UNIVERSITÀ DEGLI STUDI DI MILANO

Facoltà di Scienze e Tecnologie

Doctorate School in Chemical Sciences and Technologies

Dipartimento di Chimica

Ph.D Studies in Industrial Chemistry, XXVII Course

HETEROGENEOUS CATALYSIS FOR THE SYNTHESIS OF BIOPRODUCTS

CHIM/03

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Academic Year 2013-2014

Table of Contents

Table of Abbreviations

FAME: Fatty Acids Methyl Esters
TON: Turnover Number
CH: Chemisorption-Hydrolysis
IW: Incipient Wetness
TEM: Transmission Electron Microscopy
TPR: Temeprature Programmed Reduction
FT-IR: Fourier Transform- Infrared Spectroscopy
XPS: X-Ray Photoelectron Spectroscopy
HR-TEM: High Resolution Transmission Microscopy
THF: Tetrahydrofuran
HC-SCR: HydroCarbon-Selective Catalytic Reduction
ZSM-5: Zeolite Socony Mobil-5
TCD: Thermal Conductivity Detector
IR-DTGS: Infrared Tryglicine Sulfate Detector
TOF: Turnover Frequency
RT: Room Temperature
SBA: Santa Barbara Amorphous
TMP: Trimethylolpropane
NPG: Neopentylglycol
PE: pentaerithrol
Gly: Glycerol
BSTFA: N,O-bis(trimethylsilyl)trifluoroscetamide
GC-FID: Gaschromathoraphy Flame Ionization Detector
ASA: Amorphous Silica Aluminas
RID: Refractive Index Detector

Chapter 1:

Introduction

1.1 General introduction

One of the most challenging problem of the modern society is the continued population growth. In mid-2013 we were 7.2 billion of people, and in the 2025 the prospected population will be 8.1 billion[1]. The increasing in world population means a major consumption of resources, including fossil fuels, metals, food, energy, water and land. Most of them are not renewable, thus representing a supply problem for everyone. The immoderate use of fossil fuels not only presents the problem linked with is ending, but also a pollution problem. In fact the combustion of petrol for automotive, warming and other needs, produce tons of carbon dioxide, one of the most known greenhouse gases. In the Last years the CO_2 concentration reached 400 ppm, potentially enough to trigger a warming of 2°C, compared with pre-industrial levels[2]. Another problem is to give food to nearly 9 billion people, considering constrains of natural resources, limited farming land supplies and the water crisis[3].

The use of renewable resources and sustainable feedstock can stem these problems. Biomass is defined as a biological material coming from CO_2 fixation by natural photosynthesis[4]. From biomass it is possible to produce fuels and chemicals, preserving environment. The use of biomass as for fossil fuel replacement is considered carbon neutral, where generated carbon dioxide output is generally offset by CO_2 fixation through photosynthesis during biomass growing. Biomass is the fourth largest source of energy (following oil, coal and natural gas), and accounts for over 10% of global primary energy supply. The total primary energy supplied from biomass in 2012 reached the huge quantity of 55 EJ ($55*10^{18}$ J)[5]. To improve the biomass use and reduce CO_2 emissions, the European Commission has published, in 1997, a White Paper of Renewable Energy Sources forcing the EU members to increase to 20% the use of renewables in energy production by 2020[6]. This entails the use of biomass in a way complying with the green chemistry principles[7].

A new concept is emerging about the chemicals and fuels production: the biorefinery concept. As a petroleum refinery, that transform oil in power, fuel and chemicals, a biorefinery transforms biomass in the same products. (Figure 1.1)

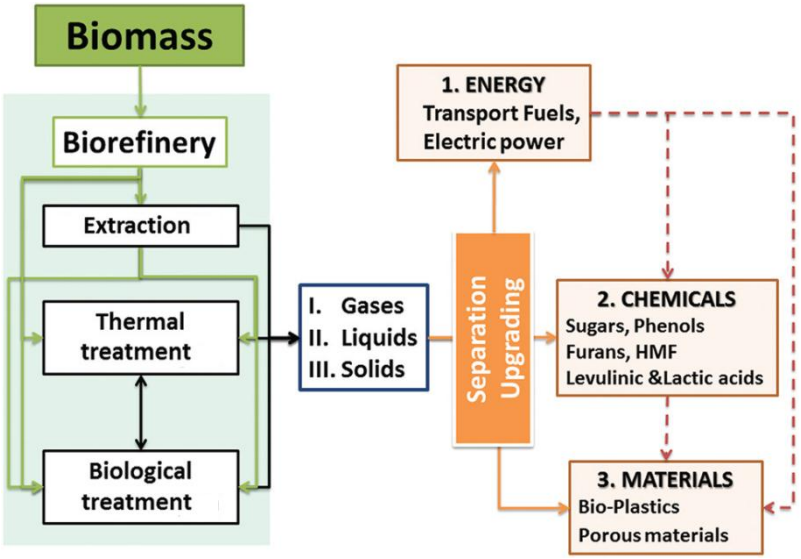

Figure 1.1 Illustration of biorefinery concept

The biorefinery allows one to processing waste feedstock, including those containing carbohydrates, lignin, fats, proteins and various other chemicals. The resulted output can be classified in two categories: high-volume low value products (fuels) and higher value lower volume chemicals (waxes, succinic acid, sorbitol, glycerol, ecc) that can be used as platform molecules in polymer and pharmaceutical industries[8]. In order to transform the starting biomass in valuable products, biorefinery needs to adopt different processes: extraction, biological and thermal treatment, allowing to switch among many biomass feedstocks[9]. Biorefineries have changed over time, passing from first to second generation ones. First generation biorefineries can produce bio-derived liquid fuels, starting from readily available food and energy crops, such as ethanol form sugarcane or biodiesel from vegetable oils and animal fats, putting significant pressure on agriculture and food provision[10]. These kind of biofuels receive severe criticisms as their production have a minimum effect on greenhouse gas emission reduction, and they also have a minimal impact on transportation fuels due to limited feedstock supplies[11]. Such a global production of biofuels results to be not sustainable, thus requiring new and more environmental friendly methodologies and feedstocks. The second generation biorefineries have been developed in order to prevent these problems, using non-food competing biomass such as waste biomass, waste food and lignocellulosic materials[12]. There are some drawbacks related to this kind of feedstock: for example the complex structure of non-food lignocellulosic materials, that contains inert material (as cellulose), the difficulty to perform a continuous process converting biomass in fuel and chemicals and the lack of low-cost processing technologies able to transform feedstock.

Second generation biochemical processing involves conversion of hemicellulose and cellulose to fermentable sugars, therefore converted into alcohols suitable as fuels[13]. Among the methods seen before for transforming the starting biomass, biochemical ones are the most energy efficient, but are time-consuming and leave lignin as waste. Thermochemical methods use heat to breakdown starting material, allowing the production of wide range of chemicals and fuels. On the other hand they suffer from a high capital input, significant energy demand and high operational costs[14]. If compared to biochemical processes, pyrolysis of biomass is less selective but still highly advantageous and it poses less restriction on the type of feedstock. If these two processes were combined in a continuous low temperature process, it would be possible to maximize both range of attainable products and their individual yields. All these biomass transformations must comply with the 12 rules of green chemistry, developed by Paul Anastas and John Warner in order to have a greener process or product:

1. **Prevention**

   It is better to prevent waste than to treat or clean up waste after it has been created.

2. **Atom economy**

   Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. **Less hazardous chemical syntheses**

   Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. **Designing Safer Chemicals**

   Chemical products should be designed to affect their desired function while minimizing their toxicity.

5. **Safer Solvents and Auxiliaries**

   The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

6. **Design for Energy Efficiency**

   Energy requirements of chemical processes should be recognized for their environmental

and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. **Use of Renewable Feedstocks**
   A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. **Reduce Derivatives**
   Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

9. **Catalysis**
   Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. **Design for Degradation**
    Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11. **Real-time analysis for Pollution Prevention**
    Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. **Inherently Safer Chemistry for Accident Prevention**
    Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Heterogeneous catalysts allow to respect the ninth rule and to avoid waste of metals, as they are recyclable. Moreover they allows to enhance yields and to obtains better product selectivity.

1.2 First generation biorefinery

First generation biorefineries are mainly devoted to biodiesel production, conversion of glycerol and bio-ethanol from starch-rich biomass. Biodiesel production is one of the most important issue in the first generation biorefinery. It is constituted by FAME, because direct use of triglycerides in

diesel engine is problematic due to their high viscosity and low volatility. Acid or base-catalyzed transesterification with methanol affords FAMES, that show lower density with respect to triglycerides[15]. Base catalyst are preferred, but triglycerides sources tend to contain significant amount of free fatty acids, which neutralize some of the bases, thus requiring larger amount of catalyst. In many cases a pre-esterification step is necessary, in order to decrease free fatty acids content in the triglycerides sources. Heterogeneous catalysts can be effective substitutes for both acid and basic catalysts, having the advantage to be greener and to simplify the downstream processes avoiding saponification and additional steps required by homogeneous catalysts[16]. For example normal CaO is practically ineffective in production of biodiesel, but in nanocrystalline state is able to produce biodiesel with 99% conversion of triglyceride, showing good recyclability, up to 5 times[17]. Similar results were obtained with nano-sized g-Al_2O_3 with 15% of KF, giving methyl esters yields up to 98%[18]. Another successful way is the enzymatic one. Immobilizing lipase enzyme on nanoparticles can catalyze transesterification reaction, under mild conditions. Xie et al. have reported methyl esters yields up to 94% grafting lipase onto magnetic Fe_3O_4 nanoparticles, that allow an easiest way to recover the catalyst[19]. The major by-product of biodiesel synthesis is glycerol and there is a growing interest in the transformation of this waste in valuable chemicals. From glycerol it is possible to obtain 1,3-propanediol, propylene glycol, acrolein and glyceric acid. 1 wt% Au/graphite shows 54% glycerol conversion and 100% selectivity in glyceric acid in mild conditions[20]. Lactic acid is another important platform molecule, that can be converted in propylene glycol, polylactic acid and lactaldehyde. It's possible to produce lactic acid from glycerol, combining oxidation catalyst Au-Pt/TiO_2 with NaOH under O_2 in atmospheric pressure at 90°C[21]. By using similar conditions with Rh/ZnO and Pt/ZnO as catalysts, it is possible to convert glycerol in a mixture of lactic acid and propylene glycol. Conversion up to 100% are reached, obtaining a mixture 70:30% of lactic acid:propylene glycol[22]. Non precious metals are also active in glycerol transformation. For example highly dispersed silica-supported copper nanoparticles can afford 99% selectivity in propylene glycol with only 19% conversion[23]. Iron oxide can catalyze transformation of glycerol in allyl alcohol through dehydration and consecutive hydrogen transfer[24]. Fermentation of glucose is the preferred method to obtain bio-ethanol, and immobilization of enzymes onto nanoparticles is the most reliable catalytic route. By changing enzyme it is possible to produce other interesting chemicals as bio-butanol or lactic acid. a-amylase, immobilized over magnetic nanoparticles showed god results, exhibiting 83% residual activity after 8 cycles[25].

1.3 Second generation biorefinery

Second generation biorefinery processes non-food biomass to obtain energy and chemicals. Main topics are: cellulosic ethanol, lactic acid from glucose, pyrolysis of lingo-cellulosic biomass, bio-oil upgrading and gasification of biomass and bio-oil into syngas. One of the most widespread biopolymer is cellulose, constituted by condensed D-glucose units. These units are connected by β-1,4-glycosidic bonds and intra/inter molecular hydrogen bonds. This particular structure results in a very stable crystalline fibrous structure, with great tensile strength and chemical inertness[26]. Cellulase is an enzyme able to break cellulose and to produce glucose, but it tends to be sensitive towards a lot of environmental factors (temperature, ecc). Heterogenisation of cellulase can enhance stability and catalytic activity of this enzyme. In their work, Chang et al. immobilized cellulase onto mesoporous silica nanoparticles, by using physisorption and covalent bonding. They showed that covalent bonded cellulase have the same performances of free enzyme, thus giving up to 80% glucose yields. The free and physisorbed enzyme lost a significant part of their catalytic activity after a prolonged storage, while bonded cellulase retains it[27]. The glucose obtained from cellulose hydrolysis undergoes fermentation giving bio-ethanol, the most used liquid biofuel. In 2010 among the 120 billion liters of biofuels produced for transport, 100 billion liters where bio-ethanol, data giving an idea of the importance of this process[28]. Continuous process is preferred to batch ones, as they give enhanced volumetric productivity that allow to use smaller bioreactor and therefore lower investment/operational costs[29]. Ivanova et al. entrapped *Saccharomyces cerevisiae* cells in an alginate matrix with magnetic nanoparticles, developing a continuous ethanol fermentation system[30]. It is possible to produce lactic acid also from glucose, for example with a combination of alkaline degradation and air oxidation of D-glucose with Pt/C as catalyst, obtaining 45% yield of lactic acid[31]. From lactic acid it is possible to obtain many others high value molecules, for example propylene glycol or lactaide. By using Ru/TiO_2 selectivities up to 95% in propylene glycol were reached[32]. With lanthanum-titanium composite oxides it is possible to dehydrate lactic acid and to obtain lactaide, that can be polymerized into polylactic acid[33]. Valorization of cellulose by means of its transformation into chemicals others than glucose, is receiving even greater attention. In fact it is possible to convert cellulose directly in ethylene glycol, hexitols and isosorbide. Heterogeneous catalysis plays a fundamental role in these transformations. Ru/zeolite is able to completely convert cellulose into hexitols with yields >90%[34]. Biomass can be directly converted into biofuels by using thermal treatment. This method

is highly versatile, in fact by changing process parameters (temperature, heating rate and residence time) it is possible to obtain different biofuels: bio-gas, bio-oil or char, from three different thermal processes: gasification, pyrolysis and torrefaction (Table 1.1).

Table 1.1 Biomass thermal treatments

Type of pyrolysis	Temperature/ °C	Heating rate/°C min^{-1}	Main product
Torrefaction	200–350	<50	Bio-char
Fast pyrolysis	400–550	100–10 000	Bio-oil
Gasification	550–1000	100–10 000	Bio-gas

Heterogeneous catalysts can influence biomass gasification, avoiding formation of tar and enhancing yield and quality of the produced gases. The use of nano-NiO supported on g-Al_2O_3 in biomass pyrolysis at 800°C gives very good results, with a tar removal efficiency of 99% and a gas composition that favors H_2 and CO at the expense of CO_2 and CH_4[35]. Bio-oil is a dark brown liquid, constituted by a mixture of different products derived from dehydration and breakdown of (hemi)-cellulose and lignin as acids, aldehydes, furans, phenols, monosaccharides and polymers. It is possible to influence the nature and distribution of the constituent of bio-oil by using heterogeneous catalysts. Nano-SnO_2 can accelerate the hazelnut shells pyrolysis increasing gas evolution[36]. By using different kind of nano-sized metal oxides, it is possible to increase levoglucosan yield in cellulose pyrolysis[37]. The applications of bio-oil are limited because of their high viscosity, poor stability and corrosivity. Many efforts have been made in order to upgrading bio-oil, for example by means of hydrogenation, esterification , hydrodeoxygenation or by blending it with diesel, but these processes are costly, use complicated equipment and procedures and the catalysts tend to foul during the process. A smart approach was proposed by Crossley, by using solid nanohybrid materials for both stabilize water-oil emulsion and catalyze biphasic hydrodeoxygenation. The catalyst was constituted by Pd nanoparticles supported onto a combination of carbon nanotubes and nanosized oxides. The authors observed TONs similar to those obtained with Pd/C in monophasic system, but reaction temperature was lower than 50°C[38]. Another example is a catalyst constituted by Ru, Pd and Pt nanoparticles with a Brønsted acidic ionic liquid, able to hydrogenate phenols to cyclohexane[39]. One of the common ways to obtain high quality biofuel is the gasification of biomass and bio-oil to syngas, that in turn can be converted in a variety of hydrocarbons with Fischer-Tropsch reaction or in methanol, for further transformations. Recently a syngas conversion to C_2-C_4 olefins with selectivity up to 60%was

reported by using iron nanoparticles promoted by sulphur and sodium on a-alumina or carbon nanofibre supports[40]. Methanol synthesis from syngas is a very important process in the chemical industry. The better catalyst is Cu supported on ZnO/Al_2O_3, but a recent study shows that copper nanoparticles are very active catalysts in *quasi* homogeneous phase, without any solid support[41]. Methanol produced from bio-syngas can be transformed in other valuable products, for example olefins. With nano a-Mn_2O_3 at 250°C methanol conversion of 35% and ethylene selectivity of 80% were obtained[42]. Heterogeneous catalysts made with metal nanoparticles seem to be very promising for biofuels and chemicals production, giving greener processing, higher yields and selectivity. The major challenge for biorefinery is to produce energy, fuels and chemicals in a competitive manner with respect to crude oil refinery. To achieve this goal there are still some important drawbacks that have to be solved:

- Sustainable design of still more active and selective nano-sized catalysts, to obtain tailored bio-oils;
- Development of more versatile nano-based catalytic systems, capable to process a wide range of biomasses, tolerating impurities such as acids, alkali metals, nitro and sulphur containing compounds, ecc;
- Development of new catalysts able to convert bio-derived sugars in biofuels and chemicals;
- In depth investigation about process intensification of nanotechnology based Fischer-Tropsch synthesis applied to bio-syngas[43]. A next generation biorefinery is being studied, and integrate high-efficiency solar cells, water electrolysis and biological CO_2 fixation mediated by cell-free synthetic cascade enzymes[44].

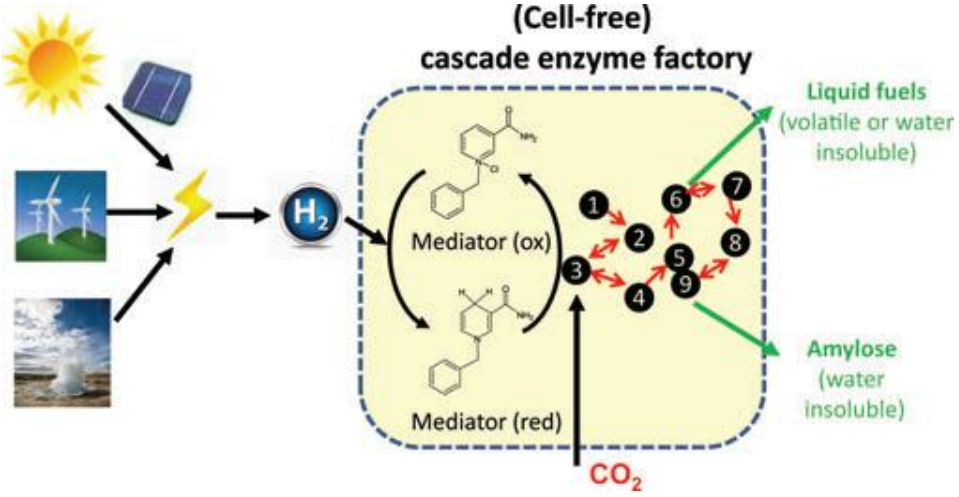

Figure 1.2 Next generation biorefinery based on artificial photosynthesis

This system, based on artificial photosynthesis, offer many advantages:

- Solar cells have a broader light absorption spectrum and higher efficiency than plant pigments. Also in it easy to concentrate nonpoint insolation to a point electricity;
- The hydrogen generated by water electrolysis at daytime can be stored and consumed at a constant rate for CO_2 fixation process at night;
- Carefully chosen product: water insoluble amylose, volatile alcohols and water insoluble fatty alcohols; in order to minimize product separation costs;
- High energy efficiency can be achieved, much better than natural processing mediated by living organism, that dissipate energy by respiration.

This system is so far only a project, but can bridge current and future primary energy utilization system and address sustainability challenges such as renewable biofuel and chemical production, CO_2 utilization and fresh water conservation[45]. In conclusion second generation biorefineries development, based on nonfood biomass, is a pressing issue because they will produce a variety of chemicals that cannot be substituted by other renewable resources. This point will be of importance for biorefineries economic viability, because natural feedstock contains multiple components. It's very important to not change current agricultural lands used for food/feed production to yield bioenergy crops, leading to a food shortage. And in the end, it's very significant to develop next generation biorefineries, based on artificial photosynthesis, that can produce carbon-containing compounds form CO_2 and H_2/electricity.

1.4 Aim of the thesis

The aim of the present Ph.D. work has been mainly focused on the application of amorphous and non-noble metal based solid catalysts for their application to the transformation of different kind of biomass derived materials. In particular we devoted our attention to the use of solid acids (amorphous mixed oxides) for esterification and hydrolysis reactions and to the use of copper catalysts for the set-up of bifunctional processes. On one hand the use of fatty acids for the preparation of biolubricants and monoglycerides has been explored. On the other hand the exploitation of poly- and disaccharide such as cellulose and lactose have been studied.

In fact, the possibility to transform into valuable molecules this kind of materials, in some cases available as by-product or wastes of industrial processes, represents an interesting point to look at within the previously described scenario, that is the biorefinery one.

1.5 References

[1] World Population Prospect: The 2012 Revision, Key Findings and Advance Tables. Working Paper No. ESA/P/WP.227., United Nation, Department of Economic and Social Affairs, Population Division 2013;

[2] The Keeling Curve: A Daily Record of Atmospheric Carbon Dioxide from Scripps Institution of Oceanography at UC San Diego: http://keelingcurve.ucsd.edu/;

[3] J. Foley et al., *Nature*, 2011, 478, 337;

[4] Y.H.P. Zhang, *Energy Science & Engineering*, 2013, 1, 27;

[5] REN21. Renewables 2013 Global Status Report, Paris 2013;

[6] M. Mascal, E.B. Nikitin, *Angew. Chem., Int. Ed.*, 2008, 47, 7924;

[7] M. Mascal, E.B. Nikitin, *ChemSusChem*, 2009, 2, 859;

[8] A. Gandini, A.J.D. Silvestre, C.P. Neto, A.F. Sousa, M. Gomes, *J. Polym. Sci. Part A: PolymChem*, 2009, 47, 295, and S.W. Breeden, J.H. Clark, T.J. Farmer, D.J. Macquarrie, J.S. Meimoun, Y. Nonne, J.E.S.J. Reid, *Green Chem*, 2013, 15, 72;

[9] V.L. Budarin, P.S. Shuttleworth, J.R. Dodson, A.J. Hunt, B. Lanigan, R. Marriot, K.J. Milkowsi, A.J. Wilson, S.W. Breeden, J.J. Fan, E.H.K. Sin, J.H. Clark *Energy Environ. Sci.*, 2011, 4, 471;

[10] M. Stocker, *Angew. Chem. Int. Ed.,* 2008, 47, 9200;

[11] T. Searchinger, R. Heimlich, R.A. Houghton, F. Dong, A. Elobeid, J. Fabiosa et al, *Science*, 2008, 319, 1238;

[12] M. FitzPatrick, P. Champagne, M.F. Cunningham, R.A. Whitney, *Bioresour. Technol.,* 2010, 101, 8915;

[13] H. Kobayashi, T. Komanoya, K. Hara, A. Fukuoka, *ChemSusChem*, 2010, 3, 440;

[14] D. Mohan, C.U. Pittman, P.H. Steele, *Energy Fuels*, 2006, 20, 848;

[15] L.C. Meher, D.V. Sagar, S.N. Naik, *Renew. Sustain. Energy Rev.* , 2006,10, 248;

[16] Z. Helwani, M.R. Othman, N. Aziz, J. Kim, W.J.N. Fernando, *Appl. Catal. A*, 2009, 363,1;

[17] C. Reddy, V. Reddy, R. Oshel, J.G. Verkade, *Energy Fuels*, 2006, 20, 1310;

[18] B. Freedman, R.O. Butterfield, E.H. Pryde, *J. Am. Oil Chem. Soc.*, 1986, 63, 1375;

[19] W.L. Xie, N. Ma, *Biomass Bioenergy*, 2010, 34, 890;

[20] S. Carrettin, P. McMorn, P. Johnston, K. Griffin, G.J. Hutchings, *Chem. Commun.*, 2002, 696;

[21] M. Dusselier, P. Van Wouwe, A. Dewaele, E. Makshina, B.F. Sels, *Energy Environ. Sci.*, 2013, 6,1415;

[22] M. Checa, F. Auneau, J. Hidalgo-Carrillo, A. Marinas, J.M. Marinas, C. Pinel, F.J. Urbano, *Catal. Today*, 2012, 196, 91;

[23] Z.W. Huang, F. Cui, H.X. Kang, J. Chen, X.Z. Zhang, C.G. Xia, *Chem. Mater.*, 2008, 20,5090;

[24] Y. Liu, H. Tuysuz, C. J. Jia, M. Schwickardi, R. Rinaldi, A.H. Lu, W. Schmidt, F. Schuth, *Chem. Commun.*, 2010, 26, 1238;

[25] D.A. Uygun, N. Ozturk, S. Akgol, A. Denizli, *J. Appl. Polym Sci.*, 2012, 123, 2574;

[26] Y.H.P. Zhang, L.R. Lynd, *Biotechnol. Bioeng.*, 2004,88,797;

[27] R.H.-Y. Chang, J. Jang, K.C.W. Wu, *Green Chem.*, 2011, 13, 2844;

[28] F.O. Licht, *World ethanol markets: The outlook to 2015*, TunbridgeWeels, UK, 2006;

[29] S. Brethauer, C.E. Wyman, *Bioresour. Technol.*, 2010, 101, 4862;

[30] V. Ivanova, P. Petrova, J. Hristov, *Int. Rev. Chem. Eng.*, 2011, 3,289;

[31] A. Onda, T. Ochi, K. Kajiyoshi, K. Yanagisawa, *Appl. Catal. A*, 2008, 343, 49;

[32] A. Primo, P. Concepcion, A. Corma, *Chem. Commun.*, 2011, 47, 3613;

[33] A. Corma, S. Iborra, A. Velty, *Chem. Rev.*, 2007, 107, 2411;

[34] J. Geboers, S. Van de Vyver, K. Carpentier, P. Jacobs, B. Sels, *Chem. Commun.*, 2011, 47, 5590;

[35] J. Li, R. Yan, B. Xiao, D.T. Liang, L. Du, *Environ. Sci. Technol.*, 2008, 42, 6224;

[36] Z. Gokdai, A. Sinag, T. Yumak, *Biomass Bioenergy*, 2010, 34, 402;

[37] C. Torri, I.G. Lesci, D. Fabbri, *J. Anal. Appl. Pyrolysis*, 2009, 85, 192;

[38] S. Crossley, J. Faria, M. Shen, D.E. Resasco, *Science*, 2010, 327, 68;

[39] N. Yan, Y. Yuan, R. Dykeman, Y. Kou, P.J. Dyson, *Angew. Chem. Int. Ed.*, 2010, 49, 5549;

[40] H.M.T. Galvis, J.H. Bitter, C.B. Khare, M. Ruitenbeek, A.I. Dugulan, K.P. de Jong, *Science*, 2012, 335, 835;

[41] S. Vukojevic, O. Trapp, J.D. Grunwaldt, C. Kiener, F. Schuth, *Angew. Chem. Int. Ed.*, 2005, 44, 7978;

[42] J. Xu, L. Ouyang, Y. Luo, X. M. Xu, Z. Yang, C. Zhang, J. Gong,*AlChe. J.*, 2012, 58, 3474;

[43] P.S. Shuttleworth, M. de Bruyn, H.L. Parker, A.J. Hunt, V.L. Budarin, A.S. Matharu, J.H. Clark, *Green Chem.*, 2014, 16, 573;

[44] Y.H.P. Zhang, *Energy Sci. Eng.*, 2013, 1, 27;

[45] Y.H.P. Zhang, W.-D. Huang, *Trends Biotechnol.*, 2012, 30, 301.

Chapter 2:

Characterization of Cu catalysts prepared by Chemisorbtion-Hydrolysis

2.1 Introduction

2.1.1 Heterogeneuos copper catalyst preparation

Several methods have been developed for the preparation of heterogeneous catalysts, but, as already mentioned, the current state-of-the-art cannot completely satisfy the demand of robust and active materials, in particular for industrial application. In this section, the main advantages and drawbacks of main catalysts preparation techniques are reported, taking also a look to the trends concerning copper catalysts.

Traditional coprecipitation and impregnation techniques are based on uncomplicated preparation steps employing simple and cheap precursors. As a drawback, catalysts prepared in this way present quite low dispersion, particularly for high metal loadings and lack in particle size control and uniformity. For example, coprecipitation techniques allow one to prepare supported, mixed and also single component catalysts, often in one step, but the process may be difficulty controlled and features low flexibility, as components in the starting homogeneous solution need to be simultaneously precipitated in a single material. Likewise, impregnation techniques are quite easy preparation procedures, but often lead to a large spectrum of catalytic sites, different in size, shape and support interaction [1] [2].

The general trend in new heterogeneous catalyst design has been driven towards the production of well-defined and uniform active sites, in order to combine the advantages of homogeneous catalysts with an easy product separation, recover, recycling and a good stability of the catalyst [3] [4] [5] [6] [7]. The latest cutting-edge of single site hetereogeneous catalysis (SSHC) is nothing but the extreme expression of this strategy. This particular approach aims at the preparation of catalytic systems where the active sites are well-defined, isolated, evenly distributed entities (single sites) with defined chemical surroundings, as in conventional homogeneous catalysts or enzymes, while showing all of the advantages of heterogeneous systems [8] [9].

A simpler alternative to SSHC is chemical vapor deposition (CVD) and related methods. CVD is an useful technique for the preparation of well dispersed catalysts with quite high metal loadings, avoiding several step of the traditional method, such as washing, drying, calcination and reduction [6] [10] [11] [12].

Unfortunately, preparation methods like SSHC and CVD, though affording the synthesis of highly active heterogeneous systems, frequently require sophisticated and tricky techniques or apparatus that lead to low reproducibility or scarce practical applicability, particularly when large scale productions are sought. The search for a particular morphology in the catalytic site calls for

highly controlled conditions in the preparation method, as much as the use of elaborate, costly and unstable complexes as metal precursors [8] [9] [11] [13].

The preparation of colloidal metal nanoparticles and their deposition on a support is an alternative persecuted route. It usually allows a good control of the shape and size of the particles at the expenses of the handiness of the protocol. The synthetic procedure is frequently complicated, leading to the coverage of the colloid surface by organic polymers that can interfere with the catalytic activity of the system: moreover the removal of these polymers may affect the stability of the nanoparticles [3] [14].

As regards copper, today heterogeneous Cu catalysts are prepared with the more traditional techniques, like impregnation and cooprecipitation, but also by means of less conventional method.

Metal vapor synthesis (MVS) has been used to obtain copper catalysts with high metal dispersion, used for Ullman reactions [15] as well as for oxygen activation [16] [17].

A different approach has been employed in the precipitation-gel technique, involving the addition of aqueous NaOH to a solution of $Cu(NO_3)_2$ to form a precipitate, following by the addition of colloidal silica to the obtained suspension, in order to stabilize the microparticles of the precipitate and simultaneously form a gel. These materials have been proposed for the glycerol hydrogenolysis into 1,2-propandiol [18].

Finally, a microwave assisted protocol introduced for noble metals has been successfully extended to copper catalysts and used for C-S coupling reactions [19].

2.1.2 Chemisorption-Hydrolysis

In the present thesis we report about the use of an unconventional technique, called Chemisorption-Hydrolysis, which enables to obtain highly versatile copper based catalytic systems in an easy and reproducible way. Chemisorption-Hydrolysis represents a fruitful trade-off, as it combines the simplicity of impregnation techniques, both in terms of handiness (easy experimental procedure, simple apparatus) and cheapness, with the high metal dispersion obtained by anchoring techniques. As previously discussed, the possibility to prepare highly dispersed smoothes the way to diverse applications of the metal oxide and in this context CH leads to different catalytic sites just by varying the inorganic matrix, while always keeping a remarkable

dispersion. On the other hand reductive treatment allows one to switch from an acidic catalyst to an hydrogenation one [1].

The preparation steps of Chemisorption-Hydrolysis are:

1. Preparation of $[Cu(NH_3)_4]^{2+}$ complex by dropping aqueous NH_3 to a $Cu(NO_3)_2 \bullet 3H_2O$ solution until pH 9 has been reached
2. Addition of support powder to the $[Cu(NH_3)_4]^{2+}$ solution
3. Dilution of the cooled slurry (0 °C)
4. Filtration and calcination (350 °C, 4 h) of the solid to obtain CuO/support (Cu^{2+}) or CuO_x/support ($Cu^{\delta+}$, $+1 \leq \delta \leq +2$) catalyst

If required by reaction conditions, an eventual reduction pretreatment (directly with H_2) leads to Cu/support catalyst, where copper is totally or partially reduced.

The pH of the solution used in Chemisorption-Hydrolysis and Incipient Wetness methods plays a fundamental role [20]. Differently to traditional impregnation method, in CH the pH of the starting aqueous solution of $Cu(NO_3)_2$ is increased until 9, well above the zero charge point of the common supports employed (e.g. SiO_2 and TiO_2), by adding NH_4OH: hence the surface of the support is negatively charged, thus favoring the adsorption of copper cations and giving the observed high dispersion of the sample, while nitrate ions are removed by washing. On the other hand, in the case of impregnation methods the pH of the impregnating solution used is 3–4, thus below the zero charge point for supports. Therefore the surface is positively charged and adsorbs anionic species, i.e. copper nitrates. Moreover, as a consequence of the quite low pH of the impregnating solution some dissolution of the support is expected: through calcination both unsupported CuO and a disordered, amorphous surface layer, containing copper, titanium, oxygen, and nitrogen, will be produced. A phase retaining some nitrogen, in Cu/SiO_2 samples prepared by wet impregnation, has been observed also by Higgs and Pritchard [21]. Thus in the case of Chemisorption-Hydrolysis the copper deposition at the surface of support is the result of an ionic exchange reaction, while in the case of wet impregnation catalyst a cupric nitrate solution simply fills the pores [20].

In 1997 Boccuzzi et al. reported a comparison between Cu/TiO_2 catalysts made by CH and Incipient Wetness, by using different characterization technique (TEM, TPR, FT-IR) [20]. The results clearly illustrate that samples having the same chemical composition can show very different properties, depending on the preparation method and on the thermal and chemical pretreatments. HR-TEM micrographs show different characteristics of the two calcined catalysts reduced by the electron beam: on IW samples the beam produces a large, amorphous layer covering the TiO_2 crystallites,

while on CH samples small particles are formed. This behavior is ascribed to the different structures of the copper containing overlayer as seen above.

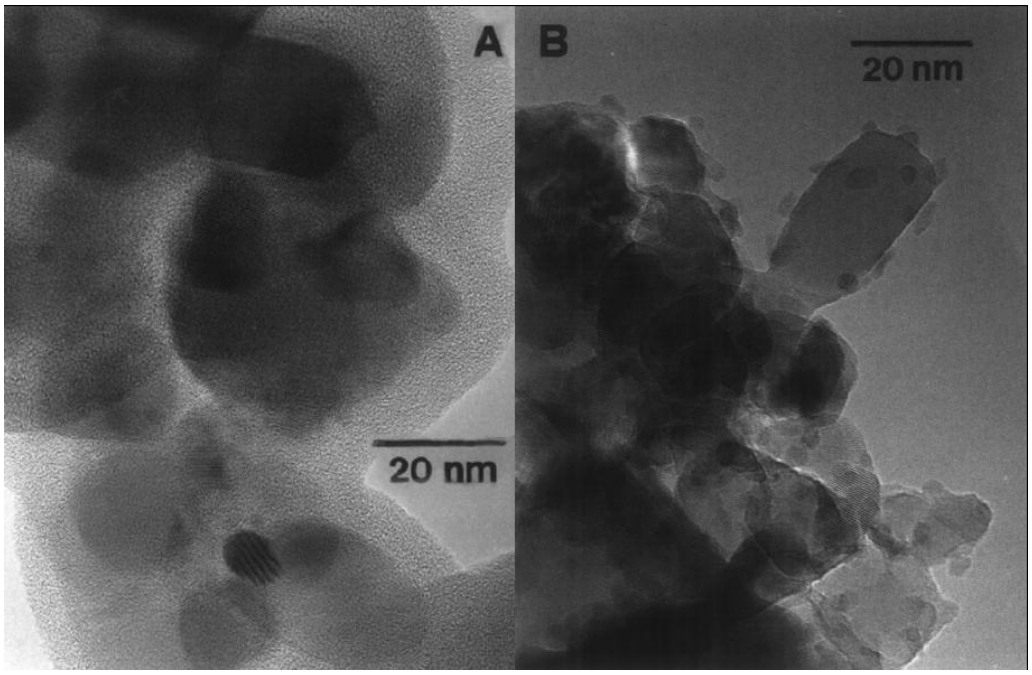

Figure 2.1 TEM images of CuO/TiO_2 samples after exposure to electron beam. (A) Cu/SiO_2 made by IW. (B) CuO/TiO_2 made by CH [20]

TPR profiles of CH and IW samples confirmed that the samples are completely different: narrow peaks in the range 180-230 °C is present for the former (reduction of CuO crystallites of different dimension), while a broad peak at 170–260 °C is seen for the latter (reduction of both unsupported CuO and a disordered phase containing copper and titania interdispersed at an atomic level, possibly with some residual anions). Finally, the interpretation of FT-IR spectra of adsorbed CO describes a situation in which isolated or two-dimensional clusters of copper are exposed on the surface of the catalyst made by Incipient Wetness, whereas the sample made by chemisorption–hydrolysis is composed by three-dimensional copper particles [20]. Therefore, it is not a coincidence that the two materials show a very different activity, e.g. in the hydrogenation of 1,3-cyclooctadiene, where the catalysts prepared by CH shows a turnover frequencies about 100 times greater than that made by IW[22].

