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Liquid phase nitration of benzene over supported ammonium salt of 12-molybdophosphoric acid catalysts prepared by sol–gel method

Shuwen Gong*, Lijun Liu, Qingxin Cui, Junhong Ding

Department of Chemistry, Liaocheng University, Liaocheng 252059, China

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ABSTRACT

A mild and clean liquid nitration of benzene with 65% nitric acid as nitrating agent over silica supported ammonium salt of 12-molybdophosphoric acid catalysts has been investigated. These catalysts with different loadings were prepared by sol–gel method and characterized by X-ray diffraction (XRD) and FTIR spectra. The acidity of these catalysts was measured by the potentiometric titration method. The XRD and IR analysis revealed that supported catalysts possess the Keggin structure which is similar to 12-molybdophosphoric acid. And it can be found that the supported catalysts had high nitration reaction catalytic activity and selectivity over nitrobenzene. The effects of various parameters such as nitric acid/benzene volume ratio, temperature and time of reaction have also been systematically studied.

1. Introduction

The nitration of benzene is a widely studied reaction of great industrial significance as nitrobenzene is known to be a starting material for producing useful substances such as aniline, benzidine, metanilic acid. Industrial-scale nitration of benzene is usually carried out in liquid phase using mixed-acids containing nitric and sulfuric acids as starting materials, where the main purpose of sulfuric acid is the protonation of nitric acid, thereby forming nitronium ions, which are the actual nitrating species. Additionally, the sulfuric acid also serves as a water binder and heat sink for the nitration as these reactions are exothermic [1,2]. Despite of the high efficiency, the nitration reaction with the mixed-acids is not very eco-friendly, as it produces large amount of acid waste, which were costly to recycle and generated environmental problems making nitration of aromatics as one of the most hazardous industrial process [1–3].

For the last 160 years, chemical engineering research on nitration processes of benzene or substituted benzenes has achieved many valuable improvements including better energy management of modern nitration plants, and various clean nitration approaches focused on dispensing the use of sulfuric acid have also been explored [2–4], in other words, nitration of aromatics without the use of sulfuric acid would be an attractive alternative. So an alternative solid–acid catalyst is desirable, as its separation from the reaction mixture and its regeneration will be easier than that of the liquid acid in the mixed-acid process [5–9].

Heteropolyacids (HPAs), particularly the 12-molybdophosphoric acid (MPA) and the 12-tungstophosphroic acid (TPA) possessing the Keggin structure, are extensively studied as acid catalysts for many reactions and industrial processes [10–14]. The salts of HPAs are also recognized as effective catalysts, in particular, industrial application of the ammonium salt of 12-molybdophosphoric acid (AMPA), possessing the Keggin structure, began with the oxidation of methacrolein to methacrylic acid in which diammonium molybdophosphoric acid [$(NH_4)_2HPMo_{12}O_{40}$] was identified as the catalytically relevant species [15]. Recently, Heravi et al. [16] reported the regioselective nitration of phenol catalyzed by $H_{3+x}PMo_{12-x}V_xO_{40}$ in heterogeneous system with different solvents and other parameters. But for salts of HPAs catalyst, they have not been exploited in nitration reaction of aromatic compounds.

Recently, in seeking to develop new synthetic methods for organic compounds by using heteropolyacids, we have prepared a series of supported ammonium salt of 12-molybdophosphoric acid catalysts, which exhibited the Keggin structure like parent MPA, and the performance and applicability of these catalysts have been studied for liquid phase nitration of benzene.

2. Experimental

2.1. Catalyst preparation

Ammonium heptamolybdate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$], ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$) and ethyl

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* Corresponding author. Tel.: +86 635 8230606; fax: +86 635 8239121.
E-mail address: gongshw@lcu.edu.cn (S. Gong).

