# Regioselective nitration of naphthalene over HZSM-5-supported phosphotungstic acid

**Pingle Liu · Wei Xiong · Xiaofei Wang · Kun Huang · Fang Hao · Liangjie Wang · He'an Luo**

**Abstract** HZSM-5-supported phosphotungstic acid (PW) has been prepared and characterized. The results indicate that 5 wt% PW/HZSM-5 calcined at 773 K has the largest surface area and high dispersion of PW. It was confirmed that Keggin units are present inside the catalyst and that the proton of PW and the silanol of HZSM-5 interact via bridging structure. The catalytic properties of PW/HZSM-5 in the regioselective nitration of naphthalene to dinitronaphthalene were investigated. The best results, i.e. 48.5 % yield of 1,5-dinitronaphthalene, 49.2 % yield of 1,8-dinitronaphthalene, and the highest ratio of 1,5-dinitronaphthalene to 1,8-dinitronaphthalene, were obtained by use of 5 wt% PW/HZSM-5.

**Keywords** Regioselective nitration · Naphthalene · Dinitronaphthalene · HZSM-5-supported phosphotungstic acid catalyst

## Introduction

Nitration of aromatic compounds is a very important industrial process for production of intermediates which are widely used in the manufacture of pharmaceutical products, dyes, polyurethane pesticides, and perfumes. Naphthalene nitration can produce 1-nitronaphthalene, 1,5-dinitronaphthalene, and 1,8-dinitronaphthalene. The product from reduction of 1,8-dinitronaphthalene is an important intermediate in the production of dyes, and that from reduction of 1,5-dinitronaphthalene can be used to produce 1,5-naphthalene diisocyanate (NDI), an important raw material for production of advanced polyurethane with perfect performance

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(high hardness, excellent elasticity, heat resistance, good dynamic capability, and wear resistance) [1]. Polyurethane elastomers based on 1,5-naphthalene diisocyanate have attracted much research interest.

Nitration of naphthalene is mainly achieved by classical processes involving large quantities of nitric acid and sulfuric acid; these have many disadvantages, including generation of large quantities of corrosive waste, low regioselectivity, and inefficient atom economy. The yield of the most desired product, 1,5-dinitronaphthalene, is low, approximately 25–30 %, whereas yields of 1,8-dinitronaphthalene and 1-nitronaphthalene are approximately 60 and 10 % [2]. An environmentally benign and economical method for preparation of dinitronaphthalene and improving the yield of 1,5-dinitronaphthalene is, therefore, urgently required.

Zolfigol et al. designed 3-methyl-1-sulfonic acid imidazolium nitrate ([Msim]NO$_3$), a new, organic, acidic ionic liquid and nitrating agent, which enables highly efficient nitration of a variety of aromatic compounds without the need for a co-catalyst [3]. Methods for nitration of naphthalene or 1-nitronaphthalene to dinitronaphthalene in nitric acid or in a nitrating mixture of nitric acid and sulfuric acid over a well-defined catalyst have been patented. The yield of 1,5-dinitronaphthalene from nitration of 1-nitronaphthalene in nitric acid and nitromethane catalyzed by zeolite is 30.6–57.3 %. Recently, Wang et al. [4] reported that 78 % yield of dinitronaphthalene can be achieved by nitration of 1-nitronaphthalene over HZSM-5 with 95 % fuming nitric acid as nitration reagent. However, the 1-nitronaphthalene must be obtained by nitration of naphthalene. In the nitration of naphthalene in nitric acid and 1,2-dichloroethane over zeolite catalyst, yields of 1,5-dinitronaphthalene, 1,8-dinitronaphthalene, and 1-nitronaphthalene are only 37.9, 46.3, and 1.0 %, respectively. The main product in the absence of catalyst is 1-nitronaphthalene (yield 62.2 %) [5].

Researchers have devoted much attention to regioselective nitration of naphthalene, phenol, toluene, and other aromatic compounds over solid acid and ionic liquid catalysts [5–9]. However, selectivity for 1,5-dinitronaphthalene in the catalytic nitration of naphthalene is only approximately 30–40 %; more 1,8-dinitronaphthalene is formed [10, 11].

