

Effective Liquid-phase Nitration of Benzene Catalyzed by a Stable Solid Acid Catalyst: Silica Supported $\text{Cs}_{2.5}\text{H}_{0.5}\text{PMo}_{12}\text{O}_{40}$

Gong Shu-wen,* Liu Li-jun, Zhang Qian, and Wang Liang-yin

Shandong Provincial Key Laboratory of Chemical Energy-Storage and Novel Cell Technology, School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, China. *E-mail: gongshw@lcu.edu.cn
Received December 8, 2011, Accepted January 26, 2012

Silica supported $\text{Cs}_{2.5}\text{H}_{0.5}\text{PMo}_{12}\text{O}_{40}$ catalyst was prepared through sol-gel method with ethyl silicate-40 as silicon resource and characterized by X-ray diffraction, infrared spectroscopy, scanning electron microscopy, nitrogen adsorption-desorption and potentiometric titration methods. The $\text{Cs}_{2.5}\text{H}_{0.5}\text{PMo}_{12}\text{O}_{40}$ particles with Keggin-type structure well dispersed on the surface of silica, and the catalyst exhibited high surface area and acidity. The catalytic performance of the catalysts for benzene liquid-phase nitration was examined with 65% nitric acid as nitrating agent, and the effects of various parameters were tested, which including temperature, time and amount of catalyst, reactants ratio, especially the recycle of catalyst was emphasized. Benzene was effectively nitrated to mononitro-benzene with high conversion (95%) in optimized conditions. Most importantly, the supported catalyst was proved has excellent stability in the nitration progress, and there were no any other organic solvent and sulfuric acid were used in the reaction system, so the liquid-phase nitration of benzene that we developed was an eco-friendly and attractive alternative for the commercial technology.

Key Words : Liquid-phase nitration, Benzene, Solid acid catalyst, Supported, Sol-gel

Introduction

Nitrobenzene is known to be a starting material for producing useful substances such as aniline, benzidine and metanilic acid.^{1,2} The commercial industrial production of nitrobenzene involves nitration of benzene with a mixture of sulfuric and nitric acids, which do not meet the environment-friendly requirements of the modern chemical industry processes. A major problem associated with the technology is that the significant consumption of sulfuric acid generates large amounts of wastes, which are very costly to treat.³⁻⁵

To overcome this drawback, considerable efforts have been put into developing of the heterogeneously catalyzed liquid or vapor phase nitration of aromatic compounds using solid acid catalysts.⁶⁻¹¹ Chaudhuri *et al.*⁷ has studied the catalytic activity of $\text{Al}(\text{H}_2\text{PO}_4)_3$ in nitration of benzene as a solid acid catalyst with nitric acid (70%), and the yield of nitrobenzene has been improved to 85%. Brei and coworkers¹² have reported the gas-phase nitration of benzene with 70% HNO_3 catalytic by superacid WO_3/ZrO_2 catalyst at 170 °C under atmospheric pressure, with the yield of nitrobenzene in the range of 65-80% and selectivity for mononitrobenzene of 99%. Although these solid acid catalysts showed good catalytic properties in nitration progress, the recycling results of these catalysts were not referred,⁹⁻¹² which are important evaluation criterions for an excellent catalyst applied in industrial production.

Heteropoly acids (HPAs), especially those of the Keggin series, have attracted considerable interest as acid catalysts for the clean synthesis of fine chemicals in heterogeneous system.^{13,14} However, solid HPAs can act as heterogeneous