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silicate-40 (CAS registry No. 18945-71-7) were used as the source of molybdenum, phosphorus and silica, respectively. Unsupported AMPA catalyst was prepared according to Ref. [17]. Stoichiometric amounts of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $NH_4H_2PO_4$ were dissolved in a minimum amount of de-ionized water and the pH of solution was adjusted to 1 using nitric acid. The aqueous solution was stirred at 343 K for 5 h and then was concentrated and dried at 393 K.

Silica supported AMPA catalysts with varying molybdenum oxide mass concentrations (5, 10, 20, 30 and 40 wt%) were prepared by the sol–gel technique. In the next step, the mixed solutions of ethyl silicate-40, distilled water and ethanol (volume ratio, 1:2:2) were stirred at 343 K for 30 min to form clear solution. In the next step, the solutions of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $NH_4H_2PO_4$ which were prepared in advance using the method mentioned above (dryness at 393 K was excepted) were added under vigorous stirring, and the stirring was conducted until the transparent gel forms. After 2 days of aging, these prepared samples were dried at 393 K and collected, which will be used for further characterizations.

The silica support was obtained by drying the gel, which was prepared by the Stober process, with the volume ratio between ethyl silicate-40 and ethanol to be 1:2. Trace amount of ammonia was added as catalyst, which was stirred at 343 K until gel was formed.

2.2. Catalyst characterization

The X-ray diffraction analysis was carried out using an X-ray diffractometer (Beijing Purkinje General Instrument Co. Ltd.) with Ni filtered Cu Kα radiation ($\lambda = 1.542$ Å) and a scanning range 2θ of 5–80°. FTIR spectra were taken using a FT6700 instrument in the range 400–4000 cm^{-1}. 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 [18].

2.3. 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 1 g catalyst were added into a 100 mL round bottom flask at 343 K 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).

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of all the catalysts prepared by sol–gel with 5, 10 and 20 wt% loadings are shown in Fig. 1. For comparison, the XRD patterns of pure support and unsupported AMPA catalyst are also included. The pattern of the support clearly indicates the presence of amorphous silica. The pattern of the unsupported catalyst shows that peaks are similar to the reference pattern for AMPA ($(NH_4)_3PMo_{12}O_{40}$) taken from the JCPDS powder diffraction file (card 09-0412). Catalysts with 10 and 20 wt% loading show highly crystalline nature with intense peaks at $2\theta = 10.8°$, 15.2°, 21.6°, 26.5°, 36.2°, etc., which is similar to the unsupported catalyst, confirming the successful preparation of AMPA on the silica support. For catalyst with 5 wt% loading, some peaks assigned to AMPA are also observed with weaker diffraction intensity than catalysts with 10 and 20 wt% loading. It is noteworthy to note that even though the AMPA is in the crystalline form at higher loading, the silica support still retains its amorphous nature, leading to the high surface area of the catalysts, which indicates that AMPA particles are well dispersed on the support when the loading is low, and the increase of loading results in the growth or aggregation of AMPA crystal particle.

