SYNTHESIS AND CHARACTERIZATION OF A CATALYST FORMED BY DIRECT INCORPORATION OF SOME HETEROPOLYACIDS INTO MESOPOROUS MATERIALS

Alexandru POPA, Viorel SASCA, Catalin IANASI,
Orsina VERDES, Livia AVRAM

Institute of Chemistry Timişoara, ROMANIA

ABSTRACT
The effect of incorporation of heteropolyacids species into organized mesoporous silica by using non-ionic and cationic surfactants were studied. The structure and texture of $H_3PMo_{12}O_{40}$ included on mesoporous silica were studied by XRD, FT-IR, BET and pore size distribution. The synthesis of silica molecular sieve containing HPAs was carried out in acidic media by using a mixture of cationic and non-ionic surfactants. FT-IR studies showed that HPAs anions preserved their Keggin structure after incorporation on molecular sieves supports. The values of specific surface area of HPAs were increased by deposition on molecular sieve supports.

1. INTRODUCTION

Heteropolyacids have attracted considerable attention as they present high acidity and favourable redox behaviour. Especially Keggin type heteropolyacids (HPAs) have been used extensively in acid-catalysed reactions as well as oxidation reactions both in the heterogeneous and homogeneous systems. Pure HPAs generally show low catalytic reactivity owing to their small surface area. In order to be more effective for catalytic reactions, HPAs are usually impregnated or incorporation on different porous materials with high surface area [1-6].

Direct incorporation of heteropolyacids (HPAs) $H_3PMo_{12}O_{40}$ (HPM) into mesoporous silica molecular sieve during the synthesis was studied. The synthesis of silica molecular sieve containing HPAs was carried out in acidic media by using a mixture of cationic and non-ionic surfactants, such as cetyltrimethylammonium bromide ($C_{16}TMABr$) and Triton (TX-100) or Tween 100 [7]. The obtained mesoporous materials were characterised by FTIR spectrometry, X-ray diffraction at low angles, thermal analysis (TG-DTA) and N_2 adsorption-desorption measurements.

FT-IR studies showed that HPAs anions preserved their Keggin structure after incorporation on molecular sieves materials. X-ray diffraction studies confirmed the uniformity of the distribution of active phase in the silica molecular sieve composites.

2. MATERIALS and METHODS

Molybdo phosphoric acid, $H_3[PMo_{12}O_{40}] \cdot 12H_2O$ (HPM) was purchased from Merck. The silicon source was tetraethoxysilane (TEOS) from Fluka. Two types of non-ionic surfactants were used in this study: polyethyleneglycol-4-tert-octylphenylether with 9-10 ethoxy groups (Triton X-100) from Fluka and polyethylene sorbitan-monostearate (Tween 60) from Merck. The cationic surfactant used is cetyltrimethylammonium bromide $C_{16}H_{33}(CH_3)_3 NBr$ (CTMABr) from Fluka. As mineralizing agent it was employed sodium floride NaF, from Fluka.

Mesoporous molecular sieves-included HPAs (denoted HPA-in-TX 100 or Tween 60) with 15 % HPA loading, were prepared by the hydrolysis of tetraethyl orthosilicate using non-ionic and cationic surfactants. The procedure described by Toufaily et. al. [7] was applied with some modifications. In first synthesis we used a mixture of TX-100 and CTMABr surfactants, while in the second we used as surfactant only Tween 60.

First synthesis was performed with the following molar composition: 1SiO_2:0.22 TX100:0.04 CTMABr:0.04 NaF:0.006 HPM:168 H_2O. In a first step, 7.4 g of TX-100 and 0.82 g of CTMABr were dissolved in 160 ml distilled water containing 4 ml of hydrochloric acid (HCl 37 wt.%). Then, after a clear solution was obtained, 11 g of TEOS were added and stirred until complete dissolution. Then a solution of 0.57 g HPM in 30 ml acidified (HCl) distilled water was added to first solution and stirred for 4 hours at room temperature. The solution was aged for 24 h at room temperature without stirring. A small amount of sodium fluoride (0.1 g) was then added in order to promote the hydrolysis of TEOS. The solution was furthermore aged at 60°C for 48h. The solid product was filtered, washed with

JOURNAL OF ENGINEERING
annals OF
FACULTY OF ENGINEERING HUNEDOARA

ANNALS OF THE FACULTY OF ENGINEERING HUNEDOARA – JOURNAL
OF ENGINEERING. TOME VII (year 2009). Fascicule 3 (ISSN 1584 – 2673)

distilled water and dried in air for 6h. Calcination for template surfactants removal was carried out under air by increasing temperature from 25 to 350°C with a rate of 2°C/min and heating at 350°C for 4h.

The second synthesis was performed by the same procedure but with Tween 60 as non-ionic surfactant. The following molar composition was used: $1SiO_2:0.067$ Tween $60:0.04$ NaF$:0.006$ HPM$:148$ H_2O. The structure and texture of HPM and HPVM included on molecular sieves were studied by XRD, FT-IR and low temperature nitrogen adsorption technique. Powder X-ray diffraction data were obtained with a XD 8 Advanced Bruker diffractometer using the Cu K_α radiation in the range $2\theta = 0.5$-$5°$ at low angles and $2\theta = 5$-$60°$.

