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- Study of zeolite based catalysts for bioethanol dehydration to ethylene
- Use of different water/ethanol ratio and addition of Ni to increase selectivity and life
- Use of real bioethanol solutions (second generation).
- Set up of a possible flowsheet and integration with the ethanol purification section

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ETHYLENE PRODUCTION FROM DILUTED BIOETHANOL SOLUTIONS

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ABSTRACT

Ethylene production by ethanol dehydration has been investigated over a set of zeolites with BEA structure in acidic form (HAlBEA). The effect on Ni addition (up to 3 wt %) is explored as a mean to improve ethylene selectivity limiting the formation of heavier byproducts. The reaction temperature has been varied between 300 and 500°C and the effect of cofeeding water has been also explored. Both an increase of the operating temperature and of the water/ethanol ratio can improve stability to coking and thus catalyst life. The use of diluted bioethanol solutions showed beneficial as for catalyst stability. The effect of possible impurities present in less purified raw materials was also checked by testing two diluted second generation bioethanol solutions (50 and 90 vol %).
A first reactor layout and the integration with the bioethanol purification strategy are also proposed, including two purification options much less energy demanding than traditional rectification.

Keywords: Ethylene production; Ethanol; Process intensification; Zeolite; Catalytic dehydration.

INTRODUCTION

At present, *ca*. 75 % of petrochemical products are produced from ethylene, including acetaldehyde, acetic acid, ethylene oxide, ethylene glycol, ethylbenzene, chloroethanol, vinyl chloride, styrene, ethylene dichloride and vinyl acetate. It is also used as monomer to produce a variety of important products such as polyethylene, polyvinyl chloride and polystyrene. The main process for ethylene production at present is cracking of hydrocarbons, leading to *ca*. 99 % of ethylene worldwide.[1,2]

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To exploit new renewable based feedstocks for ethylene production, biomass-derived ethanol can be catalytically dehydrated as a sustainable alternative route.[3,4] The bio-based polymers market is extensively growing (1.3 billion US dollar market with 35 % growth between 2006 and 2011). The demand for renewable polyethylene (PE) corresponds to 10 % of the global PE market whereas the present supply is < 1 %. However, for viable processes, a premium price for the products and/or low-cost feedstock are required and this point is still challenging.[5] Therefore, routes to ethylene starting from less expensive feedstocks should be explored.

The availability of second generation bioethanol at a reasonable price[6] may open the way to this important step towards the exploitation of biorefineries. However, the unit operations to achieve the concentration and final dehydration of the fermentation broth hugely affect bioethanol price, especially when > 99 % purity is required, as for direct combustion or gasoline mixing purposes. Therefore, the possibility to use less concentrated bioethanol solutions as feedstock is an important step towards the economical sustainability of the process.

Ethylene may be produced through ethanol dehydration, catalyzed by acidic active sites (reaction 1). The reaction is endothermal and heat is commonly provided by cofeeding steam, which also allows preventing catalyst coking (reaction 3), which is also promoted by strong acidic sites. Such reaction environment opens up the intriguing possibility to use directly diluted bioethanol mixtures. Therefore, in this work we investigated the unconventional use of a diluted ethanol solution (*ca*. 50 vol %) for ethylene production. Such feedstock may be simply obtained by flash concentration of the fermentation broth, so limiting very much the ethanol purification costs or, depending on the desired concentration, by using a feed split purification strategy which has been recently proposed by our group.[7]

$$C_2H_5OH \leftrightarrows C_2H_4 + H_2O \qquad (1)$$

$$2\ C_2H_5OH \leftrightarrows C_2H_5OC_2H_5 + H_2O \qquad (2)$$

$$C_2H_4 \rightarrow \text{polymers/aromatics} \rightarrow \text{coke} \qquad (3)$$

If water is added in the feed, with a significant amount of group VIII metals (such as > 5 wt% Ni), the steam reforming reaction (reaction 4) can also take place at relatively high temperature (>400°C), followed by water gas shift (reaction 5). Ethanol dehydration to acetaldehyde (reaction 6) may even occur, or its decomposition to methane (reaction 7).

$$C_2H_5OH + H_2O \leftrightarrows 2\ CO + 4\ H_2 \qquad (4)$$

$$CO + H_2O \leftrightarrows CO_2 + H_2 \qquad (5)$$

$C_2H_5OH \leftrightarrows CH_3CHO + H_2$ (6)

$C_2H_5OH \rightarrow CH_4 + CO + H_2$ (7)

Alumina is the most used and investigated catalyst for this application. However, besides coking problems, it suffers from competitive adsorption between ethanol and water. Therefore, the common strategy to add steam to prevent extensive deactivation induces significant drawbacks for catalytic activity. Zeolites have been suggested as alternative catalysts, but also in this case stability issues may arise due to coking and poor hydrothermal stability in the presence of steam. The catalytic performance of different zeolites have been reported for this application [2,8–11] and very recently reviewed by Sun and Wang .[12]

We here selected BEA zeolite samples with optimized acidity.[11] The BEA microporous structure is constituted by channels *ca.* 6.7 Å in size, allowing the diffusion of ethanol with limited resistance,[13] since almost all the accessible free volume of the pores is available given the characteristic molecular size of ethanol (*ca.* 3.8 Å).[14] In this work we deepened the effect of reaction conditions to optimize the selectivity to ethylene. Ni addition in different concentration has been also explored as a further mean to tune process selectivity towards ethylene. Indeed, Ni is active for the reforming of higher olefins and hydrocarbons, thus it can possibly improve catalyst selectivity to ethylene. Finally, the best performing catalyst has been tested also with real bioethanol solutions to account for possible impurities contained in a less purified feed. Once demonstrated that suitable catalytic performance can be achieved, we also coped with some process development issues.