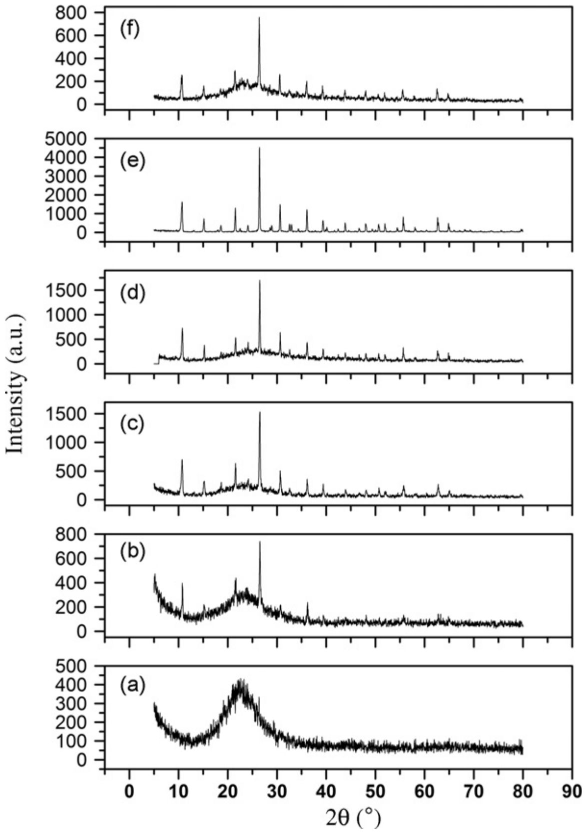

Fig. 1. XRD patterns of supported catalysts prepared by sol–gel method. (a) Support; (b) 5%; (c) 10%; (d) 20%; (e) unsupported catalyst; (f) 10% catalyst after nitration reaction.

Shown in Fig. 2 are FTIR spectra for supported catalysts with 5, 10, 20 and 40 wt% loadings as well as the spectra of support and pure AMPA are given for comparison. The IR spectra of pure sample show bands at 1062, 963, 865 and 791 cm^{-1}, that can be assigned to stretching vibrations of ($P–O_d$), ($Mo–O_t$), ($Mo–O_b–Mo$), and ($Mo–O_c–Mo$), respectively (the symbols given to oxygen atoms describe their specific positions in the Keggin structure) [17,19]. These four bands are typical bands of Keggin structure. And there are two bands at 1384 and 3139 cm^{-1} that can be attributed to the N–H of NH_4^+, and the bands of 1626 and 3434 cm^{-1} to H–O–H. In general, the unsupported catalyst is an ammonium salt with some crystal water. Due to the pure support, which shows strong shoulder bands at approximately 1200 cm^{-1}, the AMPA 1079 cm^{-1} stretching for supported samples is partially superseded. And for the catalysts with 5 wt% loading, the bands assigned to AMPA are very weaker, which may be covered by the strong absorption of silica in the region of the Keggin anion "fingerprint" [17]. On a further increase of loading to 10–20 wt%, the bands of 963 and 865 cm^{-1} are found, these two bands are typical of the Keggin anion and not observed in the silica spectrum, and the increase in intensities of these bands with increase of loading is also observed. For supported catalyst with 40 wt% loading, the band assigned to AMPA is almost observed besides the band of 1079 cm^{-1} was blanketed by the band of support, indicating that the catalyst at this loading had attained bulk nature.

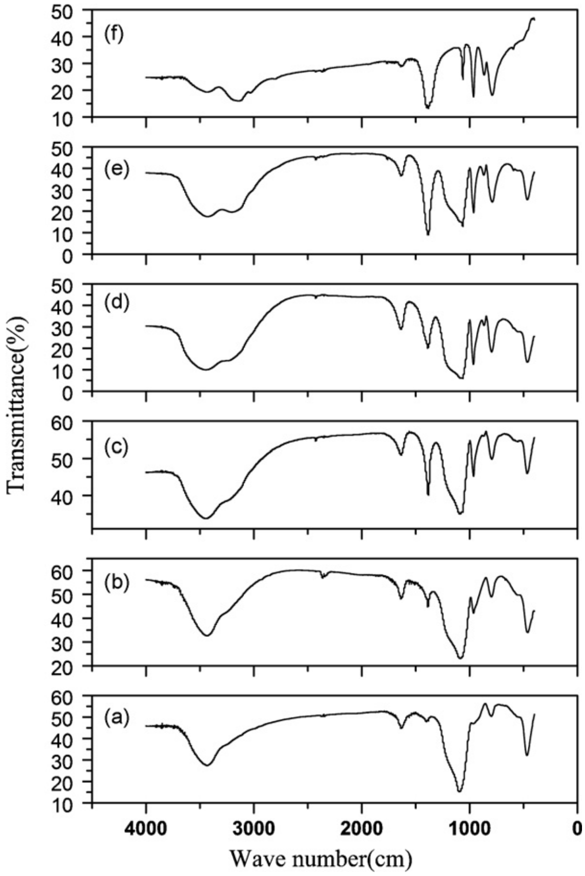

Fig. 2. FTIR spectrum of supported catalysts prepared by sol–gel method. (a) Support; (b) 5%; (c) 10%; (d) 20%; (e) 40%; (f) unsupported catalyst.

