Catalytic Activity of Heteropolytungstic Acid Encapsulated into Mesoporous Material Structure

Gonul Gunduz[*]   Rayna P. Dimitrova[†]

Selahattin Yilmaz[‡]

[*]Ege University, gonul.gunduz@ege.edu.tr

[†]Institute of Organic Chemistry, zeolab@orgchm.bas.bg

[‡]Izmir Institute of Technology, selahattinyilmaz@iyte.edu.tr

Catalytic Activity of Heteropolytungstic Acid Encapsulated into Mesoporous Material Structure[*]

Gonul Gunduz, Rayna P. Dimitrova, and Selahattin Yilmaz

Abstract

The paper presents a spectroscopic and catalytic study of encapsulated Keggin type heteropoly acid (12-tungstophosphoric acid, HPW) in the mesopores of MCM-41 molecular sieves. Nitrogen physisorption, FTIR, SEM, XRD and catalytic methods have been used to characterize and compare the properties of the samples. Methanol conversion, ?-pinene isomerization and ethyl acetate oxidation have been applied as model reactions for the evaluation of acid site activity. The combined physicochemical and catalytic investigations clearly show that the introduction of 12-tungstophosphoric acid into MCM-41 causes significant changes in the properties of the sample.

KEYWORDS: encapsulation, mesoporous material, heteropoly acid, isomerization, alpha-pinene, methanol, ethyl acetate

[*]E-Mail: gonul.gunduz@ege.edu.tr (G.Gündüz), Tel: + 90 232 3884000/2292, Fax: +90 232 3887776.

1. INTRODUCTION

A wide range of liquid-phase industrial reactions, for production of fine and specific chemicals, employ organic or inorganic acids (sulfuric acid, hydrochloric acid) as catalyst. During the product final isolation from the acidic solution, large quantities of hazardous wastes are obtained and the cost of disposal of the waste often overcharges the value of the product. Besides, as the acids are highly corrosive, expensive and durable reactors are required. The tightening of the environmental legislation, concerning the emission of hazardous pollutants, is driving factor for the industry to consider alternative processes for the catalytic proceeding.

In this aspect, the use of heterogeneous catalysts gains a considerable interest due to their simplified removal, recovery and selectivity (Wilson and Clark, 2000). The ideal heterogeneous catalyst should possess mesopores for avoiding of the diffusion constraints and for facilitating the access to the acidic and catalytic centers from bulky organic molecules.

Zeolite and molecular sieves are widely used as heterogeneous acid catalysts in various industrial processes (Asensi et al., 1998; Dimitrova et al., 2006). Zeolite application is based upon the behavior of hydrocarbons within their framework structure and is governed by two factors: the zeolite acid strength and the pore size. Unfortunately, small pore sizes of zeolite (around < 8 Å) restrict their application for reactions involving bulky substrates. The facile transport of the reagents and the products is an important factor for the liquid-phase reaction, because it minimizes the catalyst deactivation. The synthesis of M41S family of mesopores molecular sieves (MCM-41, MCM-48, and MCM-50) with pore sizes in the range of 20-100 Å opens up new possibilities for the acid catalyzed reactions of large molecules in liquid-phase. The pure silica MCM-41 has one-dimensional hexagonal arranged mesopore system with amorphous walls of the channels, thermal stability, large surface area and adsorption capacity. The pore diameters vary between 1.5 and 10 nm and can be controlled by using of different surfactants during the synthesis. The silica mesoporous MCM-41 comprises silanol OH groups (external silanol groups, bridging hydroxyl groups, silanol nests, hydroxyl pairs), which are slightly acidic. Methanol conversion and α-pinene isomerization are appropriate reactions and have been successfully applied as model reactions for the evaluation of acid site activity and for following the intermediates of the catalytic transformation in heterogeneous conditions (Dimitrova et al.,2006; Dimitrova et al., 2004). However, studies concerning the data on the catalytic properties of zeolite-like materials, such as the meso molecular sieve MCM-41, are still rather scared. Heteropoly acids (HPAs) are extremely strong acids and are widely used as catalysts. HPAs are considered as solid acids if they are physically immobilized in a porous support. Being molecules of Keggin type, HPAs are spherical with diameters around 1 nm and thus are effectively encaged and immobilized in MCM-41 molecular sieves (Nowinska and Kaleta, 2000; Mukai et al., 1997; Mukai et al., 2001; Mukai et al., 2003; Anandan et al., 2003; Grzona et al., 2005).

In the paper, 12-tungstophosphoric acid (HPW) was immobilized in the mesoporous MCM-41 molecular sieve with open cylindrical pores of uniform size and its catalytic activity was tested in the isomerization of the bulky α-pinene molecule, in methanol conversion and as a green chemistry example, in the oxidation of ethyl acetate.

