New acid catalyst comprising heteropoly acid on a mesoporous molecular sieve MCM-41

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New solid acid catalysts, consisting of heteropoly acid (HPA) $H_3PW_{12}O_{40}$ (PW) supported on a mesoporous pure-silica molecular sieve MCM-41, have been prepared and characterized by nitrogen physisorption, X-ray diffraction, FT-IR, and ^{31}P magic angle spinning NMR. The PW/MCM-41 compositions with PW loadings from 10 to 50 wt% have $\sim$ 30 Å uniformly-sized mesopores. HPA retains the Keggin structure on the MCM-41 surface and forms finely dispersed HPA species. No HPA crystal phase is developed even at HPA loadings as high as 50 wt%. PW/MCM-41 exhibits higher catalytic activity than H_2SO_4 or bulk PW in liquid-phase alkylation of 4-*t*-butylphenol (TBP) by isobutene and styrene. In the alkylation of TBP by styrene, PW/MCM-41 shows a size selectivity compared to bulk PW and PW/SiO_2, providing higher yields of a 2-(1-phenylethyl)-4-*t*-butylphenol, at the expense of the more bulky 2,6-bis-(1-phenylethyl)-4-*t*-butylphenol. The PW/MCM-41 compositions, having strong acid sites and a regular mesoporous system, are promising catalysts for the acid-type conversion and formation of organic compounds of large molecular size.

Keywords: heteropoly acid; molecular sieve MCM-41; alkylation of phenols

1. Introduction

The development of new solid acid catalysts with advanced characteristics as to acid strength, surface area, porosity, etc. has been a challenge for a long time. In particular, much attention has been paid to the design of materials, having strong acid sites, a regular structure and very narrow pore size distribution, e.g. zeolites and modified layered materials, which are capable of strictly selecting reacting and product molecules by their size (size and shape selectivity) [1–3].

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We report here the preparation and study of new solid acid catalysts having strong acid sites as well as regular arrays of uniformly-sized channels with pore diameters within the mesoporous region. These materials are based on a Keggin heteropoly acid (HPA) and a recently developed mesoporous molecular sieve, MCM-41 [4,5]. HPAs have been widely used as acid as well as oxidation catalysts [3,6–8]. They are known to possess a strong, purely Brønsted acidity, being stronger than many mineral acids or conventional solid acids such as amorphous $SiO_2-Al_2O_3$ [6]. In this work, tungstophosphoric acid, $H_3PW_{12}O_{40}$ (PW), the strongest HPA in the Keggin series [6], has been used. As an inert support, we have chosen the pure-silica mesoporous molecular sieve MCM-41, which exhibits a hexagonal arrangement of uniform pores, whose dimensions can be engineered in the range from 15 Å to greater than 100 Å [4,5]. Such dimensions allow the easy introduction of HPA molecules (~ 12 Å diameter) into the MCM-41 pores. The MCM-41 materials typically have surface areas above 700 m^2/g and pore volumes of 0.7 cm^3/g and greater [4,5]. Pure-silica MCM-41 can be heated to at least 800°C without its structural collapse [9]. Due to these properties MCM-41 can be an excellent support for the loading of HPAs.

PW/MCM-41 compositions containing 10–70 wt% PW were prepared by impregnating pure-silica MCM-41 with PW, and were characterized by N_2 physisorption, X-ray diffraction (XRD), Fourier transform infrared (FT-IR), and ^{31}P magic angle spinning (MAS) NMR spectroscopy. Their catalytic performance has been tested in the liquid-phase alkylation of 4-*t*-butylphenol with isobutene and styrene. The present catalytic compositions are potentially useful catalysts in the conversion or formation of organic compounds of large molecular size, e.g. in the synthesis of fine chemicals.