Although the two papers wrote by Boccuzzi and coworkers pointed out, once again, the great influence of the preparation method on the catalytic properties of material nominally composed of the same elements, the role of the support has not to be forgotten. Copper dispersed on SiO_2 or

SiO_2-Al_2O_3 (13% of Al_2O_3) supports by Chemisorption-Hydrolysis method revealed to be very different in nature. On SiO_2, similarly to what happens also on TiO_2, the deposition of copper generates a CuO phase well reducible to metallic Cu, by means of a reductive pretreatment. The situation is markedly different when SiO_2-Al_2O_3 is used as support: in this case isolated copper species with oxidation state ranging from (II) to (I) were formed just after the catalyst preparation and the reduction only significantly decreases the amount of the Cu(II) species in favor of Cuδ+ ($1 < \delta < 2$) and Cu(I). These differences were confirmed by a depth characterization (TPR and XPS) and, definitely, by catalytic tests which show distinct behaviors depending on the support [23] [24].

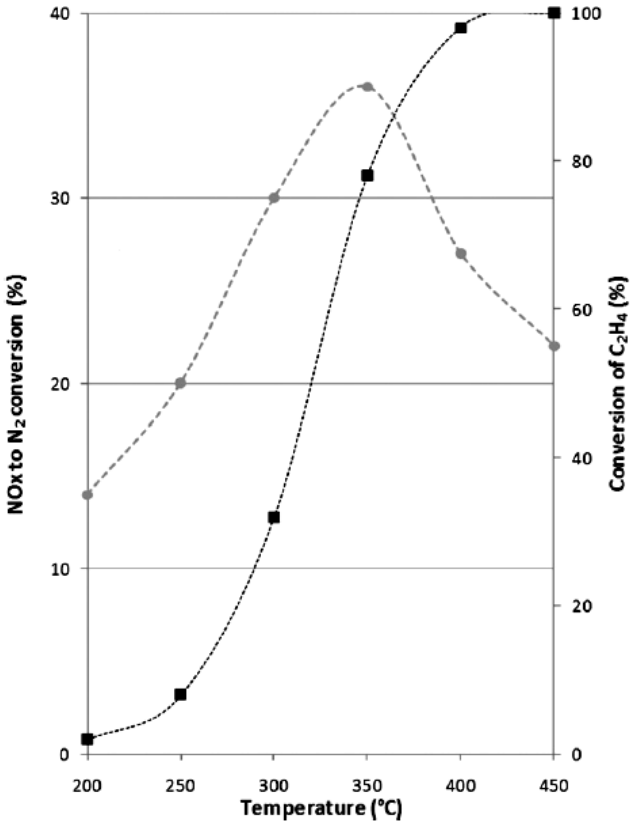

Figure 2.2 Conversion of NO_x to N_2 (gray dot) and conversion of C_2H_4 (black square) to carbon oxide as a function of reaction temperature in SCR (initial concentrations: ca. 1500 ppm of NO_x and of C_2H_4 and 15000 ppm of O_2) [1].

Even if the use of completely reducible copper species is generally required on Cu catalyzed hydrogenation reaction, the particular nature of the unreduced oxide obtained over silica alumina can conversely be exploited for several applications. Activity of Cu/SiO_2-Al_2O_3 in the carbene insertion coming from methyl phenyldiazoacetate, into one C-H bond of THF has been recently reported, thus constituting the first example of this reaction promoted by a purely inorganic catalyst [25]. In this synthetic application, Cu/SiO_2-Al_2O_3 leads to better results regarding yield and

catalyst recovery than Cu/SiO_2, confirming that different redox properties of the supported Cu phase influence the behavior of the catalyst depending on the support. The particular electronic properties of the oxidic phase when dispersed over this silica alumina can be conveniently exploited for other catalytic applications than hydrogenation. In particular, the similarity with copper-exchanged zeolites prompted to test these systems in the Selective Catalytic Reduction in oxidising atmosphere (HC-SCR) for NO_x [1,23,24]. According to Márquez-Alvarez at al., HC-SCR can be performed in any Cu-based system containing small cupric oxide particles and some acidity [26]. The catalyst preparation method is a critical factor for improving the de-NO_x activity of copper dispersed catalysts together with the choice of a suitable support with acidic properties and a wide surface to disperse the copper phase. The superior performances observed for copper-exchanged zeolites (particularly ZSM-5) compared to amorphous supported systems has been ascribed to the capacity of zeolites in disperding the active copper at atomic level [27]. On the other hand, desirable support properties are high mechanical and hydrothermal stability. Chemisorption-Hydrolysis has been revealed an adequate method to prepare nanodispersed copper catalysts supported over oxidic acidic support as SiO_2-Al_2O_3 to be used for this kind of catalytic application. Recently we reported a 35% of NO_x conversion to N_2 and 80% of C_2H_4 conversion to carbon oxides [1] (Figure 2.2). Comparable NO to N_2 conversions (41%) were reported over Cu-ZSM-5 at 250 °C [28].

A step forward in exploiting as much as possible the versatility of these kind of copper catalysts is represented by the use of dispersed copper oxide as an acidic catalyst, even if supported over non acidic matrixes. Acidic properties in heterogeneous catalysts usually derive from conventional acidic functions such as –OH groups in molecular sieves or clays or exchanged metal ions as Lewis acid [29]. Dispersed copper over a non-acidic silica obtained with the Chemisorption-Hydrolysis technique can be used as a heterogeneous acid catalyst, by virtue of its high dispersion, while catalysts made by Incipient Wetness are completely inactive. In Figure 2.3 are reported the results obtained by Zaccheria et al. is the alcoholysis reactions of epoxides with different alcohols catalyzed by CuO/SiO_2 catalyst. Good conversion and selectivity was reached with different alcohols, in general within 1 h. These results unravel the unexpected acidity of this material, where none of the partners shows acidic activity itself [30]. Although the use of Cu(II) salts as Lewis Acids is known [31] reports on CuO are lacking. The reaction proceeds truly by a heterogeneous pathway, as clearly shown by the authors: if catalyst is filtrated from the reaction media, the reaction stops immediately. Moreover the use of chromatographic silica ensured the inertness of the support

used under these conditions, in fact only SiO_2 did not lead to any reaction. On the other the sample prepared by traditional Incipient Wetness technique and with the same copper loading resulted to be almost inactive under the reaction conditions used, confirming the peculiar properties given by the particular preparation method used. Also bulk CuO resulted to be completely inert.

Alcohol	t (h)	Conv. (%)	Sel. (%)[b]
MeOH	8.5	97	92
EtOH	2	99	90
2-Propanol	0.75	100	83
	0.75	100	82[c]
2-Butanol	0.5	98	83
Isobutanol	0.5	100	81
1-Octanol	0.5	94	88
2-Octanol	0.5	100	87
Cyclohexanol	0.25	56	81
	0.5	100	78

[a] Alcohol as solvent (5 mL), 60 °C, N_2. [b] Main byproduct being phenylacetaldeide derived from the acid promoted epoxide isomerisation. [c] Reaction carried out under air.

Figure 2.3 Styrene oxide alcholysis promoted by CuO/SiO_2 [30].

Summarizing, as we seen in this section, among the preparation methods used in heterogeneous catalysis, chemisorption–hydrolysis represents a powerful technique in order to combine high activity and handiness. This protocol is reliable and versatile, giving the opportunity to properly choose the support in order to tune the catalytic activity or selectivity, thus ranging over very different kind of purposes, aimed both to fine chemicals preparation and environmental remediation [32]. Thus, the same preparation technique leads to different catalytic sites just by varying the inorganic matrix, while always keeping a remarkable dispersion. On the other hand the reductive treatment allows one to switch from an acidic catalyst to an hydrogenation one. Moreover the use of a non-noble, non-toxic and non-pyrophoric metal shelters from several economical and safety concerns.

2.1.3 Aim of the work

In this chapter preparation and characterization of different catalysts made by Chemisorption-Hydrolysis have been reported. The copper amount was chosen between 1 and 15 wt%. The preparation involved mainly two different support type: SiO_2 and SiO_2-Al_2O_3 with 13% of Al_2O_3. As regards to SiO_2, various silica with different surface area, pore diameter and pore volume were used as catalyst support. However the deeper characterization was focused mainly on silica Chrom catalysts. Other support taken into account were TiO_2, Al_2O_3, SiO_2-ZrO_2, SiO_2-TiO_2,…

Various techniques were employed for the characterization: AAS for the determination of copper loading, TPR, FT-IR of pyridine, and HR-TEM.

On the basis of these analysis the differences between reduced and unreduced Cu/SiO_2 and Cu/SiO_2-Al_2O_3 catalysts made by CH and Cu/SiO_2 catalyst made by IW were debated. The knowledge acquired will be discussed, correlated and rationalized in the next chapters according to the catalytic data of the studied reaction.

Catalysts made with different preparation methods other than CH are always clearly marked (e.g. Cu/SiO_2 IW). If preparation method is not distinctly specified, Chemisorption-Hydrolysis should be implied.

Reduced catalysts are labeled as “Cu/support” (e.g. Cu/SiO_2), while unreduced ones as “CuO/support” or “CuO_x/support” (e.g. CuO/SiO_2 and CuO_x/SiO_2-Al_2O_3). However the label “Cu/support” can simply indicate a generic catalyst, or a class of catalysts (reduced or not), if in the specific context is not necessary to underline the pretreatment conditions (e.g. a general behavior).

2.2 Experimental

2.2.1 Chemicals

All reagents were purchased from Aldrich and used without further purification.

2.2.2 Supports

Supports were purchased and used without further purification. Table 2. reports specific surface area, pore volume and pore diameter of main support used.

Table 2.1. Features of main support used in this thesis.

Support	SSA (m^2/g)	PV	DP_{av} (A)
SiO_2 332	313	1.79	114
SiO2 Chrom	480	0.75	60
SiO_2 360	564	0.99	35
SiO_2 MP04300	723	0.66	38
SiO_2 MP15300	297	1.29	156
SiO_2 MP25300	201	1.34	251
SiO_2 MP09300	478	1.04	86
SiO_2 MP20300	255	1.06	193
SiO_2 MI300	681	0.33	20
SiO_2 SP550-10022	330	1.2	-
SiO_2-Al_2O_3 13 (13% of Al_2O_3)	485	0.75	37

2.2.3 Preparation of copper catalysts

Chemisorption-Hydrolysis catalysts were prepared using the following procedure. The support powder was added to a $[Cu(NH_3)_4]^{2+}$ solution prepared by dropping aqueous NH_3 (28%) to a $Cu(NO_3)_2 \cdot 3H_2O$ solution until pH 9 had been reached. After 20 min under stirring, the slurry, held in an ice bath at 273 K, was diluted with water. The solid was separated by filtration, washed with water, dried overnight at 383 K, and calcined in air at 673 K for 4 h. The amount of $Cu(NO_3)_2 \cdot 3H_2O$ was regulated in order to obtain, as each case required (as needed), a copper loading between 1 and 15 wt%.

The Incipient Wetness sample was prepared by impregnating the support with a copper nitrate solution of proper concentration and volume in order to obtain a 8.5 % and 15% loaded catalyst.

2.2.4 AA Spectroscopy

Cu loading was determined by Atomic Absorption Spectroscopy (Atomic Absorption Spectrometer 3100 PerkinElmer; flame: acetylene/air) and an external calibration methodology, after microwave digestion of about 20 mg of oxidized sample in 3 ml of HNO_3.

2.2.5 Temperature Programmed Reduction (TPR)

TPR profiles were recorded with a modified version of the Micromeritics Pulse Chemisorb 2700 apparatus equipped with a thermal conductivity detector (TCD). The samples (25 mg) were diluted with an equal amount of quartz, calcined at 500 °C under O_2 (40 mL/min) for 1 h and then reduced at 8 °C/min with a 8% H_2/Ar mixture at 15 mL/min. The rate of hydrogen uptake was measured by an HP 3396A integrator.

2.2.6 FT-IR of adsorbed Pyridine

The FT-IR studies of pyridine adsorption and desorption were carried out with a BioRad FTS40 spectrophotometer equipped with mid-IR DTGS detector.

The experiments were performed on sample disk (15-20 mg) after eventual pre-treatment (dehydration: 270 °C, 20 min air + 20 min vacuum; reduction: 270 °C, 20 min air + 20 min vacuum + 2 min H_2) and pyridine adsorption at room temperature. Following desorption steps were carried out for 30 min at various temperature (from room temperature to 250 °C). All spectra were recorded at room temperature after pyridine desorption at each temperature and one spectrum was collected before pyridine adsorption.

2.2.7 HRTEM analysis

The morphology and distribution of the supported metal particles were evaluated by HR-TEM. The powder samples were further ground and dispersed in toluene in an ultrasonic bath. A drop of the suspension was deposited on a perforated carbon film supported on a copper TEM grid. The specimen, after solvent evaporation under vacuum, was inserted in the column of a ZEISS LIBRA 200FE HR-TEM. Pictures were taken spanning wide regions of several support grains in order to

provide a truly representative map of the catalyst system. Distribution histograms of metal particle fraction versus diameter were evaluated from about 200 to 350 counts per sample.

2.2.8 XRD analysis

X-ray powder diffraction patterns were recorded within the range of 10° to 70° 2θ, with a step of 0.02° 2θ and counting time 1 or 4 sec/step on Philips PW-3020 powder diffractometer Ni-filtered Cu Kα radiation. The peak of CuO(111) at 2θ=35.5° was used for line-broadening determinations. Copper oxide crystallite sizes were estimated using the Scherrer equation.

2.3 Results and Discussion

2.3.1 TPR analysis

Temperature reduction profile of copper catalysts are reported in this section. The reduction peaks were assigned to $Cu^{2+} \rightarrow Cu^{0}$ one step reduction and to the reduction of strongly interacting with the support copper species with an oxidation state in the range between 1 and 2 [1] [33] [34].

Figure 2.3 reports the TPR profiles of Chrom and 332 copper silica based catalysts prepared by CH.

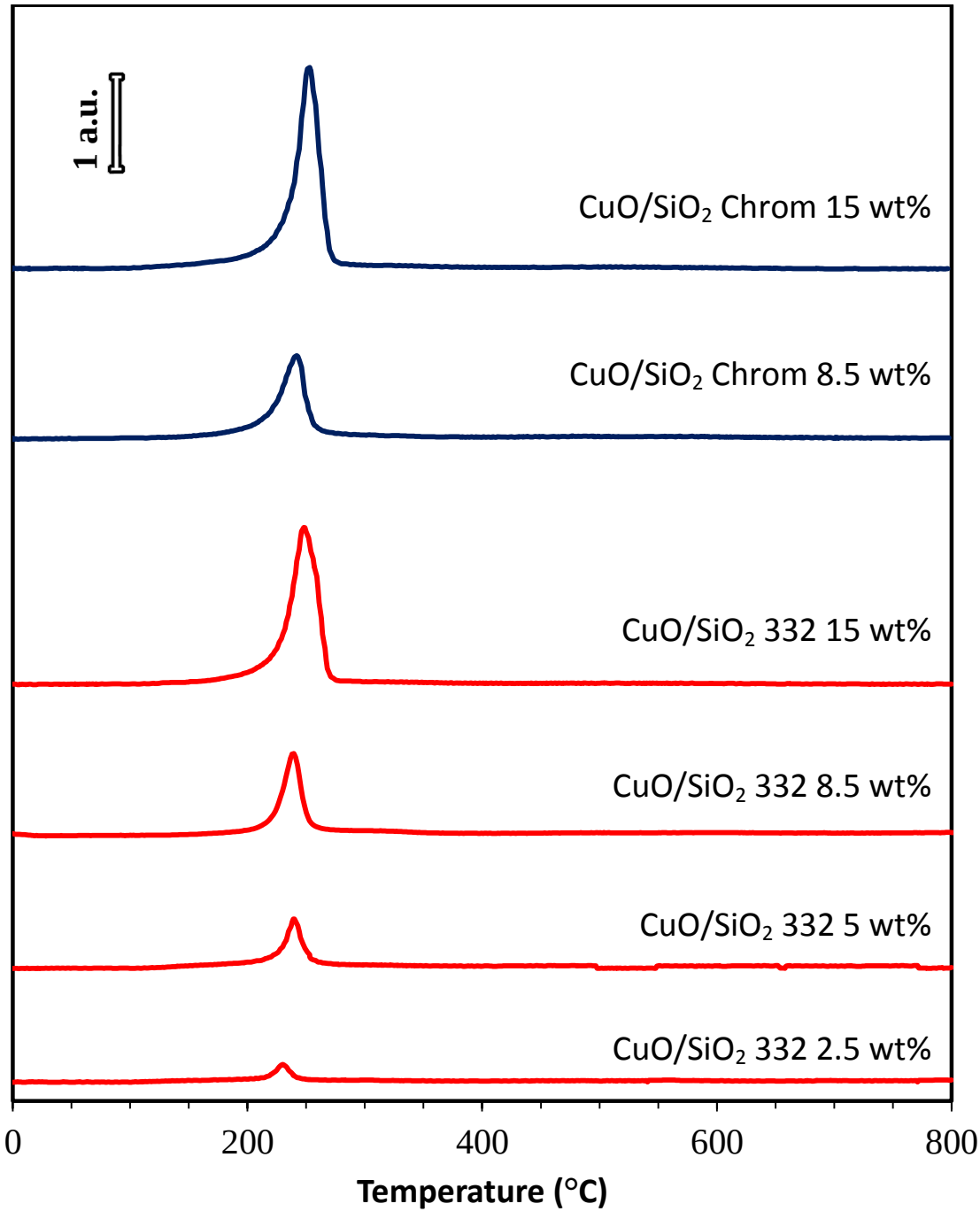

Figure 2.3 TPR profiles of CuO/SiO_2 Chrom and 332 with different copper loading made by CH.

TPR profiles of silica based catalysts show the presence of one single sharp symmetric peak centered around 240 °C. The increase of copper loading does not result in a significant shift in the peak maximum, that remains almost unchanged. On the other hand, as we expected, peak area increases. SiO_2 support does not have an important influence on copper reduction temperature, as shown by the comparison of TPR analysis of SiO_2 Chrom, SiO_2 332 (Figure 2.4) and other silica used (profiles not reported). Based on the literature, such a low temperature is diagnostic of the presence of a highly dispersed copper oxide phase in a single and reducible state, suggesting that small and well-dispersed CuO particles, easily reducible into metallic Cu small particles by treatment with H_2, are produced on catalyst surface after calcination. The reduction of CuO bulk starts indeed at low temperature (around 190 °C), with the maximum shifted to 276 °C due to the broadness of the whole peak, related to CuO dimension. On the contrary CuO/SiO_2 (IW) is less easily reducible (T_{max} = 332 °C) due to the presence of species strongly interacting with the support(Figure 2.4). The formation of a CuO phase was also confirmed by XRD (see further) and is well reported in literature[1] [35] [36] [37].

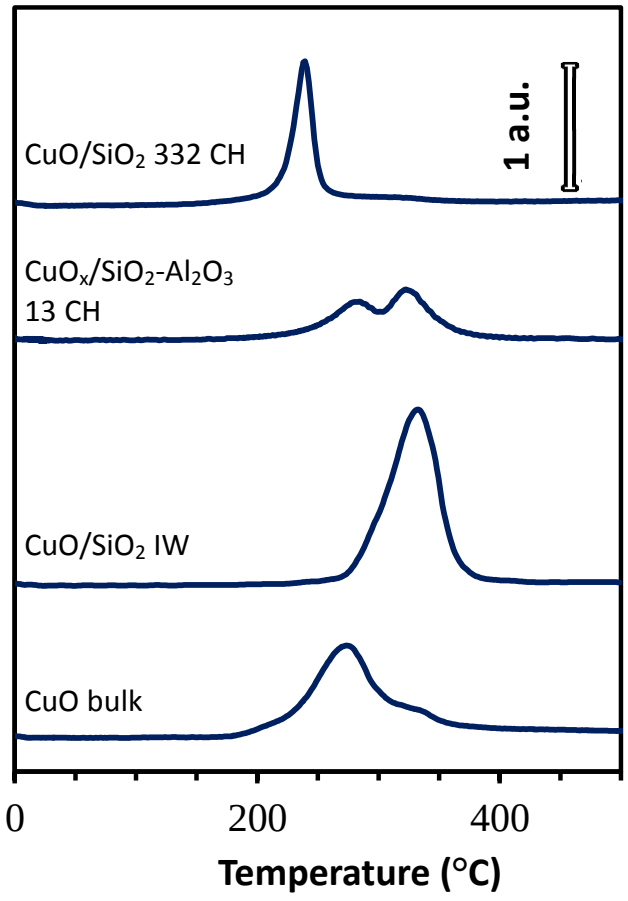

Figure 2.4 TPR profiles of different 8.5 wt% copper catalysts and CuO bulk.

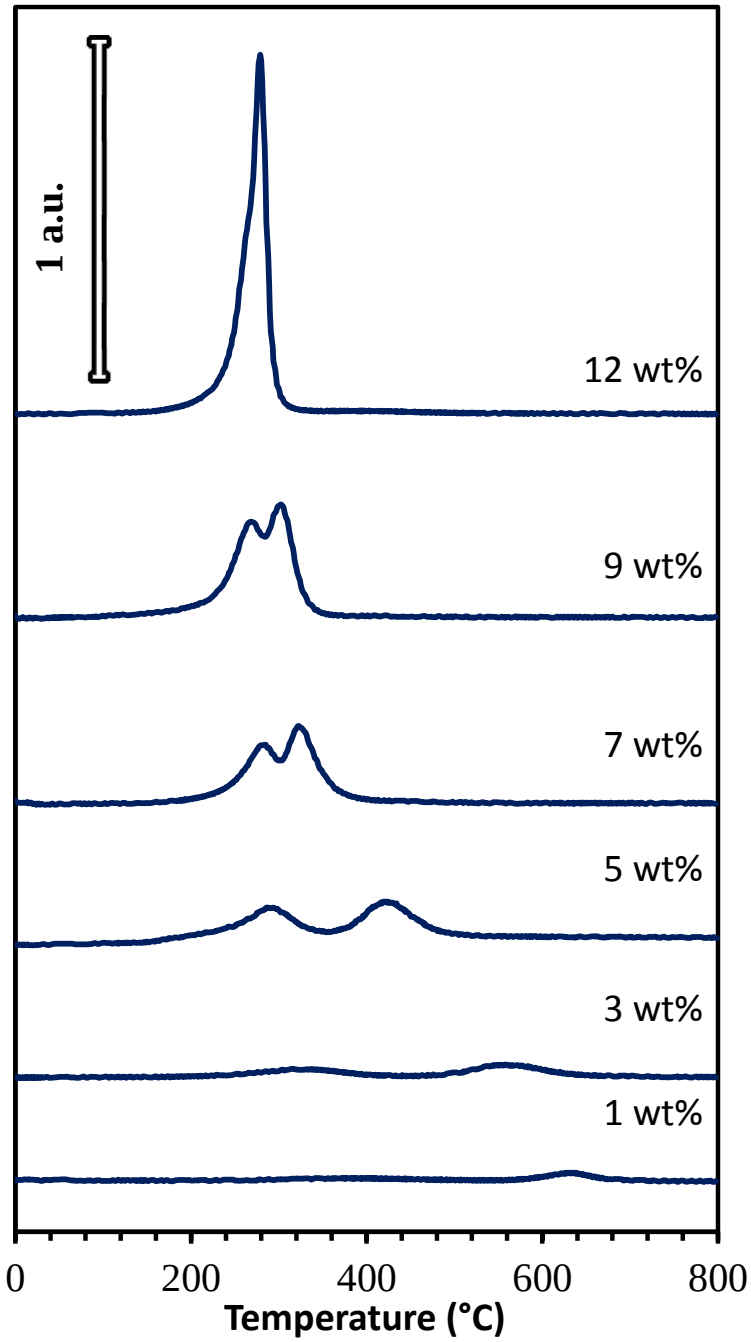

Figure 2.5 TPR profiles of different loading CuO_x/SiO_2-Al_2O_3 CH catalysts.

TPR profiles of Cu/SiO_2-Al_2O_3 13 (Figure 2.5) indicate a very different situation. Low loading copper samples show high temperature reduction peaks (over 400 °C), hardly detectable because of the low copper content. However, in reduction profile of 5 wt% catalyst two broad peaks are clearly visible: one around 288 °C and another one around 422 °C. The peak referred to the higher temperature can be assigned to the reduction of CuO_x in strong interaction with the support (Cu-aluminate-like phase), while low temperature one to the reduction of a Cu (II) species. The easy reducible fraction of metal increases with the amount of copper and CuO_x/SiO_2-Al_2O_3 13 12 wt%

shows a single narrow peak (with a small shoulder) centered at 277 °C. The TPR results are in good agreement with the literature, where oxidized 8 wt% CuO_x/SiO_2-Al_2O_3 is mainly composed of isolated copper species hardly reducible, with an oxidation state ranging from (II) to (I) [23], though this sight, in our case, appears more suitable for lower copper loading.

Therefore TPR analysis put in evidence distinctly that low loading silica and silica-alumina Cu catalysts expose a very different copper phase, while the differences were attenuated at high loadings. This was also confirmed by the different activity of the two materials. We reported, for example, the hydrogenation of 3-methylcyclohexanone to the corresponding alcohols. In this reaction 8 wt% Cu/SiO_2 catalyst reduced at 270 °C revealed outstanding performances (better rate and productivity) than the analogous on SiO_2-Al_2O_3 [1]. However similar TOFs per exposed metal site for the two catalysts were found. In fact, the proposed active site for the hydrogenation is Cu (0): as we expected, in the case of Cu/SiO_2-Al_2O_3 the metallic copper specific surface area measured by N_2O chemisorption is significantly lower than the one measured for Cu/SiO_2, as a consequence of the low reduction extent of copper on silica-alumina support. Cu/SiO_2-Al_2O_3 with a low amount of Cu should be totally inactive in this reaction.

2.3.2 HR-TEM analysis

HR-TEM image (Figure 2.) of 8.5 and 15 wt% CuO/SiO_2 Chrom were recorded. Related histograms are also reported (Figure 2.).

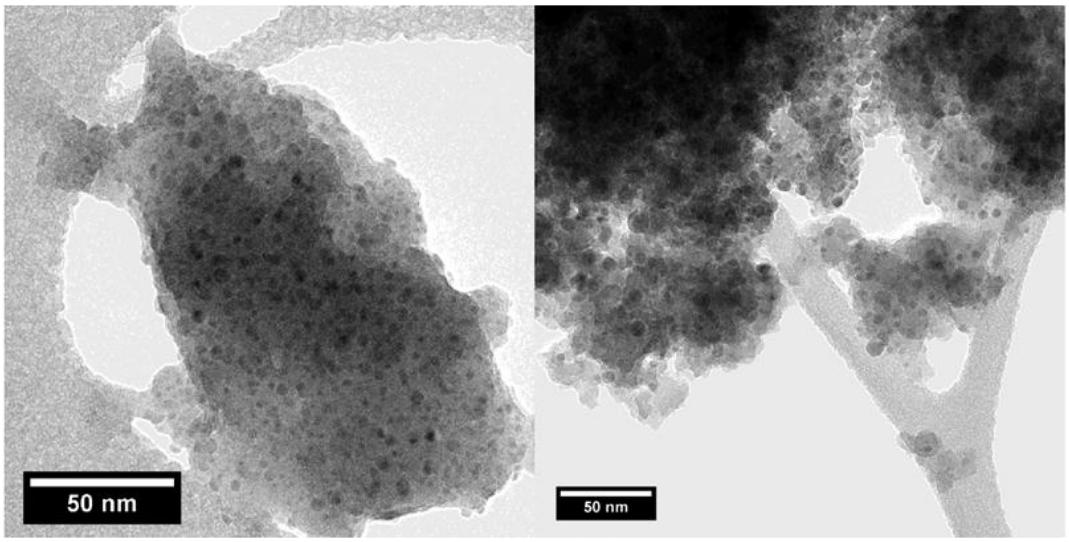

Figure 2.7 HRTEM of CuO/SiO_2: left – 8.5 wt%; right – 15 wt%.

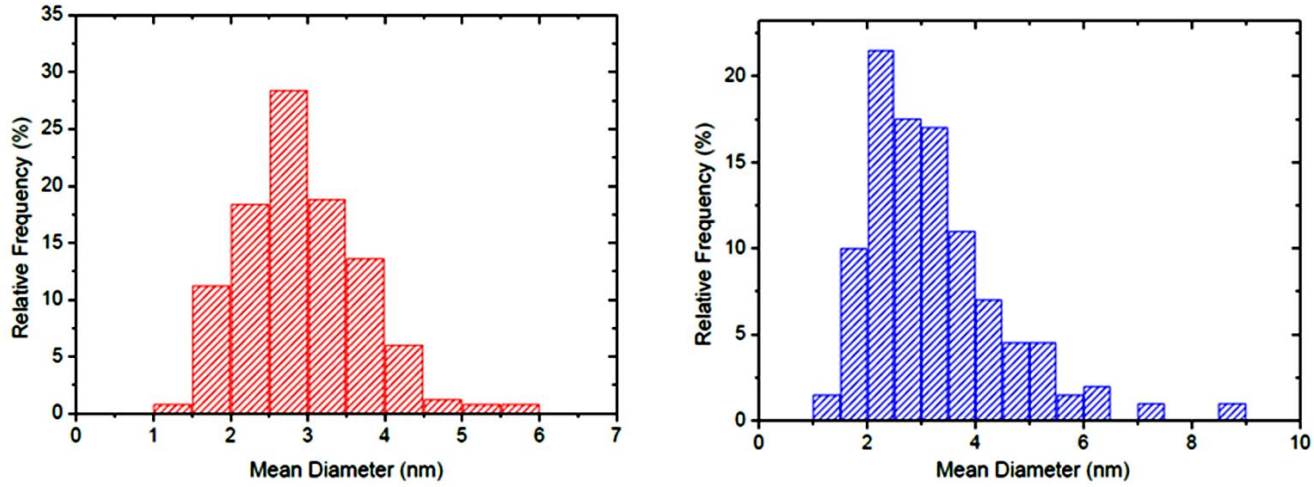

Figure 2.8 Histograms of CuO/SiO_2: left – 8.5 wt%; right – 15 wt%.

The mean diameter of nanoparticles is 2.9 nm for low loading samples and 3.2 nm for high loading one. Moreover very small nanoparticles can be most hardly detectable during TEM count it does not seem to be a coincidence that the size differs much more for smaller crystals (9 wt% catalyst). Finally, as reported later, FT-IR spectra of adsorbed carbon monoxide suggests that the in situ reduced 8.5 wt% catalyst is composed mainly from zerovalent copper cluster (thus very small particles), instead of well-structured particles. In any case, TEM measurements confirm the high dispersion of CH samples.

2.3.3 XRD analysis

XRD patterns of 15% CuO/SiO_2 Chrom IW indicates the reflections typical of CuO only for IW sample, while no significant reflections are registered in the spectrum of 15 wt% CuO/SiO_2 Chrom CH catalyst collected in same condition (2θ =10°-70°, 2θ step=0.02°, 1 sec/step), suggesting that either the structure of copper species is amorphous or their size is very small. However, an increase on the counting time (from 1 to 4 sec/step) results in a very broad signal, due to finely dispersion of copper on CH sample, in agreement also with TEM analysis. On the other hand, the estimated mean particles size for IW catalyst is of 34 nm. From these results, we can say that CH method allows to keep an high dispersion even at very high metal loading, while a classic impregnation method, such as IW, generates more than ten-times bigger particles.

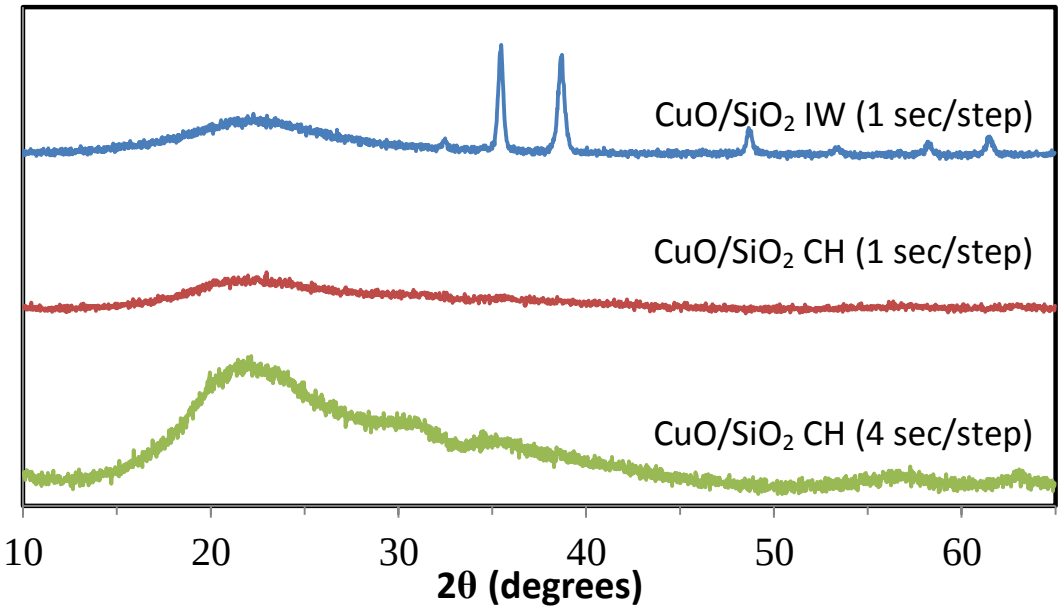

Figure 2.9 XRD spectra of 15 wt% CuO/SiO_2 Chrom catalysts.

We performed XRD analysis also on other silica catalysts prepared by CH and IW obtaining similar results [39] [40].

2.3.4 FT-IR of adsorbed pyridine

Pyridine was chosen as probe molecule for the study of acid properties (detection of Lewis or Brønsted sites) of the studied material. In this investigation pyridine desorption spectra of the fresh catalyst 15 wt% CuO/SiO_2 Chrom made by CH were compared with the spectra of dehydrated 15 wt% Chrom catalyst (vacuum at 270 °C), and of the reduced one (H_2 at 270 °C). Moreover we collected also spectra of bare SiO_2 Chrom support (fresh and dehydrated) and of 15 wt% CuO/SiO_2 Chrom made by IW.

As reported in the literature the FT-IR spectra of adsorbed pyridine show many peaks in the range of 1400-1700 cm^{-1}: bands around 1450 cm^{-1} and 1610 cm^{-1} can be assigned to pyridine bounded to Lewis acid sites, while absorption at 1550 cm^{-1} followed by other peaks near 1620 cm^{-1} and 1640 cm^{-1} is related to the presence of Brønsted acid sites. Finally a band around 1490 cm^{-1} is assigned to a combination of pyridine on Lewis and Brønsted acid sites. At last a weak interaction with the probe molecule (physisorption or hydrogen bond) results in an adsorption band in the range of 1440-1450 cm^{-1} followed by another one at 1580-1600 cm^{-1} [41] [42] [43] [44] [45] [46].

