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# Study of catalysts comprising heteropoly acid $H_3PW_{12}O_{40}$ supported on MCM-41 molecular sieve and amorphous silica

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## Abstract

With the aim of obtaining pure Keggin-type heteropoly acid (HPA) species on siliceous surfaces, the preparation of HPA catalysts, comprising of 10 to 50 wt.%  $H_3PW_{12}O_{40}$  (PW) supported on an amorphous silica or a mesoporous all-silica molecular sieve MCM-41, was studied. The state of HPA on the siliceous surface was characterized by  $^{31}P$  NMR, XRD and TEM. Impregnating MCM-41 or amorphous  $SiO_2$  with an aqueous solution of PW gave catalysts with, in general, two HPA species: one with intact Keggin structure (A) and the other with a different structure (B), supposedly,  $H_6P_2W_{18}O_{62}$  ( $P_2W_{18}$ ) and/or  $H_6P_2W_{21}O_{71}$  ( $P_2W_{21}$ ). The relative amount of species A and B depends on HPA loading, with A dominating. At higher loadings, 30–50 wt.%, A is practically the only one present on the surface; at lower loadings, both species exist, the amount of B increasing as the HPA loading decreases. In contrast, catalysts prepared by impregnation with a methanol solution of HPA contained exclusively Keggin-type A over the whole range of PW loading. In the PW/MCM-41 catalysts, as shown by TEM, the PW species are mainly located inside the MCM-41 pores. The B species was about 8 times as active as A in the liquid-phase trans-de-*t*-butylation of 2,6-di-*t*-butyl-4-methylphenol.

**Keywords:** Heteropoly acid  $H_3PW_{12}O_{40}$ ; MCM-41 molecular sieve; Silica;  $^{31}P$  NMR; XRD; TEM; Trans-de-*t*-butylation of 2,6-di-*t*-butyl-4-methylphenol

## 1. Introduction

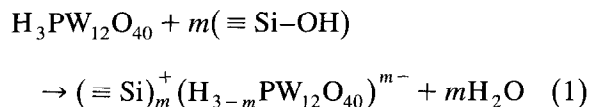
Keggin-type heteropoly acids (HPAs),  $H_{8-x}XM_{12}O_{40}$ , where X is the central atom ( $Si^{4+}$ ,  $P^{5+}$ , etc.),  $x$  its oxidation state and M the metal ion ( $Mo^{6+}$ ,  $W^{6+}$ ), are widely used as

acid catalysts due to their very strong Brønsted acidity and special structural properties [1–6]. Usually, tungsten HPAs are preferred over molybdenum HPAs as acid catalysts because of their stronger acidity, higher thermal stability and lower oxidation potential [6].  $H_3PW_{12}O_{40}$  (PW) — the strongest acid in the HPA series — is particularly recommended [6]. Supported HPA catalysts are important for applications, as bulk HPAs have a low specific surface ( $< 10 \text{ m}^2 \text{ g}^{-1}$ ). Acidic or neutral substances such as

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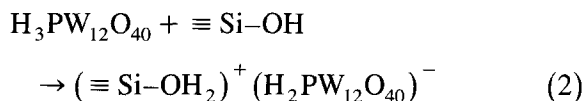
SiO<sub>2</sub>, active carbon, acidic ion-exchange resin, etc., are all suitable as supports, but SiO<sub>2</sub>, which is relatively inert towards HPAs, is the most often used ([1] and references therein). Recently, HPAs supported on the new all-silica mesoporous molecular sieve MCM-41 have attracted interest as a promising solid acid catalyst for conversion and formation of large organic molecules [7,8]. The PW/MCM-41 compositions, having uniformly sized mesopores of around 30 Å, were shown to exhibit a high catalytic activity and shape selectivity in liquid-phase phenol alkylation [7].

The state of HPAs on the SiO<sub>2</sub> surface has been reviewed recently [1]. According to earlier IR and XRD studies, PW retains the Keggin structure when supported on SiO<sub>2</sub>. However, recent investigations with <sup>31</sup>P MAS NMR, which is the most useful probe of the state of heteropolyphosphates so far [9], showed that the state of PW on SiO<sub>2</sub> is more complex, and that a chemical interaction between HPA and SiO<sub>2</sub> takes place. Supporting PW on SiO<sub>2</sub> was found to result in a shift as well as a line-broadening in the <sup>31</sup>P NMR spectrum, indicating a distortion of the HPA structure compared with that in bulk HPA [10]. <sup>1</sup>H MAS NMR [10] and microcalorimetry [11] also showed the interaction of PW with SiO<sub>2</sub> and the formation of a new type of proton sites on the silica surface, resulting in a decrease of the HPA acid strength. Protonation of surface Si–OH groups followed by dehydration was suggested ( $1 \leq m \leq 3$ ) [10]:



In a more recent <sup>31</sup>P NMR study [12] of a series of PW/SiO<sub>2</sub> catalysts, with HPA loading ranging from 13 to 87 wt.%, two partially resolved peaks were detected, one at –15.1 ppm and the other at –14.5 ppm from external 85% H<sub>3</sub>PO<sub>4</sub>. These were assigned to the bulk crystalline PW and to the ‘interacting’ form, ( $\equiv \text{Si}-\text{OH}_2$ )<sup>+</sup>(H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub>)<sup>–</sup>, respectively, the relative

amount of the latter increasing as HPA loading decreases. The interacting species may be formed by proton transfer according to (2):



