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Hexagonal mesoporous silicas with and without Zr as supports for HDS catalysts

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Abstract

Hexagonal mesoporous materials (HMS) with and without zirconium were used as supports for preparation of HDS catalysts. The catalysts prepared by modification of the supports with 12-phosphomolybdic acid (HPMo) were characterised by nitrogen adsorption, IR spectroscopy, TPD of ammonia, TPR and catalytic activity in thiophene hydrodesulphurisation. Parent silicas showed mesoporous structure with BET surface area between 1200 and 800 $m^2\,g^{-1}$, pore size diameter around 3.3 nm and acidity around 0.3 mmol $NH_3\,g^{-1}$. Molybdenum catalysts possess stronger acidity than the supports used. The catalytic activities in hydrodesulphurisation of thiophene of the molybdenum containing catalysts prepared with HMS were higher than the activity of the catalyst prepared with amorphous silica. Higher acidity of Zr–HMS supports lead to lower stability in the thiophene conversion. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrodesulphurisation; Mesoporous materials; Zirconium-containing mesoporous silicas

1. Introduction

Molybdenum-based hydroprocessing catalysts are usually loaded on suitable supports in order to improve the HDS activity [1]. In most cases γ-Al_2O_3 has been used [2]. The demand for lower content of sulphur and aromatics in the fuels requires utilisation of new materials as catalyst supports. Suitable carriers for this purpose could be recently synthesised mesoporous materials with large pore diameter [3]. MCM-41 material has a hexagonal array of mesopores. This material has been shown to be an excellent support for preparation of bifunctional catalysts [4]. Another mesoporous material, hexagonal mesoporous silica (HMS), prepared by neutral templating pathway [5] offer certain advantages over electrostatically templated MCM-41 materials [6]. The potential importance of MCM-41 and HMS also lies in their use as hosts for supramolecular assembly [7].

Introduction of Ti^{4+} and Zr^{4+} cations into the HMS materials can significantly affect their properties [8], modifying them into the catalysts active in oxidation of bulky molecules by organic peroxides [9]. Both Ti^{4+} and Zr^{4+} cations are randomly distributed in the framework of mesoporous materials and their coordinations are very close to those observed in related zeolites [8]. High specific surface area and acidic properties of these materials are essential for the reactions proceeding on the acidic sites of middle strength [10]. Recently, Corma et al. [11] utilised the MCM-41 mesoporous crystalline alumosilicate as a support for NiMo-catalyst for hydrocracking of vacuum gasoil. Superior catalytic activity of the

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NiW/Ti–HMS catalyst was also observed in hydrogenation of naphthalene [12], in comparison with a conventional alumina-supported catalyst.

Heteropoly compounds of molybdenum or tungsten are often used as active components for supported catalysts or starting material for preparation of metal-oxide catalysts. 12-Phosphomolybdic acid (HPMo), deposited on the MCM mesoporous silica, was used as a catalyst in the processes catalysed by acids [13–15].

In the present work, an HMS and zirconium-containing hexagonal mesoporous silicas (Zr–HMS) of various Zr/Si ratios were synthesised. These materials were used as supports for preparation of molybdenum catalysts. Obtained supports and catalysts were characterised by BET, TPD of ammonia, TPR, IR and catalytic activities for hydrodesulphurisation of thiophene.

2. Experimental

HMS and Zr–HMS, were synthesised from tetraethyl orthosilicate (TEOS) and zirconium oxychloride $ZrOCl_2$ $8H_2O$ (both Merck). Mixtures of the following molar compositions were used: $x SiO_2 : y ZrO_2 : 0.27$ template: $36 H_2O : 0.02 HCl : 6.5\text{-}C_2H_5OH$. The y/x ratio was varied from 0, 0.01, 0.02 and 0.04. In all experiments, dodecylamine (Fluka) was chosen as the organic template. More detailed description of the carrier preparation procedure is given in [16].

Catalysts were prepared by incipient wetness impregnation of the supports with an aqueous solution of HPMo. Wet catalysts were dried at 70°C and calcined at 350 and 500°C for 4 h. The catalysts contain 12 wt.% of molybdenum. The catalysts prepared are denoted as Mo/Zr–HMS followed by the Zr/Si ratio in parentheses.