The acidity of the catalyst was measured by potentiometric titration technique which enables the determination of the total number of acidic sites and their strength. The titration curves of the catalysts with 30% loading and pure AMPA are shown in Fig. 3. In order to 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 (mequiv. amine/g cat) can be considered as the total number of acid sites [20]. On the other hand, the acid strength of these sites may be classified according to the following scale: $E_i > 100$ mV (very strong sites), $0 < E_i < 100$ mV (strong sites), $-100 < E_i < 0$ (weak sites) and $E_i < -100$ mV (very weak sites) [20]. Fig. 4 shows the acid strength of the support samples with different AMPA loading.

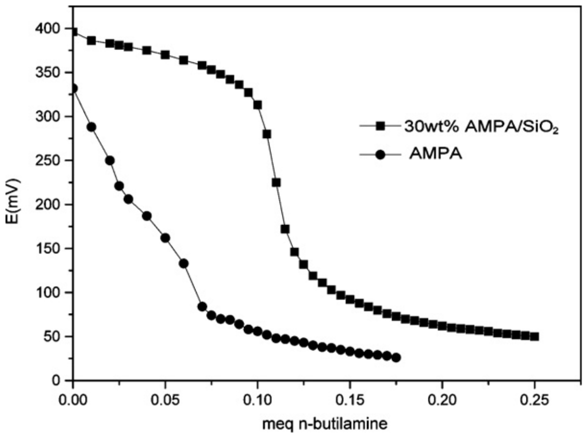

Fig. 3. Potentiometric titration curves of pure AMPA and 30% AMPA/SiO$_2$ catalysts.

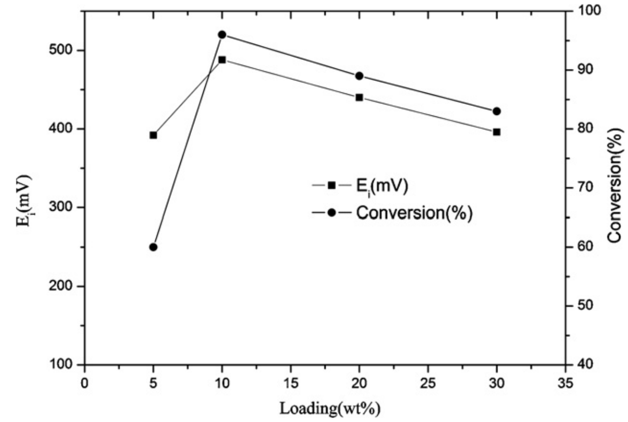

Fig. 4. Acid strength and nitration catalytic activity of supported AMPA catalysts. Reaction conditions: 10 wt% catalyst 1 g, benzene 5 mL, nitric acid 15 mL, 5 h and 343 K.

From the plot shown in Fig. 3, it can be found that the silica supported AMPA with 30% loading shows very strong acid sites ($E_i = 396$ mV), whose acid strength is higher than that of the strong sites in pure AMPA. And the total number of acid sites of the supported AMPA with 30 wt% is more than pure AMPA, which may be caused by the good dispersion of the AMPA over support. Fig. 4 reveals the change of acid strength of supported catalysts with the increase of loading. The acid strength of the support catalysts increases as the loading increases to 10 wt%. On a further increase of loading from 10 to 30 wt%; however, a continuous decrease of acid strength is observed, possibly due to the decrease of surface area of the catalysts with the increase of loading. The silica support was titrated at lower potentials ($E < 0$ mV) in the range of very weak acid sites [21].

