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Synthesis of di(methylphenyl)methane over heteropolyacids ($H_3PW_{12}O_{40}$) catalysts

Dingfeng Jin, Zhaoyin Hou*, Yongming Luo, and Xiaoming Zheng

Department of Chemistry, Institute of Catalysis, Zhejiang University, Xixi Campus, Hangzhou, 310028 P. R. China

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Catalytic synthesis of di(methylphenyl)methane ($CH_3C_6H_4CH_2C_6H_4CH_3$, DMPMs) from toluene and formaldehyde were investigated over various solids acids. At 140 °C and toluene/HCHO = 5/1, the conversion of HCHO over zeolite (Hβ, H-mordenite, HX, HY and HZSM-5) is limited, while heteropolyacids ($H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$) exhibited higher activity and DMPMs selectivity. The best yield of DMPMs reached 81.5% (conversion of HCHO nearly 100%). $H_3PW_{12}O_{40}$ could be recovered by simply drying and the recycle-used catalyst remained its activity and structure in five runs.

KEY WORDS: di(methylphenyl)methane; formaldehyde; synthesis; heteropolyacids; $H_3PW_{12}O_{40}$.

1. Introduction

Di(methylphenyl)methane ($CH_3C_6H_4CH_2C_6H_4CH_3$ or $CH_3PhCH_2PhCH_3$, DMPMs) is an important chemical and intermediate in the production of spices, pharmaceutics and dielectric fluid. And diphenylmethane dyes (e.g., auramine) are widely used in wool, paper, leather and silk industries [1].

Typically, DMPMs are produced by the condensation of xylene with benzyl chloride in the presence of a Friedel–Crafts catalyst mainly aluminium chloride or iron chloride, which gives large amount of by-products such as polymers of benzyl chloride and several compounds containing three or more benzene rings [2,3].

$$C_6H_5(CH_3)_2 + C_6H_5CH_2Cl \rightarrow CH_3C_6H_4CH_2C_6H_4CH_3 + HCl \qquad (1)$$

Several solid acid catalysts relevant to Friedel–Crafts reactions have been reported in order to replace conventional problematic homogeneous catalysts, such as montmorillonite supported transition metals [4], graphite–aluminum–chloride intercalate [5], modified alumina [6], transition metal cations [7], sulfated zirconia [8], calcined nickel sulfate [9,10], clays [11–15] and zeolite [16–18]. But these heterogeneous catalysts have shown drawbacks in lower activity or selectivity, formation of higher amount of polyalkylated products and drastic reaction conditions [19,20].

Another long-established method is the condensation of toluene with formaldehyde at low temperature using concentrated sulfuric acid as catalyst.

$$C_6H_5CH_3 + HCHO \rightarrow CH_3C_6H_4CH_2C_6H_4CH_3 + H_2O \qquad (2)$$

One problem of this process is that the starting formaldehyde is so liable to be polymerized that the reaction should be carried out at a very low temperature (−40 to −20 °C), which needs a cooling medium. At the same time, the reacted mixture must be neutralized to remove the sulfuric acid. Thus, this condensation method is not only troublesome to handle but is also low in both conversion and selectivity [2].

Recently, it was reported that one kind of modified USY zeolite exhibited significant products shape selectivity at moderate temperature, while the productivity of desired products is low due to the low HCHO/toluene ratio in feed (1/60–1/70, mole ratio) and high catalyst/HCHO ratio (l g/200 mg) [21]. Heteropolyacids have enjoyed wide acceptance as active catalysts in both homogeneous and heterogeneous systems [22–26]. Here we want to report an environmental friendly synthesis of di(methylphenyl)methane over heteropolyacids catalyst.

