

Synthesis of the novel layered amorphous and crystalline zirconium phosphate–phosphonates $\text{Zr}(\text{HPO}_4)[\text{O}_3\text{PCH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}] \cdot n\text{H}_2\text{O}$, $\text{Zr}(\text{HPO}_4)[\text{O}_3\text{PCH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2] \cdot n\text{H}_2\text{O}$, zirconium phosphonates $\text{Zr}[(\text{O}_3\text{PCH}_2)\text{NCH}_2\text{CO}_2\text{H}] \cdot n\text{H}_2\text{O}$ and the catalytic activities of their palladium complexes in hydrogenation

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Abstract

The layered amorphous and crystalline samples of zirconium [*N*-(phosphonomethyl)morpholine-phosphate] $\text{Zr}(\text{HPO}_4)[\text{O}_3\text{PCH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}] \cdot n\text{H}_2\text{O}$ (1a, 2a), zirconium [*N*-(phosphonomethyl)iminodiacetic acid-phosphate] $\text{Zr}(\text{HPO}_4)[\text{O}_3\text{PCH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2] \cdot n\text{H}_2\text{O}$ (1b, 2b) and zirconium [*N,N*-di(phosphonomethyl) acetic acid] $\text{Zr}[(\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{CO}_2\text{H}] \cdot n\text{H}_2\text{O}$ (1c, 2c) were synthesized for the first time with zirconium oxychloride, sodium dihydrogen phosphate and $\text{H}_2\text{O}_3\text{PCH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}$, $\text{H}_2\text{O}_3\text{PCH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$ or $(\text{H}_2\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{CO}_2\text{H}$ in the absence and presence of hydrofluoric acid. The samples were comparatively characterized by XRD, IR, TG and elemental analysis. XRD data showed that the crystalline samples 2a, 2b and 2c are highly crystalline with interlayer spacings of 1.606, 1.538 and 1.239 nm, respectively. The amorphous and crystalline samples lost nearly the weight calculated for their organic component over the same broad temperature range of 172–664, 184–680 and 176–668 °C, respectively. XPS data indicated that the coordination bonds formed between nitrogen and palladium in the palladium complexes. Their palladium complexes possessed good activities for the hydrogenation of the carbon–carbon double bond. The catalytic activities of the palladium complexes of amorphous 1a, 1b and 1c is 1.5–3.1 times as high as that of the palladium complexes of crystalline 2a, 2b and 2c.

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1. Introduction

Zirconium phosphates and zirconium phosphonates are types of layered multi-functional materials that can be used as ion-exchangers, catalysts or catalyst supports, adsorbents and absorbents [1]. In general, the surface areas of typical α -zirconium phosphates and phosphonates are in the range of 30–200 m²/g [2]. 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 indi-

cates that those materials are quite acid stable and possess high thermal stability. Current research in the layered zirconium phosphates or phosphonates field is active, but the bulk of this work has involved mainly ion-exchange [3–5], intercalation of organic materials [6–12], proton conduction for solid state gas sensors [13], molecular recognition [14–17] and solid acid catalytic action [18]. But few of the mixed zirconium phosphate–phosphonate $\text{Zr}(\text{HPO}_4)_{2-x}(\text{O}_3\text{PG})_x$ ($x = 0-2$, G: organic groups) in which molar content of organic groups (x) can be easily altered to meet different stereo-chemistry were reported, especially the application of their transitional metal complexes in hydrogenation and hydroformylation reactions [12]. In the light of the desirable physical properties of zirconium phosphonates, our interest in the synthesis of zirconium phosphonate containing N, O, P-complexing

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atoms grew from the prospectives in the fields of green chemistry in hydrogenation, carbonylation and hydroformylation reactions of their transitional metal complexes. In this paper the mixed amorphous and crystalline zirconium [*N*-(phosphonomethyl)morpholine-phosphate] Zr(HPO₄)(O₃PCH₂N(CH₂CH₂)₂O)·*n*H₂O, zirconium [*N*-(phosphonomethyl)iminodiacetic acid-phosphate] Zr(HPO₄)[O₃PCH₂N(CH₂CO₂H)₂]·*n*H₂O and the mixed-alike zirconium [*N,N*-di(phosphonomethyl)acetic acid] Zr[(O₃PCH₂)₂NCH₂CO₂H]·*n*H₂O whose organic groups are active complexing agents for transition metals such as palladium were prepared for the first time. The application of their palladium complexes in hydrogenation reactions was also preliminarily studied.

