

Synthetic Hydrotalcites as suitable Co-based catalysts for Fischer-Tropsch Process

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1 Introduction

Nowadays it is imperative to develop economical and energy-efficient processes for the sustainable production of alternative fuels and chemicals. Fischer Tropsch synthesis (FT) is a well-established industrial process whereby these objectives can be achieved using syngas (mixture of H₂, CO, CO₂) as raw material. Syngas can be manufactured from CH₄, coal or, as a new tendency, from biomass. FT synthesis usually requires catalysts based on cobalt or iron. The typical products range is from methane to long chain hydrocarbons (waxes) [1]. Cobalt-based catalysts have been used for FT for long time due to their long life-times, high CO conversion and high selectivity to heavy hydrocarbons; they are moreover characterized by low activity towards the water-gas shift, so avoiding the CO₂ formation.

In this work, layered double or triple hydroxides, also known as synthetic hydrotalcites, are proposed and studied as FT catalysts. The choice of these materials allows to easily prepare solid phases, essentially based on mixed metal oxides, where specific metal atoms are homogeneously dispersed at an atomic level. Hydrotalcites are represented by the empirical formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A^{n-}/n]^{x-}mH_2O$ where M(II) is a divalent cation such as Co, Mg, Zn, Ni, or Cu, M(III) is a trivalent cation such as Al, Cr, Fe or Ga; Aⁿ⁻ is an anion of charge *n* and *m* the molar amounts of co-intercalated water [2]. When calcined at proper temperatures, the random distribution of cations, characteristic of the hydroxide phase, is maintained in the resulting mixed oxide. Hydrotalcite based materials have been recently reported as good catalysts for several processes in the energy field, such as hydrogen production by steam reforming of methanol and ethanol, photocatalytic water splitting and so on [3-5].

A series of Co-Zn-Al hydrotalcites, with increasing Co contents was synthesized and characterized. Preliminary tests on their catalytic activity in the FT process resulted in a satisfactory outcome.

2 Experimental Part

2.1 Preparation

Co-Zn-Al hydrotalcites, with general formula $[Co_xZn_{(1-x-y)}Al_y(OH)_2](NO_3)_y \cdot 0.5H_2O$, were synthesized by a modification of the urea method [6]. Different volumes of 0.5 M metal nitrate solutions were mixed in order to obtain the desired molar ratios among the three metals. Solid urea was added to the solution, in the mo-

lar ratio of 4 vs. Al. The resulting solution was maintained at the reflux temperature in an open flask for 24 hr. The precipitate was separated by centrifugation, washed with water, and then dried at 80°C.

2.2 Characterization

The obtained materials were characterized by X-ray powder diffraction (XRD: PANalytical X'Pert Pro, CuK α radiation) and scanning and transmission electron microscopy (SEM: Philips XL30; TEM: Philips 208). Specific surface area was determined with the BET method by N₂ adsorption isotherms (Micromeritics ASAP2010). Temperature programmed reduction (TPR: Micromeritics Pulse Chemisorb 2705, H₂ flux, 8 bar) analyses were performed in order to determine the temperature and the amount of cobalt reduced to metallic Co, representing the active phase.

2.3 Testing Procedures

FT synthesis was performed in a fixed bed reactor, using 1 g of fresh catalyst mixed with 1 g of α -Al₂O₃, as a diluting material. This material, inert towards FT, acts as a good thermal conductor, helping to control the process temperature [7]. The calcined catalysts were initially activated in situ by flowing hydrogen for 4 hours at 90.0 Nml min⁻¹ 350°C and 0.8 MPa. Then, they were tested at the standard conditions by flowing syngas (H₂/CO = 2/1) at 46.8 Nml min⁻¹ plus 5.0 Nml min⁻¹ of N₂ as an internal standard, at 2.0 MPa and 250°C. Analyses of the gas-phase products (C₁-C₇) were performed with an on-line micro gas-chromatograph (Agilent 3000). Liquid products were collected in a trap at 5°C and 2.0 MPa and analyzed at the end of the reaction by a gas-chromatograph (Fisons Mod. 8000 Series) equipped with a Poparak-Q column. The aqueous phases were collected in a cold trap and analyzed by a TOC (Schimadzu Mod. 5000A) to quantify the amount of carbonaceous species dissolved in the water. A mass molar balance was performed for each FT run, resulting in a maximum error of $\pm 5\%$ _{moles}.

3 Results and Discussion

3.1 Catalysts Characterization

According to the XRD patterns in all the samples there is no evidence of the presence of Co oxides or hydroxides as separate phases, indicating that Co atoms are randomly distributed inside the structure of the layers.