Two species, resonating at –15.2 and +3.2 ppm, were found by <sup>31</sup>P NMR in SiO<sub>2</sub>-supported PW calcined at 300°C [13]. In PW/MCM-41, HPA retains the Keggin structure at HPA loadings above 20 wt.%, but at lower loadings two forms were also observed by <sup>31</sup>P NMR with well-resolved signals at –15.3 and –13.3 ppm [7]. The first one was attributed to finely dispersed HPA molecules, retaining the Keggin structure, and the second to a lacunary or unsaturated species, such as PW<sub>11</sub> and P<sub>2</sub>W<sub>17</sub> or P<sub>2</sub>W<sub>18</sub> and P<sub>2</sub>W<sub>21</sub>, which have similar lines in <sup>31</sup>P NMR solution spectra [9]. Therefore, at least two species originating from PW were detected on the SiO<sub>2</sub> surface; their amount depends on the HPA loading and probably on the preparation conditions.

In this work we have studied the preparation of HPA catalysts comprising PW supported on a mesoporous all-silica molecular sieve MCM-41 and on an amorphous SiO<sub>2</sub>, with the aim of obtaining certain HPA forms on the siliceous surface. The catalysts were characterized by <sup>31</sup>P MAS NMR, XRD and TEM and tested in the liquid-phase trans-de-*t*-butylation of 2,6-di-*t*-butyl-4-methylphenol.

## 2. Experimental

### 2.1. Materials

H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> · 24H<sub>2</sub>O from Janssen Chimica, containing > 99 mol% Keggin HPA (from <sup>31</sup>P NMR), was used. H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> (α/β 4:1) (P<sub>2</sub>W<sub>18</sub>) was synthesized by a known procedure [14] and purified by multiple extraction with diethyl ether; <sup>31</sup>P NMR in aqueous solution for

$\alpha$ - $P_2W_{18}$ :  $-13.0$  ppm (lit.  $-12.7$  ppm [9]); for  $\beta$ - $P_2W_{18}$ :  $-11.5$  and  $-12.2$  ppm (lit.  $-11.0$  and  $-11.6$  ppm [9]).  $H_6P_2W_{21}O_{71}$  ( $P_2W_{21}$ ) was prepared by an electromembrane method [15];  $^{31}P$  NMR in aqueous solution:  $-13.5$  ppm (lit.  $-13.3$  ppm [9]). Aerosil 380 (Degussa), was used as the amorphous silica support. All-silica mesoporous molecular sieve MCM-41 was synthesized according to a literature procedure [16]. The material showed a typical XRD pattern (Fig. 1) with a  $d_{100}$ -,  $d_{110}$ - and  $d_{200}$ -spacing of 38, 22 and 19 Å, respectively, and, from nitrogen physisorption, had a multipoint BET surface area of 1250 m<sup>2</sup>/g, pore volume of 0.93 cm<sup>3</sup>/g and uniform pores 32 Å in size.

The catalysts comprising of 10 to 50 wt.% HPA on a siliceous support were prepared by shaking a suspension of Aerosil 380 or MCM-41 (0.5–1 g) in an aqueous (3–5 ml) or methanol (around 30 ml) solution, containing a certain amount of HPA, in a glass vessel from 1 to ca. 20 h (overnight) at room temperature. The pH of the impregnating aqueous solution varied from 1 to 2 depending on the HPA loading. Evaporation of the suspensions was carried out below 60°C using a rotary vacuum evaporator. Unless otherwise stated, the catalysts were

mildly calcined at 130°C/0.3 mmHg for 1.5 h and stored in a desiccator over  $P_2O_5$ .

## 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 as described elsewhere [7]. 1%  $H_3PO_4$  in  $D_2O$  was used as an external reference. Special care was taken to protect solid samples from moisture. The accuracy of the chemical shift determination was within  $\pm 0.4$  ppm.

### 2.2.2. X-ray diffraction

XRD measurements were carried out on a Philips PW 1840 diffractometer using monochromatized Cu K $\alpha$  radiation. Patterns were recorded over the range from 0 to 40° ( $2\theta$ ) in steps of 0.02° with a count time of 2 s at each point.

### 2.2.3. Transmission electron microscopy

Transmission electron microscopy (TEM) was performed with a Philips CM 30 ST electron

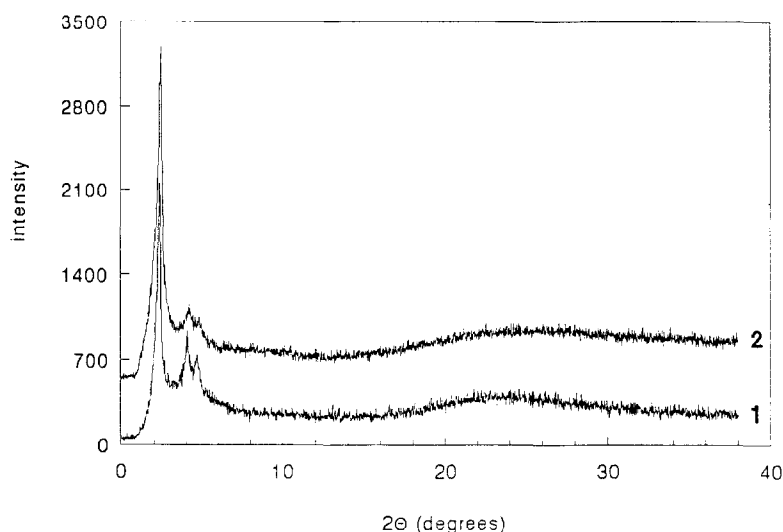


Fig. 1. XRD patterns for MCM-41 (1) and 10% PW/MCM-41 (from MeOH, 20 h) (2).

microscope with a field emission gun operated at 300 kV and equipped with an energy dispersive X-ray (EDX) element analysis system. The samples were prepared as follows. The ground PW/MCM-41 and PW/SiO<sub>2</sub> samples were suspended in n-hexane. A copper grid coated with a microgrid carbon polymer was loaded with a few drops of this suspension.