catalysts in liquid phase only in non-polar solvents because they are highly soluble in polar ones, which will result in difficulty to recycle and reuse. Additionally these compounds exhibit very low specific surfaces areas ($1\text{-}10\text{ m}^2\text{g}^{-1}$)¹⁵ and moderate thermal stability, which limit their applications in industrial chemical processes.¹⁶ To overcome these handicaps, HPAs have been supported on different solid matrices, such as silica,^{16,17} MCM-41,¹⁸ nanoparticle tin oxide,¹⁹ titania¹⁴ and so on. Preyssler type heteropoly acid, namely salts of HPAs, were prepared by partially exchanging protons of the parent HPAs with large cations, such as Cs^+ , Na^+ and NH_4^+ , which could be water insoluble and present a rather high surface area ($> 100\text{ m}^2\text{g}^{-1}$),²⁰⁻²² such as the $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ possessed a considerable BET surface area $154\text{ m}^2\text{g}^{-1}$.²² Therefore, as solid acid catalysts, the supported salts of HPAs should be more competitive than those HPAs in industrial chemical processes, while to the best of our knowledge, there was little report about the evaluation of supported salts of HPAs catalyst in nitration progress up to now.

Previously, we have reported the application of ammonium salt of 12-molybdophosphoric acid (AMPA) catalysts in the liquid-phase nitration of benzene.²³ Those catalysts show good catalytic activity in nitration, while there was a decrease of activity after recycling for several times and the stability of AMPA catalysts should improve in nitration progress. In this work, silica supported Cs salt catalyst of 12-molybdophosphoric acid ($\text{Cs}_{2.5}\text{H}_{0.5}\text{PMo}_{12}\text{O}_{40}$) was prepared *via* sol-gel technology, and its catalytic activity has been qualitatively evaluated in the liquid-phase nitration of benzene using nitric acid under solvent-free conditions.

Experimental

Synthesis of Cs Salt of Molybdophosphoric Acid. Cs salt of 12-molybdophosphoric acid ($\text{Cs}_{2.5}\text{H}_{0.5}\text{PMO}_{12}\text{O}_{40}$, which was abbreviated as CsPMA) was prepared by adding the Cs_2CO_3 solution dropwise to the 12-molybdophosphoric acid solution under vigorous stirring according to the literature method.²² After 2 h stirring, the green precipitate was obtained by dried at 110 °C overnight.

Synthesis of Supported Cs Salt Catalysts. A series of silica supported catalysts with varying molybdenum oxide mass concentrations (5, 10, 20 and 30 wt %) were prepared by the sol-gel technique. The mixed solutions of ethyl silicate-40, distilled water and ethanol (volume ratio = 1:2:2) were stirred at 70 °C for 30 min to form clear solution. Then the suspending aqueous solution of CsPMA, which prepared in advance using the method mentioned above (dryness at 110 °C was excepted) was added dropwise under constant stirring at 70 °C. And the stirring was conducted until the transparent gel forms. After two days aging, these prepared samples were dried at 110 °C and collected. The catalysts with different molybdenum oxide loading from 5 to 30 wt % were referred to as CsPMA-*x*/SiO₂ (*x* = 5, 10, 20 and 30 wt %), which will be used for further characterizations and activity estimation.

Physico-chemical Characterization. The BET surface areas of catalysts were determined from nitrogen physisorption measured on a Quantachrome Autosorb IQ-C instrument at -196 °C. Before the measurement, the samples were evacuated at 200 °C for 2 h. Powder X-ray diffraction (XRD) spectra of catalysts were recorded on a X-ray diffractometer (Beijing Purkinje General Instrument Co. Ltd) with Ni filtered Cu K α radiation ($\lambda = 1.542 \text{ \AA}$) and a scanning range 2θ of 5-80°. XRD patterns were attributed using the JCPDS database. FT-IR spectra were taken using a FT6700 instrument in KBr matrix in the range 400-4000 cm^{-1} . Scanning electron microscopy images (SEM) were obtained with a JSM6380LV instrument to observe the morphology of the prepared samples. The acidity of the solid samples was measured by the potentiometric titration method. Certain amount of solid (0.5 g) was suspended in acetonitrile and the system was then magnetically stirred for 3 h at room temperature. Then the suspension was titrated with a solution of 0.05 N *n*-butylamine in acetonitrile, with the flowing rate of 0.05 mL/min. The variation in the electrode potential was measured with an instrument having a digital pH meter, using a standard calomel electrode.²⁴

Catalytic Activity. All liquid-phase catalytic nitration reactions were carried out in a batch reactor. In a typical run, 5 mL benzene, 15 mL nitric acid (65%) and 0.5 g catalyst was added into a 100 mL round bottom flask at 70 °C under stirring. After stirring for 5 h, the catalyst was separated by filtration, and the organic layer was analyzed off-line by gas chromatography (FID, column: OV-101, 30 m length, 0.25 mm ID).