2. Experimental

Toluene and paraformaldehyde were purchased from Shanghai Chemical Reagents Co. (China) and directly used without further treatment. Zeolite (Hβ, H-mordenite, HX, HY, HZSM-5) were kindly supplied by Huahua Catalysis Co. (Wenzhou, China). A custom-designed 150 cm^3 stainless autoclave (Lanzhou, China) was employed in this study. Before the catalytic reaction, the commercial $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ (Shanghai Chemical Reagents. China) were pretreated at 250 °C for 3 h; zeolite were pretreated at 550 °C for 3 h. A mixture of toluene

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* To whom correspondence should be addressed.
E-mail: zyhou@zju.edu.cn

(450 mmol), paraformaldehyde (90 mmol of HCHO) and nitrobenzene (20 mmol, internal standard) was poured onto the catalyst (1 g). The resulting suspension was vigorously stirred with a magnetic stirrer. The reaction solution was cooled after the specified reaction time, diluted with ethanol and analyzed using a FID gas chromatography–mass spectrometry equipped with a 25 m capillary column of a cross-linked 5% phenylmethylsilicone (HP5988A, USA). All products were confirmed with the standard mass spectrum in database and that of the standard products purchased from Addrich.

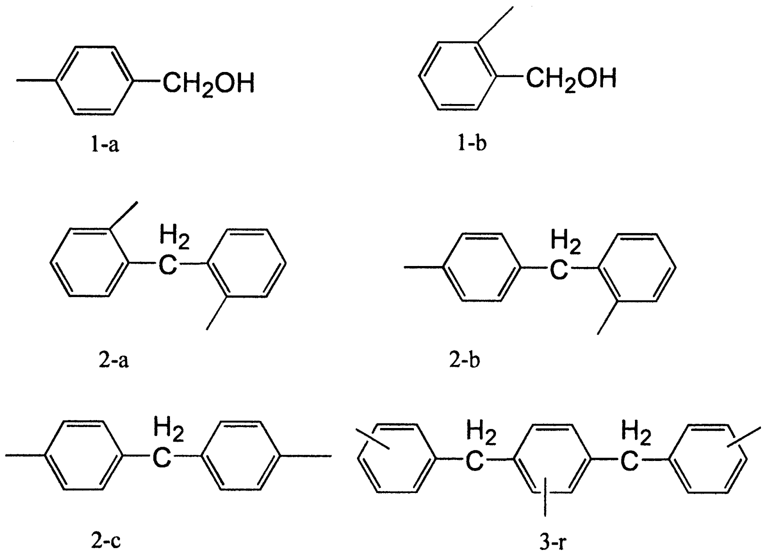
FT-IR spectra of the fresh and spent $H_3PW_{12}O_{40}$ were obtained using the KBr method (Nikolet 560, USA).

3. Results

3.1. Condensation of toluene with paraformaldehyde over solid acids catalysts

Several products were detected in the reaction mixture and the assignment of these products (see figure 1) were based on the GC-MS analysis of these peaks for the corresponding molecular ions with those of the standard database and that of the standard products purchased from Addrich. As it was expected that di(methylphenyl)methane in the *ortho–ortho′* (2-a), *ortho–para′* (2-b) and *para–para′* (2-c) positional isomers were detected in the reaction mixture. Some amount of 4-methylbenzyl alcohol (1-a), 2-methylbenzyl alcohol (1-b) and three-ring products (3-r) were also detected.

Conversion and selectivity of DMPMs synthesis from toluene and paraformaldehyde over various solid acids are summarized in table 1. It can be found that no reaction happened on Al_2O_3. Zeolite (Hβ, H-modernite, HX, HY and HZSM-5) had very low activity and the main products are the intermediate (1-a and 1-b, methylbenzyl alcohol). Heteropolyacids ($H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$) exhibited high activity and DMPMs selectivity in the condensation of toluene and HCHO. The conversion of HCHO and total yield of DMPMs over $H_3PW_{12}O_{40}$



1-a

1-b

2-a

2-b

2-c

3-r

Figure 1. Chemical species referred in this paper.

