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Calcination effect of Ca-Fe hydrocalumites supported CoMo for the hydrodesulfurization of thiophene and hydrogenation of cyclohexene

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Abstract

A Fe-Ca hydrocalumite was synthesized, calcined between 500 and 900°C, and characterized by different techniques such as: X-ray diffraction (XRD), Fourier-Transform infrared spectroscopy (FT-IR) and surface area. After that, supports were impregnated with Mo and Co. Finally, catalysts were tested in the thiophene hydrodesulfurization and cyclohexene hydrogenation as model reactions. Results showed that conversion depended of calcination temperature of support, and those were more active when the support was calcined to the highest temperature which could be associated to the present phases.

Keywords: Hydrocalumite; Iron; Calcination; Thiophene; Cyclohexene.

Efecto de la calcinación de hidrocalumitas Fe-Ca como soporte de CoMo para la hidrodesulfuración de tiofeno e hidrogenación de ciclohexeno

Resumen

Se sintetizó una hidrocalumita de Fe-Ca, se calcinó entre 500 y 900°C, y se caracterizó por diferentes técnicas tales como: difracción de rayos X (DRX), espectroscopia de infrarrojo con transformada de Fourier (FT-IR) y área superficial. Luego, los soportes fueron impregnados con Mo y Co. Finalmente, los catalizadores fueron probados en la hidrodesulfuración de tiofeno e hidrogenación de ciclohexeno como reacciones modelo. Los resultados mostraron que la actividad catalítica depende de la temperatura de calcinación del soporte, y éstos fueron más activos cuando los soportes se calcinaron a la temperatura más alta lo cual podría estar asociado a las fases presentes.

Palabras clave: Hidrocalumita; Hierro; Calcinación; Tiofeno; Ciclohexano.

Introduction

The presence of heavier crude oils in refineries has increased the use of new supports and active phases as hydrotreating catalysts in order to satisfy environmental

regulations [1, 2].

Among tested supports as hydrotreating catalysts can be mentioned: zeolites, amorphous silica, mesoporous materials, hydrotalcites and others [3-7], but little

attention have received hydrocalumite-type materials [8].

Hydrocalumite is a solid closer to hydrotalcite-type materials based in brucite-type corrugated layers with an ordered array of hepta and hexa-coordinated Ca^{2+} and M^{3+} ions, and a fixed $\text{Ca}^{2+}/\text{M}^{3+}$ ratio of 2:1 [8].

Usually hydrocalumites with Al^{3+} are successfully synthesized but other combinations with Fe^{3+} , Ga^{3+} and Sc^{3+} are also possible [9]. In addition, the calcination of these materials generates interesting properties [10].

Hydrocalumites as supports of hydrotreating catalysts have been few documented: Linares et al. [10] synthesized Al-hydrocalumites as support of hydrotreating catalysts. Results showed lower conversions than that of commercial catalyst.

Despite of these conversions, the presence of Fe in the hydrocalumite could increase the activity of these catalysts due to its properties as promoter [11]. In addition, depending iron oxides formed during the sample calcination, the acid-base properties can be modified [12, 13].

Experimental

Fe-hydrocalumite (Fe-HC) synthesis

Fe-HC was synthesized following the procedure previously reported [9]. 50 mL of a 0.33 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Mallinckrodt, 99%) and 0.66 M CaCl_2 (ERBA, 92%) solution was slowly added over 100 mL of a 1M NaOH solution. The resultant solution was agitated under a nitrogen atmosphere at room temperature during 24 h. The pH was kept <11.5. After that, the gel was filtered and washed until pH=7. An orange solid was obtained, and it was dried in oven at 60 °C during overnight.

Then, dried solid was divided in five equal portions, and calcined at: 500, 600, 700, 800 and 900 °C using a heating rate of 3 °C/min by means of a muffle.

Impregnation of calcined Fe-HC

Calcined solids were impregnated by the incipient wetness impregnation method using an ammonium heptamolybdate salt (Riedel-de Haën, 98%, 15 w/w % MoO_3). Then, the Co was co-impregnated under a $[\text{Mo}]/[\text{Co}]$ atomic ratio of 3, using a cobalt nitrate salt (BDH Chemical Ltd, 97%). Impregnated solids were dried at room temperature for 24 h. Then, these solids were calcined at 420 °C for 24 h.

