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Improving the selectivity in hydrocracking of phenanthrene over mesoporous Al-SBA-15 based Fe–W catalysts by enhancing mesoporosity and acidity

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ABSTRACT

Catalysts for heavy oil hydrocracking require an enhanced mesoporosity (higher pore diameters) and a moderate acidic function (mild acidity) to treat the bulky molecules present in this kind of feedstock and to yield middle distillates (MD). In this work, we have synthesized five different kinds of mesoporous silica based on SBA-15 by modifying some of the variables of their synthesis with the aim at enhancing mesoporosity. NH_4F and 1,3,5-trimethylbenzene (TMB) were used to modify the mesostructured arrangement in SBA-15. TMB modified SBA-15 materials exhibited the highest textural properties (2.16 $cm^3\,g^{-1}$ and 17 nm) in comparison to NH_4F modified silica (1.90 $cm^3\,g^{-1}$ and 10.8 nm) and pristine SBA-15 silica (1.03 $cm^3\,g^{-1}$ and 12 nm). The acidity of the SBA-15 based materials was modified by a post-synthesis "grafting procedure" to Si/Al molar ratios of 10, 25, and 40. SBA-15 based materials modified with both Al and TMB were used as supports for Fe–W sulfides. These catalysts were tested in the hydrocracking of phenanthrene. In general, all of the catalysts supported on Al-SBA-15 based materials were selective to the ring opening reaction of phenanthrene in contrast to the results obtained over a commercial Ni–Mo/γ-Al_2O_3 catalyst. Such trend was associated to the presence of Brönsted acid sites on the surface of the Al modified supports as shown ^{27}Al MAS NMR analysis.

1. Introduction

The increase in the demand of middle distillates (MD) production by refining heavy oils remains a challenging task [1–4]. The efficiency of conventional catalysts processing heavy oils is poor due to diffusional limitations. Therefore, researchers have focused on developing materials with larger pores to use them as supports of the catalysts aiming the conversion of heavy oils into MD [5–7].

It is possible to synthesize and modify silica based materials such as MCM-41 (Mobil Composition of Matter No 41), SBA-15 (Santa Barbara Amorphous No 5), and MCF (Mesocellular Foam), and use them as catalytic supports for upgrading heavy oils [8–11]. In particular, SBA-15 is a type of mesoporous silica, which possesses wide pore volume, narrow pore size distributions, and better hydrothermal stability as compared to, for example MCM-41 [12]. Therefore, SBA-15 is an interesting candidate for supported catalysts for hydroconversion of heavy oils [12–14]. SBA-15 is formed by a hexagonal array of tubular and uniform cylindrical channels, which is formed in strong acid media during the synthesis of the material thanks to the micelles built over triblock copolymers [9]. Such copolymers act as both surfactant and a template during the synthesis of the material [10,15,16]. Aiming pore size widening, Zhao et al., studied the use of micellar swelling agents to modify the textural and structural properties of SBA-15, obtaining silica materials with larger pore sizes by using 1,3,5-trimethylbenzene (TMB) [14,15]. It has also been reported that the use of organic co-solvents such as hexane or *n*-butanol can act as a swelling agents during the synthesis of SBA-15, hence widening pore size [8,9,16]. On the other hand, an improvement on the thickness of SBA-15 was reported after the addition of small quantities of inorganic salts during the synthesis of the material [16–18], this feature makes SBA-15 a specific mesostructured material.

Another issue when trying to apply SBA-15 as catalytic support for heavy oil hydroconversion is its modest acidity [19]. Such low acidity is explained by the fact that the structure of SBA-15 consists mainly of neutral Si atoms. To improve the acidity of SBA-15 based supports, different metals such as Al, Ti, Zr, and Sn have been used as promoters for the formation of Brönsted acid sites [20–22]. In the

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case of aluminum, aluminum loaded SBA-15 materials have been prepared by varying the Si/Al molar ratio of the materials, aiming to enhance the acidity of the materials [23–26].

In this contribution, we investigated how to enhance both the porosity and acidity of SBA-15 type materials in order to prepare catalysts for the hydroprocessing of heavy crude oils. On the other hand, the influence of adding NH_4F and TMB (1,3,5-trimethylbenzene) during the synthesis of SBA-15 on their structure and porosity was analyzed. Five different kinds of SBA-15 based mesoporous silica were thus obtained. Conversely, the acidity of selected SBA-15 based materials was modified by aluminum grafting. SBA-15 based catalytic supports of different Si/Al molar ratios: 10, 25, and 40 were thus synthesized. The active phase of the SBA-15 type catalysts was based on a combination of Fe–W. In general, iron based active phases have received less attention from researchers, despite of being cheaper than conventional Ni and Co based catalysts [7,27–31]. The synthesized catalytic materials were tested in hydroprocessing of phenanthrene, as a model reaction for processing vacuum gas oil (VGO). Catalysts were characterized by different techniques: N_2 physisorption to calculate textural properties, XRD to study the changes in the structure of the materials, SEM to observe changes in morphology, ^{27}Al MAS NMR to identify the Al species on the surface of the selected materials, and PAD to study the nature of OH groups on the surface of the materials and their overall acidity. Therefore, the effect of both, textural and acid properties of the Al-SBA-15 based materials in hydroprocessing reactions is given.