### 2.3. Reactions

Liquid-phase trans-de-*t*-butylation of 2,6-di-*t*-butyl-4-methylphenol (DBMP) with *o*-xylene as *t*-butyl group acceptor and suspended solid HPA catalysts was carried out as described elsewhere [17]. DBMP (Janssen Chimica, 99%) was used without purification. The products — 2-*t*-butyl-4-methylphenol, *p*-cresol and 1,2-dimethyl-4-*t*-butylbenzene — were analyzed by GLC (a Varian Star 3400 CX instrument with 25 m × 0.32 mm CP Sil 5 CB column) using undecane as internal standard.

## 3. Results

Having observed different HPA forms in PW/MCM-41 [7] and also in PW/C catalysts [18], we supposed that PW could partially decompose to form lacunary and/or unsaturated HPA species when preparing the catalysts. In particular, this is likely at low HPA loadings, i.e. at a low PW concentration in the impregnating solutions [7,18]. In aqueous solution, Keggin HPAs are known to decompose as the pH increases up to a certain level. Thus PW transforms to lacunary PW<sub>11</sub>O<sub>39</sub><sup>7-</sup> (PW<sub>11</sub>) species at pH ≥ 2 [9,19], which is close to the pH in our impregnating solutions. This process may be promoted by a solid support, especially if the latter includes basic impurities. On the other hand, Keggin HPAs are more stable in polar organic solvents than in aqueous solutions [6], which could be used for the preparation of supported HPA catalysts to prevent the decomposition of the Keggin-type species. Methanol is

a particularly useful organic solvent due to its high stability towards acids and the high solubility of PW therein. It is easily removed from the catalysts.

The conditions of catalyst preparation and pretreatment may also influence the stability of supported HPA. In this work, we used milder conditions (see Section 2) than those in the works [12,13] mentioned above.

### 3.1. PW supported on SiO<sub>2</sub>

Fig. 2 shows the <sup>31</sup>P MAS NMR spectra for bulk crystalline PW and PW/SiO<sub>2</sub> catalysts at PW loadings ranging from 10 to 50 wt.% obtained by impregnating in water. The spectrum (1) of the bulk PW is a well-known resonance at around -15 ppm and ca. 50 Hz linewidth, depending on the amount of water of crystallization in the sample. In the spectra of PW/SiO<sub>2</sub>, there are generally two lines: one (A) at around -15 ppm from the PW species with intact Keggin structure and the other (B) at around -14 ppm which reflects the presence of a species with a different structure. The relative amount of these species depends on the HPA loading, form A dominating. At higher loadings (30–50 wt.%), form A is practically the only one present on the SiO<sub>2</sub> surface. At lower loadings, both forms exist, the amount of B increasing as the HPA loading decreases, in agreement with data [12].

In aqueous systems, no decomposition of the HPA Keggin structure was observed during shaking SiO<sub>2</sub> with HPA aqueous solution (PW/SiO<sub>2</sub> 1:4 wt./wt.) at room temperature for 1 to 20 h, as evidenced by <sup>31</sup>P solution NMR after removing SiO<sub>2</sub> from the system. Thus, the transformation of the Keggin units possibly takes place during the drying of the SiO<sub>2</sub> + PW + H<sub>2</sub>O mixture at an elevated temperature and the calcination of wet catalysts. Probably as a result of this, a rather poor reproducibility of the A/B ratio was observed in parallel preparations.

Pretreating SiO<sub>2</sub> with 0.1 M HCl aqueous

solution followed by washing until neutral did not affect the state of the HPA species on the silica surface. The same occurred with MCM-41 (see below). This means that either basic impurities were absent in our supports or they did not affect HPA.

Fig. 3 shows the  $^{31}\text{P}$  MAS NMR spectra of 10–20 wt.% PW/SiO<sub>2</sub> catalysts obtained by impregnating PW into silica from MeOH for 20 h. In these catalysts, only form A was observed even at a HPA loading as low as 10 wt.%, in contrast to the impregnation from aqueous systems.

To examine the influence of the calcination temperature, two catalysts 20 wt.% PW/SiO<sub>2</sub>, one prepared in methanol and containing only form A (Fig. 3, spectrum 1), the other prepared in water and containing 40 mol% form B (Fig. 2, spectrum 5), were additionally calcined at 350°C/0.3 mmHg for 0.5 h. After the calcination, both catalysts, initially white, turned blue, and the intensity of their  $^{31}\text{P}$  resonances was somewhat reduced. However, the first one did

not change its NMR spectrum, while in the second the signal of the form B decreased and a new signal appeared at –11.6 ppm, whereas the signal of form A remained unchanged (Fig. 2, spectrum 6). This may indicate the decomposition of form B upon calcination at 350°C.

The XRD patterns for 10 and 20 wt.% PW/SiO<sub>2</sub> catalysts prepared in H<sub>2</sub>O or MeOH as well as for PW + SiO<sub>2</sub> (1:9 wt.) mixture are shown in Fig. 4. Neither of the PW/SiO<sub>2</sub> catalysts shows an HPA crystallinity regardless of the state of HPA therein. This is in agreement with the literature data [20,21] that the HPA crystal phase on the SiO<sub>2</sub> surface ( $S_{\text{BET}}$  200–300 m<sup>2</sup>/g) appears at HPA loadings above 20 wt.%.