2. Experimental

2.1. MATERIALS

PW crystalline hydrate was prepared from $Na_2WO_4 \cdot 2H_2O$ and NaH_2PO_4 [10] and recrystallized from water. According to ^{31}P NMR it contained >99 mol% Keggin HPA. Pure-silica MCM-41 was synthesized using the procedure of Beck et al. [5], modified by substituting the $C_{16}H_{33}(CH_3)_3NOH$ solution by equivalent amounts of $C_{16}H_{33}(CH_3)_3NCl$ and NaOH [11]. Silica sources were HiSil (PPG Industries) and tetramethylammonium silicate. The reaction mixture was statically heated in a polypropylene bottle at 100°C for 48 h. The resulting solid product was recovered by filtration, washed with deionized water, dried in air at ambient temperature and then calcined in air at 540°C for 10 h. XRD patterns for the prepared material (fig. 1, curve 1) are in good agreement with the literature data [5,9]. So are its surface area and porosity. From N_2 adsorption isotherms the material was characterized as having a BET surface area of 1200 m^2/g, uniform pores 32 Å in size and with a pore volume of 0.95 ml/g.

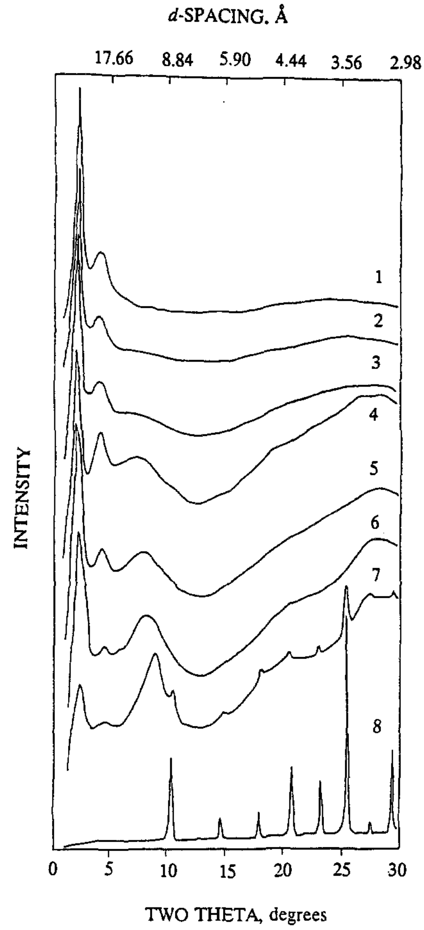


Fig. 1. XRD patterns: (1) MCM-41, (2) 10 wt% PW/MCM-41, (3) 20 wt% PW/MCM-41, (4) 30 wt% PW/MCM-41, (5) 40 wt% PW/MCM-41, (6) 50 wt% PW/MCM-41, (7) 70 wt% PW/MCM-41, (8) PW+MCM-41 1 : 9 (wt) physical mixture.

The catalysts were prepared by shaking MCM-41 (1.0 g) with a PW aqueous solution (10 ml, 0.01–0.1 g HPA/ml) at room temperature overnight. The product was dried at room temperature in vacuum over P_2O_5.

Isobutene ⩾99% (Fluka AG) and 4-*t*-butylphenol 97% (Janssen Chimica) were used without purification. Styrene was distilled prior to use.

2.2. TECHNIQUES

2.2.1. NMR spectroscopy

161.90 MHz ^{31}P MAS NMR spectra were measured at room temperature on a Varian VXR-400S spectrometer, equipped with a Doty Scientific 5 mm Solids MAS Probe. A few hundred transient responses from 4 μs (45° flip angle) pulses, with repetition time of 2.0 s were collected. Spin rate 6 kHz. Exponential multiplication with 3 Hz line-broadening was applied prior to Fourier transformation. 1% H_3PO_4 in D_2O was used as an external reference. Special care was taken to protect solid samples from moisture.

2.2.2. *Infrared spectroscopy*

FT-IR spectra were recorded on a Bruker IFS 66 spectrometer in KBr pellets over the range of 600–1300 cm^{-1} under atmospheric conditions without special precautions.