SEM and TEM images (Fig. 1) show that the samples were obtained in the form of homogeneous aggregates of hexagonal platelets, about 2 μm large and some hundreds of nm thick. Composition maps, obtained with coupled TEM-EDX analysis, showed that Co, Zn and Al are homogeneously dispersed over the entire analyzed spot area, without creating single-metal domains, thus confirming the good distribution of the metals in the samples in their entirety. XRD analysis confirmed the absence of crystalline metallic Co phases [8].

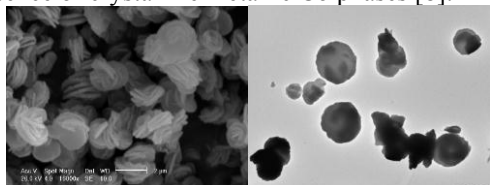


Fig. 1. SEM (left) and TEM (right) images of Co70

Catalytic activity of these materials depends on the presence of metallic Co centres on the surface. Basing on the TPR data, they were therefore activated at 350°C for 4 hours under hydrogen atmosphere, in order to reduce the Co ions to metallic Co.

3.2 Catalytic Results

The activated samples characterized by different cobalt loadings were tested at different temperatures in the FT plant, as reported in the experimental part. Catalytic tests resulted in a very satisfactory outcome, as displayed in Fig. 3, where the CO conversion vs. the reaction temperature is reported for all the catalysts. The products selectivity results are displayed in Table 2.

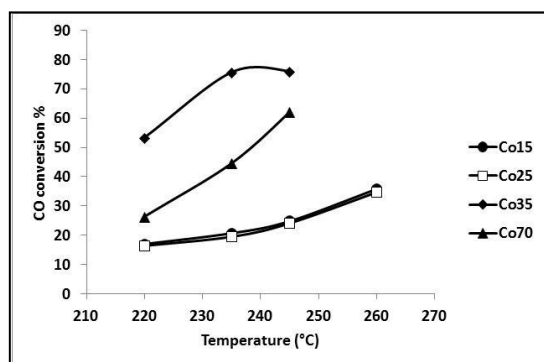


Fig. 3. CO conversion using catalysts with different Co loadings at various temperatures.

Table 2. FT products selectivity using catalysts with different Co loadings at various temperatures. Sel. = products selectivity; <C₇: all the hydrocarbons in the range C₂-C₇; >C₇: all the hydrocarbons greater than C₇.

Catalyst	Temp. (°C)	% Sel.			
		CO ₂	CH ₄	<C ₇	>C ₇
Co15	220	0.3	2.9	3.3	93.4
	235	0.3	5.9	10.4	83.4
	245	1.1	8.5	12.7	77.6
	260	1.9	14.1	16.0	67.9
Co25	220	3.2	2.6	9.8	84.4
	235	3.8	4.9	14.3	76.9
	245	3.3	6.0	15.4	75.3
	260	8.1	16.3	41.3	34.3
Co35	220	1.4	10.1	17.0	70.5
	235	8.1	26.2	47.3	18.5
Co70	220	1.4	3.9	10.3	84.4
	235	1.8	9.6	23.4	65.1

As expected, for each catalyst the activity is strongly influenced by the reaction temperature: the higher the temperature, the higher the CO conversion, but also the selectivity towards CO₂, CH₄ and light hydrocarbons is favoured by the increase of the temperature. The obtained CO conversions are similar for the samples Co15 and Co25, while they are higher at all the selected temperatures for the two samples characterized by a higher amount of cobalt (i.e. Co15 \approx Co25 < Co70 < Co35: the maximum CO conversion was obtained using the Co35 catalyst), as displayed in Fig.3. In the FT synthesis it is fundamental to obtain low quantities of CH₄ and CO₂ (undesired products). For this reason, temperatures in the range 220-235°C are more suitable than the higher ones. The sample Co35 gives the highest CO conversion, being characterized by an high Co amount, but it results at the same time in a high CH₄ selectivity. Samples characterized by lower cobalt amounts give lower CO conversion but a more convenient products distribution.

4 Conclusions

The CO conversion, as expected, is directly dependent on the increase of the temperature.

Despite the Co35 shows the highest CO conversion, the best choice is represented by the sample Co15. According to the obtained results that samples with lower cobalt amounts give the higher selectivity towards heavy hydrocarbons at lower temperatures.

The obtained data suggest the possibility of using synthetic HTlc as a suitable Co-based catalysts for FTS and open the expectation for a subsequent study of synthetic hydrotalcite as a suitable support for Co for FTS.

5 References

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