Table 1

Conversion and selectivity of DMPMs from toluene and paraformaldehyde with various solid acids

Catalyst (1 gram)	Conversion (mol%)	total Yield of DMPMs (mol%)	TON [a]	Selectivity (mol%)				
				2-a	2-b	2-c	3-r	(l-a) + (l-b)
Al_2O_3	0.0	–	–	–	–	–	–	–
Hβ (Si/Al = 10)	11.3	9.5	6.7	8.9	42.1	33.1	0	16.0
H-mordenite (Si/Al = 19)	0.2	< 0.1	0.2	9.2	23.5	15.2	0	52.1
HX (Si/Al = 3.0)	0.2	< 0.1	0.0	10.2	24.1	18.3	0	47.5
HY (Si/Al = 12.0)	5.4	2.3	3.8	15.0	13.0	13.8	0	58.3
HZSM-5(Si/Al = 25)	1.3	0.4	1.8	8.3	12.1	10.9	0	78.8
$H_3PW_{12}O_{40}$	88.9	77.9	76.8	1.2	39.1	47.4	11.4	0.9
$H_3PMo_{12}O_{40}$	44.0	39.6	24.1	9.4	35.9	44.7	6.9	3.1
$H_4SiW_{12}O_{40}$	74.0	62.1	47.8	6.3	31.8	45.8	13.8	2.4

Reaction conditions: toluene 450 mmol, paraformaldehyde 90 mmol, catalyst 1.0 g, reaction temperature 141°C and 4 h.

[a] TON = (mole of reacted HCHO)/(mole of protons in catalyst), and the amount of proton in zeolite was estimated from the composition (Si/Al ratio).

reached to 88.9% and 77.9%, respectively. Among the desired products, the mole ratio of *ortho–ortho′* (2-a), *ortho–para′* (2-b) and *para–para′* (2-c) isomers was 1.2/39.1/47.4, and both the selectivity and the yield of *para–para′* (2-c) isomer are higher than that of traditional $AlCl_3$, H_2SO_4 catalysts and recently reported USY catalyst [21].

As it was reported that the condensation between toluene and HCHO to DMPMs involves two consecutive electrophilic attacks to an aromatic ring with an *ortho–para* directing substituent, both of these attacks need to be catalyzed by acid catalysts, and only strong acid sites are active [21,27]. In table 1, the calculated TON (turnover numbers, defined as (mole of reacted HCHO)/(mole of protons in catalyst)) indicates that the catalytic activity decrease in the order of $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_3PMO_{12}O_{40} > H\beta >$ HY, which follows well with their acidity. In this case, the poor activity of Al_2O_3, H-mordenite, HX and the lower activity of $H\beta$, HY zeolite are reasonable. It can also be found from the reaction equation (equation (2)) that H_2O formed during the reaction, and the formed water had strong poisoning effect to active sites of zeolite, which might also decrease their activity. The higher activity of $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ for the condensation between toluene and paraformaldehyde could be firstly attributed to their strong acidity in organic solution. At the same time the formed water would dissolve in the bulk structure of the heteropoly anions and exhibited no influence on its activity (this property was also defined as water-tolerant ability) [22–24].

3.2. *Time course of condensation between toluene and HCHO catalyzed by $H_3PW_{12}O_{40}$*

The conversion of HCHO and the selectivity of all detected products at different reaction time at 140 °C are shown in figure 2. It was found that the conversion of HCHO increased with the reaction time, nearly 100% conversion was attained after 5 h and the best yield of DMPMs reached 81.5%. While the selectivity of DMPMs (total of two-rings products) decreased slightly as the amount of consecutive three-rings products increased with the reaction time. As it was expected that the selectivity of intermediated product (1-a) decreased with the reaction time.

3.3. *Effect of the amount of $H_3PW_{12}O_{40}$*

Figure 3 shows the relationship between the amount of $H_3PW_{12}O_{40}$ and the selectivity of detected products. It can be found that the conversion of HCHO increased from 82% to 100% with the added amounts of catalysts increased from 0.5 to 2.5 g. While the selectivity of DMPMs decreased and the selectivity of three-rings products increased with increased amount of catalyst. That is, higher amount of catalyst is helpful for the conversion of HCHO, but it will catalyze the consecutive reaction of desired product.

