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Synthesis and Characterization of Aminophosphonates Zirconium as New Mesoporous Materials

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Abstract: A serial of aminophosphonates zirconium with the different arm lengths of –(CH_2)n– organic chains (n=2–6) was synthesized for the first time. These compounds are characterized by FT-IR, SEM, TEM, TG and nitrogen adsorption-desorption. And based on the experimental data, these materials not only have layer structure mesoporous and good thermal stability such as zirconium phosphate, but also can be adjusted the layer distance, pore size and pore volume. So aminophosphonates zirconium posses special excellent properties and will have potential prospect applications.

Keywords: Mesoporous materials; Aminophosphonates Zirconium; Synthesis and Characterization.

Introduction

Zirconium phosphonate and its derivatives are very important compounds to use in the field of catalysis, adsorption, ion exchange and/or functional materials. If the P-OH bonds in the molecule of zirconium phosphonate are whole or part changed to the P-R, the compounds become organic zirconium phosphonates or their derivatives [1-3]. The common inorganic materials such as mesoporous, macroporous silica gel and molecular sieve with surface of single hydroxyl have difficult to be further modified [4-6]. A variety of functional groups of zirconium phosphonates can overcome this problem. By controlling the synthesis conditions, zirconium phosphonates with different groups and spacing of layers can be prepared. Zirconium phosphonates as supports in catalysis have recently been highlighted as a new option for the immobilization of homogeneous catalysts [7-8].

They generally have amorphous structure with high specific surface area that let reactive sites fully expanded. And the container effects of micropores and mesopores of zirconium phosphonates are benefit to chemical reaction sufficient occurring.

In this paper, a serial of aminophosphonates zirconium with the different arm lengths of $-(CH_2)n-$ organic chains (n=2–6) was synthesized for the first time. These compounds are characterized by FT-IR, SEM, TEM, TG and nitrogen adsorption-desorption.

Experimental

Material and Methods:

FT-IR spectra were recorded on Bruker RFS100/S spectrophotometer (USA) using KBr pellets in the 400–4000 cm^{-1} range. ^1H, ^{13}C and ^{31}P NMR spectra were recorded by using an av-300 NMR instrument at 300, 75 and 121 MHz, respectively. TG analyses were performed on a SBTQ600 Thermal Analyzer (USA) with the heating rate of 20°C/min in the temperature range of 30–1200°C under flowing N_2 (100 mL/min). N_2 adsorption–desorption isotherms carried out at 77 K on Autosorb-1 apparatus (Quantachrome). The surface areas were determined by using the BET equation, and the average pore size was estimated according to the BJH model. Scanning electron microscopy (SEM) analysis was performed on S-4800 FE-SEM instrument (Hitachi). Transmission electron microscopy (TEM) analysis was recoded on a TECNAI10 (PHILIPS, Holland) apparatus.

Phthalimide was purchased from Alfa Aesar. Other commercially available chemicals were laboratory-grade reagents from local suppliers.

Synthesis of Aminophosphonates Zirconium:

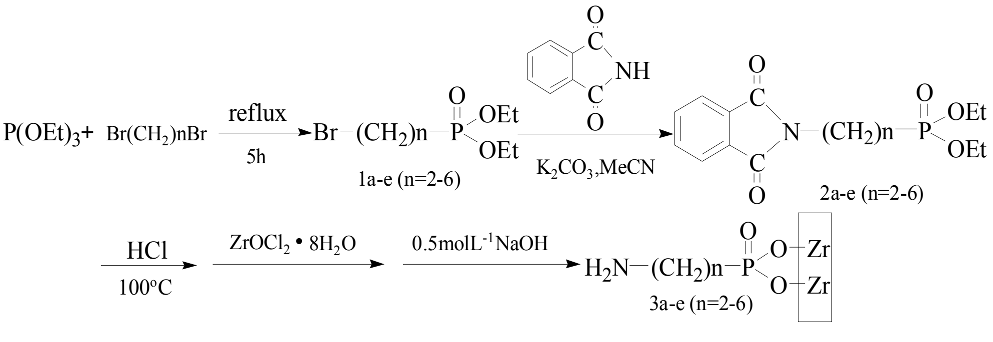

Figure 1. The synthese route of aminophosphonates zirconium.

(1) In the dried three-necked flask (250 mL) was charged ω-alkane dibromide (n=2–6) (237mmol) and followed by dropwise addition of triethyl phosphate (13.11g, 79 mmol)

refluxed for 5 h with the tracking of TLC. The reaction mixture was chromatographed on a silica gel column eluted with petroleum ether (60–90°C)/ethyl acetate (10:1 in volume) to give 1a–e [10], respectively in 75–85% yield.

