Synthesis of dimethyldiphenylmethane over supported 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$)

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Abstract

SiO_2, MCM-41 and activated carbon supported 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, HPW) were used in the direct synthesis of dimethyldiphenylmethane ($CH_3C_6H_4CH_2C_6H_4CH_3$, DMDPMs) from toluene and formaldehyde, and characterized by FT-IR, XRD and nitrogen adsorption. It was found that SiO_2 supported HPW exhibited higher activity and DMDPMs selectivity, and the yield of DMDPMs increased with the loading amount of HPW. The best yield of DMDPMs reached 61.3% when the loading of HPW increased to 60 wt.% on SiO_2. FT-IR and XRD analysis indicated that HPW dispersed highly on the surface of these supports. Highly dispersed HPW exhibited higher activity (higher TON) than that of pure HPW. While MCM-41 suffered severe structural distortions when the loading amount of HPW is high.
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1. Introduction

Dimethyldiphenylmethane ($CH_3PhCH_2PhCH_3$, DMDPMs) is an important chemical and intermediate in the production of spices, pharmaceutics and dielectric fluid. And diphenylmethane dyes (e.g. auramine, also called as Basic Yellow, such as $NH:C[PhN(CH_3)_2]_2$) are widely used in wool, paper, leather and silk industries [1]. Typically, DMDPMs is produced by the condensation of xylene with benzyl chloride in the presence of a Friedel–Crafts catalyst such as aluminium chloride or iron chloride, which gives large amount of by-products such as polymers of benzyl chloride and several compounds having three or more benzene rings (Eq. (1)) [2,3].

$$CH_3C_6H_4CH_3 + C_6H_5CH_2Cl \rightarrow CH_3PhCH_2PhCH_3 + HCl \tag{1}$$
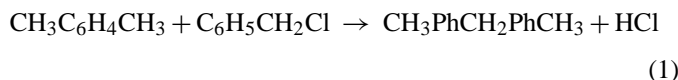
Several solid acid catalysts relevant to Friedel–Crafts reactions had been reported in order to replace conventional problematic homogeneous catalysts, such as montmorillonite-supported transition metals, the graphite–aluminum-chloride intercalate, modified alumina, transition-metal cations, sulphated zirconia,

calcined nickel sulphate and clays [4–15]. But these catalysts had shown drawbacks such as lower selectivity, formation of higher amount of polyalkylated products and drastic reaction conditions [16].

In the past three decades, the use of heteropoly compounds (HPAs) in acid catalyzed reactions had opened new expectations for processes requiring acidities higher than those present on zeolites [17–19]. Previous work found that 12-tungstophosphoric acid exhibited good activity for the condensation of benzene and formaldehyde [20–22], and high activity for the condensation of toluene and formaldehyde (Eq. (2)) [23].

$$2C_6H_5CH_3 + HCHO \rightarrow CH_3PhCH_2PhCH_3 + H_2O \tag{2}$$

This process is economical and environmental favorable as the only by-product is water. While the solid state heteropoly acids catalyst changed into a slurry state after reaction due to the formation of water, which brought difficulties in the following separation process and the loss of catalyst in the recycle usage [23]. In order to use HPAs as solid catalysts, it was desirable to support them on an appropriate carrier since the surface area of these materials was very small ($<10\,m^2\,g^{-1}$). The high dispersed heteropoly acids on carriers with large surface area would increase the accessibility of the reactants to the active sites and enhance the efficiency of the catalyst. At the same time, the solid

state catalyst was facile in separation process. The present contribution concerned the immobilization of 12-tungstophosphoric acid on SiO_2, MCM-41 and activated carbon, and their utilization in the condensation of toluene and formaldehyde.

2. Experimental

2.1. Preparation of catalysts

12-Tungstophosphoric acid ($H_3PW_{12}O_{40}$, HPW) and SiO_2 were purchased from Shanghai Chemical Reagent Co. (China) and used directly without further treatment. Pure-silica MCM-41 was synthesized following a procedure as described in literature [24]. A commercial activated carbon (Shanghai Chemical Reagent Co.) was treated in 0.1 M HNO_3, washed with water and dried at 130 °C for 3 h in vacuum before the catalyst preparation.

SiO_2, MCM-41 and activated carbon supported 12-tungstophosphoric acid catalysts with different loading amount were prepared by impregnation an equal volume adsorption (of support materials) of aqueous solution of HPW (with identified amount of HPW). The impregnated precursor was dried at 150 °C in vacuum for overnight and finally calcined at 300 °C in nitrogen for 3 h.