Characterization of catalysts

Fe-HC, calcined Fe-HC and CoMo/Fe-HC samples were characterized by X-ray diffraction (XRD, with Phillips PW3710, Ni-filtered $\text{CuK}\alpha$ radiation at 1.542 Å), Fourier-Transform infrared spectroscopy (FT-IR, Perkin Elmer model AAnalyst 200, by the KBr pellet method) and BET surface area measurements (Micromeritics ASAP 2010 by N_2 physisorption).

Catalytic conversion

Catalytic precursors were tested in thiophene hydrodesulfurization (HDS) and cyclohexene hydrogenation (HYD) reactions. Thiophene HDS and cyclohexene HYD were carried out in a continuous flow reactor working at atmospheric pressure. All catalysts were presulfided in situ at 400 °C for 2 h prior to catalytic tests using a 0.17 mL.min⁻¹ stream of CS_2 (10 v/v %)/n-heptane solution vaporized and mixed with a H_2 stream (100 mL.min⁻¹) and kept at these conditions for 2 h. Then, the reaction took place on 200 mg samples of catalyst using a liquid feed (1.62 10⁻² mL.min⁻¹) composed of 6 v/v % of thiophene or cyclohexene in n-heptane vaporized and mixed with a H_2 stream (15 mL.min⁻¹) at 325 °C. All lines of the reaction system were covered with a heating mantle (150 °C) in order to avoid any condensation of the reactants and reaction products. Reaction products and unreacted feed were analyzed with a Varian 3800 (AutoSystem XL) gas chromatograph equipped with a flame ionization detector and a capillary column.

Results and discussion

Characterization of CoMo/calcined Fe-HC samples

Fig. 1 shows FT-IR spectra of CoMo/Fe-HC samples calcined at different temperatures. For not calcined sample (Fe-HC, spectrum a), bands between 3400 and 3600 cm⁻¹ were attributed to OH- groups corresponding superficial OH- groups from $\text{Ca}(\text{OH})_2$ of Fe-HC [8, 9]. The band closes to 2362 cm⁻¹ corresponds to physisorbed CO_2 during the preparation of KBr pastilles [14]. The presence of CO_3^{2-} anions was corroborated by a series of bands around 1477 cm⁻¹. Bands at 1691 cm⁻¹ and 1560 cm⁻¹ were adjudicated to water molecules placed between Fe-HC interlayers. According to Campos et al. [15], the band at 858 cm⁻¹ was related to the C-O bonds from CaCO_3 .

When samples are calcined to 500 °C, the FT-IR spectrum

shows that the intensity of bands corresponding to OH-groups from $\text{Ca}(\text{OH})_2$ and water molecules are diminished which indicates that the HC structure is dehydrated and the water molecules are expelled [9, 16, 17], and other phases could be formed.

Then, at temperatures superior to 600 °C, FT-IR spectra are very close. Two bands are emerged at 876 cm^{-1} and between 1400 and 1500 cm^{-1} . Both bands are associated to CaCO_3 [16]. During the calcination, it is observed that both bands are diminished and new band close to 541 cm^{-1} is increased which could be due to formation of CaO by decomposition of CaCO_3 [18].

For the sample calcined at 900 °C, bands between 3400 and 3600 cm^{-1} , 1400 and 1500 cm^{-1} and 799 cm^{-1} are almost disappeared. Together to the bands previously observed in calcined Fe-HC, other new bands were determined in these catalytic precursors. Bands around 876 and 800 cm^{-1} are adjudicated to Mo-O-Mo bonds from MoO_3 [19]. In addition, bands at 1523 cm^{-1} and those found to low frequency (< 600 cm^{-1}) could be associated to Fe-O and Ca-O bonds from Fe-HC decomposition due to the calcination treatment [8, 20].

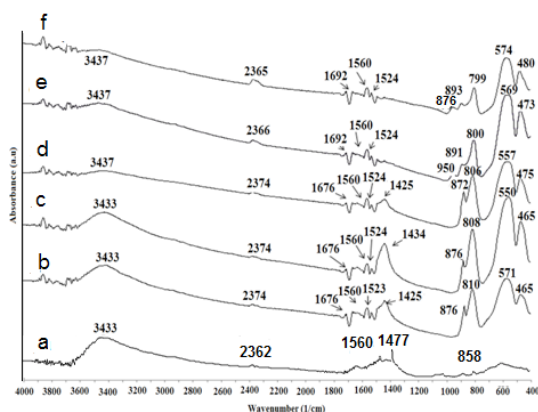


Figure 1. FT-IR spectra of catalytic precursor calcined at: a) room temperature, b) 500 °C, c) 600 °C, d) 700 °C, e) 800 °C and f) 900 °C.