(2) In the dried three-necked flask (250 mL) was charged anhydrous K_2CO_3 (5.5g, 40 mmol) and phthalimide (5.88g, 40mmol), flushed three times with nitrogen at room temperature, added dropwise 100mL acetonitrile solution of 1a–e (n=2–6) (40mmol) then refluxed for 48 h with the tracking of TLC. The reaction mixture was concentrated under reduced pressure. After removal of the solvent, the residue was diluted with $CHCl_3$ (100 mL) and then was washed with brine (30 mL×3), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the pale yellow liquid. The crude product was purified by silica gel column chromatography using petroleum ether (60–90°C)/$CHCl_3$ (4:1 in volume) to give 2a–e, respectively in 58–64% yield.

(3) A mixture of 2a–e (n=2–6) (2 mmol), 15 mL of hydrochloric acid (36%) was stirred at 100°C for 24 h and concentrated under reduced pressure. Zirconium oxychloride (1.7g, 6 mmol) in 15 mL of deionized water was added dropwise and stirred at room temperature for another 16 h. The white solid was filtered, dispersed in 50 mL of water, adjusted to pH= 6–7 by using sodium carbonate (0.5mol/L) and filtered again. The mud cake was washed with deionized water till chloride ion was not detected by using ion chromatography, and then dried at 60°C for 24 h under reduced pressure to afford aminophosphonates zirconium 3a-e, respectively in 52–63% yield.

Results and Discussion

Infrared Spectroscopy:

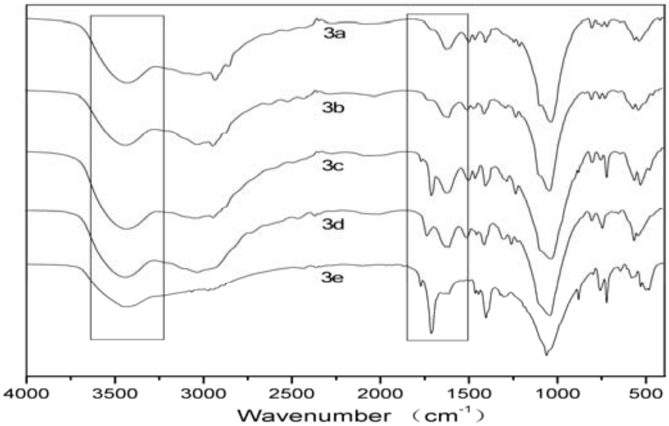

Figure 2. IR spectra of 3a-e.

The FT-IR spectra of the parent supports 3a–e had the similar infrared spectroscopy in the 4000–500cm^{-1} range. The 3a-e exhibited bands at 3600-3200cm^{-1} assigned to the characteristic vibration of the –NH groups. The several absorption peaks in the scan range 1686-1650cm^{-1} for 3a–e were attributed to the N–H vibrations of the appended organic moieties. Therefore, based on IR spectra of 3a-e, it was demonstrated that aminophosphonates zirconium were successfully prepared.

Surface Morphology:

Scanning electron micrograph (SEM) was recorded to understand morphology of the surface of aminophosphonates zirconium in solid state. From the SEM images shown in Fig. 3(a), 3a were conglomerated with the globular aggregates with the diameters of about 0.1–0.2 um, which indicated that the diameter of the particles of the material was in submicron. Also, it showed that the material was loose, and had various caves, holes and porous. Interestingly, 3a in the organic solvents were easily swollen, which could be verified by the TEM images. After the samples 4a–e were dispersed in cyclohexane and stirred for 2h, their morphologies of the filiform structure with thickness about 20–50 nm and length about several micrometers was observed in Fig. 3(b). The similar SEM and TEM images and results were obtained for the other four compounds 3b–e.

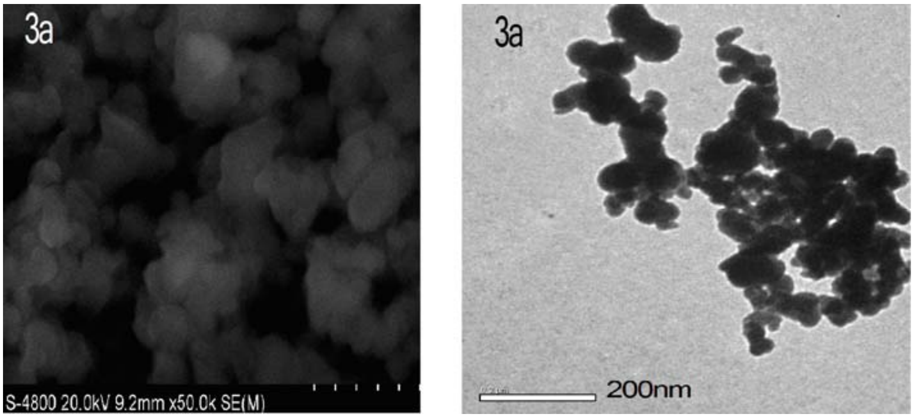

Figure 3. (a) SEM image of aminophosphonates zirconium 3a and (b) TEM image of aminophosphonates zirconium 3a.