This approach is novel, allowing the use of diluted, much cheaper feed for the production of this bulk chemical. Furthermore, the addition of a metallic function to a properly selected zeolite, together with properly optimized reaction conditions, allows to achieve very high selectivity to ethylene. Thus, very simple separation processes can be designed to purify ethylene. Indeed, significantly better selectivity and ethylene productivity can be achieved in the present case, with respect to a benchmark alumina catalyst.

MATERIALS AND METHODS

Catalyst Preparation

Details on catalyst preparation can be found elsewhere.[11] Briefly, a tetraethylammonium BEA (TEABEA) zeolite with Si/Al ratio of 17 (mol/mol) nominal, provided by RIPP (China) was calcined in air (100 °C/h) at 550 °C for 15 h to remove the organic template and then treated two times with 400 mL of 0.1 mol/L NH_4NO_3 solution for 3 h in order to exchange K^+ and Na^+ ions present in industrial BEA zeolite with NH_4^+ ion. The obtained material was washed with distilled water and dried overnight at 90 °C. The NH_4AlBEA samples was calcined in air (100 °C/h) for 3 h at 500 °C to remove NH_3 and obtain the acidic form of the zeolite BEA, HAlBEA.

Ni was added by wet impregnation from a $Ni(NO_3)_2 \cdot 6H_2O$ solution. Proper amount of Ni precursor was dissolved in 200 mL water and the solid suspension was stirred for 24 h at room temperature at pH of 3.3. Then, the suspension was stirred in evaporator under vacuum of a water pump for 2 h in air at 60 °C until water was evaporated. Three samples with 0.5, 1.5 and 3.0 wt % of Ni were obtained and labeled as $Ni_{0.5}$HAlBEA, $Ni_{1.5}$HAlBEA and $Ni_{3.0}$HAlBEA (Table 1). The composition of the tested samples is reported in Table 1.

Table 1. Nomenclature, preparation parameters and main physical-chemical properties of the samples prepared.

Sample	Code	Initial Si/Al (atom/atom)	Post-treatment	Ni content (wt %)
1	HAlBEA	17	Calcination	0
2	$Ni_{0.5}$HAlBEA	17	Calcination	0.5
3	$Ni_{1.5}$HAlBEA	17	Calcination	1.5
4	$Ni_{3.0}$HAlBEA	17	Calcination	3.0

Activity Testing

Details on the equipment for activity testing have been previously reported elsewhere.[15,16] Briefly, the catalysts (*ca*. 0.5 g, 0.15-0.25 mm particle size) were diluted 1:3 (vol/vol) with SiC of the same size. The void space of the reactor was filled with quartz beads, *ca*. 1 mm in size. The sample was activated in 3 L/h of a 20 % H_2/N_2 gas mixture, while heating by 600 °C/h up to 625 °C for 1 h. Activity testing was carried out by feeding 0.00102 L/h of a X:1 (mol/mol) $H_2O:CH_3CH_2OH$ (X = 3, 2, 1, 0) liquid mixture by means of a Hitachi, mod. L7100, HPLC pump, added with 3.36 L/h of N_2, used as internal standard, and 10.44 L/h of He. Such dilution of the feed stream was calibrated so to keep the reactants mixture in the vapour phase even at zero conversion at the reactor outlet. We selected 3 as upper limit of the water/ethanol ratio since it corresponds to a composition easily obtainable by one-stage distillation (flash) as described in the last section (*vide infra*).

The activity tests were carried out at atmospheric pressure, at a GHSV = 2500 h^{-1} (Gas Hourly Space Velocity) referred to the ethanol + water gaseous mixture (76500 h^{-1} including the inert gases flow rate), and at temperatures ranging from 300 to 500 °C. Both the total flow and GHSV were kept constant while varying the composition.

The analysis of the out-flowing gas was carried out by GC analysis. The analytical system allows to quantify simultaneously ethanol, ethylene, water, ethane, H_2, CO, CO_2, acetaldehyde, propane, propylene, diethylether and higher hydrocarbons if needed. Repeated analyses of the effluent gas were carried out every hour and the whole duration of every test at each temperature was 8 h. The raw data, expressed as molar flow of each species outflowing from the reactor, averaged after 4-8 h-on-stream (period after which steady state conditions were normally achieved, based on constant conversion, temperature and products distribution) have been elaborated as described here below:

Products distribution: $Y_i = \text{mol } i / \Sigma(\text{mol } i)$

C balance:

$100 - (((\text{mol } CH_3CH_2OH * 2)_{in} - \Sigma\, (\text{mol } C_i * \chi_i)_{out}) / (\text{mol } CH_3CH_2OH * 2)_{in})*100$

Conversion: $X = (\text{mol } i_{\,in} - \text{mol } i_{\,out}) / \text{mol } i_{\,in}$ $\quad i = CH_3CH_2OH$

Selectivity: $S_i = (\text{mol } i / \nu_i) / (\text{mol ethanol}_{\,in} - \text{mol ethanol}_{\,out})$

where *i* = products detected, dry basis; χ_i = number of C atoms in the *i*-th molecule; ν_i = stoichiometric coefficient of species *i* in the dehydration or other parasitic reaction.