3.2. *Catalytic reaction*

Benzene nitration was carried out using a series of catalysts with different loading and the results are summarized in Fig. 4. For catalyst with 5 wt% loading, the conversion of benzene was 60%. With the increase of the loading, the conversion increased rapidly and attained the maximum of 96% for the sample with 10 wt% loading and then decreased gradually, reaching 83% for 30 wt% loading. The significative result is that from Fig. 4, it can be observed that the conversion trend of benzene is in accord with the change of acid strength from loading 5 to 30 wt%.

It should be mentioned that a disadvantage for nitration with mixed-acid method is reaction is unselective, which lead to the formation of some undesirable multi-nitro compounds [1]. While for the prepared unsupported and supported catalyst, there only exists the nitrobenzene in the product, in other words, the selectivity for nitrobenzene was 100%. On the other hand, AMPA is an attractive alternative sulfuric acid also because it not only reduces pollution caused by the spent acid, but also facilitates the separation issues of the undesired products, which is in accordance with the principles of green chemistry.

The effect of volume ratio between nitric acid and benzene on the nitration reaction at 343 K over 1 g of 10 wt% catalyst was investigated, and the results are shown in Fig. 5. It was observed that the conversion of benzene was low when the volume ratio between nitric acid and benzene is 1:1, and it increased with the molar ratio of nitric acid to benzene ranged from 1 to 7. The selectivity for nitrobenzene remained almost constant and there were no dinitro-benzene or other products formation.

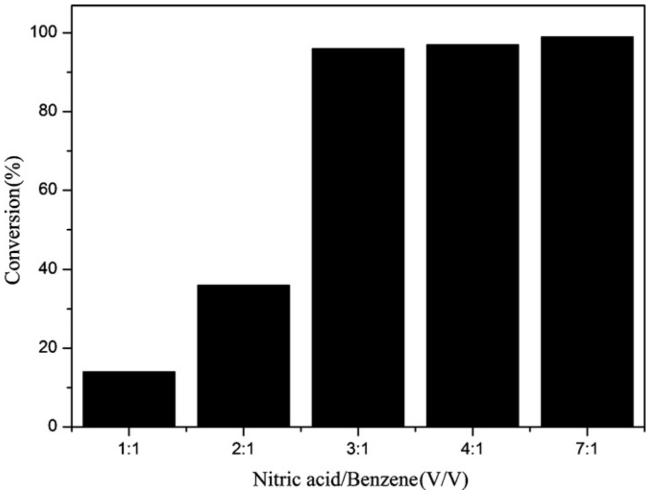

Fig. 5. Effect of volume ratio of nitric acid to benzene on yield of nitrobenzene. Reaction conditions: 10 wt% catalyst 1 g, benzene 5 mL, 5 h and 343 K.

The effect of reaction time at 343 K over 1 g of 10 wt% catalyst was also investigated. As shown in Fig. 6, there was a gradual increase in benzene conversion up to 5 h and thereafter no notable increase of the conversion with further increase of the reaction time. Additionally, the product was still only nitrobenzene after 7 h. Thus, the selectivity towards nitrobenzene was not significantly affected by the reaction time.

The nitration was carried out at different temperatures. The reaction was carried out in the presence of 1 g of 10 wt% catalyst with the volume ratio between nitric acid and benzene volume ratio 3:1 and the reaction temperatures varied from 323 to 383 K. The results are presented in Fig. 7. The conversion of benzene increased with the increase of reaction temperature from 323 to 363 K. Generally, the conversion is lower when the reactions are carried out at lower temperatures. It is believed that the higher temperature favors for the acceleration of the reaction. However, little decrease of benzene conversion was observed when the reaction temperature increased from 363 to 383 K, which may be associated with exothermic character of the nitration reaction itself.