2. EXPERIMENTAL

2.1 Materials and Characterization

The 12-tungstophosphoric acid (HPW) was a commercial product from Merck ($H_3PW_{12}O_{40}$.). MCM-41 molecular sieve was synthesized by a method described in (Lin et al., 1997). The template solution was prepared by mixing 3.825 g HTMABr (99% pure hexadecyltrimethylammoniumbromide, Merck,) and 29.3 ml water under stirring for 20 minutes. 14.2 ml water glass (Aldrich) was added to the clear aqueous solution under stirring till the formation of a gel mixture. After 20 minutes stirring at room temperature, 1.10 M H_2SO_4 (Merck) was added drop wise till 10.1 pH. The component molar ratio in the resulting gel was: 1 SiO_2 /0.25 Na_2O /0.11 HTMABr /0.26 H_2SO_4 /38.18 H_2O. The viscous and milky gel was then poured into Teflon lined autoclave and aged at 373 K for 48 h. After that, the autoclave was quenched to ambient temperature and the obtained MCM-41 sample was filtered and washed with 1 liter of demineralized water. The MCM-41 sample was dried for two days at room temperature and calcined at 833

K for 6 h (5 °C/minute) to remove the occluded organic species in the channels. The MCM-41 sample was cooled with air (5 °C/minute) to room temperature.

The HPW was introduced into MCM-41 sample from a 30 % (in weight) HPW methanol solution under refluxing for 3 h, as described in (Nowinska and Kaleta, 2000). The obtained HPW/MCM-41 sample was thoroughly washed with demineralized hot water, dried at 373 K and calcined at 573 K for 2 h (Mukai et al., 1997). The HPW amount was about 76 wt %, as measured by atomic absorption spectrometry (Varian 10 plus). The morphological characterization of HPW/MCM-41 and MCM-41 samples was performed by various methods. The SEM microphotographs were taken on Philips XL 30S model scanning electron microscope. The crystalline structures were determined by Philips X'Pert diffractometer with CuK_α radiation. Nitrogen physisorption studies were performed at 77 K using micromeritics ASAP 2010 model static volumetric adsorption instrument. Prior to adsorption experiment, the samples were degassed at 673 K for 24 hours under 5 μm Hg vacuum. The FTIR spectra were collected on a Brucker spectrometer (Vector 22) using KBr pellet technique. The samples were dried at 423 K for 3 h in the experimental camera under vacuum before the FTIR spectra.

2.2 Catalytic Tests

The alpha-pinene isomerization was carried out at atmospheric pressure with 0.5 g catalyst and 25 ml alpha-pinene (Acros) at 373 K under nitrogen atmosphere. Analysis of the products was accomplished periodically during the course of the reaction and analyzed with a gas chromatograph (Hewlett-Packard 5980/2 with HP-Carbowax 20 M capillary column) equipped with flame ionization detector (FID). Temperature programming (2°C/min from 333 to 403 K and 3 °C/min until 500 K) and a flow of 1 ml/min N_2 were applied for products separation.

The catalytic experiments of methanol conversion and ethyl acetate oxidation were performed in a fixed bed reactor at atmospheric pressure. The catalyst (0.5 g) in powder form was diluted with a three-fold amount of glass. The methanol conversion was studied at temperatures above 550 K with a WHSV of 1.5 h^{-1}, methanol partial pressure of 1.57 kPa and argon used as a carrier gas. The oxidation of ethyl acetate (EA) was performed with a mixture of ethyl acetate (1.21 vol. %) in air and WHSV-100 h^{-1}. The on-line gas chromatographic analysis was done on 2 m Porapak Q and 2 m Durapak columns on Varian 3700. The products yields were calculated using an absolute carbon base calibration. Catalytic tests were also carried out on Cabosil (SiO_2) sample in order to follow most fully the differences in samples active centers.