Textural characteristics of the outgassed samples were obtained from nitrogen physisorption using a Quantachrome instrument, Nova 2000 series. The specific surface area S_{BET}, mean cylindrical pore diameters d_p and adsorption pore volume V_{pN2} were determined. Prior to the measurements the samples were degassed to 10^{-5}Pa at 250°C. The BET specific surface area was calculated by using the standard Brunauer, Emmett and Teller method on the basis of the adsorption data. The pore size distributions were calculated applying the Barrett-Joyner-Halenda (BJH) method to the desorption branches of the isotherms. The IUPAC classification of pores and isotherms were used in this study.

The IR absorption spectra were recorded with a Jasco 430 spectrometer (spectral range 4000-400 cm^{-1} range, 256 scans, and resolution 2 cm^{-1}) using KBr pellets.

3. RESULTS AND DISCUSSION

For all synthesized materials the N_2 adsorption-desorption isotherms exhibit a type IV isotherm (Fig. 1 a, b). The specific surface area, pore volume and pore diameter determined from the isotherm using the BJH method are given in Table 1.
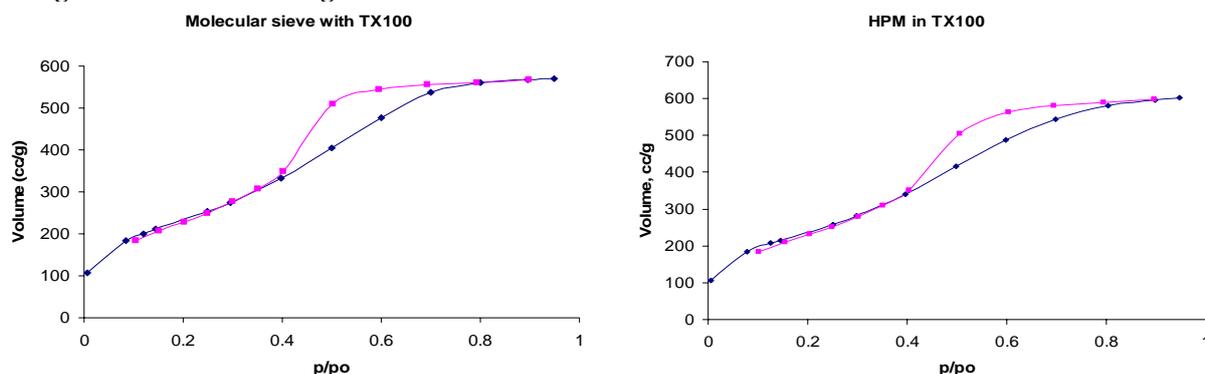
Figure 1. Nitrogen adsorption-desorption plot of molecular sieve with TX 100 (a) and HPM included on TX 100 (b)

Table 1 Textural properties of molecular sieves and included HPM

Sample	Specific surface area (m²/g)	Pore volume BJH_{Des} (cc/g)	Average pore diameter BJH_{Des} (nm)
TX 100	841.65	0.881	3.66
Tween 60	877.67	1.012	3.64
HPM in TX100	857.04	0.931	3.67
HPM in Tween 60	762.01	0.867	3.66

The pore size distribution curves of parent molecular sieves with TX 100 plus CTMABr and Tween 60 respectively, have narrow pore size distribution within mesopore range with a maximum at 37 Å and 36 Å, respectively.

After HPM incorporation in molecular sieves matrix, the pore volumes of samples decreased with the increase of the concentration of active phase and also the surface area decreased with the increase in HPAs loading. The pore size distribution curves of HPM included on molecular sieves with TX 100 plus CTMABr and Tween 60 respectively, have one maximum within mesopore range at approximately the same values as in the case of pure molecular sieves.

The XRD patterns at low angles for the initial molecular sieves show a broad diffraction peak below 2.5° (2θ) for both materials prepared with TX 100 plus CTMABr and Tween 60, respectively (not shown).

For the two HPM included on molecular sieves the diffraction peaks at low angles are presented but with diminished intensity. The diffraction peak of included HPM appears like a shoulder. It can be asserted that the long – range order of molecular sieve is decreased evidently even for loading of 15 wt. % HPAs.

In order to confirm the presence of the Keggin anion on silica-HPA composites, the samples were analysed by FTIR. The $PMo_{12}O_{40}^{3-}$ Keggin ion structure consists of a PO_4 tetrahedron

surrounding by four Mo_3O_{13} formed by edge-sharing octahedra. These groups are connected each other by corner-sharing oxygen. This structure give rise to four types of oxygen, being responsible for the fingerprints bands of Keggin anion between 1200 cm⁻¹ and 700 cm⁻¹.

