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SIZE-DEPENDENT EFFECTS

Effect of preparation technique on the properties of Mo-containing Al-MCM-41

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Abstract The Al-MCM-41 has been used as support to prepare Mo-containing catalysts. The 12- molybdophosphoric heteropoly acid (HPMo) is used as initial compound. The catalysts are synthesized by two different methods: incipient impregnation with aqueous solution of the acid and mechanochemical synthesis. The samples were tested in the reaction of the thiophene hydrodesulfurization after activation with mixture H_2 + H_2S. The effect of the preparation method of the catalysts on their physicochemical and catalytic properties has been studied. A partial destruction of the loaded compound is observed in mechanochemically treated sample whereas the aggregates are formed from the particles of different size in the impregnated sample. The specific surface area of the sample prepared by mechanical–chemical treatment decreases 2–3 times, while the total pore volume is about four times lower. The HDS activity is higher on the impregnated sample than on the mechanochemically treated one.

Introduction

Stricter fuel specifications demand redrawing of refinery flow sheets with inclusion of hydrodesulfurization unit at many stages of petroleum refining. The new legislation in many countries up to 20 ppm sulfur in gasoline and diesel in 2010 requires [1] the new catalysts using. There are many approaches to prepare better catalysts to meet these challenges, like changing the active component, varying the preparation method and changing the supports or such permutations and combinations.

In recent years, there has been heightened interest in new supports for HDS catalysts, due to the need to develop better catalysts [2].

In 1992, the preparation of MCM-41, the first member of the family of mesoporous molecular sieves, opened a new area in the preparation of heterogeneous catalysts [3] because it offers an uniform pore of 1.5–10 nm and specific surface area of over 1000 m^2/g. Landau et al. [4] reported that the AlMCM-41 supported showed a higher performance in deep HDS than alumina supported catalysts.

Nowadays the heteropoly compounds are used in the HDS catalyst synthesis. A major disadvantage of bulk heteropoly acids (HPAs), when used as catalysts lies in the low specific surface area, not exceeding 10 m^2/g, which can be improved by immobilization on solid supports [5]. In this aspect owing to a very large surface area (~1000 m^2/g) and a uniform large pore size (2 nm), the MCM-41 materials can act as an excellent support for expanding the catalytic capability of traditional acidic materials [6].

The method of the catalyst preparation is very important to improve their catalytic activity. Different methods are used in practice: impregnation, co-precipitation, sol–gel, and mechanochemical treatment [7, 8].

The aim of this paper is to study the effect of the preparation method of the HDS catalysts on their

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physicochemical and catalytic properties. The AlMCM-41 support and 12-molybdophosphoric heteropoly acid (HPM) are used. The catalysts have been characterized with XRD, IR, DRS, TPR, and BET techniques.

Experimental

Catalyst preparation

Catalysts were prepared by incipient wetness impregnation of the AlMCM-41 support (1000 m^2/g) with aqueous solution of $H_3PMo_{12}O_{40}$ heteropolyacid (denoted HPM-Imp) and mechanochemical treatment of initial materials (denoted HPM-MCh). All catalysts were dried 4 h at 378 K and calcined 2 h at 623 K. The catalysts contain 12 wt.% Mo.

Catalysts characterization

X-ray powder diffraction (XRD) data for phase identification were scanned in the angle interval 7–42°(2θ) with a step of 0.02°(2θ) and a counting time of 1s per step. The measurements were performed on a DRON automatic powder diffractometer, using CuK_α filtered radiation and a Bragg-Brentano geometry. Equal amounts of powdered samples and identical sample holders were used for the measurements. The identification of the phases was carried out using the powder diffraction file of the international center for diffraction date [9].

The surface area of the catalysts was estimated by measuring of the adsorption–desorption isotherms of nitrogen at 78 K (BET method).

IR spectra (400–1200 cm^{-1}) were recorded at room temperature on a Bruker IFS-25 Fourier transform IR spectrometer. The catalysts were pressed with KBr in ratio 1:150.

Diffuse reflectance spectra (DRS) of the samples were recorded at room temperature on a Beckman 5270 spectrophotometer, equipped with a DR spectra accessory, in the wavelength range 240–800 nm. $BaSO_4$ has been used as reference. The spectra were evaluated by means of a Kubelka–Munk function $F(R_\infty)$.

