

Preparation and catalytic property of the solid base supported on the mixed zirconium phosphate phosphonate for Knoevenagel condensation

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Abstract

A new type of the mixed zirconium phosphate phosphonate support and the solid base were prepared and characterized by elemental analysis, IR, XRPD, ³¹P MAS NMR, TG, DTG and DSC. IR spectra showed that there were some differences between the support and the solid base in the vibration frequencies. XRPD indicated that the supports were amorphous. The ³¹P MAS NMR spectrum of each solid base exhibited three main resonances, and thermogravimetry indicated that the solid base had two or three step weight loss at temperatures of up 900 °C. The Knoevenagel condensation of benzaldehyde with diethylmalonate or malononitrile, cyclohexanone with malononitrile was catalyzed by the solid base ($H_{-} = 12.2$) in high catalytic activity and simple work-up, the catalyst could be reused four times and easy to be regenerated.

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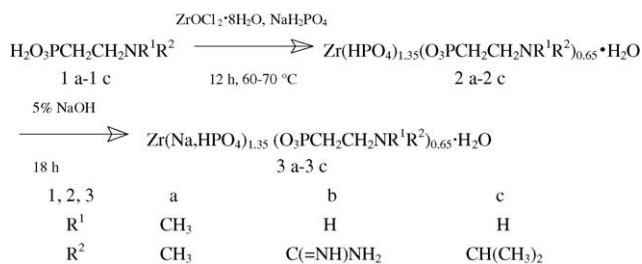
Keywords: The mixed zirconium phosphate phosphonate; Support; Solid base; Heterogeneous catalysis; Knoevenagel condensation

1. Introduction

Heterogeneous catalysts are easier to work-up, simpler to separate and purify, and safer to operate in the industrial process, as far as environmental and economic concern, there has been increasing attention on the design and use of new environmentally benign heterogeneous catalysts targeted to minimize the emission of effluents in the chemical industry. Heterogeneous acid catalysis has received much attention due to its importance in petroleum refining and petrochemical processes, in comparison, heterogeneous base catalysis, although it play a decisive role in a number of organic reactions [1,2], is much less numerous. The Knoevenagel

condensation has wide application in the organic synthesis [3–5], and it is usually catalysed by homogeneous bases or acids [6,7], however, the use of heterogeneous catalysts (i.e., zeolite molecular sieves and inorganic mesoporous material MCM-41 [8–11]; anionic resin [12,13]; hydrotalcite [14,15]; fluorapatite, hydroxyapatite, Aluminophosphate, phosphate, diphosphate ($\text{Na}_2\text{CaP}_2\text{O}_7$) and K^+ exchanged layered zirconium phosphate [16–21]; organic-silicate hybrid material and basic microporous titanosilicate ETS-10 [22,23]) has been reported in recent year, in addition, ultrasound, microwave irradiation and imidazolium ionic liquids [24–26] have also been applied. Zirconium phosphates and phosphonates have been extensively researched, their characteristics make them very interesting both from a fundamental point of view and in many application fields, they are easily obtained as multifunctional materials, used as ion exchanger, catalyst or cat-

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Scheme 1.

alyst support, adsorbent [27–30]. In general, the surface areas of typical α -zirconium phosphates and phosphonates are in the range of 30–200 m²/g [31]. No matter whether crystalline, semi-crystalline or amorphous, all organic groups are located on the surface of the layer and in the interlamellar region, the accumulated data indicates that those materials are high thermal and chemical stabilities. Current research in the zirconium phosphates and phosphonates field is active, they have involved mainly ion exchange [32,33], intercalation chemistry [34,35], sensor and proton conductivity [36], catalysis area [37–40]. However, few of the mixed zirconium phosphate phosphonates $\text{Zr}(\text{HPO}_4)_{2-x}(\text{O}_3\text{PG})_x$ ($x=0-2$, G: organic groups) in which inorganic/organic molar ratio and organic group can be modulated for special purposes are reported, especially the application of the solid base catalyst in heterogeneous catalysis. In previous papers we reported that the mixed zirconium phosphate phosphonates were used as solid acid catalyst [41,42]. In this paper, a new type of the mixed zirconium phosphate phosphonate support was designed for heterogeneous base catalysis, the preparation route of the solid base was outlined in Scheme 1. The application of the solid catalyst in Knoevenagel condensation of benzaldehyde with diethylmalonate or malononitrile, and cyclohexanone with malononitrile was preliminarily investigated.