2.2. Characterizations

The primary structure of the supported 12-tungstophosphoric acid catalysts were detected by means of FT-IR spectroscopy in a Nikolet 560 apparatus (USA). Samples were prepared by compressing a well mixed 3 mg of catalysts powder with 200 mg of potassium bromide (KBr).

The structure of the carriers and the prepared catalysts were measured by nitrogen adsorption at −196 °C using an OMNISORP 100CX system (COULTER Co., USA). All samples were pretreated at 250 °C in high vacuum, and the pore structure was calculated from the adsorption isotherm. Pore size (diameter) distribution in the range of 0.55–1.8 nm was calculated by the Horvath–Kawazoe method and pore size in the range of 3.0–100.0 nm was calculated by the Barret–Joyner–Halenda method.

X-ray diffraction patterns were obtained with X-ray diffractometer in a D8 ADVANCE (BRUKER, Germany) equipment using nickel-filtered Cu Kα radiation at 40 kV and 40 mA. Diffraction data were recorded using continuous scanning with a rate of 0.01°/s.

2.3. Catalytic reaction

A custom-designed 150 cm^3 stainless autoclave (Lanzhou, China) was employed in this study. The mixture of toluene (450 mmol), paraformaldehyde (90 mmol of HCHO) and nitrobenzene (20 mmol, internal standard) was poured into the catalyst. The suspension was vigorously stirred with a magnetic stirrer. After reaction, the reactor was cooled to room temperature, solid catalyst was separated by centrifuging, the organic reactant solution was diluted with ethanol and analyzed using an FID gas chromatography–mass spectrometry equipped with

a 25 m capillary column of a cross-linked 5% phenylmethylsilicone (HP5988A, USA). 4,4′-Dimethyldiphenylmethane (4,4′-DMDPM) was confirmed with the standard mass spectrum in database and that of the standard products purchased from TCI (Beijing Branch, China). 2,2′-Dimethyldiphenylmethane (2,2′-DMDPM), 2,4′-dimethyldiphenylmethane (2,4′-DMDPM) and three-benzene-ring products (3-rings) were confirmed with the standard mass spectrum in database. And the amount of dimethyldiphenylmethanes was calculated on the basis of external standard (commercial 4,4′-DMDPM). The selectivity of the dimethyldiphenylmethanes was calculated on the basis of HCHO according to the following equations:

$$\frac{\text{mol of DMDPM}}{\text{total mol of DMDPMs} + 2} \times 100\%.$$
$$\times \text{ mol of three ring products}$$

In this contribution, the mass balance calculated on the basis of HCHO lying in 96–100%.

3. Results and discussion

3.1. Characterizations of supported 12-tungstophosphoric acid catalysts

The IR spectrum of the SiO_2 and MCM-41 supported 12-tungstophosphoric acid catalysts are shown in Figs. 1 and 2. Pure 12-tungstophosphoric acid exhibited the typical IR bands at vas (P–O_a) = 1080 cm^{-1}, vas (W=O_d) = 982 cm^{-1}, vas (W–O_b–W) = 890 cm^{-1} and vas (W–O_c–W) = 810 cm^{-1} asymmetric vibrations associated to the Keggin ions, where a–d designated specific positions of the oxygen atoms in the Keggin structure, namely, P–O_a–W, W–O_b–W and W–O_c–W connecting two W_3O_{13} units by corner sharing and edge sharing, O_d=W [25]. In SiO_2 supported catalysts, apart from the detected intensity of asymmetric vibrations of W–O_b–W increased slightly with the loading amount of HPW, other three adsorption peaks of HPW acid changed slightly due to the overlapped vibrations peaks of HPW to those of SiO_2 (Fig. 1). No clear adsorption
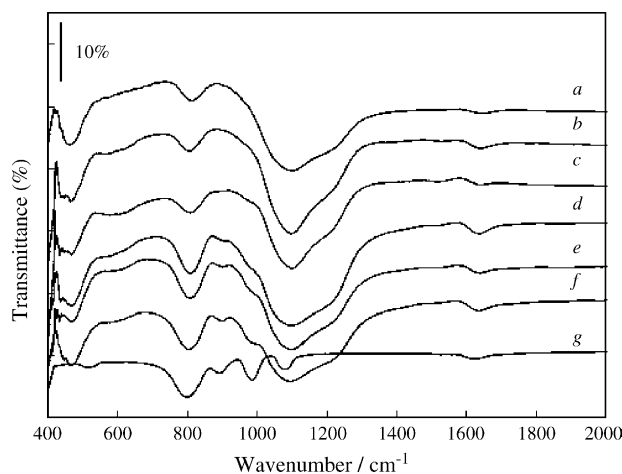

