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Short Communication

Synthesis of zirconia porous phosphate heterostructures (Zr-PPH) for Prins condensation

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ABSTRACT

Porous phosphate heterostructure materials with zirconia galleries have been prepared. Their acid properties were studied via 2,6-di-*tert*-butyl-pyridine adsorption, infrared spectra of pyridine adsorption and potentiometric titration. The samples prepared in alcohol media are more thermal stable than those prepared in aqueous media. They are very active and selective for the Prins condensation of β-pinene with paraformaldehyde because of large amount of Lewis acid sites as well as proper L/B ratio. The selectivity towards Nopol can be further improved by ion-exchanging with sodium cations, due to the elimination of Brønsted acid sites which suppresses the by-reactions such as isomerization of β-pinene.

1. Introduction

Heterogeneous solid acid catalysts are of increasing interest in fine chemical reactions due to their environmentally benign nature with respect to corrosiveness, safety, less waste and ease of separation and recovery [1]. Among them, metal oxide pillared layered metal (IV) phosphates are promising catalysts, due to their high surface area, large pore volume and high stability. Furthermore, the pillared phosphates are more versatile in framework chemical variety and composition compared with other mesoporous materials, which are indeed of importance to the heterogeneous catalysis. These materials are already found catalytically active for various acid-catalyzed reactions, such as dehydration of isopropanol [2,3], cumene cracking [3], and polymerization of pyrrole [4].

Recently, a novel kind of porous phosphate heterostructure (PPH) material with a layered structure has been synthesized by a co-templated method [5,6]. These materials possess much larger surface area and better porous structure as compared with the silica pillared zirconium phosphate by the traditional method [7]. Chemical properties of these materials can be modified by doping or replacing the silica galleries with different elements. Cu-PPHs and Ru-PPHs were reported in the selective catalytic reduction of NO_x and hydrotreating of aromatic hydrocarbons, respectively [8,9]. Mixed silica/zirconia pillared and mixed silica/titania pillared zirconium phosphates were also prepared as new solid acids [10].

Nopol, widely used in manufacturing household products, is commercially synthesized by the condensation of β-pinene and paraformaldehyde. In accordance with the concept of green chemistry, heterogeneous catalysts especially metal-doping mesoporous materials such as ZnMCM-41 [11,12], SnMCM-41 [12,13], SnSBA-15 [14,15], ZrSBA-15 [16], $ZnCl_2$/montmorillonite [17] and mesoporous iron phosphate [18], were explored and utilized in this reaction in the past decades. In this work, zirconia galleries were inserted into the PPH materials due to the excellent catalytic behaviors of zirconia which come from its unique acid and base properties. The catalytic application in Prins condensation of β-pinene with paraformaldehyde was conducted. The reusability and regeneration of the catalyst were also studied.

2. Experimental

2.1. Sample preparation

Cetyltrimethylammonium bromide expanded zirconium phosphates (CTAB-ZrP) were prepared following the procedures in the literature [5,6]. Zirconia galleries were inserted in aqueous media as follows: 1 g CTAB-ZrP (≥99%, Guoyao) was suspended in 100 ml water. Hexadecylamine (90%, Alfa) in *n*-propanol (35 g/l) solution was added into the water with hexadecylamine/P molar ratio of 0.4. After stirred for one day at 40 °C, zirconium (IV) propoxide (70% Aldrich) with Zr/P molar ratio of 2 was added. This suspension was stirred for three days at 40 °C. The solid obtained was centrifuged, washed several times with ethanol. The surfactants were removed by refluxing in 200 ml ethanol with 1.5 ml of concentrated hydrochloric acid at 70 °C overnight, washed with ethanol, dried at 60 °C, and finally calcined for 3 h. The inserting in alcohol media follows the same procedures except that CTAB-ZrP was suspended in 100 ml *n*-propanol at the beginning. The obtained materials in aqueous and

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n-propanol media were denoted as ZrO_2–ZrP-w-*T* and ZrO_2–ZrP-a-*T*, respectively, where *T* is the calcination temperature.