2. Experimental

2.1. Starting materials and methods

$\text{H}_2\text{O}_3\text{PCH}_2\text{CH}_2\text{NR}^1\text{R}^2$ were prepared according to [43] and affirmed by ¹H NMR and IR. All other materials used were of analytical grade.

C, H and N analysis was performed on a Perkin-Elmer 2400 elemental instrument. ¹H NMR was performed on a dpx-300 NMR instrument. IR spectra of the samples were recorded on Spectrum GX (KBr pellet). X-ray powder diffraction was performed on a D/MAX-3C automatic diffractometer with Cu K α radiation. ³¹P MAS NMR spectra were recorded on Bruker AV-300 spectrometer with NaH₂PO₄ as reference. Thermal analysis was performed on a DELTA SERIES instrument. GC analysis was carried out with GC-9A instrument. HPLC analysis was carried out with LC-6A instrument.

2.2. Preparation of amorphous support

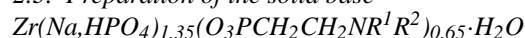
$\text{Zr}(\text{HPO}_4)_{1.35}(\text{O}_3\text{PCH}_2\text{CH}_2\text{NR}^1\text{R}^2)_{0.65} \cdot \text{H}_2\text{O}$

$\text{H}_2\text{O}_3\text{PCH}_2\text{CH}_2\text{NR}^1\text{R}^2$ (13 mmol) and NaH₂PO₄ (3.24 g, 27 mmol) in water (100 ml) was added to the solution of ZrOCl₂·8H₂O (6.45 g, 20 mmol) in water (100 ml) with stirring, then the reaction mixture was stirred for 12 h at 60–70 °C, filtered, washed with water to pH 5 and dried in vacuo. White solids of 2a (6.3 g, 93.6%), 2b (6.5 g, 93.9%), and 2c (6.6 g, 95.4%) were obtained [44].

IR (KBr, ν , cm⁻¹) 2a: 3451 (s, b), 1636 (w), 1053 (vs), 610 (m), 517 (m). 2b: 3426 (s, b), 1651 (w), 1051 (vs), 600 (m), 517 (m). 2c: 3458 (s, b), 1633 (w), 1067 (vs), 606 (m), 515 (m).

The anal. calc. for amorphous 2a were: C, 9.26; H, 2.92; N, 2.70; found: C, 9.18; H, 2.81; N, 2.59. 2b: C, 6.76; H, 2.47; N, 7.89; found: C, 6.64; H, 2.35; N, 7.72. 2c: C, 11.28; H, 3.22; N, 2.63; found: C, 11.13; H, 3.07; N, 2.45.

2.3. Preparation of the solid base



The support 2 (10 mmol) was added to 5% of sodium hydroxide (40 ml), the reaction mixture was stirred for 18 h at room temperature, filtered, washed with water to pH 8 and dried in vacuo. White solids of 3a, 3b, and 3c were obtained.

IR (KBr, ν , cm⁻¹) 3 a: 3412 (s, b), 1657 (w), 1121 (s), 982 (vs), 544 (m). 3 b: 3432 (s, b), 1642 (w), 1015 (vs), 563 (m). 3 c: 3434 (s, b), 1651 (w), 1011 (vs), 561 (m).

The basic numbers of different strengths could be measured by titration with benzoic acid [1].