### 3.2. PW supported on MCM-41

Fig. 5 shows the  $^{31}\text{P}$  MAS NMR spectra for 20–50 wt.% PW/MCM-41 catalysts prepared in H<sub>2</sub>O (20 h). They have already been discussed elsewhere [7]. Like PW/SiO<sub>2</sub>, the

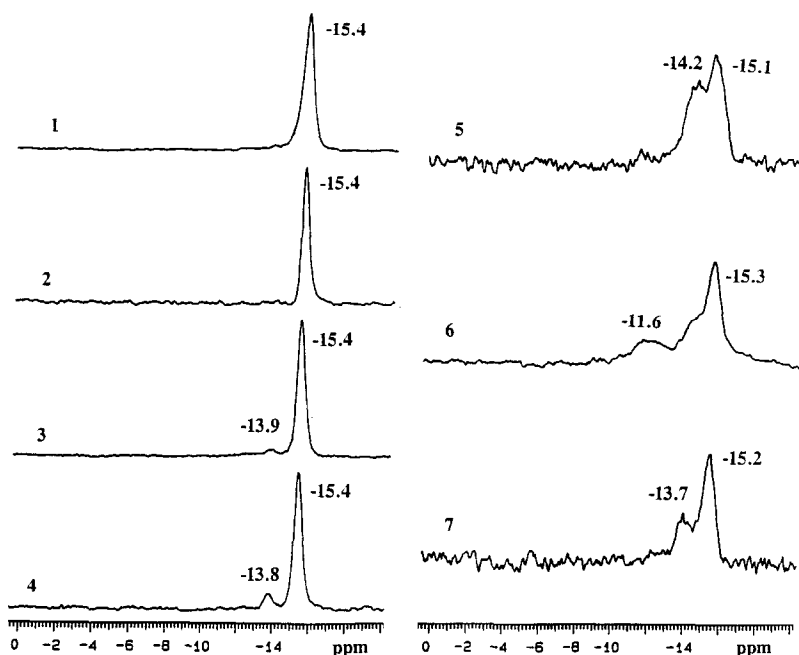


Fig. 2.  $^{31}\text{P}$  MAS NMR spectra for PW (1) and PW/SiO<sub>2</sub> (from H<sub>2</sub>O) at various PW loadings and impregnation times: (2) 50%, 3 h; (3) 40%, 20 h; (4) 25%, 20 h; (5) 20%, 3 h; (6) same sample calcined at 350°C/0.3 mmHg for 0.5 h; (7) 10%, 3 h.

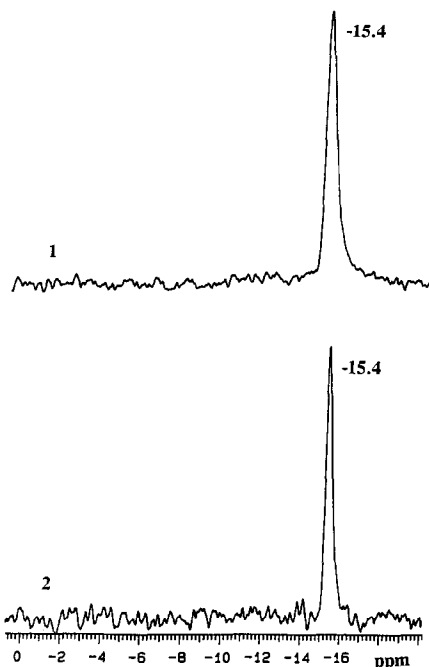


Fig. 3.  $^{31}\text{P}$  MAS NMR spectra for PW/SiO<sub>2</sub> (from MeOH, 20 h) at two PW loadings: (1) 20%; (2) 10%.

PW/MCM-41 catalysts at higher loadings, 30–50 wt.%, consist of practically pure form A, while at lower loadings form B is also present.

The  $^{31}\text{P}$  MAS NMR spectra for 10–40 wt.%

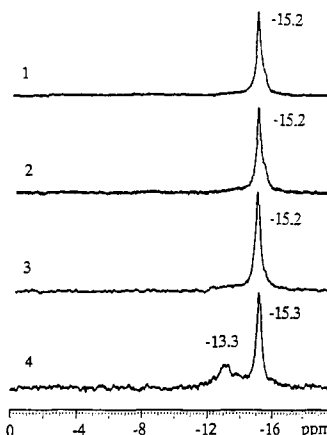


Fig. 5.  $^{31}\text{P}$  MAS NMR spectra for PW/MCM-41 (from H<sub>2</sub>O, 20 h) at various PW loadings: (1) 50%; (2) 40%; (3) 30%; (4) 20% [7].

PW/MCM-41 prepared in MeOH (20 h) are presented in Fig. 6. As is clearly seen, only form A is present in the catalysts over the whole range of PW loading, as with PW/SiO<sub>2</sub>.