RESULTS AND DISCUSSION

Thermodynamic Considerations

Using water + ethanol mixtures for ethylene production by dehydration is not intuitive, being a dehydration reaction, and the operating conditions should be properly checked from a thermodynamic point of view. The equilibrium products distribution has been evaluated by using the Aspen Plus® process simulation tool, adopting i) the predictive Soave-Redlich-Kwong (PSRK) thermodynamic package and ii) the Non-Random-Two-Liquid (NRTL) model with Wilson mixing rules to model non-ideality in the liquid phase, coupled with the SRK equation of state to model real gas phases. Both models gave rise to the same results.

Equilibrium composition has been evaluated by using a Gibb's reactor model. The reactor feed was defined (pure ethanol or ethanol + water) and a population of allowed compounds was associated to the reactor, including the reactants and all the products of the reactions that are likely to occur in the reactor itself. These include all the compounds appearing in the reactions described in the Introduction. As molecules to also account for coke production (reaction 3) we selected benzene and light polycondensed aromatic species, such as naphthalene and anthracene. The choice of possible products is very critical, because if some reactions are neglected, unreliable and inconsistent product previsions may be obtained.

A detailed thermodynamic analysis of the process, carried out in the presence and in the absence of water, is reported elsewhere.[11] According to those results, even if the addition of water slightly unfavoured ethanol conversion (with negligible effect on the selectivity to ethylene), it helped in limiting coke formation. A temperature window between 350 and 500°C was obtained, where the model molecules selected as coke precursors (aromatics) were completely absent when cofeeding water/ethanol = 3:1 mol/mol. The thermodynamically favoured pathway at low temperature was ethanol decomposition to form methane (reaction 7), whereas at higher temperature (> 500 °C) syngas was the favoured product, due to ethanol steam reforming (reaction 4).

These considerations allow concluding that when ethylene is the desired outcome, the optimisation of catalyst selectivity should be carefully carried out. The catalyst should turn the reaction pathway towards thermodynamically less favourable routes, *i.e.* ethanol dehydration rather than decomposition. Therefore, materials and conditions must be selected to drive the reaction under kinetic regime and not under thermodynamic control, which is not the typical scope in designing catalysts. In this way, it is possible to achieve the desired ethylene selectivity by using diluted bioethanol solutions, a much cheaper feedstock than pure ethanol.

Effect of Ni Loading on Ethanol Dehydration to Ethylene

The effect of acidity on catalyst performance has been recently investigated elsewhere.[11] The zeolite HAlBEA was selected for the present work due to its superior selectivity to ethylene when preliminarily tested at 500 °C, water/ethanol ratio = 3:1 (mol/mol) and 1.5 wt % Ni loading. Under such reaction conditions the catalyst completely converted ethanol, with 99 ± 3 % selectivity to ethylene. A life test was also performed on the same $Ni_{1.5}$HAlBEA for 80 h-on-stream, without any evidence of significant deactivation.

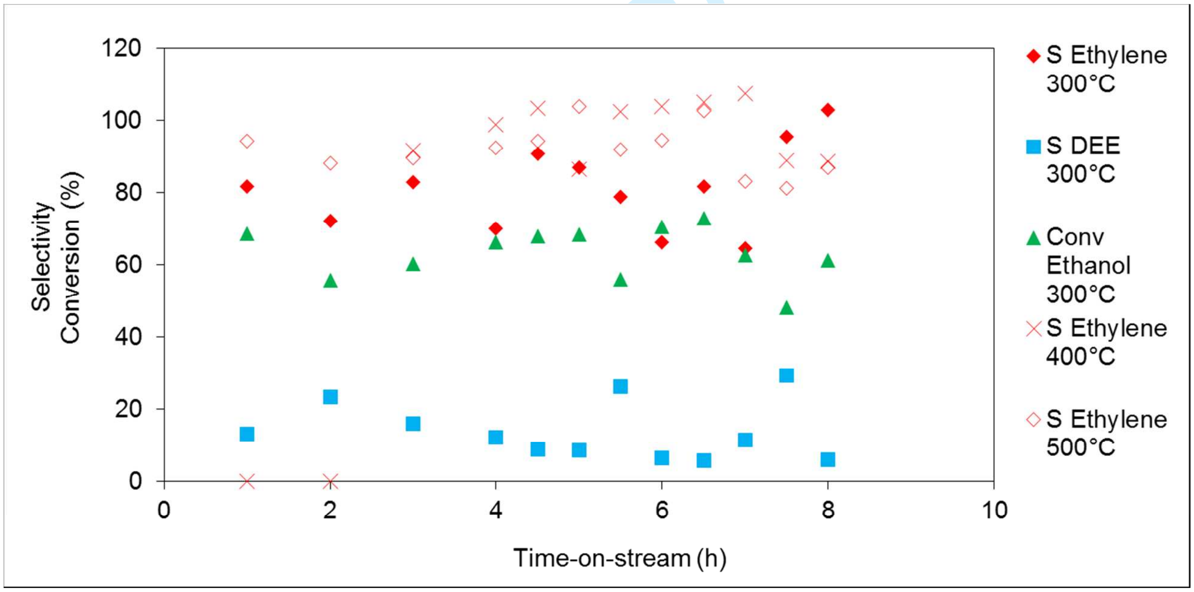
A comparative test performed on commercial γ-Al_2O_3, of the type used for industrial ethanol dehydration, led to complete ethanol conversion, but much more limited selectivity to ethylene, *i.e.* 80 ± 7 %.