Results and Discussion

Catalyst Characterization. The powder XRD patterns of the samples are shown in Figure 1. The patterns suggested that the silica support and CsPMA-5/SiO₂ were in amorphous phase. For the CsPMA-10/SiO₂ sample, the main peaks were observed at $2\theta = 10.4^\circ, 18.2^\circ, 23.8^\circ, 26.0^\circ, 30.3^\circ, 35.3^\circ,$ and 38.6° , which were assigned to the diffraction of unsupported CsPMA. It is noteworthy that the intensities of these diffraction peaks were increasing with the increase of loadings. Compared with unsupported CsPMA, there was no modification in the XRD patterns of the CsPMA/SiO₂ samples except the amorphous character at about $2\theta = 25^\circ$, indicating that there was no structural change in the units of CsPMA that are arranged on the amorphous silica support.

Figure 2 presents the FT-IR spectra of unsupported and supported CsPMA samples. The spectra of CsPMA showed the characteristic signature of Keggin structure with absorp-

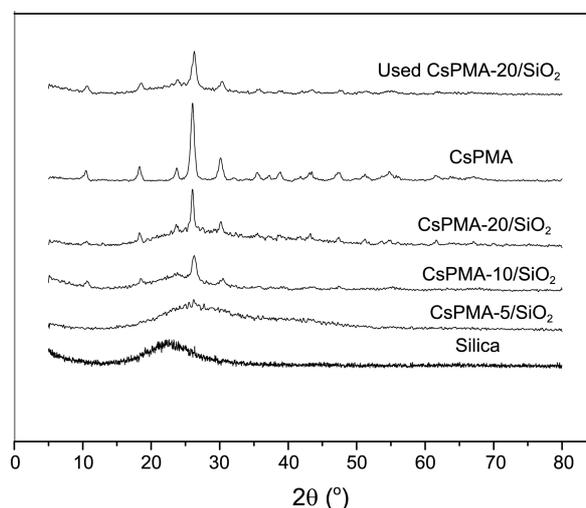


Figure 1. XRD patterns of supported catalysts prepared by sol-gel method.

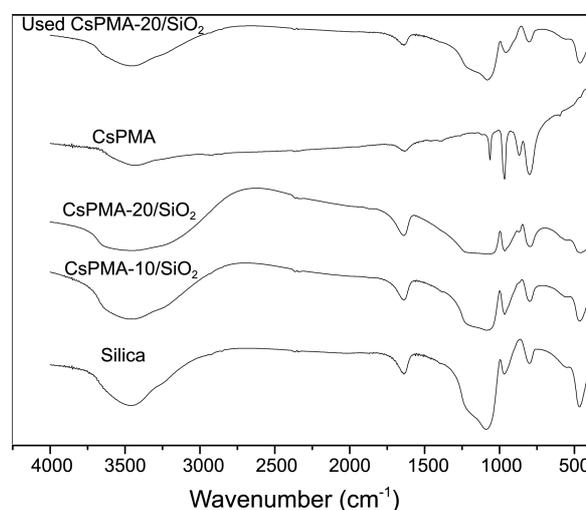


Figure 2. FTIR spectrum of supported catalysts prepared by sol-gel method.