3.4. *Effect of reaction temperature*

Figure 4 shows the effect of reaction temperature on the activity of $H_3PW_{12}O_{40}$ catalyzed condensation between toluene and HCHO. The conversion of HCHO increased quickly from 36.2% to 88.9% with the reac-

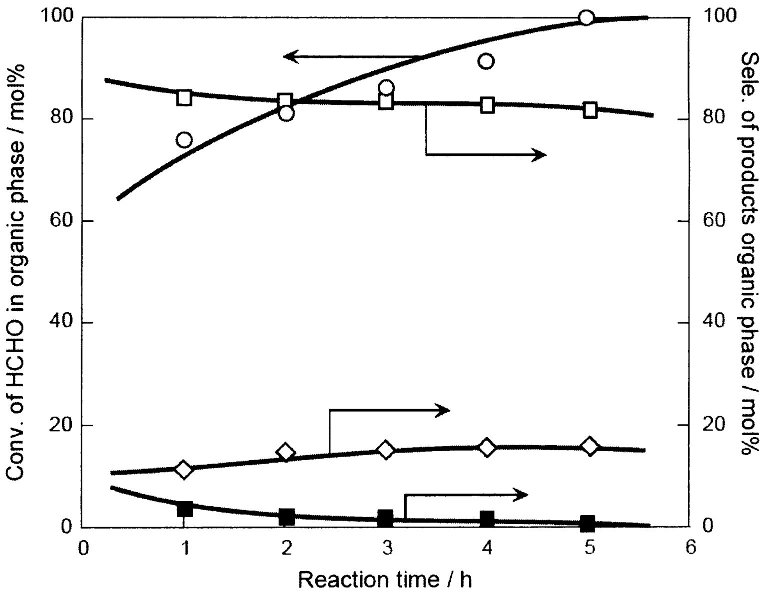


Figure 2. Time course of the condensation between toluene and HCHO using $H_3PW_{12}O_{40}$ (○) conversion of HCHO, (□) selectivity of DMPMs, (◇) selectivity of three-rings product and (■) selectivity of benzyl alcohol. Reaction conditions: toluene 450 mmol, paraformaldehyde 90 mmol, catalyst 1.0 g, reaction temperature 140 °C.

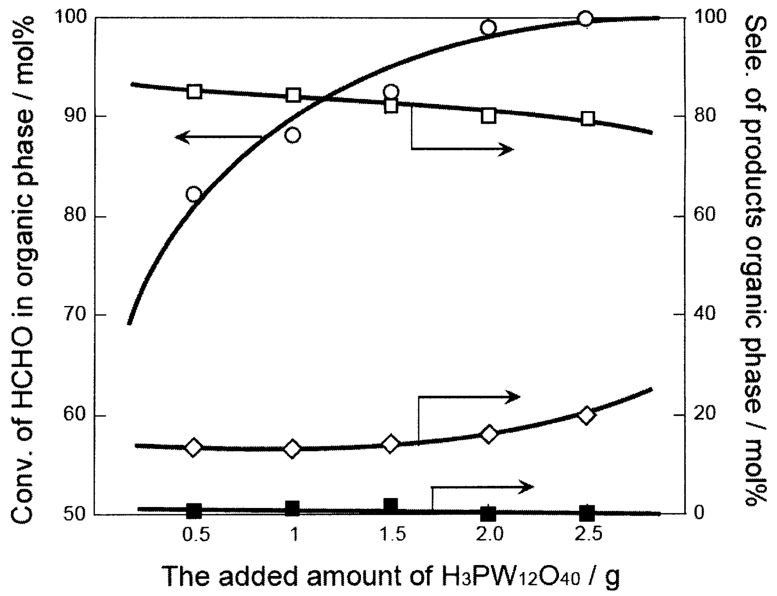


Figure 3. Effects of the added amount of $H_3PW_{12}O_{40}$ catalyst (○) conversion of HCHO, (□) selectivity of DMPMs, (◇) selectivity of three-rings product and (■) selectivity of benzyl alcohol. Reaction conditions: toluene 450 mmol, paraformaldehyde 90 mmol, reaction temperature 140 °C, 4 h.

tion temperature raised from 100 to 140 °C, and then increased slightly. While the selectivity of DMPMs decreased with the reaction temperature and the selectivity of three-rings products increased at higher temperature.