Fig. 1. IR spectra of SiO_2 supported $H_3PW_{12}O_{40}$. The loading amount of HPW (per 1 g support) were: (a) 0 g, (b) 0.05 g, (c) 0.15 g, (d) 0.25 g, (e) 0.4 g, (f) 0.6 g and (g) pure $H_3PW_{12}O_{40}$.

Fig. 2. IR spectra of MCM-41 supported $H_3PW_{12}O_{40}$. The loading amount of HPW (per 1 g support) were: (a) 0 g, (b) 0.05 g, (c) 0.15 g, (d) 0.25 g, (e) 0.4 g, (f) 0.6 g and (g) pure $H_3PW_{12}O_{40} \times 5$.
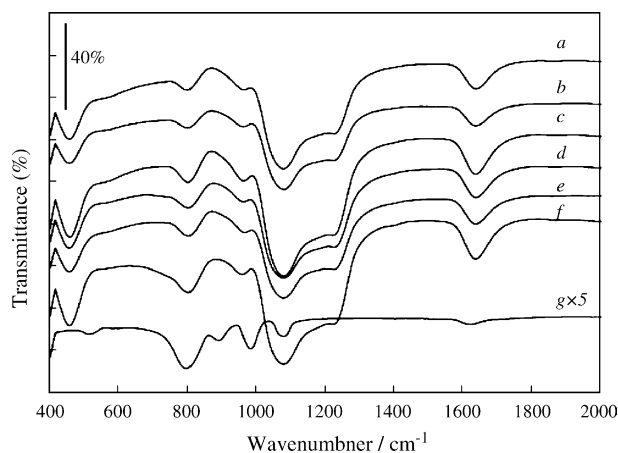

Fig. 4. XRD patterns of pure HPW and HPW (0.6 g/g-support) on different supports. The species of supports: (a) pure $H_3PW_{12}O_{40}$, (b) SiO_2, (c) MCM-41 and (d) activated carbon.

peak of HPW could be identified on MCM-41 support (Fig. 2). These results indicated that 12-tungstophosphoric acid dispersed highly on the surface of SiO_2 and MCM-41.

Fig. 3 shows the XRD spectrum of SiO_2 supported 12-tungstophosphoric acid with different loading amount. It could be found that no diffraction peak of 12-tungstophosphoric acid was detected when the loading amount less than 0.25 g/g-support. After this point, the diffraction peaks of 12-tungstophosphoric acid became obvious. Similar results were also detected in MCM-41 and activated carbon supported catalysts (Fig. 4). These results indicating that the primary structure of 12-tungstophosphoric acid was preserved even at high loading amount.

Fig. 5 illustrated the XRD spectrum of the fresh MCM-41 and MCM-41 supported 12-tungstophosphoric acid catalyst (0.6 g/g-support). Fresh MCM-41 exhibited a strong reflection at high d_{100}-spacing (ca. 3.5 nm) and a few weak peaks at higher angles with corresponding d-spacing in the range ca. 2.3–1.5 nm. While in MCM-41 supported catalyst, 12-tungstophosphoric acid had a striking effect on the width and intensity of the main reflection at high d_{100}-spacing and this line became broader and weaker. This suggested that the long-range order of MCM-41 was decreased noticeably by the presence of 12-
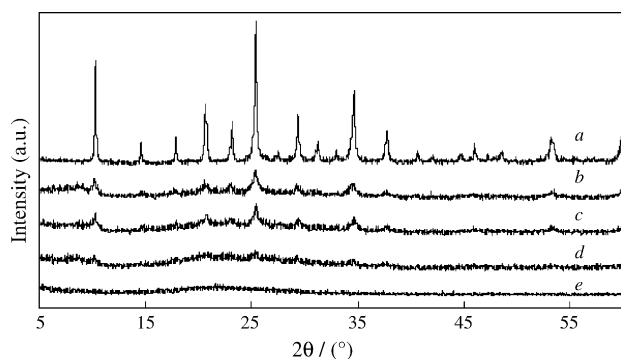
tungstophosphoric acid. There is increased disorder within the pores following deposition of HPW crystallites.