Hydrodesulphurisation of thiophene was carried out in a continuous flow reactor at 350°C and atmospheric pressure with 0.1 g of catalyst for 4 h. Two ways of pre-treatment of the catalysts were used: (i) the samples were heated for 1.5 h in hydrogen flow (40 ml min^{-1}) prior to the introduction of thiophene and (ii) the samples were standardised by in situ calcination in argon at 350°C for 0.5 h. The calcined catalyst was activated by sulphidation with H_2S (350°C, flow rate 40 ml min^{-1}, 0.5 h). After activation had been completed, the catalyst was flushed with argon at the same temperature for 0.5 h, and then, feeding of the reaction mixture (of 6 mol% of thiophene in hydrogen with WHSV 25 ml min^{-1} begins. The reaction products were analysed using on-line gas chromatograph equipped with thermal conductivity detector [17].

Textural properties of the supports and catalysts were determined from nitrogen adsorption isotherms obtained at −198°C after evacuation at 350°C for 5 h on ASAP 2100M, Micromeritics, USA. The pore size distribution of the catalyst samples was derived from the nitrogen desorption isotherms by BJH analysis [18]. Surface area and volume of mesopores were determined by Schneider's method [19].

The FTIR spectra (400–4000 cm^{-1}) were recorded on a Bruker-IFS spectrometer. The samples were pressed with KBr in the ratio 1:150.

Temperature-programmed desorption (TPD) of ammonia was used to determine acidity of the samples. The apparatus and procedure were described earlier [20]. Measurements were carried out using 0.05 g of a catalyst and helium as carrier gas (flow rate 15 ml h^{-1}). Prior to the ammonia desorption, all supports and catalysts were calcined up to 350°C. The rate of temperature rise was maintained at 20°C min^{-1}. Then, 30 doses (840 μl each) of ammonia were injected into the helium stream at 30°C. The excess of ammonia was removed by helium flowing 1 h through the sample. After that, TPD of ammonia was started and finished when temperature 350°C was reached. Peak Fitting Module of Origin program (Microcal Software) was used to analyse the overall desorption peaks (evaluation of peaks maxima and their proportions).

Experiments of temperature-programmed reduction (TPR) were carried out on the apparatus for the TPD measurements. A hydrogen–nitrogen mixture (10 mol% of H_2) was used to reduce samples at a flow rate of 17 ml min^{-1}. The temperature was increased up to 850°C at a rate of 20°C min^{-1}.

3. Results and discussion

The thiophene conversions as a function of time-on-stream (TOS) on pre-sulphided molybdenum-

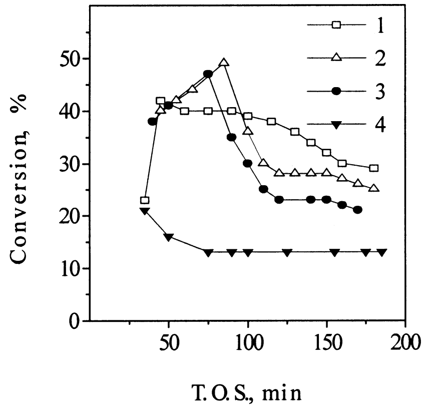

Fig. 1. Evolution of thiophene conversion with TOS over catalysts: (1) Mo/HMS; (2) Mo/Zr–HMS (0.01); (3) Mo/Zr–HMS (0.02); (4) Mo/SiO_2.

based catalysts are represented in Fig. 1. The curves are with maxima in the first hour of reaction.

The HDS activities of the Mo/HMS catalysts are compared with Mo/SiO_2 sample of the same molybdenum loading. This sample was prepared by impregnation of amorphous silica (Cab–O–Sil, $S_{BET} = 290\,m^2\,g^{-1}$) with HPMo (Fig. 1). The Mo/Zr–HMS catalysts have higher activities than the reference Mo/SiO_2 catalyst.