As shown earlier by XRD [7], no HPA crystal phase exists in the PW/MCM-41 catalysts obtained in water at the HPA loading as high as 50 wt.% due to the huge surface area of MCM-41. Fig. 1 shows the XRD pattern for the 10 wt.% PW/MCM-41 prepared from MeOH (20

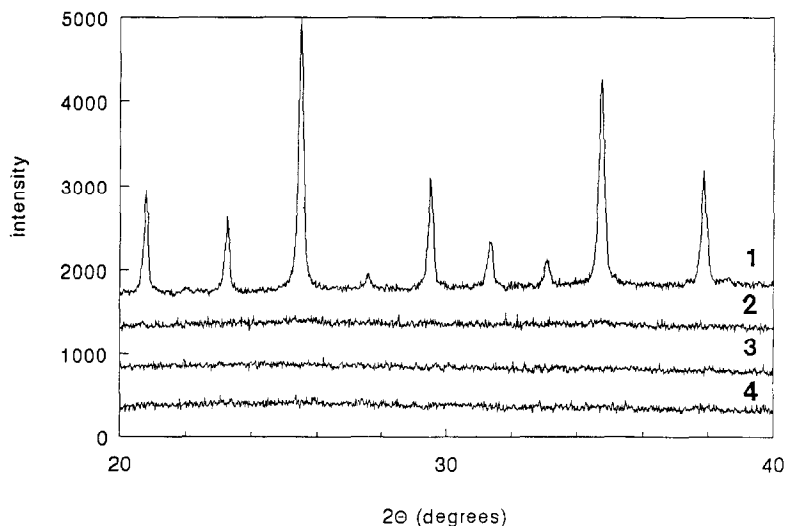


Fig. 4. XRD patterns for: (1) PW + SiO<sub>2</sub> 1:9 wt. mixture; (2) 20% PW/SiO<sub>2</sub> (from H<sub>2</sub>O, 3 h); (3) 10% PW/SiO<sub>2</sub> (from MeOH, 20 h); (4) 10% PW/SiO<sub>2</sub> (from H<sub>2</sub>O, 3 h).

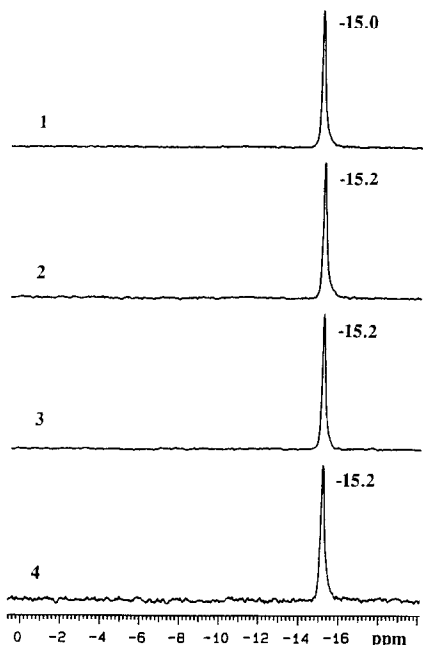


Fig. 6.  $^{31}\text{P}$  MAS NMR spectra for PW/MCM-41 (from MeOH, 20 h) at various PW loadings: (1) 40%; (2) 30%; (3) 20%; (4) 10%.

h). As expected, there is no HPA crystallinity either. In addition, the hexagonal morphology of the MCM-41 support after PW loading remained intact while the unit cell dimension was decreased from 44 to 42 Å, probably as a result of acid catalyzed condensation of silanol groups [22].

TEM analysis was performed on some PW/MCM-41 and PW/SiO<sub>2</sub> samples to determine the location and the size of the PW species which can be distinguished as dark dots in TEM images (Fig. 7 and Fig. 8). The TEM image of the MCM-41 structure is rather dominant, which makes it difficult to detect the supported PW species. For this reason the MCM-41 lattice was subjected to amorphization using the electron beam. The TEM image (Fig. 7b) of a thinner part of 40 wt.% PW/MCM-41 sample (from MeOH, 20 h) shows that in this catalyst there is practically no PW species on the edges of the MCM-41 particles. The PW species range from

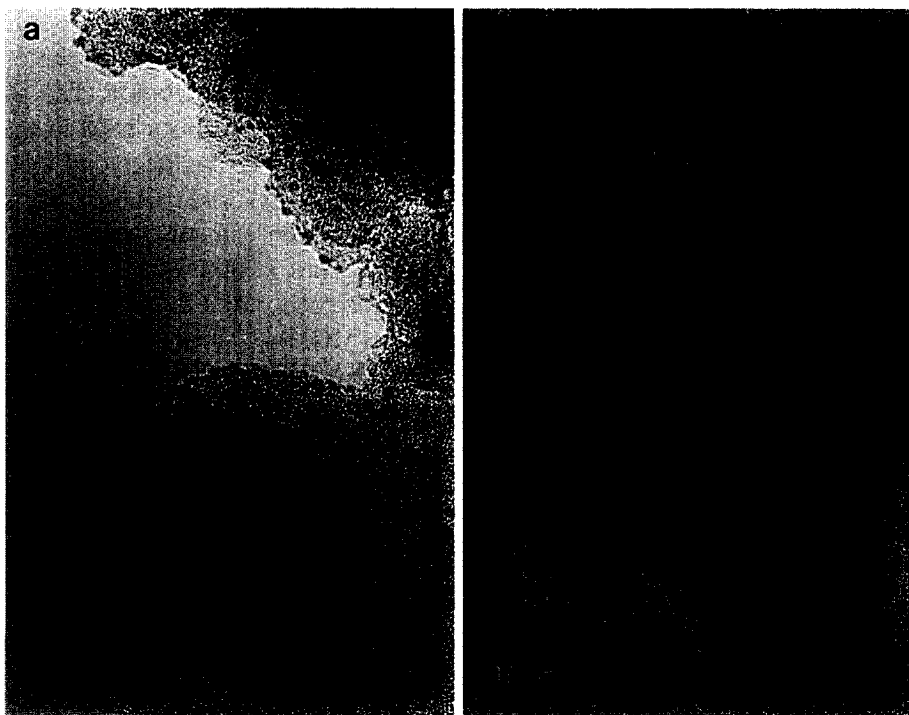


Fig. 7. TEM images: (a) 35% PW/SiO<sub>2</sub> (from H<sub>2</sub>O, 6 h) and (b) 40% PW/MCM-41 (from MeOH, 20 h) after amorphization.