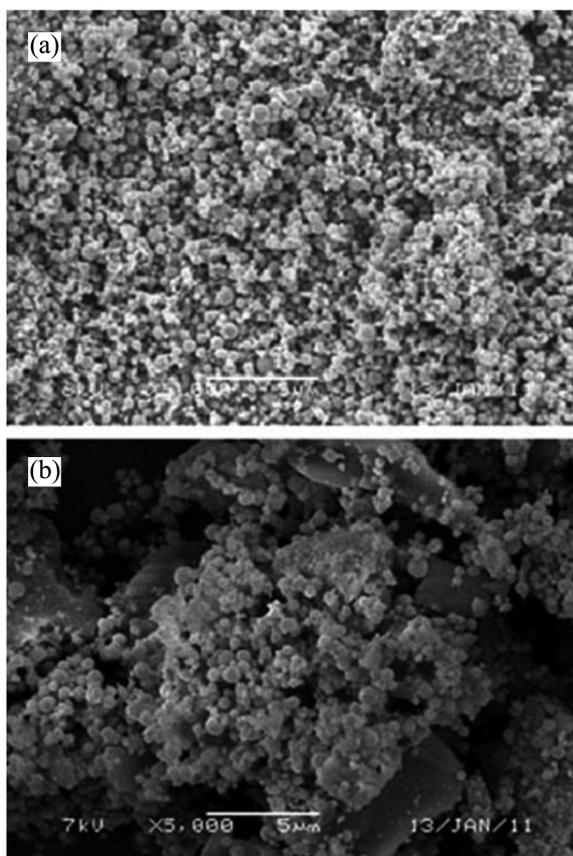


Figure 3. Scanning electron microscopy images of (a) CsPMA. (b) CsPMA-30/SiO₂.

tion bands at 1063, 966, 868, and 800 cm⁻¹. For supported CsPMA samples, the spectra shown a broad band around 3100-3600 cm⁻¹, which may be ascribed to adsorbed water molecules. The absorption band at 1640 cm⁻¹ was according to H–O–H bending vibration of water. The broad absorption band around 1090 cm⁻¹ was attributed to Si–O asymmetric stretching vibrations of Si–O–Si bridges.²² The informative fingerprint about the presence of Keggin structure was also given in FT-IR spectra of CsPMA-20/SiO₂ with two weak characteristic band at 966 and 868 cm⁻¹ that were not observed in spectra of silica, indicating that CsPMA still retained its Keggin structure after supported on silica by sol-gel technology.

The SEM images of CsPMA and CsPMA-30/SiO₂ are shown in Figure 3. It revealed that CsPMA was made up of submicrometer sized free standing or aggregated sphere shaped particles and the average particle size was in the range of 0.5-1 μm. Similar type of morphology was observed in the case of CsPMA-30/SiO₂ and these sphere shaped particles were well dispersed on the surface of plank shaped silica support, which may conducive to the increase of specific surface area.

Table 1 shows the BET surface areas of CsPMA-*x*/SiO₂ samples. As well known, neat H₃PMO₁₂O₄₀ has a low specific surface area (< 10 m²/g).¹⁵ The substitution of 2.5 H⁺ in H₃PMO₁₂O₄₀ by 2.5 Cs⁺ brought about a change, the prepared CsPMA has a surface area of 88 m²/g. For the series of

Table 1. Physicochemical characterization, effects of loading on nitration of benzene

Catalyst	BET surface area (m ² /g)	E _i (mV) potentiometric titration	Conversion ^a (%)
CsPMA-5/SiO ₂	779	161	69.1
CsPMA-10/SiO ₂	598	358	93.7
CsPMA-20/SiO ₂	526	375	95.1
CsPMA-30/SiO ₂	358	219	87.6
CsPMA	88	275	88.8

^aThe reaction conditions are the ratio by volume of benzene: Nitric acid is 1:3, the catalyst weight is 0.5 g, and the reaction is carried out at 70 °C under stirring for 5 h.

CsPMA-*x*/SiO₂ samples prepared by sol-gel technique, the surface area of CsPMA-5/SiO₂ was 779 m²/g. Although the values decreased gradually with the loadings increasing, the surface area of CsPMA-30/SiO₂ was still 358 m²/g and much higher than the pure CsPMA, indicating the sol-gel method is effectively to increase the surface area of CsPMA catalyst.