3. RESULTS AND DISCUSSION

The nitrogen physisorption isotherms and the corresponding calculated parameters for the parent MCM-41 and the modified HPW/MCM-41 samples are presented in Figure 1 and Table 1, respectively. In the latter, the results from the nitrogen adsorption measurements are compared with Horvath-Kawazoe method. The isotherm of MCM-41 material shows type IV profile (IUPAC classification), typical of mesoporous materials. A sharp capillary condensation step, indicative of a narrow pore size distribution, is registered at 0.2-0.4 relative pressure. The nitrogen sorption isotherm with somewhat less pronounced condensation step is obtained for HPW/MCM-41 sample.
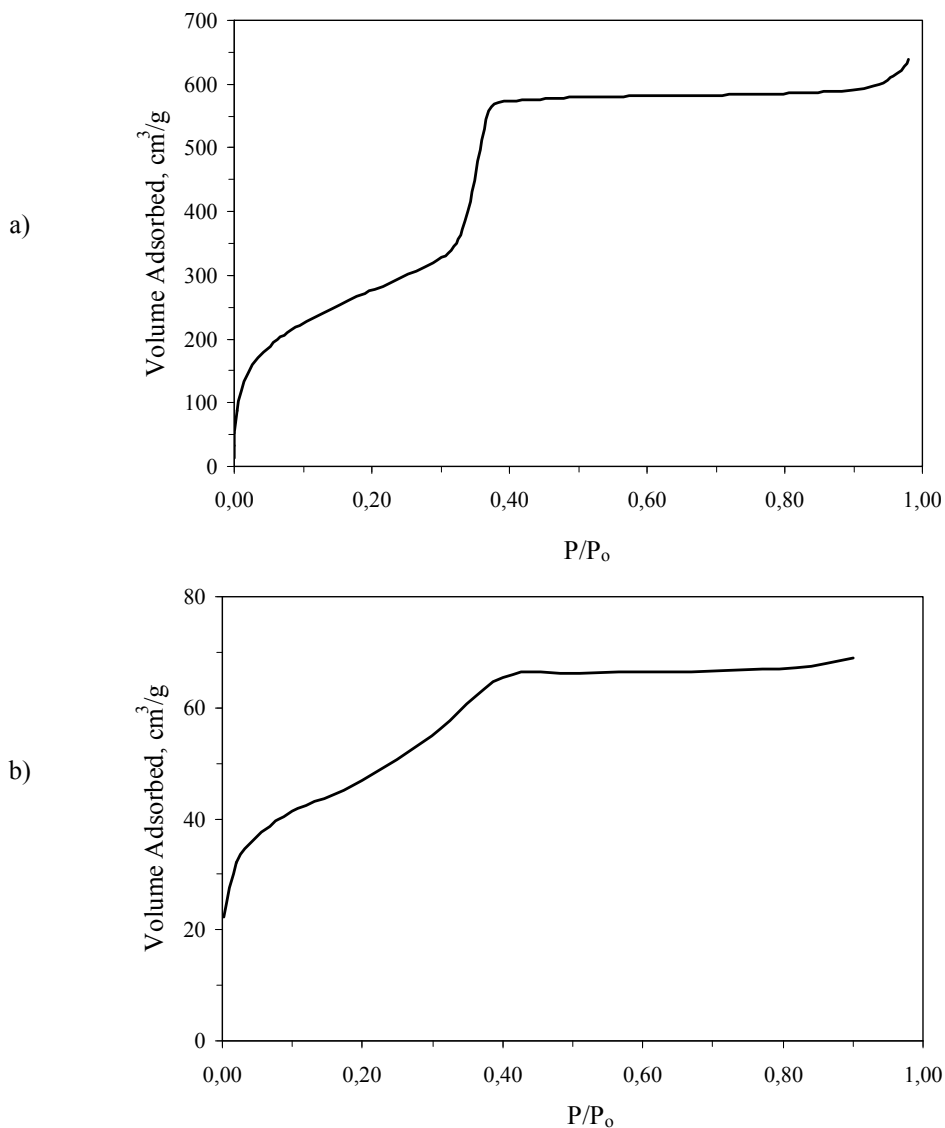
Figure 1. Nitrogen adsorption isotherms of samples: a) MCM-41, b)HPW/MCM-41.

A significant decrease of the BET surface area and pore volume (up to 14 %) was observed for HPW/MCM-41 sample (Table 1). The effect could depend both on the increased sample specific mass and on the partial pores filling of the support. A "correction" of the sorption data, concerning the increased sample masses after modification (76 wt %, of HPW), indicates for more pronounced location of the HPW inside the pores of MCM-41 silica structures.

Table 1. Adsorption characteristics of MCM-41 and HPW/MCM-41 samples

Samples	BET surface area, m²/g	Langmuir surface area, m²/g	A_{micro} m²/g	V_{micro} cm³/g	Total pore volume cm³/g	V_{max} cm³/g	Average pore diameter, Nm
MCM-41	1148.9	1692.3	298.3	0.0244	0.450	560.2 [1]	2.4
HPW/MCM-41	169.3	225.1	42.0	0.0169	0.064	69.4 [2]	2.5

$A_{micro} = A_{BET} - A_{(t-plot)}$
V_{micro} = micropore volume, from t-plot
[1] V_{max} = maximum amount adsorbed at relative pressure $P/P_0 = 0.92$
[2] V_{max} = maximum amount adsorbed at relative pressure $P/P_0 = 0.9$

   The SEM images of MCM-41 and HPW/MCM-41 samples are shown in Figure 2. MCM-41 consists of spherical particles with a size of around 0.5μm. The introduction of HPW changes the surface morphology of MCM-41 (Figure 2-b).
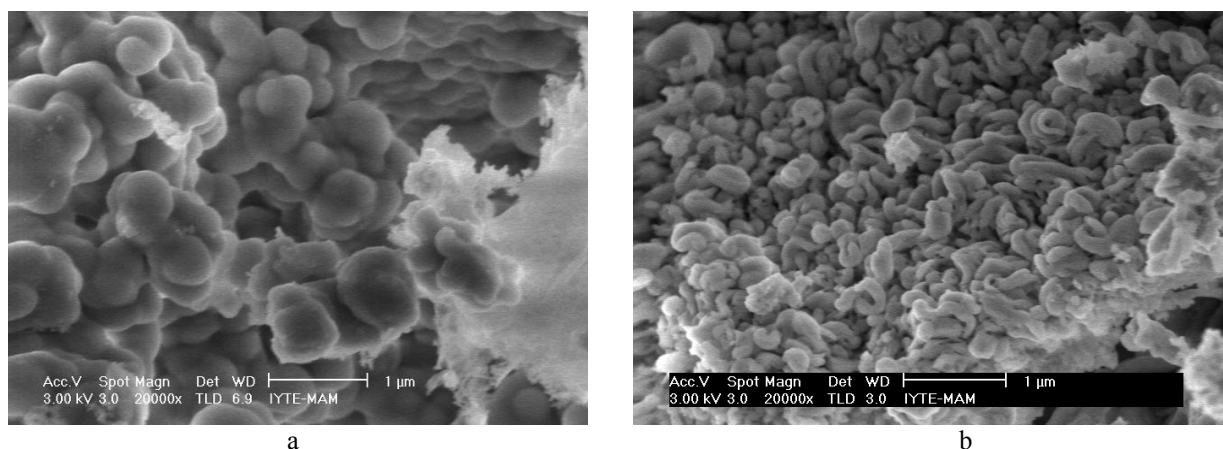

a   b

Figure 2. SEM images of: (a) MCM-41,   (b) HPW/MCM-41.