The RT spectra of SiO_2 and dehydrated SiO_2 (Figure 2.) show two characteristic peaks at 1447 cm^{-1} and 1598 cm^{-1} due to the physisorbed (or hydrogen bonded) pyridine to surface OH group of SiO_2 support. In fact, the outgassing at 50 °C leads to almost complete disappearance of this two bands, that are not clearly detectable at 100 °C, indicating only a weak interaction between the probe molecule and silica. Moreover, as reported clearly by Parry, the low shift of the band at 1440 cm^{-1}, present in free pyridine spectrum (ν_{19b}), to 1447 cm^{-1} is not large enough to indicate a Lewis interaction[47] [48] [49]. From the comparison of two spectra of SiO_2 Chrom we can observe that the dehydration does not result in any change in the pyridine absorption.

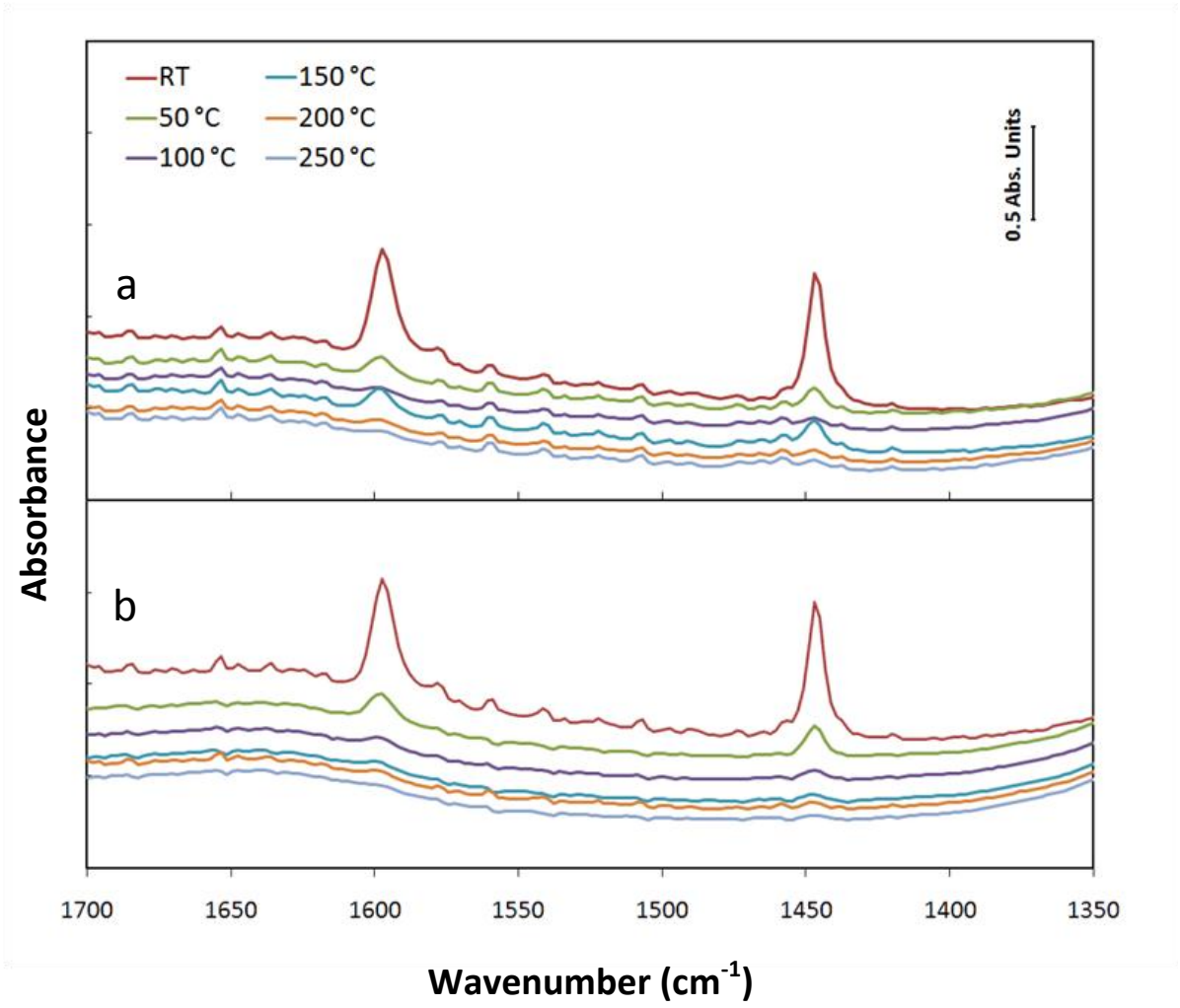

Figure 2.10 Desorption spectra of pyridine on: (a) fresh SiO_2 Chrom; (b) dehydrated SiO_2 Chrom.

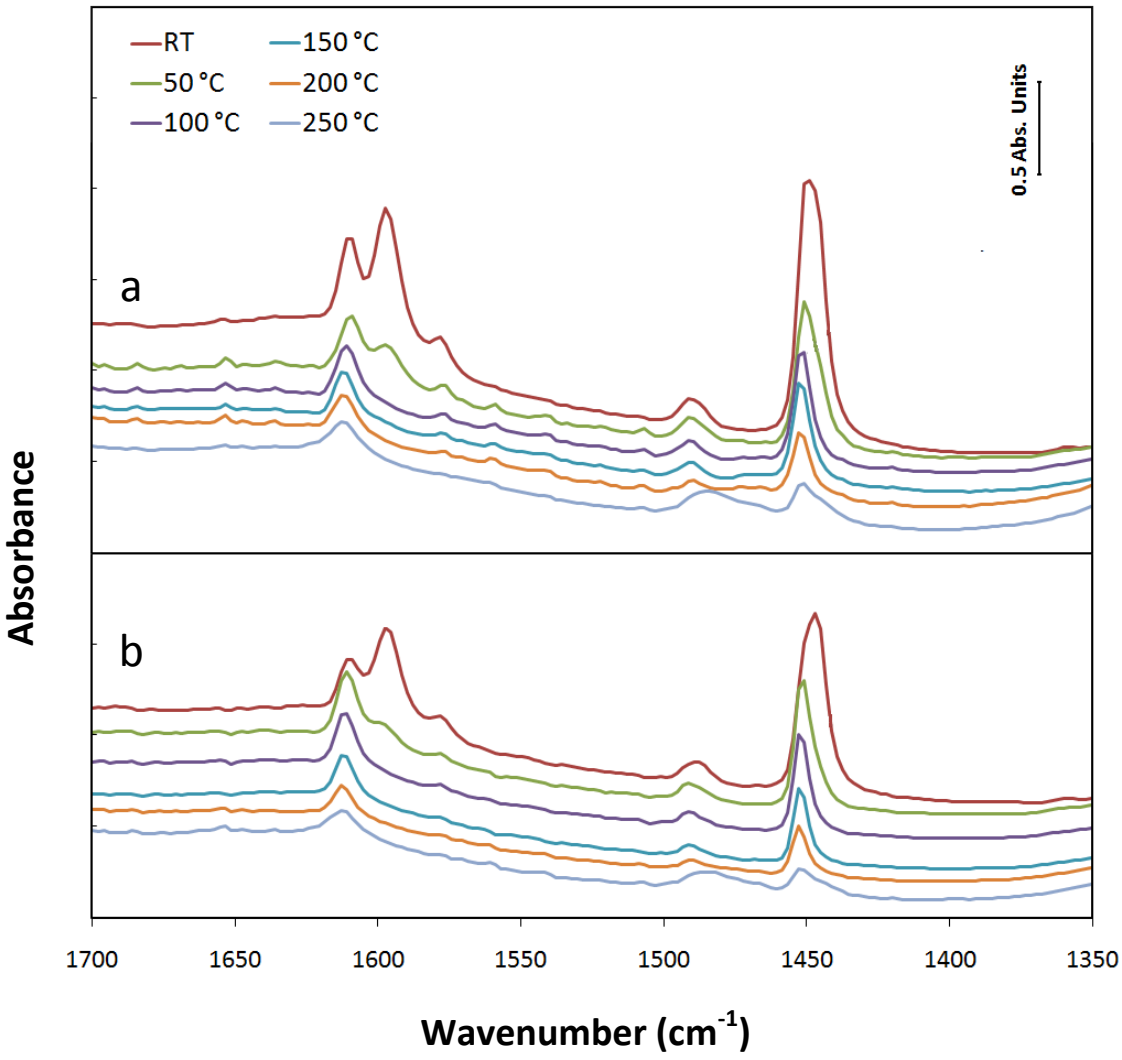

Figure 2.11 Desorption spectra of pyridine on: (a) fresh CuO/SiO_2 Chrom CH; (b) dehydrated CuO/SiO_2 Chrom CH.

Figure 2.11 shows the spectra of CuO/SiO_2 and dehydrated CuO/SiO_2 made by CH. The RT spectra show five main adsorption bands: an intense and broad one at 1449 cm^{-1}, two small peaks at 1488 and 1578 cm^{-1} and finally two intense peaks 1597 and 1610 cm^{-1}. The absorption at 1578 cm^{-1} is not very well characterized: Glen and Dumesic does not clearly distinguish this band between physisorbed pyridine or Lewis/Brønsted acid sites, while Parry assign an adsorption around these frequency to a Lewis acid sites. On the other hand, as above mentioned, the band at 1488 cm^{-1} is not indicative of an specific acid site. By outgassing even at 100 °C the maximum of the broad band at 1449 cm^{-1} shifts to 1453 cm^{-1} indicating the presence of two component: physisorbed pyridine coming from the silica support (with maximum at 1446 cm^{-1}, as we seen before) and a strong absorption at 1453 cm^{-1}, due to the interaction with CuO. The evacuation results also in the desorption of the second physisorption peak at 1597 cm^{-1}. Thus, spectrum recorded at 100 °C only bands at 1611 (slightly shifted respect to the same band at 1610 cm^{-1} at RT), 1488 and 1453 cm^{-1}

are still present, both for fresh and dehydrated CuO/SiO_2. The bands at 1611 and 1453 cm^{-1} can be unambiguously assigned to pyridine adsorbed on Lewis acid sites, while peaks clearly corresponding to Brønsted acid site are not visible (bands at 1550 cm^{-1}, 1620 cm^{-1} and 1640 cm^{-1} are totally absent). Moreover shape and adsorption frequencies of the CuO/SiO_2 spectra recorded at 100 °C (after physisorbed pyridine removal) resemble those of the spectrum of pyridine adsorbed on a Lewis acid (BH_3) presented by Yasuyuki at al.[50]. Again no important differences are seen for hydrated and dehydrated CuO/SiO_2 material.

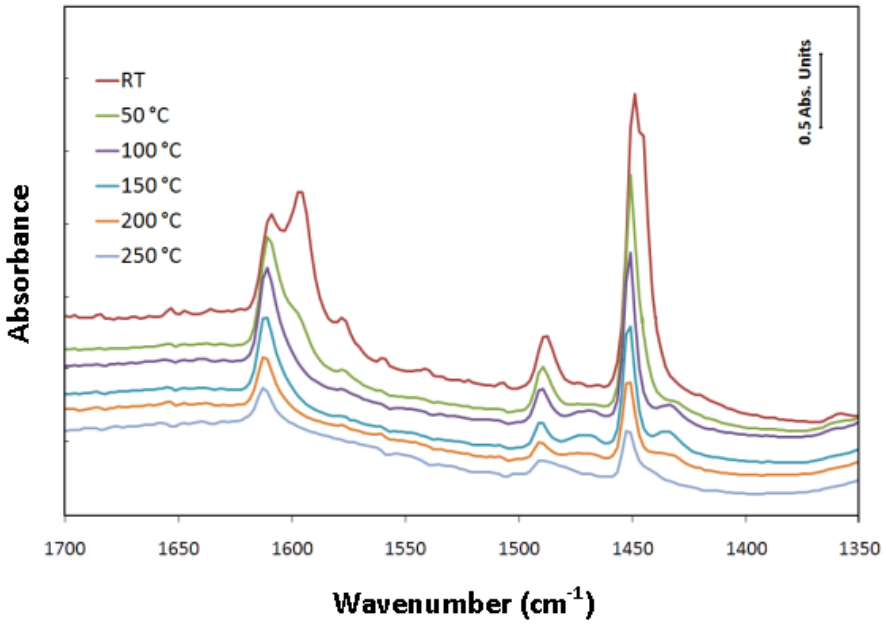

Figure 2.12 Desorption spectra of pyridine on reduced Cu/SiO_2 Chrom CH.

The spectra of reduced catalyst made by CH (Figure 2.12) does not show marked differences with fresh and dehydrate CuO/SiO_2 profiles: the adsorption bands kept after outgassing at 100 °C (or more) at 1453, 1488 and 1611 cm^{-1} are explainable with the presence of Lewis acid sites.

On the other hand desorption spectra of 15 wt% CuO/SiO_2 Chrom made by IW show only weak interaction with pyridine (Figure 2.): the desorption is almost complete even at 100 °C, thus this sample does not show acidity. Figure 2. reports the comparison between pyridine desorption spectra (RT and 150 °C) of CH CuO/SiO_2, IW CuO/SiO_2 and SiO_2: this picture distinctly shows how IW catalyst behaves like Chrom support.

The non-acid behavior of 15 wt% CuO/SiO_2 made by IW is attributed to the low dispersion of the material (as shown by XRD), while the high dispersion of the Chemisorption-Hydrolysis catalyst is responsible of the Lewis acidity. Very small CuO particles can be electronically unsatured in nature and/or the interaction with the support, even if weak, can influence the properties of copper

phase. We confirmed this surprising difference between CH and IW preparation method on 8 wt% copper silica catalysts made on different support other than Chrom (e.g. SiO_2 332 and SBA spectra not reported) [40].

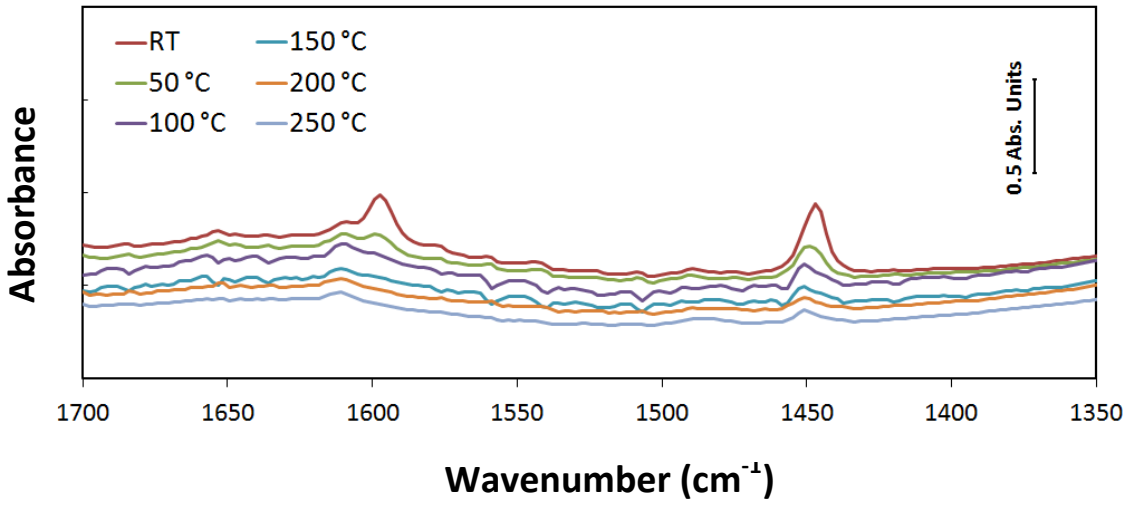

Figure 2.13 Desorption spectra of pyridine on reduced CuO/SiO_2 Chrom IW.

If pyridine desorption analysis can again leave some doubts, in agreement with these experimental evidences we reported the direct etherification of 4-methoxyphenylethanol with 2-propanol over CuO/SiO_2 CH catalysts [1]. Ether formation is traditionally performed with the Williamson reaction starting from an alcohol and a halide by using a strong base for the alkoxide formation. Nonetheless, Brønsted acid catalysts are known to promote ether formation starting from the corresponding alcohols by means of a dehydration process [51]. The bare Chrom silica resulted to be completely inactive under the reaction conditions used (as confirmed also by pyridine desorption profile), whereas the unreduced copper catalyst supported over the same chromatographic silica is able to promote the condensation reaction with excellent selectivity and good activity (60% of conversion and 100% of selectivity after 5 h). The sample prepared by traditional Incipient Wetness technique with the same copper loading resulted to be almost inactive under the reaction conditions used, confirming the peculiar properties given by the particular preparation method used.

A similar behavior was recently reported, as previously discussed in the introduction of this chapters [30].

In conclusion, pyridine adsorption spectra clearly show the presence of Lewis acid sites on both CuO/SiO_2 and Cu/SiO_2, while the presence of Brønsted acid site can be excluded. The dehydration or the reduction do not appear to substantially modify the acidity of starting fresh material. Lewis

acidity is attributed to high dispersion of the sample: low dispersed IW made material does not show any acid features. In the case of Cu/SiO_2-Al_2O_3 catalysts, the proper acidity of the support should not allow to separate the intrinsic acid character of small copper nanoparticles from that of SiO_2-Al_2O_3.

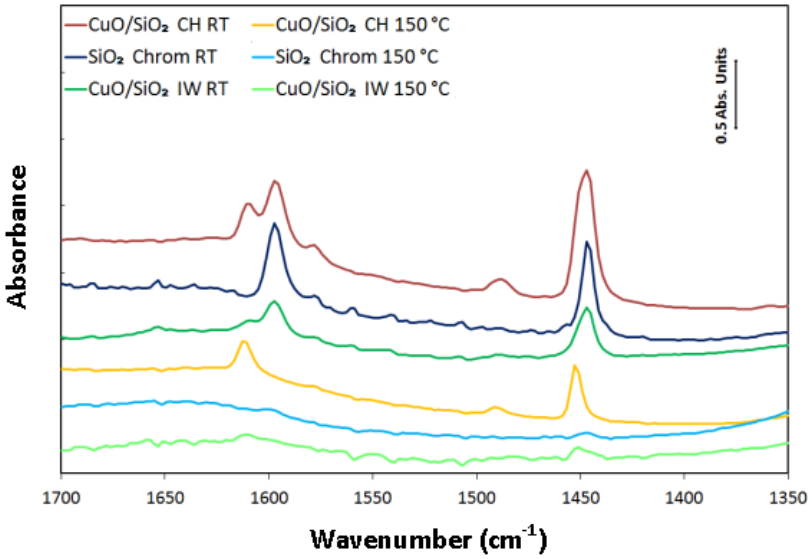

Figure 2.14 Desorption spectra of pyridine (RT and 150 °C) on CuO/SiO_2 CH, CuO/SiO_2 Chrom IW and SiO_2.

2.4 Conclusions

The behaviour Cu/SiO_2 catalysts can be outlined in Figure 2..

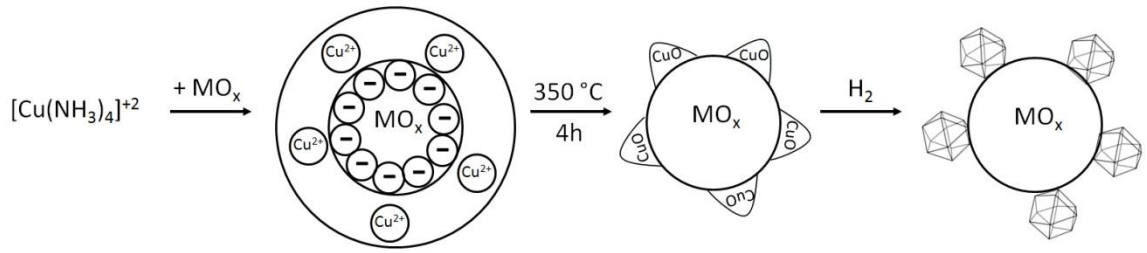

Figure 2.15 Cu/SiO_2 catalysts prepare by Chemisorption-Hydrolysis.

All the characterization technique agree with the formation of finely dispersed phase of CuO on silica, easily reducible to metal copper at any copper loading for CH samples. While unreduced silica catalyst shows acid properties, the metal copper nanoparticles formed after treatment with H_2 keep the acid feature, but, as well reported in the literature, evidence also a good activity in hydrogenation reactions. The size of the particles, as estimated by TEM analysis, is very small (between 1.5-3.5 nm) for all silica supports employed, even if at high copper loading. Usually, literature reports that only low loading (1-5%) catalysts are active, because of the drop of

dispersion as the amount of the metal increases. On the contrary Chemisorption-Hydrolysis method allows one to keep a great dispersion obtaining very small copper particles also to an high metal loading (up to 15%), with a potential beneficial effect on the productivity of the catalysts. The same catalysts prepared by Incipient Wetness present very large copper crystals (34 nm as estimated by XRD). Lewis acidity appears to be truly a consequence of high dispersion: in fact materials made by IW does not show acid behavior both in pyridine adsorption and as catalyst in acid reactions. FT-IR spectra of adsorbed CO on reduced (270 °C) Cu/SiO_2 Chrom made by CH show the presence of well-formed copper crystal exposing (111) facets on 15 wt% catalyst, while 8.5 wt% sample is composed mainly of small zerovalent clusters.

Cu/SiO_2-Al_2O_3 catalysts show a behavior which depends on the copper amount and influences catalytic properties: up to 5 wt% only hardly reducible $Cu^{\delta+}$ ($+1 \leq \delta \leq +2$) is formed on the catalyst, while after this loading a CuO phase easily reducible (at low temperature) to well-formed Cu(0) crystallites begins to form on the surface.

2.5 References

[1] N. Scotti, D. Monticelli, F. Zaccheria, *Inorg. Chim. Acta* 2012, 380, 194;

[2] I. Chorkendoff, J.W. Niemantsverdriet, *Concepts of Modern Catalysis and Kinetics*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2003;

[3] C.-J. Jia, F. Schüth, *Phys. Chem. Chem. Phys*., 2011, 13, 2457;

[4] M. Campanati, G. Fornasari, A. Vaccari, *Catal. Today* , 2003,77, 299;

[5] J. C. Park, J. U. Bang, J. Lee, C. H. Ko, H. Song, J. *Mater. Chem.*,2010, 20, 1239;

[6] M. A. Botavina, C. Evangelisti, Yu. A. Agafonov, N. A. Gaidai, N. Panziera, A. L. Lapidus, G. Martra*, Chem. Eng. J.*, 2011, 166, 1132;

[7] G. W. Coates, *Chem. Rev.*, 2000, 100, 1223;

[8] J. M. Thomas, R. Raja, D. W. Lewis*, Angew. Chem. Int. Ed.*, 2005, 44, 6456;

[9] J. M. Thomas, R. Raja, *Top. Catal.*, 2006, 40, 3;

[10] A. E. Aksoylu, J. L. Faria, M. F. R. Pereira, J. L. Figueiredo, P. Serp, J.-C. Hierso, R. Feurer, Y. Kihn, P. Kalck, *Appl. Catal. A: Gen.*, 2003, 243, 357;

[11] H. O. Pierson, *Handbook of Chemical Vapor Deposition*, Second Edition, Noyes Publications/William Andrew Publishing, LLC Norwich, New York, U.S.A., 1999.

[12] C. Thurier, P. Doppelt, Coord. *Chem. Rev.*, 2008, 252, 155;

[13] V. Dal Santo, F. Liguori, C. Pirovano, M. Guidotti, *Molecules*, 2010, 15, 3829;

[14] X. Wang, P. Sonström, D. Arndt, J. Stöver, V. Zielasek, H. Borchert, K. Thiel, K. Al-Shamery, M. Bäumer, *J. Catal.*, 2011, 278, 143;

[15] A. A. Ponce, K. J. Klabunde, *J. Mol. Catal. A: Chem.*, 2005, 225, 1;

[16] G. Vitulli, M. Bernini, S. Bertozzi, E. Pitzalis, P. Salvadori, S. Coluccia, G. Martra, *Chem. Mater.*, 2002, 14, 1183;

[17] C. Evangelisti, G. Vitulli, E. Schiavi, M. Vitulli, S. Bertozzi, P. Salvadori, M. Bertinetti, G. Martra, *Catal. Lett.*, 2007, 116, 57;

[18] Z. Huang, F. Cui, H. Kang, J. Chen, X. Zhang, C. Xia, *Chem. Mater.*, 2008, 20, 5090;

[19] C. Gonzalez-Arellano, R. Luque, D. J. Macquarrie, *Chem. Commun.*, 2009, 1410;

[20] F. Boccuzzi, A. Chiorino, G. Martra, M. Gargano, N. Ravasio, B. Carrozzini, *J. Catal.*, 1997, 165, 129;

[21] V. Higgs, J. Pritchard, *Appl. Catal.*, 1986, 25, 149;

[22] F. Boccuzzi, A. Chiorino, M. Gargano, N. Ravasio, *J. Catal.*, 1997, 165, 140;

[23] A. Gervasini, M. Manzoli, G. Martra, A. Ponti, N. Ravasio, L. Sordelli, F. Zaccheria, *J. Phys. Chem. B*, 2006, 110, 7851;

[24] S. Bennici, A. Gervasini, N. Ravasio, F. Zaccheria, *J. Phys. Chem. B,* 2003, 107,5168;

[25] F. Liao, Y. Huang, J. Ge, W. Zheng, K. Tedsree, P. Collier, X. Hong, S. C. Tsang, *Angew. Chem. Int. Ed.*, 2011, 50, 2162;

[26] F. Zaccheria, N. Ravasio, R. Psaro, A. Fusi, *Tetrahedron Lett.*, 2005, 46, 3695;

[27] F. Zaccheria, N. Ravasio, R. Psaro, A. Fusi, *Chem. Eur. J.*, 2006, 24, 6426;

[28] H. Yahiro; M. Iwamoto, *Appl. Catal. A: Gen.*, 2001, 222, 163;

[29] A. Corma and H. Garcia, *Chem. Rev.*, 2003, 103, 4307;

[30] F. Zaccheria, F. Santoro, R. Psaro, N. Ravasio, *Green Chem.*, 2011, 13, 545;

[31] M. P. Sibi, G. R. Cook, *Lewis Acids in Organic Synthesis*, ed. H. Yamamoto, Wiley VCH, 2008, pp. 543–574;

[32] F. Zaccheria, N. Ravasio, in: B. Pignataro (Ed.), *Tomorrow's Chemistry Today*, 593 Wiley, VCH, 2008, p. 321;

[33] H. Tounsi, S. Djemel, A. Ghorbel, G. Delahay, L. C. de Menorval, B. Coq, React. *Kinet. Catal. Lett.*, 2004, 81, 33;

[34] B. Bridier, N. López, J. Pérez-Ramírez, *J. Catal.*, 2010, 269, 80;

[35] G.C. Bond, S.N. Namijo, J.S. Wakeman, *J. Mol. Catal.*, 1991, 64, 305;

[36] G.C. Bond, S.N. Namijo, *J. Catal.*, 1989, 118, 507;

[37] F.-W. Chang, W.-Y. Kuo, K.-C. Lee, *App. Catal. A: Gen.*, 2003, 246, 253;

[38] G. Busca, *J. Mol. Catal.*, 1987, 43, 225;

[39] A. Dandekar, M. A.Vannice, *J. Catal.*, 1998, 178, 621;

[40] N.Y. Topsoe, H. Topsoe, *J. Mol. Catal. A:Chem.*, 1999, 141, 95;

[41] A. Gervasini, S. Bennici, A. Auroux, C. Guimon, *App. Catal. A: Gen.*, 2007, 331, 129;

[42] Á. Szegedi, M. Popova, V. Mavrodinova, C. Minchev, *App. Catal. A: Gen.*, 2008, 338, 44;

[43] D. R. Brown, C. N. Rhodes, *Catal. Lett.*, 1997, 45, 35;

[44] G. Busca, G. Martra. A. Zecchina, *Catal. Tod.*, 2000, 56, 361;

[45] V. Sánchez Escribano, C. del Hoyo Martínez, E. Fernández López, J. M. Gallardo Amores, G. Busca, *Catal. Comm.*, 2009, 10, 861;

[46] E. P. Parry, *J. Catal.*, 1963, 2, 371;

[47] R. Ferwerda, J. H. van der Maas, F. B. van Duijneveldt, *J. Mol. Catal. A: Chem.*, 1996, 104, 319;

[48] M. Yurdakoç, M. Akçay , Y. Tonbul, K. Yurdakoç, *Turk. J. Chem.*, 1999, 23, 319;

[49] M. Yasuyuki, H. Keiji, Y. Satohiro, *J. Mol. Catal.*, 1991, 69, L19;

[50] J. G. Larsen, E. Lotero, M. Marquez, H. Silva*, J. Catal.*, 1995, 157, 645;

[51] A. Corma, M. Renz, *Angew. Chem., Int. Ed.*, 2007, 46, 298.

Chapter 3:

Biolubricants and

Monoglycerides

3.1 Biolubricants

The need of renewable and biodegradable lubricants is growing, because environmental concerns about pollution and contaminations. In fact the worldwide lubricant consumption is estimated around 37 million metric tons per year[1], but about 50% of hydraulic liquids are lost by total loss applications, spillage, evaporation and accidents, resulting in severe pollution of soil, water and air[2]. Around 95% of these materials are mineral oil-based or non-renewable. The market for biolubricant is estimated between 1% and 3.6%, but growth rates are higher than for the overall lubricant market. In fact over 90% of all lubricant can be replaced by biolubricants, giving a potential market in Europe of 5 Mt/year.

Lubricant is a material used in order to facilitate the relative motions of solid bodies, minimizing friction and wear between interacting surfaces. Lubricant oils are also employed in removal of heat, prevention of corrosion and transfer of power. In addition, they provide a liquid seal at moving contacts and remove wear particles. In order to carry out these works lubricant oils must have specific physical and chemical properties. One of the fundamental requirements is that the oil should remain liquid in a wide range of temperature. This range is limited between the pour point, at low temperatures, and the flash point, at high temperatures. Pour point should be low in order to ensure that the oil is pump-able when the equipment is started or used at low temperatures[3]. Flash point should be as high to allow the safe operation and minimum volatilization at the maximum operating temperature. Biodegradability is the most important aspect with regard to the environmental impact of a substance. Primary degradation is the first step of the breakdown of a compound, involving the disappearance of a molecule. It is also important the determination of ultimate degradability, or the mineralization of the molecule in CO_2 and H_2O, because it guarantees the safe reintegration of organic material in the natural carbon cycle. The biodegradability depends more on the chemical structure of the lubricant than on its water solubility. All the lubricants that are rapidly biodegradated and non-toxic for human and aquatic environment are called biolubricants. A biolubricant can be plant-oil based or derived from synthetic esters manufactured from modified renewable oils or from mineral-based products. These kinds of materials have many benefits: less emissions, absence of polyaromatic hydrocarbons, compatibility with skin and safeness with respect to normal lubricants. Market of these materials is huge, approximatively 40000 metric tons of biolubricants are sold annually in European Union, and almost similar amount in USA[4]. Plant oils are composed mainly of

triacylglycerol (98%), constituted by different fatty acid chains linked to a glycerol molecule. They can also contain a minor amount of mono and diglycerides (0.5%), free fatty acids (0.1%), sterols and tocopherols (0.4%)[5]. Fatty acids are mainly long chain unbranched aliphatic acids (C_{18}-C_{24}) and can be saturated, unsaturated or polyunsaturated. The presence of one or more double bonds decrease the melting point, and usually they are liquid at room temperature[6]. Mineral oils are instead a complex mixture of C_{20}-C_{50} hydrocarbons, containing linear alkanes (waxes), branched alkanes (paraffinics), alicyclic (naphthenic), olefinic and aromatic species. Mineral oils are cheaper, more stable and readily available than natural oils, and can be found in a wider range of viscosities. Moreover there are some drawbacks related to the use of mineral oils, for example the low molecular weight components, that tend to volatilize thickening the oil during use and decreasing the flash point. Other issues are the presence of heteroatoms and the difference of features related to the origin of the oils. On the other hand, the direct application of plant oils as lubricants has some disadvantages, due to different factors. In fact they have poor oxidative stability, due to the presence of acyl groups and because of the tertiary β-hydrogen on the glycerol backbone, that make thermally unstable the oil.

There are some troubleshooting for this problem: additives or chemical modifications. The first one is easier to be applied. Usually they account 1-2% of total volume in hydrodynamic fluids or 30% in transmission oils. Typical additives are antioxidants, corrosion inhibitors, de-emulsifiers, wear reducers and hydrolysis inhibitors. They are mostly used for mineral and plant oils, but the toxicity of these kind of additives require development of new bio-based materials[7]. On the other hand there are different chemical transformations in order to improve technical properties of lubricants and their thermal stability. The main transformations are: epoxidation, estolides formation and transesterification with polyols[8].

One of the most important lubricant is trimethylolpropane trioleate, industrially produced by reaction between trimethylolpropane and free fatty acid or esters, catalyzed by homogeneous or heterogeneous catalysts such as mineral acids, acidic oxides or enzymes[9].

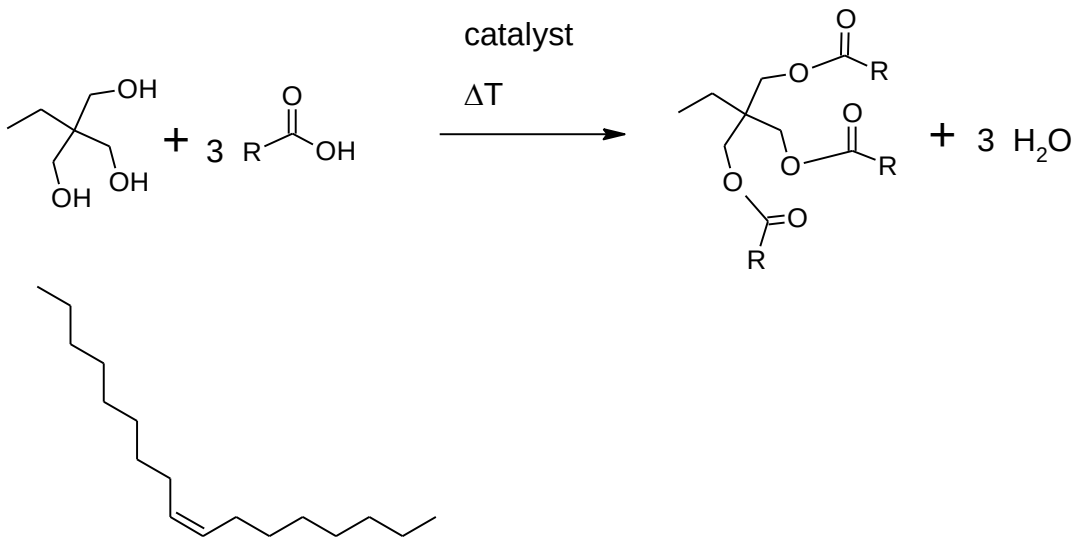

Figure3.1 Esterification of oleic acid and trimethylolpropane to give trimethylolpropane trioleate

By comparing three different catalysts, two heterogeneous (silica-sulphuric acid and Amberlyst 15) and one enzyme (immobilized lipase B from C. Antarctica, commercially known as Novozym 435) it is possible to see that all three solid materials were able to efficiently esterify oleic acid and trimethylolpropane. All three catalysts reach conversions close to 80% in 24 hours, but only the ester obtained with Novozym 435 shows a Gardner index of 2, thus indicating a very clear product color. In the opposite ways the two solid acidic catalysts give a brown product.

3.2 Monoglycerides

Biodiesel production from oils or fats transesterification is a quite inefficient reaction, in fact a huge amount of glycerol is obtained as co-product, accounting for around 10% of the biodiesel production. Considering the world production of biodiesel, 28 million tons per year only for European Union, USA, Brazil and Argentina, the glycerol surplus is becoming a very urgent environmental and economic problem, because of its depreciation, biodiesel producers are forced to burn glycerol or to sell it without refining[10]. Already exist some interesting utilization for glycerol, for example it is used in food products, cosmetics and pharmaceuticals industry, liquid detergents and antifreeze[11]. Other interesting uses for this biomass-derived compound are: synthesis of hydrogen[12], liquid fuels[13], fuel additives[14] and chemicals[15]. Among the chemical commodities, monoglycerides play importance big role, because of their chemical structure.