The surface area of pure 12-tungstophosphoric acid, SiO_2, MCM-41, activated carbon and the supported catalysts are summarized in Table 1. The average pore diameter of SiO_2, MCM-41 and activated carbon were 10.2, 3.0 and 1.0 nm, respectively. Pure 12-tungstophosphoric acid possesses a limited surface ($<10.0 \, m^2/g$), small pore volume (0.02 cm^3/g) and large interparticles average pore diameter (3.7 nm). This interparticles pore of 12-tungstophosphoric acid also appeared on MCM-41 and activated carbon supported catalysts (3.7 nm diameter), while the main pore diameter of these carriers remained, which inferred that big 12-tungstophosphoric acid particles might form on the surface of MCM-41 and activated carbon (Fig. 6). Only one unique pore (ca. 9.6 nm) was detected in SiO_2 supported catalyst, and its diameter is smaller than that of pure SiO_2 (ca. 10.2 nm, Table 1). This indicated that 12-tungstophosphoric acid were immobilized in the channels of SiO_2 and fully dispersed in a monolayer on SiO_2 surface [26]. On the another hand, micropores (0.6 nm) appeared in MCM-41 supported catalyst, while surface area of HPW/MCM-41 remains relatively high, it might be increased disorder within the pores following deposition of HPW crystallites. The adsorption isotherms of MCM-41 and HPW/MCM-41 also confirmed this increased disorder within

Fig. 3. XRD patterns of HPW and SiO_2 supported HPW catalysts. The loading amount of HPW (per 1 g support) were: (a) pure $H_3PW_{12}O_{40}$, (b) 0.6 g, (c) 0.4 g, (d) 0.25 g and (e) 0.05 g.
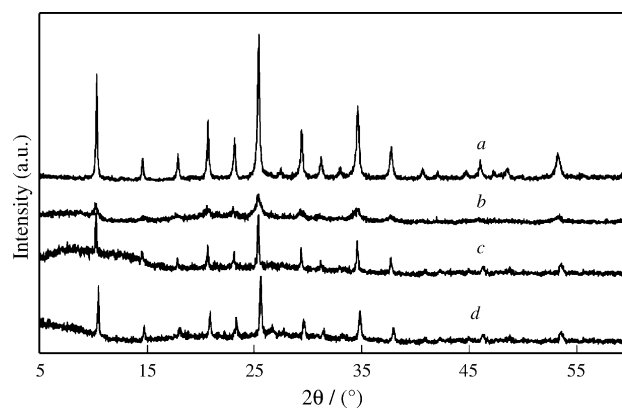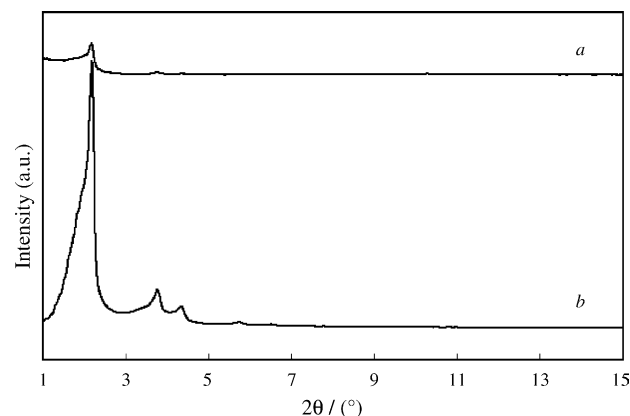

Fig. 5. XRD patterns of MCM-41 and MCM-41 supported $H_3PW_{12}O_{40}$ catalyst. (a) MCM-41 supported $H_3PW_{12}O_{40}$ and (b) MCM-41.