   The XRD patterns of MCM-41 and HPW/MCM-41 samples are compared in Figure 3. The reflections in the small-angle region for the initial MCM-41 material are indexed to mesophases with a hexagonal pore symmetry (Figure 3a). No significant changes in the patterns are observed after the introduction of Keggin type heteropoly acid, demonstrating the preservation of the silica support long-range order. In the wide-angle region, peaks with very low intensities at 2θ about 10°, 25° and 35° are registered in the XRD spectrum of HPW/MCM-41 characteristic for the immobilized solid HPW (Nowinska and Kaleta, 2000; Izumi et al., 1983; Kozhevnikov et al., 2001). The result is in agreement with the data for introduction of heteropoly compounds in various supports (Nowinska and Kaleta, 2000; Nowinska et al., 2003; Kozhevnikov et al., 1996).
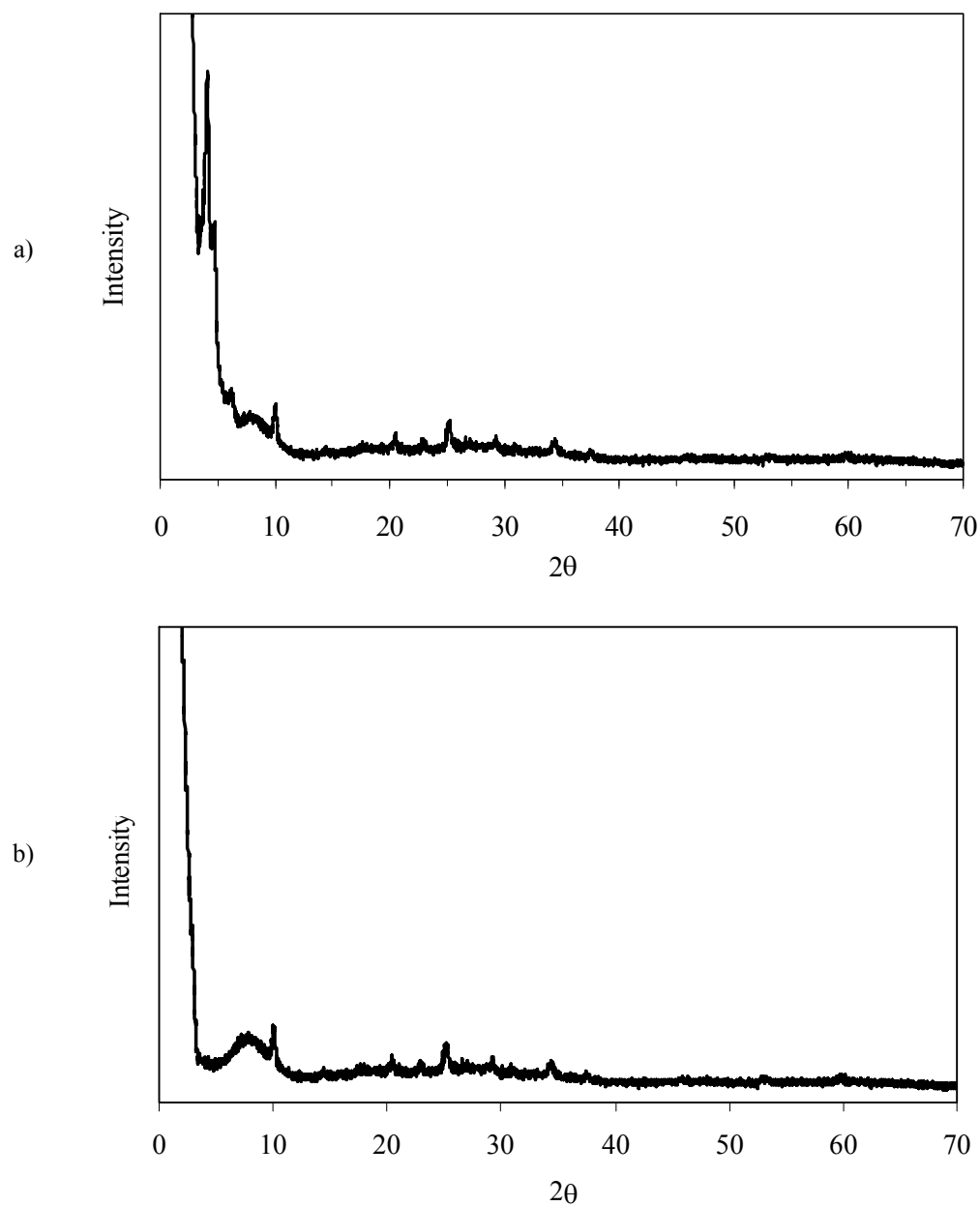
Figure 3. XRD Patterns of: (a) MCM-41, (b) HPW/MCM-41.

