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Fischer-Tropsch synthesis. Influence of the crystal size of iron active species on the activity and selectivity

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ABSTRACT

In order to analyze the influence of the crystal size of the active phase in the Fischer-Tropsch synthesis (FTS), two iron catalysts, supported on MCM-41 and SBA-15, were prepared by incipient wetness impregnation and tested in this reaction. The solids were characterized by atomic absorption spectroscopy, N_2 adsorption, X-ray diffraction at low angles and Mössbauer spectroscopy. The activated catalysts showed the same iron species. However, the average crystal size of the active phase is about three times higher in SBA-15 than in MCM-41. Besides, both systems displayed a narrow size distribution. The catalyst with higher crystal size (Fe/SBA-15) presented higher conversion, higher chain growth and lower CH_4 production. These results would indicate that the FTS is a "structure sensitive" reaction in a sizes range within, approximately, 3–10 nm.

1. Introduction

The Fischer-Tropsch synthesis (FTS) is a process used to produce a broad distribution of "clean" hydrocarbons from syngas ($CO:H_2$ mixture in a determined ratio). Although, this is a process that has been industrially used for decades, the still unsolved major problem is to achieve good selectivity toward certain products of interest. For this purpose two different methodologies have been applied: the control of the synthesis process conditions or the change of certain structural properties of the catalysts. This last option seems to be the most appropriate one since the reaction is kinetically controlled. There are several possible methods to achieve the second objective, two of them are: the use of promoters added to the conventional Fischer-Tropsch catalyst (Fe or Co) or the control of crystal size of the active phase. The last method is based on the fact that in some heterogeneous catalytic reactions, the activity of the solid is a function of the crystal size of the active phase, generally in 1–10 nm range. These reactions are known to be "structure sensitive" [1]. Today, the concept of "structure sensitive" involves the activity and selectivity of the catalyst. In the literature there is some early evidence that the FTS is "structure sensitive" [2] and, more recently, this property would be confirmed using Co supported catalysts [3]. Therefore, it would be possible to achieve an improvement in the catalyst selectivity if particles of supported Fe oxides, with determined average diameters and narrow size distribution, were obtained. The average diameter should not be extremely small, since the growing of the product chains would be hindered [4], leading to a high methane production. Therefore, it is necessary to overcome certain minimum value. On the other hand, the diameter should not be too large since the chains grow up without control and the selectivity would be lost. It is possible to estimate values between 3 and 10 nm as adequate for the control selectivity.

The first step to obtain a catalyst of this type is to select an "inert" support with a narrow pore size distribution and thermal stability during the preparation steps and use of the catalyst. Besides, the pore diameter of the support must allow locating the iron oxide crystals within the channels, avoiding their migration to the outer surface during the activation steps. The challenge is to find a support having all these properties simultaneously. The mesoporous solids MCM-41 and SBA-15 seem to fulfill the above conditions. Thus, MCM-41 has a hexagonal arrangement of uniform pores, high specific surface area between 1000 and 1200 m^2/g, tailored channel dimensions between 1.5 and 10 nm and thermal stability [5] and the mesoporous solid SBA-15 has a narrow pore size distribution, with hexagonal arrangement, whose diameters can be varied between 5 and 30 nm, wall thicknesses between 3 and 6 nm and specific surface area between 700 and 1000 m^2/g [6,7].

However, the greater challenge to produce a narrow crystal size distribution in the desired size range of the active Fe species

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involves the introduction of the total iron species inside the channels of these solids.

Thus, the aim of the present work is to prepare two iron catalysts supported on MCM-41 and SBA-15 with different average crystal size of active species, in order to determine the influence of these sizes on the activity and selectivity in the FTS. In order to achieve this scope, it will be necessary to introduce the total or the greater possible quantity of the iron loading inside the channels of the mesoporous supports.

2. Experimental

2.1. Catalysts preparation

MCM-41 support was prepared according to the methodology proposed by Ryoo and Kim [5] using sodium silicate as silica source, cetyl-trimethyl-ammonium chloride as surfactant and pH control during the hydrothermal synthesis. Thus, 40 g of sodium silicate (26.1% SiO_2) were dissolved into 74 g of water. The solution was then slowly added to 38 ml of cetyl-trimethyl-ammonium chloride and 0.65 ml of NH_3 with vigorous stirring at room temperature. This mixture was heated in a polypropylene bottle, without stirring to 373 K for 24 h, afterwards, it was cooled to room temperature. The pH was regulated to approximately 11 by drop wise addition of acetic acid with vigorous stirring. The reaction mixture was heated again to 373 K for 24 h. This procedure for pH control and subsequent heating was repeated twice. The resulting solid was filtered, washed and dried in air at room temperature. The surfactant was removed by calcination in N_2 flow (150 cm^3/min) using the following thermal program: from room temperature (RT) to 783 K with a heating rate of 8 K/min and kept at this temperature for 1 h. Subsequently, the N_2 flow is replaced by air, keeping the last temperature for 6 h.