Indeed the general formula for a monoglyceride consists in a hydrophilic head and a hydrophobic tail, that impart surfactant and emulsifying properties.

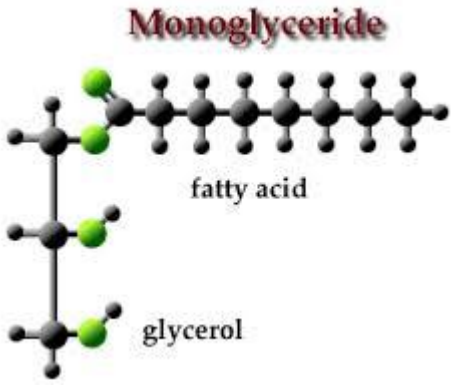

Figure 3.2 General monoglyceride structure

Therefore monoglycerides can help in mixing hydrophobic and hydrophilic substances and are very appreciated in food, detergents, plasticizer, cosmetics and pharmaceutical formulations. A monoglyceride is the monoester of glycerol and one molecule of a fatty acid and can be synthetized by 3 different pathways: 1) the direct esterification of glycerol and free fatty acid, 2) the transesterification of fatty acid methyl esters (FAMEs) and glycerol or 3) triglycerides glycerolysis. All these methods present pros and cons, but generally transesterification of FAMEs is considered better, as the starting material is not corrosive as free fatty acids and are less hydrophobic than triglycerides, showing better solubility in glycerol. Anyhow the real problem is to catalyze the reaction. In fact enzyme are expensive and not very efficient, due to their difficult to be reused. Homogeneous catalysis with strong mineral acid or base give problem of corrosion and disposal of spent acid or basic materials. The alternative is heterogeneous catalysis, with evident environmental and technical advantages: the possibility to separate and reuse the catalyst, the biggest conversion because of the possibility to tune the structure and the acid-base properties of the catalyst. It is also possible to improve the reaction selectivity, thus avoiding additional purifications steps like the expensive molecular distillation, for obtain food or pharmaceutical grade monoglycerides[16].

3.3 Results and discussion

3.3.1 Polyolesters

The synthesis of a wide series of polyolesters has been carried out by direct esterification of different fatty acids with trimethylolpropane (TMP) in the presence of different amorphous solid acids.

The use of solid acids allows one to overcome several significant drawbacks related to the widespread use of sulfuric acid or organosulfonic acids. Thus, solid acids are not corrosive, they can be easily separated from reaction mixtures, their use allows one to avoid neutralization and washing steps forming large amount of waste water and inorganic salts to be disposed of and sometimes they can be reused. All these properties ensure that the process is green and environmental sustainable.

Textural properties of the solid used are reported in Table 3.1. Their surface areas fall in the range 300-500 m^2/g, they show high porosity with pore size in the range of mesoporosity, that is 15-200 Å . All of them are silica modified with a second oxide with Lewis acid activity, namely alumina, titania or zirconia.

Table 3.1 Textural properties of solid used

Oxide	**% co-oxide**	**Surface area (m^2/g)**	**PV (ml/g)**	**DP (Å)**
SiO_2		480	0,75	60
SiO_2-Al_2O_3	0.6	488	1,43	117
SiO_2-Al_2O_3	13	485	0,79	33
SiO_2-TiO_2	2,3	297	1,26	84
SiO_2-ZrO_2	4.7	405	2,19	167

Dispersion of this second oxide on the surface of silica enhances their Lewis acid activity as shown by the FT-IR spectra of absorbed pyridine (Figure 3.3).

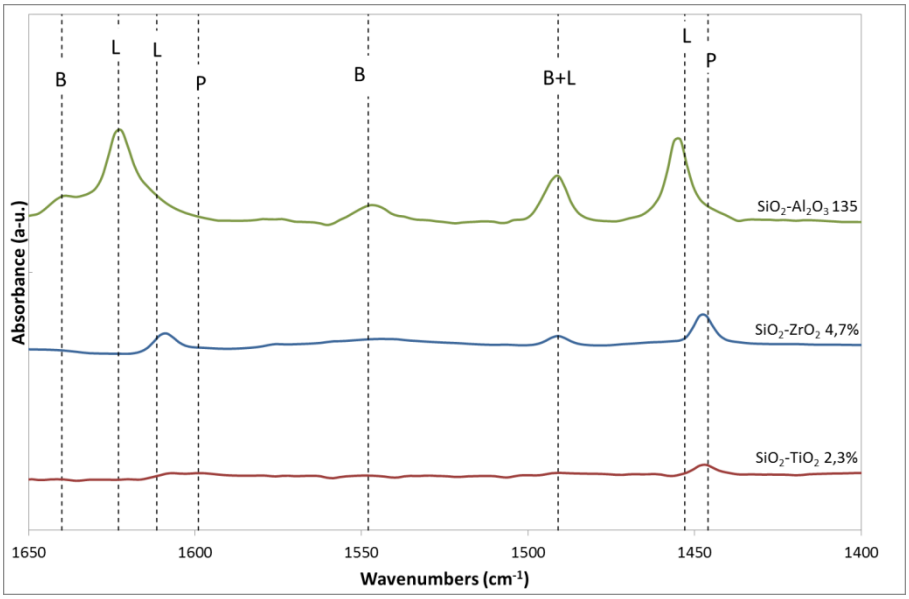

Figure 3.3 FT-IR of adsorbed pyridine of three different mixed oxides

Reactions were carried out without solvent by using a Claisen condenser and a weak nitrogen flow, in order to make easier the removal of water formed in the esterification thus shifting the equilibrium position toward product formation.

Results obtained are reported in Table 3.2. From the table it is apparent the solid materials used are very active, giving up to 99% conversion. This high activity may be due to both dispersion of the Lewis acid sites and high porosity allowing the access of this big molecules.

Table 3.2[a] Results related to esterification reactions

Entry	Polyol	Fatty Acid	Catalyst	Exp. Cond.	t (h)	Conv (%)	Sel (%)
1	TMP	Nonanoic (C9)	SiO_2-ZrO_2	5% exc TMP	6	99	-
2	TMP	"	SiO_2-TiO_2	5% exc TMP	6	94	-
3	TMP	"	SiO_2-Al_2O_3 135	5% exc TMP	6	94	-
4	TMP	Caprilic (C8)	SiO_2-ZrO_2	5% exc TMP	6	98	-
5	TMP	"	SiO_2-TiO_2	5% exc TMP	6	92	-
6	TMP	"	SiO_2-Al_2O_3 135	5% exc TMP	6	92	-
7	TMP	Oleic (C18)	SiO_2-ZrO_2	5% exc TMP	6	98	-
8	TMP	"	SiO_2-TiO_2	5% exc TMP	6	95	-
9	TMP	"	SiO_2-Al_2O_3 135	5% exc TMP	6	89	-
10	TMP	"	SiO_2-TiO_2	stoichiometric	6	87	-
11	NPG	Oleic	SiO_2-ZrO_2	5% exc fatty acid	6	92	-
12	PE	Oleic	SiO_2-ZrO_2	5% exc fatty acid	6	99	-
13	TMP	Oleic	SiO_2-ZrO_2 [c]	5% exc fatty acid	6	99,8	95
14	TMP	Oleic	SiO_2-ZrO_2 [b]	5% exc fatty acid	6	99,3	96
15	TMP	Oleic	SiO_2-ZrO_2	5% exc fatty acid	6	99,0	91
16	TMP	Oleic	SnO	"	6	92,0	89

[a] = 2,5% by weight; b = 5%; c =10%

According with his equilibrium nature, the esterification reaction carried out under stoichiometric conditions gave poor results in terms of activity (entry 10) , while both an excess of the alcohol

and an excess of the fatty acid gave conversion higher than 90% . Concerning the effect of the C atoms chain length in the fatty acid molecule no significative differences were observed, particularly with Silica zirconia, as shown by Figure 3.4 reporting conversion vs time for the reaction of the 3 different fatty acids with TMP.

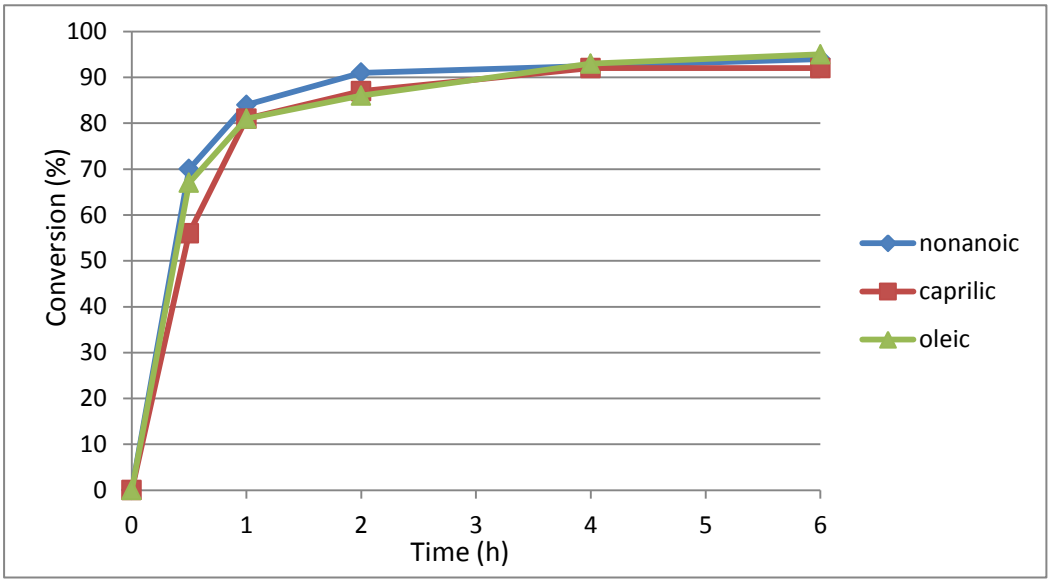

Figure 3.4 Conversion vs Time graph for reaction between TMP and three different fatty acids

This is quite interesting because quite big differences were reported for sulfuric acid adsorbed on silica, a sulphonic resin, Amberlyst 15 and a immobilized lipase , Novozym 435 (Figure 3.5)[9].

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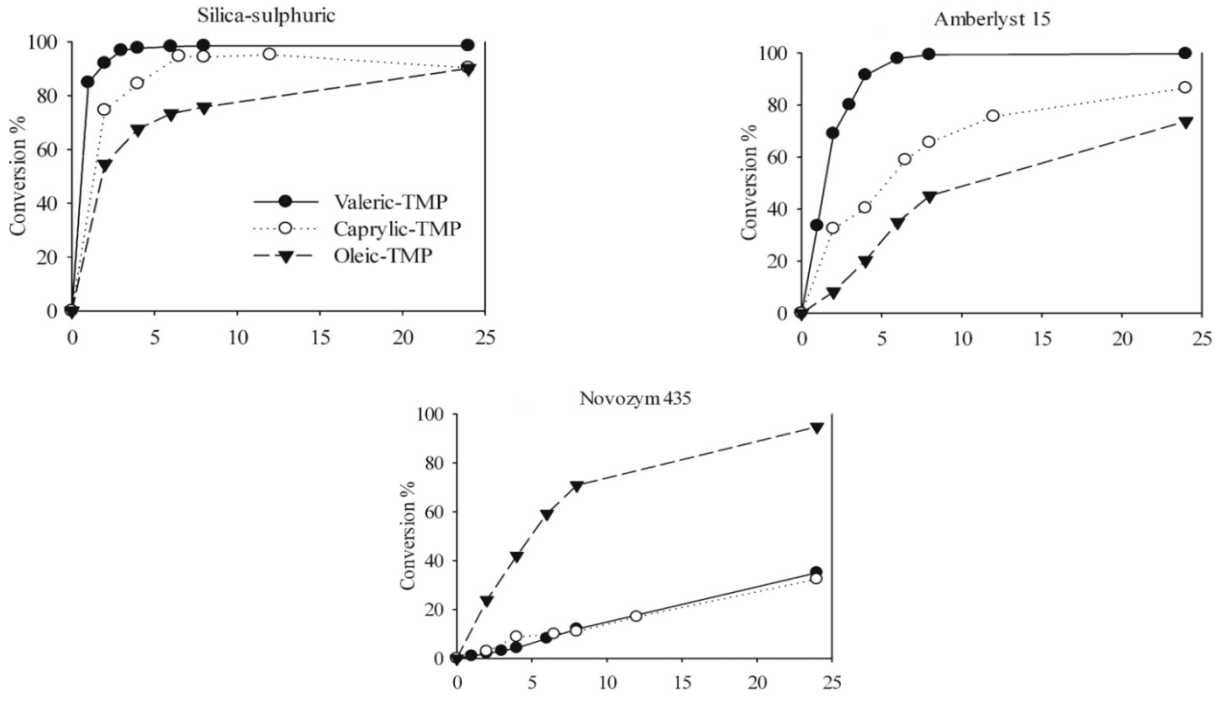


Figure 3.5 Conversion vs Time graph for three different catalysts in the esterification of oleic acid with TMP

In the first two cases oleic acid was found to react slower and not reaching 100% conversion in 25 hours whereas with the enzyme it was possible to reach total conversion in 25 hour for oleic acid, but the system don't work for the other two, namely caprylic (C8) and valeric (C5).

Very high activity was observed in the presence of Silica zirconia, particularly with oleic acid also with neo-pentylglycol and pentaerithrol as polyols (entry 11 and 12). In the case of oleic acid and TMP the activity was higher than that observed in the presence of SnO, widely used in the lubricant industry, under the same experimental conditions (entry 15 vs 16) while a quantitative transformation could be obtained by operating with an excess of fatty acid. Moreover, selectivity to tri-esters was very high.

This very high selectivity toward tri-esters is witnessed by the excellent physical properties of the raw esters, reported in Table 3.3

Table 3.3 Physical properties of obtained triesters

Entry	**Acid**	**Catalyst**	**Viscosity (cSt)**		**Viscosity Index**
			40°C	100°C	
1	Caprilic	SiO_2-ZrO_2	19,9	4,3	124
2	Nonanoic	SiO_2-ZrO_2	22,3	4,5	118
3	Oleic	SiO_2-ZrO_2	46,6	9,3	188
4	Oleic	SiO_2-TiO_2	46,7	9,1	181

It is worth noting that when these reaction are carried out with Brønsted acids, such as sulfuric acid, sulfonated silicas or sulfonated resins selectivity is much lower as due to the reactivity of sulfuric acid with the double bond in the fatty acid molecule that causes the darkening of the product due to formation of estolides or polymers[9]. In the case of solid acids tested here only in the presence of silica alumina we could observe a darkening of the mixture in agreement with the Brønsted–like character of this solid (Figure 3.6).

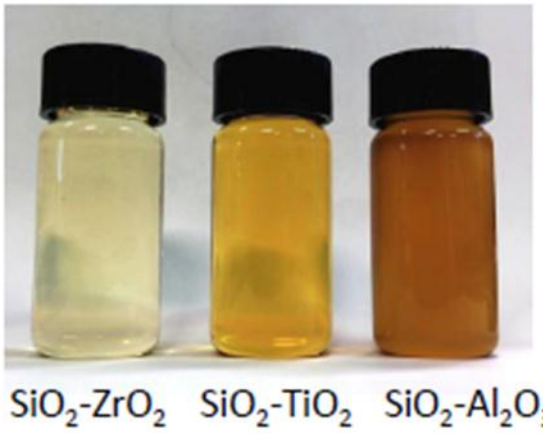


Figure 3.6 Aspect of the triolesters obtained with different acid mixed oxides

However, the search for estolides, using gel-permeation chromatography, in the reaction mixture of oleic acid with TMP gave negative results.

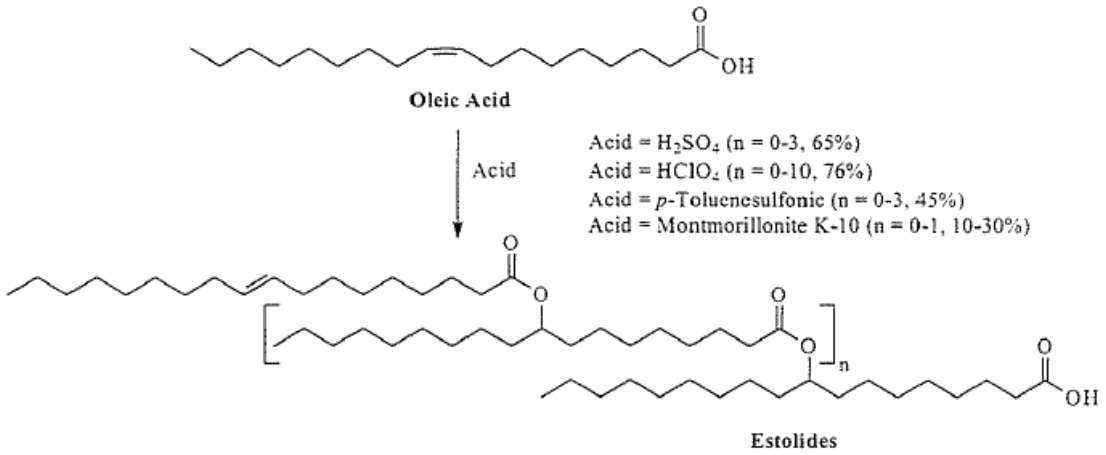


Figure 3.7 Estolides formation

To extend the scope of this work, I've performed esterification of different fatty acids, in particular lauric and valeric, with glycerol, obtaining triglycerides. The reaction condition are the same, except for the temperature (170°C for lauric and 150°C for valeric) because of the lower boiling point of these acids.

Table 3.4 Esterification of glycerol with different fatty acids

Entry	Polyol	Fatty Acid	Cat (%)	Exp. Cond.	t (h)	Conv (%)	Sel (%)
1	Gly	Lauric	SiO_2-Al_2O_3 135(2,5%)	stoichiometric	6	72	49
2	Gly	Lauric	SiO_2-TiO_2(2,5%)	stoichiometric	6	70	56
3	Gly	Valeric	TRYSIL 300 (2,5%)	stoichiometric	6	65	33
4	Gly	Valeric	SiO_2-Al_2O_3 0,6% (2,5%)	stoichiometric	6	64	30
5	Gly	Valeric	TRYSIL (2,5%)	stoichiometric	6	65	33
6	Gly	Valeric	TRYSIL (5%)	stoichiometric 170°C	6	75	94
7	Gly	Valeric	SiO_2-TiO_2(5%)	Stoichiometric 170°C	6	76	77

Valeric acid was chosen as substrate because di and trivalerate glycerides are compatible with diesel in some important properties, providing also lubricity benefits to diesel[17].

There are numerous differences between glycerol and TMP, in fact all the conversion are lower respect the TMP. Lauric acids give satisfactory conversions and with silica-titania acceptable selectivity in triglycerides are reached (entry 2). In the case of valeric acid the reaction carried out at 150°C (entry 3,4, and 5) shows low conversions and bad selectivity. This is problematic in the separation step, that usually request a very expensive molecular distillation. In order to improve both conversion and selectivity I try to increase temperature and catalyst loading (entry 6 and 7). Surprisingly the conversions increase a little bit, but with trysil catalyst the selectivity reach 94%.

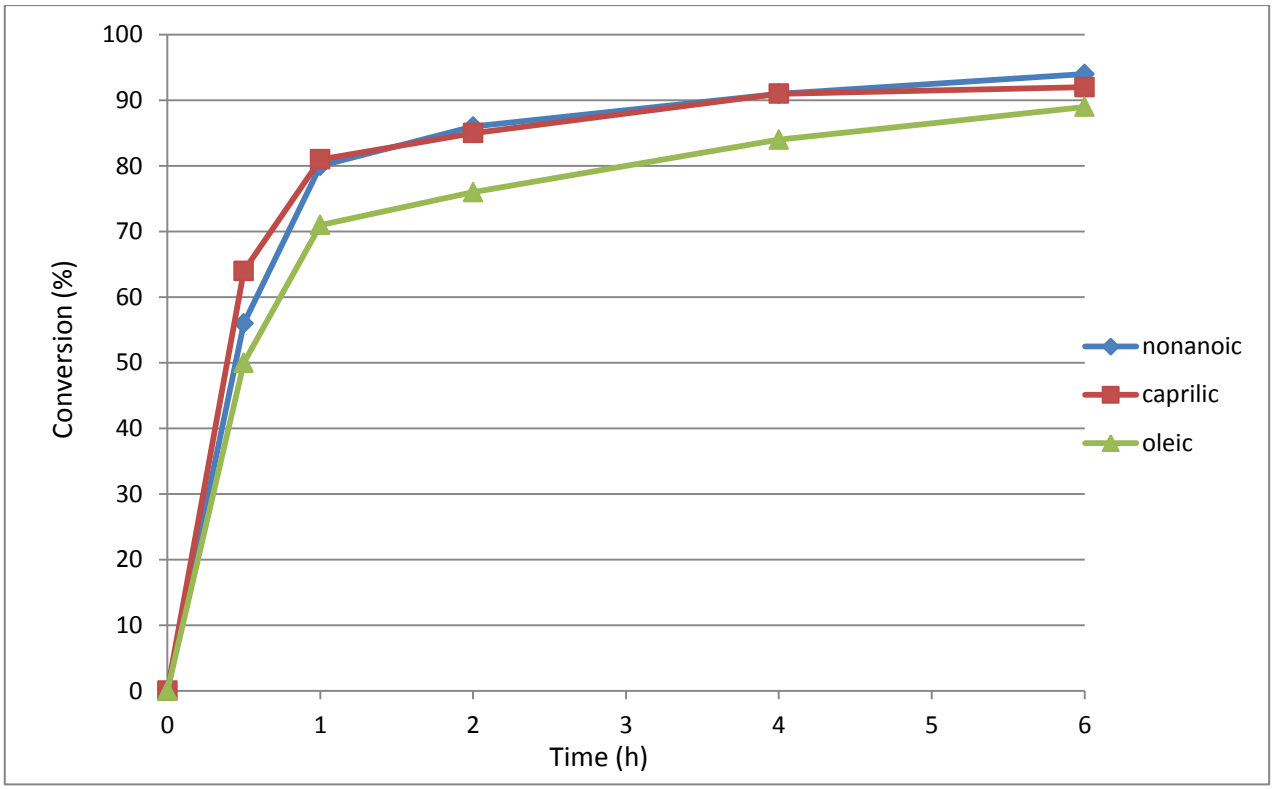


Figure 3.8 Esterification of TMP with different fatty acids and silica-alumina as catalyst

In the case of silica-alumina we can see a marked difference between the acids, in fact oleic acid convert (Figure 3.8).

3.3.2 Monoglycerides

We used the same approach ant the same catalysts to produce monoglycerides.

In the literature there are a lot of examples of synthesis of lauric acid (C12) monoglycerides using mesoporous acid solids, showing Brønsted acidity, like MCM-41 functionalized with sulfonic groups or SBA-15 also with $–SO_3H$ groups. As shown in Table 3.5 generally both selectivity and conversion are not satisfactory, except for sulfonated silicas. The catalyst loading is high (up to 13.5 %), sometimes there is the need to carry out the reaction under vacuum and to use a glycerol:acid ratio of 4:1. Above all this huge amount of glycerol poses big separation problems in the purification step. For all of these drawbacks we think to use solid acid catalysts with Lewis acidity for perform the same reactions, and here I'll show the results.

Table 3.5 Literature data for monoglycerides of lauric acid

Catalyst	Cat loading (%)	Gly/FFA	T(°C)	t (h)	Conv (%)	Sel (%)	Yield (%)
H-Beta	7.5	1:1	100	10		20	
H-USY	2.3	1:1	110	24	58		36
Amberlyst15	2.3		110	12			44
Silica-SO_3H	2.3		110	8	80		51
HMS-SO3H			"	10	80	65	52
MCM41-SO3H	2.3		"	24	75	71	53
"	7.5		"	"	80	75	60
SZ SBA-15*	13.5	4:1	160	6	62	68	42
SBA15-SO_3H		"			94	70	66
pTSA	0.5			4			44

- 508 mbar

These literature results are comparable with those obtained with our solid acidic catalysts. In particular with SiO_2-TiO_2 we reached conversions, selectivities and yields very similar to those of SZ SBA-15 and SBA15-SO_3H. But authors use an glycerol/free fatty acid ratio of 4:1, we used an 3:1 ratio allowing a saving of glycerol. In the other cases data are similar to our results, and it is important to note that high selectivity and yields in monoglycerides facilitates or avoiding the subsequent expensive step of molecular distillation.

Table 3.6 Our results for monoglycerides formation

Entry	Fatty Acid	Catalyst	Gly/FFA	Conv (%)	Mono (%)	Di (%)	Tri (%)	Yeld (%)
1	Lauric C12	SiO_2-Al_2O_3 135	1:1	76,2	49,8	43,5	6,4	37,9
2	"	SiO_2-TiO_2	"	86,0	42,4	50,2	7,4	36,4
3	"	TRISYL 300	"	81,8	49,2	44,7	6,1	40,2
4	"	TRISYL 300	3:1	84,4	62,0	32,1	6,0	52,3
5	"	SiO_2-TiO_2	"	93,9	62,4	32,9	4,7	58,6
6	Valeric C5	TRISYL	1:1	91,8	31,3	33,7	35,0	28,7
7	"	SiO_2-Al_2O_3 135	"	81,0	72,2	26,2	1,6	59,0
8	"	SiO_2-TiO_2	"	84,9	74,3	24,4	1,3	63,1
9	"	SiO_2-Al_2O_3 0.6%	"	83,5	64,5	33,1	2,4	53,4
10	"	TRISYL	"	81,0	64,1	32,9	3,0	52,0
11	Stearic C18:0	SiO_2-TiO_2	1:1	93,9	52,7	28,4	18,9	49,5
12	"	TRYSIL	"	85,6	40,8	42,3	16,9	35,0
13	"	SiO_2-Al_2O_3 135	"	86,9	21,1	44,0	34,9	18,3
14	"	SiO_2-ZrO_2	"	90,6	14,9	53,4	31,7	13,5
15	"	SiO_2-TiO_2	2:1	93,3	52,2	42,1	5,7	48,7
16	"	TRYSIL	"	91,7	43,3	41,1	15,6	39,7
17	Oleic C18:1	SiO_2-TiO_2	1:1	99,0	49,0	20,0	29,0	48,5
18	"	SiO_2-Al_2O_3 0.6%	"	97,0	37,0	62,0	<<1,0	35,9
19	"	SiO_2-Al_2O_3 135	"	96,0	78,0	19,0	2,0	75,0
20	"	SiO_2-ZrO_2	"	97,0	77,0	20,0	2,0	74,7

In order to compare our catalysts (Table 3.6) with literature we started to perform reaction with glycerol and lauric acid.

For the first three entries I've used an equimolar quantity of glycerol and lauric acid, obtaining good conversion, up to 86%, but scarce selectivity in monoglycerides. Bringing the molar ratio

glycerol:acid to 3:1 (entries 4 and 5) is possible to increase a bit conversions and much more selectivity. Anyway our catalytic systems are comparable with literature with regard to selectivity and conversion.

I've tried also to synthesize monoglycerides of valeric acid, that are important product for feed animal industry. In entry 6 the reaction was carried on at 170°C and with 5% of catalyst, we can observe a good conversion, but a statistical product distribution. Then for the other reaction I've lower the temperature to 150°C and the catalyst loading to 2,5%.

The changes have the effect to decrease a bit conversions, but selectivity in monoglycerides where more than doubled. In particular silica-titania (entry 8) shows the best performances.

Another acid that I've used is stearic acid, the conversions appears very good for all entries, so we tried to increase glycerol:acid ration up to 2:1 (entries 15 and 16), trying to enhance selectivity. The result show an increase in monoglycerides selectivity, but also a diglycerides selectivity at the expense of triglycerides. Again silica-titania seem s to be the best catalyst for this reaction, with glycerol:acid ratio 1:1.

The last acid was oleic and it was chosen because is monoglycerides are very used in food industry. In this case our results are very good, in fact it's possible to reach almost complete conversion in all cases and very good selectivity to monoglycerides with silica-zirconia (entry 20) and silica-alumina (entry 19).

The different behavior of stearic and oleic acid can be explained by their molecular structure. In fact stearic acid is a linear molecule (Figure 3.9), and after the formation of a molecule of monoglyceride there is no stearic hindrance for a second molecule of acid to react and form diglycerides. Oleic acid present a double bond in a cis conformation (Figure 3.10), that create a folding of the molecular structure, that prevents the access to a second molecule of acid.

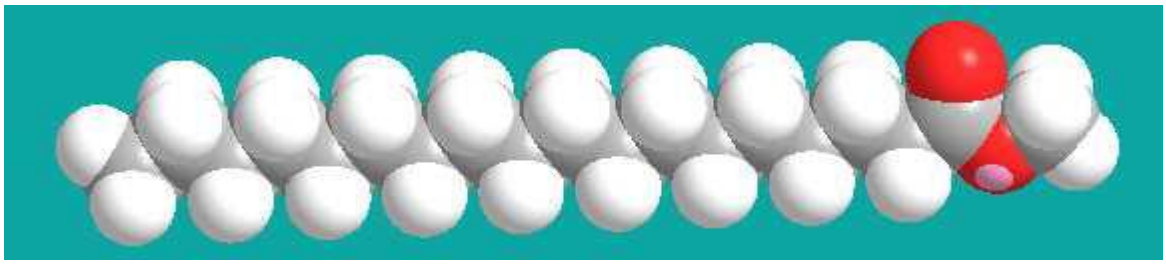


Figure 3.9 Stearic acid conformation

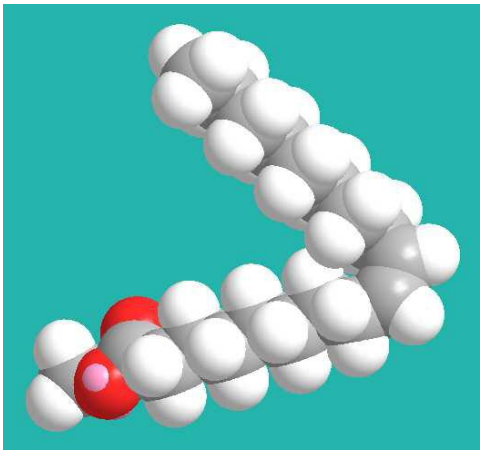


Figure 3.10 Oleic acid conformation

3.4 Experimental part

3.4.1 Chemicals

All fatty acids (oleic, lauric, stearic and valeric) were purchased from Sigma Aldrich, glycerol and trimethylolpropane (TMP) were purchased from Sigma Aldrich. Sodium hydroxide solution 0,1N Fixanal, ethyl ether and absolute ethanol were purchased from Sigma Aldrich. All reactions were performed in glassware equipment.

3.4.2 Instruments

For GC analysis an Agilent 6890 N equipped with FID analyzer and a capillary column AT1 12 m x 0.32 mm x 0.1 m was used.

3.4.3 Analysis

Acidity percentage (according to the method NGD C 10-1976)

0.1 g of sample were dissolved in a mixture of 20 mL of ethyl ether and 10 mL of absolute ethanol. Then 5 drops of phenolphthalein are added, and the solution was titrated with an aqueous solution of NaOH 0.1N until weak and persistent purple colour. The percentage of acidity was calculated in accordance with the formula:

$$\%\ of\ acidity = \frac{V * N * MW\ acid}{m * 10}$$

where:

V= volume of NaOH 0.1N used for the titration in mL;

N= normality of the NaOH solution;

MW acid= molar mass of the used acid;

M= mass of the sample taken, in grams.

Determination of bonded glycerol content (according to the Italian norm UNI 22053)

Internal standard solutions

Glyceril α-mono-nonadecanoate

In a 100 mL volumetric flask weigh 50 mg of glyceril α-mono-nonadecanoate, dissolve it and bring it to volume with chloroform. The solution should be stored closed in fridge at temperature of 4°C, and warmed at RT before use.

Glyceril dinonadecanoate

In a 100 mL volumetric flask weigh 50 mg of glyceril dinonadecanoate, dissolve it and bring it to volume with chloroform. The solution should be stored closed in fridge at temperature of 4°C, and warmed at RT before use.

Glyceril trinonadecanoate

In a 100 mL volumetric flask weigh 50 mg of glyceril trinonadecanoate, dissolve it and bring it to volume with chloroform. The solution should be stored closed in fridge at temperature of 4°C, and warmed at RT before use.

Reference solution of internal standard for analysis

In a 100 mL volumetric flask weigh 50 mg of methyl eptadecanoate and dissolve it in few milliliters of hexane. Add to the solution, with a volumetric pipette, 5 mL of each solution of glyceril -mono-nonadecanoate, glyceril dinonadecanoate and glyceril trinonadecanoate prepared before and bring to volume with hexane. The solution should be stored closed in fridge at temperature of 4°C, and warmed at RT before use.

Sample preparation

In a 50 mL volumetric flask weigh 0.5 g of sample, dissolve it and bring to volume with hexane. With a volumetric pipette take 1ml and transfer it in a 10 mL centrifuge tube, and add, with a volumetric pipette, 2 mL of reference solution. Remove the solvent with a nitrogen flow, avoiding warming and splashing. To the dry sample, add 200 L of pyridine and 200 L of silanizing agent (N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA)). Plug the tube and let react the mixture for 20 minutes at RT, then evaporate pyridine and BSTFA with a nitrogen flow, avoiding warming. Add 8 mL of heptane and inject in a GC-FID.

GC-FID analysis

For chromatographic analysis there is necessity of a gas chromatograph equipped with:

- FID detector;
- cold on column injector;
- capillary column from 5 to 7 m of length, internal diameter of 0.32 mm, stationary phase methylsiloxane or methylsiloxane with 5% of methylphenylsiloxane and film thickness of 0.1 μm.

The temperature program is:

- 80°C, then 30°C/min until 120°C and then 8°C/min until 340°C;
- Detector temperature: 350°C;
- Carrier gas linear velocity: from 20 to 35 cm/s.

The retention times where:

- 17 min for glyceril -mono-nonadecanoate;
- 30 min for glyceril dinonadecanoate;
- 41 min for glyceril trinonadecanoate;
- Between 26 and 30 min for diglycerides;
- Between 34 and 41 for triglycerides.

The percentage of mono, di and triglycerides were calculated using the following formula:

$$\% = 100 * \frac{Tx * Cx}{Ax * M}$$

Where:

Tx= summation of areas related to mono, di or triglyceride;

Cx= mass in mg of mono, di or triglyceride use as internal standard;

Ax= area of mono, di or triglyceride use as internal standard;

M= mass of sample weigh in mg.