The acidity of these CsPMA-*x*/SiO₂ samples were measured by potentiometric titration technique with *n*-butylamine as the titrant, which was recommended by Cid and Pecchi²⁴ to evaluate the strength and the total number of acid sites on the surface of solid acid catalyst. The titration curves of the electrode potential as a function of mL *n*-butylamine added are shown in Figure 4. It can be found that as the acid sites of these CsPMA-*x*/SiO₂ samples become neutralized, a buffer behavior was more apparent, which in turn was related to the volume of *n*-butylamine added. In order to further interpret the results, it is suggested that the initial electrode potential (*E_i*) be taken as the maximum acidic strength of the surface sites and the range where the plateau is reached can be considered as the total number of acid sites.²⁵ On the other hand, the acid strength of these sites may be classified according to the following scale²⁵: *E_i* > 100 mV (very strong sites), 0 < *E_i* < 100 mV (strong sites), -100 < *E_i* < 0 mV (weak sites) and *E_i* < -100 mV (very weak sites). The *E_i* values of CsPMA-*x*/SiO₂ samples with different loadings are

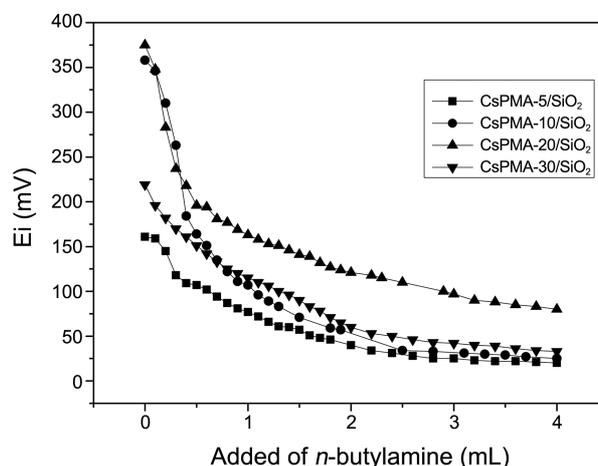


Figure 4. Potentiometric titration curves of supported catalysts.

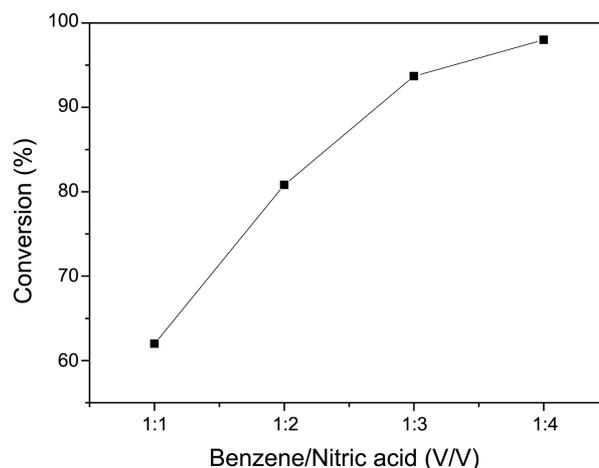
Table 2. Influence of catalyst re-used on conversion of benzene

Used times	Catalyst	Temperature (°C)	Benzene/nitric acid (V/V)	Time (h)	Conversion (%)
1	CsPMA-20/SiO ₂	70	1:3	5	95.1
2	CsPMA-20/SiO ₂	70	1:3	5	93.6
3	CsPMA-20/SiO ₂	70	1:3	5	92
4	CsPMA-20/SiO ₂	70	1:3	5	90.9
5	CsPMA-20/SiO ₂	70	1:3	5	89.2
6	CsPMA-20/SiO ₂	70	1:3	5	90

shown in Table 1. All CsPMA-*x*/SiO₂ samples exhibited high E_i value, indicating these samples had very strong acid sites. And the acid strength of the CsPMA-*x*/SiO₂ catalysts increases as the loading increases to 20 wt %. On a further increase of loading to 30 wt %, however, a decrease of acid strength is observed, possibly due to the decline in surface area and the aggregation of the catalysts with the high loading.