The values of maxima achieved of thiophene conversion decrease linearly with increase of zirconium content in the catalysts for the studied Zr/Si ratio interval (Fig. 2). The zirconium-free Mo/HMS catalyst has a higher steady-state conversion than the zirconium-containing samples.

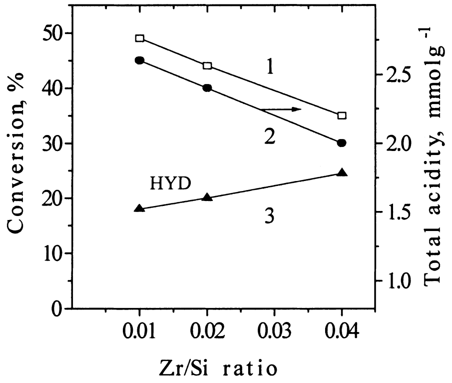

Fig. 2. Effect of Zr/Si ratio in Mo/Zr–HMS catalysts on: (1) the value of maxima of thiophene conversion; (2) total acidity; (3) the selectivity to *n*-butane (HYD).

The thiophene conversion products observed over Mo/Zr–HMS catalysts are hydrogen sulphide, *n*-butane, 1-butene, *cis*/*trans*-2-butenes, and lighter C_1–C_3 hydrocarbons. The cracking products are more abundant for the pre-sulphided Mo/Zr–HMS (0.04) catalyst. On the other hand, no cracking products were observed for the catalyst Mo/Zr–HMS (0.01). Since *n*-butane is the product of the butenes hydrogenation, the hydrogenation function of the catalysts is defined by its amount in the reaction mixtures. Hydrogenation activity (HYD) of the catalysts, evaluated as the ratio of *n*-butane to all C_4-hydrocarbon products, is stable with increasing TOS. All the pre-sulphided Mo/Zr–HMS catalysts are characterised with high hydrogenation activity, which linearly increases with zirconium content (Fig. 2).

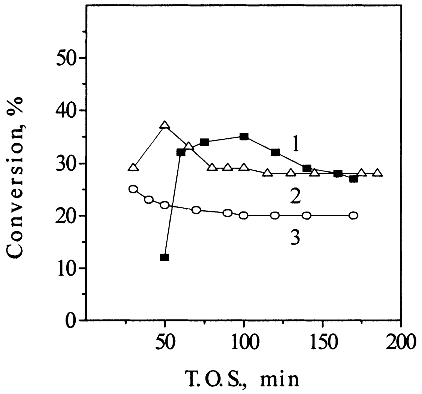

Fig. 3. Effect of catalyst pre-treatment on thiophene conversion with TOS for Mo/Zr–HMS (0.04): (1) pre-sulphided; (2) pre-reduced; (3) calcined at 500°C and pre-sulphided.

Fig. 3 shows the influence of pre-treatment conditions on the degree of thiophene conversion over the Mo/Zr–HMS (0.04) sample. The catalyst calcined in air at 500°C manifested a lower but very stable conversion of thiophene. Only MoO_3 phase was present in the catalyst calcined at such high temperature. No cracking products were found for the pre-reduced catalysts. Behaviour of the Mo/Zr–HMS catalysts is similar. With the pre-reduced Mo/Zr–HMS catalyst, the selectivity to *n*-butane is 100% in the first hour of TOS. During the catalytic test, evolved H_2S is consumed for a sulphidation of the pre-reduced sample.

Table 1
Porous structure parameters of the parent hexagonal silicas and the corresponding catalysts

Sample	S_{BET} ($\mathrm{m^2\,g^{-1}}$)	S_{meso} ($\mathrm{m^2\,g^{-1}}$)	V_{meso} ($\mathrm{cm^3\,g^{-1}}$)	d_{max} (nm)
HMS	818	570	0.51	4.5
Mo/HMS	532	419	0.81	4.6
Zr–HMS (0.01)	1040	736	2.04	5.4
Mo/Zr–HMS (0.01)	740	552	1.43	5.4
Zr–HMS (0.02)	932	645	0.94	3.6
Mo/Zr–HMS (0.02)	581	423	0.60	3.3
Zr–HMS (0.04)	816	657	0.77	3.1
Mo/Zr–HMS (0.04)	523	347	0.52	3.5