The recycling performance of the catalyst was investigated by isolating the catalyst by filtration and recycling it. The filtered catalyst was only dried and reused with the fresh charge of benzene and nitric acid. The results are given in Table 1. Although the activity of catalyst was found to be deactivated, conversion of 78% was also obtained after 10 wt% catalyst was reused for three times and the selectivity for nitrobenzene was still 100%. Interestingly, the catalyst after being used for three times was collected and analyzed again by XRD, given in Fig. 1. It can be seen that its XRD pattern does not show significant changes except for the lower intensities of the peaks than original samples, suggesting the stability of structure of the catalyst.

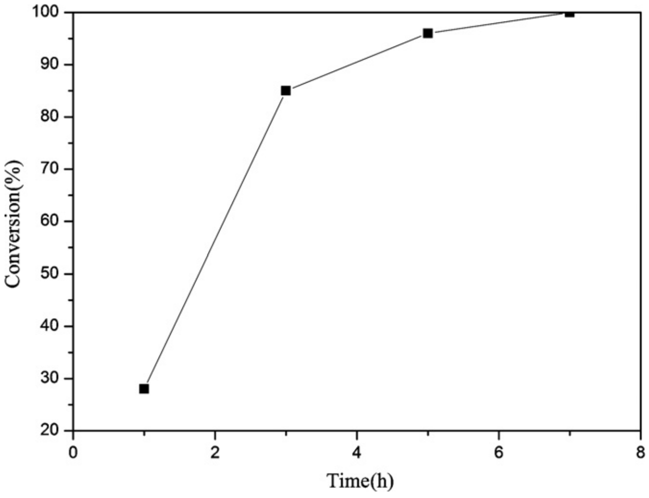

Fig. 6. Effect of reaction time on the yield of nitrobenzene. Reaction conditions: 10 wt% catalyst 1 g, benzene 5 mL, nitric acid 15 mL and 343 K.

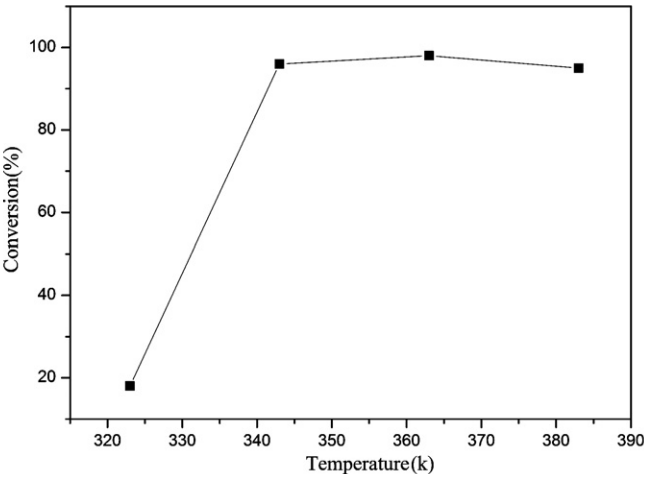

Fig. 7. Effect of reaction temperature on the yield of nitrobenzene. Reaction conditions: 10 wt% catalyst 1 g, benzene 5 mL, nitric acid 15 mL and 5 h.

Table 1
Results of catalyst recycle studies.

Catalyst	Recycle times	Conversion (%)
10%AMPA/SiO_2	0	96
10%AMPA/SiO_2	1	90
10%AMPA/SiO_2	2	86
10%AMPA/SiO_2	3	78

Reaction conditions: catalyst 1 g, benzene 5 mL, nitric acid 15 mL, 5 h and 343 K.

4. Conclusion

Nitration of benzene to nitrobenzene was achieved using a series of supported ammonium salt of 12-molybdophosphoric acid catalysts, which were prepared via sol–gel technique, with high conversion and selectivity. Nitric acid was used as nitrating agent without the use of sulfuric acid, which makes this process environmentally benign. And it was found that the nitration of benzene can be affected by the catalyst loading, volume ratio of nitric acid to benzene, nitration time and temperature. And after recycling three times, the supported AMPA catalyst still exhibits high stability and catalytic activity.

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