TPR measurements were carried out in the apparatus described earlier [10]. Hydrogen/nitrogen mixture (10 mol % H_2) was used to reduce catalysts at the flow rate 17 $cm^3\ min^{-1}$. The temperature was linearly raised at a rate of 20 K min^{-1} from 293 K up to 1123 K.

HDS of thiophene was carried out in a continuous flow reactor at 623 K and at 0.1 MPa. Each experiment was carried out with a fresh catalyst (0.1 g) that was standardized by in-situ calcination (30 min) in argon at 623 K. Calcined catalyst was activated by sulfidation with a mixture of $H_2S + H_2$ during 1 h at temperature 623 K and flow rate 40 $cm^3\ min^{-1}$. We have found out in our preliminary experiments that this sulfidation treatment gives maximal catalytic activity of the catalysts. After activation the catalyst was flushed (30 min) with argon at the same temperature, and then, the mixture of 6 mol% thiophene in hydrogen was fed into the reactor. Activity of catalysts was valued as the thiophene conversion to hydrocarbons (C_4).

Results and discussion

X-ray diffraction (XRD)

XRD spectra of the samples in oxide form have been registered after the thermal treatment. The XRD analysis of the support shows a strong reflection at about 1.5–2.0° (2Θ) that is typical for aluminosilicates of the MCM-41 type [11]. The intensity of these lines decreases after impregnation of the HPMo heteropoly compound.

The strong reflection at about 1.5–2.0° (2Θ) in the XRD spectra of the mechanochemically synthesized samples decreases. The decrease in the peak intensity detects disorganization at long range of the mesoporous structure. The spectra of the mechanochemically synthesized sample reveal the diffraction lines characteristic of the $H_3PMo_{12}O_{40} \times H_2O$.

Figure 1 shows XRD patterns of the initial HPM and the catalysts. No crystalline phases are revealed in the sample HPM-imp.

The results obtained allow to suggest that the most of the HPMo species are localized inside the mesopores, being dispersed on the wall surface of MCM-41 or forming small clusters which could not be detected by XRD. The clusters aggregate outside the mesopores to form small agglomerates.

The results mean that the loaded compounds in the impregnated samples have higher dispersity in comparison with that in the mechanochemically treated samples. The low dispersity of the loaded compounds in these catalysts could be explained with a formation of the clusters.

Specific surface area, pore volume and pore size distribution

The specific surface area of the samples (S_{BET}) and the total pore volume (V_t) of the catalysts, prior to the

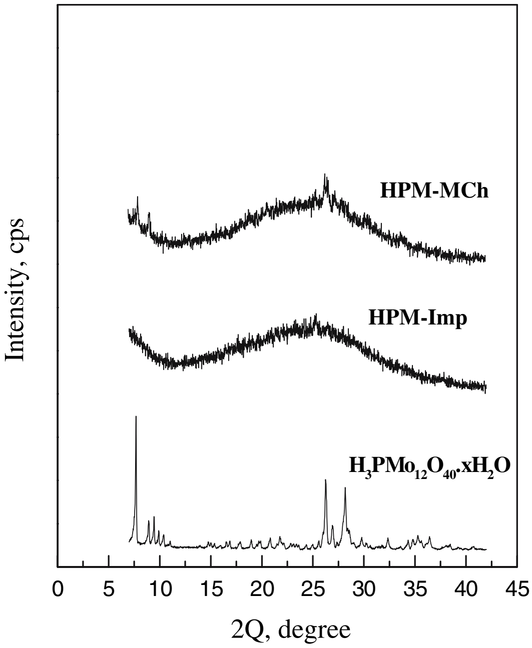

Fig. 1 X-ray diffractograms of the $H_3PMo_{12}O_{40}$ (PDF = 751588) and the catalysts

mechanical–chemical treatment and incipient wetness impregnation, are represented in Table 1.

It is seen that the specific surface area of the samples prepared by mechanical–chemical treatment decreases 2–3 times, while the total pore volume is about four times lower.

The surface area of the impregnated samples decreases negligibly.

We suppose that the sharp decrease in the specific surface area and total pore volume of the mechanochemically treated samples is the result of the local overheating of the supporting phase, its migration and blockage of the pores. The plastic deformation, which takes place during the catalyst samples activation, induces a number of non-steady-state processes, an appearance of defects and/or destruction of the crystal lattice, a variation in the form and the size of the particles, as well as changes in the specific surface area and in the porosity [12, 13].