3.4.4 Triolesters

Esterification of oleic acid with TMP (excess of 5% of acid) (MM03)

Reagent	Grams (g)	Mols (mol)
Oleic acid	35.53	0.126
TMP	5.2696	0.039
SiO_2-ZrO_2 4.7%	0.8753 (2.5% by respect to acid)	

The solid catalyst was activated in a reactor (150°C in air for 30 min, and 150°C in vacuum for 30 min), the solid was placed in a three-necked flask of 100 mL with oleic acid and TMP. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on using a membrane pump (400 mbar) and the temperature was setted to 200°C. When the was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The initial yellow color become brown dark in the end.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1208	3.70	86.4
1	0.1130	1.20	30.0
2	0.1030	0.53	14.2
4	0.1158	0.28	6.8
6	0.1121	0.24	6.0

Yeld: 94.0%

GC ANALYSIS

Diglycerides : 10.35%

Triglycerides: 88.40%

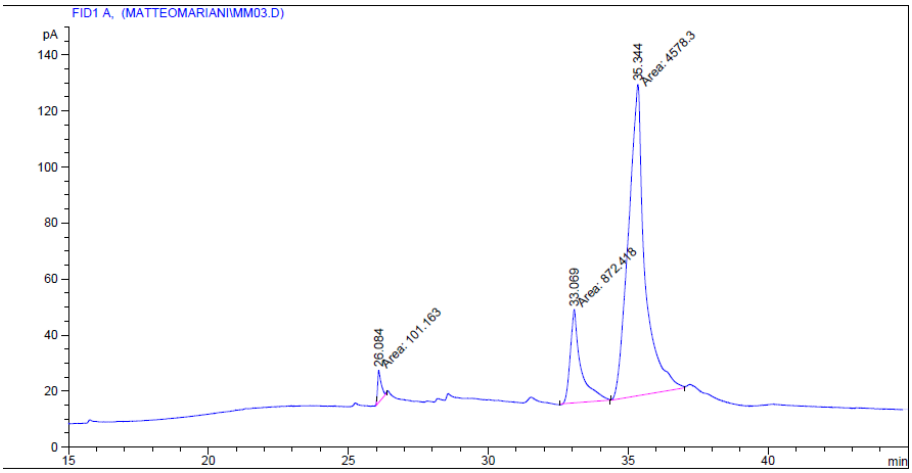


Figure 3.11 Chromatogram of reaction MM03

Esterification of oleic acid with TMP (stoichiometric amount of reagents) (MM04)

Reagent	Grams (g)	Mols (mol)
Oleic acid	35.17	0.125
TMP	5.5650	0.042
SiO_2-ZrO_2 4.7%	0.8750 (2.5% by respect to acid)	

The solid catalyst was activated in a reactor (150°C in air for 30 min, and 150°C in vacuum for 30 min), the solid was placed in a three-necked flask of 100 mL with oleic acid and TMP. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture remain yellow during all the reaction time.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1177	2.74	65.6
1	0.1096	0.89	25.2
2	0.1260	0.68	15.2
4	0.2827	0.96	9.8
6	0.1354	0.38	7.9
7	0.1145	0.24	5.9
8	0.1045	0.20	5.4
10	0.1207	0.20	4.7
12	0.1140	0.20	4.9

Yeld: 95.1%

GC ANALYSIS

Diglycerides : 8.74%

Triglycerides: 86.80%

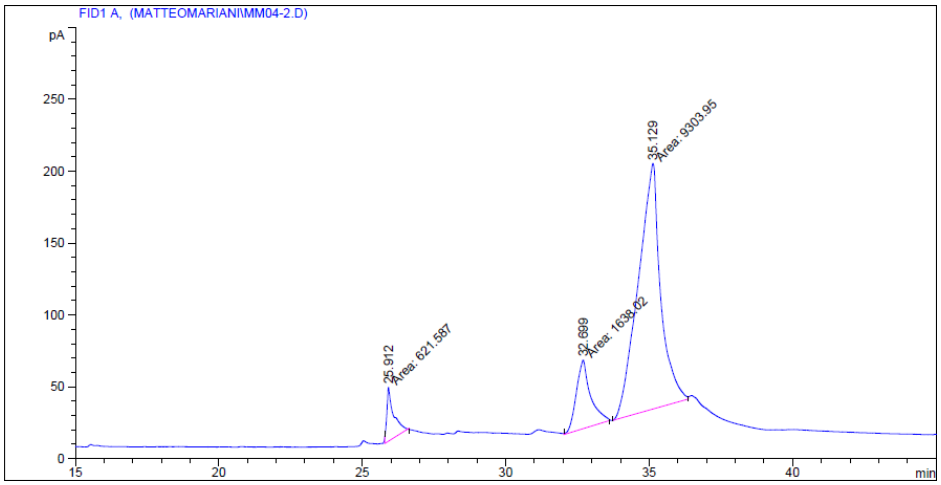


Figure 3.12 Chromatogram of reaction MM04

Esterification of oleic acid with TMP (excess of 5% of TMP) (MM10)

Reagent	Grams (g)	Mols (mol)
Oleic acid	33.33	0.118
TMP	5.7018	0.042
SiO_2-ZrO_2 4.7%	0.8751 (2.5% by respect to acid)	

The solid catalyst was activated in a reactor (150°C in air for 30 min, and 150°C in vacuum for 30 min), the solid was placed in a three-necked flask of 100 mL with oleic acid and TMP. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture remain yellow during all the reaction time.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1201	3.62	85.0
1	0.1107	1.20	30.6
2	0.1110	0.74	18.8
4	0.1106	0.20	5.1
6	0.1022	0.16	4.4
7	0.1101	0.08	2.0
8	0.1072	0.06	1.6
10	0.1157	0.04	0.9
12	0.1028	0.04	1.0

Yeld: 99.0%

GC ANALYSIS

Diglycerides : 11.10%

Triglycerides: 87.63%

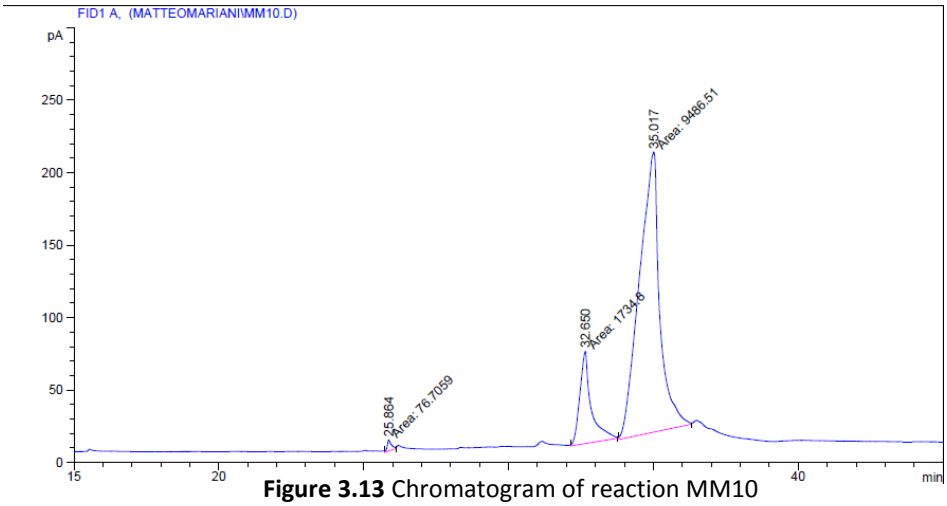


Figure 3.13 Chromatogram of reaction MM10

Esterification of oleic acid with TMP (stoichiometric amount of reagents) (MM22)

Reagent	Grams (g)	Mols (mol)
Oleic acid	35.74	0.127
TMP	5.6746	0.042
SiO_2-TiO_2 2.3%	0.8756 (2.5% by respect to acid)	

The solid catalyst was activated in a reactor (150°C in air for 30 min, and 150°C in vacuum for 30 min), the solid was placed in a three-necked flask of 100 mL with oleic acid and TMP. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1144	3.50	61.6
1	0.1150	1.66	40.7
2	0.1123	0.98	24.6
4	0.1002	0.54	15.2
6	0.1016	0.40	11.1
7	0.1203	0.56	13.1
8	0.1179	0.42	10.0
10	0.1075	0.32	8.4
12	0.1086	0.24	6.2

Yeld: 93.8%

Esterification of oleic acid with TMP (stoichiometric amount of reagents) (MM23)

Reagent	Grams (g)	Mols (mol)
Oleic acid	35.19	0.125
TMP	5.5065	0.042
o-benzenedisulfonimide	0.4013 (2.5% by respect to acid)	0.002

In a three-necked flask of 100 mL where inserted oleic acid, TMP and o-benzenedisulfonimide. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 180°C. When the temperature was 180°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down. The catalyst dissolved into the reaction mixture, that became dark.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1158	3.52	85.7
1	0.1175	0.82	19.7
2	0.1128	0.56	14.0
4	0.1061	0.40	10.6
6	0.1060	0.38	10.1

Yeld: 90.0%

Esterification of oleic acid with TMP (stoichiometric amount of reagents) (MM24)

Reagent	Grams (g)	Mols (mol)
Oleic acid	35.17	0.125
TMP	5.4904	0.042
SiO_2-ZrO_2 1%	0.8760 (2.5% by respect to acid)	

The solid catalyst was activated in a reactor (150°C in air for 30 min, and 150°C in vacuum for 30 min), the solid was placed in a three-necked flask of 100 mL with oleic acid and TMP. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture remain yellow.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1194	3.68	87.0
1	0.1092	1.64	42.3
2	0.1140	1.14	28.2
4	0.1175	0.86	20.6
6	0.1080	0.72	19.0
7	0.1172	0.68	16.4
8	0.1168	0.60	14.5
10	0.1139	0.48	12.0
12	0.1022	0.34	9.4

Yeld: 91.0%

Esterification of oleic acid with TMP (excess of 5% of acid) (MM33)

Reagent	Grams (g)	Mols (mol)
Oleic acid	35.32	0.125
TMP	5.2228	0.039
SiO_2-TiO_2 0.3%	0.8843 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with oleic acid and TMP. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on using a membrane pump (400 mbar) and the temperature was setted to 200°C. When the was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The initial yellow color become brown dark in the end.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1170	1.82	43.9
1	0.1102	1.16	30.0
2	0.1128	0.92	23.0
4	0.1014	0.62	17.2
6	0.1025	0.56	15.4

Yeld: 84.6%

Esterification of tall oil with TMP (stoichiometric amount of reagents) (MM58)

Reagent	Grams (g)	Mols (mol)
Tall oil	35.09	0.124
TMP	5.51	0.041
SiO_2-ZrO_2 SP1987	0.8764 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with oleic acid and TMP. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1144	3.50	61.6
1	0.1150	1.66	40.7
2	0.1123	0.98	24.6
4	0.1002	0.54	15.2
6	0.1016	0.40	11.1
7	0.1203	0.56	13.1
8	0.1179	0.42	10.0
10	0.1075	0.32	8.4
12	0.1086	0.24	6.2

Yeld: 93.8%

Esterification of oleic acid with TMP (excess of 5% of TMP) (DOMUS 19)

Reagent	Grams (g)	Mols (mol)
Oleic acid	34.00	0.121
TMP	6.0439	0.045
TRYSIL	0.8516 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with oleic acid and TMP. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 2 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1151	1.80	44.1
1	0.1183	1.00	23.8
2	0.1073	0.70	18.4
4	0.1024	0.40	11.0
6	0.1124	0.34	8.5
8	0.1017	0.26	7.2

Yeld: 93.0%

Esterification of oleic acid with TMP (excess of 5% of TMP cat recycle) (DOMUS 20)

Reagent	Grams (g)	Mols (mol)
Oleic acid	35.03	0.125
TMP	6.0716	0.045
TRYSIL	0.8515 (2.5% by respect to acid)	from DOMUS19

The solid catalyst was placed in a three-necked flask of 100 mL with oleic acid and TMP. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 2 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1100	1.16	29.7
1	0.1062	0.78	20.7
2	0.1135	0.56	13.9
4	0.1183	0.46	10.9
6	0.1056	0.38	10.1
8	0.1074	0.26	6.8

Yeld: 93.0%

Esterification of oleic acid with TMP (excess of 5% of TMP) (DOMUS 24)

Reagent	Grams (g)	Mols (mol)
Oleic acid	34.21	0.122
TMP	6.05	0.045
DAVICAT 332	0.8554	

The solid catalyst was placed in a three-necked flask of 100 mL with oleic acid and TMP. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1187	2.12	50.4
1	0.1083	1.00	26.0
2	0.1113	0.74	18.7
4	0.1070	0.42	11.1
6	0.1057	0.34	9.1

Yeld: 91.0%

Esterification of oleic acid with glycerol (5% excess of oleic acid) (MM11)

Reagent	Grams (g)	Mols (mol)
Oleic acid	35.63	0.126
Glycerol	3.6147	0.039
SiO_2-ZrO_2 4.7%	0.8753 (2.5% by respect to acid)	

The solid catalyst was activated in a reactor (150°C in air for 30 min, and 150°C in vacuum for 30 min), the solid was placed in a three-necked flask of 100 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1085	3.80	99.0
1	0.1051	2.30	62.0
2	0.1062	1.82	48.3
4	0.1156	1.52	37.1
6	0.1028	1.30	38.0
7	0.1071	1.30	34.2
8	0.1148	1.32	32.4
10	0.1079	1.18	31.0
12	0.1028	1.12	30.7

Yeld: 70.0%

Esterification of oleic acid with glycerol (stoichiometric amount of reagents) (MM12)

Reagent	Grams (g)	Mols (mol)
Oleic acid	35.55	0.126
Glycerol	3.9432	0.043
SiO_2-ZrO_2 4.7%	0.8750 (2.5% by respect to acid)	

The solid catalyst was activated in a reactor (150°C in air for 30 min, and 150°C in vacuum for 30 min), the solid was placed in a three-necked flask of 100 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 220°C. When the temperature was 220°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1064	3.66	97.0
1	0.1076	2.22	58.1
2	0.1013	1.64	46.0
4	0.1083	1.28	33.3
6	0.1086	0.90	21.4
7	0.1016	0.60	16.6
8	0.1077	0.54	14.1
10	0.1168	0.40	9.6
12	0.1063	0.18	4.8

Yeld: 95.0%

Esterification of oleic acid with glycerol (5% excess of glycerol) (MM13)

Reagent	Grams (g)	Mols (mol)
Oleic acid	35.54	0.126
Glycerol	4.0934	0.044
SiO_2-ZrO_2 4.7%	0.8752 (2.5% by respect to acid)	

The solid catalyst was activated in a reactor (150°C in air for 30 min, and 150°C in vacuum for 30 min), the solid was placed in a three-necked flask of 100 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 220°C. When the temperature was 220°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1008	3.30	92.3
1	0.1143	2.26	55.7
2	0.1051	1.50	40.2
4	0.1029	1.02	27.9
6	0.1028	0.70	19.2
7	0.1020	0.52	14.4
8	0.1070	0.52	13.7
10	0.1107	0.40	10.2
12	0.1036	0.30	8.2

Yeld: 92.0%

Esterification of oleic acid with glycerol (5% excess of glycerol) (MM15)

Reagent	Grams (g)	Mols (mol)
Oleic acid	35.48	0.126
Glycerol	3.8842	0.042
Montmorillonite K10	0.8759 (2.5% by respect to acid)	

The solid catalyst was activated in a reactor (150°C in air for 30 min, and 150°C in vacuum for 30 min), the solid was placed in a three-necked flask of 100 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1177	3.92	99.0
1	0.1104	2.36	60.3
2	0.1012	1.66	46.2
4	0.1064	1.32	35.0
6	0.1191	1.26	30.0
7	0.1028	1.10	30.1
8	0.1186	1.10	26.1
10	0.1139	0.98	24.3
12	0.1062	0.90	23.8

Yeld: 76.0%

Esterification of oleic acid with glycerol (stoichiometric amount of reagents) (MM16)

Reagent	Grams (g)	Mols (mol)
Oleic acid	35.34	0.125
Glycerol	3.8553	0.042
Montmorillonite KSF	0.8758 (2.5% by respect to acid)	

The solid catalyst was activated in a reactor (150°C in air for 30 min, and 150°C in vacuum for 30 min), the solid was placed in a three-necked flask of 100 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1036	3.74	101.8
1	0.1147	2.88	71.0
2	0.1189	2.26	53.6
4	0.1061	1.58	42.0
6	0.1182	1.56	37.2
7	0.1042	1.26	34.1
8	0.1086	1.28	33.2
10	0.1075	1.10	29.0
12	0.1021	0.94	26.0

Yeld: 74.0%

ACIDIC TREATMENT OF SEPIOLITE

SEPAC 1

1g of sepiolite was stirred with 10 mL of HNO_3 1M for 1 hour, at RT. The solid was separated with a Büchner funnel, washed with distilled water until pH 5 and dried for 15 hours at 60°C.

SEPAC 3

1g of sepiolite was stirred with 10 mL of HNO_3 1M for 3 hours, at RT. The solid was separated with a Büchner funnel, washed with distilled water until pH 5 and dried for 15 hours at 60°C.

These two solids are used as heterogeneous catalysts for oleic acid esterification with glycerol.

Esterification of oleic acid with glycerol (stoichiometric amount of reagents) (MM17)

Reagent	Grams (g)	Mols (mol)
Oleic acid	35.72	0.127
Glycerol	3.8938	0.042
SEPAC 1	0.8749 (2.5% by respect to acid)	

The solid catalyst was activated in a reactor (150°C in air for 30 min, and 150°C in vacuum for 30 min), the solid was placed in a three-necked flask of 100 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1182	3.96	94.4
1	0.1157	2.74	67.0
2	0.1166	2.10	51.0
4	0.1178	1.60	38.3
6	0.1054	1.22	32.6
7	0.1133	1.26	31.4
8	0.1017	1.02	28.3
10	0.1186	1.12	26.6
12	0.1034	0.94	25.6

Yeld: 74.4%

Esterification of oleic acid with glycerol (stoichiometric amount of reagents) (MM18)

Reagent	Grams (g)	Mols (mol)
Oleic acid	35.22	0.125
Glycerol	3.8347	0.042
SEPAC 3	0.7059 (2.5% by respect to acid)	

The solid catalyst was activated in a reactor (150°C in air for 30 min, and 150°C in vacuum for 30 min), the solid was placed in a three-necked flask of 100 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1071	4.00	105.3
1	0.1023	2.54	70.0
2	0.1161	2.20	53.4
4	0.1019	1.42	39.3
6	0.1133	1.34	33.3

Yeld: 66.7%

Esterification of oleic acid with glycerol (stoichiometric amount of reagents) (MM20)

Reagent	Grams (g)	Mols (mol)
Oleic acid	35.68	0.127
Glycerol	3.9005	0.042
ZrO_2-SiO_2 3.5%	0.8755 (2.5% by respect to acid)	

The solid catalyst was activated in a reactor (150°C in air for 30 min, and 150°C in vacuum for 30 min), the solid was placed in a three-necked flask of 100 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2 and 4 reaction hours, in order to evaluate the acidity decrease. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1112	3.24	82.2
1	0.1111	2.90	73.6
2	0.1147	2.22	54.6
4	0.1080	1.66	43.3

Yeld: 56.7%

Esterification of oleic acid with glycerol (stoichiometric amount of reagents) (MM21)

Reagent	Grams (g)	Mols (mol)
Oleic acid	35.74	0.127
Glycerol	3.9163	0.043
SiO_2-TiO_2 2.3%	0.8760 (2.5% by respect to acid)	

The solid catalyst was activated in a reactor (150°C in air for 30 min, and 150°C in vacuum for 30 min), the solid was placed in a three-necked flask of 100 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1114	4.20	106.3
1	0.1057	2.28	61.0
2	0.1068	1.52	40.1
4	0.1109	0.94	24.0
6	0.1027	0.64	17.6
7	0.1057	0.54	14.4
8	0.1057	0.48	13.0
10	0.1085	0.38	10.0
12	0.1123	0.36	9.04

Yeld: 91.0%

Esterification of valeric acid with glycerol (stoichiometric amount of reagents) (MM54)

Reagent	Grams (g)	Mols (mol)
Valeric acid	35.82	0.351
Glycerol	10.87	0.118
SiO_2-Al_2O_3 135	0.8959 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with valeric acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 160°C. When the temperature was 160°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1083	7.58	71.5
1	0.1084	6.04	57.0
2	0.1112	5.96	55.0
4	0.1122	5.28	48.0
6	0.1092	4.58	43.0

Yeld: 57.0%

GC ANALYSIS

Monoglycerides: 30.25%

Diglycerides : 57.33%

Triglycerides: 12.42%

Esterification of nonanoic acid with glycerol (stoichiometric amount of reagents) (DOMUS 21)

Reagent	Grams (g)	Mols (mol)
Nonanoic acid	35.13	0.247
Glycerol	6.44	0.070
SiO_2-ZrO_2 4.7%	0.8793 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with nonanoic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1060	3.80	51.0
1	0.1005	2.40	34.0
2	0.1006	1.60	23.0
4	0.1023	1.42	19.7
6	0.1088	1.26	16.4

Yeld: 84.0%

GC ANALYSIS

Monoglycerides: 0.32%

Diglycerides : 1.02%

Triglycerides: 97.66%

Esterification of valeric acid with glycerol (stoichiometric amount of reagents) (DOMUS 22)

Reagent	Grams (g)	Mols (mol)
Valeric acid	35.82	0.351
Glycerol	10.87	0.118
TRYSIL	0.8959 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with valeric acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 160°C. When the temperature was 160°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1087	3.48	45.5
1	0.1057	2.20	29.5
2	0.1064	1.72	23.0
4	0.1011	1.24	17.4
6	0.1005	1.06	15.0

Yeld: 85.0%

GC ANALYSIS

Monoglycerides: 0.79%

Diglycerides : 0.73%

Triglycerides: 97.48%

Esterification of nonanoic acid with TMP (5% excess of TMP) (DOMUS57)

Reagent	Grams (g)	Mols (mol)
Nonanoic acid	105.58	0.67
TMP	31.2251	0.23
SiO_2-ZrO_2 3rd	2.6362 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with nonanoic acid and TMP. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.3308	8.24	39.4
1	0.1053	1.06	16.0
2	0.1063	0.56	8.3
4	0.1069	0.14	2.1
6	0.1105	0.1	1.4

Yeld: 98.6%

Esterification of nonanoic acid with TMP (5% excess of TMP) (DOMUS58)

Reagent	Grams (g)	Mols (mol)
Nonanoic acid	35.0540	0.22
TMP	10.4422	0.078
SiO_2-TiO_2 2.3%	0.8705 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with nonanoic acid and TMP. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1046	2.0	30.2
1	0.1132	1.16	16.2
4	0.1172	0.66	8.9
6	0.1050	0.42	6.3

Yeld: 93.7%

Esterification of nonanoic acid with TMP (5% excess of TMP) (DOMUS59)

Reagent	Grams (g)	Mols (mol)
Nonanoic acid	35.3250	0.22
TMP	10.4241	0.078
SiO_2-Al_2O_3 135	0.8853 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with nonanoic acid and TMP. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1131	3.12	43.6
1	0.1059	1.36	20.3
2	0.1040	0.90	13.7
4	0.1061	0.58	8.6
6	0.1198	0.48	6.3

Yeld: 93.7%

Esterification of caprilic acid with TMP (5% excess of TMP) (DOMUS54)

Reagent	Grams (g)	Mols (mol)
Caprilic acid	115.01	0.73
TMP	31.30	0.23
SiO_2-ZrO_2 3rd	2.67 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with caprilic acid and TMP. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.2880	6.88	38.0
1	0.2032	3.12	24.3
2	0.2602	2.48	15.1
4	0.2304	1.46	10.0
6	0.2776	0.84	4.8

Yeld: 95.2%

Esterification of caprilic acid with TMP (5% excess of TMP) (DOMUS52)

Reagent	Grams (g)	Mols (mol)
Caprilic acid	35.0137	0.22
TMP	10.4378	0.08
SiO_2-TiO_2 2.3%	0.8827 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with caprilic acid and TMP. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.2342	6.52	44.0
1	0.3285	4.02	19.3
2	0.2124	1.70	12.6
4	0.2366	1.20	8.0
6	0.1051	0.52	7.8

Yeld: 92.2%

Esterification of caprilic acid with TMP (5% excess of TMP) (DOMUS51)

Reagent	Grams (g)	Mols (mol)
Caprilic acid	35.0208	0.22
TMP	10.476	0.08
SiO_2-Al_2O_3 135	0.8716 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with caprilic acid and TMP. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1135	2.60	36.2
1	0.3004	3.62	19.0
2	0.1180	1.10	14.7
4	0.2362	1.32	8.8
6	0.1780	0.90	7.9

Yeld: 92.1%

Esterification of oleic acid with TMP (5% excess of TMP) (DOMUS48)

Reagent	Grams (g)	Mols (mol)
Oleic acid	34.10	0.12
TMP	6.0640	0.04
SiO_2-ZrO_2 3rd	0.8546 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with oleic acid and TMP. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1045	2.44	65.8
1	0.1137	0.50	12.4
2	0.1076	0.22	5.8
4	0.1101	0.12	3.1
6	0.1052	0.08	2.1

Yeld: 97.9%

Esterification of oleic acid with TMP (5% excess of TMP) (DOMUS14)

Reagent	Grams (g)	Mols (mol)
Oleic acid	34.09	0.12
TMP	6.0617	0.04
SiO_2-TiO_2 2.3%	0.8528 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with oleic acid and TMP. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1104	1.28	32.7
1	0.1040	0.70	19.0
2	0.1091	0.54	14.0
4	0.1121	0.30	7.5
6	0.1111	0.20	5.0

Yeld: 95.0%

Esterification of oleic acid with TMP (5% excess of TMP) (DOMUS60)

Reagent	Grams (g)	Mols (mol)
Oleic acid	35.0665	0.12
TMP	5.7700	0.04
SiO_2-ZrO_2 3rd	0.8761 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with oleic acid and TMP. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. After 6 hours reaction the mixture was cooled down and the day after was carried on for other 6 hours. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1141	2.02	50.0
1	0.2186	2.24	28.9
2	0.0993	0.84	23.8
4	0.2120	1.18	15.7
6	0.1493	0.59	11.1

Yeld: 88.9%

3.4.5 Monoglycerides

Esterification of oleic acid with glycerol (MM38)

Reagent	Grams (g)	Mols (mol)
Oleic acid	34.96	0.124
Glycerol	11.44	0.124
SiO_2-TiO_2 2.3%	0.8754 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,3,4 and 5 reaction hours, in order to evaluate the acidity decrease. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1065	0.80	21.2
1	0.1126	0.28	7.0
2	0.1034	0.14	3.8
3	0.1028	0.08	2.2
4	0.1183	0.06	1.4
5	0.1231	0.04	0.9

Yeld: 99.1%

GC ANALYSIS

Monoglycerides: 49.4%

Diglycerides : 20.5%

Triglycerides: 29.0%

Esterification of oleic acid with glycerol (MM39)

Reagent	Grams (g)	Mols (mol)
Oleic acid	34.91	0.124
Glycerol	11.45	0.124
SiO_2-Al_2O_3 135	0.8747 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 5 reaction hours, in order to evaluate the acidity decrease. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1104	1.26	32.2
1	0.1146	0.66	16.2
2	0.1122	0.38	9.6
4	0.1136	0.20	5.0
5	0.1110	0.14	3.6

Yeld: 96.4%

GC ANALYSIS

Monoglycerides: 78.0%

Diglycerides : 19.1%

Triglycerides: 1.5%

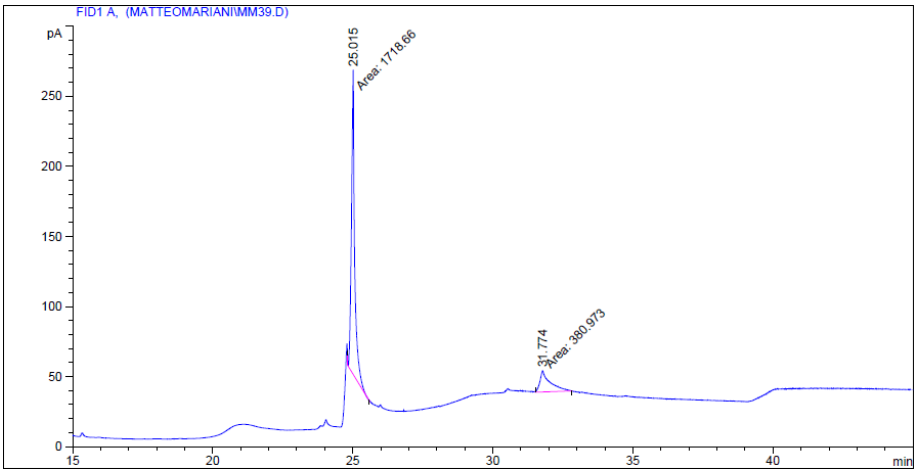


Figure 3.14 Chromatogram of reaction MM39

Esterification of oleic acid with glycerol (MM40)

Reagent	Grams (g)	Mols (mol)
Oleic acid	35.07	0.124
Glycerol	11.68	0.124
SiO_2-ZrO_2 4.7%	0.8769 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,3,4 and 5 reaction hours, in order to evaluate the acidity decrease. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1028	0.52	13.5
1	0.1040	0.30	8.1
2	0.1143	0.22	5.4
3	0.1104	0.20	5.1
4	0.1026	0.16	4.4
5	0.1143	0.14	3.4

Yeld: 96.6%

GC ANALYSIS

Monoglycerides: 77.0%

Diglycerides : 18.0%

Triglycerides: 2.0%

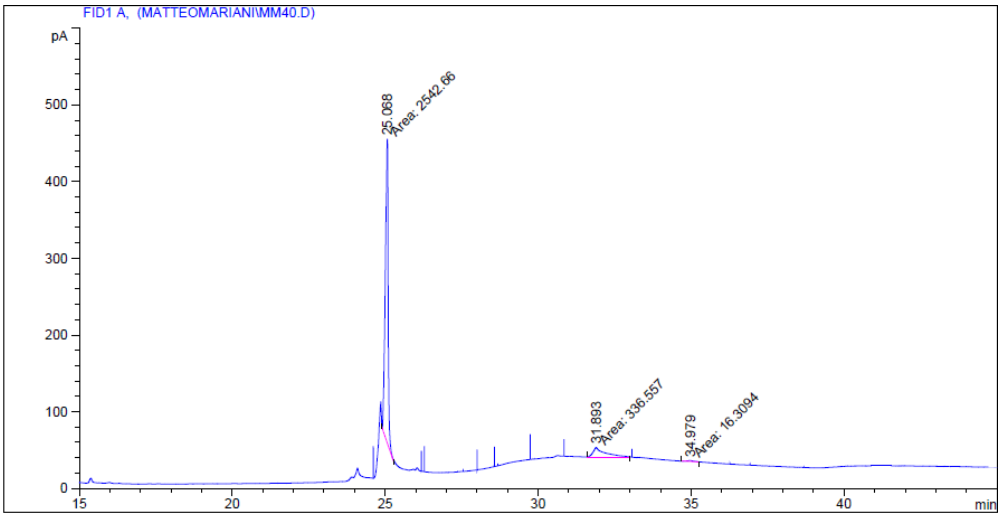


Figure 3.12 Chromatogram of reaction MM40

Esterification of oleic acid with glycerol (MM41)

Reagent	Grams (g)	Mols (mol)
Oleic acid	34.99	0.124
Glycerol	11.42	0.124
SiO_2-Al_2O_3 0.6%	0.8748 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,3,4 and 5 reaction hours, in order to evaluate the acidity decrease. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1089	0.96	25.0
1	0.1160	0.54	13.1
2	0.1005	0.32	9.0
3	0.1177	0.26	6.2
4	0.1070	0.16	4.2
5	0.1177	0.12	3.0

Yeld: 97.0%

GC ANALYSIS

Monoglycerides: 37.0%

Diglycerides : 62.0%

Triglycerides: 0.0%

Esterification of valeric acid with glycerol (MM47)

Reagent	Grams (g)	Mols (mol)
Valeric acid	35.17	0.344
Glycerol	31.92	0.347
TRYSIL	1.7584 (5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 170°C. When the temperature was 170°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1078	3.04	29.0
1	0.1100	2.32	21.5
2	0.1075	1.70	16.1
4	0.1110	1.18	11.0
6	0.1077	0.86	8.2

Yeld: 92.0%

GC ANALYSIS

Monoglycerides: 31.4%

Diglycerides : 33.7%

Triglycerides: 35.0%

Esterification of valeric acid with glycerol (MM49)

Reagent	Grams (g)	Mols (mol)
Valeric acid	13.28	0.130
Glycerol	11.93	0.129
SiO_2-Al_2O_3 135	0.3882 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 50 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 150°C. When the temperature was 150°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1058	4.56	44.0
1	0.1030	3.54	35.1
2	0.1133	3.26	29.4
4	0.1029	2.28	22.6
6	0.1040	1.94	19.0

Yeld: 81.0%

GC ANALYSIS

Monoglycerides: 72.2%

Diglycerides : 26.0%

Triglycerides: 1.7%

Esterification of valeric acid with glycerol (MM52)

Reagent	Grams (g)	Mols (mol)
Valeric acid	35.60	0.349
Glycerol	32.36	0.351
SiO_2-TiO_2 2.3%	0.8962 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 150°C. When the temperature was 150°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1117	5.38	49.2
1	0.1068	3.74	36.0
2	0.1192	3.38	29.0
4	0.1114	2.44	22.4
6	0.1148	1.70	15.1

Yeld: 85.0%

GC ANALYSIS

Monoglycerides: 74.3%

Diglycerides : 24.4%

Triglycerides: 1.3%

Esterification of valeric acid with glycerol (MM53)

Reagent	Grams (g)	Mols (mol)
Valeric acid	34.87	0.341
Glycerol	31.4151	0.341
SiO_2-Al_2O_3 0.6%	0.8690 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 150°C. When the temperature was 150°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1087	5.44	51.1
1	0.1134	4.26	38.4
2	0.1122	3.36	30.6
4	0.1216	2.50	21.0
6	0.1040	1.68	16.5

Yeld: 83.5%

GC ANALYSIS

Monoglycerides: 64.5%

Diglycerides : 33.1%

Triglycerides: 2.4%

3.4.6 Acidic oils valorization

Esterification of acidic olive oil with glycerol (MM31)

Reagent	Grams (g)	Mols (mol)
Oleine Bunge	35.50 (25.74 g of oleic acid)	0.091
Glycerol	2.8093	0.030
SiO_2-ZrO_2 4.7%	0.6438 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4,6 and 8 reaction hours, in order to evaluate the acidity decrease. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became dark brown during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1013	1.90	53.0
1	0.1046	1.24	33.4
2	0.1093	0.80	20.6
4	0.1046	0.58	15.6
6	0.1121	0.42	10.6
8	0.1114	0.32	8.1

Yeld: 92.0%

Esterification of acidic olive oil with glycerol (MM32)

Reagent	Grams (g)	Mols (mol)
Oleine Bunge	35.34 (25.62 g of oleic acid)	0.091
Glycerol	2.8078	0.030
SiO_2-TiO_2 2.3%	0.6403 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4,6 and 8 reaction hours, in order to evaluate the acidity decrease. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became dark brown during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1058	1.82	48.5
1	0.1094	1.08	28.0
2	0.1126	0.86	21.5
4	0.1110	0.58	15.0
6	0.1099	0.40	10.3
8	0.1119	0.20	5.0

Yeld: 95.0%

Esterification of acidic olive oil with dirty glycerol (MM34)

Reagent	Grams (g)	Mols (mol)
Oleine Bunge	35.50 (25.74 g of oleic acid)	0.091
Glycerol Oxem	2.8241	0.031
SiO_2-TiO_2 2.3%	0.6444 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with oleic acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4,6 and 8 reaction hours, in order to evaluate the acidity decrease. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became dark brown during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1050	1.58	42.4
1	0.1029	1.16	32.0
2	0.1012	0.88	24.5
4	0.1175	0.72	17.3
6	0.1081	0.48	12.5
8	0.1140	0.42	10.4

Yeld: 90.0%

Esterification of rice bran oil with glycerol (stoichiometric amount of reagents) (MM57)

Reagent	Grams (g)	Mols (mol)
Rice bran oil	17.0957 (13.6766 g of oleic acid)	0.050 of oleic acid
Glycerol	1.7560	0.019
SiO_2-Al_2O_3 135	0.4092 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with valeric acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1362	1.70	44.0
1	0.1146	1.20	36.0
2	0.1104	0.94	30.0
4	0.1043	0.68	23.0
6	0.1040	0.56	19.0

Yeld: 81.0%

GC ANALYSIS

Diglycerides : 33.40%

Triglycerides: 66.60%

Esterification of rice bran oil with glycerol (stoichiometric amount of reagents) (MM56)

Reagent	Grams (g)	Mols (mol)
Rice bran oil	20.0018 (16.0014 g of oleic acid)	0.057 of oleic acid
Glycerol	1.5070	0.016
SiO_2-TiO_2 2.3%	0.4047 (2.5% by respect to acid)	

The solid catalyst was placed in a three-necked flask of 100 mL with valeric acid and glycerol. The flask was equipped with a thermometer, a Claisen condenser and a bubbler. The reaction was carried on in a weak nitrogen flow (0.2 L/h) and the temperature was setted to 200°C. When the temperature was 200°C a sample was taken for acidity titration. Other samples were taken after 1,2,4 and 6 reaction hours, in order to evaluate the acidity decrease. Then was centrifuged at 3000 rpm for 5 min, in order to separate the solid catalyst. The reaction mixture became yellow-orange during the reaction.