2.2.3. *X-ray diffraction*

XRD measurements were carried out on a Philips PW 1840 diffractometer using monochromatized Cu Kα radiation. Patterns were recorded over the range from 1 to 30° (2θ) in steps of 0.02° with a count time of 1 s at each point.

2.2.4. *Nitrogen physisorption measurements*

BET surface areas and pore size distributions of the catalysts were calculated from N_2 adsorption isotherms at 77 K in a Micromeritics ASAP 2400 equipment.

2.3. REACTIONS

The alkylation of 4-*t*-butylphenol (TBP) with isobutene and styrene was carried out in a 75 ml glass reaction vessel equipped with a magnetic stirrer, a condenser and a gas inlet. The reactor was charged with the substrate (1.0 g) and a hydrocarbon solvent (1–2 g) and heated to 70–90°C. Then the catalyst was added and the olefin supply was started. Gaseous isobutene was supplied at a constant flow rate of 15 ml/min. For the rate of the TBP alkylation with isobutene to be estimated, the stirring intensity was kept high enough to overcome gas–liquid diffusion limitations on the reaction rate. Styrene was fed dropwise over a 1–2 h period during the reaction. The reactions were followed by GLC (a Packard 428 gas chromatograph, 50 m × 0.5 mm capillary column with CP Sil 5 CB stationary phase). Products were identified by GLC-MS (a VG70-250S/SE instrument) as well as by GLC, using authentic samples. All the PW containing catalysts were dried at room temperature in vacuum and stored over P_2O_5.

3. Results and discussion

3.1. CHARACTERIZATION OF PW/MCM-41 CATALYSTS

3.1.1. *XRD patterns*

Fig. 1 shows the XRD patterns for the initial MCM-41 and the PW/MCM-41 catalysts with various HPA loadings. The starting MCM-41 has a typical XRD pattern [5,9]; the sample exhibits a very strong peak at a *d*-spacing of 39.9 Å and weak peak(s) at 19.5 Å.

On HPA loading, the intensity of the peak at 39.9 Å decreases, as expected. With HPA content increasing from 10 to 70 wt%, a featureless broad bump appears in the region of XRD patterns of crystalline PW, $2\theta > 10°$. Another narrower bump of unknown origin is gradually rising at 8–9° (2θ). However, no patterns from the PW crystal phase are observed even at an HPA loading as high as 50 wt%; only at 70 wt% HPA content such pattern can be seen. Note that a 1 : 9 wt/wt physical mixture of PW and MCM-41 clearly shows the pattern of the HPA crystal phase. Therefore, the XRD data indicate that PW is finely dispersed on the MCM-41 surface, no HPA crystallinity being observed at an HPA loading as high as 50 wt%. This result can be explained by the easy access of HPA molecules (ϕ 12 Å) to the MCM-41 mesopores and the huge surface area of the material (1200 m^2/g). Assuming the cross-sectional area of the HPA molecule to be equal to 100 Å, one can calculate that, at 50 wt% PW loading, HPA occupies at most only 1/6 of the MCM-41 total surface area. Recently we have obtained similar results for HPAs supported on activated carbon [12]. In contrast, when loading HPA on amorphous silica (S_{BET} 200–300 m^2/g), HPA crystallinity already appears at ca. 20 wt% HPA content [13,14].

3.1.2. Surface and porosity

Table 1 shows BET surface areas (S_{BET}), mean pore diameters (d), and pore volumes (V_p) for the starting MCM-41 and the samples loaded with 20 and 40 wt% PW/MCM-41, as calculated from N_2 physisorption. S_{BET}, d and V_p all decrease when loading PW on MCM-41. However, even at high HPA loading the materials have rather large surface areas and, most importantly, they retain the uniformity of their mesopores. Thus, 40 wt% PW/MCM-41 has S_{BET} 580 m^2/g and uniform pores 30 Å in diameter. The pore size distribution for this sample is shown in fig. 2.