The GHSV was fixed in order to explore the effect of temperature, water/ethanol ratio and catalyst formulation. It has been selected based on the feeding pump range, reactor size and possibility to keep all the outflowing mixture in gas phase to allow one single GC analysis. It also represents a feasible value for scale up.

At constant, low Ni loading, acidity was decreased by increasing the Si/Al ratio either by selecting different native zeolites or by postsynthesis dealumination, leading to decreasing acidity. The sample characterised by very strong Lewis acid sites led to high dehydration activity, but followed by progressive coking of the strongest acidic sites. By contrast, too low acidity led to lower dehydration activity. The alumina commercial catalyst for ethanol dehydration led to lower ethylene selectivity and lower carbon balance due to stronger Lewis acidity than the present BEA zeolites.

The native HAlBEA zeolite, without Ni addition, was active for ethanol dehydration and led to higher selectivity than the reference alumina sample. However, it also led to the formation of undesired byproducts, such as diethylether. Furthermore, catalyst performance was rather unstable during time-on-stream (Fig. 1). Heavier compounds as diethylether have been frequently reported in the literature as byproducts for this process. In order to limit their selectivity we explored the addition of a metal phase, e.g. Ni, in order to promote their possible decomposition, being more reformable compounds with respect to ethanol and ethylene.

Fig. 1: Ethanol conversion and selectivity to ethylene and diethylether (DEE) at different temperature on catalyst HAlBEA.



The results are reported in *Table 2*. Ni addition, without significantly lowering selectivity to ethylene, allowed indeed stabilising catalyst performance. This is visible by the lower spread of the carbon balance and selectivity to ethylene for the Ni containing catalysts with respect to the acidic ones. Furthermore, Ni containing catalysts completely suppressed the formation of heavier byproducts, such as diethylether, possibly present at the lowest temperature (*Fig. 1* and *Table 2*).

Table 2. Results of activity testing at different temperatures after activation at 800 °C, water/ethanol = 3:1 mol/mol, GHSV = 2500 h^{-1}. Effect of Ni loading and temperature on HAlBEA zeolite. Commercial alumina as reference.

T (°C)	**Ni loading (wt %)**	**0**	**0.5**	**1.5**	**3.0**	**γ-Al_2O_3**
500	Ethanol conversion (%)	100	100	100	100	100 ± 0.00
	C balance (%)	96 ± 8	96 ± 2	98 ± 3	98 ± 2	88 ± 7
	Selectivity ethylene (%)	92 ± 7	88 ± 4	99 ± 3	72 ± 3	80 ± 7
400	Ethanol conversion (%)	100	100	-	100	-
	C balance (%)	102 ± 8	102 ± 2	-	103 ± 2	-
	Selectivity ethylene (%)	98 ± 8	99 ± 2	-	96.6 ± 1.3	-
300	Ethanol conversion (%)	64 ± 7	67 ± 7	-	89 ± 5	-
	C balance (%)	105 ± 13	100 ± 7	-	103 ± 3	-
	Selectivity ethylene (%)	82 ± 13	82 ± 7	-	98 ± 2	-
	Selectivity diethylether (%)	15	15	-	-	-

Effect of Reaction Conditions

Table 2 reports the effect of Ni loading and reaction temperature, whereas in *Table 3* we show the effect of the water/ethanol ratio and of the ethanol feedstock at fixed Ni loading (0.5 wt %) and temperature (400 °C).

Full ethanol conversion was always observed at 500°C. However, the products distribution was different. At low or nil Ni amount the main byproducts, besides ethylene, were acetaldehyde and hydrogen, whereas at high Ni loading the steam reforming products (H_2, CO and CO_2) were predominant. In the case of the bare alumina catalyst the carbon balance was unacceptably low, indicating coke accumulation over the surface.

A decrease of temperature to 400°C allowed maintaining full ethanol conversion and 100% selectivity to ethylene especially at low or nil Ni loading. A further decrease of the reaction temperature to 300°C decreased ethanol conversion unacceptably if no enough Ni was present. The higher ethanol conversion for the highest Ni loading (3 wt%) could be possibly attributed to higher steam reforming activity, but this hypothesis is ruled out as demonstrated by the almost quantitative selectivity to ethylene (98%, the only by-product being acetaldehyde). On the contrary, a high Ni amount likely led to the formation of additional middle strength Lewis acidic sites that were beneficial for this application at very low reaction temperature, as demonstrated in previous investigations.[11] By looking to the products spectrum, a process can be designed that in one step can fully convert ethanol to ethylene. If water is added, it can be rather easily separated by condensation at reactor outlet together with water formed during the dehydration reaction. In this light, optimal reaction conditions were then considered to be 400 °C and 0.5 wt % Ni loading, at least among those here tested.

Table 3. Results of activity testing at 400 °C for the $Ni_{0.5}$HAlBEA catalyst after activation at 800 °C, water/ethanol = 3:1 mol/mol, GHSV = 2500 h^{-1}. Effect of water/ethanol ratio and of ethanol origin. BE = 2nd generation bioethanol with concentration 50 vol% (BE50) or 90 vol% (BE90).