TITRATION

Time (h)	g of reaction	mL NaOH 0.1N	Acidity %
0	0.1170	1.26	38.0
1	0.1082	0.66	21.5
2	0.1055	0.38	13.0
4	0.1115	0.26	8.2
6	0.1108	0.22	7.0

Yeld: 93.0%

GC ANALYSIS

Diglycerides : 25.24%

Triglycerides: 74.76%

3.5 References

[1] T. Mang, W Dresel, Lubricants and Lubrication, Wiley-VCH 2001;

[2] S. Tang, C.L. Jones, H. Zhao, *Bioresour. Tech.* 2013, 129, 667;

[3] M.T. Benchaita, F.E. Lockwood, *Lubr. Sci.*, 1993, 5, 259;

[4] B. Cunningham, N. Batterby, W. Wehrmeyer, C. Fothergill, *J. Ind. Ecol.* 2004, 7, 179;

[5] S.J. Randles, Formulation of Environmentally AcceptablLubricants, 49th STLE Annual Meeting, Pittsburgh, May 1–5 1994;

[6] A. Adhvaryu, B.K. Sharm, H.S. Hwang, S.Z. Erhan, *Ind. Eng. Chem. Res.*2006, 45, 928;

[7] M.P. Schneider, *J. Sci. Food Agric.*2006, 86, 1769;

[8] B.K. Sharma,A. Adhvaryu, Z. Liu, S.Z. Erhan, *J. Am. Oil Chem. Soc.*2006, 83, 129;

[9] C.O. Åkerman, Y. Gaber, N. AbdGhani, M. Lamsa, R. Hatti-Kaul, *J. Mol. Catal. B: Enzym.*, 2011, 72,263;

[10] C.A. Ferretti, A. Soldano, C.R. Apesteguia, J.I. Di Cosimo, *Chem. Eng. J.*, 2010, 161, 346;

[11] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* 2007, 107, 2411;

[12] J.W. Shabaker, G.W. Huber, J.A. Dumesic*, J. Catal.* 2004, 222,180;

[13] A. Corma, G.W. Huber, L. Sauvanaud, P. O'Connor, *J. Catal.*, 2007, 247, 307;

[14] R.S. Karinen, A.O.I. Krause, *Appl. Catal. A: Gen.* 2006, 306, 128;

[15] Y. Zheng, X. Chen, Y. Shen, *Chem. Rev.*, 2008, 108, 5253;

[16] A. Corma, S.B.A. Hamid, S. Iborra, A. Velty, *J. Catal.*, 2005, 234, 340;

[17] Lange J.P., Price R., Ayoub P.M., Louis J., Petrus L., Clarke L., Gosselink H., *Angew. Chem. Int Ed.,* 49, 2010, 4479.

Chapter 4:

Cellulose

4.1 Introduction

Plants use carbon dioxide and water to obtain sugar building blocks and oxygen, with the help of solar energy and chlorophyll:

$$nCO_2 + nH_2O + \text{light} \xrightarrow[\text{chlorophyll}]{} (CH_2O)_n + nO_2$$

Figure 4.1 Chlorophyllian photosynthesis

The sugars are stored in polymers such as cellulose, hemicellulose and starch, containing part of the solar energy used for the synthesis, that can be used to produce fuels and chemicals. It's important to find an inexpensive, abundant and ethical way to obtain these biomass feedstocks. One of the promising material is cellulose, as it is present in big amount (50%) in agricultural and wood wastes and it is not edible, so its utilization does not exempt food for humans and land for cultivation. Cellulose is a crystalline polymer constituted by linear polysaccharide with b-1,4 bonds of D-glucopyranose monomers[1]. This material possesses an extended, flat, 2-fold helical conformation, with hydrogen bonds that help to maintain and reinforce the flat, linear conformation of the chain. Top and bottom of cellulose chains are hydrophobic, and therefore the sides are hydrophilic and capable of hydrogen bonding, because all the aliphatic hydrogen atoms are in axial position, and the polar hydroxyl groups are in equatorial position.

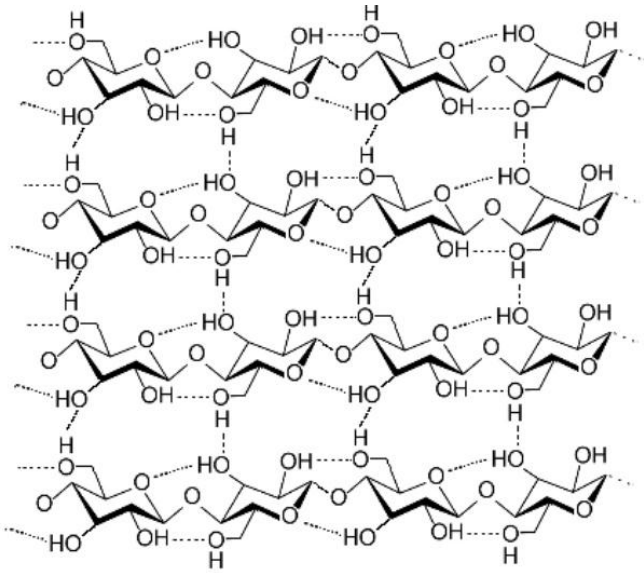


Figure 4.2 Cellulose structure

The main problem of cellulose is its insolubility in all the common solvents, and therefore the impossibility to hydrolyze it and to obtain glucose. One possible solution is the use of ionic liquids, such as 1-butyl-3-methylimidazolium chloride, that can dissolve cellulose and facilitate its hydrolysis[2]. There are other methods to solubilize cellulose, but they request particular solvents or mixture of inorganic salts and solvents[3].

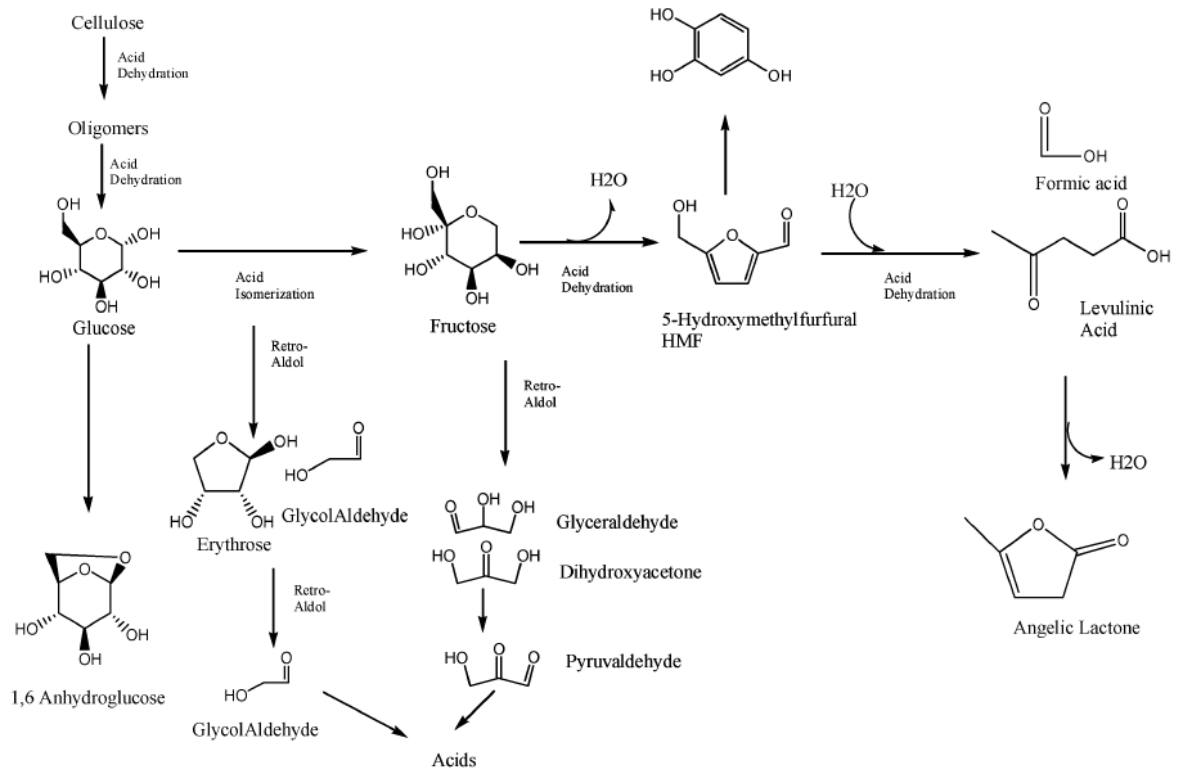


Figure4.3 Cellulose hydrolysis

In order to obtain interesting chemicals from cellulose, it is important to hydrolyze the glycosidic bond, mainly getting glucose, but also dehydrated products such as hydroxymethylfurfural (HMF) and organic acids. The traditional method foresees the use of concentrated inorganic acids, typically sulfuric acid, that are able to swell cellulose and to break the glycosidic bonds[4]. Acid promotes cellulose solubilization when its concentration is above 62% w/v, then glycosidic bonds are attached by water molecules, catalyzed by acid, and then hydrolyzed to give oligomers, glucose and dehydrated products[5]. This direct hydrolysis has low energy consumption because it operates at 20-50°C and at atmospheric pressure. On the other hand the process has strict requirements on water content of raw material, heavy problems related to the corrosive nature of the homogeneous catalyst and reuse of the acid. Also diluted solutions of mineral acids can act as catalysts. The hydrated protons can protonate the oxygen atom in glycosidic bonds, activating them. With diluted acids the reaction temperature are higher with respect to what observed with

concentrated acids, usually 180°C and 1.2-1.3 MPa, with reaction times ranging from minutes to hours and high cellulose conversion, but low glucose selectivity[6]. Biomass can be hydrolyzed by simple water under hydrothermal conditions, with T<300°C and pressures of 10-15 MPa. The hydrolysis under hydrothermal conditions is promoted by the enhanced ion product of water, as proton and hydroxyl concentration increases[7]. Enzymatic hydrolysis of cellulose to glucose is receiving attention, both from academia and industry. The most used system are cellulose, a mixture of three different enzymes: endoglucanases, exoglucanases and cellobiohydrolases. The mechanism of action is complex and consists of three passages:

I) Endoglucanase cleave b-1,4 glycosidic bonds, creating free ends;

II) Exoglucanase act on the reducing and non-reducing ends, to liberates oligosaccharides;

III) Cellobiohydrolase cleave the polymer from reducing end, to liberate cellobiose.

The produced cellobiose inhibits cellulase activity, and it is important to remove it from reaction[8]. Other factors affecting the enzyme activity are: substrate concentration, end-product inhibition, reaction temperature and pH[9].

Some of the drawbacks related with the use of homogeneous acid catalysts (corrosion and impossibility to reuse the catalyst) can be overcome by the use of solid acids. This kind of materials exhibits acidic center, principally placed on the surface of the catalyst. During the reaction these centers are able to donate protons or to accept electrons. Heterogeneous catalysts show better properties if compared to their homogeneous counterpart, for example selectivity, catalyst life, and easiness in recovery and reuse. On the other hand they show some drawbacks, mainly in hydrothermal catalytic hydrolysis, as water can significantly decrease their catalytic activity[10]; moreover some catalysts do not have active sites strong enough to break glycosidic bonds, cannot reach a close contact with b-1,4-glucans. There is a wide variety of solid acids that can be used for cellulose hydrolysis, with different properties: zeolites, metal oxides, cation-exchanging resins, heteropoly acids and various supported acidic species. Zeolites are widely used in catalysis due to their shape-selective abilities, and because they can provide stereo- and region-control in the reaction. The number of Brønsted acid sites in the H-form zeolites is related to the atomic ratio Al/Si and high ratios give high acidity[11]. The mechanism seems to foresee the coordination of one water molecule to an acid site of the H-form zeolite, via hydrogen bond. Then the soluble polysaccharide diffuses in the pores, undergoes hydrolysis over the acid sites and the product diffuses out of the pores. Cellulosic materials have to be dissolved in a solvent to be converted into sugars, so ionic liquids are used for this scope[12]. Even though zeolites have large surface

areas and strong acidity they are not so effective in cellulose hydrolysis. The main problem is the accessibility to the active site, in fact the small pore size of zeolites limits the cellulose contact with protons in the pores. Metal oxides are composed by cations possessing Lewis acid sites and anions with Brønsted base sites; they can be classified as single metal oxides or mixed metal oxides. These materials are mesoporous, thus allowing the access of the reactant to active sites. Other properties of metal oxides are: high specific surface area, adjustable pore size and enhanced thermal stability. Some examples of widely used metal oxides are: Nb_2O_5, WO_3[13], and TiO_2[14]. Cation-exchange resins are polyvinyl styrene based polymers, with cationic groups, usually sulfonic ones. They are commercially used as solid acid catalysts in many organic reactions, such as esterification, alkylation and condensation. It is possible to use them for cellulose hydrolysis, obtaining a maximum glucose conversion of 39% with NKC-9 acidic resin[15]. One advantage in using acidic resins is that the catalyst also acts as membrane, thus allowing permeation of products during the reaction. This process allows to remove the inhibiting compound, playing a positive role in following fermentation processes[16]. The acidic resins present big stability problems at temperature higher than 100°C, making hard to reuse the catalyst due to large leaching of sulfate ions[17]. Another class of acid material suitable for cellulose deconstruction are the supported solid acid catalysts. They are promising because they possess significant surface acidic species and specific functional groups. It is possible to use a wide range of supports: silica[18], zeolites[19], amorphous carbon[20], ecc. Metal oxides are often used as supports for the catalytic phase, due to their mechanical and thermal stability, high specific surface areas, large pore size and pore volume. Because solid acids act as H^+ for cellulose hydrolysis, sulfonated metal oxides (SO_4^{2-}/Al_2O_3, SO_4^{2-}/TiO_2 and SO_4^{2-}/V_2O_5)can supply many acidic species. Pt and Ru supported over metal oxides are very active in transforming cellulose in sugar alcohols with 31% yield and 88% glucose selectivity[21]. There is only one problem related to the use of these materials: the active species become leached from support under hydrolytic conditions. Carbonaceous solid acids seem to be the most effective solid acid catalysts investigated so far. They derived from sulfonation of carbonized D-glucose or sucrose[22] and present $-SO_3H$ groups as active sites. The reaction mechanism is similar to the one involved when using sulfuric acid, as protons in $-SO_3H$ groups attack the glycosidic bonds in cellulose. These solids can convert cellulose into saccharides with high efficiency at temperature of 100°C in 6 hours and are recyclable[23]. The only drawback observed is the separation and recovery of un-hydrolyzed cellulose residues. Heteropolyacids possess acidic strength similar to the one of sulfuric acid, and in water solution their mechanism is

the same. These acids show good glucose selectivity and yield (92% and 51% respectively) at 180°C for 2 hours[24]. Recovery of this homogeneous catalyst is very difficult, and 9% of solid acid was lost after 6 runs of extractions. Heteropolyacids can be immobilized over different supports, thus providing a greener way to perform cellulose deconstruction[25].

4.2 Results and discussion

Figure 4.4A sums up the most significant results obtained by using different supported Copper catalysts compared with the corresponding bare supports (Figure 4.4B). All the bare supports tested under our experimental conditions show moderate conversions in terms of soluble products. This is quite significant taking into account that the use of these solids for cellulose deconstruction has seldom been reported.

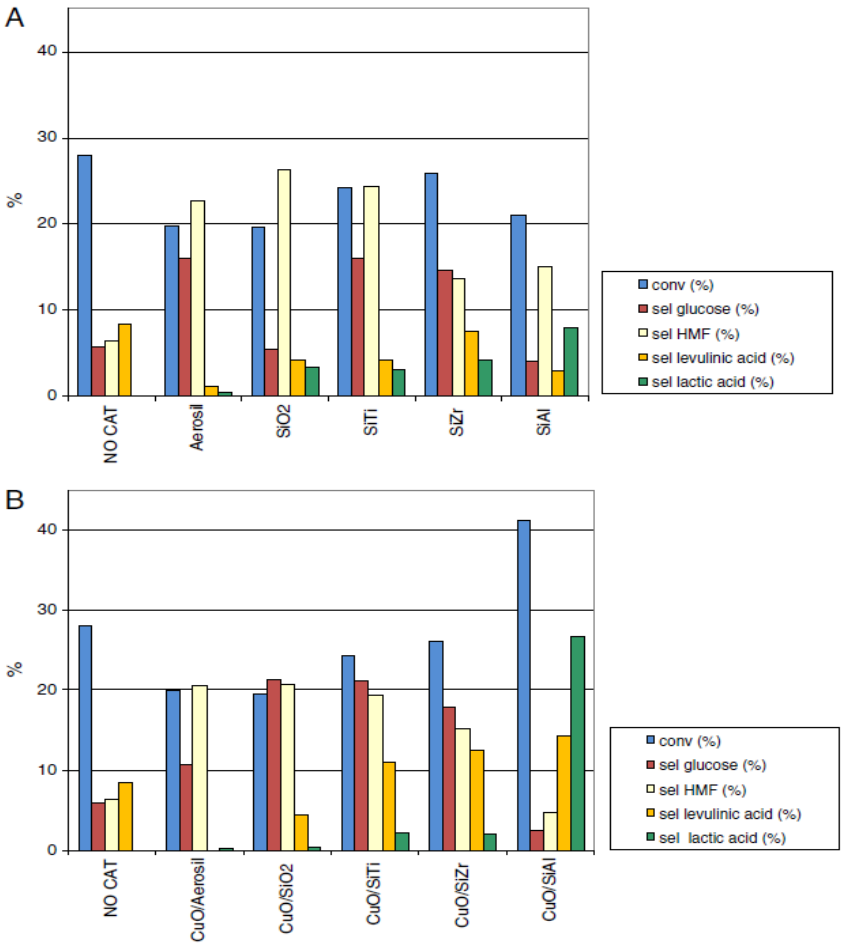


Figure 4.4 Cellulose depolymerization carried out by using (A) different oxides and (B) supported copper catalysts

Thus, the use of silica or amorphous mixed oxides without any post-synthesis functionalization, such as the introduction of sulfonic groups as strong Brønsted acid sites, is not commonly envisaged. Amorphous silica aluminas (ASA) are indeed acid catalysts much weaker than zeolites, in particular, it is generally accepted that ASA contain sites that are similar to the Brønsted acid sites in zeolites but somehow of lower strength[26]. Conversions into soluble C products are quite similar by varying the different supports ranging from 20% to 26%, while selectivity observed with

respect to glucose, HMF, levulinic and lactic acid chosen as reference products are quite different. However, the use of these catalysts allows one to obtain the mentioned products with selectivity higher with respect to the non-catalyzed reaction. Thus, the blank experiment leads to conversion into soluble products up to 27%, but with very poor selectivity in glucose (5.8%), in HMF (6.2%) and in levulinic acid (8.4%). Within catalyzed reactions, the effect of porosity is quite evident, as the use of pyrogenic silica (entry 9, Table 4.1) gives quite low conversion and does not allow the formation of levulinic or lactic acid.

Table 4.1 Textural properties of support and corresponding 8% loaded copper catalysts

Entry	Catalyst	% Co-oxide	SSA (m^2/g)	PV (mL/g)	RP_{av}[a] (Å)
1	SiO_2	–	480	0.75	30
2	CuO/SiO_2	–	363	0.68	36
3	SiO_2-Al_2O_3(SiAl)	13	485	0.79	33
4	CuO/SiO_2-Al_2O_3		412	0.75	37
5	SiO_2-TiO_2 (SiTi)	2.3	297	1.26	84
6	CuO/SiO_2-TiO_2		318	1.01	64
7	SiO_2-ZrO_2(SiZr)	1	453	0.91	80
8	CuO/SiO_2-ZrO_2		382	0.75	79
9	Aerosil	–	380	–	–
10	CuO/Aerosil	–	n.d.	n.d.	n.d.

[a] Average radius pore.

On the contrary, mesoporous silica gives conversion around 20% but increasing amount in HMF, levulinic and lactic acid. The presence of a low amount of a co-oxide like ZrO_2 or TiO_2 in mesoporous materials leads to a decrease in HMF and to an increase in levulinic and lactic acid. Interesting insights can be drawn from results obtained by moving to copper catalysts. We recently reported on the acidic behavior expressed by heterogeneous copper oxide catalysts prepared by the chemisorption–hydrolysis technique[27]. Catalytic systems prepared with this method reveal unexpected acidic properties by virtue of the high dispersion of the copper oxide phase. The preparation method, based on the electrostatic interaction of the precursor and the support during the chemisorption step, grants the formation of coordinatively unsaturated copper oxide nanoparticles (≈3 nm). Results obtained in cellulose deconstruction in the presence of copper catalysts (Figure 4.4B) show no improvement in conversion but some interesting effect on selectivity. In particular, no changes were observed when the pyrogenic silica was used, while in the case of CuO/Si, CuO/SiTi and CuO/SiZr a sharp increase in glucose and levulinic acid formation took place. It is worth noting that catalysts with moderate Lewis acidity have already been reported to show higher performances in glucose formation with respect to typically Brønsted ones[28]. Moreover, very recent results reported by Vlachos et al[29]. highlight the promotion effect

obtained by adding Lewis acids to Brønsted ones towards formation of levulinic acid starting from glucose. The product distribution obtained with the copper catalysts comes close to that observed with Silica modified with a small amount of ZrO_2. This is in agreement with the presence of very well dispersed Lewis acid sites on both species, well evident in the pyridine adsorption spectra that are quite similar[30], thus accounting for the activity observed in the aminolysis of styrene oxide. A more pronounced Lewis acidity like the one expressed by dispersed copper oxide in epoxide alcoholysis[31] does not stand out in the present case. The ability of coordinating the substrate by displacement of coordinated water at the Lewis acid site clearly does not hold when working in aqueous solution. However, the role of CuO in tuning the selectivity towards glucose could play a major role in setting up bifunctional catalysts for the production of sugar alcohols. Copper-based catalysts have been used for the reduction of monosaccharides since the beginning of the 20th century[32], and they have been recently tested in the hydrogenolysis of cellulose to C1–C3 alcohols[33] showing high activity. The hydrolysis of cellulose or starch to glucose and in situ hydrogenation of the formed glucose to thermally stable sugar alcohols has been widely explored as a way to avoid decomposition to low value products. The most used catalysts are Ru/C[34] eventually in the presence of heteropolyacids[35] or Pt catalysts[36]. Only Fukuoka et al.[37] compared the activity of a Ru/C catalyst with that of the parent support in the absence of H_2 and found an increase in glucose yield from 16% to 31% together with a decrease in oligosaccharides yield from 22% to 5% when working in the presence of the metal. They identified 1 nm diameter $RuO_2{\cdot}2H_2O$ particles on the catalyst and ascribed the higher activity in hydrolyzing oligosaccharides to the high valence of the Ru species, similar to a tri-valent Ru-polyoxometalates[38]. A unique case is represented by the CuO/SiAl system and its parent support. Despite the presence of some strong Brønsted acid sites, bare silica alumina shows conversion and product distribution very similar to the other silica-based materials but for a higher amount of levulinic and lactic acid. On the contrary, the CuO/SiAl material stands among all the copper-based systems as far as both conversion and selectivity are concerned. Thus, conversion jumps to a remarkable 40% while selectivity to lactic acid reaches 25% at the expenses of HMF production and leaving the other products unaffected. This behavior has to be ascribed to the peculiar nature of the metallic phase on this catalyst. The use of chemisorption–hydrolysis technique for the deposition of copper oxide over this silica alumina generates isolated copper species, hardly reducible to an oxidation state lower than monovalent copper, as evidenced by several techniques[39]. Thus, the presence on this support of strong acidic sites similar to those determined

for a H-Beta zeolite[40] makes a pure ion exchange mechanism of these sites with the $[Cu(NH_3)_4]^{2+}$ solution competitive with the electrostatic interaction one, which gives rise to the CuO dispersed phase on the other systems. The presence of ionic copper species therefore leads to marked Lewis acidic properties, similarly to what observed for Cu exchanged zeolites. It is known that for Cu zeolites, upon copper introduction, Brønsted sites are transformed into Lewis acid sites[41]. These result seems to strongly confirm the influence of Lewis acid sites on this system, and they are in full agreement with the work by Chambon et al.[42]. They reported evidences on the role of Lewis acid sites in promoting both cellulose conversion and formation of lactic acid reaching 47% conversion and 60% selectivity to lactic acid in the presence of tungstated alumina, a solid exhibiting almost exclusively Lewis acidity. The importance of the presence of both acid site types is moreover claimed as a prerequisite to realize fast and selective sugar conversion. Thus, the combination of strong Lewis acid sites obtained by grafting Sn(IV) on a high surface mesoporous silica with weak Brønsted acid sites allowed to reach quantitative conversion of triose to ethyl lactate in ethanol[43]. To get a deeper insight into the acidic sites distribution on the surface of CuO/SiAl, we carried out a series of catalytic tests by varying the metal loading and checking by IR the acidic sites distribution. Figure 4.5 sums up results obtained in terms of conversion and selectivity with copper loading increasing from 2.5% to 8% compared with the bare support. Both conversion and selectivity to lactic acid increase linearly with the Cu loading, reaching a maximum with the 8% Cu catalyst. This interesting trend fits very well with a different distribution of Lewis and Brønsted sites in the corresponding catalysts as revealed by IR analysis of adsorbed pyridine.

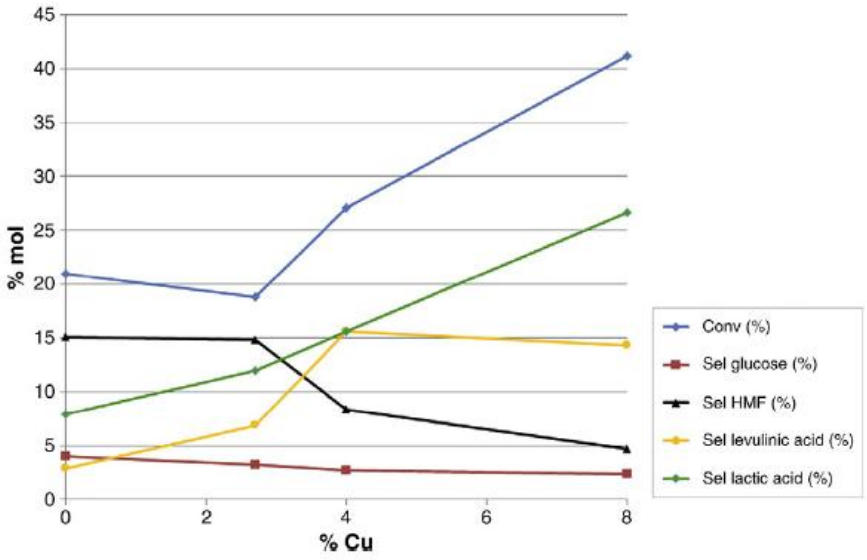


Figure 4.5 Conversion and selectivities obtained in cellulose deconstruction by using different loaded copper catalysts over silica alumina

Figure 4.6 shows the spectra recorded for the four catalysts and the bare support after outgassing at 150 °C and their comparison with CuO/SiO_2. The bands at 1640, 1547 and 1492 cm^{-1} in the sample of SiAl without copper are the most intense modes of pyridinium cations associated with a total proton transfer from the Brønsted acidic surface -OH group to the basic molecule, whereas bands at 1623 and 1455 cm^{-1} are due to the pyridine molecularly coordinated on Al^{3+} cations, acting as Lewis acid sites[44]. When analyzing the spectra of adsorbed pyridine on copper catalysts, it is worth noting the progressive growth of a band at 1610 cm^{-1} ascribable to Lewis acid sites. This particular band, observed also on the surface of CuO supported on silica increases in intensity by increasing the copper content, while the bands at 1640 and 1492 cm^{-1} significantly decrease. The presence of important Lewis acidic sites, deriving both from Al^{3+} and dispersed copper oxide strongly interacting with the surface, could therefore be the reason for such a sharp increase in conversion and selectivity into lactic acid. Thus, a mechanism similar to the one hypothesized with AlW involving the direct coordination with –OH group belonging to soluble oligomers to Lewis sites, followed by intra cyclic C-O and C-C cleavage, could also take place in the present case.

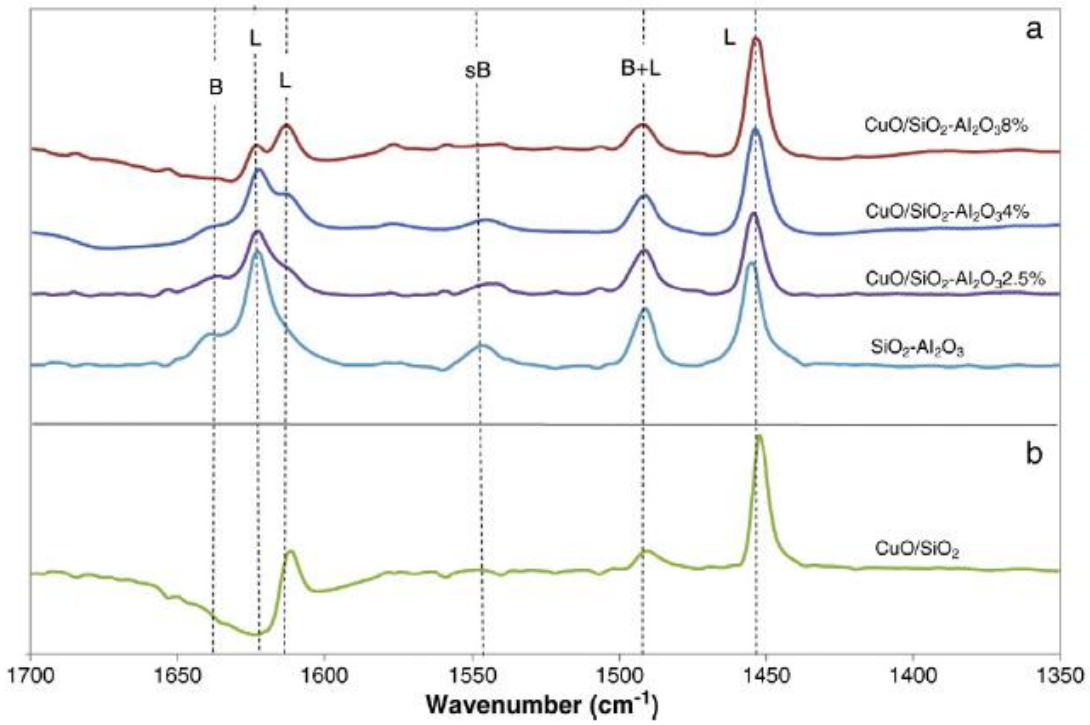


Figure 4.6 Pyridine adsorption IR spectra after outgassing at 150°C for CuO/SiAl 2,5%, CuO/SiAl 4%, CuO/SiAl 8%, SiAl and CuO/SiO_2

4.3 Experimental part

4.3.1 Chemicals

α-cellulose and silica were purchased from Sigma Aldrich, the other oxides were purchased from Grace and TiO_2 P25 was from Evonik. The copper catalysts were synthesized as reported (see Chapter 2). The desired amount of $Cu(NO_3)_2$*3 H_2O was dissolved in 20 mL of distilled water and bring to pH 9 with NH_4OH 27%. The oxide support was mixed with the copper amino complex, and the slurry was stirred for 20 minutes. After 20 minutes, the suspension was poured in a 5 L 2-necked flask, inserted in ice bath and equipped with mechanic stirrer. During 3 hours, 3 L of distilled water are dropped in the flask; after the suspension was filtered by a Büchner funnel, dried at 120°C overnight and calcined at 350°C for 4 hours in static air.
Before use the catalysts were dehydrated at 270°C for 20 minutes in air and in vacuum.

4.3.2 Instruments

All the reactions were carried on in a hastelloy Parr Instrument autoclave with an internal volume of 0.1L, and an HEL parallel reactor system.
The HPLC analysis where performed using an Agilent 1260 Infinity equipped with UV and RID detectors, a MetaCarb H Plus Guard Column 50 x 4,6 mm and a MetaCarb H Plus Column 300 x 7,8 mm. The TOC analysis were performed with a Shimadzu TOC-L analyzer.
<u>Retention times</u>
Glucose: 18,4 min at RID
Fructose: 19,4 min at RID
Lactic acid: 25,5 min at RID
Levulinic acid: 32,6 min at RID
HMF: 60,5 min at RID

4.3.3 Analysis

The conversion in soluble organic compound was calculated using TOC. 1 mL of reaction solution was poured in 10 mL of distilled water, 8 mL of this solution were diluted with 40 mL of distilled water and used for TOC analysis. The conversion was calculated with the following formula:

$$conv\% = \left(\frac{ppm\ TOC}{20000}\right) * 100$$

ppm TOC = mg/L of soluble organic compound;

20000 = maximum theoretical mg/L of C.

The conversion was also calculated with the solid residual of reaction, subtracting the weight of the catalyst.

Selectivity in chosen compounds was calculated using HPLC. 1 mL of reaction solution was diluted in 10 mL and injected (loop 20 mL). Analysis condition: flow 0,4 mL/min, temperature 323 K, eluent solution of H_2SO_4 0.0085 N in MilliQ water.

$$sel\% = \left(\frac{conc\ x}{ppm\ TOC}\right) * 100$$

conc x = concentration of compound derived from HPLC analysis;

ppm TOC = mg/L of soluble organic compound.