For a better determination of present phases during the calcination, X-ray diffraction was carried out (Fig. 2). The presence of Fe into the hydrocalumite sample is a possibility, further characterization, as the Mössbauer technique should be done in order to confirm the presence of this element in the hydrocalumite structure.

Peaks possible corresponding to: molibdate MoO_3 (COD:

96-101-1074), hematite Fe_2O_3 (COD: 96-900-0140), calcium ferrite CaFe_2O_5 (COD: 96-901-3960), powellite CaMoO_4 (COD: 96-900-9634), brownmillerite $\text{Ca}_2\text{Fe}_2\text{O}_5$ (COD: 96-900-4372), lime CaO (COD: 96-900-6742), magnetite Fe_3O_4 (COD: 96-900-2333), srebrodolskite $\text{Ca}_2\text{Fe}_2\text{O}_5$ (COD: 96-900-3470), goethite FeO_2 (COD: 96-901-6060), schwertmannite Fe_8O_{17} (COD: 96-901-5186) and banfordite $\text{FeMo}_2\text{O}_{10}$ (COD: 96-900-1903) were observed for these catalytic precursors. In Fig. 2 are only shown the most intense peaks. The identifications some peaks were also observed by FT-IR.

The MoO_3 phase is produced by the impregnation of supports with the molybdenum salt. Co phases were not observed which could be associated to a good dispersion of this element on the support surface [20].

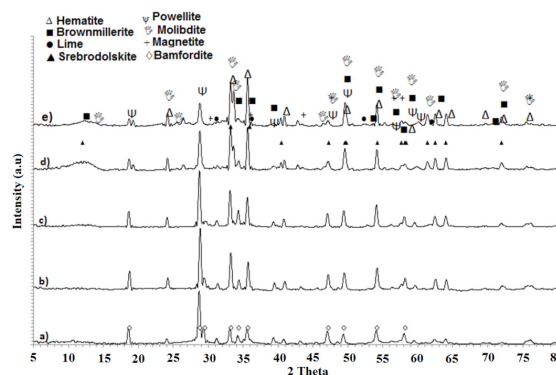


Figure 2. XRD of catalytic precursors calcined at a) 500 °C, b) 600 °C, c) 700 °C, d) 800 °C and e) 900 °C.

An approximate quantification of phases showed in X-ray diffractograms could be done by the relation of peak intensities of different compounds (Table 1).

As it can be seen, as the calcination temperature increased, the hematite phase is also increased but the brownmillerite phase is diminished. Also, phases such as banfordite, schwertmannite and goethite which were identified at 600 and 700 °C, almost disappear when the temperature is increased.

The powellite phase which appears in a high proportion for samples calcined between 500 and 800 °C, it is few active for the hydrotreating reactions. This phase is produced by the reaction with calcium ions from hydrocalumite and the impregnated Mo. In turn, the molibdate phase which is responsible of the catalytic activity, it was determined in low proportion for these samples before mentioned

However, for sample calcined at 900 °C, the powellite phase is found in low concentration in comparison to the

molibdate phase. We do not have a clear explanation for these results found for the sample calcined at 900 °C, but it is very possible that the high temperature of calcination does not allow a high mobility of calcium ions, and they can remain inside the calcined hydrocalumite structure. This low mobility of calcium ions allows a high proportion of the molibdate phase which is responsible of the activity of this catalyst.

On the other hand, these phases previously determined, are very sensible to high temperatures and stable phases are formed. Hematite and magnetite are resistant to high temperature and high pH; therefore, they are competitive phases.

Results of BET surface areas are observed on Table 1. As it can be seen, the calcination of Fe-HC produces the diminution of BET surface area as the calcination temperature is increased, which could be related to the formation of dense phases as it was before mentioned. Otherwise, the specific areas of catalytic precursors were similar to those reported for its corresponding supports which could be associated to high dispersion of the Co and Mo. In turn, for sample calcined at 500 °C, the surface area was diminished in comparison to its support which could be due to blocking of porous by the impregnation of molybdenum and cobalt salts (Table 1).

Catalytic reactions

HDS of thiophene

Fig. 3.a exhibits the catalytic behavior of the diverse catalytic precursors calcined at different temperatures in the HDS reaction of thiophene compared with a commercial CoMo/ γ -Al₂O₃ catalyst. As it can be seen, the traditional catalyst reported a conversion close to 17 % in the stationary state; then, the rest of catalysts showed conversion lower than that the commercial catalyst. An exception was observed for catalyst calcined at 900°C which showed a superior conversion than that CoMo/ γ -Al₂O₃ catalyst.