The sodium ion-exchanged samples were obtained by ion-exchanging ZrO_2–ZrP-a-*T* three times with 1 M NaCl (1 g/10 ml) at 80 °C for 4 h, and designated as Na–ZrO_2–ZrP-a-*T*.

2.2. Catalyst characterization

The N_2 adsorption/desorption isotherms were measured on a Tristar 3000 porosimeter at liquid N_2 temperature. Surface areas of the samples were calculated by BET method, and the pore size distributions by Cranston and Inkley method [19]. Scanning electron microscopic (SEM) images were obtained on a Philips XL-30 scanning electron microscope.

DTBPy adsorption in liquid phase was tested by adding 20 mg catalyst into 2 ml DTBPy/xylene solution (0.004 mol/l). Trace amount of tetradecane was utilized as internal standard. The mixture was stirred for 5 h at room temperature. The remaining DTBPy was analyzed by a gas chromatograph equipped with a SE-30 capillary column (30 m × 0.25 mm × 0.3 μm).

Py-IR spectra were recorded on a Nicolet Nexus 470 FT-IR spectrometer at 100 °C. Quantitative determination of Brønsted and Lewis acid sites was derived from the integrated areas of the IR bands at 1540 and 1450 cm^{-1}, respectively. Extinction coefficients ($E_B = 0.73$ cm/μmol and $E_L = 1.11$ cm/μmol) were obtained from previous work of Dakta et al. [20].

The acidity was measured by means of potentiometric titration [21,22]. The 0.05 g catalyst was suspended in 10 ml acetonitrile, and titrated with 0.1 mol/l butylamine in acetonitrile. The electrode potential variation was recorded with a Mettler Toledo FE20 potentiometer. The acid strength can be classified according to the following scale: $E_i > 100$ mV (very strong sites), $0 < E_i < 100$ mV (strong sites) and $-100 < E_i < 0$ mV (weak sites) [21,22].

2.3. Catalytic tests

The Prins condensation of β-pinene with paraformaldehyde was carried out in a three-necked flask equipped with a condenser. Typically, 50 mg catalyst, 1 mmol (0.136 g) β-pinene, 2 mmol (0.06 g) paraformaldehyde and 5 ml toluene were added with magnetic stirring at 80 °C for 4 h. The products were analyzed by a gas chromatograph equipped with a SE-30 capillary column (30 m × 0.25 mm × 0.3 μm).

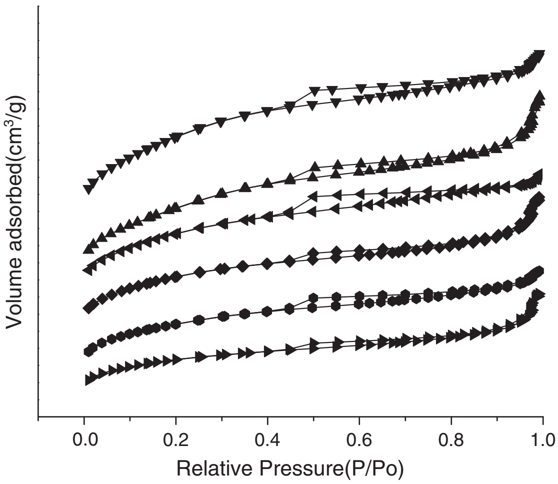

Fig. 1. N_2 adsorption/desorption isotherms for (▼) ZrO_2–ZrP-a-150, (▲) ZrO_2–ZrP-w-150, (◄) ZrO_2–ZrP-a-350, (♦) ZrO_2–ZrP-w-350, (●) ZrO_2–ZrP-a-550, (►) ZrO_2–ZrP-w-550.