2.4. General procedure for Knoevenagel condensation

Benzaldehyde (5.3 g, 50 mmol) was added dropwise to the solution of diethyl malonate (8.1 g, 50 mmol) and solid base (2.0 g) in solvent (40 ml) with stirring, then the reaction mixture was stirred for appropriate time at reflux temperature, cooled to room temperature after water separation, filtrated, the condensation product was given by the solvent removal, purified and affirmed by chromatography, ¹H NMR, IR, respectively.

The reaction of benzaldehyde or cyclohexanone with malononitrile was treated by the same procedure.

3. Results and discussion

3.1. Basic strength and basic number

The solid possessed basic sites stronger than H₋ = 12.2 by indicator methods.

When the reaction of ZrOCl₂·8H₂O and NaH₂PO₄ with 1 a was for 1, 2, 3.5, 5, 9, 12, 15, 18, 20, 22 h at 60–70 °C, the basic number with H₋ = 9.3 for 3a was 1.75, 1.72, 1.59,

1.67, 1.80, 2.00, 1.68, 1.34, 1.55, 1.71 mmol/g, respectively, the results showed that the reaction time had a profound effect on the basic number. The reaction of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and NaH_2PO_4 with 1b or 1c was for 12 h at 60–70 °C, the basic number with $\text{H}^- = 9.3$ for 3b, 3c was 2.26, 1.80 mmol/g, respectively.

3.2. Infrared spectra

The infrared spectra of the solid bases or supports exhibited broad bands centered at 3410–3460 cm^{-1} representing OH, NH, and water stretching vibrations, the frequencies of the band for 3a, 3c were lower than those of the support 20–40 cm^{-1} , however the band for 3b was shifted to higher frequency, the weak band at 1633–1657 cm^{-1} represented water bending vibration, the band for 3a or 3c was shifted to higher frequency, in contrast, the band for 3b was shifted to lower frequency. The region from 980 to 1121 cm^{-1} consisted of several broad overlapping bands that resulted from phosphate stretching vibration. In general, IR spectra showed that there were some differences between support and solid base in the vibration frequencies, which indicated that the support 2 had interacted with sodium hydroxide.

3.3. XRPD and ^{31}P MAS NMR

The supports did not diffract (Fig. 1), which indicated that the supports were amorphous. In order to obtain detailed structure information of the solid base, ^{31}P MAS NMR measurements were performed (Fig. 2), each showed three main resonances, first at about $\delta = -28$ ppm for NaPO_4 , second at about $\delta = -22$ ppm due to HPO_4 and third at about $\delta = -7$ ppm attributed to the phosphonate phosphorus atom.

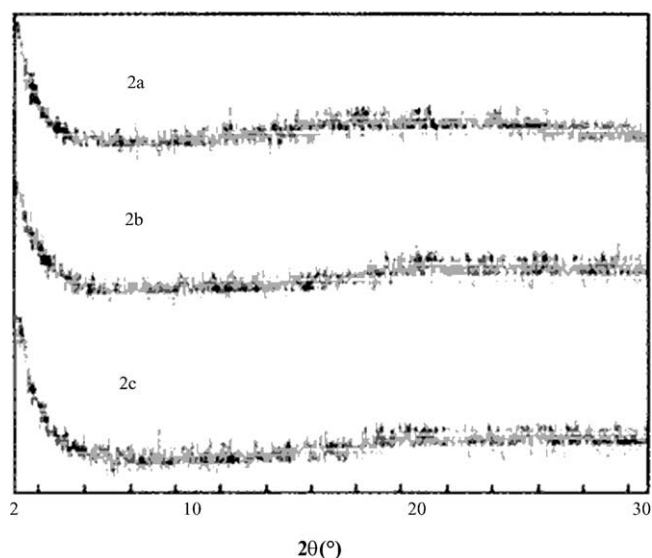


Fig. 1. XRPD profiles of 2a, 2b, 2c.