2. Experimental

2.1. Mesoporous silica synthesis

Five kinds of SBA-15 based materials were prepared by adapting the procedures employed in some literature reports [8,15,17]. Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, M_{av} = 5800, Aldrich) was used as a structural direction agent (SDA), and tetraethylortosilicate (TEOS, 98% Aldrich) as a silica source. Synthesis was conducted in strong acid media conditions (pH < 1) in accordance to the following nominal molar ratio: 1.0 TEOS:0.0169 P123:4.42 HCl:186 H_2O. The effect of NH_4F and TMB (1,3,5-trimethylbenzene) addition to the structure of SBA-15 was studied. NH_4F (99% Aldrich) and TMB (98%, Alfa Aesar) were always added to the synthesis mixture before TEOS incorporation.

In a typical synthesis of SBA-15, 10 g of P123 were completely dissolved in an aqueous solution of 1.3 M HCl (37 vol.%, Merck) and under stirring (500 rpm). Then, 24 mL of TEOS was added dropwise and kept under stirring for 1 h. Subsequently temperature was increased to 311 K and thus kept during 24 h. The milky suspension thus obtained was then transferred into a 500 mL PTFE vessel, and placed inside a muffle furnace at 403 K for 24 h for the hydrothermal treatment. Afterwards, the vessel was allowed to cool down. The recovered solid product was filtered and washed with deionized water, and left to dry at ambient conditions. The recovered powder was calcined, with a heating rate of 2 K/min in a flow of dry air (100 mL/min) at 773 K during 6 h in order to remove the template.

NH_4F modified silica materials were synthesized by adding 0.10 g and 0.15 g of NH_4F to the synthesis mixture before TEOS incorporation, those samples were labeled: SBA-F(0.10) and SBA-F(0.15), the value in brackets indicates the amount of NH_4F added.

TMB modified silica materials were obtained adding the required amount of TMB to get TMB:P123 mass ratios of 0.15 and 0.75 before dropwise TEOS incorporation and kept under stirring for 1 h. Those materials were labeled: SBA-TMB(0.15) and SBA-TMB(0.75), the value in brackets indicates the TMB:P123 mass ratio. The other steps remained the same as SBA-15 preparation.

2.2. Aluminum incorporation into the SBA-15 type silica

Surface acidity of the supports was obtained by an Al post-synthesis grafting procedure [29]. A 0.02 M ethanol (Merck, 98%) solution of aluminum isopropoxide ($C_9H_{21}AlO_3$, Merck 98%) was used as aluminum source. Powdered samples (5 g) of SBA-15 and SBA-TMB(0.75) were grafted by soaking them in the $C_9H_{21}AlO_3$ solution, thence keeping the resulting suspension under constant stirring (500 rpm) for 18 h. Grafting was performed at pH between 9.0 and 9.5 using NH_4OH (28 vol.%, Aldrich, 98%). Appropriate amounts of the aluminum precursor were employed to obtain materials with Si/Al molar ratios of 10, 25, and 40. The grafted materials were filtered and washed with ethanol to remove residua from the aluminum precursor. Then, the recovered materials were calcined in dry air (100 mL/min) at 773 K for 6 h. Al-modified materials were labeled following the nomenclature: Al-SBA-15-*x* and Al-SBA-TMB(0.75)-*x*, where "*x*" indicates the Si/Al molar ratio.

2.3. Catalysts preparation

Fe–W catalysts supported on γ-Al_2O_3 (Protocatalyse), Al-SBA-15-*x* and Al-SBA-TMB(0.75)-*x* were prepared by the successive incipient wetness impregnation method. $Fe(NO_3)_3{\cdot}9H_2O$ (98%, Aldrich) and $(NH_4)_6H_2W_{12}O_{40}.H_2O$ (98%, Aldrich) aqueous solutions (30% in excess of the required amount to fill pore volume of catalysts) were used as Fe and W precursors, respectively. After each impregnation step, materials were dried at 393 K (heating rate of 2 K/min) during 12 h, and then calcined in dry air flow (100 mL/min) at 773 K during 6 h. Fe_2O_3 and WO_3 loadings were 3 wt.% and 15 wt.%, respectively. The thus obtained materials were labeled as Fe–W/Al-SBA-15-*x* and Fe–W/Al-SBA-TMB(0.75)-*x*. All catalysts were sieved down to a particle size range between 25 μm and 75 μm.

2.4. Characterization of supports and catalyst

2.4.1. Textural characteristics

The BET specific surface area (S_{BET}, $m^2\,g^{-1}$) of the materials was determined by N_2 adsorption–desorption isotherms measured at 77 K in a 3FLEX apparatus from Micromeritics.

Samples of 0.2 g of the materials were degassed in vacuum (3 Pa) at 393 K for 12 h before the analysis.

S_{BET} was calculated from data taken in the range of relative pressures (P/P_0) between 0.04 and 0.24 according to IUPAC recommendation [32]. Pore size distributions were estimated from N_2-DFT models provided by Micromeritics depending on the geometry of the pores. For SBA-15 based materials, a model based on cylindrical pores oxide surface, and for SBA-TMB(0.75) catalysts a model based on slit pores was employed. Total pore volumes were calculated from the amount of nitrogen adsorbed at a relative pressure (P/P_0) of 0.9.

2.4.2. XRD patterns

XRD patterns of the materials were recorded in a Bruker Advance diffractometer with Da Vinci geometry using Ni-filtered CuKα1 radiation (40 kV, 30 mA) instrument. Samples (0.2 g) were grinded in an agate mortar down to a particle size of 38 μm. Low angle spectra were recorded to identify changes in the material ordering pattern. $2\theta^\circ$ range was scanned between 0.5° and 8° with a step size of 0.01526°, and a counting time of 0.4 s per step. Qualitative analysis of the observed peaks was carried out by comparing the observed profile with the diffraction profile reported in the database PDF-4 + ICDD (SiO_2-00-058-0344). Wide angle analyses were performed for all catalysts in order to confirm the occurrence