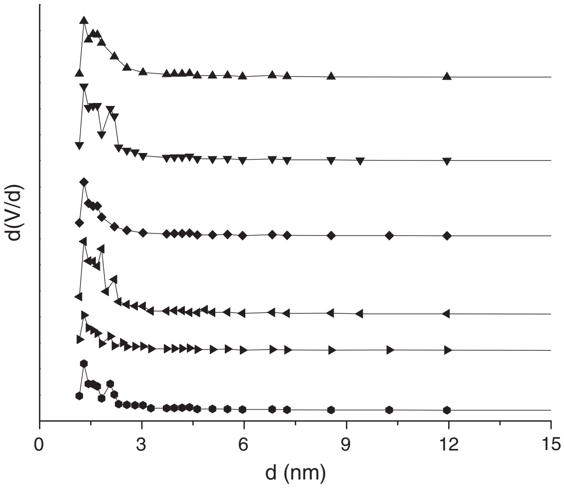

Fig. 2. The isotherms of the pore size distribution for (▲) ZrO_2–ZrP-w-150, (▼) ZrO_2–ZrP-a-150, (♦) ZrO_2–ZrP-w-350, (◄) ZrO_2–ZrP-a-350, (►) ZrO_2–ZrP-w-550, (●) ZrO_2–ZrP-a-550.

2.4. Catalyst poisoning by DTBPy

Catalyst poisoning was done by adding calculated amount of DTBPy to the mixture of catalysts and solvent (toluene) prior to the addition of reactants. The above mixture was stirred under room temperature overnight. After that, catalytic tests were done as described in Section 2.3.

3. Results and discussion

3.1. Textural properties of the catalysts

The N_2 adsorption–desorption isotherms of porous phosphate heterostructure materials with zirconia galleries are shown in Fig. 1. Type IV isotherms can be observed for all the samples prepared, showing that mesopores were generated after the zirconia inserting. This was proved by the pore size distribution curves of the above materials, as shown in Fig. 2. These obtained samples exhibit high BET surface area and large pore volume as compared with the calcined CTAB-ZrP (Table 1), indicating the presence of zirconia galleries between the interlayer spaces of the phosphate, which resulted in a porous structure accessible to the N_2 molecules. The surface area and pore volume decrease with the increasing of the calcination temperature, since the pore structure may shrink or partially collapse due to self-condensation of P-OH groups [23]. This decrement changes with the preparative media. The samples obtained from alcohol media are more thermal stable than those from aqueous one. After calcinations at 550 °C, the variation of pore volume is 36% for alcohol media sample. While for aqueous media

Table 1
Textural properties of the samples.

Catalysts	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter[c] (nm)	Adsorbed DTBPy (mmol/g)
CTAB-ZrP[a]	24	0.03	–[b]	–[b]
ZrO_2–ZrP-w-150	455	0.45	4.0	0.12
ZrO_2–ZrP-w-350	378	0.34	3.6	0.04
ZrO_2–ZrP-w-550	265	0.26	3.9	0.04
ZrO_2–ZrP-a-150	543	0.42	3.1	0.25
ZrO_2–ZrP-a-350	426	0.27	2.5	0.20
ZrO_2–ZrP-a-550	342	0.27	3.2	0.08
Na–ZrO_2–ZrP-a-150	483	0.49	4.1	–[b]
Na–ZrO_2–ZrP-a-350	310	0.33	4.3	–[b]

[a] Calcined at 550 °C for 6 h.
[b] Not detected.
[c] Obtained by 4 V/A.

