FISCHER TROPSCH SYNTHESIS USING A Co -BASED CATALYST DEPOSITED ON AlSBA-15 UNDER ATMOSPHERIC PRESSURE

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AlSBA-15 support was impregnated with cobalt, manganese and calcium nitrates and reduced to metallic phase. The obtained catalyst was characterized by N_2 adsorption-desorption isotherm and scanning electron microscopy. Co-based catalyst deposited on AlSBA-15 was tested in the Fischer Tropsch process under atmospheric conditions. The temperature and CO:H_2 molar ratio were varied in order to optimize the catalytic activity and selectivity for olefins. Experiments were performed in the temperature range of 250° - 350 °C. Different CO:H_2 molar ratio values, from 1:1 to 1:2 were tested. The selectivity for C_2 -C_4 olefins is influenced by temperature and CO: H_2 molar ratio. The best results are obtained at temperatures of 300°-325°C and at CO: H_2 molar ratios of 1:1 and 1:1.25.

Keywords: Fischer-Tropsch; Co-based catalyst; AlSBA-15 support

1. Introduction

Fossil fuels have been intensively used in the past 100 years. In most cases crude oil is separated into light components such as liquefied petroleum gas, gasoline and heavier components such as diesel, tars and waxes, by rectification [1]. Also in some cases, certain fractions are sought after and the conversion of other products into useful products is required. Thus processes like fluid catalytic cracking (FCC) and pyrolysis have to be implemented in refineries. Also FCC and pyrolysis have a larger environmental impact regarding their emissions in the atmosphere despite numerous attempts to solve this issue [2].

The Fischer-Tropsch (F-T) process consists in the reaction of H_2 with CO (or in some cases CO_2) that leads to the formation of hydrocarbons [3]. The catalyst used in this process consists in an active metal (usually Fe, Co or Ni) [4,5,6] which is deposited onto a support [7]. Supports for most F-T catalysts vary

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from aluminosilicates [8] to TiO_2 [9] or carbon nanotubes [10] (the latter being the most expensive). The use of a support is required in order to avoid the premature deactivation of the catalyst [11]. In time, on the F-T catalyst, a layer of carbon is formed on its surface that blocks the metallic active sites [10]. The F-T process operates at high temperatures (usually from 200°C to 400°C) and pressures of 5-10 atmospheres [11]. Working at higher pressures leads to an increase in the hydrocarbon length and an enhanced amount of saturated hydrocarbons, however this increase in hydrocarbon length and saturation also results in a high amount of oxygenated compounds [12]. Using a lower pressure eliminates these problems, but raises the challenge of countering the excessive formation of methane and reducing the selectivity for other hydrocarbons [13].

The aim of the work was to determine the most favorable F-T reaction conditions in order to obtain light olefins under atmospheric pressure. For this study AlSBA-15 supported Co-based catalyst was used. AlSBA-15 was chosen as catalyst support due its favorable textural properties (high specific surface area, optimum pores diameter) that allow a good diffusivity through the supports mesochannels [14,15].

2. Experimental section

Experimental setup

Carbon monoxide and hydrogen have been used as the reaction gases. Hydrogen in a mixture with nitrogen was used for the catalyst activation and regeneration. For the catalyst activation, a temperature of 400 °C, a flow of 1:1 molar ratio N_2:H_2 and a flow rate of 80 mL/min were used. The flow rate was controlled by mass flow controllers (MFC) from Sierra instruments. To perform the F-T reaction at atmospheric pressure, the catalyst was placed in a quartz tube reactor conventionally heated and the reaction gas mixture pressure was monitored before and after the reaction in order to avoid eventual pressure drops [15]. The gas hourly space velocity used was of 300 h^{-1}. The reaction mixture was analyzed by a Buck type 910 gas chromatograph.

Preparation of the catalyst

The catalyst consists in an AlSBA-15 support, which was impregnated with cobalt, manganese and calcium nitrates corresponding to 10% (wt.) metallic phase that were thermally decomposed and then the formed metallic oxides were reduced at corresponding metals.

For AlSBA-15 support, 3.8 g nonionic triblock copolymer $EO_{20}PO_{70}EO_{20}$ Pluronic P 123, used as the structure directing agent, was dissolved in 120 mL H_2O along with 1.335 g of $Al_2(SO_4)_3 \cdot 18H_2O$, which served as the aluminum source. The mixture was let for 24 h at room temperature, under magnetic stirring and then 8.85 mL tetraethyl orthosilicate were added. The reaction mixture was

aged at 40 °C for 24 h and then hydrothermally treated at 100 °C for 48 h at auto-generated pressure. The formed solid was filtered off, intensively washed with water and ethanol and dried at room temperature. For removal of structure directing agent, a calcination step at 550 °C for 5 h was performed [16].