When H_2S appears at the outlet of the reactor, isomerisation activity of the catalyst can be observed. From this moment the selectivity to butane was stabilised at 16%. HYD activity increased to 50% when the catalyst was pre-sulphided with H_2S. Sulphidation of the catalysts at 350°C leads to simultaneous molybdenum reduction and to substitution of oxygen with sulphur in molybdenum surrounding. Probably, an increase in the amount of strongly bonded sulphur in the $\mathrm{Mo^{5+}}$–O, S surrounding [21] might be a reason for deactivation of the Mo–Zr/HMS catalysts.

Textural properties of the supports and the catalysts were determined by physical adsorption of nitrogen. All the samples showed adsorption–desorption isotherms of similar character. Surface areas of mesopores S_{meso} and volumes of mesopores V_{meso} obtained are summarised in Table 1.

All supports are characterised with high BET surface areas within the limits of 1040–820 $\mathrm{m^2\,g^{-1}}$. In comparison with them, surface areas of mesopores calculated by Schneider's method are somewhat lower (within limits of 740–570 $\mathrm{m^2\,g^{-1}}$). With increasing amount of zirconium, surface area of mesopores decreased.

After impregnation of the supports with HPMo, surface areas and pore volumes of the catalysts decreased. This effect is demonstrated in Fig. 4 for the Zr–HMS (0.02) support and corresponding catalyst. As the size of Keggin anion of the HPMo acid is about 1.2 nm [13,22], we assume that the mesoporous structure of the silicas with pore diameter about 3.5 nm enable the HPMo molecule to enter the pores. A part of mesopores are probably blocked (Table 1) after loading the supports with HPMo. Roughly speaking, pore size distributions of all molybdenum catalysts replicate mesoporous structure of their supports. Only the Mo/HMS and Mo/Zr–HMS (0.01) catalysts include additional mesopores. Formation of the additional mesopores of larger diameter could be associated with a less stable structure of the HMS and Zr–HMS (0.01) supports whose mesoporous structure could be disordered after loading HPMo.

TPD of ammonia is applied for the characterisation of acidity of the samples. In Table 2, total amount of ammonia desorbed in the temperature range of 20–300°C from the parent HMSs is given together with the other values characterising acidic properties of the materials (relative portion in total desorption spectrum, peak temperature maxima of individual peaks).

With all parent silicas, TPD curves show one broad peak that include two overlapping peaks. The first one having temperature maximum around 90°C and the second around 120°C. Low temperatures of both desorption peaks indicate that acidic sites of all par-

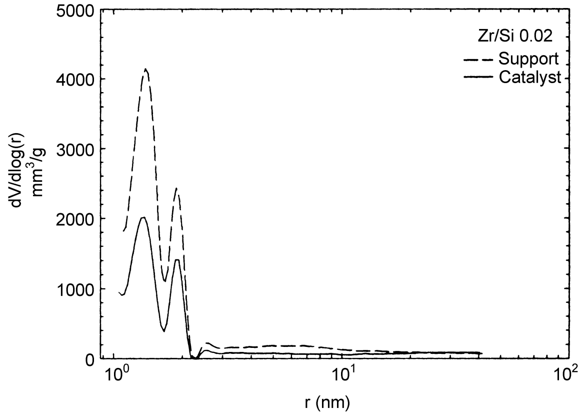

Fig. 4. Pore size distributions of the Zr–HMS (0.02) support and corresponding catalyst vs pore radii.