3.1.3. ^{31}P MAS NMR spectra

^{31}P NMR is the most revealing method for examining the state of phosphorous heteropoly compounds [15]. Fig. 3 shows ^{31}P MAS NMR spectra for bulk PW and PW/MCM-41. The spectrum for bulk PW agrees well with the literature data

Table 1
Surface and porosity of PW/MCM-41

Sample	T_{max} [a] (°C)	S_{BET} (m^2/g)	d (Å)	V_p (ml/g)
MCM-41	300	1200	32	0.95
20 wt% PW/MCM-41	250	970	30	0.65
40 wt% PW/MCM-41	250	580	30	0.38

[a] Pretreatment temperature.

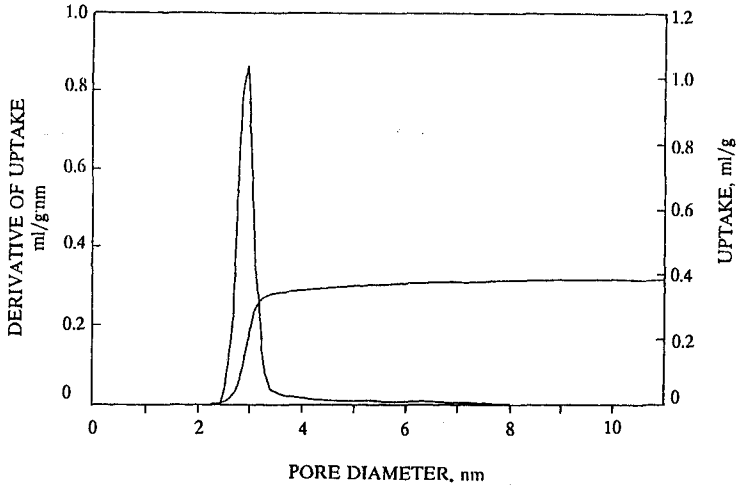


Fig. 2. Pore size distribution for 40 wt% PW/MCM-41 calculated from N_2 adsorption isotherms.

[16,17]. It consists of one single line at ~ 15.8 ppm, $\Delta\nu_{1/2} = 55$ Hz. It should be noted that in this case the chemical shift and linewidth depend on the water content in the sample, ranging from −15.0 to −15.8 ppm and from 50 to 65 Hz, respectively, in our experiments.

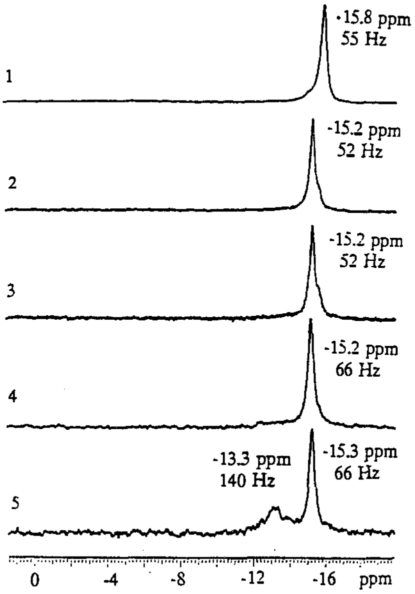


Fig. 3. ^{31}P MAS NMR spectra (ref.: external 1% H_3PO_4 in D_2O): (1) PW, (2) 50 wt% PW/MCM-41, (3) 40 wt% PW/MCM-41, (4) 30 wt% PW/MCM-41, (5) 20 wt% PW/MCM-41. The chemical shifts and $\Delta_{1/2}$ are given for each peak. The samples were dried at room temperature in vacuum and stored over P_2O_5.