Table 1
The BET area of pure 12-tungstophosphoric acid, SiO$_2$, MCM-41, activated carbon and the supported catalysts

Pure carriers	BET area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)	Supported catalysts (0.6 g HPW/g-support)	BET area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
SiO$_2$	324.7	10.2	1.2	HPW/SiO$_2$	177.3	9.6	0.5
MCM-41	1064.5	3.0	0.8	HPW/MCM-41	616.8	0.6, 2.8, 3.7	0.6
Activated carbon	1134.9	1.0	0.6	HPW/activated carbon	694.4	1.0, 3.7	0.4
				Pure HPW	10.0	3.7	0.0

the pores (Fig. 7). The micropores of the activated carbons (ca. 1.0 nm) were in the majority. This kind of micropore was too narrow to accommodate a 12-tungstophosphoric acid molecule (diameter is 1.2 nm). It can also be found that the surface area of supported catalysts (with 0.6 g loading amount of HPW) decreased obviously compared with the pure carriers. And we thought that there might be a progressive decrease in surface area with the increasing loading amount of HPW.

3.2. DMDPMs synthesis over 12-tungstophosphoric acid

The catalytic performance of 12-tungstophosphoric acid for directly synthesis of DMDPMs via the condensation of toluene and formaldehyde are summarized in Table 2. Manily 4,4′-DMDPM (with a selectivity of 51.2–65.3%) and 2,4′-DMDPM (with a selectivity of 29.7–38.9%) was detected in the reaction mixture. It could be found that the conversion of HCHO increased from 26.9 to 80.1% with the added amounts of 12-tungstophosphoric acid increased from 0.1 to 0.5 g. While the selectivity of total DMDPMs decreased slightly from 96.3 to 89.9% and the selectivity of 3-rings products increased with increasing conversion of HCHO. That is, higher amount of catalyst was helpful for the conversion of HCHO, but it would

catalyze the consecutive reaction of formed by-product. The calculated TON value (turnover numbers, defined as (mole of reacted HCHO)/(mole of protons in catalyst)) decreased slightly from 232.8 to 141.9 with the amount of catalyst from 0.1 to 0.5 g.

3.3. DMDPMs synthesis on supported 12-tungstophosphoric acid catalysts

The activity of SiO$_2$, MCM-41 and activated carbon supported 12-tungstophosphoric acid catalysts with different loading amounts are summarized in Tables 3–5. On SiO$_2$ supported catalysts, the conversion of HCHO increased obviously from 23.6 to 75.8% with the loading amount of 12-tungstophosphoric acid and the selectivity of total DMDPMs decreased from 90.0 to 80.9%. Though the calculated TON decreased from 469.1 to 174.6 with the increase of loading amount of HPW, these data are higher than that of unsupported 12-tungstophosphoric acid at the same amount. We think that the increased TON of H$^+$ on SiO$_2$ supported catalysts is due to the highly dispersion of 12-tungstophosphoric acid and the highly dispersed proton increased the accessibility of the reactants to the active sites and enhance the efficiency of the catalyst. This allowed us to conclude that on SiO$_2$ support 12-tungstophosphoric acid was molecularly dispersed and retained their protons without modification of their strength and were immobilized in the channels by weak interaction with the walls, presumably by hydrogen
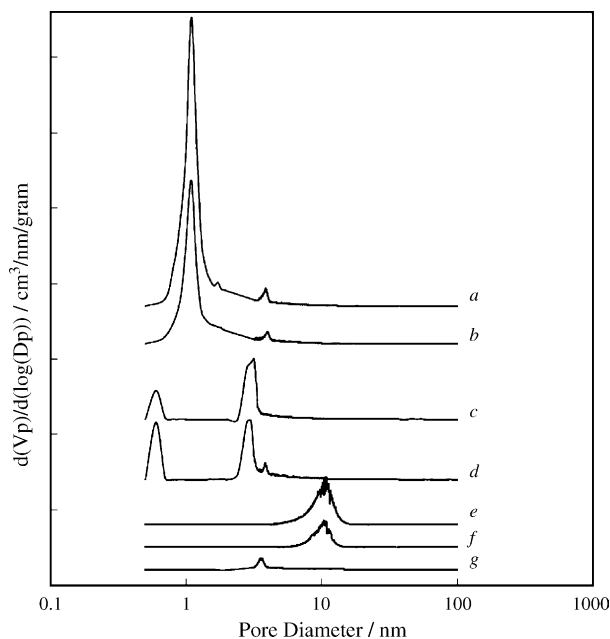