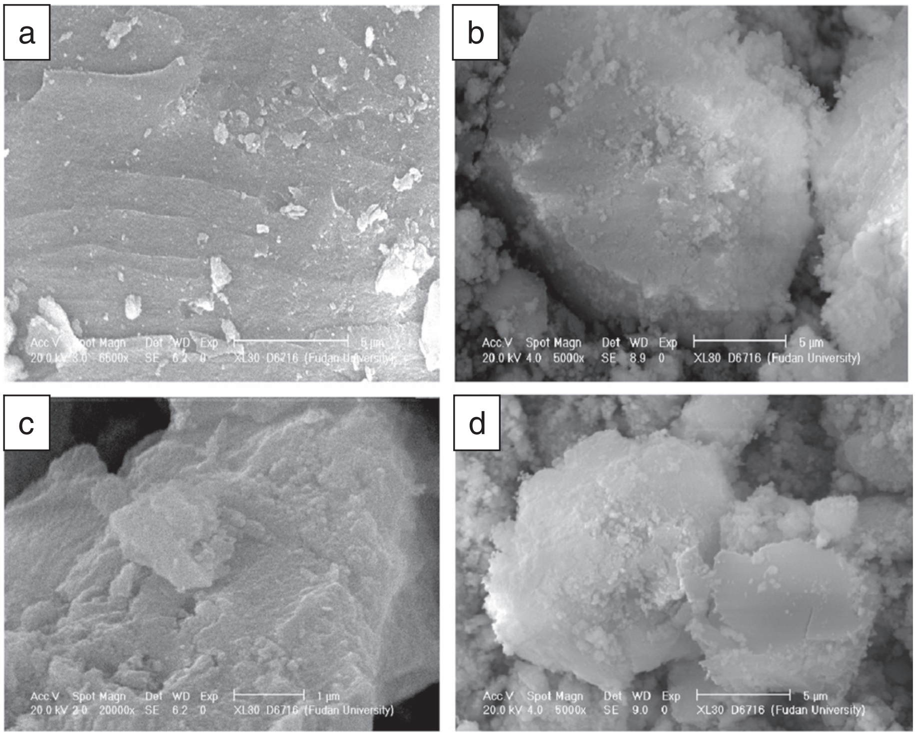

Fig. 3. SEM images for (a) ZrO_2–ZrP-a-150, (b) ZrO_2–ZrP-w-150, (c) ZrO_2–ZrP-a-350, (d) ZrO_2–ZrP-w-350.

one, the value is 42%. Furthermore, the surface area of the catalyst prepared in *n*-propanol is higher than that of the sample prepared in water under the same calcination temperature.

Liquid phase DTBPy adsorption reflects the capability of catalysts for bulky molecular reactants since DTBPy was a moderate base with relatively large size (~0.79 nm in diameter). As seen in Table 1, the amount of adsorbed DTBPy decreased with the increasing of the calcination temperature, from 0.12 mmol/g to 0.04 mmol/g for aqueous media sample and from 0.25 mmol/g to 0.08 mmol/g for alcohol media one, indicating the decrement of the possible active sites for the catalytic reactions. However, the DTBPy amount of the catalyst prepared in propanol was always higher than that of the sample prepared in aqueous media under the same calcination temperature, which is in agreement with the BET results.

The SEM images of the ZrO_2–ZrP-a-150, ZrO_2–ZrP-w-150, ZrO_2–ZrP-a-350 and ZrO_2–ZrP-w-350 are shown in Fig. 3. The lamellar nature of the obtained materials prepared in propanol (Fig. 3a and c) can be observed from their platelike crystal morphology while similar structure is not so clear for the materials obtained in aqueous medium (Fig. 3b and d), which is due to the quick hydrolysis of zirconium(IV) propoxide in water than in propanol. The particles of the four samples are all nonuniform.

Table 2
Acidic properties of the catalysts obtained by titration.

Catalysts	Amount of acid sites (mmol/g)			
	Strong acid[a]	Mild acid[b]	Weak acid[c]	Total
ZrO_2–ZrP-a-150	1.60	0.60	0.70	2.9
Na–ZrO_2–ZrP-a-150	0.13	1.20	0.60	1.9
ZrO_2–ZrP-a-350	0.90	0.20	0.69	1.8
Na–ZrO_2–ZrP-a-350	0.57	0.25	0.28	1.1

[a] $E_i > 100$ mV.
[b] $100 \text{ mV} > E_i > 0$ mV.
[c] $0 \text{ mV} > E_i > -100$ mV.

3.2. Acidity measurements

The acidity of the catalysts was characterized by means of potentiometric titration. The acid sites with different acid strengths can be seen in Table 2. The total amount of acid sites decreases markedly after calcination, which may be caused by the condensation of free P-OH groups [23]. Ion-exchanging by sodium cations also reduces the amount of acid sites, since the Brønsted acid sites have been ion-exchanged. The acid sites for the four catalysts has the order of ZrO_2–ZrP-a-150 > Na–ZrO_2–ZrP-a-150 ≈ ZrO_2–ZrP-a-350 > Na–ZrO_2–ZrP-a-350.