The PW/MCM-41 samples with higher PW content (30–50 wt%) exhibit practically the same spectra as bulk PW. This indicates unambiguously that the Keggin structure is retained when loading PW on MCM-41. The same was found earlier for silica-supported PW [17]. In contrast, the spectra for PW/MCM-41 at lower PW content show a partial decomposition of the Keggin structure. Thus, in the spectrum of 20 wt% PW/MCM-41, besides the intense line of PW, there is another resonance of lower intensity at −13.3 ppm, $\Delta\nu_{1/2} = 140$ Hz. This line may well be assigned to lacunary (defect) heteropoly anions such as, e.g. $PW_{11}O_{39}^{7-}$ and $P_2W_{17}O_{61}^{10-}$, or unsaturated anions like $P_2W_{18}O_{62}^{6-}$ and $P_2W_{21}O_{71}^{6-}$ [15], which can be formed via the decomposition of the PW Keggin structure. The question arises what causes the decomposition. It may be either chemical interaction of PW with the support, or destruction of PW in the impregnating aqueous solution [12]. The latter seems to be the most probable, because otherwise the line at −13.3 ppm should also be present in the spectra of 30–50 wt% PW/MCM-41. It is known that the PW anion decomposes in aqueous solution at $pH \geqslant 2$ to form the lacunary $PW_{11}O_{39}^{7-}$ anion [15]. This may well be the case when preparing PW/MCM-41 compositions with lower PW content, for, when preparing 20 wt% PW/MCM-41, one has to use a highly diluted $\sim$ 1 wt% PW impregnating solution (pH $\approx$ 2). Under such conditions, basic impurities in MCM-41 can possibly promote the decomposition of PW. Furthermore, we earlier observed the decomposition of PW in the case of carbon-supported PW at lower HPA content [12].

3.1.4. FT-IR spectra

FT-IR spectra of bulk PW as well as of 20 and 30 wt% PW/MCM-41 are shown in fig. 4. The spectrum of bulk PW is in good agreement with the spectra reported

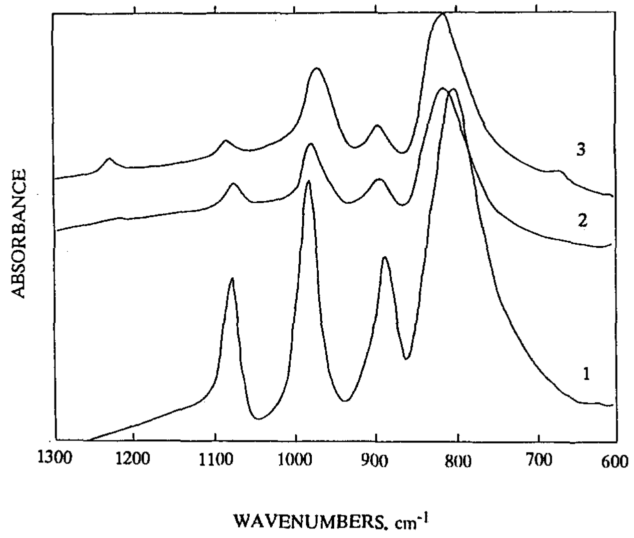


Fig. 4. FT-IR spectra (KBr): (1) PW, (2) 30 wt% PW/MCM-41, (3) 20 wt% PW/MCM-41.

elsewhere [18] (cm^{-1}): 1081 (P–O), 985 (W=O) and 897, 803 (W–O–W). The spectrum of 30 wt% MCM-41 agrees well with that of bulk PW. This supports our conclusion from ^{31}P NMR data, that the PW Keggin structure is retained in this sample. It is seen that the bands for outer groups (W=O, corner- and edge-bridging W–O–W) show small 4–12 cm^{-1} shifts compared to that in the spectrum of bulk PW, probably due to chemical interaction between the HPA anion and the MCM-41 inner surface. The magnitude of the shifts is the same as for outer-sphere cation effects on the vibrational spectra of HPAs [18]. The spectrum of 20 wt% PW/MCM-41 contains a band at 1232 cm^{-1} besides the bands typical of HPA. This may indicate the partial decomposition of HPA, in agreement with our NMR data.