The textural characterization of the samples provide evidence that the mesoscopic order in HPW/MCM-41 sample has been maintained, despite the relatively high amount of introduced HPW and the significant change in the pore characteristics.

The FTIR spectra of HPW/MCM-41 and MCM-41 samples are presented in Figure 4. For comparison the spectrum of Cabosil (SiO_2) is drawn. A significant difference was observed in the spectra of the mesoporous molecular sieves and the pure SiO_2. The existence of silanol groups, situated as "silanol nests" in the mesoporous

structures is verified by band around 960 cm^{-1}. An appearance of a band centered at 960 cm^{-1} for MCM-41 and bands at 940 and 960 cm^{-1} in the spectra of HPW/MCM-41 are clearly distinguished (Figure 4, lines 2 and 1). Both bands are absent in the Cabosil spectrum (Figure 4, line 3). The characteristic bands at 3640 cm^{-1} and 1640 cm^{-1} recorded for all samples, ascribe the presence of terminal Si-OH groups and intermolecular O–H bonding on samples surface, respectively (Apelian et al., 1996).
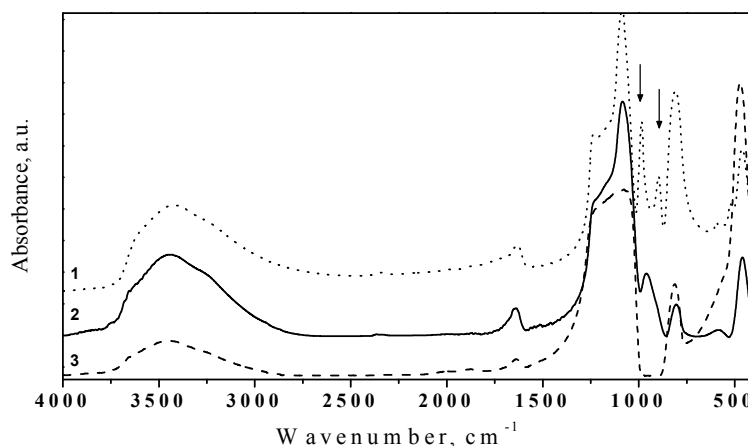

Figure 4. FTIR spectra of: HPW/MCM-41 - line 1; MCM-41–line 2; Cabosil - line 3.

The growth in the intensity of the bands at 960 cm^{-1} and 3640 cm^{-1} as well as an appearance of a new one at 940 cm^{-1} in the HPW/MCM-41 spectrum evidenced for the immobilization of the HPW through interaction with the mesoporous silanol groups.

The catalytic behavior of the silica molecular sieves is closely related to the number and the type of the catalytic active sites. The overall conversion of the bulky α-pinene and the reaction mixture composition after a reaction time of 3 h are presented in Table 2 for MCM-41 and HPW/MCM-41 samples. The corresponding data for HPW dried at 373 K in vacuum for 7.5 h and for HPW calcined at 573 K in air for 2 h are given for comparison. It is seen that the introduction of HPW into MCM-41 channels influence significantly the catalyst activity in the acid catalyzed α-pinene isomerization.

Table 2. α-pinene conversion ($x_α$) and weight percentages of products after 3h reaction.

Catalyst	$x_α$	1	2	3	4	5	6	LRTP[a]	UP[b]	HRTP[c]
MCM-41	2.9	85.88	2.14	-	1.76	0.62	0.38	-	3.2	6.02
HPW/MCM-41	98.3	1.70	15.30	5.79	0.25	19.73	-	4.98	1.85	50.39
HPW(at 373 K)	6.2	93.58	3.09	0.44	0.87	0.28	-	-	1.38	0.36
HPW(at 573 K)	5.6	92.15	3.72	1.81	1.57	0.47	-	-	1.19	0.18

1, α-pinene; 2, camphene; 3, terpinenes; 4, limonene; 5, p-cymene; 6, terpinolenes
[a] Products with a retention time lower than α-pinene (low retention time products)
[b] Products with a retention time in the range between α-pinene and terpinolene (unidentified products)
[c] Products with a retention time higher than terpinolene (high retention time products)

The HPW and MCM-41 are not active in α-pinene isomerization. HPW reveales low activity in spite of its high acidity, due to its very low surface area (below 10 m^2/g) (Nowinska and Kaleta, 2000). The different temperature pretreatment had no significant effect on HPW activity. A low α-pinene conversion was registered in presence of MCM-41 sample, despite its large external area and is related to its low total acidity (desorbed ammonia 0.50 mmol/g (Dimitrova et al., 2006). As stated in our previous study, an appropriate balance between sample acidity and mesoporous structure is obligatory for the acid catalyzed isomerization of the bulky α-pinene

molecule. Encapsulation of HPW into MCM-41 leads to an increase in the total sample acidity, mainly in Brönsted acidity,causing high α-pinene conversion (Atalay, 2003).