2. Experimental

2.1. Starting materials and methods

H₂O₃PCH₂N(CH₂CH₂)O, H₂O₃PCH₂N(CH₂CO₂H)₂ and (H₂O₃PCH₂)₂NCH₂CO₂H were prepared according to the literature [19] and affirmed by ¹H NMR and IR. All other materials used are of analytical grade.

C, H and N elemental analysis were performed on a Perkin-Elmer 2400 elemental instrument. IR spectra of the samples were recorded on Spectrum GX using polystyrene as a standard (KBr pellet). TG/DTA analyses were performed on a Q-Derivatograph thermal analyzer. The inter-layer spacings were obtained on a D/MAX-3C automatic X-ray diffractometer. XPS was performed on a KRATDS XSAM800 instrument. Pd content of the complexes supplied was measured by WYX-401 atomic adsorption spectroscopy.

2.2. Synthesis of amorphous zirconium

[*N*-(phosphonomethyl)morpholine-phosphate] Zr(HPO₄)(O₃PCH₂N(CH₂CH₂)₂O)·2H₂O (1a), zirconium [*N*-(phosphonomethyl)iminodiacetic acid-phosphate] Zr(HPO₄)[O₃PCH₂N(CH₂CO₂H)₂]·2H₂O (1b) and zirconium [*N,N*-di(phosphonomethyl)acetic acid] Zr[(O₃PCH₂)₂NCH₂CO₂H]·2H₂O (1c)

The mixture of (3.6 g, 20 mmol) or H₂O₃PCH₂N(CH₂CO₂H)₂ (4.5 g, 20 mmol) and NaH₂PO₄ (2.4 g, 20 mmol) in water (80 ml) was added to the solution of zirconium oxychloride (6.45 g, 20 mmol) in water (80 ml) with stirring, then the reaction mixture was stirred for 3–4 h at 60–70 °C, filtered, washed with water to pH = 5–6 and dried in vacuo. White solids of 1a (7.3 g, 95.0%) and 1b (8.1 g, 93.5%) were obtained [20]. Amorphous 1c (6.5 g, 96.2%) was also obtained by addition of (H₂O₃PCH₂)₂NCH₂CO₂H to the solution of zirconium oxychloride only in the absence of NaH₂PO₄ by the same steps. The anal. calc. for amorphous 1a were: C, 14.99; H, 3.75; N, 3.50; found: C, 14.74; H, 3.68; N, 3.44. 1b: C, 13.40; H, 2.90; N, 3.12; found: C, 13.36;

H, 2.84; N, 3.02. 1c: C, 13.52; H, 3.10; N, 3.94; found: C, 13.50; H, 3.08; N, 3.86.

2.3. Synthesis of crystalline

Zr(HPO₄)[O₃PCH₂N(CH₂CH₂)₂O]·H₂O (2a), Zr(HPO₄)[O₃PCH₂N(CH₂CO₂H)₂]·H₂O (2b) and Zr[(O₃PCH₂)₂NCH₂CO₂H]·H₂O (2c)

At molar ratio of F⁻/Zr⁴⁺ = 10 and H₂PO₄⁻/Zr⁴⁺ = 1, crystalline layered 2a and 2b were synthesized as follows. The solution of H₂O₃PCH₂N(CH₂CH₂)₂O (3.6 g, 20 mmol) or H₂O₃PCH₂N(CH₂CO₂H)₂ (4.5 g, 20 mmol) and NaH₂PO₄ (2.4 g, 20 mmol) in water (80 ml) was added with stirring to the mixture of zirconium oxychloride (6.45 g, 20 mmol) and hydrogen fluoride (40%, 10 ml, 0.20 mol) in water (80 ml), then stirred for 72 h at 60–70 °C, filtered, washed with water to pH = 5–6 and dried in vacuo. Crystalline layered 2c was obtained by adding (H₂O₃PCH₂)₂NCH₂CO₂H (4.6 g, 20 mmol) to the mixture of zirconium oxychloride and hydrogen fluoride in water only in the absence of NaH₂PO₄ by the same steps. White solids of 2a (4.9 g), 2b (5.2 g) and 2c (4.8 g) were obtained (yield 63.6, 60.0 and 71.0%, respectively). The anal. calc. for crystalline 2a were: C, 15.62; H, 3.38; N, 3.64; found: C, 15.57; H, 3.32; N, 3.58. 2b: C, 13.96; H, 2.56; N, 3.25; found: C, 13.92; H, 2.54; N, 3.23. 2c: C, 14.25; H, 2.67; N, 4.15; found: C, 14.20; H, 2.64; N, 4.09.