Water/ethanol (mol/mol)	**3:1**	**2:1**	**1:1**	**0:1**	**3:1 BE50**	**3:1 BE90**
Ethanol conversion (%)	100	100	100	100	100	100
C balance (%)	102 ± 2	98 ± 5	99 ± 7	100 ± 3	99 ± 2	103 ± 2
Selectivity ethylene (%)	99 ± 2	95 ± 5	96 ± 7	98 ± 3	96 ± 2	98 ± 3

Therefore, further experiments were carried out on this sample at 400°C by varying the water/ethanol ratio. According to the results of *Table 3*, no significant variation of catalyst performance was observed by using pure ethanol or diluted ethanol solutions, confirming the intriguing possibility to adopt such less purified, thus less expensive, raw material for ethylene production. Indeed, full conversion was always achieved, with satisfactory carbon balance and substantially quantitative selectivity to ethylene. Thus, the addition of water to ethanol under the present reaction conditions did not inhibit the dehydration reaction. On the contrary, a more stable behaviour of the catalyst during time-on-stream tests was observed at the highest water/ethanol ratio.

The highest productivity of ethylene has been obtained at 400°C with both the 0.5 and 3 wt % NiHAlBEA catalysts and resulted to be ca. 18 kmol/h kg_{cat}, corresponding to the complete conversion of the ethanol in the feed.

Performance with Real Bioethanol Feed

In order to explore the effect of possible impurities present in a less purified bioethanol feedstock, we collected two samples of second generation bioethanol, kindly supplied by the Mossi&Ghisolfi group (*Table 3*).

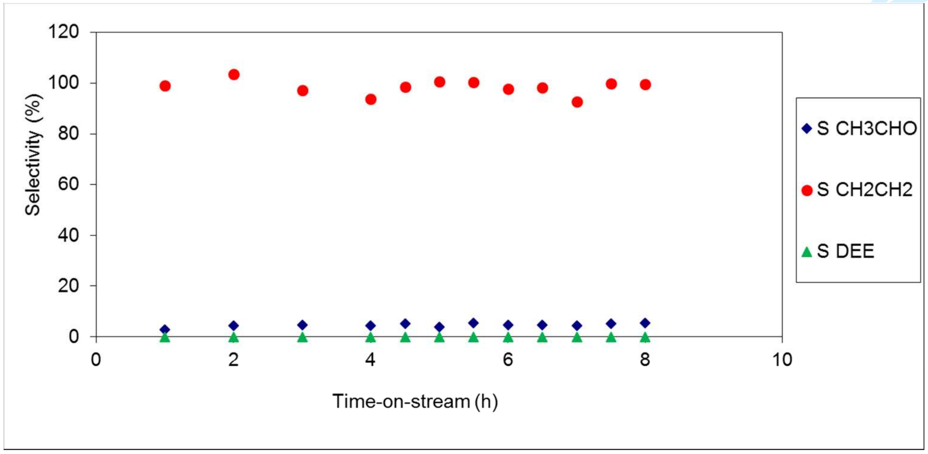
The samples were obtained by fermentation of Arundo Donax (a common cane), added with agriculture residua available at the Crescentino site (Italy). More information on the Proesa process is available on the following website: http://www.betarenewables.com/en/proesa/feedstock.

The two samples were obtained after flash separation (50 vol %, called BE50) and after rectification (90 vol %, called BE90) of the raw beer. Their preliminary characterisation revealed the presence of compounds of possible concern. Indeed, higher alcohols were found (C_3-C_5 saturated alcohols up to 0.37 wt % for BE90 and 0.15 wt % for BE50), which may lead to more reactive and easily polymerisable olefins upon dehydration. Being these data expressed as wt %, their absolute amount is substantially identical in the two samples (their wt % changes just following dilution) and thus they are not effectively eliminated by rectification. In addition, sulphates (0.86 ppm for BE90, 1 ppm for BE50) and reduced sulphur-based compounds, possible poisons for the catalyst (0.3 ppm for BE90 and 0.7 ppm for BE50) were present. These latter S-containing compounds can be decreased by rectification, though not fully eliminated in BE90, and may cause catalyst deactivation. These impurities may vary depending on the biomass used for fermentation.

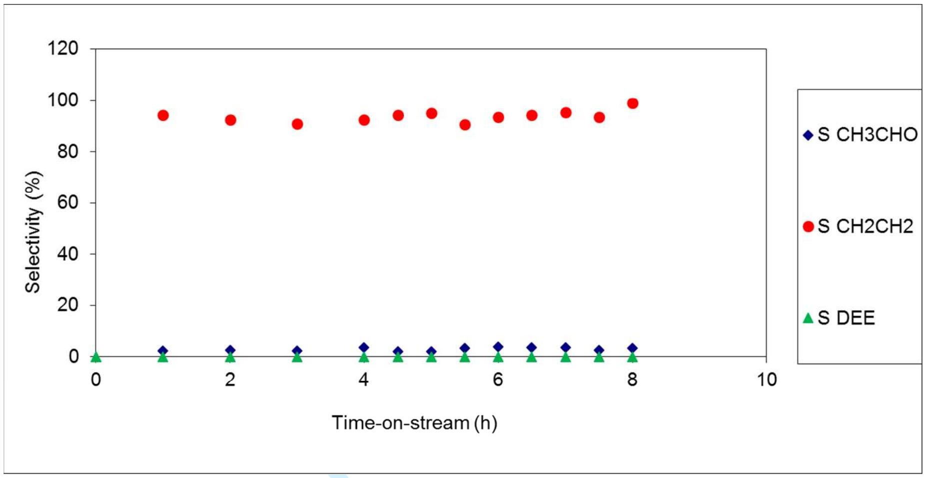
By looking at the results in *Table 3* and in Fig. 2, similar selectivity to ethylene was obtained when using BE50 or BE90 with respect to pure ethanol (*i.e.* 99.9 vol %).