Py-IR was taken to study the nature of acid sites [24]. The characteristic bands of pyridine coordinately bonded to Lewis acid sites at ca. 1450 cm^{-1}, as well as the bands at ca. 1540 cm^{-1} assigned to protonation of pyridine by Brønsted acid sites can be observed on the catalysts. The amount of Brønsted and Lewis acid sites was quantified and summarized in Table 3. The total number of acid sites has the sequence of ZrO_2–ZrP-a-150 > ZrO_2–ZrP-a-350 > Na–ZrO_2–ZrP-a-150 > Na–ZrO_2–ZrP-a-350. Calcining or ion-exchanging with Na^+ mainly reduced the Brønsted acid sites while keeping the Lewis acid sites almost unchanged, resulting the great increase of L/B ratio.

3.3. Catalytic activity

The activities of the prepared zirconia pillared zirconium phosphate catalysts for the reaction were investigated and the results are listed in Table 4. All catalysts were very active for this condensation, higher than

Table 3
Acidity of the catalysts determined by pyridine absorbed FT-IR.

Catalysts	Brønsted acid s ites (mmol/g)	Lewis acid sites (mmol/g)	Total acid sites (mmol/g)	L/B ratio
ZrO_2–ZrP-a-150	0.72	0.60	1.32	0.83
Na–ZrO_2–ZrP-a-150	0.36	0.68	1.04	1.9
ZrO_2–ZrP–a-350	0.60	0.69	1.29	1.1
Na–ZrO_2–ZrP-a-350	0.08	0.64	0.72	8.5

Table 4
Activities of the catalysts for Prins condensation.[a]

Catalysts	Conv. (%)	Selectivity (%)				Yield of Nopol (%)
		Nopol	Camphene	Limonene	Others[b]	
ZrO_2–ZrP-a-150	98	79	9	5	7	77
Na–ZrO_2–ZrP-a-150	92	82	6	3	9	75
ZrO_2–ZrP-a-350	89	77	9	5	9	68
Na–ZrO_2–ZrP-a-350	86	87	5	3	5	75

[a] Reaction condition: 50 mg catalyst, 1 mmol β-pinene and 2 mmol paraformaldehyde, 5 ml toluene as solvent, 80 °C for 4 h.

[b] Including terpinolenes, terpinenes and α-pinene.

the recent results over Zr-SBA-15 [16]. The sequence of the activity is as follows: ZrO_2–ZrP-a-150 > Na–ZrO_2–ZrP-a-150 > ZrO_2–ZrP-a-350 > Na–ZrO_2–ZrP-a-350, which is the same as that of the total amount of acid sites by titration, since the reaction is thought to be catalyzed by acid sites. However, the selectivity towards Nopol has an opposite trend. It was reported that the existence of Brønsted acid sites is also favorable to form monoisomers through pinene isomerization rather than Nopol through condensation [16]. The formation of isomers is irreversible so that if isomerization is predominant, less β-pinene is available for condensation. The selectivity can be improved by eliminating the Brønsted acid sites through ion-exchanging with sodium ions. This is the reason why the catalyst Na–ZrO_2–ZrP-a-350 with the lowest Brønsted acid sites has the highest selectivity to Nopol.