A correlation was observed between the surface area and the catalytic conversion, and those catalysts with high surface area were more active with an exception for the catalysts calcined at 900 °C whose behavior was superior to the CoMo/ γ -Al₂O₃ catalyst despite its low surface area.

Moreover, catalysts calcined at 500, 600 and 800 °C showed a similar conversion which could be associated to a similar phase composition: the magnetite phase is higher proportion and the MoO₃ active phase is in lower composition (Table 1). Both phases have influence in the catalytic development as will be referred.

Table 1. Composition estimation of catalytic precursors supported on Fe-HC calcined at different temperatures and BET surface area measurements.

Samples (%)	500 °C	600 °C	700 °C	800 °C	900 °C
Hematite	16.3	41.8	42.0	44.0	52.6
Srebrodskite	7.7	-	-	26.4	-
Powellite	24.3	35.9	29.4	18.4	7.6
Molibdite	4.5	4.3	2.9	5.8	10.0
Lime	3.2	3.9	2.4	3.0	1.9
Magnetite	3.1	6.5	9.6	2.4	2.3
Brownmillerite	7.9	7.7	7.5	-	6.9
Banfordite	8.4	-	-	-	-
Schwertmannite	14.4	-	-	-	-
Goethite	4.0	-	-	-	-
BET surfacea	50	24	16	8	3
BET surfaceb	35	21	13	8	6

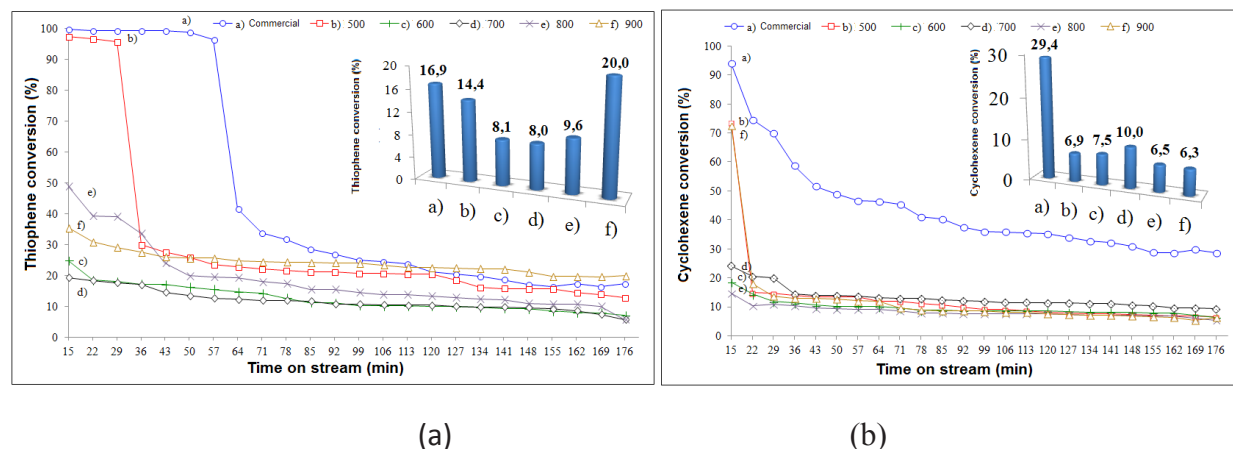


Figure 3. a) HDS of thiophene b) HYD of cyclohexene. Samples at: a) CoMo/ γ -Al₂O₃, b) 500 °C, c) 600 °C, d) 700 °C, e) 800 °C and f) 900 °C.

In another way, the catalyst calcined at 900 °C, showed the highest catalytic conversion for the HDS reaction of thiophene. This catalyst has a very low surface area close to 8 m²/g but the composition for this catalyst shows high values of hematite (52.6%) and molybdenum oxide (10%), and low composition in magnetite and lime. Cornell and Schwertmann [12] studied the surface acidity of different iron oxides. Results showed that the hematite phase is basic while the magnetite phase presents an acid character. According to Breyse et al. [13], the basic supports could favor a high stability and dispersion of the molybdenum oxide phase which reduce the coke formation with a high catalytic conversion, despite the low surface area.

HYD of cyclohexene

For this reaction, all catalysts showed a low conversion (<10%) in relation to the commercial catalyst (\approx 30%) (Fig 3.b). The lowest values were obtained for the catalysts calcined at 800 and 900 °C, while the highest values were found for those catalysts with major presence of magnetite which shows acidic properties. Studies carried out using the adsorption of CO by FT-IR, shows an electron deficiency of the catalytic centers which is increased with the acidity of support raising the hydrogenation activity [21]. On the other hand, the surface area does not seem to affect the obtained results.