The AlSBA-15 support was impregnated with a mixture of cobalt, manganese and calcium nitrates in a 10:1:1 molar ratio. The metal loading of the final catalyst consisted of 20% (wt). The nitrates impregnated support was dried under vacuum and then was calcined at 400 °C for the thermal decomposition of the nitrates to the corresponding oxides.

The support and fresh catalyst were analyzed by nitrogen adsorption-desorption isotherm recorded at 77 K on a Quantachrom Autosorb iQ$_2$ in order to determine the textural parameters and by scanning electron microscopy (SEM). The chemical composition of catalyst was determined by energy dispersive X-ray analysis coupled with scanning electron microscope (Tescan Vega 3 LM).

3. Results and discussion

Catalyst characterization

The textural properties of the support and fresh catalyst were determined from N$_2$ adsorption-desorption isotherms recorded at 77 K by using Brunauer Emmet Teller (BET) method for specific surface area (S_{BET}) and Barrett Joyner Halenda (BJH) for average pore size (d_{BJH}), which are listed in Table 1. The total pore volume (V_{pore}) was determined at relative pressure, P/P_0=0.9900. The isotherms of AlSBA-15 support and fresh catalyst are type IV characteristic for mesoporous materials (Fig. 1). As expected the fresh catalyst has lower porosity than the corresponding support. Also the average pore diameter of the fresh catalyst is lower than for support, meaning that the metallic oxide particles did not block the support pores.
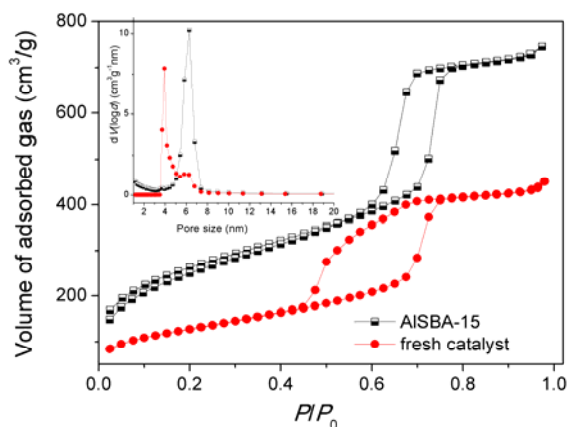

Fig. 1. N$_2$ adsorption-desorption isotherm for AlSBA-15 support and fresh catalyst

Textural properties for the AlSBA-15 support and catalyst

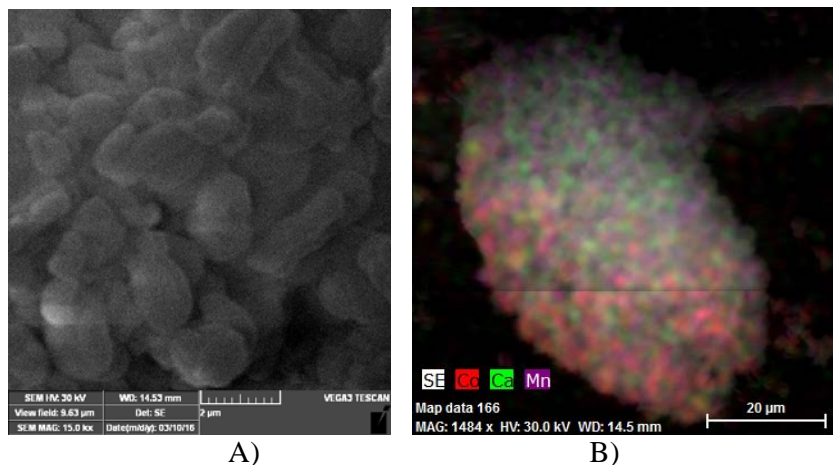| Name	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	d_{BJH} (nm)
AlSBA-15	955	1.25	6.29
Fresh catalyst	459	0.76	3.94

Fig. 2. SEM images of fresh catalyst

The morphology of the catalyst was investigated by scanning electron microscopy. The catalyst presents rods and particles of micron size (Fig. 2A). The energy dispersive X-ray analysis showed a uniform distribution of metallic oxide particles on the mesoporous aluminosilicate support (Fig.2B). The EDX analysis revealed that the total metallic phase content was 11.1% (wt.) with a Co:Ca:Mn molar ratio of 13:1:1 compared with the theoretical value of 10% (wt) and 10:1:1, respectively. The Si/Al molar ratio of the aluminosilicate support was found 20.