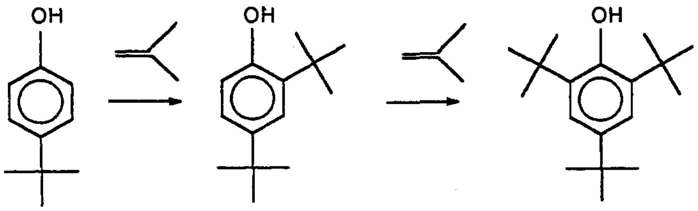
3.2. CATALYTIC TESTING

The catalytic performance of the PW/MCM-41 compositions is demonstrated in the liquid-phase alkylation of 4-*t*-butylphenol (TBP) with olefins such as isobutene and styrene. Bulk and SiO_2-supported tungsten HPAs have been found to be excellent catalysts for the alkylation and dealkylation of phenols that are widely used in organic synthesis [6]. In these reactions, HPAs are far more active than many of the conventional acid catalysts, e.g. H_2SO_4, SiO_2–Al_2O_3, acidic ion-exchange resins, etc. The acid-catalyzed alkylation of phenols with olefins proceeds via the interaction of carbenium ion, generated from the olefins, with the phenol. The ortho-alkylation of TBP with HPAs has been studied recently [19]. This reaction probably proceeds via the intermediate formation of an ether, followed by its rearrangement to the ortho-alkylated product [18].

The purpose of the present study of the alkylation of TBP is: (1) to compare the catalytic activity of PW/MCM-41 with that of other acid catalysts, such as H_2SO_4, bulk PW, and SiO_2-supported PW, in order to estimate the acidity of PW/MCM-41; and (2) to test whether or not the selectivity of this catalyst is sensitive to the substrate molecular size (shape selectivity). The acid properties of PW supported on amorphous SiO_2 have been studied in detail (ref. [6] and references therein). The acid strength of PW/MCM-41 is probably the same as that of PW/SiO_2.

3.2.1. Alkylation of TBP with isobutene

The ortho-*t*-butylation of TBP is a consecutive reaction to give 2,4-di-*t*-butylphenol (DTBP) followed by 2,4,6-tri-*t*-butylphenol (TTBP):



Isobutene oligomers are also formed as side products, mainly at the end of the reaction. With all the HPA catalysts the reaction is a heterogeneous one under the conditions studied. So the reaction practically stops as the catalyst is filtered off.

Fig. 5 shows typical kinetic curves for the homogeneous (with H_2SO_4) and heterogeneous (with PW based catalysts) alkylation of TBP. In the homogeneous reaction, both the first and the second step are fairly fast, finally yielding 90% TTBP. In the heterogeneous reaction, the first step is also fast, but the second one goes rather slowly, probably due to a significant steric hindrance for the conversion of bulky DTBP on the catalyst surface. This results in a significantly higher selectivity to DTBP at the expense of TTBP in the heterogeneous process.

Table 2 presents the catalytic activities in terms of the half-times, $\tau_{1/2}$, of TBP conversion in the first step as well as the selectivities to DTBP and TTBP at a 95% TBP conversion for all the catalysts studied. Bulk PW and H_2SO_4 show almost the same activity in terms of the rate per equal catalyst weight. But in terms of the rate per equal amount of accessible protons, in agreement with data [19], PW is 10^4 times more active than H_2SO_4 (estimated, assuming S_{BET} 1 m^2/g for bulk PW and a cross-sectional area of 100 $Å^2$ for the PW molecule). The PW/MCM-41 compositions are three to four times more active than bulk PW per unit weight of PW. This is apparently due to the fine PW dispersion on the MCM-41 surface, providing far more surface proton sites than bulk PW. It is noteworthy that PW supported on MCM-41 and on amorphous SiO_2 have the same activity, which, as expected, indicates the similarity of their acid strengths. $PW/SiO_2-Al_2O_3$ shows the lowest activity of all the catalysts studied. A possible explanation for this is the interaction of HPA with the Al^{3+} cation [6].