Cellulose depolymerization (CELL38)

Reagent	Grams (g)	mL
α-cellulose	1.5031	
CuO/SiO_2 CHROM 16% Cu	0.8022	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 150°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 17 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	528	2.4
17	1365.5	6.1
24	2786	12.5

Conversion by weight: 36.0%

Selectivity (after 24 h):

glucose: 14.6%

fructose: 9.6%

levulinic acid: 0%

HMF: 9.6%

lactic acid: 1.1%

Cellulose depolymerization (CELL39)

Reagent	Grams (g)	mL
α-cellulose	1.5137	
CuO/SiO_2 CHROM 16% Cu	0.8030	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 17 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	7875	35.1
17	4494	22.5
24	6195	27.6

Conversion by weight: 58.0%

Selectivity (after 24 h):

glucose: 10.7%

fructose: 1.4%

levulinic acid: 7.3%

HMF: 14.4%

lactic acid: 2.7%

Cellulose depolymerization (CELL42)

Reagent	Grams (g)	mL
α-cellulose	0.2716	
H2SO4 0.01M		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 150°C and stirred with a mechanic stirrer at 100 rpm for 16 hours. After 2 and 16 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	1733.5	43.1
16	3283	81.6

Conversion by weight: 11.0%

Selectivity (after 16 h):

glucose: 1.2%

fructose: 0.2%

levulinic acid: 10.6%

HMF: 0.0%

Cellulose depolymerization (CELL43)

Reagent	Grams (g)	mL
α-cellulose	1.5068	
water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2,19 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	2387	10.7
19	1588.5	7.12
24	6930	31.0

Conversion by weight: 36.0%

Selectivity (after 24 h):

glucose: 5.8%

fructose: 3.5%

levulinic acid: 8.7%

HMF: 6.6%

lactic acid: 4.6%

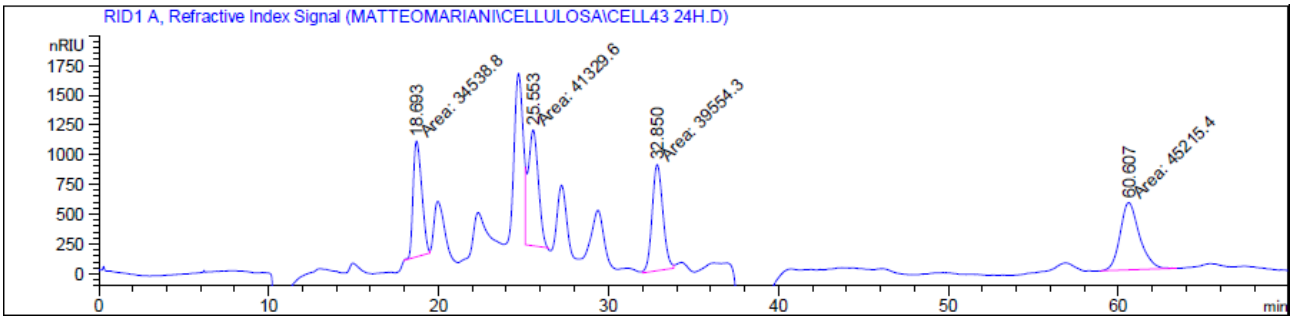


Figure4.6 Chromatogram of reaction CELL43

Cellulose depolymerization (CELL44)

Reagent	Grams (g)	mL
α-cellulose	1.5061	
CuO/SiO_2-Al_2O_3 135 8% Cu	0.8030	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 19 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	4185.5	18.8
19	2384	10.7
24	9200	41.2

Conversion by weight: 58.0%

Selectivity (after 24 h):

glucose: 2.4%

fructose: 1.0%

levulinic acid: 14.3%

HMF: 4.7%

lactic acid: 26.6%

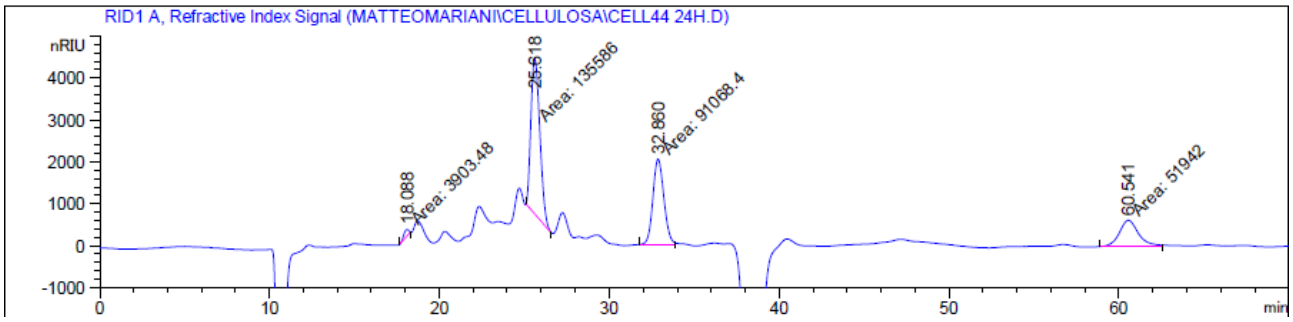


Figure 4.7 Chromatogram of reaction CELL44

Cellulose depolymerization (CELL45)

Reagent	Grams (g)	mL
α-cellulose	1.5095	
CuO/SiO_2-TiO_2 2.3% 8% Cu	0.8004	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 19 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	2823	12.6
19	2943	13.2
24	5425	24.3

Conversion by weight: 34.0%

Selectivity (after 24 h):

glucose: 21.3%

fructose: 2.4%

levulinic acid: 11.1%

HMF: 19.4%

lactic acid: 2.1%

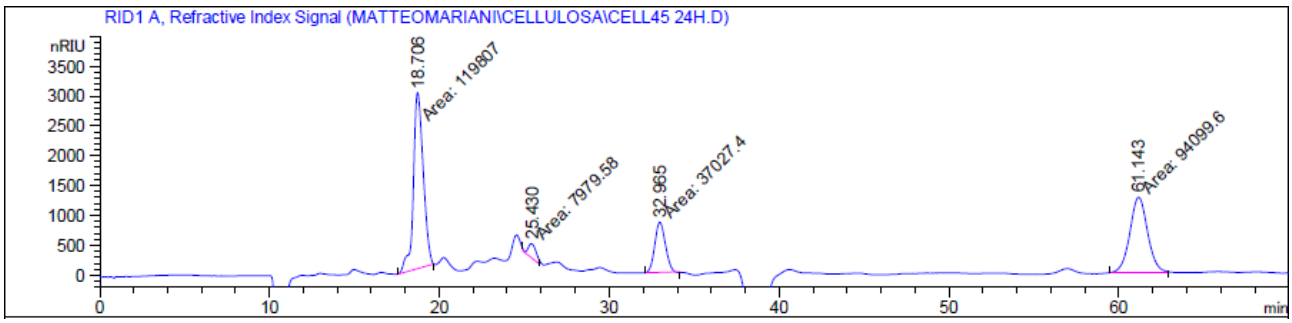


Figure 4.8 Chromatogram of reaction CELL45

Cellulose depolymerization (CELL46)

Reagent	Grams (g)	mL
α-cellulose	1.5072	
SiO_2 CHROM	0.8035	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 19 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	3709.5	16.6
19	2464.5	11.0
24	4365	19.6

Conversion by weight: 50.0%

Selectivity (after 24 h):

glucose: 5.5%

fructose: 2.0%

levulinic acid: 4.1%

HMF: 26.4%

lactic acid: 3.3%

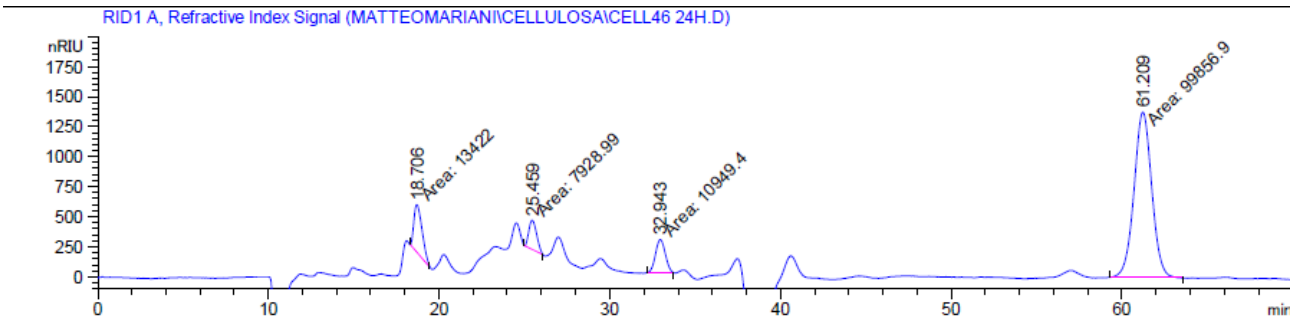


Figure 4.9 Chromatogram of reaction CELL46

Cellulose depolymerization (CELL47)

Reagent	Grams (g)	mL
α-cellulose	1.5095	
SiO_2-Al_2O_3 135	0.8047	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 19 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	3210.5	14.4
19	2665	12.0
24	4688	21.0

Conversion by weight: 51.0%

Selectivity (after 24 h):

glucose: 4.0%

fructose: 1.4%

levulinic acid: 3.0%

HMF: 15.1%

lactic acid: 8.0%

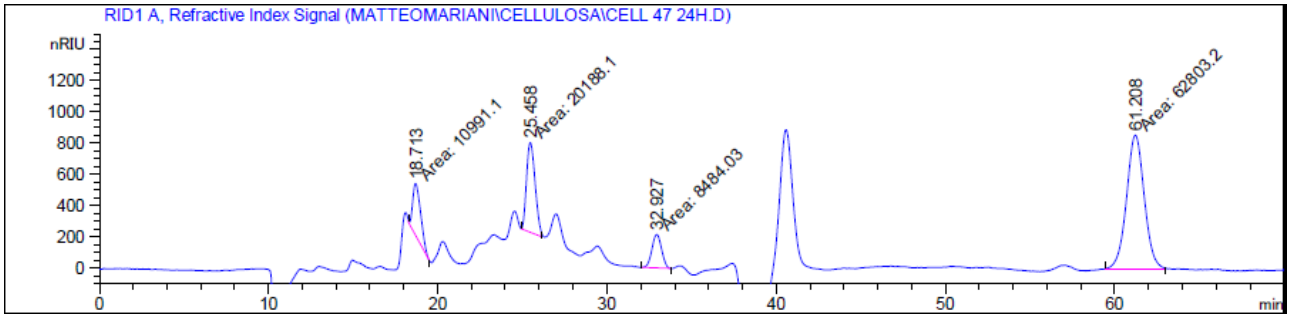


Figure 4.10 Chromatogram of reaction CELL47

Cellulose depolymerization (CELL48)

Reagent	Grams (g)	mL
α-cellulose	1.5009	
SiO_2-TiO_2 2.3%	0.8074	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 19 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	2884.5	13.0
19	2520.5	11.3
24	5370	24.2

Conversion by weight: 50.3%

Selectivity (after 24 h):

glucose: 16.1%

fructose: 2.6%

levulinic acid: 4.1%

HMF: 24.4%

lactic acid: 3.1%

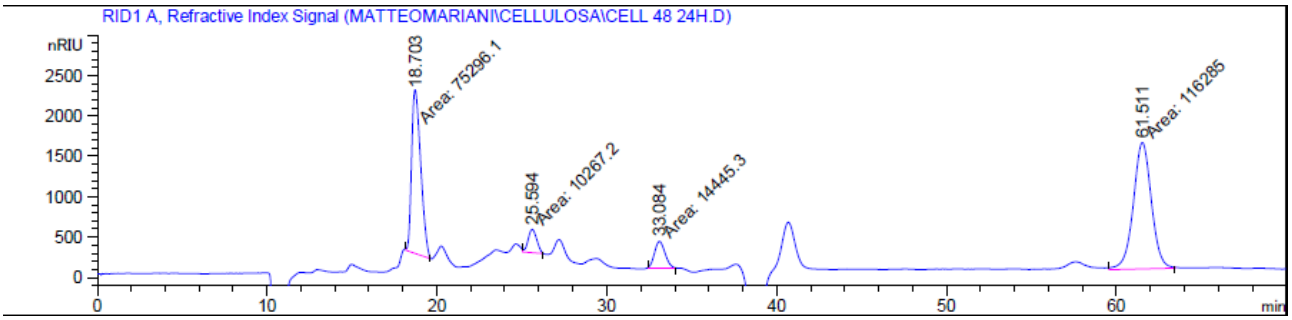


Figure 4.11 Chromatogram of reaction CELL48

Cellulose depolymerization (CELL54)

Reagent	Grams (g)	mL
α-cellulose	1.5025	
CuO/TRYSIL 8% Cu	0.8106	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 16 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	1504	6.6
16	2115	9.2
24	5610	24.4

Conversion by weight: 88.0%

Selectivity (after 24 h):

glucose: 20.0%

fructose: 0.8%

levulinic acid: 9.0%

HMF: 16.3%

lactic acid: 0.7%

Cellulose depolymerization (CELL56)

Reagent	Grams (g)	mL
α-cellulose	1.5001	
CuO/AEROSIL 16% Cu	0.8069	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 16 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	5295	23.8
16	2427.5	11.0
24	4450	20.0

Conversion by weight: 55.0%

Selectivity (after 24 h):

glucose: 10.7%

fructose: 1.4%

levulinic acid: 0.0%

HMF: 20.5%

lactic acid: 0.2%

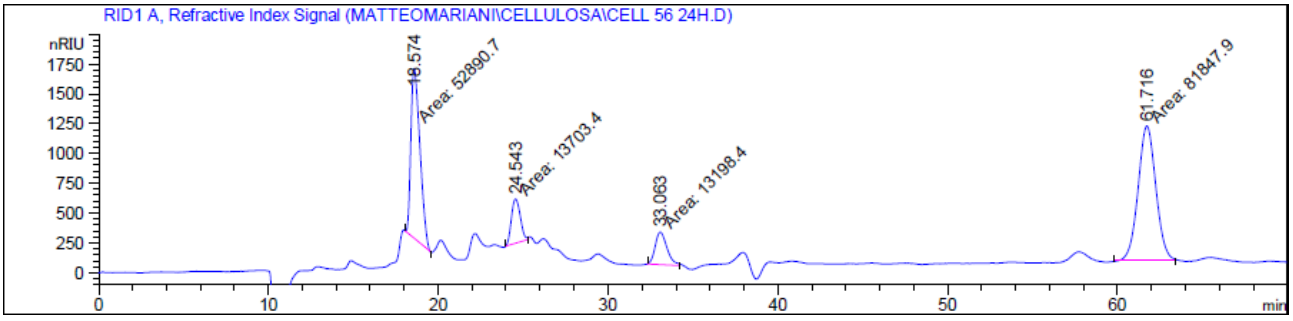


Figure 4.12 Chromatogram of reaction CELL56

Cellulose depolymerization (CELL57)

Reagent	Grams (g)	mL
α-cellulose	1.5004	
CuO/TiO_2 8% Cu	0.8023	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 16 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	4108	18.5
16	2693	12.1
24	5910	26.6

Conversion by weight: 77.2%

Selectivity (after 24 h):

glucose: 15.0%

fructose: 0.7%

levulinic acid: 10.5%

HMF: 10.7%

lactic acid: 3.0%

Cellulose depolymerization (CELL65)

Reagent	Grams (g)	mL
α-cellulose	1.5006	
TRYSIL	0.8059	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 16 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	1779.5	8.0
16	8510	38.3
24	4965.5	22.3

Conversion by weight: 70.0%

Selectivity (after 24 h):

glucose: 4.5%

fructose: 0.8%

levulinic acid: 2.0%

HMF: 14.2%

lactic acid: 4.0%

Cellulose depolymerization (CELL68)

Reagent	Grams (g)	mL
α-cellulose	1.5027	
CuO/Al_2O_3 Puralox 8%Cu	0.8020	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 16 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	1787	8.0
16	3755	16.9
24	3667	16.5

Conversion by weight: 33.0%

Selectivity (after 24 h):

glucose: 1.7%

fructose: 1.0%

levulinic acid: 0.6%

HMF: 8.8%

lactic acid: 24.3%

Cellulose depolymerization (CELL69)

Reagent	Grams (g)	mL
α-cellulose	1.5018	
Al_2O_3 Puralox	0.8082	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 16 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	2042.5	9.2
16	3558	16.0
24	3930	17.7

Conversion by weight: 40.2%

Selectivity (after 24 h):

glucose: 2.1%

fructose: 0.7%

levulinic acid: 0.4%

HMF: 7.4%

lactic acid: 27.8%

Cellulose depolymerization (CELL70)

Reagent	Grams (g)	mL
α-cellulose	1.5044	
CuO/SiO_2-ZrO_2 (1%) 8%Cu	0.8049	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 16 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	2910	13.1
16	3751.5	16.8
24	5810	26.1

Conversion by weight: 40.2%

Selectivity (after 24 h):

glucose: 18.0%

fructose: 0.8%

levulinic acid: 12.5%

HMF: 15.2%

lactic acid: 2.0%

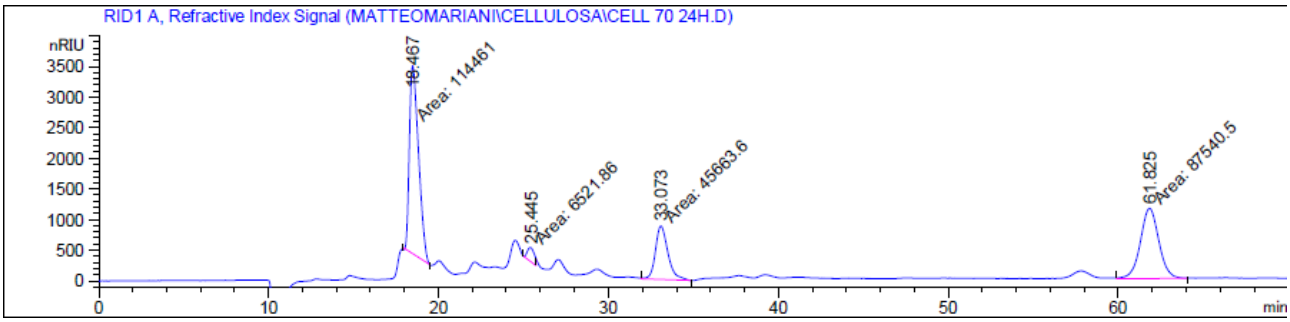


Figure 4.13 Chromatogram of reaction CELL70

Cellulose depolymerization (CELL71)

Reagent	Grams (g)	mL
α-cellulose	1.5059	
SiO_2-ZrO_2 (1%)	0.8048	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 16 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	1370	6.1
16	2400	10.8
24	5285	23.7

Conversion by weight: 43.0%

Selectivity (after 24 h):

glucose: 16.1%

fructose: 0.7%

levulinic acid: 8.3%

HMF: 15.0%

lactic acid: 4.2%

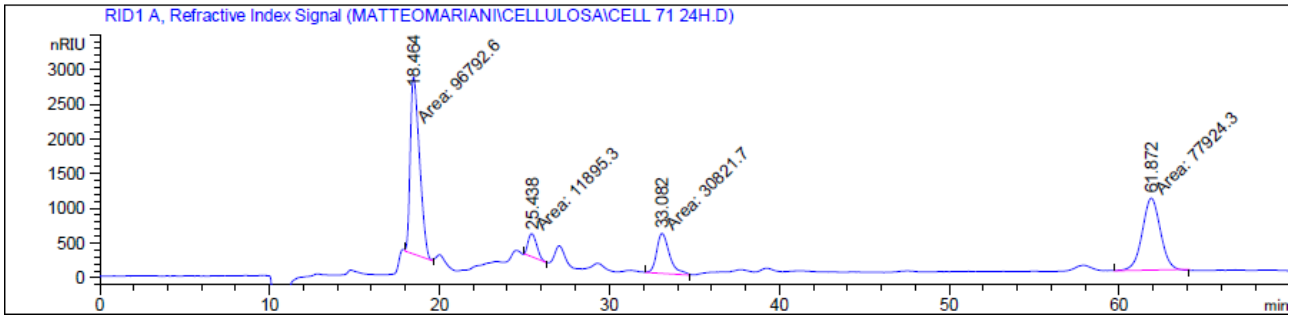


Figure 4.14 Chromatogram of reaction CELL71

Cellulose depolymerization (CELL73)

Reagent	Grams (g)	mL
α-cellulose	1.5030	
TRYSIL 300	0.8118	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 16 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	3708.5	16.7
16	3705.5	16.7
24	3775.5	17.0

Conversion by weight: 69.0%

Selectivity (after 24 h):

glucose: 16.6%

fructose: 0.7%

levulinic acid: 6.0%

HMF: 23.4%

lactic acid: 0.6%

Cellulose depolymerization (CELL74)

Reagent	Grams (g)	mL
α-cellulose	1.5047	
CuO/SiO_2 MP04300 8% Cu	0.8052	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 16 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	2062.5	9.3
16	3218.5	14.4
24	3300	14.8

Conversion by weight: 68.0%

Selectivity (after 24 h):

glucose: 24.4%

fructose: 0.0%

levulinic acid: 7.0%

HMF: 21.0%

Cellulose depolymerization (CELL75)

Reagent	Grams (g)	mL
α-cellulose	1.5029	
AEROSIL 380	0.8035	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 16 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	574	2.6
16	1931.5	8.7
24	4421.5	20.0

Conversion by weight: 27.0%

Selectivity (after 24 h):

glucose: 16.1%

fructose: 2.0%

levulinic acid: 1.0%

HMF: 23.0%

lactic acid: 0.5%

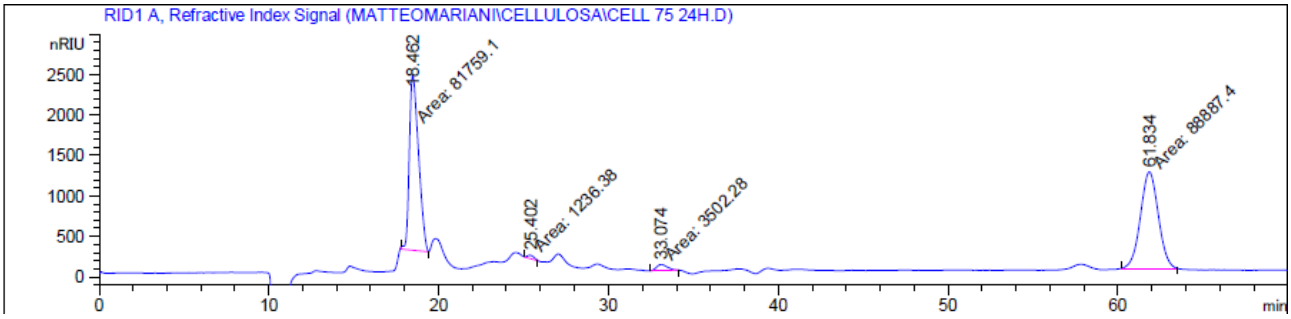


Figure 4-15 Chromatogram of reaction CELL75

Cellulose depolymerization (CELL76)

Reagent	Grams (g)	mL
α-cellulose	1.5054	
TiO_2 P25	0.8007	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 16 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	2641	11.8
16	2054	9.2
24	6165	27.6

Conversion by weight: 70.0%

Selectivity (after 24 h):

glucose: 20.3%

fructose: 0.4%

levulinic acid: 13.2%

HMF: 7.8%

lactic acid: 2.5%

Cellulose depolymerization (CELL77)

Reagent	Grams (g)	mL
α-cellulose	1.5057	
CuO/SiO_2 CHROM 16% Cu	0.8015	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 210°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 1, 2 and 3 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
1	3466.5	15.5
2	3960.5	17.8
3	6470	29.0

Conversion by weight: 46.0%

Selectivity (after 24 h):

glucose: 26.5%

fructose: 0.7%

levulinic acid: 2.7%

HMF: 23.5%

Cellulose depolymerization (CELL78)

Reagent	Grams (g)	mL
α-cellulose	1.5000	
CuO/TRYSIL 300 8% Cu	0.8053	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 16 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	2415.5	10.9
16	3691.5	16.6
24	5775	26.0

Conversion by weight: 47.4%

Selectivity (after 24 h):

glucose: 30.0%

fructose: 0.3%

levulinic acid: 9.0%

HMF: 15.0%

Cellulose depolymerization (CELL79)

Reagent	Grams (g)	mL
α-cellulose	1.5021	
CuO/SiO_2-Al_2O_3 D 4% Cu	0.8028	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 16 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	3274.5	14.7
16	2561.5	11.5
24	6025	27.1

Conversion by weight: 48.6%

Selectivity (after 24 h):

glucose: 2.7%

fructose: 1.4%

levulinic acid: 15.6%

HMF: 8.4%

lactic acid: 15.6%

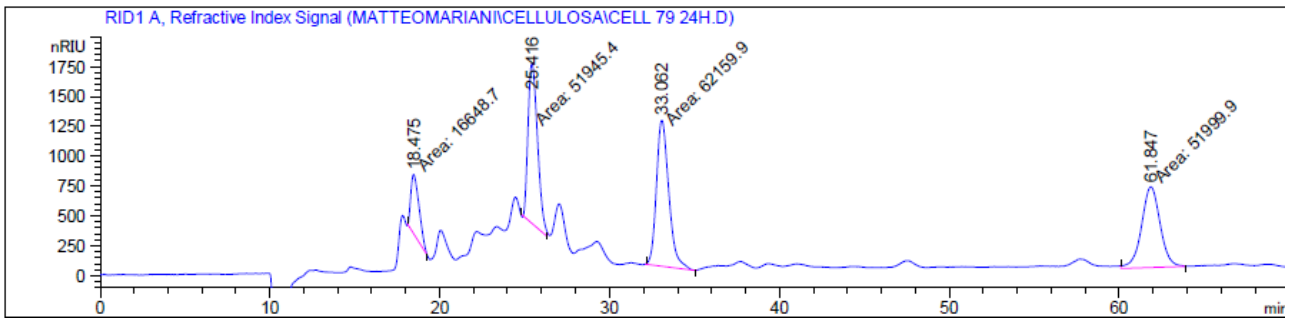


Figure 4.16 Chromatogram of reaction CELL79

Cellulose depolymerization (CELL80)

Reagent	Grams (g)	mL
α-cellulose	1.5042	
CuO/SiO_2-Al_2O_3 D 3% Cu	0.8072	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 16 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	2945	13.2
16	4592	20.6
24	4197	18.8

Conversion by weight: 39.0%

Selectivity (after 24 h):

glucose: 3.3%

fructose: 1.6%

levulinic acid: 6.8%

HMF: 14.8%

lactic acid: 12.0%

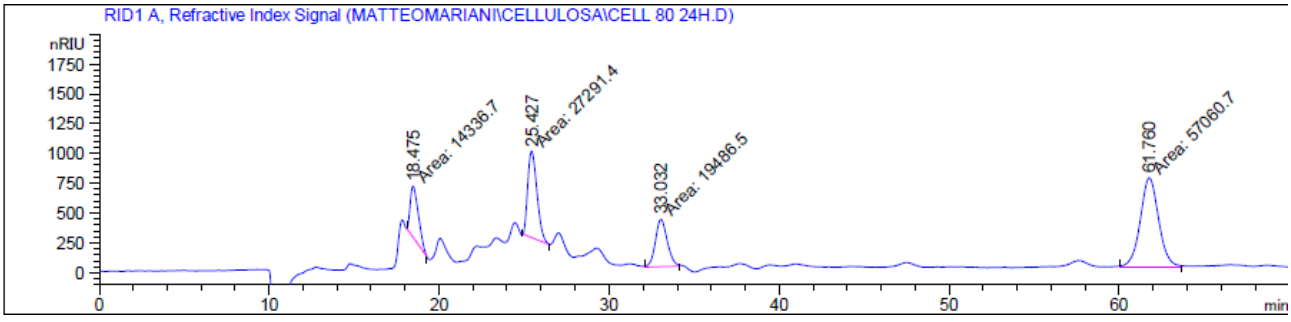


Figure 4.17 Chromatogram of reaction CELL80

Cellulose depolymerization (CELL81)

Reagent	Grams (g)	mL
α-cellulose	1.5039	
SiO_2 MP04300	0.8026	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 16 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	2398	10.8
16	3289.5	14.8
24	4988.5	22.4

Conversion by weight: 57.0%

Selectivity (after 24 h):

glucose: 18.0%

fructose: 1.5%

levulinic acid: 2.1%

HMF: 24.1%

lactic acid: 0.6%

Cellulose depolymerization (CELL82)

Reagent	Grams (g)	mL
α-cellulose	1.5003	
CuO/SiO_2-Al_2O_3 D 12.4% Cu	0.8018	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 16 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	3815.5	17.2
16	3108	14.0
24	3321	15.0

Conversion by weight: 54.2%

Selectivity (after 24 h):

glucose: 0.0%

fructose: 0.1%

levulinic acid: 7.0%

HMF: 1.0%

lactic acid 5.7%

Cellulose depolymerization (CELL83)

Reagent	Grams (g)	mL
α-cellulose	1.5028	
CuO/SiO_2 CHROM 8% Cu	0.8037	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 16 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	3224	14.5
16	2830.5	12.7
24	4345.5	19.5

Conversion by weight: 40.0%

Selectivity (after 24 h):

glucose: 21.4%

fructose: 1.0%

levulinic acid: 4.4%

HMF: 20.7%

lactic acid: 0.5%

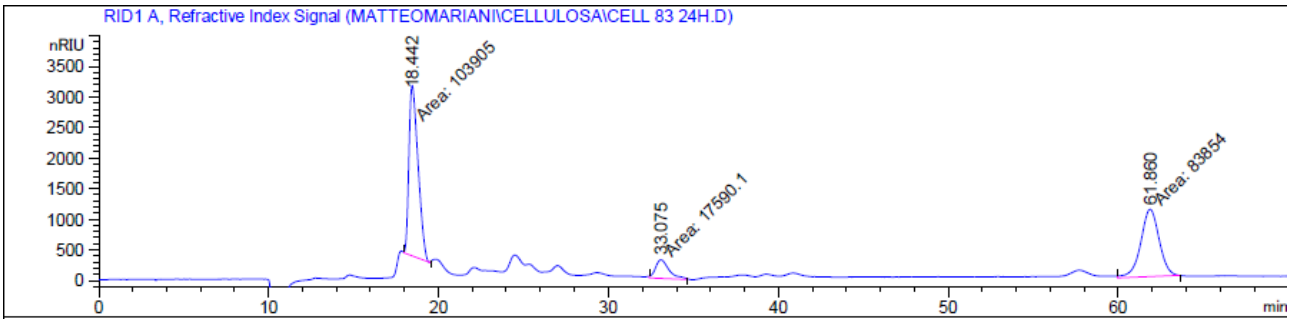


Figure 4.18 Chromatogram of reaction CELL83

Cellulose depolymerization (CELL84)

Reagent	Grams (g)	mL
α-cellulose	1.5023	
CuO/ZSM5 8%	0.8010	
Water		30

All reagents were inserted in the autoclave, the system was evacuated and filled with dinitrogen 3 times; then 4 bar of N_2 were introduced. The reactor was heated at 180°C and stirred with a mechanic stirrer at 1000 rpm for 24 hours. After 2, 16 and 24 hours reaction a sample was taken, for HPLC and TOC analysis. When the reaction is finished, the suspension was filtered with a paper filter, obtaining a dark solid and a dark yellow solution. The solid was dried at RT and weighed for the conversion.

Time (h)	ppm C (TOC)	Conversion (%)
2	3917.5	17.6
16	3176.5	14.3
24	4057	18.2

Conversion by weight: 64.1%

Selectivity (after 24 h):

glucose: 3.4%

fructose: 0.2%

levulinic acid: 37.5%

HMF: 3.6%

lactic acid: 0.8%

4.4 References

[1] C.E. Wyman, S.R. Decker, M.E. Himmel, J.W. Brady, C.E. Skopec, L. Viikari, *Polysaccharides*, 2nded, S. Dumitriu, Ed, Marcel Dekker, New York, 2005;

[2] R. Rinaldi, R. Palkovitz, F. Schüt, *Angew.Chem. Int. Ed.*, 2008,120, 8167;

[3] F. Guo, Z. Fang, C.C. Xu, R.L. Smith, *Progress in Energy and Combustion Science,* 2012, 38, 672;

[4] J.F. Saeman, J.L. Bubl, E.E. Harris, *Ind. Eng. Chem. Anal. Ed.,* 1945, 17,35;

[5] F. Camacho, P. Gonzalez-Tello, E. Jurado, A. Robles, *J. Chem. Technol. Biotechnol.,* 1996, 67, 350;

[6] Nanjing, Forestry Institute. Plant Hydrolysis Technology. 1st edition, Beijing,: Agricultural Press; 1961;

[7] M. Sasaki, Z. Fang, Y. Fukushima, T. Adschiri, K. Arai, *Ind. Eng. Chem. Res.,*2000, 39,2883;

[8] M.J. Zhang, R.G. Su, W. Qi, Z.M. He, *Appl. Biochem. Biotech.,* 2010, 160, 1407;

[9] S. Kim, B.E. Dale, *Biomass Bioenerg.,* 2004, 26, 361;

[10] J.A. Bootsma, B.H. Shanks, *Appl. Catal. A: Gen.,*2007, 327, 44;

[11] N. Salman, C.H. Rüscher, J.C. Buhl, W. Lutz, H. Toufar, M. Stöcker, *Micropor. Mesopor. Mat.,*2006, 67, 1741;

[12] Z. Zhang, Z.K. Zhao, *Carbohyd. Res.,* 2009, 344, 2069;

[13] C. Tagusakawa, A. Takagaki, A. Iguchi, K. Takanabe, J.N. Kondo, K. Ebitani, *Angew. Chem. Int. Ed.,*2010, 49, 1128;

[14] J.N. Kondo, T. Yamashita, K. Nakajima, D. Lu, M. Hara, K. Domen, *J. Mater. Chem.,* 2005, 15, 2035;

[15] Z. Zhang, Z.K. Zhao, *Carbohyd. Res.,* 2009, 344, 2069;

[16] N.O. Nilvebrant, A. Riemann, S. Larsson, L.J. Jönsson, *Appl. Biochem. Biotechnol.,* 2001, 91-93, 35;

[17] A. Onda, T. Ochi, K. Yanagisawa, *Green Chem.,* 2008, 10,1033;

[18] V. Degirmenici, D. Uner, B. Cinlar, B.H. Shanks, A. Yilmaz, R.A. Santen, *Catal. Lett.,* 2011, 141, 33;

[19] Z. Zhang, Z.K. Zhao, *Carbohyd. Res.,* 2009, 344, 2069;

[20] S. Suganuma, K. Nagajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi, *J. Am. Chem. Soc.,* 2008, 130, 12787;

[21] A. Fukuoka, P.L. Dhepe, *Angew. Chem. Int. Ed.,* 2006, 45, 5161;

[22] M. Toda, A. Takagaki, M. Okamura, J.N. Kondo, S. Hayashi, K. Domen, *Nature,* 2005, 438, 178;

[23] S. Suganuma, K. Nagajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi, *Solid State Sci.,* 2010, 12, 1029;

[24] J. Tian, J. Wang, S. Zhao, C. Jiang, X. Zhang, X. Wang, *Cellulose,* 2010, 17, 587;

[25] T. Okuhara, *Chem. Rev.,* 2002, 102, 3641;

[26] E.J.M. Hensen, D.G. Poduval, V. Degirmenci, D.A.J. Michel Ligthart, W. Chen, F. Maugé, M.S. Rigutto, J.A.R. van Veen, *Journal of Physical Chemistry C,* 2012, 116, 21416 ;

[27] F. Zaccheria, N. Scotti, M. Marelli, R. Psaro, N. Ravasio, *Dalton Transactions*, 2013, 42 (5), 1319;

[28] K. Shimizu, H. Furukawa, N. Kobayashi, Y. Itaya, A. Satsuma, *Green Chemistry*, 2009, 11, 1627;

[29] V. Choudhary, S.H. Mushrif, C. Ho, A. Anderko, V. Nikolakis, N.S. Marinkovic, A.I. Frenkel, S.I. Sandler, D.G. Vlachos, *JACS*, 2013, 135, 3997;

[30] F. Santoro, F. Zaccheria, N.I. Shaikh, N. Ravasio, *Topics in Catalysis*, 2012, 55, 606;

[31] F. Zaccheria, F. Santoro, R. Psaro, N. Ravasio, *Green Chemistry*, 2011, 13 (3), 545;

[32] A.M. Ruppert, K.Weinberg, R. Palkovits, *Angewandte Chemie, International Edition*, 2012, 51, 2564;

[33] K. Tajvidi, K. Pupovac, M. Kukrek, R. Palkovits*, ChemSusChem* 2012, 5, 2139;

[34] H. Kobayashi, T. Komanoya, K. Hara, A. Fukuoka, *ChemSusChem*, 2010, 3, 440;

[35] B. Op de Beeck, J. Geboers, S. Van de Vyver, J. Van Lishout, J. Snelders, W.J.J. Huijgen, C.M. Courtin, P. Jacobs, B.F. Sels, *ChemSusChem*, 2013, 6 (1), 199;

[36] V. Jollet, F. Chambon, F. Rataboul, A. Cabiac, C. Pinel, E. Guillon, N. Essayem*, Green Chemistry*, 2009, 11, 2052;

[37] H. Kobayashi, T. Komanoya, S.K. Guha, K. Hara, A. Fukuoka, *Applied Catalysis A: General*, 2011, 409–410, 13;

[38] T. Komanoya, H. Kobayashi, K. Hara, W.J. Chun, A. Fukuoka, *Applied Catalysis A: General,* 2011, 407, 188;

[39] A. Gervasini, M. Manzoli, G. Martra, A. Ponti, N. Ravasio, L. Sordelli, F. Zaccheria, *The Journal of Physical Chemistry: B*, 2006, 110, 7851;

[40] B. Dragoi, A. Gervasini, E. Dumitriu, A. Auroux, *Thermochimica Acta,* 2004, 420, 127;

[41] G. Boskovic, T. Vulic, E. Kis, P. Putanov, *Chemical Engineering and Technology*, 2001, 24, 3;

[42] F. Chambon, F. Rataboul, C. Pinel, A. Cabiac, E. Guillon, N. Essayem*, Applied Catalysis B: Environmental*, 2011, 105, 171;

[43] F. de Clippel, M. Dusselier, R. Van Rompaey, P. Vanelderen, J. Dijkmans, E. Makshina, L. Giebeler, S. Oswald, G.V. Baron, J.F.M. Denayer, P.P. Pescarmona, P.A. Jacobs, B.F. Sels, *JACS*, 2012, 134, 10089;
[44] M. Trombetta, G. Busca, S. Rossini, V. Piccoli, U. Cornaro, A. Guercio, R. Catani, R. Willey, *Journal of Catalysis*, 1998, 179, 581;

Chapter 5:

Lactose

5.1 Introduction

Lactose is a disaccharide formed by one D-glucose unit connected to a D-galactose unit by a β-1,4 glycosidic bond.