3.5. Reactivity of recycled $H_3PW_{12}O_{40}$

The activities of recycled $H_3PW_{12}O_{40}$ are summarized in table 2. When the reaction was repeated using recycled $H_3PW_{12}O_{40}$ (by simply drying the slurry $H_3PW_{12}O_{40}$ at 100 °C in air), the conversion of HCHO and the yield of DMPMs decreased slightly from 88.9% and 77.9% to 66.4% and 61.9%, respectively. While it should be noted that the amount of remained catalyst during these cycles decreased from 1.0 to 0.47 g after the fifth run due to the adherent of $H_3PW_{12}O_{40}$ on the wall of recycled equipment. Compared with the activity of fresh $H_3PW_{12}O_{40}$ in the same amount (0.5 g in figure 3), we think that $H_3PW_{12}O_{40}$ could remain its activity at least in five cycles, FT-IR analysis indicated that the

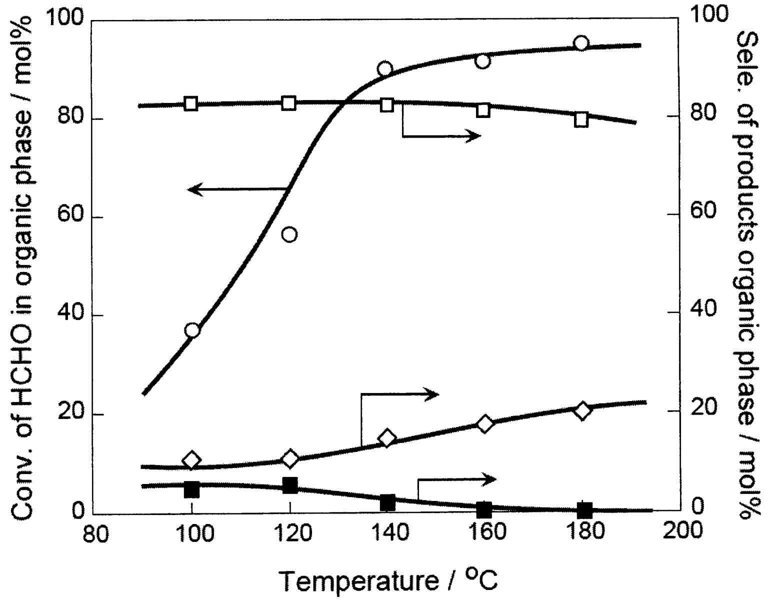


Figure 4. Condensation between toluene and HCHO at different temperatures using $H_3PW_{12}O_{40}$ (○) conversion of HCHO, (□) selectivity of DMPMs, (◇) selectivity of three-rings product and (■) selectivity of benzyl alcohol. Reaction conditions: toluene 450 mmol, paraformaldehyde 90 mmol, catalyst 1.0 g, 4 h.

Table 2
Conversion and selectivity of DMPMs from toluene and paraformaldehyde with recycle used $H_3PW_{12}O_{40}$

Runs	Conversion (mol%)	total Yield of DMPMs (mol%)	Selectivity (mol%)				
			2-a	2-b	2-c	3-r	(1-a) + (1-b)
1st (1.00 g)	88.9	77.9	1.2	39.1	47.4	11.4	0.9
2nd	80.8	66.7	1.0	36.5	45.2	15.6	1.8
3rd	78.5	65.3	1.1	37.7	44.4	14.7	2.2
4th	70.7	64.7	1.1	40.7	49.7	8.2	0.4
5th (0.47 g)	66.4	61.9	1.1	44.4	47.8	6.5	0.3

Reaction conditions: toluene 450 mmol, paraformaldehyde 90 mmol, reaction temperature 140 °C and 4 h.

main Keggin structure of the spent catalyst was completely remained after the fifth runs at 140 °C (figure 5).

4. Conclusions

In this paper, we found that heteropolyacids ($H_3PW_{12}O_{40}$) exhibited a high activity and selectivity for the production of DMPMs via condensation of toluene with formaldehyde. The best yield of DMPMs reached 81.5% at 140 °C, toluene/HCHO = 5/1, 5 h. And the most important is that this kind of catalysts could be used in recycle without loss of its structure and activity.