Fig. 6. Pore distribution of supports and HPW (0.6 g/g-support) on different supports. (a) Activated carbon, (b) HPW/AC, (c) MCM-41, (d) HPW/MVM-41, (e) SiO$_2$, (f) HPW/SiO$_2$ and (g) pure H$_3$PW$_{12}$O$_{40}$.
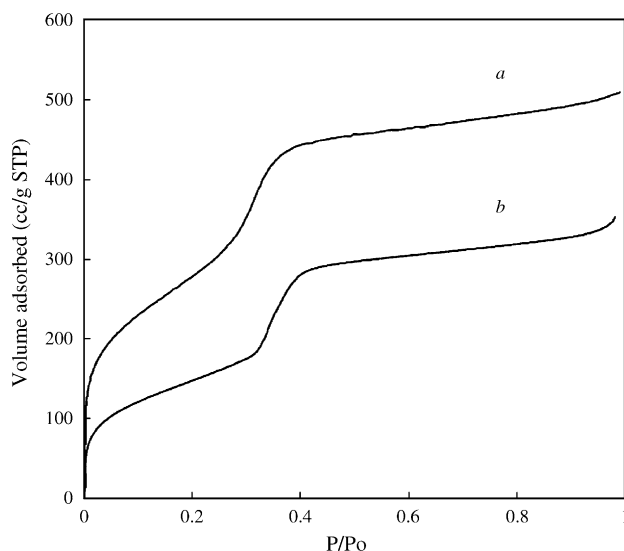

Fig. 7. N$_2$ adsorption isotherms of MCM-41 and MCM-41 supported HPW catalysts. (a) MCM-41 and (b) HPW/MVM-41.

Table 2
Condensation of toluene and HCHO on $H_3PW_{12}O_{40}$ catalysts

Amount of HPW (g)	Conversion (of HCHO %)	TON[a]	Selectivity (on the basis of HCHO) (mol%)[b]			
			2,2′-DMDPM	2,4′-DMDPM	4,4′-DMDPM	3-ring products
0.1	26.9	232.8	1.2	38.9	56.2	3.7
0.2	47.7	206.3	1.0	29.7	65.3	4.0
0.3	64.5	174.4	1.1	32.5	59.4	7.0
0.4	76.5	152.3	1.3	36.3	51.2	11.2
0.5	82.1	141.9	1.4	35.4	53.1	10.1

Reaction conditions: toluene, 450 mmol; paraformaldehyde, 90 mmol; catalyst, 1.0 g; reaction temperature, 140 °C; 4 h.

[a] TON: turnover numbers, defined as (mole of reacted HCHO)/(mole of protons in catalyst).

[b] The selectivity of DMDPMs were calculated as (mol of DMDPM)/(total mol of DMDPMs + 2 × mol of 3-ring products) × 100%.

Table 3
Condensation of toluene and HCHO on SiO_2 supported $H_3PW_{12}O_{40}$ catalysts

Loading amount/g-HPW/g-SiO$_2$	Conversion (of HCHO %)	TON[a]	Selectivity (on the basis of HCHO) (mol%)[b]			
			2,2′-DMDPM	2,4′-DMDPM	4,4′-DMDPM	3-ring products
0.05	17.6	429.1	1.8	26.7	61.5	10.0
0.15	54.7	362.6	1.1	32.5	50.3	16.2
0.25	66.4	286.7	1.1	30.5	50.2	18.2
0.40	71.8	217.1	1.0	31.7	49.1	18.2
0.60	75.8	174.6	1.2	32.5	47.2	19.1

Reaction conditions: toluene, 450 mmol; paraformaldehyde, 90 mmol; catalyst, 1.0 g; reaction temperature, 140 °C; 4 h.

[a] TON: turnover numbers, defined as (mole of reacted HCHO)/(mole of protons in catalyst).

[b] The selectivity of DMDPMs were calculated as (mol of DMDPM)/(total mol of DMDPMs + 2 × mol of 3-ring products) × 100%.

Table 4
Condensation of toluene and HCHO on MCM-41 supported $H_3PW_{12}O_{40}$ catalysts

Loading amount (g-HPW/g-MCM)	Conversion (of HCHO %)	TON[a]	Selectivity (on the basis of HCHO) (mol%)[b]			
			2,2′-DMDPM	2,4′-DMDPM	4,4′-DMDPM	3-ring products
0.05	26.8	532.2	1.3	36.1	54.3	8.3
0.15	52.1	385.1	1.2	35.9	50.3	12.6
0.25	63.2	289.4	1.2	34.2	50.5	14.1
0.40	69.2	217.8	1.1	34.0	50.1	14.8
0.60	76.4	176.7	1.1	31.9	49.1	17.9

Reaction conditions: toluene, 450 mmol; paraformaldehyde, 90 mmol; catalyst, 1.0 g; reaction temperature, 140 °C; 4 h.