Catalytic Activity. As catalyst of liquid-phase nitration of benzene, pure CsPMA and CsPMA-*x*/SiO₂ with different loadings were evaluated and the result is summarized in Table 1. The reaction were carried out with the volume ratio of benzene : nitric acid of 1:3 and the catalyst weight of 0.5 g. The reaction mixture was stirred for 5 h at 70 °C. Take CsPMA as catalyst, the conversion of benzene was about 89% and there were no other multi-nitro compounds formed besides mononitro-benzene, indicating that CsPMA had high catalytic activity and selectivity over nitrobenzene. In other words, CsPMA exhibited excellent potential as the alternative of sulfuric acid in the nitration progress of benzene. For CsPMA-5/SiO₂, the conversion of benzene was 69%. With the increase of the loading, the conversion increased rapidly and attained the maximum of 95% for CsPMA-20/SiO₂ sample and then decreased gradually, reaching 87.6% for CsPMA-30/SiO₂. More significant result could be observed from Table 1, the change of catalytic activity was consistent with the change of acid strength of pure and supported samples.

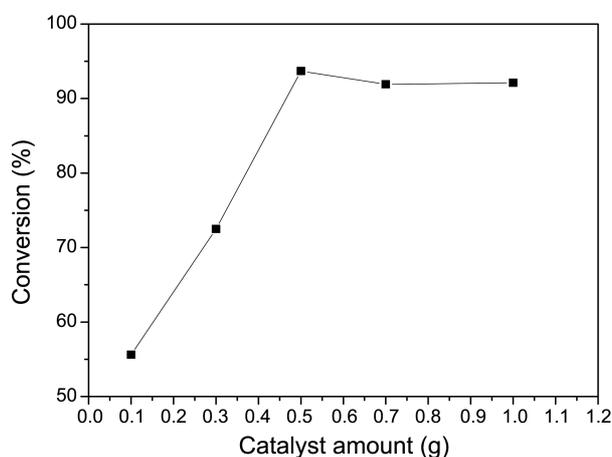
Compared with pure CsPMA, silica supported samples with suitable loadings not only improve the catalytic activity, but also to optimize the recycling performance of the catalyst in reaction progress. The recycle of CsPMA-20/SiO₂ was only by leaching from the reaction system and dried at 110 °C before used next time with fresh benzene and nitric acid. The recycling result is shown in Table 2. The conversion of benzene still reached 90% even after reusing five times, indicating CsPMA-20/SiO₂ catalyst had excellent stability under nitration reaction conditions. After being reused for five times, the possible change of CsPMA-20/SiO₂ catalyst in reaction progress was analyzed by XRD and potentiometric titration technique. XRD pattern (Fig. 1) of used CsPMA-20/SiO₂ catalyst was almost same as that of before nitration and only these diffraction peaks ascribed CsPMA were observed, indicating that there was no structural change in nitration progress. The potentiometric titra-

**Figure 5.** Influence of volume ratio of nitric acid to benzene on conversion of benzene.

tion result indicated reused catalyst also had very strong acid sites ($E_i = 295$ mV), which may be the main reason that this catalyst still exhibited high catalytic activity after repetitious usage. These results also demonstrated the initial idea that combined the support technology and partially substitution of protons by large cations, could improve the stability of HPAs catalysts.

To deeply evaluate the catalytic performance of silica supported CsPMA catalyst, the effects of reaction parameters on the nitration of benzene had been investigated in details, such as the catalyst amount, temperature, time, the volume ratio of benzene and nitric acid. CsPMA-10/SiO₂ was selected as the evaluated catalyst. Figure 5 shows the effect of volume ratio between nitric acid and benzene on the nitration reaction at 70 °C over 0.5 g catalyst. The conversion of benzene was 62% when the volume ratio of benzene and nitric acid was 1:1, and it increased with the increase of the amount of nitric acid. Almost completely conversion (98%) with 100% selectivity of mononitrobenzene was obtained when the volume ratio of nitric acid to benzene was increased to 4:1.