2.4. Preparation of corresponding palladium complexes

A mixture of 5 g of 1a, 1b, 1c, 2a, 2b or 2c (150 mesh), 60 mg of PdCl₂·2H₂O and ethanol (50 ml) was stirred at refluxing temperature for 12–16 h. The white powder became gray in reaction medium, the ethanol solution became colorless and transparent during the reaction. Then the complexes that contained 0.56–0.58% of the palladium were obtained by filtration, washing with ethanol (10 ml × 2) and drying in vacuo.

Catalytic hydrogenation reactions were carried out at atmospheric pressure.

3. Results and discussion

3.1. IR spectra

Comparing the IR spectra of the amorphous compound 1a, 1b and 1c with that of crystalline 2a, 2b and 2c, respectively, it was found that there were some differences between amorphous and crystalline samples in the vibration frequencies and shapes.

The absorption bands of amorphous 1a, 1b and 1c were wide and structureless, but for the crystalline materials 2a, 2b and 2c were sharp and narrow, which indicated that those groups such as PO₃(OH), C=O have a wider variety of chemical environments in the different crystal states.

3.2. Thermogravimetric analysis

On heating the samples 1a, 1b, 1c, 2a, 2b or 2c, their similar behaviors of their thermo-stability in comparing the amorphous and crystalline states over a broad temperature range of 40–900 °C were observed. Amorphous 1a, 1b and 1c lost the exact weight calculated for two waters of hydration in the temperature range of 40–172, 40–184 and 40–176 °C, respectively, whereas crystalline 2a, 2b and 2c only contained one water molecule. In general, the amorphous state has a larger internal surface than the crystalline state. Larger the surface areas, the more hydration water is encased. The thermolytic dissociation of the organic moiety $-\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}$, $-\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$ and $(-\text{CH}_2)_2\text{NCH}_2\text{CO}_2\text{H}$ in amorphous and crystalline samples 1a and 2a, 1b and 2b and 1c and 2c carried out apparently in the temperature range of 172–664, 184–680 and 176–668 °C, respectively. The 25.7, 33.4 and 27.6% weight losses in amorphous and crystalline samples 1a and 2a, 1b and 2b and 1c and 2c, respectively, are in accord with the theoretical content of their pendant organic component. It was demonstrated that there was the same thermolytic behavior of pendant organic moiety between amorphous samples with crystalline samples. In the temperature range of 710–900 °C the losses were attributed to the dehydrolysis of $\text{Zr}(\text{HPO}_4)_2$ to ZrP_2O_7 .

3.3. XRD results

Although amorphous 1a, 1b and 1c did not diffract, XRD data showed that the crystalline 2a, 2b and 2c were regularly layered compounds whose interlayer spacings were 1.606, 1.538 and 1.239 nm, respectively (Fig. 1). For crystalline 2a,

at $2\theta = 5.500, 11.140, 22.520$ and 28.460° there are four strong diffraction peaks, the interstices of corresponding crystal faces are 1.606, 0.794, 0.395 and 0.313 nm, respectively. The interstice 1.606 nm (d_{002}) at $2\theta = 5.500$ is the interlayer spacing of crystalline 2a. Due to the rigidity of cyclic ether in crystalline 2a the longest interlayer spacing was obtained among the three designed crystalline samples. But for crystalline sample 2c, the pendant organic groups $(-\text{CH}_2)_2\text{NCH}_2\text{CO}_2\text{H}$ has enough space to act and lack of rigidity, the shortest interlayer spacing was obtained. It was demonstrated that the different affixed organic groups could lengthen different interlayer spacings of zirconium phosphonate.