As to selectivity, all the PW based solid catalysts, including PW/MCM-41, show practically the same performance in this reaction, sharply differing from

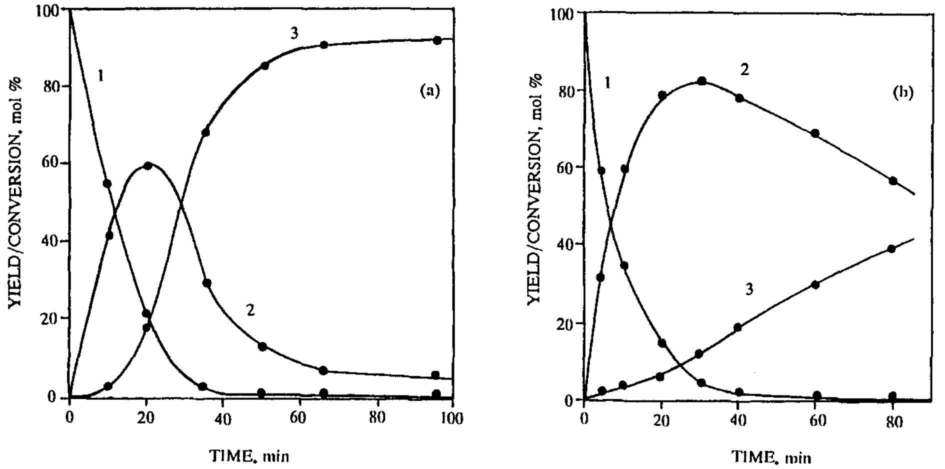


Fig. 5. Plot of yield/conversion versus time for the TBP alkylation with isobutene catalyzed by (a) H_2SO_4 (5.0 wt%) and (b) 50 wt% PW/MCM-41 (2.5 wt%) in benzene (70°C, TBP/C_6H_6 50 : 50 wt/wt): (1) TBP, (2) DTBP, (3) TTBP.

Table 2
Alkylation of TBP with isobutene in benzene (70°C, TBP/C_6H_6 50 : 50 wt/wt)

Catalyst[a]	Amount[b] (wt%)	$\tau_{1/2}$[c] (min)	Selectivity[d] (mol%)	
			DTBP	TTBP
97% H_2SO_4	2.5	21	46	54
Amberlyst-15	5.0	41	57	43
PW	2.5	15	89	11
20% PW/MCM-41	2.5	20	86	14
40% PW/MCM-41	2.5	11	87	13
50% PW/MCM-41	2.5	8	91	9
20% PW/SiO_2[e]	2.5	20	89	11
20% PW/SiO_2–Al_2O_3[f]	5.0	125	87	13

[a] All the PW catalysts were prepared by impregnation, dried at room temperature in vacuum and stored over P_2O_5.

[b] The percentage of the catalyst based on the total amount of the reaction mixture.

[c] The half-time of the TBP conversion.

[d] The selectivity based on TBP at 95% TBP conversion, 0.5–1 h.

[e] As a carrier Aerosil 380 (Degussa AG) was used.

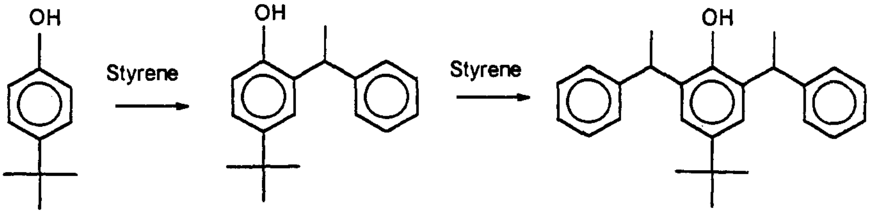
[f] As a carrier an amorphous aluminosilicate LA-SHPV 708 (AKZO) with S_{BET} 539 m^2/g and Si/Al 20 was used.