Zeolites are well known for their shape-selective behavior and phosphotungstic acid is widely used as a catalyst because of its strong acidity, high oxidizing ability, and thermal stability [12–17]. In this paper, we report the nitration of naphthalene with nitric acid over a zeolite-supported phosphotungstic acid catalyst without use of sulfuric acid. This is a mild, environmentally benign, and economical method for preparation of dinitronaphthalene.

## Experimental

### Catalyst preparation

NaZSM-5 zeolite was ion-exchanged in 1.0 M NH$_4$Cl aqueous solution at 298 K for 12 h, washed, dried at 293 K for 10 h, and calcined at 723 K for 12 h in air to obtain HZSM-5 zeolite.

HZSM-5-supported PW catalysts were prepared by impregnation. Phosphotungstic acid solutions were prepared by dissolving appropriate amounts of the acid in 30 mL of a 1:1 (v/v) mixture of ethanol and water. The HZSM-5 zeolite was then impregnated in this solution, with stirring, for 4 h. The mixture was then dried at 393 K for 12 h and calcined at different temperatures in the range 623–823 K for 4 h.

## Catalyst characterization

Specific surface area, pore volume, and pore size distribution of the samples were determined by use of a NOVA-2200e automated gas sorption system to study nitrogen adsorption–desorption. X-ray diffraction (XRD) data in the range $2\theta = 10$–$50°$ were acquired by use of a Rigaku (Japan) D/Max 2550 VB$^+$ X-ray diffractometer; the scanning rate was 1° min$^{-1}$. Fourier-transform infrared (FT-IR) spectra in the wavenumber range 400–4,000 cm$^{-1}$ were recorded on a Nicolet 380 spectrometer. Ultraviolet–visible spectra in the range 100–500 nm were recorded on a UV-2550 spectrometer.

## Typical reaction procedure

Nitration of naphthalene was performed in a three-necked, round-bottomed flask with a reflux condenser. Naphthalene (10 mmol) was placed in a flask containing 0.3 g catalyst, and excess nitric acid (65 wt%) was added. The reaction mixture was stirred at 338 K for 3 h. When reaction was complete, unreacted nitric acid was recovered by filtration. The remaining solid mixture was dissolved in acetonitrile and the catalyst was separated by filtration. The reaction products were analyzed by liquid chromatography with an LC-20AT solvent-delivery unit, 55:35:10 CH$_3$OH–C$_2$H$_3$N–H$_2$O as mobile phase, and detection at 254 nm (SPD-20A).

The concentration of the specimen and the selectivity for 1,5-dinitronaphthalene were calculated by use of the formulas (Eqs. 1, 2):

$$W_s = A_s \times W_i/A_i, \tag{1}$$

where $W_s$ and $W_I$ are the concentrations of the specimen and the standard sample, respectively, and $A_s$ and $A_I$ are the peak areas for the specimen and the standard sample, respectively, and

$$\text{Selectivity (\%)} = \frac{\text{the amount (mol) of dinitronaphthalene}}{\text{the amount (mol) of reacted naphthalene}} \times 100\ \% \tag{2}$$

## Results and discussion

### Characterization of the catalysts

The textures of catalysts with different PW loading calcined at 773 K are summarized in Table 1. The surface area of the HZSM-5 was 352.61 m$^2$ g$^{-1}$; this

increased when the HZSM-5 was used as a support for PW, possibly because formation of a secondary pore structure in the alumina framework. Surface area was largest (443.17 m$^2$ g$^{-1}$) for 5 wt% PW/HZSM-5 and decreased with increased PW loading, possibly because of coverage of the pore structure by large amounts of PW. Hence, pore volume also decreases with increased PW loading.

XRD patterns obtained from catalysts with different PW loading are shown in Fig. 1 (5 wt% PW/HZSM-5 (a), 10 wt% PW/HZSM-5 (b), and 30 wt% PW/HZSM-5 ©)). XRD patterns obtained from 5 wt% PW/HZSM-5 calcined at different temperatures are shown in Fig. 2 (623 K (a), 673 K (b), 723 K ©), 773 K (d), and 823 K (e)). The characteristic diffraction peaks at $2\theta = 22°–25°$ for all the samples are indicative of the presence of the HZSM-5 structure, i.e. this structure was not destroyed during catalyst preparation. For the 5 and 10 wt% PW/HZSM-5 samples, the characteristic peaks of PW crystals are barely visible, indicating that the PW is highly dispersed throughout the large-surface-area porous framework of HZSM-5. However, when PW loading reaches 30 wt%, the characteristic diffraction peaks of solid-state PW appear at $2\theta = 10.5°$, $20°$, and $35°$ [18, 19], indicating that Keggin units are present inside the pores and on the walls outside the pores and interact with the framework for 30 wt% loading.