The pure HPAs show an IR spectrum with the specific lines of the Keggin structure containing the main absorption bands at 1064 cm⁻¹, 965 cm⁻¹, 864 cm⁻¹, 785 cm⁻¹ assigned to the stretching vibrations ν_{as} P -O, ν_{as} Mo=O$_t$, ν_{as} Mo-O$_c$-Mo and ν_{as} Mo-O$_e$-Mo [4, 5]. These bands are preserved on the molecular sieves - HPA composites, but they are broadened and partially obscured because of the strong absorption bands of silica (1090, 812 and 456 cm⁻¹) (Figure 2).

The introduction of heteropolyacids into the silica matrix slightly influenced the structure of resulted composite (Figure 2). The vibration band at ca. 1090 cm⁻¹ can be assigned to ν_{as}(Si-O-Si) and decreased to 1072 cm⁻¹ by incorporation of HPAs into the structure of the silica. The band at ca. 966 cm⁻¹ present in the spectrum of included HPM sample can be assigned to the ν_{as} Mo=O$_t$ stretching vibration. The bands at 812 and 454 cm⁻¹ can be assigned to ν_s (Si-O-Si) and δ(Si-O-Si) bonds, respectively [6].

The bands of HPAs included on silica in the 1300-400 cm⁻¹ region are partially or completely overlapped by the bands of the silica matrix. The band assigned to the P –O asymmetric stretching vibration at 1064 cm⁻¹ is completely overlapped by the strong band at 1090 cm⁻¹ of the silica.

Two IR bands in the spectra of included HPM appeared at 966 and 660 cm⁻¹, which can be assigned to the ν_{as} Mo=O$_t$ stretching vibration and to δ (O-P-O) of the HPAs.
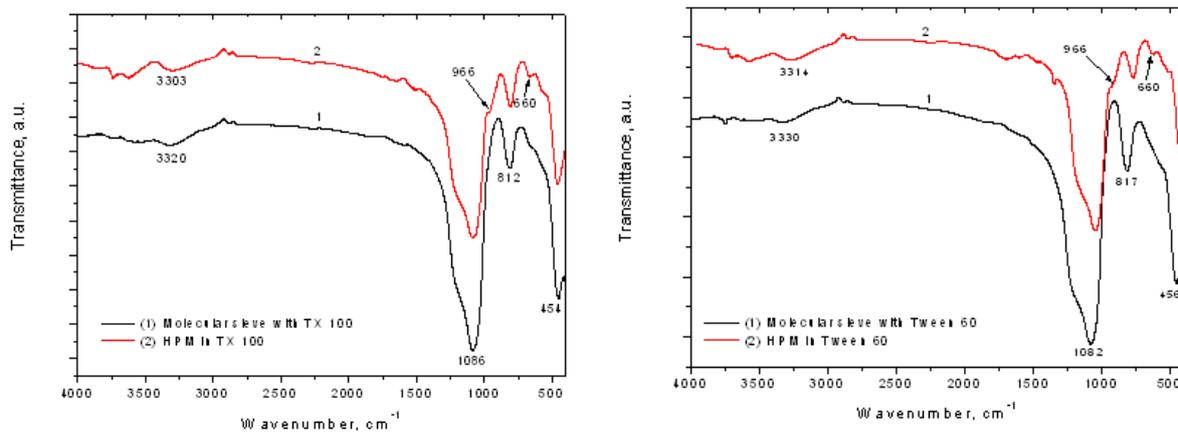
Fig. 2 FTIR spectra of molecular sieves - heteropolyacids composites

4. CONCLUSIONS

The HPAs anions preserved their Keggin structure on the surface of molecular sieves-HPA composites and forms finely dispersed HPAs species. The molecular sieves-HPM composites exhibit differential pore size distribution in the mesoporosity range.

It can be asserted that the long – range order of molecular sieve is decreased evidently even for loading of 15 wt. % HPAs.

The favourable effect of HPAs incorporation on silica molecular sieve is the increasing of pore volume and specific surface area, which in fact make the silica-HPA composites proper for heterogeneous catalysis.

LIST OF REFERENCES
[1] F.Cavani, Catal. Today 41, (1998) 73-86
[2] Alexandru Popa, V. Sasca and J. Halasz, Applied Surface Science, 255 (5 PART I), (2008)1830-1835
[3] Alexandru Popa, V. Sasca, E.E. Kiš, R. Marinkovic-Neducin and J. Halasz, J. Optoelectron. Adv. Mater., 10(6), (2008) 1401-1407
[4] A.Molnar, C. Keresszegi, B. Torok - Appl. Catal. A: General, 189 (1999) 217 - 224.
[5] A.Kukovecz, Zs.Balogi, Z.Konya, M.Toba, P.Lentz, S.-I.Niwa, F.Mizukami, A.Molnar, J.B.Nagy, I.Kiricsi, Appl. Catal. A:General 5921 (2002) 1-12.
[6] S.C. Laha, P.Mukherjee, S.R. Sainkar, R.Kumar, J.Catal.. 207 (2002) 213 -220
[7] J.Toufaily, M.Soulard, J-L.Guth, J.Patarin, L.Delmonte, T.Hamieh, M.Kodeih, D.Naoufal, H.Hamad, Colloids and Surfaces A: Phys.Eng. Aspects, 316 (2008) 285-291
[8] A.J.Bridgeman, Chem Phys. 287 (2003) 55-69