Selectivity of reactions

In order to understand the base-acid properties of these catalysts, one way, it was to determine the products of reactions of HDS of thiophene for two selected catalysts.

This reaction can be carried out by means of two ways: the hydrogenolysis (C-S bound hydrogenolysis, HDS) way or the hydrogenation way (HID). The high selectivity towards the formation of butenes (59 %) by the commercial catalyst shows its preference towards the hydrogenolysis route in comparison to the hydrogenation route (formation of butadienes, tetrahydrothiophenes and butanes).

Likewise, Fig. 4.a shows the selectivity of HDS of thiophene using the catalyst calcined at 900 °C. One can see that this catalyst has a clear and high preference towards the formation of butenes (82.5%) and a low formation of tetrathiophenes which infers the preference to the hydrogenolysis route. These results are associated to the basic properties of these supports based in its high composition in hematite as was previously mentioned. The formation of butenes is interesting because they can improve the octane numbers by alkylation of butenes.

Moreover, HDS of thiophene/HYD of cyclohexene selectivity was determined for calcined catalysts obtained from Fe-hydrocalumite and a commercial catalyst (Fig. 4.b). The catalyst calcined at 900 °C showed a high capacity towards the hydrodesulfurization reaction in comparison to the hydrogenation reaction, it can be associated to the high proportion of the hematite phase which promotes the basicity of the catalyst as was before mentioned.

On the other hand, catalysts calcined at 600, 700 and 800 °C, were more active to the hydrogenation route. These results could be associated to the magnetite phase (acid properties) and a low MoO₃ concentration available as active phase [22].

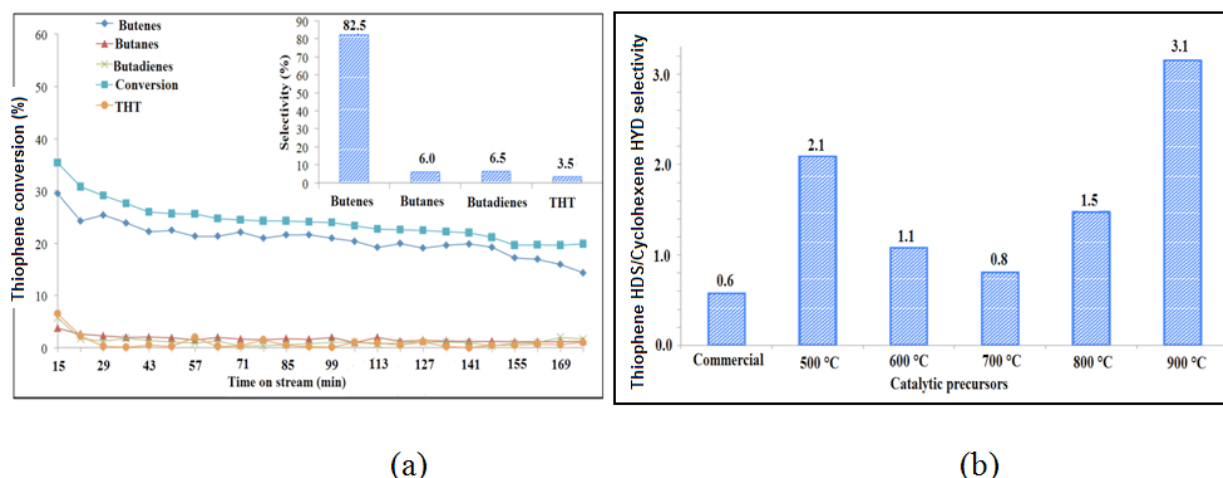


Figure 4. a) Conversion and selectivity for the HDS reaction of thiophene using the catalyst calcined at 900 °C. b) HDS of thiophene/HYD of cyclohexene selectivity for studied catalyst.

Conclusions

It was possible the synthesis and characterization of hydrocalumites containing iron in its structure. The calcination of this sample at different temperature produced different phases which could change the acid-base properties according to calcination temperature. The presence of high concentration of the hematite phase (basic properties) and high concentration of the MoO_3 phase showed for the catalyst calcined at 900 °C, increased the conversion of HDS of thiophene and decreased the conversion of HYD of cyclohexene. The obtained results for this catalyst could improve the quality of gasoline.

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