Table 2
Total acidity and distribution of the acidic sites measured by the TPD of NH_3

Sample	T_{max} (°C)			Portion of individual peaks (%)			Acidity (mmol g^{-1}), ΣA
	T_1	T_2	T_3	A_1	A_2	A_3	
HMS	80	102	–	26	74	–	0.33
Zr–HMS (0.01)	96	136	–	45	55	–	0.34
Zr–HMS (0.02)	95	118	–	48	52	–	0.35
Zr–HMS (0.04)	81	115	–	46	54	–	0.39
Mo/HMS	97	182	–	29	71	–	2.2
Mo/Zr–HMS(0.01)	91	160	244	33	41	26	2.6
Mo/Zr–HMS(0.02)	95	160	260	36	32	32	2.4
Mo/Zr–HMS(0.04)	101	166	270	30	36	34	2.0

ent hexagonal silicates are not strong. Total acidity of the parent silicas slightly grew with increasing Zr/Si ratio. Pure mesoporous silica (HMS) was characterised by the lowest acidity and this is in agreement with the data of Tuel [8]. Acidic sites on the zirconium-containing mesoporous silicas are probably of Lewis type. Using IR spectroscopy of pyridine Tuel [8] observed only Lewis and no Broensted acidic sites on the surface of Zr–HMS with $Zr/Si = 0.04$. Certain amount of Broensted acidic sites were observed with a titanium-modified HMS in the case of substantially higher titanium amount [8].

Acidity of all molybdenum-modified hexagonal silicas were very close keeping within limits 2–2.6 mmol g^{-1} (Table 2). Comparing the data with acidities of the parent silicas, modification with HPMo causes substantial increase in total acidity of the resulted catalysts. The increase in acidity of the catalyst samples can be ascribed to the presence of phosphomolybdic acid on the support surface. Non-linear relationship between acidity of the samples and the amount of zirconium present in the silicas exists.

Deconvolution of the desorption peaks of ammonia from molybdenum catalysts showed presence of three peaks. First one is identical with the first desorption peak of the parent mesoporous silicas. Second peak of the desorption curves of the catalysts is shifted to higher temperatures (around 170°C) and indicates higher strength of these acidic sites. The third peak (around 240–270°C) is observed with the catalyst prepared with Zirconium-modified hexagonal silicas. With increasing amount of zirconium in the silicas, the integral intensity of the peak with T_{max} around 250°C is increasing. The lowest strength of acidic sites (without the presence of third desorption peak) is observed for the Mo/HMS catalyst sample prepared with pure mesoporous silica.

IR spectra of the all silica HMS, Zirconium-modified mesoporous silica Zr–HMS (0.01) and of the dried and calcined Mo/Zr–HMS catalyst are shown in Fig. 5. In the spectrum of the all silica HMS (Fig. 5(1)), the intense band with maximum at about 1120 cm^{-1} and large shoulder around 1200 cm^{-1} assigned to Si–O–(Si) vibrations is observed. In addition, the bands, at about 960, 800 and 475 cm^{-1} appear too.

Introduction of zirconium into HMS caused an enlargement of the shoulder at 1200 cm^{-1} shifting it to 1260 cm^{-1} (Fig. 5(2)). The band at 960 cm^{-1} was clearly visible in the spectra of all zirconium-modified hexagonal silicas. Intensity of the band at about 960 cm^{-1} increased whereas that of the band at

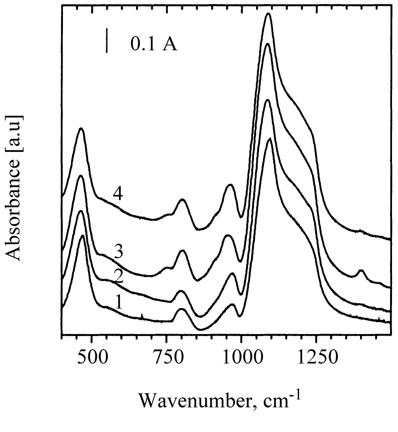

Fig. 5. IR spectra of the supports: (1) HMS; (2) Zr–HMS (0.01); (3) catalyst Mo/Zr–HMS (0.01): dried at 70°C; (4) calcined at 350°C.

800 cm^{-1} practically did not change. The ratio of band intensities at 960 and 800 cm^{-1} could be a criterion of this incorporation [23]. Calculated ratio of both bands intensities for Zr–HMS (0.01) showed that its value is higher than that for pure silica. With respect to this observation, zirconium is probably included in the structure of zirconium-modified silica.