Fig. 2: Selectivity to ethylene and other by-products for catalyst $Ni_{0.5}HAlBEA$, T = 400 °C, water/ethanol = 3, with a) BE90, b) BE50. DEE = diethylether.

a)



b)



According to the proposed results, suitable catalytic performance has been achieved to support the use of the present catalysts for ethylene production from ethanol. Nevertheless, some applicative issues can arise, relative to the conceptual design of an integrated process for ethanol production, purification and dehydration to ethylene. We will account for these issues in the next section.

Process Integration

Dehydration reactor

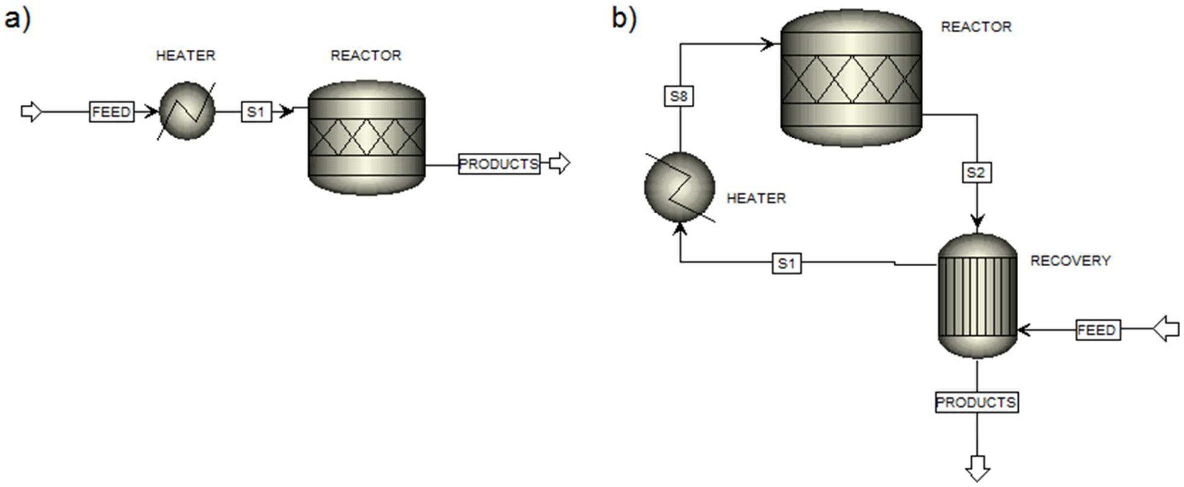
The selected water/ethanol = 3 mol/mol feed is particularly interesting for different reasons. This composition corresponds to a *ca*. 50 vol % mixture, which can be easily obtained from a fermentation broth by flash separation.[7] This mixture has to be further rectified with huge costs if absolute ethanol is desired. Therefore, the possibility to use 50 vol % ethanol allows a feed sufficiently purified from minerals and heavier compounds, but its separation costs are minimal with respect to further azeotropic distillation and anhydrification.[7] In a biorefinery scenario, bioethanol is produced and transformed into chemicals locally. Thus, using a cheaper feedstock with high water content is more economically advantageous and environmentally sustainable.

Another key point is to check the sustainability of the process when using excess water in the feed. Indeed, cofeeding water requires additional heat input (additional cost) to vaporize water, which is not a reactant. In order to quantify the impact of this choice, two different cases have been considered, represented in Fig. 3. In case a) a heater accomplishes the preheating and vaporisation of the feed with external heat input. The heat provided to the reactor to support the endothermal dehydration reaction is computed separately. In case b) internal heat recovery is accomplished, so that the spent steam is used to preheat the feed, to vaporise the ethanol and the possibly cofed water. This internal heat recovery is even more efficient, since water is produced during the dehydration reactor, so that the steam available at reactor outlet, which is used as heating medium for the feed, is given by the sum of the water fed in the diluted ethanol solution + the amount formed during the reaction. Therefore this is a very effective strategy to limit the net heat input to the process. Additionally, water condensation carried out in the heat recovery exchanger represents a very easy method for the purification of ethylene, since no other significant byproducts are present, unlike what reported in most literature.

The duty of the heater (Fig. 3*a*) to bring the feed (0.25 kmol/h ethanol + 0.75 kmol/h water) from 25 °C to 500 °C is *ca*. 19 kW. Additional 3.2 kW should be furnished to the dehydration reactor. The reactor was operated at 500 °C and completely converted ethanol to 0.25 kmol/h ethylene + 1 kmol/h water (the feed + reaction product), as in our best case. If the configuration is the one reported in Fig. 3*b*, the heater just brings the temperature to specification, requiring *ca.* 1 kW, because most of the heat needed to vaporise the feed is obtained by cooling and condensation of the water outflowing the reactor. No significant change of the duty is observed while operating the reactor at 300 °C (1.05 kW) with respect to 500 °C (1.08 kW) in this last configuration (Fig. 3*b*).