H_2SO_4 and the related catalyst Amberlyst-15. The PW catalysts allow to obtain the more valuable intermediate product DTBP in a 86–91% selectivity at a 95% TBP conversion, whereas H_2SO_4 gives only 46% selectivity. More generally, the HPA catalyzed *t*-butylation may be useful for obtaining 4-alkyl-2-*t*-butylphenols which are important intermediates in organic synthesis.

Therefore, in the TBP *t*-butylation, PW/MCM-41 shows higher catalytic activity compared to H_2SO_4 and bulk PW. However, in this case, the regularity of the MCM-41 pore system provides no advantage in selectivity over bulk and SiO_2-supported PW.

3.2.2. Alkylation of TBP with styrene

This reaction gives more bulky alkylation products: 2-(1-phenylethyl)-4-*t*-butylphenol (I) and 2,6-bis-(1-phenylethyl)-4-*t*-butylphenol (II) as well as a small amount of DTBP and its alkylation product together with styrene oligomers [19]:



I II

In this case, the uniformly-sized mesoporous PW/MCM-41 does show advantages in selectivity over bulk non-porous PW and PW supported on amorphous silica.

Three systems have been tested: 40 wt% PW/MCM-41, bulk PW and 40 wt% PW/SiO_2. The latter has a significant fraction of PW in the crystalline phase [14]. Table 3 presents the selectivities of the TBP alkylation with styrene at 90 and 99% TBP conversions. As seen, at 90% TBP conversion, PW/MCM-41 shows a three times higher selectivity to I than the other two catalysts. At 99% TBP conversion, all three catalysts perform more or less the same, providing 60–73% II, the least again with PW/MCM-41. Apparently, these results can be explained in terms of size selectivity. Since II is too bulky, there may be certain restraints on the formation of the corresponding transition state. Indeed, the size of the II molecule is comparable with the dimension of the free size in MCM-41 mesopores (~ 20 Å), which is equal to the difference between the mean pore diameter (32 Å) and the diameter of the PW molecule (12 Å). Clearly, this is not the case with non-porous bulk PW. Nor can such limitations play any significant role in the case of big PW crystallites supported on amorphous silica.

4. Conclusion

For the first time, solid acid catalytic compositions comprising a recently developed mesoporous pure siliceous molecular sieve MCM-41 and Keggin-type heteropoly acid PW have been prepared and characterized. HPA retains the Keggin structure on the MCM-41 surface and forms finely dispersed HPA species. No HPA detectable crystal phase is developed at HPA loading even as high as 50 wt%. Compared to bulk HPA, which has a small surface area of 1–5 m^2/g and, therefore, few surface acid sites, the PW/MCM-41 materials have a large number of surface acid sites. These materials have strong Brønsted sites provided by HPA, with the acid strength being about the same as that of PW supported on an amorphous silica. At the same time, they have a large surface area and, most importantly, their

Table 3
Alkylation of TBP with styrene in *n*-octane (150°C, TBP/styrene 1 : 1.2 mol/mol, TBP/*n*-octane 1 : 2.5 wt/wt, 4.0 wt% catalyst, 1.5–2 h)

Catalyst[a]	Selectivity[b] (mol%)		
	I	II	other products[c]
PW	23 (17)	68 (73)	9 (10)
40% PW/MCM-41	66 (27)	21 (60)	13 (13)
40% PW/SiO_2	24 (20)	64 (69)	12 (11)

[a] See table 2.

[b] The selectivity based on TBP at 90% TBP conversion; in parentheses at 99% TBP conversion.

[c] DTBP and 6-(1-phenylethyl)-2,4-di-*t*-butylphenol.

pores are regularly spaced and narrowly distributed in size (pore diameter ≈ 30 Å). These new catalytic compositions may be useful in acid-catalyzed conversions of organic compounds of large molecular size with steric configurations too bulky to undergo similar reactions with conventional large pore size zeolites such as zeolite Y, beta, etc. They may be particularly useful for catalyzing relatively low-temperature reactions in the liquid phase, e.g. for the synthesis of organic (fine) chemicals.

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