Fuel Processing Technology 132 (2015) 105–110

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Applications of CoMo/calcined quaternary hydrotalcites for hydrotreatment reactions

Carlos F. Linares [a,*], Maryuri Vásquez [a,b], Rafhael Castillo [a,b], Pablo Bretto [a], Roger Solano [c], Anaís Rincón [c]

[a] Unidad de Síntesis de Materiales y Metales de Transición, Departamento de Química, Facultad de Ciencias, Universidad de Carabobo, Valencia, Venezuela
[b] Escuela de Química, Universidad de Carabobo, Facultad de Ingeniería, Valencia, Venezuela
[c] Instituto de Superficies y Catálisis (INSUC), Facultad de Ingeniería, Universidad del Zulia, Venezuela

ARTICLE INFO

Article history:
Received 30 June 2014
Received in revised form 24 December 2014
Accepted 29 December 2014
Available online 13 January 2015

Keywords:
Quaternary hydrotalcite
Hydrodesulfurization
Hydrogenation
Thiophene
Cyclohexene

ABSTRACT

Co^{2+}, Ni^{2+}, Zn^{2+} and Al^{3+} quaternary hydrotalcite-type materials were synthesized at: 0.33; 0.25 and 0.20 $(M^{3+})/(M^{3+}+M^{2+})$ ratios. Then, these as-synthesized hydrotalcites were calcined and impregnated with Mo (15 wt.% MoO_3) and Co (3Mo:Co) to obtain the catalytic precursors. As-synthesized and impregnated calcined hydrotalcites were characterized by different physico-chemical techniques such as: X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), BET surface area measurements and NH_3-temperature programmed desorption (NH_3-TPD). Finally, CoMo/calcined hydrotalcites were tested in hydrodesulfurization (HDS) and hydrogenation (HYS) reactions of thiophene and cyclohexene. Results showed that the 0.25 $(M^{3+})/(M^{3+}+M^{2+})$ ratio was the most active for the HDS reaction of thiophene, while the 0.33 $(M^{3+})/(M^{3+}+M^{2+})$ ratio showed the best performance for the HYD reaction of cyclohexene.

1. Introduction

Hydrotalcite is a very versatile material. This material is composed by divalent and trivalent cations in definite proportions forming layered double hydroxides (LDHs). These compounds are closely related to that of brucite natural mineral ($Mg(OH)_2$ which is constructed with positively charged octahedral sheets, alternating with anions such as: carbonates, nitrates, chlorides, sulfates and others, together with water molecules. The general formula of LDHs is $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}[A^{n-}{}_{x/n}.mH_2O]^{x-}$; where M^{2+} and M^{3+} are respectively divalent and trivalent cations, and A^{n-} is an n-valent anion; x is a $(M^{3+})/(M^{3+}+M^{2+})$ proportion ratio between $0.2 < x < 0.4$, and m is the number of water molecules [1,2].

During the synthesis of these hydrotalcite-type materials two, three or four di- and trivalent cations can be incorporated, provided that the $M^{3+}/(M^{3+}+M^{2+})$ relationship is respected; thus binary, tertiary or quaternary hydrotalcites can be efficiently synthesized [3,4].

On the other hand, the LDHs can be thermally decomposed forming mixed oxides with high surface area, high distribution of M^{2+} and M^{3+} oxides, high metal dispersion after reduction, small crystals, stability against sintering and homogeneous solid solution [5]. These advantages can be used for highly varied potential applications, including catalysts, catalyst supports, ion-exchangers, adsorbents, medical applications, flame-retardants, corrosion inhibitor, pigments, etc. [5].

Likewise, many efforts have been done to avoid the environmental pollution due to combustion of fuel by hundreds of millions of motor vehicles driving worldwide. During the fuel combustion, sulfur and nitrogen oxides are released to environment producing the acid rain, greenhouse effect, human respiratory diseases and other [6].

Usually, hydrotreating (HDT) process is employed to control these environmental contaminants. Hydrotreatment is mainly used to remove several elements such as: N, S, metals, O from oil cuts by using high H_2 pressures and high temperatures in the presence of an adequate catalyst, usually Co–Mo or Ni–Mo pairs supported on γ-alumina. However, the presence of larger amounts of heavy crude in oil refineries has led to study and improvement these currently employed catalysts because those seem less effective against these heavy crude cuts [7].