**Table 1** Textural properties of catalysts with different PW loading

| Sample | Surface area (m$^2$ g$^{-1}$) | Pore diameter (nm) | Pore volume (cm$^3$ g$^{-1}$) |
|---|---|---|---|
| HZSM-5 | 352.61 | 2.11 | 0.171 |
| 5 wt% PW/HZSM-5 | 443.17 | 1.94 | 0.078 |
| 10 wt% PW/HZSM-5 | 397.64 | 1.80 | 0.066 |
| 30 wt% PW/HZSM-5 | 394.42 | 1.70 | 0.049 |
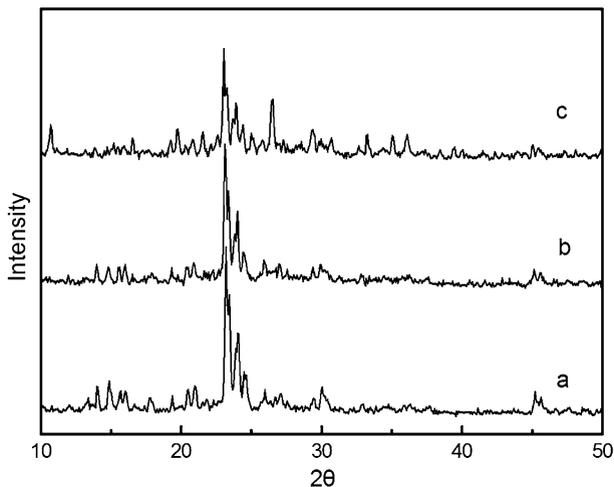


**Fig. 1** XRD patterns of PW/HZSM-5 with different PW loading: *a* 5 wt% PW/HZSM-5; *b* 10 wt% PW/HZSM-5; *c* 30 wt% PW/HZSM-5
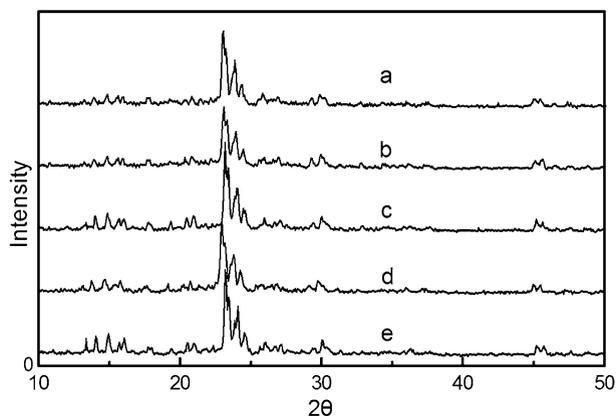
**Fig. 2** XRD patterns of 5 wt% PW/HZSM-5 calcined at different temperatures: *a* 623 K; *b* 673 K; *c* 723 K; *d* 773 K; *e* 823 K

**Fig. 3** UV–visible DRS of HZSM-5 and PW/HZSM-5 with different PW loading: *a* HZSM-5; *b* 5 wt% PW/HZSM-5; *c* 10 wt% PW/HZSM-5; *d* 30 wt% PW/HZSM-5
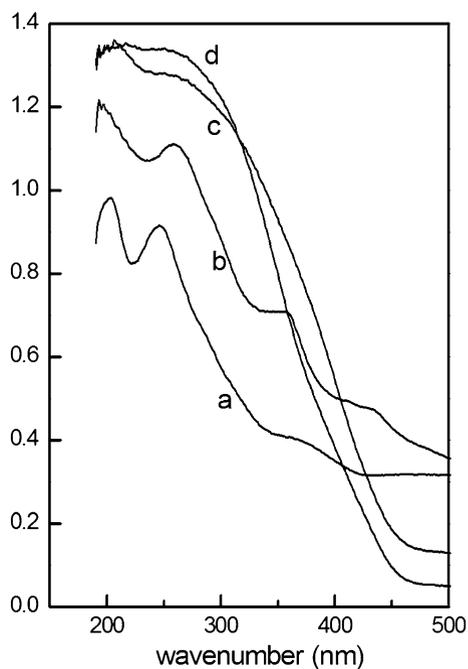