To further study the influence of the acidity on the Prins condensation, the activities of the catalysts poisoned by DTBPy have been investigated. The relevance of the DTBPy amount added and the Nopol yield over ZrO_2–ZrP-a-150 and Na–ZrO_2–ZrP-a-350 was illustrated in Fig. 4. The yield decreases slowly with the rise of DTBPy amount over both catalysts. When the DTBPy amount is 2.0 mmol/g, the yields on both catalysts are still as high as 80% of the original ones. Since DTBPy molecule was thought to adsorb mainly on the accessible Brønsted acid sites [25], the above results indicate that the uncovered Lewis acid sites can motivate the condensation efficiently without Brønsted acid sites. However, the changing tendencies for the two catalysts are different. The yield of Nopol over Na–ZrO_2–ZrP-a-350 drops quickly in the beginning of poisoning test, and then changes little afterwards. Since the Brønsted acid sites on Na–ZrO_2–ZrP-a-350 are few, which are easy to be poisoned by small amount of DTBPy added, the abrupt reduction between 0 and 0.50 mmol/g shows the promotion effect of Brønsted acid sites on the condensation reaction. Similar promotion effect can be observed over ZrO_2–ZrP-a-150. The yield decreases with the reduction of Brønsted acid sites. But this is decreasing more gradually between 0 and 2.0 mmol/g, since the amount of Brønsted acid sites on ZrO_2–ZrP-a-150 is much larger, they were difficult to be totally poisoned by the addition of DTBPy.

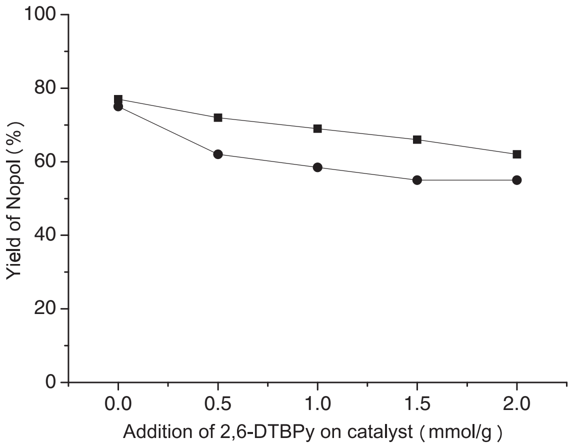

Fig. 4. Relevance of the addition of poisoning reagent DTBPy and the yield of Nopol on (■) poisoned ZrO_2–ZrP-a-150, (●) poisoned Na–ZrO_2–ZrP-a-350.

Table 5
Reusability of Na–ZrO_2–ZrP-a-350 in the Prins condensation.

Catalysts	Conversion of β-pinene (%)	Selectivity of Nopol (%)	Yield of Nopol (%)
Fresh	86	87	75
1st reuse	79	89	70
2nd reuse	73	88	64
3rd reuse	56	91	51
After regeneration[a]	83	82	68

[a] Catalyst was washed with acetone and recalcined at 350 °C for 3 h before use.

The promotion effect of Brønsted acid can be also proved by the fact that the yield of Nopol over ZrO_2–ZrP-a-150 is always higher than that over Na–ZrO_2–ZrP-a-350 with same amount of DTBPy added, since Py-IR results showed that the amount of Brønsted acid sites of ZrO_2–ZrP-a-150 was much more than that of Na–ZrO_2–ZrP-a-350 while the amount of Lewis acid sites was nearly equal. Thus, it can be concluded that the amount of Lewis acid sites as well as proper L/B ratio plays an important role in Nopol production through condensation.

The reusability of the catalyst was also studied and the results are listed in Table 5. After reaction, the catalyst was recovered by filtration, washed with acetone for several times, dried at 80 °C and then reused. An obvious deactivation is observed. After three runs, the conversion drops from 86% to 56%. Tar or polymeric compound deposition on the catalyst is probably the cause for the reduction in catalytic activity. Hence, the catalyst was recalcined at 350 °C for 3 h after four runs. The catalytic activity was recovered mostly. The conversion over the recalcined sample was 83% which is comparable to that of the fresh catalyst (Table 5).

4. Conclusions

The zirconia pillared zirconium phosphate has been synthesized successfully. The samples prepared in *n*-propanol are more thermal stable and higher acidic than that prepared in water. These materials showed good activity and selectivity in the Prins condensation of β-pinene and paraformaldehyde. A Nopol yield of 75% with 87% selectivity was obtained over Na–ZrO_2–ZrP-a-350. The catalysts can be reused just by recalcination. The amount of Lewis acid sites as well as proper L/B ratio plays an important role in selective synthesis of Nopol.

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