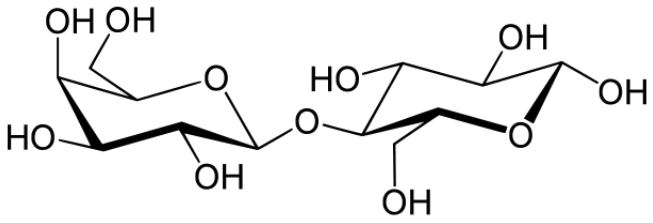


Figure 5.2 Lactose structure

The estimated annual worldwide availability of lactose, from cheese production, is several million tons[1]. In spite of this huge amount of lactose, only 400000 t/a of lactose are processed further from cheese whey[2]. In fact whey contains about 60-80% of its dry weight of lactose, and the disposal of this waste is very difficult, due to its high biological and chemical oxygen demand. There are two main limitations to lactose use: its relatively low solubility, and the inability of lactose-intolerant people to digest this milk sugar. Milk whey, and lactose in particular, are becoming very problematic substances and their valorization could become a very interesting point to look at within the biorefinery concept. Lactitol, lactulose and lactobionic acid are the most important lactose derivatives from industrial us[3]. Moreover, the two hydrolysis products glucose and galactose can be oxidized in order to obtain valuable materials (ascorbic and erythorbic acid) used in the pharmaceutical industry[4]. Lactitol is a sugar alcohol, derived from the reduction of glucose contained in lactose. It is suitable for the preparation of sugar-free, reduced calories and low-glycemic index products, showing non-cariogenic and prebiotics properties. Lactitol is metabolized independently of insulin, and for this reasons it is suitable for a diabetic diet; moreover it can substitute sucrose in most applications, due to its similar physical properties[5].
In addition it can be used as sweetener and as laxative[6]. Industrially it is produced by catalytic hydrogenation of lactose with Raney Ni catalyst. Lactulose is produced by isomerization of lactose[7] and has many applications in food and pharmaceutical field, for example as sweetener for diabetics or in the treatment of hepatic encephalopathy[8]. It is industrially produced by enzymatic or chemical methods[9]. Lactobionic acid is an antioxidant compound, that can replace formalin as organ preservation liquid, with the advantage of being less toxic[10], and it can be used in the cosmetic industry. Lactose oxidation into lactiobionic acid is carried out with heterogeneous catalysts, usually noble metals supported onto silica, alumina, titania, carbon, ecc. Sorbitol and

galactitol find applications similar to Lactitol, and can be obtained from lactose *via* hydrolysis reaction, followed by hydrogenation of the two sugars.

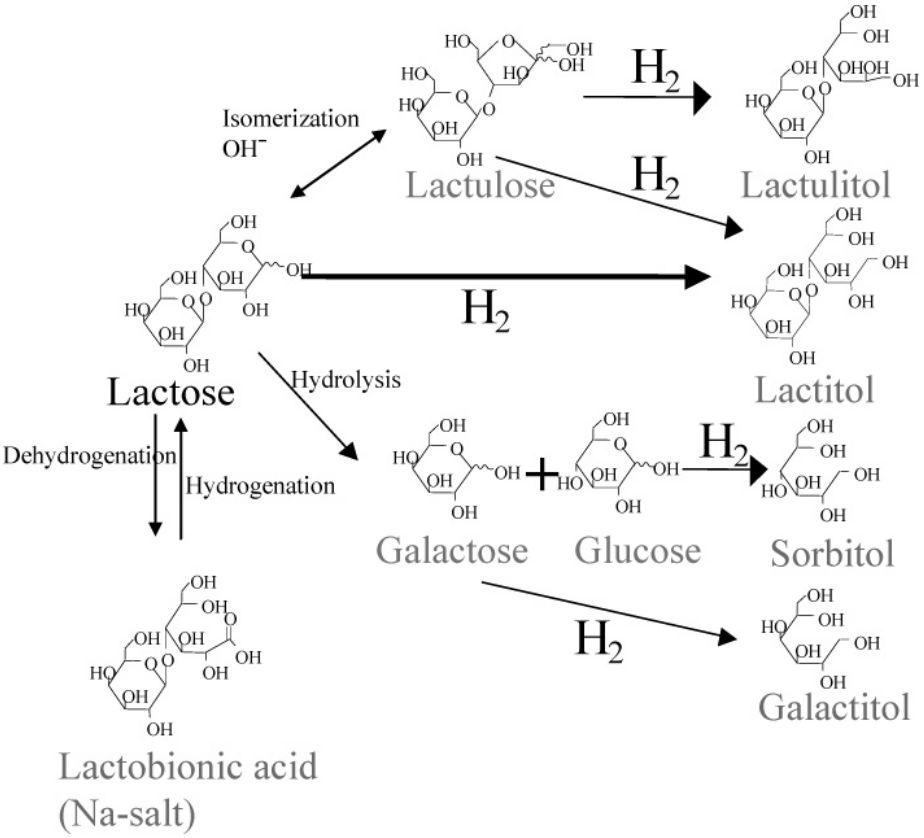


Figure 5.3 Lactose reactions

5.2 Results and discussion

Valorization of lactose is a very interesting reaction because is the major constituent of milk whey, the principal waste of dairy industry. Starting from our experience with cellulose hydrolysis , we thought to obtain high added value products, starting from this waste. In fact hydrolysis of lactose give the two sugars that compose lactose: glucose and galactose. A subsequent hydrogenation of this two sugars permits to obtain dulcitol and sorbitol(Figure 5.3). Sorbitol is very used in food industry in sugar-free and low calories products, and dulcitol can have same uses although unexplored up to now due to scarce availability of this sugar.

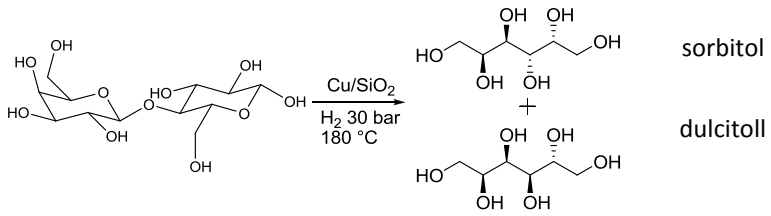


Figure 5.3 One-pot hydrolysis and hydrogenation of lactose

This transformation requires to carry out two reactions in one pot: the first reaction is the hydrolysis of lactose into glucose and galactose, the second one is the hydrogenation of the two sugars into corresponding polyols. Pre-reduced Cu/SiO_2 catalysts should be able to perform these two reactions at the same time. Thus, it has already been shown by the research group with whom I did my thesis[11] that reduction of the CuO phase, showing Lewis acidity, to the metallic state increases the acidity of the material. This allows one to set up bifunctional processes where the catalyst shows both acidic and hydrogenation activity.

This is due to the high dispersion of the CuO phase, making it very easily to reduce. In fact TPR profile shows a very sharp peak at lower temperature, with respect to the same catalyst prepared by incipient wetness or respect to the copper oxide bulk.

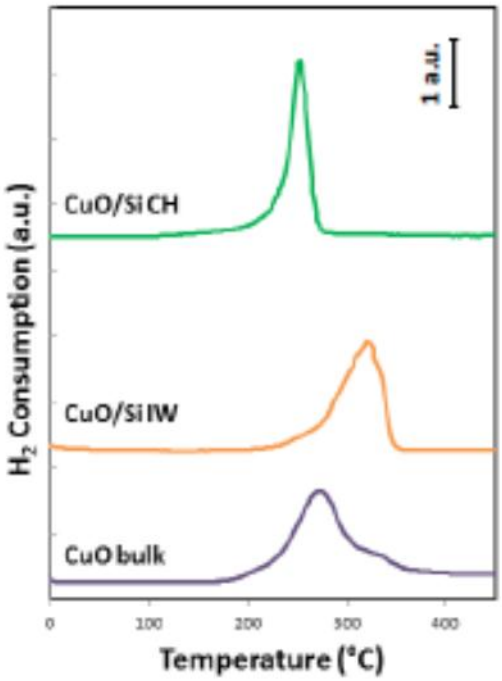


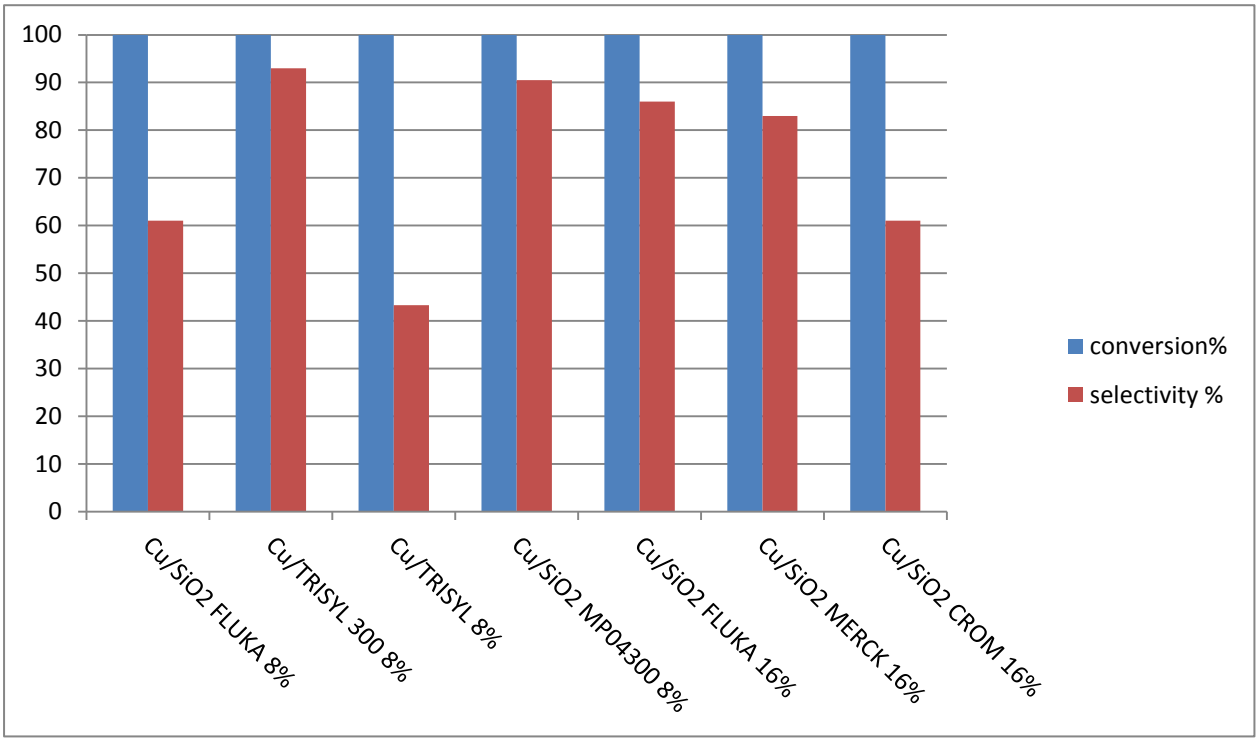
Figure 5.4 TPR profile for CuO/SiO_2 prepared by CH and by IW and compared with CuO bulk

The sharpening of the peak relative to the catalyst prepared by CH method is index of the good dispersion of the copper phase. Starting from these data we thought to use the catalyst for hydrolysis-hydrogenation of lactose.

In this work we explored some important parameters in heterogeneous catalysis: the metal loading and the support influence. As one might expect, the greater is the copper loading the higher is the conversion. In fact comparing the two catalysts Cu/SiO_2 FLUKA with 8% or with 16% of copper, it's possible to note the difference in polyols selectivity.

Changing the support is possible to obtain diverging behaviors, with the same metallic phase. In this case, comparing the two similar silicas TRISYL and TRISYL 300 we can see an opposite behavior. TRISYL 300 is a support able to helping Cu^0 phase to reduce sugars, whereas TRISYL decreases this capacity, and this catalyst gives lower selectivity in reduced sugars.

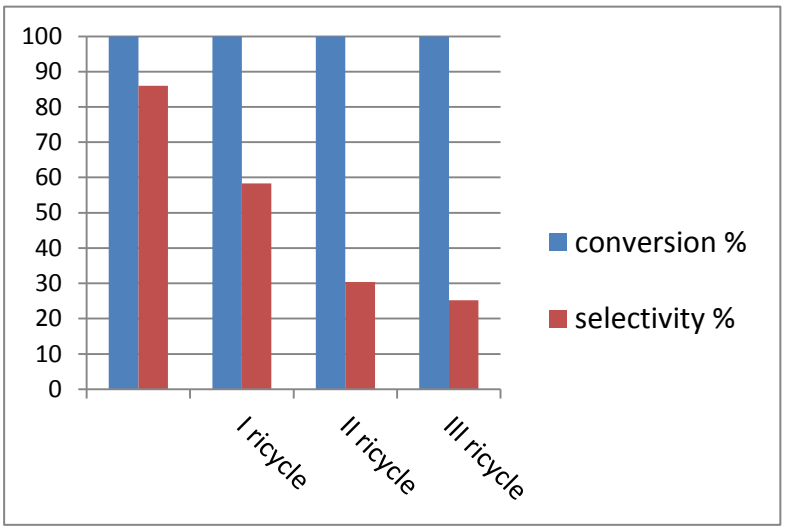
From all the tested catalysts we decide to use Cu/SiO_2 FLUKA 16% of Cu, because gives satisfactory selectivities in reduced sugars and the support is easy to find.



Graph 5-1 Results obtained in lactose hydrolysis-hydrogenation with different copper catalysts

The second step was trying to use milk whey as reactant, in order to perform the reaction with the raw material. Unfortunately it was impossible to obtain reduced sugars in this way, and also the elimination of milk proteins and fixing pH to a value of 7 didn't help.

After the failures with whey, we try to recycle catalyst in order to reuse it several times. We performed the recycle tests by removing the solution of products and by charging a new lactose solution. The results were not good, in fact the catalyst deactivate very fast, because the oxidation of metallic copper phase.



Graph 5.2 Rrecycle tests with Cu/SiO_2 16% Cu

5.3 Experimental part

5.3.1 Chemicals

β-lactose, D-(+)-glucose an D-(+)-galactose were purchased from Sigma Aldrich, the catalysts were prepared as described elsewhere.

5.3.2 Instruments

All the reactions were carried on in a hastelloy Parr Instrument autoclave with an internal volume of 0.1L, and an HEL parallel reactor system.

The HPLC analysis where performed using an Agilent 1260 Infinity equipped with UV and RID detectors, a MetaCarb H Plus Guard Column 50 x 4,6 mm and a MetaCarb H Plus Column 300 x 7,8 mm.

Retention time

Glucose: 18,4 min at RID

Galactose: 19,8 min at RID

Sorbitol and dulcitol: 21 min at RID

5.3.3 Analysis

Conversion and selectivity in reduced sugars were determined with HPLC analysis . 100 mL of reaction solution was diluted in 1 mL of distilled water and injected (loop 20 μL). Analysis condition: flow 0,4 mL/min, temperature 323 K, eluent solution of H_2SO_4 0.0085 N in MilliQ water.

β-lactose hydrolysis and reduction (LA09)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0045	0.0029	
Cu/SiO_2 CHROM 16%Cu	0.4025 (40% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 24 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 78.6%

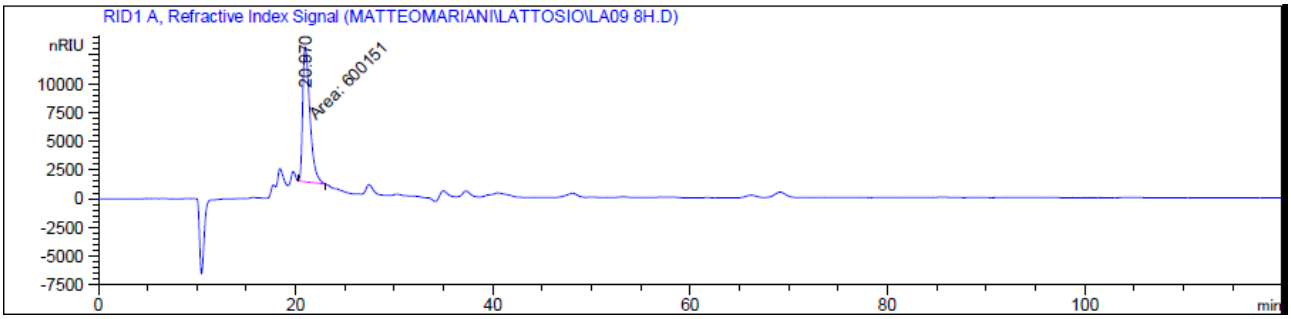


Figure 5.5 Chromatogram of reaction LA09

β-lactose hydrolysis and reduction (LA11)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0095	0.0029	
Cu/SiO_2 CHROM 16%Cu	0.4024 (40% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 160°C and stirred at 1000 rpm for 24 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 65.4%

D-(+)-galactose reduction (LA12)

Reagent	Grams (g)	Mols (mol)	mL
D-(+)-galactose	1.0058	0.0056	
Cu/SiO_2 CHROM 16%Cu	0.4024 (40% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 24 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 98.7%

Selectivity in reduced sugars: 49.5%

D-(+)-glucose reduction (LA14)

Reagent	Grams (g)	Mols (mol)	mL
D-(+)-glucose	1.0075	0.0056	
Cu/SiO_2 CHROM 16%Cu	0.4019 (40% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 24 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 98.0%

Selectivity in reduced sugars: 11.3%

β-lactose hydrolysis and reduction (LA15)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0025	0.0029	
Cu/SiO_2 CHROM 16%Cu	0.4028 (40% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 4 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 28.8%

β-lactose hydrolysis and reduction (LA16)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0015	0.0029	
Cu/SiO_2 CHROM 16%Cu	0.4009 (40% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 200°C and stirred at 1000 rpm for 4 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 46.8%

β-lactose hydrolysis and reduction (LA20)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0014	0.0029	
Cu/SiO_2 CHROM 16%Cu	0.4007 (40% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 50 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 8 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 96.0%

β-lactose hydrolysis and reduction (LA21)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0045	0.0029	
Cu/SiO_2 FLUKA 16%Cu	0.4020 (40% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 8 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 86.0%

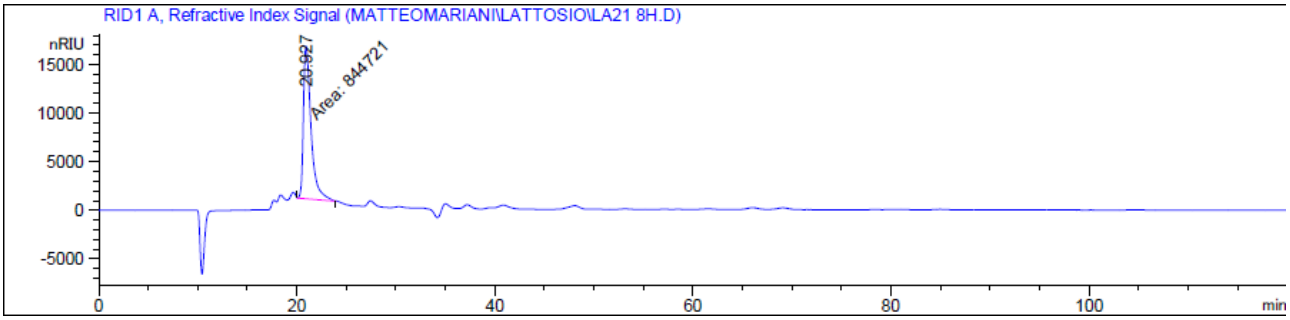


Figure 5.6 Chromatogram of reaction LA21

β-lactose hydrolysis and reduction (LA26)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0057	0.0029	
Distilled water			40

Lactose and water were introduced in the autoclave ,the pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 8 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a dark yellow solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 0.4%

β-lactose hydrolysis and reduction (LA27)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0043	0.0029	
Cu/TRYSIL 300 8%Cu	0.4041 (40% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 8 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 93.0%

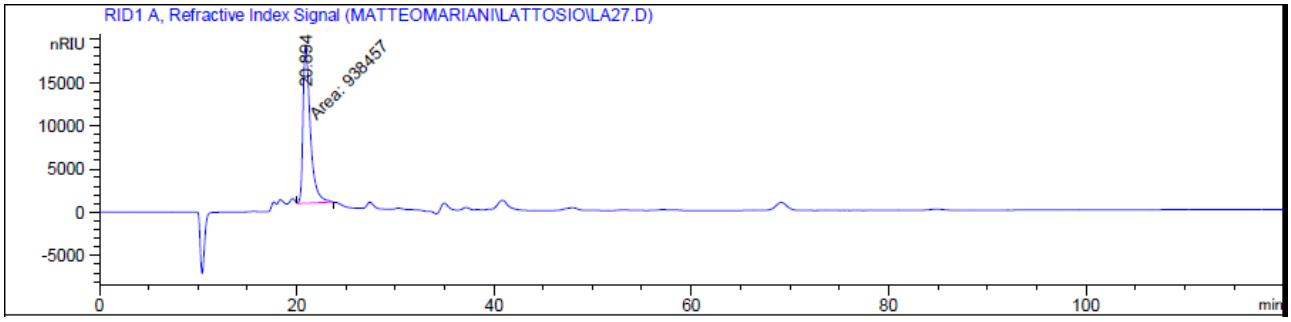


Figure 5.7 Chromatogram of reaction LA27

β-lactose hydrolysis and reduction (LA29)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0091	0.0029	
Cu/TRYSIL 8%Cu	0.4009 (40% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 8 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 1.7%

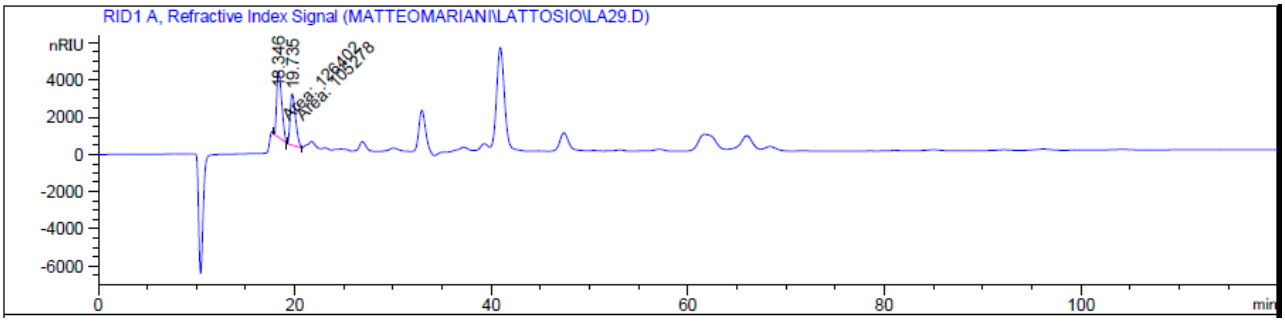


Figure 5.8 Chromatogram of reaction LA29

β-lactose hydrolysis and reduction (LA30)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0050	0.0029	
Cu/SiO_2 FLUKA 8%Cu	0.4017 (40% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 8 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 61.0%

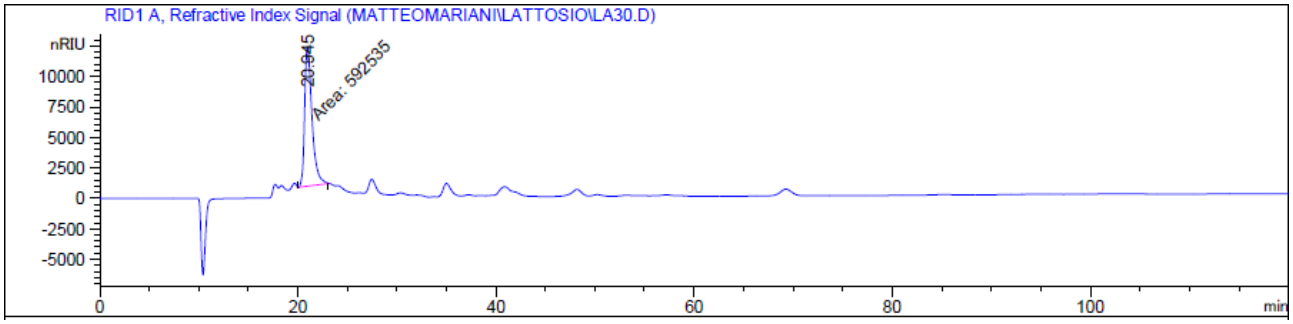


Figure 5.9 Chromatogram of reaction LA30

β-lactose hydrolysis and reduction (LA31)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0079	0.0029	
Cu/SiO_2 MP04300 8%Cu	0.4018 (40% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 8 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 90.5%

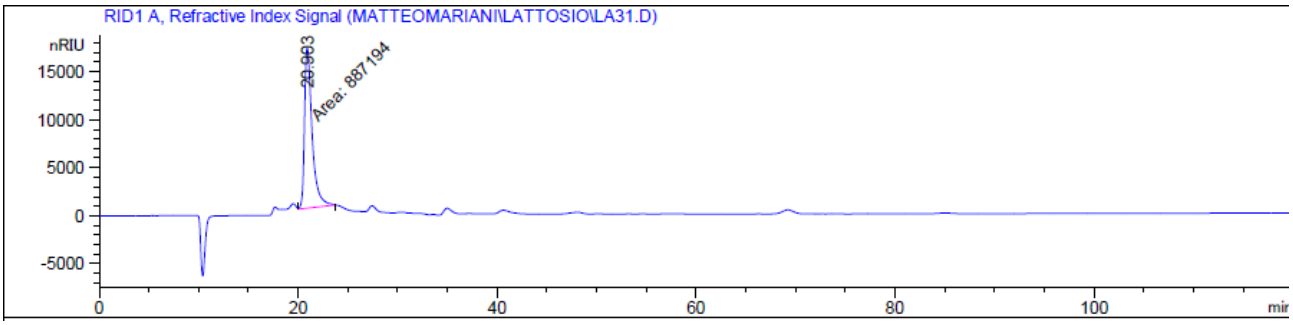


Figure 5.10 Chromatogram of reaction LA31

β-lactose hydrolysis and reduction (LA34)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0066	0.0029	
Cu/SiO_2-Al_2O_3 135 8%Cu	0.4030 (40% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 8 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 1.0%

β-lactose hydrolysis and reduction (LA40)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0040	0.0029	
Fe/SiO_2 CHROM 10%Fe	0.4033 (40% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 500°C for 20 min in air, then 500°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 8 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 92.0%

Selectivity in reduced sugars: 0.0%

β-lactose hydrolysis and reduction (LA43)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0047	0.0029	
Cu/SiO_2 MERCK 16%Cu	0.4008 (40% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 8 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 83.0%

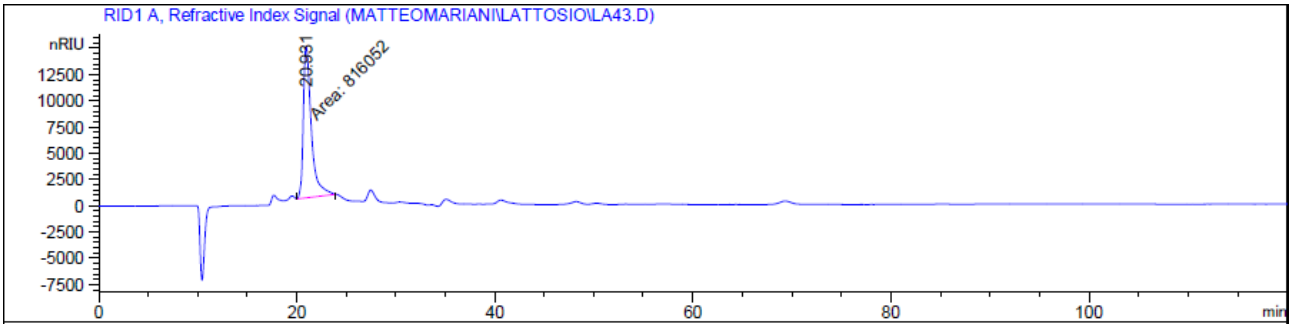


Figure 5.11 Chromatogram of reaction LA43

β-lactose hydrolysis and reduction (LA45)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0063	0.0029	
Cu/SiO_2-ZrO_2 (4.7%) 16%Cu	0.4005 (40% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 8 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 0.0%

β-lactose hydrolysis and reduction (LA46)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0071	0.0029	
Cu/SiO_2 FLUKA 16%Cu	0.2017 (20% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 8 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 90.4%

β-lactose hydrolysis and reduction (LA47)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0040	0.0029	
Cu/SiO_2 FLUKA 16%Cu	0.1008 (40% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 8 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 15.5%

β-lactose hydrolysis and reduction (LA48)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	2.0042	0.006	
Cu/SiO_2 FLUKA 16%Cu	0.2016 (20% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 8 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 9.1%

β-lactose hydrolysis and reduction (LA49)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0054	0.0029	
Cu/SiO_2 FLUKA 16%Cu	0.2010 (20% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 1 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 8 hours with a mechanic stirrer. The reaction mixture was filtered over a paper filter recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 0.0%

β-lactose hydrolysis and reduction (LA52)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0104	0.0029	
Cu/SiO_2 FLUKA 16%Cu	0.2008 (20% by respect to sugar)		
Distilled water			40

The catalyst was reduced before the reaction, in a Schlenck reactor: 270°C for 20 min in air, then 270°C for 20 min in vacuum and three vacuum/hydrogen cycles. Lactose was introduced in the autoclave and the catalyst was transferred using distilled water. The pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 8 hours with a mechanic stirrer. The catalyst was separated with a cannula, recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 25.2%

β-lactose hydrolysis and reduction (LA53)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0019	0.0029	
Cu/SiO_2 FLUKA 16%Cu	0.2008 (20% by respect to sugar) from LA52		
Distilled water			40

Lactose, water and the recovered catalyst were introduced in the autoclave , the pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 8 hours with a mechanic stirrer. The catalyst was separated with a cannula, recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 58.3%

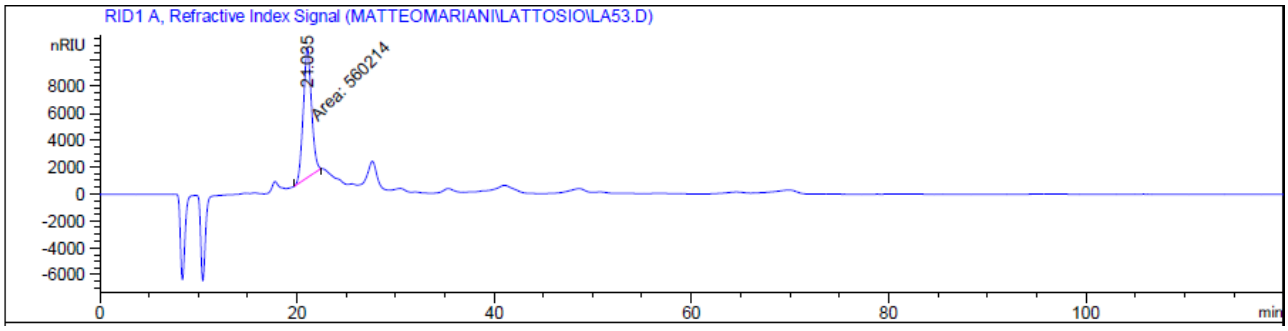


Figure 5.12 Chromatogram of reaction LA53

β-lactose hydrolysis and reduction (LA54)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0024	0.0029	
Cu/SiO_2 FLUKA 16%Cu	0.2008 (20% by respect to sugar) from LA53		
Distilled water			40

Lactose, water and the recovered catalyst were introduced in the autoclave , the pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 8 hours with a mechanic stirrer. The catalyst was separated with a cannula, recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 30.4%

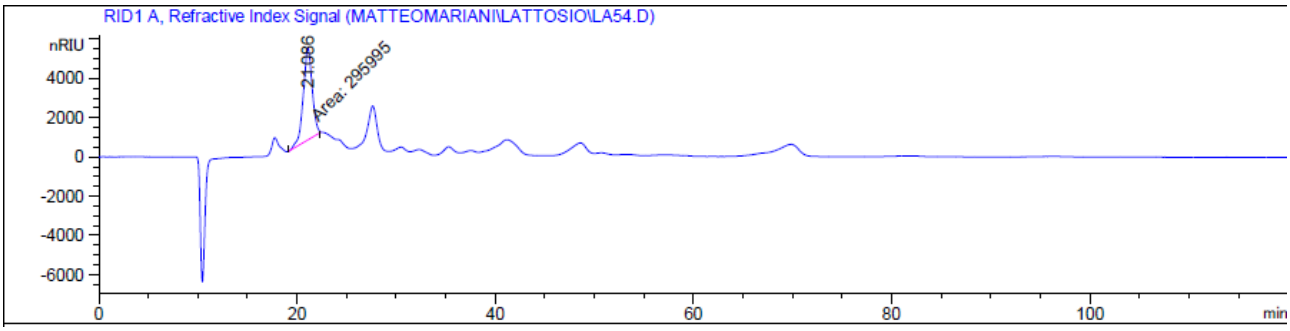


Figure 5.13 Chromatogram of reaction LA54

β-lactose hydrolysis and reduction (LA55)

Reagent	Grams (g)	Mols (mol)	mL
β-lactose	1.0080	0.0029	
Cu/SiO_2 FLUKA 16%Cu	0.2008 (20% by respect to sugar) from LA54		
Distilled water			40

Lactose, water and the recovered catalyst were introduced in the autoclave , the pressure reactor was closed, evacuated and filled with hydrogen three times, then 30 bar of hydrogen were introduced. The reactor was heated at 180°C and stirred at 1000 rpm for 8 hours with a mechanic stirrer. The catalyst was separated with a cannula, recovering a clear solution and a black solid.

Conversion: 100%

Selectivity in reduced sugars: 15.2%

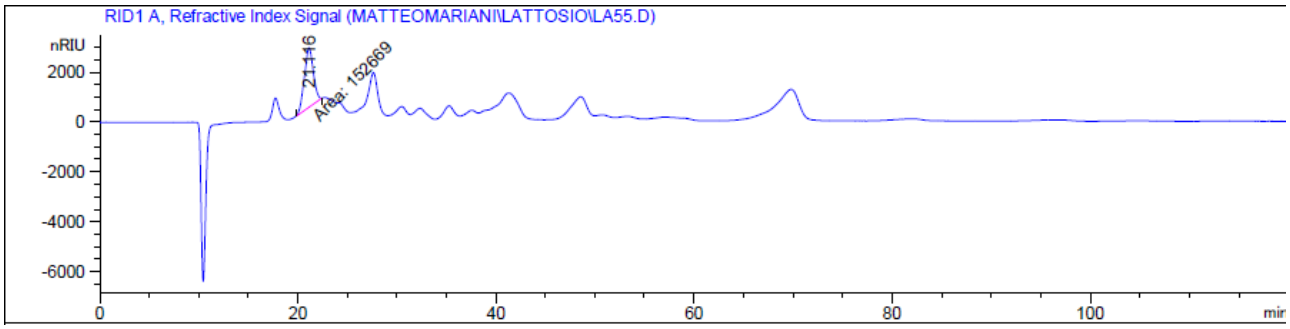


Figure 5.14 Chromatogram of reaction LA55

5.4 References

[1] M. Hu, M.J. Kurth, Y.-L- Hsieh, J.M. Krochta, *J. Agric. Food Chem.,* 1996, 44,3757;

[2] K.G. Gerling, *International Dairy Federation*, Whey proceedings of the second international whey conference, 1998, 251;

[3] M. Harju,*Bull. Int. Dairy Fed.* 1993, 289, 27;

[4] A. Abbadi, K.F. Gotlieb, J.B.M. Meiberg, H. van Bekkum,*Green Chem.,*2003, 5, 47;

[5] J. Kuusisto,J.-P.Mikkola, M.Sparv, J. Wärnå, H. Heikkilä, R. Perälä, J. Väyrynen, T.Salmi, *Ind. Eng. Chem. Res.* 2006,*45,* 5900;

[6] J. Kuusisto, A.V. Tokarev, E.V. Murzin, M.U. Roslund, J.-P. Mikkola, D.Y. Murzin,T. Salmi, *Catal. Today,* 2007, 121, 92;

[7] P.S. Panesar, S. Kumari, *Biotechnol. Adv.,* 2011, 29, 940;

[8] B. Sharma, P. Sharma, A. Agrawal, S. Sarin, *Gastroenterology* 2009, 137, 885;

[9] L. Mayer, B. Kranz, L. Fisher, *J.Biotechnol.,* 2010, 145, 389;

[10] J.H. Southard, F.O. Belzer*, Ann. Rev. Med.*, 1995, 46, 235;

[11] N. Scotti, M. Dangate, A. Gervasini, C. Evangelisti, N. Ravasio, F. Zaccheria , *ACS Catalysis*, 2014, 4, 2818;