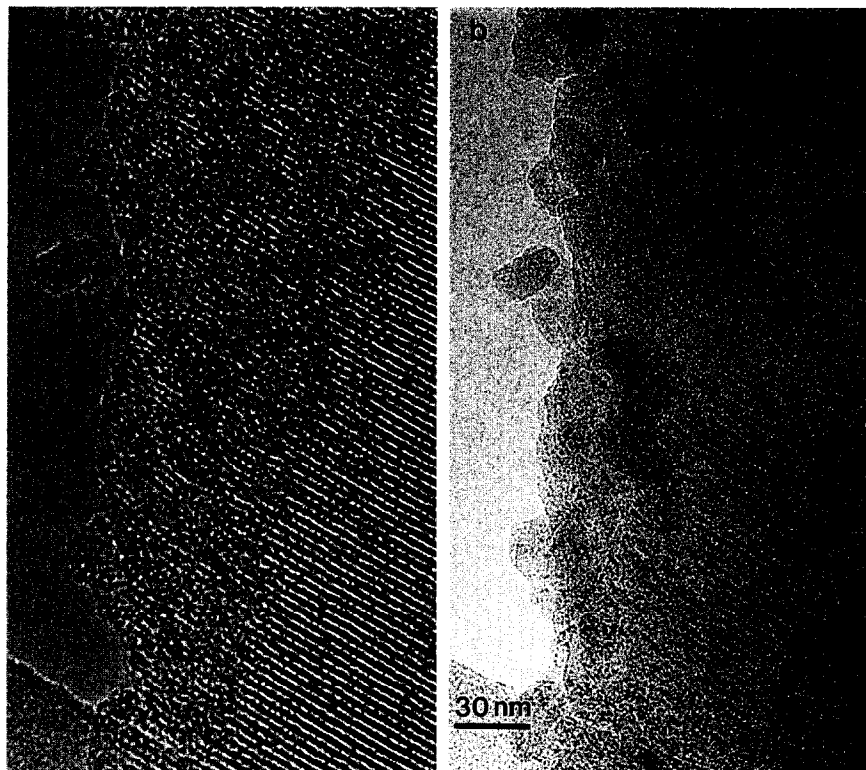


Fig. 8. TEM images of the same area of 40% PW/MCM-41 (from MeOH, 20 h): (a) before and (b) after amorphization.

10 to 15 Å close to the molecular size of HPA (12 Å). It should be noted that this is only a rough estimate because of the difficulty in size determination due to the blurring by the amorphous matrix. In contrast, in 35 wt.% PW/SiO<sub>2</sub> (from H<sub>2</sub>O, 6 h) (Fig. 7a), there are many PW species on the edges of the SiO<sub>2</sub> particles, indicating that PW is situated on the outer surface of the non-porous support. Fig. 8a and Fig. 8b show the micrographs of the same area of

the 40 wt.% PW/MCM-41 before and after amorphization, respectively. The sample before amorphization exhibits a TEM image with strong contrast dark lines indicative of the regular crystal lattice of MCM-41. Remarkably, after amorphization, the similar structure although with less contrast is observed. In this case, the dark lines originate from the PW species which were in the MCM-41 channels before the amorphization. No indication of PW clustering during

Table 1  
Trans-*de-t*-butylation of DBMP with HPA catalysts

| Catalyst   | Time <sup>a</sup> (min) | Relative activity per 1 mol HPA | Selectivity <sup>b</sup> mol% |
|--|-------------------------|---------------------------------|-------------------------------|
| 20% PW/SiO <sub>2</sub> (100% A, from MeOH)                      | 64                      | 1                               | 100                           |
| 20% PW/SiO <sub>2</sub> (60/40 A/B, from H <sub>2</sub> O)       | 27                      | 8 <sup>c</sup>                  | 100                           |
| 20% P <sub>2</sub> W <sub>18</sub> /SiO <sub>2</sub> (from MeOH) | 16                      | 6                               | 100                           |

70°C, [*o*-xylene]/[DBMP] = 20 mol/mol, 4.5 wt.% catalyst.

<sup>a</sup> Corresponding to a 30% DBMP conversion.

<sup>b</sup> Selectivity to 2-*t*-butyl-4-methylphenol.

<sup>c</sup> Activity of form B per P<sub>2</sub> entity.



amorphization was obtained. In addition, no PW species are observed on the edges of the MCM-41 particles. This is a clear indication that the PW species are mainly located inside the MCM-41 pores, which is supported by EDX elemental analysis. Thin parts of a given MCM-41 particle showed the same W/Si ratio as the much thicker parts. If PW species were mainly located on the surface, the W/Si ratio of the thick parts would be much smaller.

### 3.3. Catalyst testing

The catalysts were tested in the *trans-de-t*-butylation of DBMP (Eq. 3) as a model reaction. This reaction is of potential interest as a step in the synthesis of stabilizers [1]; it was studied in detail earlier with both bulk and SiO<sub>2</sub>-supported PW [17].