IR spectra

In the IR spectra of samples, presented in Fig. 2, the broad envelope due to OH^- stretch of water in higher energy region and the corresponding $-OH_2$ bending mode around 1637 cm^{-1} very well correlate with the water adsorption property (hydrophilic property) of the catalysts.

The spectra of the initial HPA with Keggin structure show four strong bands: at about 1064 cm^{-1} (P–O), 960 cm^{-1} (M = O), 785 and 875 cm^{-1} (Mo–O–Mo).

The framework bands of AlMCM-41 at about 1236, 1090, 964, 800 and 465 cm^{-1}, overlap slightly with those of $H_3PMo_{12}O_{40}$. In the IR spectra of the samples splitted bands at about 956 and 913 cm^{-1} instead of the band in the AlMCM-41 spectrum at about 964 cm^{-1} appear (Fig. 2). The absorption band at 916 cm^{-1}, which is observed for impregnated sample, can be assigned to Mo–O vibrations in tetrahedral molybdate species attached to the surface [14]. The intensity of the band at 916 cm^{-1} is higher in spectrum of Mo catalyst prepared by impregnation in comparison with the one prepared by mechanochemical approach (Fig. 2). This means a strong interaction between support and 12-molybdophosphoric acid has occurred during impregnation. The Keggin unit opens and the bridging Mo–O–Mo bonds are broken forming MoO_6 octahedral groups. Those easily interact with the support forming Si–O–Mo, Mo–OH [15].

The new-formed species preserve the nuclear structure of the Keggin ion. In the spectra of the Mo/Al-MCM-41 samples (Fig. 2), the band at about 800 cm^{-1} broadens and its intensity increases. This confirms the Keggin cluster presence [16, 17].

UV-VIS DR spectra

Intensive bands can be observed in the UV region (Fig. 3).

HPMo-MCh sample reveals two bands at about 240 and 300 nm indicating the presence of Mo^{6+}(Td) and Mo^{6+}(Oh) species [18]. In the case of the impregnated sample the band shifts towards higher wavelength. It

Table 1 Description of the catalyst samples and TPR data

No.	Catalysts	TPRData		S_{BET} m^2/g	$V_t(cm^3/g)$
		mmol H_2/g (20–650 °C)	Mmol H_2/g (20–850 °C)		
1	Al-MCM	–	–	1020	–
2	HPM-Imp	1.28	1.93	978	–
3	HPM-MCh	1.40	2.44	376	0.23

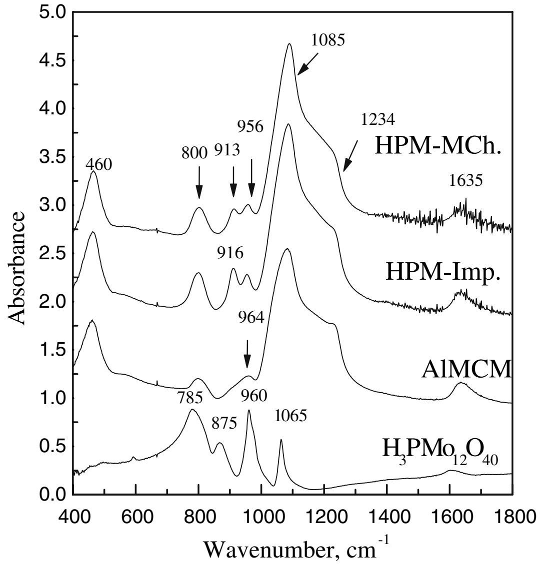

Fig. 2 IR spectra of the $H_3PMo_{12}O_{40}$, Al-MCM and catalysts

means an increase of the Mo^{6+}(Oh) species in this sample. The end in of the bands (λ_{end}) for the sample HPM-imp is situated at 495 nm, while for the sample HPM-MCh it was found at 475 nm. This proves the existence of isolated molybdate ions MoO_4^{2-}. This shifting means the Mo^{6+}(Oh) transfer in the Mo^{6+}(Td) as it was shown with the IR results (Fig. 2).

The band at 770 nm indicates the presence of the reduced molybdenum. Additionally a blue shift of the absorption edge λ_{end} was observed for the mechanochemically synthesized sample in comparison with the one prepared by impregnation suggesting a decrease in the size of the molybdenum species [19].