The effect of the catalyst amount (0.1, 0.3, 0.5, 0.7 and 1.0

**Figure 6.** Influence of catalyst amount on conversion of benzene.

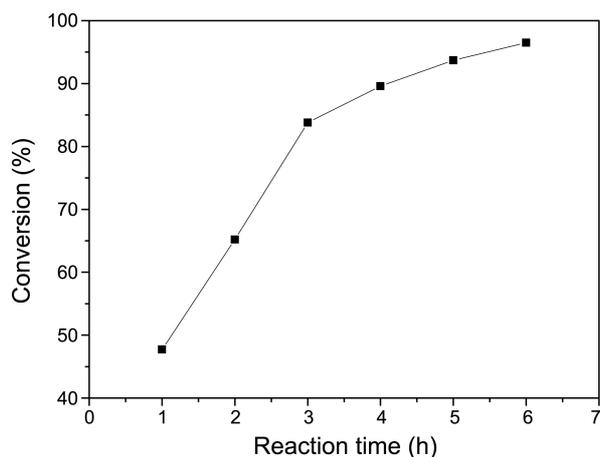


Figure 7. Influence of reaction time on conversion of benzene.

g) was investigated with the volume ratio of nitric acid to benzene being 3:1 at 70 °C for 5 h, and the result is presented in Figure 6. The conversion of benzene increases from 55.6% to 93.7% with an increase in the catalyst amount from 0.1 to 0.5 g and then remained almost constant with further increase of catalyst amount up to 1.0 g.

The effect of reaction time was studied at a volume ratio of 1:3 using 0.5 g of CsPMA-10/SiO₂ catalyst at 70 °C. As illustrated in Figure 7, the percentage of conversion increased from 47.7% to 93.7% with an increase in reaction time from 1 to 5 h. No notable increase of the conversion with further increasing of the reaction time. Additionally, the product was still only nitrobenzene after 6 h reaction, indicating the selectivity towards nitrobenzene did not significantly be affected by reaction time.

The effect of reaction temperature on the conversion of benzene is shown in Figure 8. The reaction was carried out in the temperature region 40-90 °C over 0.5 g catalyst with the nitric acid to benzene volume ratio of 3:1 for 5 h. The conversion of benzene increased with the increase of reaction temperature, indicating that the higher temperature favored the acceleration of the reaction. But further increase

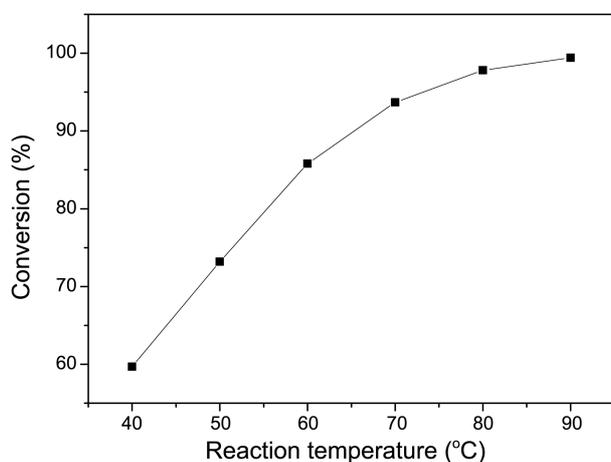


Figure 8. Influence of reaction temperature on the conversion of benzene.

in reaction temperature up to 80 °C obviously accelerated the decomposition of nitric acid. As a result, the suitable nitration temperature was 70 °C.

Conclusions

An environment-friendly liquid-phase nitration of benzene with mild conditions was developed. The Cs salt of phosphomolybdic acid exhibited good potential as alternative catalyst of sulfuric acid in nitration of benzene, and the catalytic activity can be effectively improved through the loading of Cs_{2.5}H_{0.5}PMo₁₂O₄₀ on silica support by sol-gel method with ethyl silicate-40 as silicon resource. For the supported catalyst, the Cs_{2.5}H_{0.5}PMo₁₂O₄₀ particles with Keggin-type structure were well dispersed on the surface of silica, which resulted in the obvious increase of surface area and acidity, and then optimized the catalytic performance, especially the stability of catalyst in liquid-phase nitration of benzene.