Catalytic activity

The catalyst was activated in a mixture of hydrogen and nitrogen on a 1:1 molar ratio under a flowrate of 80 mL/min at a temperature of 400 °C for 10 h. The catalyst activation was performed in order to reduce the metallic oxides to the corresponding metals. The catalyst was employed in F-T reaction at different temperature and CO:H$_2$ molar ratios in order to investigate its catalytic activity. The working temperatures were 250 °C, 300 °C, 325 °C, 350 °C and the CO:H$_2$ molar ratio for each temperature set were 1:1, 1:1.25, 1:1.5 and 1:2.

At each temperature and molar ratio, several gas samples were collected in order to make sure that the chemical reaction achieves steady state. In order to observe the catalyst stability in the Fischer Tropsch reaction, two series of catalytic tests were run, one after the catalyst activation and the other after the catalyst had been used in the Fischer Tropsch reaction for 24 h.

The CO conversion increases with the enhancement of hydrogen content in the feed gas. In figure 3a are presented the results obtained in F-T reaction performed right after the catalyst had been regenerated. The conversion increases with temperature and H_2: CO molar ratio. Figure 3b shows a slight decrease in the conversion in comparison to the data obtained for the fresh catalyst. This could be attributed to the formation of a layer of carbon on the catalysts surface, thus partially deactivating it.
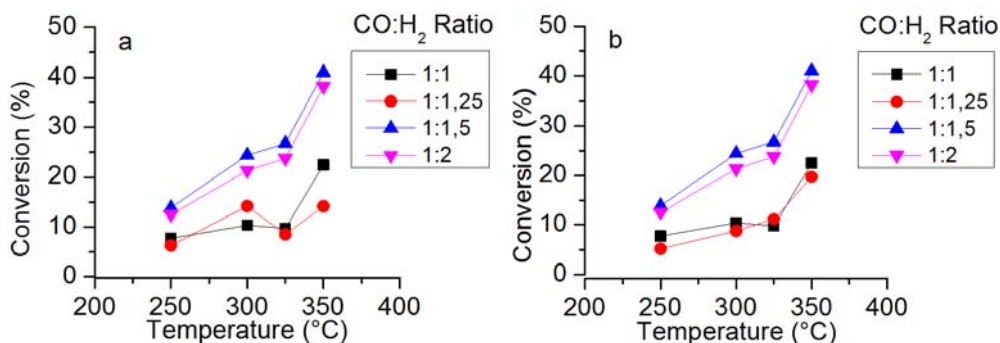

Fig. 3. CO conversion at various temperatures and CO: H_2 ratios (a) fresh (b) used catalyst.
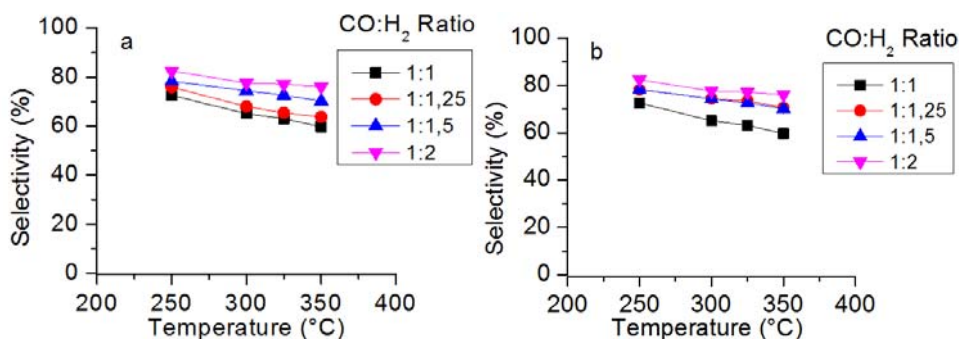

Fig. 4. CH_4 selectivity at various temperatures and CO: H_2 ratios (a) fresh (b) used catalyst.

Because the reaction has been performed at atmospheric pressure, a high selectivity for methane is obtained (Fig. 4a and b), which could be explained by the Anderson-Schulz-Flory mechanism [17]. The selectivity for carbon dioxide increases with temperature and decreases with the enhancement of H_2: CO molar ratio (Fig. 5a and b). The saturated hydrocarbons show a lower selectivity (Fig. 6a and b) than the unsaturated ones (Fig. 7a and b).