Some of the recently studied catalysts include mixed oxides from hydrotalcites as catalyst supports. Thus, several patents have been developed using Mg–Al hydrotalcites as support of hydrodesulfurization and hydrogenation catalysts. Results show an increasing in the HDS reaction and low olefin saturation [8–10]. Zhao et al. [11] studied different hydrotalcites such as: magnesium–alumina, copper–aluminum and zinc–aluminum in the hydrodesulfurization reaction of FCC gasoline. Although the CoMo/γ-alumina catalyst was more active than those of CoMo/calcined hydrotalcites in hydrodesulfurization (HDS) of FCC gasoline, the last ones produced lower levels of olefin hydrogenation and lower octane reduction. Rana et al. [12] found that the incorporation of MgO to Al_2O_3 by preparation of hydrotalcites, favors the hydrogenolysis of dibenzothiophene (DBT) when it is compared to a traditional catalyst (CoMo/γ-alumina). Álvarez et al. [13] synthesized

* Corresponding author.
E-mail address: clinares@uc.edu.ve (C.F. Linares).

http://dx.doi.org/10.1016/j.fuproc.2014.12.043
0378-3820/

hydrotalcites with variable Al/(Al + Zn) mol ratio from 0 to 1. Catalysts were tested in HDS of thiophene. Results showed a catalytic activity maximum at 0.25 ratio; then, the activity decreased as Al content increased [13].

Therefore, the presence of effective promoters for hydrotreatment reactions such as a mixture of Co, Ni and Zn oxides inside an alumina matrix could be interesting.

In order to study the influence of mixed oxides from calcined hydrotalcites, we synthesized quaternary hydrotalcites (Al, Co, Ni and Zn) in different proportions. These calcined hydrotalcites were impregnated with Co and Mo to determine their activity in HDS of thiophene and hydrogenation (HYD) of cyclohexene. The selectivity between hydrodesulfurization and hydrogenation reactions is also discussed in this paper.

2. Experimental

2.1. Preparation of quaternary hydrotalcites

Hydrotalcites were synthesized by the co-precipitation method as it was previously reported [13,14]. Two aqueous solutions were prepared: A and B. 100-mL-solution A was prepared dissolving $CoCl_2 \cdot 6H_2O$ (BDH Chemical Ltd, 97%), $Al(NO)_3 \cdot 9H_2O$ (Riedel-de Haën, 98%), $Ni(NO_3)_2 \cdot 6H_2O$ (Riedel-de Haën, 97%) and $Zn(NO_3)_2$ (Riedel-de Haën, 98%) in deionized water at $(M^{3+})/(M^{3+} + M^{2+})$ molar ratios of: 0.20, 0.25 and 0.33 respectively where M^{3+} is Al^{3+}, and M^{2+} is: $Co^{2+} + Ni^{2+} + Zn^{2+}$ for a final concentration of 1 M in cations. The relationship between cations is given in Table 1. Then, 75-mL-solution B was prepared dissolving Na_2CO_3 (0.66 M) and NaOH (1.33 M).

Solution A was slowly added over solution B under vigorous stirring at 60 °C for 24 h. The pH was kept at 9.00. Finally, solids were filtered and washed up with abundant distillated water until reaching a neutral pH. The powder was dried for 12 h at 60 °C. Samples were named as HT-x where x is the $(M^{3+})/(M^{3+} + M^{2+})$ ratio equal to: 0.20, 0.25 or 0.33.

After dried, solids were calcined by using a heating rate of 5 °C/min from room temperature to 600 °C for 3 h.

2.2. Preparation of catalytic precursors

Mixed oxides from calcined hydrotalcites (catalytic precursors) were successively impregnated with aqueous solutions of ammonium heptamolybdate tetrahydrate (Riedel-de Haën, 98%) and cobalt nitrate hexahydrate (BDH Chemical Ltd, 97%), by a standard incipient wetness technique. First: Mo was impregnated at a nominal composition of 15 wt.% as MoO_3. These solids were dried at 80 °C for 24 h and then co-impregnated with a Co aqueous solution in order to get a 3Mo:Co atomic ratio. Solids were dried at 80 °C for 24 h and finally calcined at 450 °C for 3 h.