In Figure 5, the product distribution as a function of reaction time over HPW/MCM-41 sample is presented. The HPW/MCM-41 sample revealed high activity of in α-pinene conversion. Higher amounts of HRTPs, products of terpinenes and terpinolenes disproportionation, are registered on HPW/MCM-41 in comparison with the ones obtained in presence of MCM-41 sample. The results support the statement that at high α-pinene conversion, the formed limonene (being a more reactive molecule than α-pinene) isomerizes to terpinolenes and terpinenes, that further are transformed into HRTPs products (Dimitrova et al., 2006; Dimitrova et al., 2004).
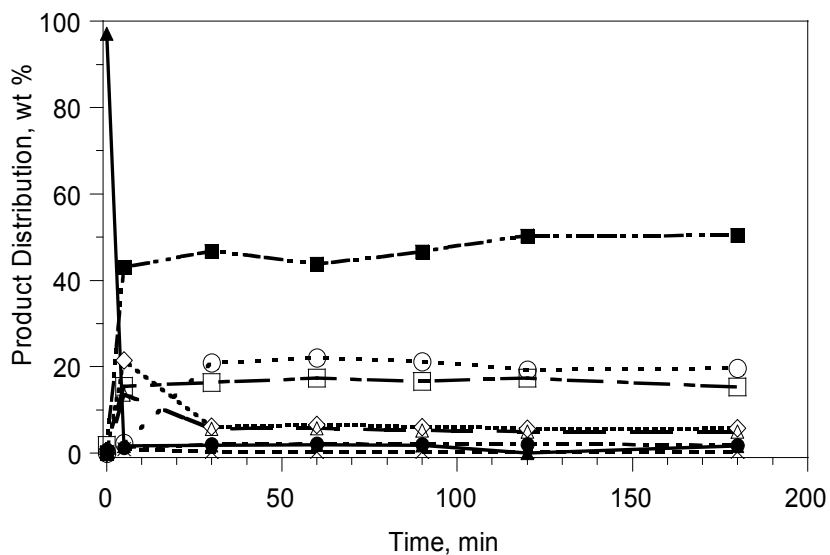

Figure 5. Product distribution in α-pinene isomerization over HPW/MCM-41: (▲) α-pinene (□)camphene; (◊) Terpinenes; (x) Limonene; (○) p-cymene; (Δ) LRTP; (●) UP; (■) HRTP

The conversion of methanol on MCM-41 and HPW/MCM-41 samples is presented in Figure 6a. As found in (Dimitrova et al., 2006; Dimitrova et al., 2004), the conversion of methanol at low reaction temperatures is dominated by the formation of dimethyl ether. The DME is the only product registered in the temperature range 425-475 K on HPW/MCM-41, while its formation begins at temperature of 550 K on both MCM-41 and Cabosil samples. The obtained data are in a good correlation with samples acidity, since the extent of methanol dehydration depend on samples total acidity. When raising the reaction temperature above 575 K, significant amounts of light olefins (predominantly alkenes and negligible amount of methane) are registered.
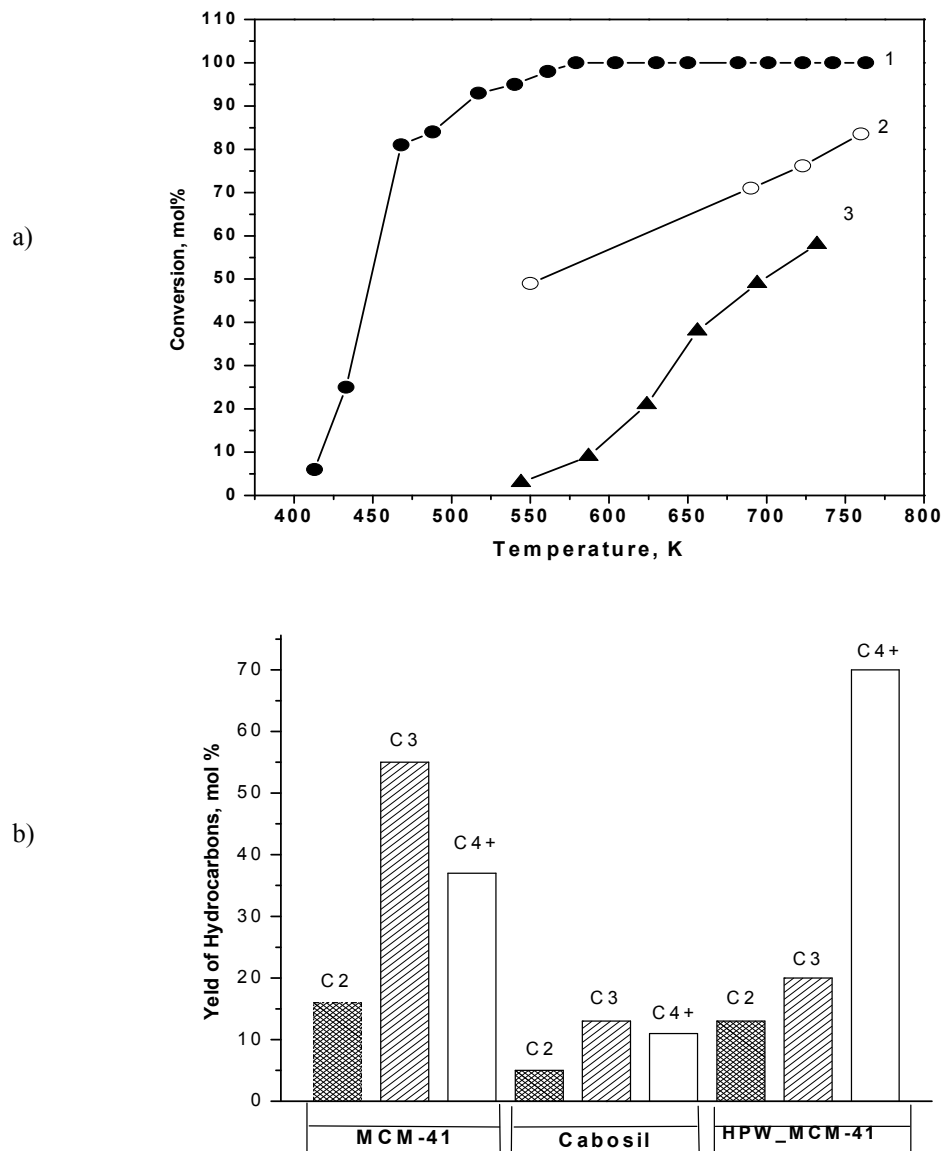
a)