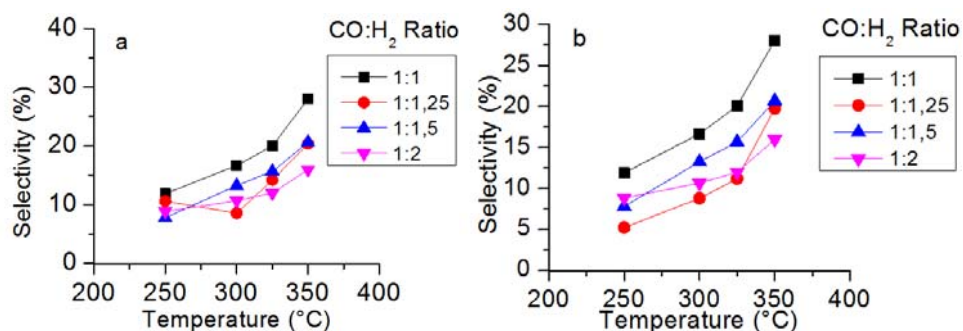Fig. 5. CO_2 selectivity at various temperatures and CO: H_2 ratios (a) fresh (b) used catalyst.
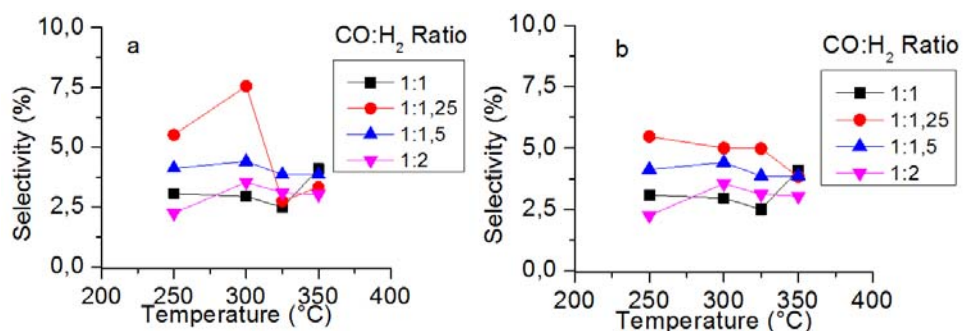

Fig. 6. Saturated hydrocarbon selectivity at various temperatures and CO: H_2 ratios (a) fresh (b) used catalyst.
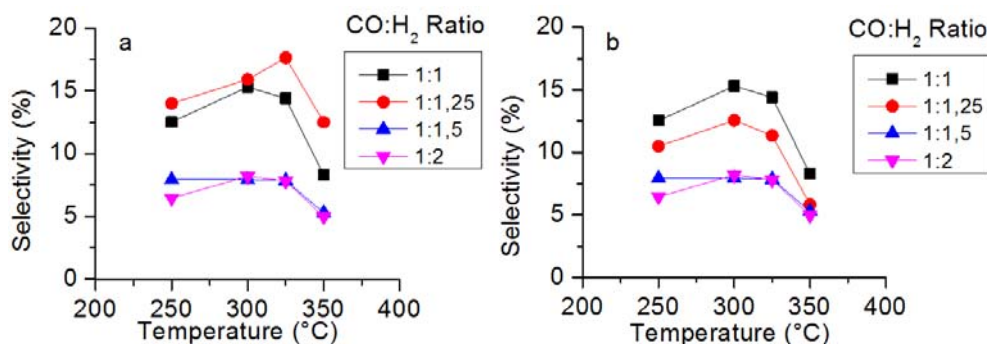

Fig. 7. Olefin selectivity at various temperatures and CO: H_2 ratios (a) fresh (b) used catalyst.

The selectivity for C_2 -C_4 olefins is strongly influenced by temperature and CO: H_2 molar ratio. The best results are obtained at temperatures of 300°-325°C and at CO: H_2 ratios of 1:1 and 1:1.25.

Compared with Fe-Ni catalyst supported on SBA-15 tested for F-T reaction under atmospheric pressure [18], which reached the highest selectivity in olefins of 12% at 350°C for a CO:H_2 molar ratio of 1:1, the catalyst reported

herein showed higher selectivity (15%) at lower temperature (325°C). However, slightly higher selectivity for olefins in F-T reaction performed in the presence of Co-based catalysts deposited on SBA-15 was reported for above atmospheric pressure [19].

4. Conclusions

In the F-T reaction, typical pressures vary from one to several tens of atmospheres; a high pressure favors an increase of hydrocarbons chain. Here, we reported results in the F-T reaction performed under atmospheric conditions by using a Co-based catalyst deposited on AlSBA-15 support with high porosity, which was used in order to obtain light hydrocarbons (C_2-C_4).

The F-T synthesis can be performed under low pressure, maintaining the catalysts activity for a prolonged duration. In this case the main reaction products are methane and small hydrocarbons (C_2-C_4) with a significant content of olefins when compared to the saturated hydrocarbons. If the syn gas is obtained from renewable sources (biomass or waste) the process could be valuable.

On using atmospheric pressure, high quantities of CO_2 are formed. The optimal reaction conditions are those in which the CO_2 selectivity is limited and the amount of light olefins is high. The optimal reaction conditions were obtained at around 325 °C and a CO: H_2 ratio of 1:1.25.

Acknowledgements

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