2.3. Characterization of catalytic precursors

Calcined hydrotalcites and CoMo/calcined hydrotalcite samples were characterized by X-ray diffraction (XRD, Phillips PW3710, Ni-filtered Cukα 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 (Micromeritc ASAP 2010 by N_2 physisorption). The surface acidity was characterized by NH_3-TPD (temperature programmed desorption of NH_3). Measurements were carried out in a stainless steel reaction line coupled to a thermal conductivity detector (TCD) using pulse method. 100 mg of sample was dried at 150 °C for 1 h in N_2 (30 $cm^3\ min^{-1}$). Then, the sample was cooled down to 100 °C and NH_3 was injected repeatedly until no adsorption was detected. When the treatment was finished, the sample was cooled down to 40 °C. At this temperature, heating began until 500 °C (rate 10 °C min^{-1}) and the NH_3 desorption was registered.

Table 1
Conditions as-synthesized quaternary hydrotalcites (90 °C, 24 h, pH = 9).

$(M^{3+})/(M^{3+} + M^{2+})$	Al^{3+}/Co^{2+}	Al^{3+}/Ni^{2+}	Al^{3+}/Zn^{2+}
0.20	0.38	1.09	0.56
0.25	1.27	1.45	0.74
0.33	1.63	1.88	0.38

2.4. Catalytic activity measurements

Catalytic precursors were tested in thiophene hydrodesulfurization (HDS) and cyclohexene hydrogenation (HYD) reactions. The thiophene HDS and cyclohexene HYD reactions were carried out in a continuous flow reactor working at atmospheric pressure. All catalytic precursors were presulfided in situ at 400 °C for 2 h prior to catalytic tests using a 10 mL h^{-1} stream of CS_2 (10 vol.%)/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 of catalytic precursors using a liquid feed (2.7×10^{-4} $cm^3\ s^{-1}$) composed by 6 vol.% of thiophene (or cyclohexene) in n-heptane vaporized and mixed with a H_2 stream (0.25 $cm^3\ s^{-1}$) at 325 °C. All reaction lines were covered with a heating mantle (150 °C) in order to avoid any condensation of the reactants or 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 (25 m, 0.25 μm i.d, CP-Sil 5 CB).

3. Results and discussion

3.1. Characterization of materials

Fig. 1 shows powder X-ray diffraction patterns of as-synthesized quaternary hydrotalcite samples. The presence of sharp and symmetric reflections for the basal planes (003) and (006), together to broad and asymmetric reflections for the non-basal (012), (015) and (018) correspond to hydrotalcite-type material (JCPDS: 22-0700) [15]. Collateral phases were not identified for these diffractograms. However, one can see, that HT-0.20 was less crystalline than those HT-0.25 or HT-0.33 hydrotalcites. HT-0.20 is in borderline of preparation of hydrotalcites; it could affect the crystallinity of this material [16].

Fig. 2 shows the X-ray diffraction patterns of catalytic precursors. As can be seen, the diffraction pattern of hydrotalcite changed due to the material calcination.

For these impregnated and calcined hydrotalcites, the following phases: ZnO (JCPDS-80-0075), $ZnAl_2O_3$ (JCPDS-82-1043), MoO_3 (JCPDS-80-0347), MoO_2 (JCPDS-86-0135), Co_3O_4 (JCPDS-80-1545), $ZnCo_2O_4$ (JCPDS-23-1390), Al_2O_3 (JCPDS-86-1410) and $NiAl_2O_4$ (JCPDS-71-0965) were basically identified for all catalytic precursors.

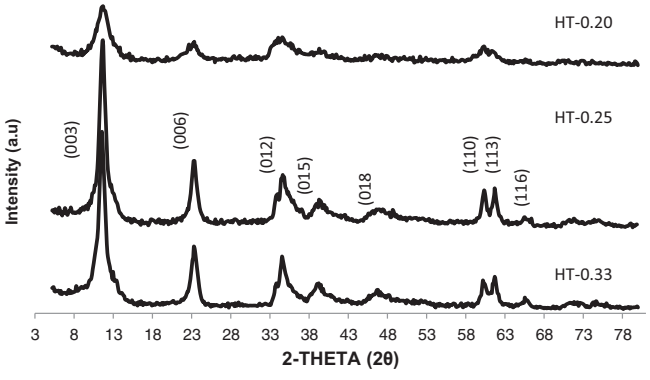

Fig. 1. X-ray diffraction patterns of as-synthesized quaternary hydrotalcites.