Therefore, with the present results we demonstrate the possibility to use cofeeding water, *i.e.* diluted bioethanol solutions to achieve full ethanol conversion and *ca.* 99% selectivity to ethylene, without heavier byproducts. Furthermore, we also introduced the use of higher operating temperature, possibly higher than those observed in the literature (250-350 °C), to achieve better performance in a coke free region. This has important practical implications from the point of view of products separation easiness and to improve catalyst life.

Fig. 3: Feed vaporisation scheme: a) base case without internal heat recovery or b) with a recovery heat exchanger.



Bioethanol purification

The production of diluted bioethanol to be used for ethylene production reaction can involve purification strategies different from those commonly adopted for producing the raw material designated for gasoline blending, which has to meet much higher purity levels (> 99 vol %).

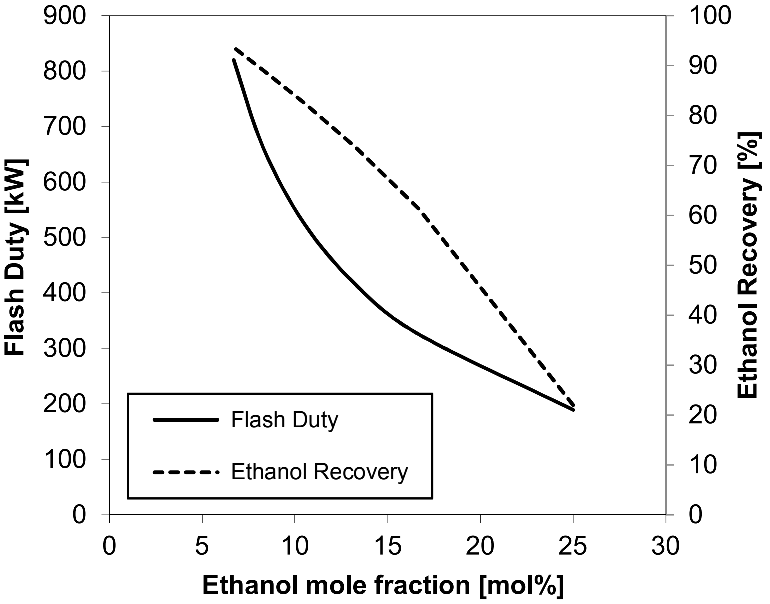
We already demonstrated that the use of diluted ethanol is also technically feasible for the co-generation of heat and power (hereafter denoted as CHP unit) described in a previous work.[7] Therefore, to cope with these two different applications where limited bioethanol purification is required, the purification strategy has been investigated for determining a suitable solution, which allows to reduce the purification costs. The competitiveness of the whole technology can thus be improved.

A first solution is to use a single stage unit for bioethanol purification, *i.e.* a flash drum. This kind of equipment is characterized by very limited installation costs with respect to a rectification column and the main operating cost is represented by the duty. If a 10 wt % (*i.e.*, about 4 mol %) bioethanol mixture were concentrated in a flash drum, very limited duty would be required to obtain *ca.* 25 mol % ethanol (Fig. 4), corresponding to the highest water/ethanol molar ratio here explored. However, the required duty would severely increase in case of lower desired ethanol concentrations (*i.e.*, more diluted mixtures to be fed to the dehydration reactor) due to a larger amount of water to be vaporized and the recovery of ethanol in the vapor phase would increase up to 93.6 % (Fig. 4).

This can feasibly allow to produce a relatively diluted mixture with the upper water/ethanol ratio here tested, *i.e.* 3:1 mol/mol, in a rather economical way. This concentration step allows to improve ethanol purity and leads to reasonably similar catalytic performance than the fully dehydrated ethanol (BE50).

The only byproduct observed when using BE50 or BE90 was acetaldehyde, which is easily separable from ethylene during the condensation step in the heat recovery exchanger described in Fig.3*b*. As for catalyst life, possible poisoning may occur by coking, especially related to the higher content of higher alcohols. This deactivation route is ruled out thanks to the better gasification achieved thanks to excess water in the feed. Sulphur concentration, higher in BE50 than BE90, may also be critical as poison for the metallic function, which is however a co-catalyst here, not related with the main catalytic active sites (acidic sites).

Figure 4. Duty and ethanol recovery for concentration of a 10 wt % bioethanol solution in a flush drum.



A different process scheme has been also explored in order to increase the ethanol recovery, while limiting the energy consumption of the concentration step. The scheme, already described by Rossetti et al. [7] and illustrated in Figure 5 for the sake of clarity, processes only a fraction of the fermentation broth by concentration in a distillation column whose energy consumption at the bottom reboiler is lower for more diluted bioethanol mixtures (Fig. 6). This system can be conveniently used to achieve more diluted solutions (ethanol concentration lower than 25 mol%) while providing a lower duty than that which is necessary to achieve the same concentration level in the flash unit. This approach is suitable, provided that no poisons for the catalyst are contained in the bypassed feed. Indeed, no mean is provided to eliminate possible contaminants from the bypassed feed, so that they would inevitably come into contact with the ethanol dehydration catalyst if this concentration strategy is followed.

Therefore, depending on the desired water/ethanol ratio selected for this specific application, different purification strategies can be available to minimize process costs and improve efficiency. This strategy can be also useful to tune the desired concentration of the critical compounds contained in the feed (higher alcohols and sulphur-containing compounds) below a given limit. This may be helpful to cope with widely different biomasses that can be used for ethanol production, which may induce different concentration of possible contaminants.