Layered crystalline zirconium phosphate, $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, presents an ideal model on which to test the foregoing ideas [21]. It contains on its lamellar surfaces a hexagonal array of hydroxyl groups spaced about 0.53 nm apart. This leads to an area per site of 0.24 nm^2 , which is quite suitable as a cross-sectional limit for many affixed substituents.

The structure of zirconium phosphonate [$\text{Zr}(\text{O}_3\text{PG})_2 \cdot \text{H}_2\text{O}$, $x = 2$, G are organic groups] is considered to be the complete substitution of hydroxy groups on lamellar surfaces of $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ by organic groups. But mixed zirconium phosphate–phosphonate $\text{Zr}(\text{HPO}_4)_{2-x}(\text{O}_3\text{PG})_x \cdot \text{H}_2\text{O}$ ($x = 0\text{--}2$) is generated by partial substitution of hydroxy groups by organic groups which can be designed according to the needs. In this paper only mixed zirconium phosphate–phosphonate $\text{Zr}(\text{HPO}_4)_{2-x}(\text{O}_3\text{PG})_x \cdot \text{H}_2\text{O}$ ($x = 1$) was emphasized. Due to steric exclusion between neighbor $-\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}$ or $-\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$ it is difficult for organic groups in crystalline 2a, 2b to be randomly distributed. The ideal structure of $\text{Zr}(\text{HPO}_4)(\text{O}_3\text{PG}) \cdot \text{H}_2\text{O}$ ($x = 1$) may be considered that the hydroxy groups on its

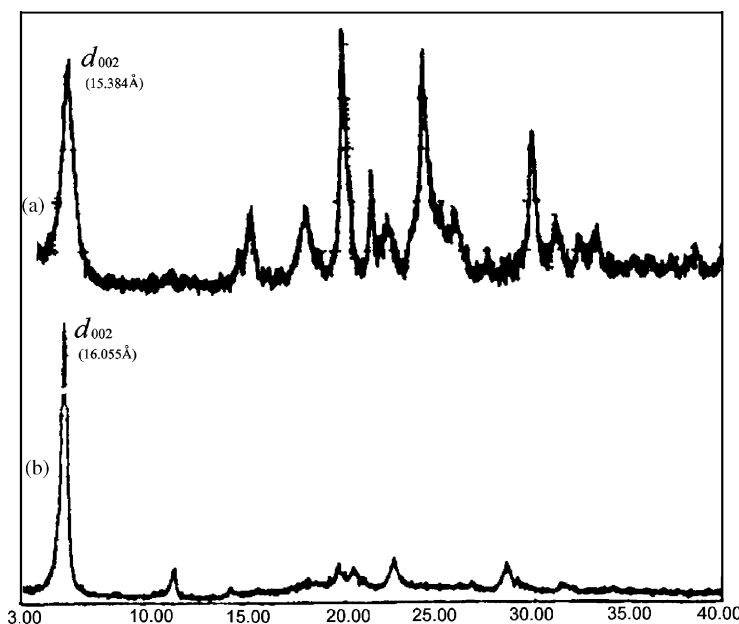


Fig. 1. XRD profile of the samples 2a and 2b: (a) crystalline 2b; (b) crystalline 2a.

Table 1
XPS data for amorphous or crystalline samples and their palladium complexes

E_b (eV)	1a	1a-Pd	1b	1b-Pd	1c	1c-Pd	2a	2a-Pd	2b	2b-Pd	2c	2c-Pd	PdCl ₂ (Pd ⁰)
N _{1s}	402.5	403.5	401.4	402.5	401.6	402.5	402.5	403.6	401.4	402.3	401.4	402.3	337.9 (335.7)
Pd _{3d(5/2)}		336.3		336.2		336.6		337.0		336.6		337.0	

Table 2
The initial hydrogenation rates of various substrates catalyzed by the Pd complexes of amorphous or crystalline samples 1a–2c

Complexes	Acrylonitrile	Acrylic ester	Propenol	Vinyl acetate	Styrene	Acrylic acid
1a	157	137	86	98	98	26
1b	123	130	82	91	103	30
1c	122	112	78	87	83	25
2a	51	39	34	45	34	17
2b	40	48	34	38	39	20
2c	40	46	33	37	36	19