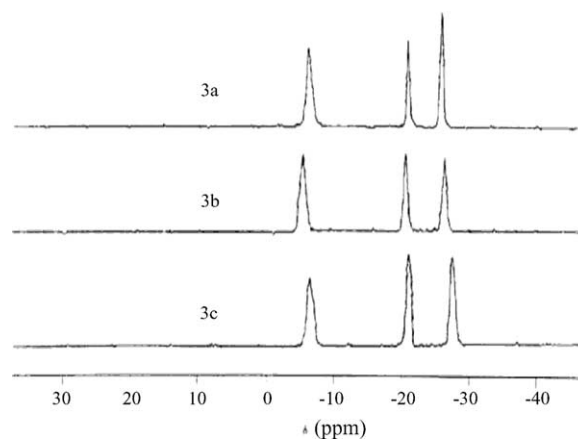


Fig. 2. ^{31}P MAS NMR spectra of 3a, 3b, 3c.

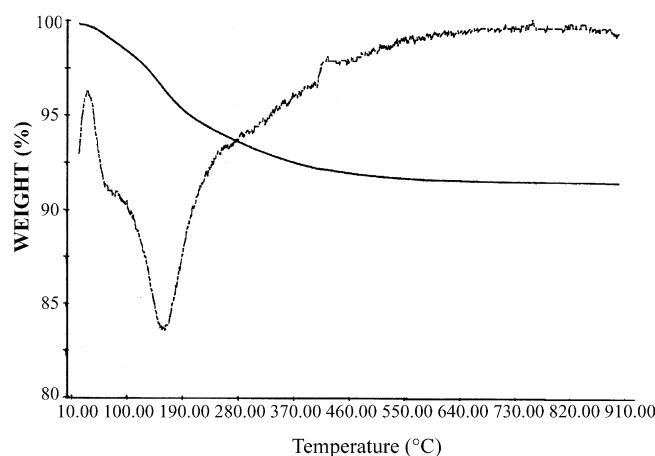


Fig. 3. TG, DTG curves of 3a.

3.4. Thermal analysis

TG and DTG curves for 3a and 3b, and 3c showed two or three steps at temperatures of up 900 °C in Figs. 3–5. The first weight loss due to the dehydration of the adsorption and crystallization water was 6.2, 6.3% at below 270 °C, the

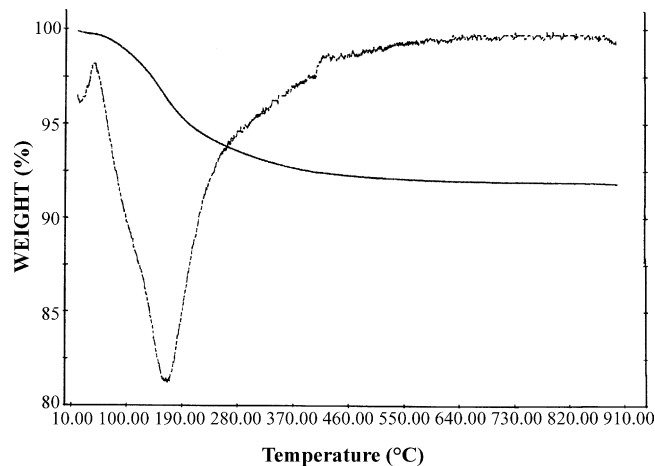


Fig. 4. TG, DTG curves of 3b.

Table 1
Knoevenagel condensation results catalyzed by solid base 3a

Entry	Reactants	Time (h)	Solvent	Yield (%)
1	Benzaldehyde with diethyl malonate	4.0	Toluene	90.2
2	Benzaldehyde with diethyl malonate	5.0	Dioxone	85.2
3	Benzaldehyde with diethyl malonate	5.5	Benzene	88.0
4	Benzaldehyde with malononitrile	4.0	Toluene	89.8
5	Benzaldehyde with malononitrile	4.5	Dichloromethane	90.2
6	Cyclohexanone with malononitrile	4.5	Dichloromethane	89.5