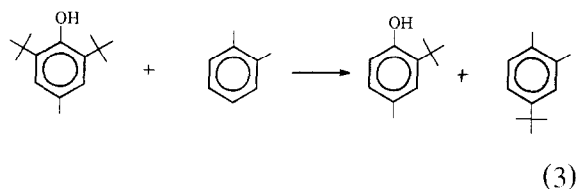


Table 1 shows the testing results for the authentic specimen 20 wt.% P<sub>2</sub>W<sub>18</sub>/SiO<sub>2</sub> (from MeOH) and two catalysts with the same loading 20 wt.% PW/SiO<sub>2</sub> obtained from methanol or water, one containing the pure form A (see Fig. 3, spectrum 1), and the other containing the maximum amount of form B, A/B 60/40 mol% based on phosphorous (Fig. 2, spectrum 5). The catalytic activity was characterized as the time corresponding to a 30% DBMP conversion, the selectivity to 2-*t*-butyl-4-methylphenol being 100%; at higher conversions, *p*-cresol was also formed as a result of the *de-t*-butylation of 2-*t*-butyl-4-methylphenol. The 60/40 mol% A/B catalyst (from H<sub>2</sub>O) appeared to be twice as active as the 100% A catalyst (from MeOH) per catalyst weight, and P<sub>2</sub>W<sub>18</sub>/SiO<sub>2</sub> was the most active in the series. It should be noted that 20 wt.% P<sub>2</sub>W<sub>21</sub>/SiO<sub>2</sub>, which might be expected

to be nearly as active as the P<sub>2</sub>W<sub>18</sub>/SiO<sub>2</sub> catalyst, showed about two times lower activity than P<sub>2</sub>W<sub>18</sub>/SiO<sub>2</sub>. This may be due to incomplete exchange of Na<sup>+</sup> by H<sup>+</sup> in the electromembrane synthesis of P<sub>2</sub>W<sub>21</sub> [15].

## 4. Discussion

Despite the relative inertness of the silica towards tungsten HPAs, the catalysts, comprising PW supported on pure siliceous supports — amorphous SiO<sub>2</sub> or mesoporous molecular sieve MCM-41 — prepared by conventional impregnation with an aqueous PW solution include at least two HPA forms, which can well be discriminated by <sup>31</sup>P MAS NMR [7,12]. One (A) with intact Keggin structure and the other (B) with a different structure. The relative amount of the two depends on the HPA loading and the preparation method. Under our conditions, form A is the dominating one, the amount of B increasing with decreasing of HPA loading. Maximally about 40 mol% form B has been observed in 20 wt.% PW/SiO<sub>2</sub> (Fig. 2, spectrum 5), which is somewhat less than that found in Ref. [12]. This may be explained by the difference in preparation conditions. It is worth noting that the pure Keggin-type PW species on SiO<sub>2</sub> or MCM-41 surface can be prepared from water at higher loadings, 30–50 wt.%.

With the less stable molybdenum HPAs, the decomposition of the Keggin units on the SiO<sub>2</sub> surface, depending on the HPA loading, was shown elsewhere [23] (for a review see [1]). Thus PMo, SiMo and PMo<sub>10</sub>V<sub>2</sub> retain the Keggin structure at high loadings, like PW, but decompose to form MoO<sub>3</sub> and practically lose their acidity at a very low loadings due to their strong interactions with surface silanol groups. On the other hand, thermally decomposed Keggin structure of molybdenum HPAs on the silica surface may be reconstructed on exposure to water vapor [23].

The important result of this work is the preparation of the catalysts, comprising the

purely Keggin-type PW species on the siliceous surface over a wide range of PW loading. This is conveniently done by PW impregnation from an organic solution, viz. methanol. The major reason why it succeeds is thought to be the greater stability of the Keggin units towards hydrolysis in organic solvents compared to aqueous solutions [6]. Both  $\text{SiO}_2$ - and MCM-41-supported PW catalysts can be prepared in this way.

Let us now consider the nature of species A and B. Earlier in the study of PW/ $\text{SiO}_2$  catalysts with higher PW loadings (up to 87 wt.%), form A was assigned to the bulk crystalline PW on the  $\text{SiO}_2$  surface, as based on the  $^{31}\text{P}$  NMR together with XRD data; the latter indeed indicated the presence of the PW crystal phase on the surface [12]. In our case, as shown by XRD, and regardless of the solvent used, no PW crystal phase is present in PW/MCM-41 at loadings in the range of 10 to 50 wt.% [7]; nor is there PW crystallinity in PW/ $\text{SiO}_2$  at the loadings below 20 wt.%. As found by TEM, these catalysts include finely dispersed species, mainly discrete PW molecules on the surface of siliceous support. In the case of PW/MCM-41, the PW species are mostly situated inside the channels rather than on the outer surface of the molecular sieve. Therefore, not only can form A be assigned to the bulk PW species on the silica surface, as in the PW/ $\text{SiO}_2$  catalysts with higher PW loadings [12], but also to the discrete surface HPA molecules with intact Keggin structure, as observed in this work. These two species have  $^{31}\text{P}$  NMR spectra similar to those of crystalline PW and PW in solution [9].

Less certain is the nature of form B. This species was supposed to be the ‘interacting’ Keggin-type HPA formed via reaction (2) [12] or the products of a partial decomposition and transformation of the Keggin structure, e.g. the lacunary species, like  $\text{PW}_{11}$  or  $\text{P}_2\text{W}_{17}$ , or unsaturated HPAs  $\text{P}_2\text{W}_{18}$  or  $\text{P}_2\text{W}_{21}$ , having  $^{31}\text{P}$  NMR solution resonances in the same region [9]. The latter seems to be more likely for the following reasons:

(1) Form B is not present in the catalysts prepared from MeOH, as expected from the greater stability of the Keggin HPAs in MeOH compared to water [6]. On the other hand, reactions (1) and (2) could proceed without any solvent on the catalyst surface and, therefore, would not be affected by solvent.