[a] TON: turnover numbers, defined as (mole of reacted HCHO)/(mole of protons in catalyst).

[b] The selectivity of DMDPMs were calculated as (mol of DMDPM)/(total mol of DMDPMs + 2 × mol of 3-ring products) × 100%.

bonding with silanol groups as suggested in ref. [27]. But the negative effect of these immobilized 12-tungstophosphoric acid catalysts is that they enhanced the formation of 3-rings products due to the consecutive electrophilic attacks to the DMDPMs.

On MCM-41 supported 12-tungstophosphoric acid catalysts, the conversion of HCHO increased quickly from 29.3 to 67.0% with the loading amount of HPW raised from 0.05 to 0.25 g, and then increased slightly. The selectivity of total DMDPMs

Table 5
Condensation of toluene and HCHO on activated carbon supported $H_3PW_{12}O_{40}$ catalysts

Loading amount (g-HPW/g-SiO$_2$)	Conversion (of HCHO %)	TON[a]	Selectivity (on the basis of HCHO) (mol%)[b]			
			2,2′-DMDPM	2,4′-DMDPM	4,4′-DMDPM	3-ring products
0.05	2.7	48.8	2.0	29.7	65.8	2.5
0.15	7.3	48.5	2.2	28.5	67.1	2.2
0.25	11.0	47.7	2.3	27.8	64.7	5.2
0.40	14.7	44.6	2.4	29.2	62.8	5.6
0.60	15.7	36.1	2.2	28.6	63.7	5.5

Reaction conditions: toluene, 450 mmol; paraformaldehyde, 90 mmol; catalyst, 1.0 g; reaction temperature, 140 °C; 4 h.

[a] TON: turnover numbers, defined as (mole of reacted HCHO)/(mole of protons in catalyst).

[b] The selectivity of DMDPMs were calculated as (mol of DMDPM)/(total mol of DMDPMs + 2 × mol of 3-ring products) × 100%.

decreased slightly with the loading amount of HPW increased. The calculated TON of H^+ in MCM-41 supported catalysts are also higher than that of unsupported 12-tungstophosphoric acid at the same amount. Though the surface area of MCM-41 ($1064.5\,m^2/g$) is several times higher than that of SiO_2 ($324.7\,m^2/g$, Table 1), 12-tungstophosphoric acid supported on MCM-41 did not exhibit any predominance compared to SiO_2. We thought that this might be due to the poor stability of the MCM-41. That is, the long-range order meso-porous MCM-41 was destroyed in some extent and there is increased disorder within the pores during the impregnation step as the strong acidity of the aqueous solution of 12-tungstophosphoric acid.

The activity of activated carbon supported 12-tungstophosphoric acid was poor for the synthesis of DMDPMs directly from toluene and HCHO. The detected conversion of HCHO and TON were even lower than that of unsupported 12-tungstophosphoric acid. Previous work found that the condensation between toluene and HCHO to DMPMs involves two consecutive electrophonic attacks to an aromatic ring and both of these attacks need to be catalyzed by acid catalysts, and only strong acid sites are active [23]. While the 12-tungstophosphoric acid adsorbed strongly on activated carbon, and the adsorption was believed to involve proton transfer from the HPW to the carbon [28]. As a result the acid strength of 12-tungstophosphoric acid supported on active carbon was weaker than that of pure 12-tungstophosphoric acid.

4. Conclusion

As a conclusion, we found that 12-tungstophosphoric acid could be dispersed highly on the surface of SiO_2 and MCM-41. These supported 12-tungstophosphoric acid catalysts are facile in separation and would increase the accessibility of the reactants to the active sites in the condensation of toluene and formaldehyde. SiO_2 and MCM-41 supported 12-tungstophosphoric acid catalysts exhibited higher activity than that of unsupported 12-tungstophosphoric acid. The best yield of total DMDPMs reached 61.3% on SiO_2 supported HPW (with 0.6 g loading amount of HPW). While the main drawback of MCM-41 supported catalysts is that the long-range order meso-porous MCM-41 was destroyed in some extent during the impregnation step as the strong acidity of the aqueous solution of 12-tungstophosphoric acid. And active carbon supported 12-tungstophosphoric acid showed a low activity for this reaction due to the decreased acidity.

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