Acknowledgments. The authors are grateful for the support of the Doctor Foundation of Shandong Province (BS2010CL011) and the National Basic Research Program (2010CB234601).

References

- Olah, G. A.; Malhotra, R.; Narang, S. C. *Nitration: Method and Mechanism*; VCH: New York, 1989; pp 5-15.
- Hu, Y.; Yang, J.; Yang, X.; Wang, G. *Chinese J. Catal.* **2009**, *30*, 891-895.
- Chaubal, N. S.; Sawant, M. R. *Catal. Commun. A* **2007**, *8*, 845-849.
- Mao, W.; Ma, H.; Wang, B. *J. Hazard. Mater.* **2009**, *167*, 707-712.
- German, A.; Akouz, T.; Figueras, F. J. *Catal.* **1994**, *147*, 163-170.
- Adamiak, J.; Kalinowska-Alichnewicz, D.; Szadkowski, M.; Skupiński, W. *J. Hazard. Mater.* **2011**, *195*, 195-200.
- Bharadwaj, S. K.; Hussain, S.; Kar, M.; Chaudhuri, M. K. *Appl. Catal. A* **2008**, *343*, 62-67.
- Chaubal, N. S.; Sawant, M. R. *Catal. Commun.* **2007**, *8*, 845-849.
- Kemdeoa, S. M.; Sapkal, V. S.; Chaudharia, G. N. *J. Mol. Catal. A* **2010**, *323*, 70-77.
- Mishra, T. *Catal. Commun.* **2008**, *9*, 21-26.
- Zolfigol, M. A.; Mirjalili, B. F.; Bamoniri, A.; Zarchi, M. A. K.; Zarei, A.; Khazdooz, L.; Noei, J. *Bull. Korean Chem. Soc.* **2004**, *25*, 1414-1416.
- Brei, V. V.; Prudius, S. V.; Melezhyk, O. V. *Appl. Catal. A* **2003**, *239*, 11-16.
- Alsalmeh, A.; Kozhevnikova, E. F.; Kozhevnikov, I. V. *Appl. Catal. A* **2008**, *349*, 170-176.
- Kumbar, S. M.; Halligudi, S. B. *Catal. Commun.* **2007**, *8*, 800-806.
- Kozhevnikov, I. V. *Catal. Rev. Sci. Eng.* **1995**, *37*, 311-352.
- Rocchiccioli-Deltcheff, C.; Aouissi, A.; Launay, S.; Fournier, M. *J. Mol. Catal. A* **1996**, *114*, 331-342.
- Rafiee, E.; Shahbazi, F.; Joshaghani, M.; Tork, F. *J. Mol. Catal. A* **2005**, *242*, 129-133.
- Carriazo, D.; Domingo, C.; Martín, C.; Rives, V. *J. Solid State Chem.* **2008**, *181*, 2046-2057.
- Ahmed, A. I.; El-Hakam, S. A.; Abd Elghany, M. A.; Abo El-Yazeed, W. S. *Appl. Catal. A* **2011**, *407*, 40-48.
- Bamoharrama, F. F.; Heravi, M. M.; Roshani, M.; Gharib, A.; Jahangir, M. *J. Mol. Catal. A* **2006**, *252*, 90-95.

21. Heravi, M. M.; Khorasani, M.; Derikvand, F.; Oskooie, H. A.; Bamoharram, F. F. *Catal. Commun.* **2007**, 8, 1886-1890.
 22. Parida, K. M.; Rana, S.; Mallick, S.; Rath, D. *J. Colloid Interf. Sci.* **2010**, 350, 132-139.
 23. Gong, S.; Liu, L.; Cui, Q.; Ding, J. *J. Hazard. Mater.* **2010**, 78, 404-408.
 24. Cid, R.; Pecci, G. *Appl. Catal. A* **1985**, 14, 15-21.
 25. Romanelli, G. P.; Autino, J. C.; Blanco, M. N.; Pizzio, L. R. *Appl. Catal. A* **2005**, 295, 209-215.
-