(2) Given form A for both the bulk PW and the discrete PW molecules on the surface, from the chemical point of view, there is hardly any difference between the surface PW molecule and the ‘interacting’ species like  $(\equiv \text{Si}-\text{OH}_2)^+(\text{H}_2\text{PW}_{12}\text{O}_{40})^-$ .

(3) The  $^{31}\text{P}$  MAS NMR spectra of the species  $(\equiv \text{Si}-\text{OH}_2)^+(\text{H}_2\text{PW}_{12}\text{O}_{40})^-$  and the bulk PW are unlikely to be different because PW in aqueous solution, where it is completely deprotonated [6], and the solid bulk PW with the protons localized thereon exhibits  $^{31}\text{P}$  resonances at the same positions.

The lacunary species are possibly not stable enough to sustain evaporation and calcination. More likely these species, if formed in the  $\text{SiO}_2 + \text{PW} + \text{H}_2\text{O}$  system, transform to dimeric HPAs like  $\text{P}_2\text{W}_{18}$  or  $\text{P}_2\text{W}_{21}$  and uncertain W(VI)

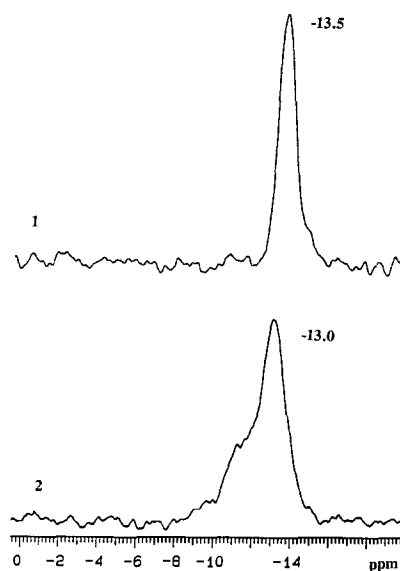


Fig. 9.  $^{31}\text{P}$  MAS NMR spectra for 20% HPA/ $\text{SiO}_2$  (from MeOH, 20 h): (1)  $\text{P}_2\text{W}_{21}/\text{SiO}_2$  and (2)  $\text{P}_2\text{W}_{18}/\text{SiO}_2$ . In the spectrum of 20%  $\text{P}_2\text{W}_{18}/\text{SiO}_2$ , the signals at  $-13.0$  and around  $-11$  ppm are from  $\alpha\text{-P}_2\text{W}_{18}$  and  $\beta\text{-P}_2\text{W}_{21}$ , respectively.

species. Mechanisms of such transformations are quite complex and scarcely understood [9]. The  $\alpha$ - $P_2W_{18}O_{62}^{6-}$  and  $P_2W_{21}O_{71}^{6-}$  heteropolyanions exhibit in the solution  $^{31}P$  NMR spectra the signals at  $-12.7$  and  $-13.3$  ppm, respectively [9]. As we found in this work,  $^{31}P$  MAS NMR spectra of 20 wt.%  $P_2W_{18}/SiO_2$  and 20 wt.%  $P_2W_{21}/SiO_2$  (from MeOH, 20 h) also have the lines at  $-13.0$  and  $-13.5$  ppm, respectively (Fig. 9), which is in agreement with the spectrum B (Fig. 2 and Fig. 5).  $P_2W_{18}$  and  $P_2W_{21}$  are thermally less stable than PW. Thus they were found to decompose at  $350^\circ C$  and showed no activity in the cracking of n-hexane at this temperature, while PW was intact and active [24]. The products of decomposition of bulk and  $SiO_2$ -supported  $P_2W_{18}$  and  $P_2W_{21}$  exhibited broad signals in  $^{31}P$  NMR spectra in the range from  $-10$  to  $-12$  ppm [24] similar to what we have observed after calcining 20 wt.% PW/ $SiO_2$ , containing 40 mol% form B, at  $350^\circ C$  (Fig. 2, spectrum 6).

Table 1 shows the relative molar catalytic activities of A, B and  $P_2W_{18}$  species on the  $SiO_2$  surface in the de-*t*-butylation of DBMP. The activity of B is in good agreement with that of  $P_2W_{18}$ , which supports our suggestion of the nature of B. Unexpectedly, B species is around 8 times more active than A despite  $P_2W_{18}$  and  $P_2W_{21}$  are nearly as strong acids as PW [15,25,26]. Possible explanation of this is that the acid strength of the surface dimeric species B decreases to a lesser extent compared to the Keggin species A due to the interaction with

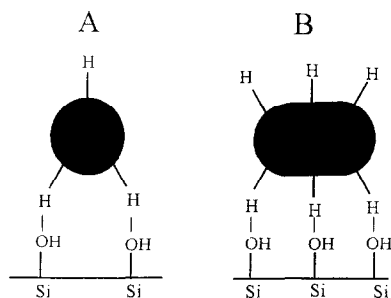


Fig. 10. The binding of A and B to the siliceous surface (schematic).

Si–OH groups, as illustrated schematically in Fig. 10. However, in high-temperature reactions the catalysts containing form B may be less active than those with pure Keggin form A due to the possible decomposition of form B, as found in n-hexane cracking [24].

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