b)

Figure 6. a) Methanol conversion at different temperatures on HPW/MCM-41 - line 1;MCM-41–line 2;Cabosil - line 3, b). Yield of olefins on HPW/MCM-41, MCM-41and on Cabosil at 750 K.

In Figure 6b, the light olefins yields distribution (ethene, propene, and butenes) produced at 750 K over the different samples are compared. It was determined that the decrease of the amount of the strong Brønsted sites (due to coke formation) was the dominating factor leading to light olefins formation (Stöcker, 1999). The correlation between the olefins amounts with higher than two carbon atoms was in accordance with catalysts mesoporosity so that the butenes were formed at values about 70 mol % on HPW/MCM-41.

As green chemistry example, oxidation of ethyl acetate was carried out on the samples. The temperature dependence of the ethylacetate oxidation is presented in Figure 7A.
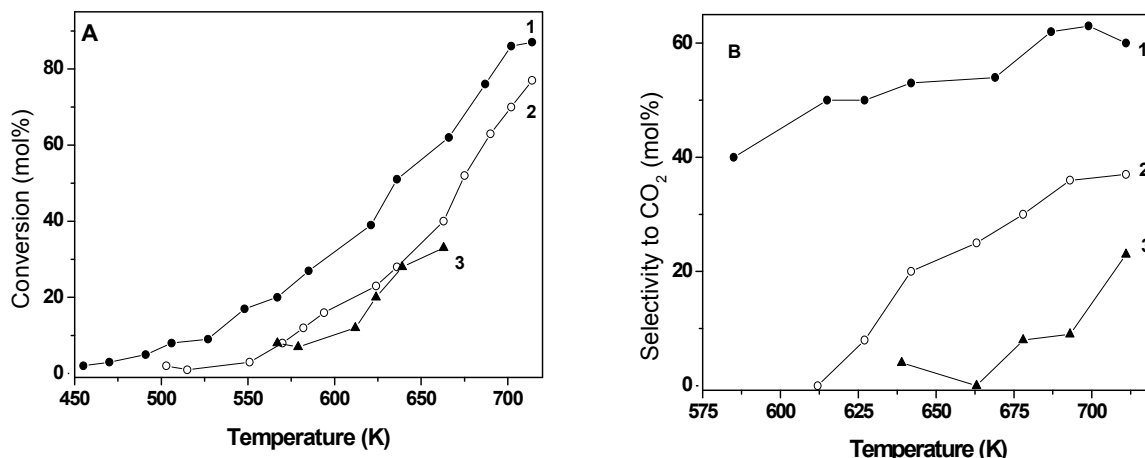
Figure 7. Ethyl acetate oxidation (A) and CO_2 selectivity vs temperature (B) on: HPW/MCM/41 - line 1; MCM-41–line 2; Cabosil - line 3.

Significant ethylacetate conversion was obtained above 600 K, as ethanol, acetic acid and CO_2 are the main registered products on MCM-41 and HPW/MCM-41 samples. It is found that Cabosil possesses a low activity. The reason should be searched in sample selectivity to CO_2 (Figure 7B).

A well defined tendency of the CO_2 selectivity increase with temperature was observed for Cabosil and MCM-41 materials, while the selectivity to CO_2 was high even at low temperature for HPW/MCM-41. As a whole, it could be stated that the porosity did not influence the catalytic activity of the samples.

CONCLUSION

The combined physicochemical and catalytic investigations clearly showed that the introduction of HPW into silica mesoporous MCM-41 sample influenced in a great extent the catalytic properties of the HPW/MCM-41 sample.

The introduction of HPW into silica mesoporous MCM-41, exhibit good catalytic stability and high activity in methanol and ethylacetate conversion at lower temperatures in comparison with the corresponding mesoporous MCM-41 sample and pure SiO_2 cabosil. We also found that the catalytic activity of the HPW/MCM-41 sample towards bulky organic molecules as α-pinene, strongly depends on its mesoporosity. High amounts of HRTPs were obtained on HPW/MCM-41 in the reaction of α-pinene isomerization in comparison with MCM-41. This supported the results obtained in our previous studies that a further transformation of limonene through terpinolenes and terpinenes into HRTPs took place.