Temperature programmed reduction (TPR)

Two TPR peaks are observed in the TPR picture of the HPM-imp sample (Fig. 4).

The first peak with T_{max} 500 °C in agreement with [20] can be assigned to partial reduction of highly dispersed polymolybdate Mo^{6+} species to Mo^{4+}.

The high temperature peak at about 770 °C is related to further reduction steps of molybdenum [20]. The TPR profiles of the catalysts prepared using mechanochemical treatment of the components are characterized with broadening of the first peak at about T_{max} 520 °C and overlapping with a number of the low intensive peaks at a higher temperature.

This method of catalyst preparation facilitates the formation of phases, which are reduced easily. The H_2 consumption is higher on the MCh samples than on the impregnated ones (Table 1). Most probably it is related to the different phases and their amount in the catalysts.

Catalytic activity measurements

The HDS activity is higher on the samples prepared using impregnation of the heteropoly compounds in comparison to the samples mechanochemically treated.

The difference in the activity could be explained with the change in the structure of the support, the quantity and the type of the active sites precursors as well as their dispersity during mechanochemical treatment (Fig. 5). This explanation is confirmed with the TPR and IR spectra. During the grinding the support and the heteropoly acid structures are changed and separated particles agglomerate.

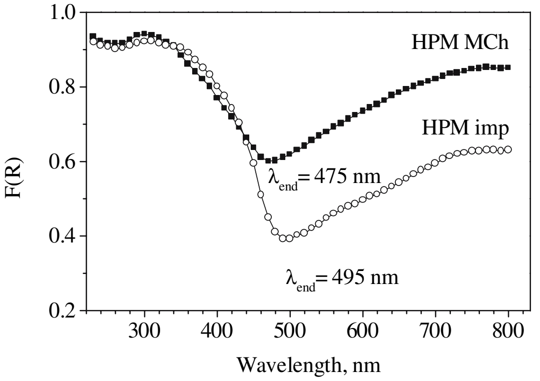

Fig. 3 UV-VIS DR spectra of the Mo state in the samples: 1-HPMo-imp and 2. HPMo-MCh

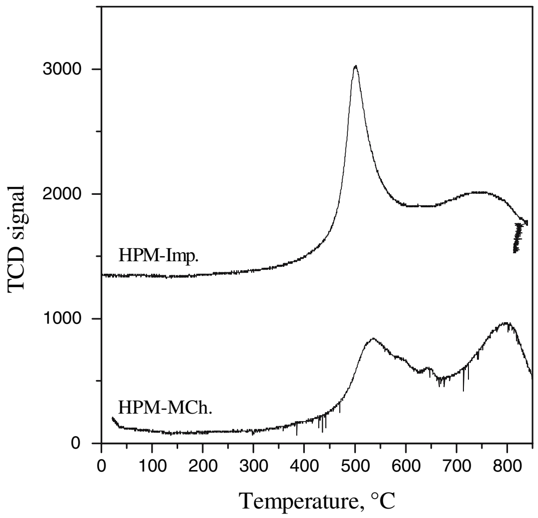

Fig. 4 TPR profiles of the catalysts

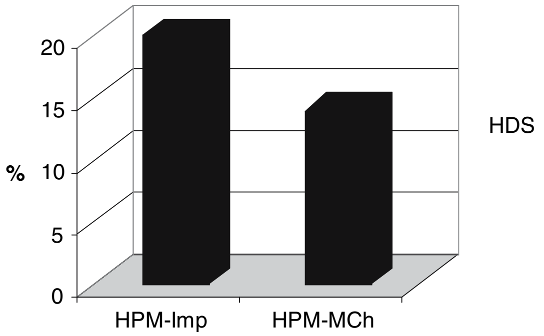

Fig. 5 Thiophene conversion (HDS) the catalysts

So, the mechanochemical method of the catalyst synthesis decreases the surface and the interaction between the components. This leads to the size increase of the active phase species and finally to a decrease of the activity.

Conclusions

The preparation technique strongly affects the physicochemical properties and HDS activity of the Al-MCM-41 supported Mo-containing catalysts.

A partial destruction of the loaded compound is observed in the impregnated sample whereas the aggregates are formed from the particles of different size in the mechanochemically treated sample.

The specific surface area of the sample prepared by mechanical–chemical treatment decreases 2–3 times, while the total pore volume is about four times lower.

The HDS activity is higher on the impregnated sample being compared to the mechanochemically treated one.

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