SBA-15 support was synthesized according to the methodology proposed by Zhao et al. [6,7] using Pluronic P123 (EO_{20}-PO_{70}-EO_{20}) as organic structure-directing agent. Thus, 12 g of Pluronic P123 were dissolved in 360 ml of water and 60 ml of HCl solution (37%, w/w) with stirring at 313 K for 3 h. Then, 27 ml of TEOS (tetraethyl orthosilicate), as silica source, were added and the solution was kept stirring at 313 K for 24 h. The mixture was aged at 363 K overnight, without stirring. The solid was recovered by filtration, washed and dried in air at RT. Calcination in air was carried out from RT to 773 K at 1 K/min and kept at 773 K for 6 h.

MCM-41 support was impregnated with a $Fe(NO_3)_3 \cdot 9H_2O$ aqueous solution and SBA-15 was impregnated with an ethanolic solution, in order to obtain the highest nominal iron concentration in a single step, using the incipient wetness impregnation method. The solids were dried using a rotary evaporator at 313 K for 24 h. Fe/MCM-41 was subsequently calcined in N_2 flow (60 cm^3/min) from 298 to 603 K with a heating rate of 0.2 K/min and kept at this temperature for 1 h. This sample was called p-Fe/MCM-41. Fe/SBA-15 was calcined under an air flow from RT to 723 K with a heating rate of 1 K/min and kept at this temperature for 4 h. The differences in the preparative steps are based on the constraints imposed by the supports used and in the previous experience of our laboratory.

2.2. Catalysts characterization

The samples were characterized by atomic absorption spectroscopy (AAS), X-ray diffraction at low angles (XRD), N_2 adsorption (BET), Fourier transform infrared spectroscopy (FT-IR), and Mössbauer spectroscopy (MS).

The Fe content of the solids was determined in atomic absorption equipment AA/AE Spectrophotometer 457 of Instrumentation Laboratory Inc. The samples were attacked with a mixture of HCl and HF acids up to complete dissolution and then were treated according to conventional methods for this technique.

All XRD patterns were measured using a standard automated powder X-ray diffraction system Philips PW 1710 with diffracted-beam graphite monochromator using Cu Kα radiation (λ = 1.5406 Å). Data were taken between $2\theta = 0.5^\circ$ and 9° with steps of 0.02° and counting time of 2 s/step.

The textural properties were measured in a Micromeritics equipment ASAP 2020.

The FT-IR absorption spectra were acquired with a Bruker IFS66 spectrometer with 1 cm^{-1} resolution by co-addition of 32 scans. The samples were prepared as potassium bromide discs, in a 1:100 proportion.

The Mössbauer spectra were obtained in transmission geometry with a 512-channel constant acceleration spectrometer. A source of ^{57}Co in Rh matrix of nominally 50 mCi was used. Velocity calibration was performed against a 12 μm-thick α-Fe foil. All isomer shifts (δ) mentioned in this paper are referred to this standard. The temperature between 25 and 298 K was varied using a Displex DE-202 Closed Cycle Cryogenic System. The Mössbauer spectra were evaluated using a commercial program with constraints named Recoil [8]. Lorentzian lines were considered with equal widths for each spectrum component. The spectra were folded to minimize geometric effects. The spectra of the reduced samples were obtained in the activation atmosphere using a cell specially built by us for this purpose to be used inside the cryogenic system [9].

Activity and selectivity measurements in FTS were carried out in a stainless steel fixed bed reactor at a total pressure of 1 atm, with H_2:CO ratio of 2:1, a space velocity of 1176 h^{-1} (400 mg catalyst and a total flow of 20 cm^3/min), at 703 K of reaction temperature. Before the reaction, the precursors were activated in H_2:CO = 2:1 flow, from 298 to 703 K with a heating rate of 9 K/min. This time is considered the zero reaction time. The gases passed through filters to remove oxygen, water traces and carbonyls. The activated solids are called c-Fe/MCM-41 and c-Fe/SBA-15. The reaction products were analyzed online by gas chromatography using FID and TCD detectors with GS-Gas Pro capillary column and a HAYESEP DB 100/120 packed one, respectively. After the reactor, the tubing lines were kept at about 503 K to avoid product condensation. This hot stream goes through a heated six-way injection valve that collected 1.8 ml of gas sample to be injected in the capillary column for hydrocarbons using a split ratio of 20:1. After, the stream goes through a second heated six-way valve, and the permanent gases were injected in the packed column.

3. Results and discussion

The structure of the mesoporous solids MCM-41 and SBA-15, used as supports, was verified by XRD (Fig. 1). On the other hand, their textural properties are typical of this type of solids (Table 1).

Both supports have walls constituted by amorphous SiO_2 with straight cylindrical pores in hexagonal arrangement. They differ in the diameter of their channels. Another possible difference between both supports could be the concentration of the surface silanol groups. A difference of about 5% in this value between both supports was observed using FT-IR. This value was obtained relating the height of the peak at 970 cm^{-1} (assigned to silanol groups [10]) with the height of symmetric stretching vibration peak of the Si–O network at 800 cm^{-1} [10] (Fig. 2). Therefore, we consider that both solids are equal (within the experimental errors) in their chemical and superficial properties, in this way, the different supports would not affect the catalytic properties of the catalysts.

The impregnation with iron salt and the calcination treatments that led to the production of p-Fe/MCM-41 and p-Fe/SBA-15 do not modify the structural properties of the mesoporous supports, as it