Figure 3 shows UV–visible diffuse reflectance spectra (DRS) of HZSM-5 and of HZSM-5-supported PW with different loading (5 wt% (a), 10 wt% (b), 30 wt% ©)). The spectrum of HZSM-5 (Fig. 3a) contains absorption bands near 200 and 250 nm. The spectra of the HZSM-5-supported PW samples contain a peak at 260 nm, indicating the presence of undegraded $H_3PW_{12}O_{40}$ species on the HZSM-5 support, which means the Keggin phase remains intact after calcination of PW-loaded HZSM-5 at 773 K [20, 21].

FT-IR spectra of PW/HZSM-5 with different loading are shown in Fig. 4 (5 wt% (a), 10 wt% (b), 30 wt% ©)). All the spectra contain bands at 530 and 802 $cm^{-1}$. The absorption at 530 $cm^{-1}$ is characteristic of vibration of the heteropolyanion [22] and the band at 802 $cm^{-1}$ is assigned to W–O–W vibration of edge-shared octahedra, indicating the presence of Keggin-type phosphotungstic acid [21, 23]. The absorption peaks at 550 and 450 $cm^{-1}$ are assigned to the framework vibration of HZSM-5. The absorption bands at 3,677 and 1,629 $cm^{-1}$, are assigned to –OH stretching vibration and H–O–H deformation vibration, respectively, of molecular water [24, 25]. Presumably the proton of PW and the silanol of HZSM-5 interact via a bridging structure. A model of the possible structure of the PW/HZSM-5 catalyst is shown in Fig. 5.
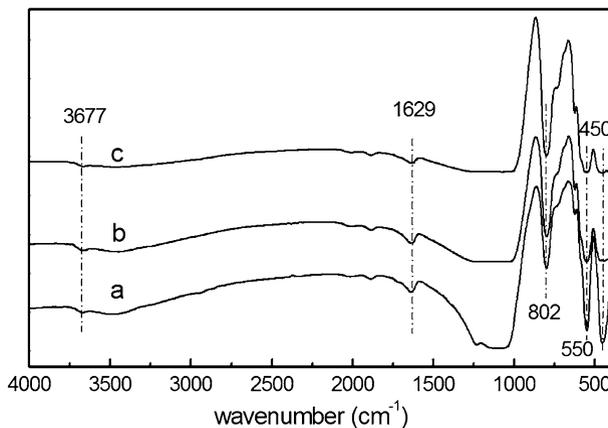


**Fig. 4** FT-IR spectra of PW/HZSM-5 with different PW loading: *a* 5 wt% PW/HZSM-5; *b* 10 wt% PW/HZSM-5; *c* 30 wt% PW/HZSM-5
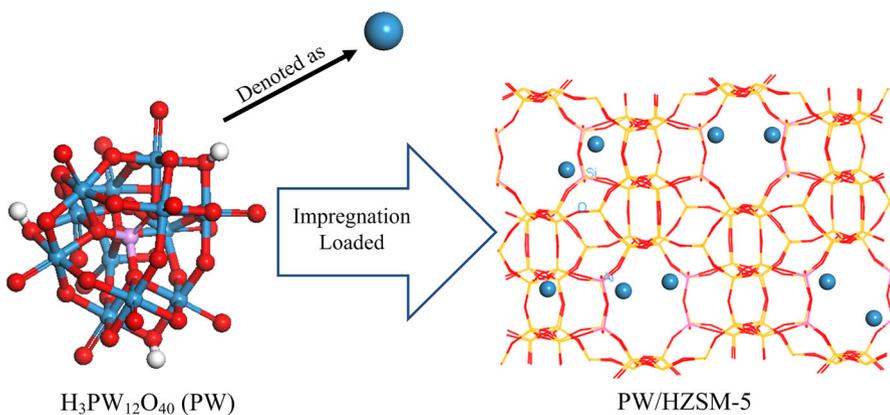