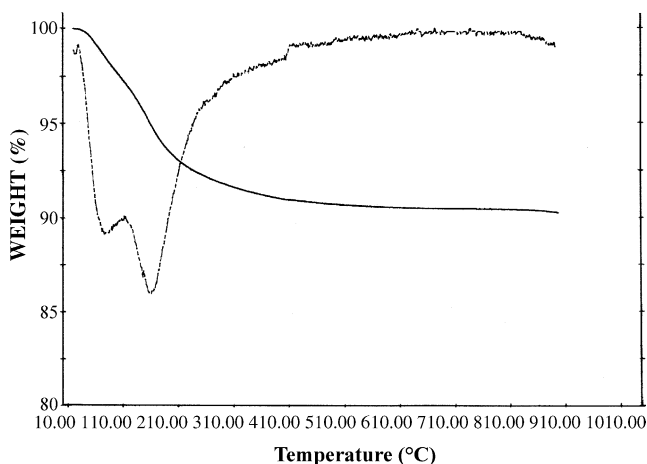


Fig. 5. TG, DTG curves of 3c.

second due to the decomposition of partial organic groups was 2.4, 1.2% in the temperature range of 270–640 °C for 3a and 3b, respectively. DSC curves for 3a (Fig. 6) showed the endothermic peak at 60 and 280 °C. The first weight loss assignable to the dehydration of the adsorption water was 2.8% at below 115 °C, the second assignable to the dehydration of the crystallization water was 4.5% in the temperature range of 115–200 °C, the third assignable to the decomposition of partial organic groups was 2.5% in the temperature range of 200–610 °C. The total weight loss for 3a, 3b, and 3c was found to be 8.6, 7.5, 9.8%, respectively, and all sample

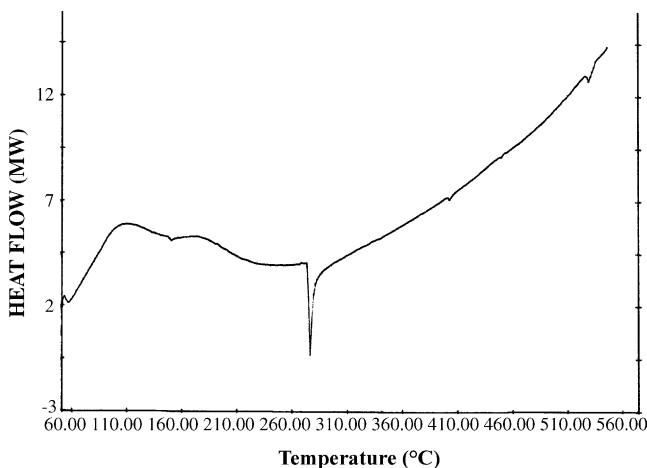


Fig. 6. DSC curve of 3a.

weight almost changed at above 610 °C, this indicated that the thermal stability of the solid base was markedly different from that of α -zirconium phosphate.

3.5. Catalytic activity

This condensation results (Table 1) clearly demonstrated that the solid was a practical base catalyst in Knoevenagel condensation with the following advantages: (1) high catalytic activity, (2) mild reaction condition, (3) simple work-up, (4) use of environmentally benign catalyst. The catalyst washed with dichloromethane and dried in vacuum could be reused for four times, the yield of product was 90.2, 89.6, 88.5, 86.3%, respectively, this indicated that the solid base did not significantly decrease in catalytic activity, and the solid base catalyst could be easily regenerated by sodium hydroxide solution disposal.

4. Conclusion

Based on our results, the mixed zirconium phosphate phosphonate solid base possessed basic sites stronger than $H_{-} = 12.2$; their active basic sites were possible to be amine group, partial P-ONa exchanged. The Knoevenagel condensation of benzaldehyde with diethyl malonate or malononitrile, cyclohexanone with malononitrile was catalysed by the solid base in high catalytic activity and the reusable nature, this implies that the solid base is a new type of environmentally benign catalyst.

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