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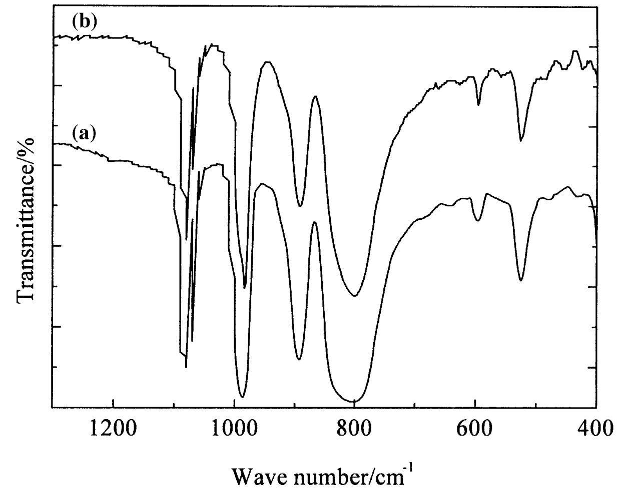

Figure 5. IR spectrum of $H_3PW_{12}O_{40}$ before and after five round recycles (a) fresh $H_3PW_{12}O_{40}$, (b) spent $H_3PW_{12}O_{40}$.

References

[1] R. Commandeur, N. Berger, P. Jay and J. Kervennal, European Patent 0442986 (1991)..

[2] M. Akatsu and H. Takayama, European Patent 0428081B1 (1990)..

[3] Y. Izumi, N. Natsume, H. Takamine, J. Tamaoki and K. Urabe, Bull. Chem. Soc. Jpn. 62 (1989) 2159.

[4] J.H. Clark, A.P. Kybett, D.J. Macquarrie, S.J. Barlow and P. Landon, J. Chem. Soc. Chem. Comm. (1989) 1353.

[5] J.M. Lalancette, U.S. Patent 3880944 (1975).

[6] H. Schmall and W. Schunack, Sci. Pharm. 42 (1974) 248.

[7] P. Laszlo and A. Mathy, Helv. Chim. Acta 70 (1987) 577.

[8] T.S. Thorat, P.S. Khumbar and G.D. Yadav, Tetrahedron Lett. 34 (1993) 529.

[9] K. Tanabe, T. Yamagata and T. Takeshita, J. Res. Inst. Catal. Hokkaido Univ. 12 (1965) 230.

[10] T. Takeshita, K. Arata, T. Sano and K. Tanabe, Kogyo Kagaku Zasshi 69 (1966) 916.

[11] A. Cornelis, C. Dony, P. Laszlo and K.M. Nsunda, Tetrahedron Lett. 34 (1993) 529.

[12] E. Herdieckerhoff and W. Sutter, German Patent 1051864 (1959).

[13] J. Haydn and H. Holzrichter, German Patent 1089168 (1960).

[14] R. Stroh, J. Ebersberger, H. Haberland and W. Hahn, German Patent 1051271(1959).

[15] R. Van Helden, C.F. Kohl and H.D. Scharf, British Patent 1110029 (1968).

[16] A.P. Singh and A.K. Pandey, Catal. Lett. 60 (1999) 157.

[17] K. Sato, Y. Nishimura and H. Shimada, Catal. Lett. 60 (1999) 83.

[18] V.R. Choudhary, S.K. Jana and B.P. Kiran, Catal. Lett. 59 (1999) 217.

[19] A.P. Singh, B. Jacob and S. Sugunan, Appl. Catal. A. 174 (1998) 51.

[20] K.B. Sherly and T.B. Venugopal, React. Kinet. Catal. Lett. 75 (2002) 239.

[21] M.J. Climent, A. Corma, H. Garcia and J. Primo, J. Catal. 130 (1991) 138.

[22] T. Okuhara, Chem. Rev. 102 (2002) 3641.

[23] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171.

[24] N. Mizuno and M. Misono, Chem. Rev. 99 (1999) 199.

[25] A. Corma, Chem. Rev. 95 (1995) 559.

[26] M. Misono, Catal. Rev. Sci. Eng. 29 (1987) 269.

[27] M.J. Climent, A. Corma and H. Garcia, Appl. Catal. 51 (1989) 113.