**Fig. 5** Possible structure of the PW/HZSM-5 catalyst

## Catalytic performance in the nitration of naphthalene

Liquid phase nitration of naphthalene with nitric acid was performed over HZSM-5-supported PW catalysts. The main products were 1-nitronaphthalene, 1,5-dinitro-naphthalene, and 1,8-dinitronaphthalene (Scheme 1). A possible reaction mechanism is proposed in Scheme 2. The reaction proceeds because of the acidity of Keggin-type phosphotungstic acid, which replaces the sulfuric acid used in traditional mixed-acid nitration of naphthalene. The mechanism for nitration of naphthalene is electrophilic aromatic nitration. Under these reaction conditions, $HNO_3$ forms the nitronium ion $(NO_2^+)$ in the presence of phosphotungstic acid.
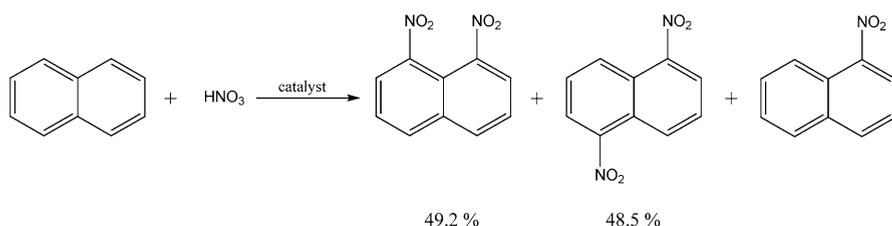


**Scheme 1** Nitration of naphthalene
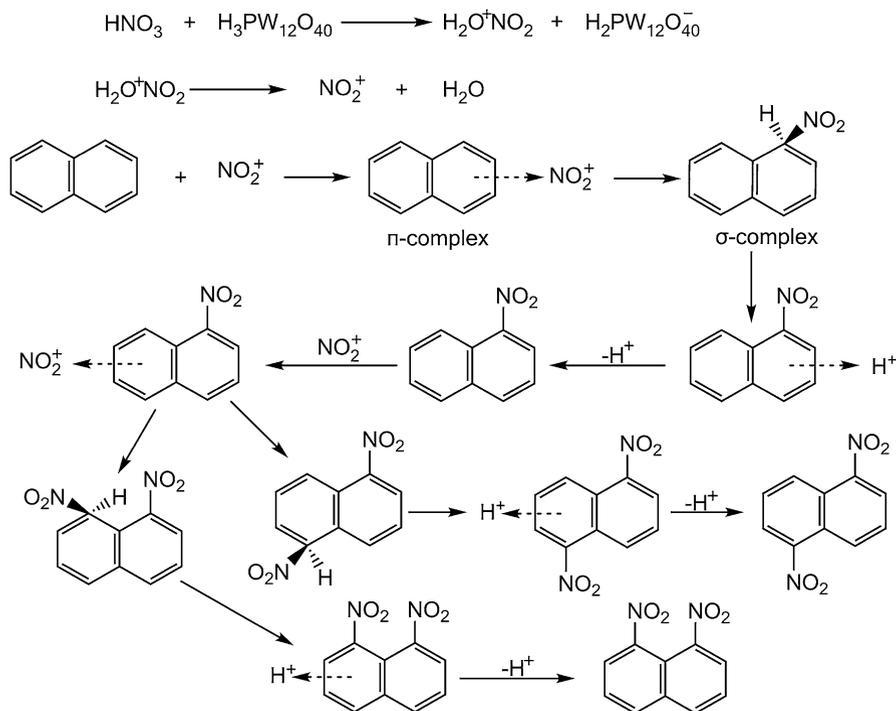


**Scheme 2** Possible reaction mechanism for nitration of naphthalene

This ion then interacts with naphthalene to form a π-complex intermediate; this is formed rapidly, because of its low activation energy. A second intermediate, a σ-complex, is formed by electron transfer from the aromatic compound to the nitronium ion in the π-complex intermediate. The σ-complex can then participate in further transformations. The first step is proton elimination leading to 1-nitronaphthalene; this reacts further with nitronium ion ($NO_2^+$) to form dinitronaphthalene by the same mechanism. The predominant dinitronaphthalene products under these reaction conditions are 1,5-dinitronaphthalene and 1,8-dinitronaphthalene.