REFERENCES

Anandan, S., Ryu, S.Y., Cho, W., Yoon, M., "Heteropolytungstic Acid ($H_3PW_{12}O_{40}$) Encapsulated into the Titanium-exchanged HY (TiHY) Zeolite: A Novel Photocatalyst for Photo reduction of Methyl Orange", J.Mol.Cat. A: Chem., Vol.195, No.1-2, 201-208 (2003).

Apelian, M.R., Fung, A.S., Kennedy, G.J., Degnan, T.F., "Dealumination of Zeolite β via Dicarboxylic Acid Treatment", J.Phys.Chem., Vol.100, No.41, 16577-16583 (1996).

Asensi, M.A., Corma, A., Martinez, A., Derewinski, M., Krysciak, J., Tamhankar, S.S., "Isomorphous Substitution in ZSM-22 Zeolite. The Role of Zeolite Acidity and Crystal Size During the Skeletal isomerization of n-Butene", App.Cat.A: General, Vol. 174, No.1-2, 163-175 (1998) .

Atalay, B., " Isomerization of α-pinene over Superacidic and Heteropolyacidic Catalysts", MSc Thesis,Ege University,Izmir/Turkey (2003) .

Dimitrova, R., Gündüz, G., Dimitrov, L., Tsoncheva, T., Yılmaz, S., Urquieta-Gonzalez, E.A., " Acidic size in Beta Zeolites in Dependence of the Preparation Methods", J. Mol. Catal. A: Chem., Vol. 214, 265-268, No.2, (2004) and refs there in.

Dimitrova, R., Gündüz, G., Spassova, M., "A Comparative Study on the Structural and Catalytic Properties of Zeolites Type ZSM-5, Mordenite, Beta and MCM-41", J. Mol. Catal. A: Chemical, Vol.243, No.1, 17-23 (2006).

Grzona, L., Masini, O., Comelli N., Ponzi,E.,Ponzi,M., "Deactivation of $H_3PW_{12}O_{40}/TiO_2$ Catalyst used in the Production of Camphene", Reaction Kinetics and Catalysis Letters, Vol.84, No.1, 199-204 (2005).

Izumi, Y., Hasebe, R., Urabe, K., J., "Catalysis by Heterogeneous Supported Heteropoly Acid", J.Catalysis, Vol.84,No.2, 402-409 (1983).

Kozhevnikov, I.V., Holmes, S., Siddiqui, M.R.H., "Coking and regeneration of $H_3PW_{12}O_{40}/SiO_2$ Catalysts", Appl.Catal.A: Gen., Vol.214, No.1, 47-58 (2001).

Kozhevnikov, I.V., Kloestra, K.R., Sirinema, A., Zandbergen, H.W., van Bekkum, H., " Study of Catalysts Comprising Heteropoly Acid $H_3PW_{12}O_{40}$ Supported on MCM-41 Molecular Sieve and Amorphous Silica", J. Mol. Catal. A: Chemical, Vol.114, No.1-3, 287-298 (1996).

Lin, H.P., Cheng, S., Mou, C.Y., "Effect of Delayed Neutralization on the Synthesis of Mesoporous MCM-41 Molecular Sieves", Microporous Mater., Vol.10, No.1-3, 111-121 (1997).

Mukai, S.R., Lin, L., Masuda, T., Hashimoto, K., "Key Factors for the Encapsulation of Keggin-Type Heteropoly Acids in the Supercages of Y-Type Zeolite", Chem.Eng.Science, Vol.56, No.3, 799-804 (2001).

Mukai, S.R., Masuda, T., Ogino, I., Hashimoto, K., "Preparation of Encaged Heteropoly Acid Catalyst by Synthesizing 12-Molybdophosphoric Acid in Supercages of Y-Type Zeolite", Appl.Catal.A: Gen., Vol.165, No.1-2, 219-226 (1997).

Mukai, S.R., Shimoda, M., Lin, L., Tamon, H., Masuda, T., "Improvement of the Preparation Method of 'Ship in The Bottle' Type 12- Molybdophosphoric Acid Encaged Y-Type Zeolite Catalyst", App.Catal.A: Gen., Vol.256, No1-2, 107-113 (2003).

Nowinska, K., Formaniak, R., Kaleta, W., Waclaw, A.,"Heteropoly Compounds Incorporated into Mesoporous Material Structure", App.Catal.A: General, Vol.256, No.1-2, 115-123 (2003).

Nowinska, K., Kaleta, W., "Sythesis of Bisphenol-A over Heteropoly Compounds Encapsulated into Mesoporous Molecular Sieves", Appl. Catal. A: Gen., Vol.203, No.1, 91-100 (2000).

Stöcker M., "Methanol-to-hydrocarbons: Catalytic Materials and Their Behavior", Microporous and Mesoporous Materials. Vol.29, No.1-2, 3-48 (1999).

Wilson, K., Clark, J.H., "Solid Acids and Their Use as Environmentaly Friendly Catalysts in Organic Synthesis", Pure Appl. Chem., Vol.72, No.7, 1313-1319 (2000).