Fig. 4 and 6 can be used as a guide for the design of an integrated process, from biomass to ethylene, to compute the duty required for ethanol purification depending on the desired concentration and type of concentration strategy selected.

Figure 5. Scheme of the concentration section proposed for producing diluted bioethanol limiting the energy consumptions.

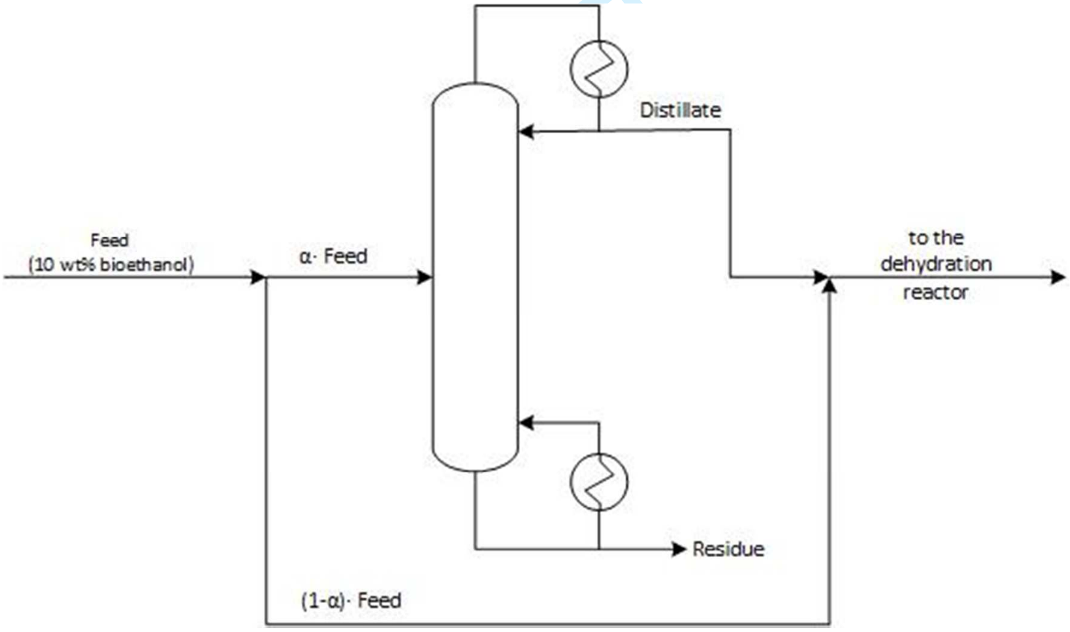
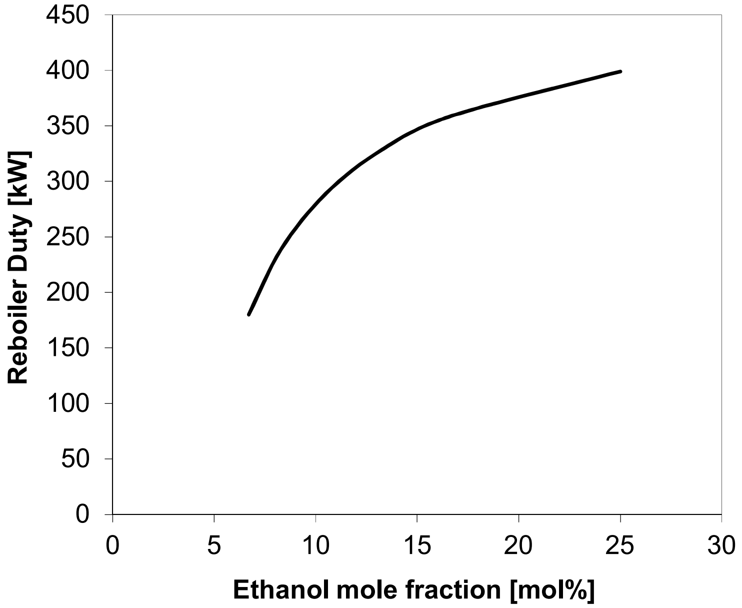


Figure 6. Reboiler duty required for bioethanol concentration by the process scheme illustrated in Figure 5.



CONCLUSIONS

The ethanol dehydration reaction to ethylene has been carried out over HAlBEA and Ni-containing HAlBEA catalysts. Full conversion of the reactant has been attained at temperature higher than 300 °C. Ethylene was the main product, accompanied by diethylether at the lowest operating temperature. In order to limit byproducts formation and to improve both the selectivity to ethylene and the stability of the catalyst, small amounts of Ni were added to HAlBEA zeolite. This induced some additional acidity to improve activity at low temperature, but most of all led to quantitative selectivity to ethylene.

The addition of water in different amounts in the feed was also explored as a method to improve the stability towards coking. The satisfactory performance of the catalysts at relatively high water/ethanol ratio (up to 3:1 mol/mol) opens the way to the use of diluted, *i.e.* less purified and less expensive, bioethanol solutions for this application. Therefore, two samples of diluted second generation bioethanol (50 and 90 vol %) were used to check for the effect of possible impurities, which was negligible.

Two different purification strategies have been then compared, leading to possible options to obtain diluted and poorly expensive bioethanol solutions. One is the concentration through a flash drum, the other involves the splitting of the feed stream and the concentration of part of it in a distillation column, each one convenient in different concentration ranges. A possible configuration for heat recovery across the reactor has been also discussed to improve the efficiency of the process.

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