The effect of PW loading of PW/HZSM-5 on total yield and 1,5-dinitronaphthalene selectivity is shown in Table 2. Over HZSM-5 the yield of 1-nitronaphthalene is 78.5 % and the total yield of dinitronaphthalene is only 16.8 %. The total yield of dinitronaphthalene increases substantially when the reaction is catalyzed by HZSM-5-supported PW catalyst, possibly because interaction between the surface silanol and the anion of PW furnishes more acidic sites for the reaction. However, higher loading of PW leads to the poor dispersion of PW on HZSM-5 and lower surface area, pore diameter, and pore volume, which do not favor the reaction.

For comparison, the parent phosphotungstic acid, and HY, $ZrO_2$, and $SiO_2$-supported PW catalysts were also tested; the results are shown in Table 3. The total yield of dinitronaphthalene is 65.2 % over PW alone, much more than over HZSM-5 alone, indicating that the acidity of PW is important in the reaction. Moreover, the best result for total yield of dinitronaphthalenes, and, in particular, the highest yield of 1,5-dinitronaphthalene and the highest ratio of 1,5-dinitronaphthalene to 1,8-dinitronaphthalene, approximately 1:1, is obtained when the HZSM-5 is treated with PW. The surface areas of HY, $ZrO_2$, and $SiO_2$ range from 120 to 170 $m^2$ $g^{-1}$, which are much smaller than that of HZSM-5. The better dispersion of PW on HZSM-5 results in better catalytic performance.

Table 4 shows the effect of the amount of nitric acid on naphthalene nitration. For comparison, nitration of naphthalene was also conducted in the absence of the catalyst; the result, also shown in Table 4, indicates that a large amount of 1-nitronaphthalene is produced when the amount of nitric acid or catalyst is insufficient. In general, when naphthalene is nitrated with mixed nitric and sulfuric acids, sulfuric acid favors formation of $NO_2^+$, which promotes nitration. However,

**Table 2** Nitration of naphthalene over PW/HZSM-5 with different PW loading

| Catalyst | Conversion (%) | Selectivity (%) | | |
|---|---|---|---|---|
| | | 1,5-Dinitronaphthalene | 1,8-Dinitronaphthalene | 1-Nitronaphthalene |
| HZSM-5 | 100 | 6.2 | 10.6 | 78.5 |
| 5 wt% PW/ HZSM-5 | 100 | 16.0 | 20.7 | 58.2 |
| 10 wt% PW/ HZSM-5 | 100 | 13.2 | 18.6 | 65.2 |
| 30 wt% PW/ HZSM-5 | 100 | 13.0 | 15.5 | 69.5 |

Reaction conditions: naphthalene: 0.01 mol; 65 wt% nitric acid: 0.1 mol; catalyst: 0.3 g; temperature: 338 K; reaction time: 3 h

**Table 3** Effect of the catalyst support on nitration of naphthalene

| Catalyst | Conversion (%) | Selectivity (%) | | |
|---|---|---|---|---|
| | | 1,5-Dinitronaphthalene | 1,8-Dinitronaphthalene | 1-Nitronaphthalene |
| PW | 100 | 28.5 | 36.7 | 31.5 |
| PW/HY | 100 | 37.1 | 59.5 | – |
| PW/ZrO$_2$ | 100 | 39.8 | 55.3 | 2.4 |
| PW/SiO$_2$ | 100 | 40.4 | 53.7 | 2.5 |
| PW/HZSM-5 | 100 | 48.5 | 49.2 | – |

Reaction conditions: naphthalene: 0.01 mol; 65 wt% nitric acid: 0.3 mol; catalyst: 0.3 g; temperature: 338 K; reaction time: 3 h

**Table 4** Effect of the amount of nitric acid on nitration of naphthalene

| Amount of nitric acid (mol) | Conversion (%) | Selectivity (%) | | |
|---|---|---|---|---|
| | | 1,5-Dinitronaphthalene | 1,8-Dinitronaphthalene | 1-Nitronaphthalene |
| 0.1 | 100 | 16.0 | 20.7 | 58.2 |
| 0.2 | 100 | 31.5 | 35.7 | 38.6 |
| 0.3 | 100 | 48.5 | 49.2 | – |
| 0.3[a] | 100 | 21.2 | 33.1 | 43.3 |

Reaction conditions: naphthalene: 0.01 mol; 5 wt% PW/HZSM-5 catalyst: 0.3 g; temperature: 338 K; reaction time: 3 h

[a] Without catalyst

use of mixed acids causes recycling problems and serious environment pollution. Thus it is necessary to appropriately increase the concentration of nitric acid to ensure the formation of dinitronaphthalene.