Conditions: substrate (5 mmol), 70 mg cat., 15 ml of methanol as solvent, 35 °C. Unit: mol H₂ min⁻¹ mol⁻¹ Pd.

lamellar surfaces are regularly and alternately substituted by organic groups (G), and the ABABAB distribution of the organic groups (G) and the hydroxy groups (–OH) (A = OH, B = G) in a two-dimensional surface ideally forms (Fig. 2). Although zirconium [*N,N*-di(phosphonomethyl) acetic acid], Zr[(O₃PCH₂)₂NCH₂CO₂H]·*n*H₂O (*n* = 1, 2), is considered to be the complete substitution of hydroxy groups by organic groups (–CH₂)₂NCH₂CO₂H], the inter space between organic groups –NCH₂CO₂H on lamellar surfaces is similar with that of mixed zirconium phosphate–phosphonate Zr(HPO₄)_{2–*x*}(O₃PG)_{*x*}·H₂O (*x* = 1) because *N,N*-di(phosphonomethyl) acetic acid is a diposphonic acid which can easily and simultaneously bond to two neighbor zirconium atoms.

3.4. Preliminary results in hydrogenation reactions

XPS data of the samples 1a, 1b, 1c, 2a, 2b and 2c their palladium complexes are listed in Table 1. After complexed with Pd²⁺, the binding energy of N_{1s} increased 0.6–1.1 eV and that of Pd_{3d(5/2)} decreased 0.9–1.7 eV. However, the

binding energies of O_{1s}, P_{2p} and Zr_{3d} only changed by 0.2, 0.2 and 0.1 eV, respectively. It was indicated that coordination bonds formed between nitrogen and palladium atoms in the complexes studied.

The preliminary results showed that the palladium complexes of amorphous and crystalline samples have good activities in hydrogenation reactions for carbon–carbon double bond (Table 2). From Table 2, it can be seen that the catalytic hydrogenation activities of the palladium complexes of amorphous 1a, 1b and 1c was 1.5–3.1 times as high as that of the palladium complexes of crystalline 2a, 2b and 2c. In general, the amorphous zirconium phosphonates have the more external surface areas. Perhaps in the palladium complexes supported by crystalline samples 2a, 2b and 2c, Pd atoms undergo complexation only on the surface. Therefore, the pendant organic groups –CH₂N(CH₂CH₂)₂O, –CH₂N(CH₂–CO₂H)₂ and (–CH₂)₂NCH₂CO₂H in the inner layers have no contribution to the complexation reactions and catalytic activities.

The hydrogenation reactions were carried out easily in some solvents with intermediate dielectric constant such as alcohol, acetone and especially methanol. But in some solvents with high or low dielectric constant such as glycol and chloroform, the palladium complexes lost their catalytic activities in hydrogenation. The solvent effect may be attributed to the solubility and mutual solubility of catalytic center in the palladium complexes, solvents and substrates each other in the catalytic system.

4. Conclusion

The ligand containing N, O atoms can be bound to the amorphous and layered zirconium phosphate to form a new type of the mixed zirconium phosphate–phosphonate carrier with different interlayer spacings due to different pendant organic moieties in phosphonates. Their palladium complexes are efficient in liquid phase hydrogenation of carbon–carbon

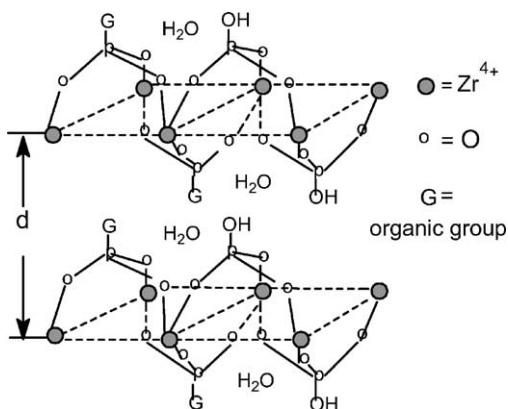


Fig. 2. Ideal model of zirconium phosphate–phosphonate Zr(HPO₄)-(O₃PG)·H₂O.

double bond in small molecules under atmospheric pressure.

Acknowledgements

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