IR spectrum of the HPMo-modified HMS dried at 70°C (Fig. 5(3)) showed a new band in the region below 750 cm^{-1}, a new shoulder at around 910–920 cm^{-1} and an increase in intensity of the band at about 950–960 cm^{-1} when compared with the spectrum of the corresponding support. Interaction of molybdenum compound with the silica support can explain the changes in the spectrum of the catalyst [24]. Complexity of the spectra of the molybdenum-containing samples does not allow us full elucidation of phosphomolybdic acid interaction with silicas. A part of HPMo molecules probably deforms some Si–O–Si bonds, whereas another part could form Si–O–Mo or Zr–O–Mo bonds. The presence of the band at frequencies lower than 750 cm^{-1} in the IR spectrum of the Mo/HMS sample could be a result of HPMo interaction with the silica. Formation of lacunar $[PMo_{11}O_{39}]^{7-}$ anion [25] could also be expected. IR spectrum of the Mo/Zr–HMS (0.01) sample did not change after calcination (Fig. 5(4)). It could indicate that zirconium can increase thermal stability of the molybdenum species arising from HPMo interaction with the silica.

Reduction profiles of the molybdenum-containing catalysts show one main reduction peak appearing around 500°C (Fig. 6) which can be assigned to the first reduction step of Mo^{6+} to Mo^{4+} in polymolybdate structure. Another peak at about 750°C is revealed in the TPR pattern of Mo/HMS and Mo/SiO_2 samples. These results indicate that at least two types of molybdenum species are present on the catalyst surface. It should be marked that in zirconium-containing catalysts increasing amount of zirconium in the silica shifts the low-temperature peak to higher temperatures, i.e. on the catalyst surfaces there are molybdenum species reduced more hardly. The low T_{max} at 502°C for the Mo/Zr–HMS (0.01) shifts to 529°C for Mo/Zr–HMS (0.04) sample. Simultaneously the T_{max} at about 700°C observed in the TPR spectrum of Mo/HMS decreases its intensity in the Mo/Zr–HMS (0.01) sample.

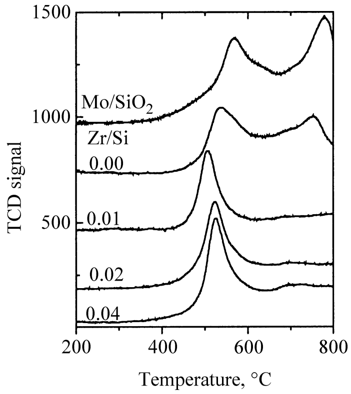

Fig. 6. TPR patterns of the molybdenum catalysts prepared on the hexagonal mesoporous silicas with different Zr/Si ratio.

However with growing of zirconium in the samples (Fig. 6, curves 0.02, 0.04) the intensity of this peak increases. These results indicate change of the coordination in a part of molybdenum species (Mo_{Oh} in polymolybdates transfers in hardly reduced Mo_{Td}) [26]. This effect of zirconium is discussed in detail in the forthcoming paper [27]. However, there is no direct correlation of reducibility with HDS activity of the Mo/Zr–HMS catalysts. Most probably HDS activity of the samples under investigation generally depends on their acidity. The lower steady state thiophene conversion on the zirconium-containing catalysts is due to their higher amount of weak acid sites in comparison with Mo/HMS. Similar decrease in activity with TOS was observed in the thiophene hydrogenolysis on acidic catalysts [28]. On the other hand, H_2S and thiophene competing for adsorption on the same sites of the pre-sulphided catalysts could decrease HDS activity. Removing adsorbed H_2S a flush of H_2 restores the initial catalyst activity [21].

4. Conclusions

The synthesised mesoporous materials (HMS) have been shown to be perspective supports for preparing of HDS catalysts owing to high surface area of HMS and their peculiar porosity. Their HDS activity is higher than that of the Mo/SiO_2 catalyst. Zirconium improves hydrogenation activities of the samples.

Correlation between total acidity of the catalysts and their initial HDS activity has been shown. Zirconium in the catalysts makes easier reducibility of the supported molybdenum species and decreases total acidity.

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