The effect of calcination temperature is shown in Table 5. Although the total yield of dinitronaphthalene is barely affected, selectivity for 1,5-dinitronaphthalene first increases and then decreases with increasing calcination temperature. The Keggin structure of PW is destroyed at 801 K, and formation of mixed oxides starts at approximately 845 K. The decomposition temperature is also reduced somewhat when PW is loaded on the support. The results from FT-IR spectroscopy show the Keggin structure is present in 5 wt% PW/HZSM-5 calcined at 773 K. However, the PW starts to decompose when the calcination temperature is increased to 823 K. This may be the reason for the decrease in selectivity for 1,5-dinitronaphthalene when the calcination temperature is close to the decomposition temperature.

The effect of solvent on naphthalene nitration is shown in Table 6. When acetic acid is used as solvent, a small amount of 1-nitronaphthalene produced, the total yield of dinitronaphthalene is approximately 75.1 %, and the yield of 1,5-dinitronaphthalene is only 32.6 %. When nitromethane and 1,2-dichloroethane are used as solvents, the yield of dinitronaphthalene is little different. Nitration efficiency and selectivity for 1,5-dinitronaphthalene are highest when no solvent is used.

**Table 5** Effect of calcination temperature on nitration of naphthalene

| Calcination temperature (K) | Conversion (%) | Selectivity (%) | |
| --- | --- | --- | --- |
| | | 1,5-Dinitronaphthalene | 1,8-Dinitronaphthalene |
| 623 | 100 | 41.9 | 56.5 |
| 673 | 100 | 43.2 | 54.6 |
| 723 | 100 | 46.0 | 50.7 |
| 773 | 100 | 48.5 | 49.2 |
| 823 | 100 | 43.7 | 53.8 |

Reaction conditions: naphthalene: 0.01 mol; 65 wt% nitric acid: 0.3 mol; 5 wt% PW/HZSM-5 catalyst: 0.3 g; temperature: 338 K; reaction time: 3 h

**Table 6** Effect of solvent on nitration of naphthalene

| Solvent | Conversion (%) | Selectivity (%) | | |
| --- | --- | --- | --- | --- |
| | | 1,5-Dinitronaphthalene | 1,8-Dinitronaphthalene | 1-Nitronaphthalene |
| Acetic acid | 100 | 32.6 | 42.5 | 22.5 |
| 1,2-Dichloroethane | 100 | 40.4 | 56.8 | – |
| Nitromethane | 100 | 42.8 | 54.1 | – |
| – | 100 | 48.5 | 49.2 | – |

Reaction conditions: naphthalene: 0.01 mol; 65 wt% nitric acid: 0.3 mol; 5 wt% PW/HZSM-5 catalyst: 0.3 g; temperature: 338 K; reaction time: 3 h

Finally, 5 wt% PW/HZSM-5 catalyst was used for recycling experiments. After reaction, the catalyst was separated and washed with acetonitrile, dried at 393 K for 2 h, and used for nitration of naphthalene. It was found the recycled catalyst retained its original activity and selectivity throughout three cycles.

## Conclusions

HZSM-5-supported PW catalysts were prepared and characterized by XRD, BET, and FT-IR and UV–visible spectroscopy. The results indicate that 5 wt% PW/HZSM-5 calcined at 773 K has the largest surface area and high dispersion of PW. Keggin units are present inside the PW/HZSM-5 catalysts and the proton of PW and the silanol of HZSM-5 interact via a bridging structure. The catalytic properties of the material in regioselective nitration of naphthalene were investigated. The best results, i.e. 48.5 % yield of 1,5-dinitronaphthalene and 49.2 % yield of 1,8-dinitronaphthalene, were obtained by use of 5 wt% PW/HZSM-5, for which the yield of 1,5-dinitronaphthalene and the ratio of 1,5-dinitronaphthalene to 1,8-dinitronaphthalene were much higher. It was also found that the catalyst retains its original activity and selectivity when recycled three times.

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