Thermal Gravimetric Analysis:

On heating the samples of aminophosphonates zirconium 3a, the thermolysis over a broad temperature range of 40–1200°C with three steps of weight loss were observed (Fig. 4). The first slope curve was due to the desorption of the surface-bound or intercalated water from the pore channels at 50-100°C. In the 100-200°C, the thermal gravimetric curve is relatively flat. The sharp weight loss in the temperature range of 200–500°C, accompanied by endothermic peaks in the DSC curves at 250°C, corresponded to the decomposition of the appended organic fragments. Finally, in the temperature range of 600–1200°C, the third slope curve was attributed to the dehydrolysis of $Zr(HPO_4)_2$ to ZrP_2O_7. The similar thermal gravimetric curves and results were obtained for the other four compounds 3b–e.

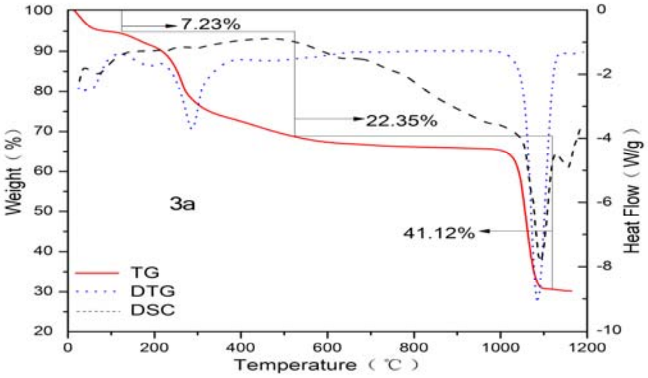

Figure 4. The thermal gravimetric curves of 3a.

Nitrogen Adsorption–Desorption Isotherms:

The materials 3a-e all have the similar nitrogen adsorption-desorption isotherms (Fig. 5). The textural parameters of 3a–e calculated by N_2 adsorption and desorption isotherms at 77 K were presented in Table 1. As expected, it was shown that 4a–e (n = 2–6) were porous solid materials with the surface areas of 22.12–88.98 m^2/g, pore volumes of 0.072–0.445cc/g and average pore sizes of 13.95–99.49 Å. With the increase in arm chain lengths n from 2 to 6, it was observed that the surface areas of 3a–e increased and average pore sizes decreased respectively.

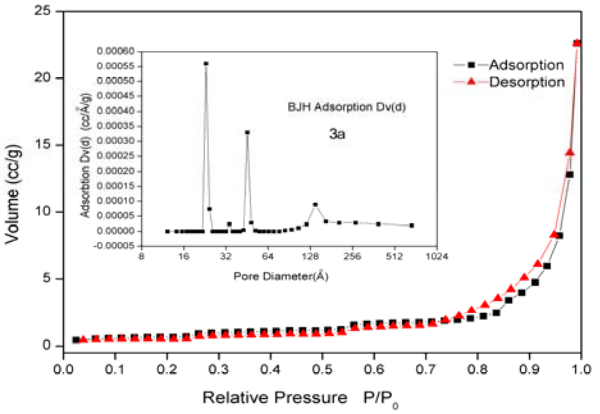

Figure 5. The nitrogen adsorption-desorption isotherms of 3a.

Table 1. The surface area, pore diameter and pore volume of 3a-e.

Samples[a]	S_{BET} (m^2/g) [b]	Pore Size (Å) [c]	Pore Volume [cc/g] [d]
3a	22.12	99.49	0.445
3b	48.57	40.08	0.147
3c	53.44	25.61	0.095
3d	73.31	21.73	0.089
3e	88.98	13.95	0.072

[a] The samples were degassed at 100ºC for 5 h.
[b] Surface based on multipoint BET method.
[c] Pore size based on the desorption data using BJH method.
[d] Pore volume based on the desorption data of BJH method.

A reasonable and plausible explanation of this change in surface area and average pore size was that the longer arm chain lengths n from 2 to 6 made the inorganic zirconium layers more expanded and amorphous, and then the more surface areas were obtained. In the other hand, the organic moieties with the arm chain lengths n from 2 to 6 between the neighbor zirconium layers tended to be more close packing in the interlayer region, which caused the less free pores and the decrease in the average pore sizes from 99.49 to 13.95 Å.

Conclusions

In summary, the materials of aminophosphonates zirconium were successfully prepared for the first time. Owing to their layered mesoporous structures, these aminophosphonates zirconium could act as catalyst supports, enabling one to take advantage of the rigid frame, the confinement effect and the cooperation effect, and bridging the gap between heterogeneous catalysts and homogeneous catalysts.

Acknowledgments

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