

Two-dimensional composite zirconium phosphonates: preparation and catalytic activities

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Abstract

Composite zirconium phosphonates in single crystal phase have been investigated and characterized by XRD, ^{13}C -, and ^{31}P -MASNMR. These compounds are lamellar structures comprising zirconium organophosphonates. Each layer consists of planes of zirconium bridged through phosphonate groups that alternate above and below the Zr atom planes, oriented away from the basal surfaces in a bilayered fashion in the interlayer region. The catalytic performance over zirconium phosphonates is evaluated by esterification of acetic acid. When the composite zirconium phosphonate includes an acidic function and with a hydrophobic function in single crystal phase, the catalytic activity showed a higher activity than that of sulfonic acid catalyst. The composite zirconium phosphonates become accessible to any reactant molecule and improve hydrophobicity around acidic sites. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently, several kinds of layered compounds have been proposed for use as catalysts, including silicates, graphite, and acid salts of tetravalent metals. Acid salts of tetravalent metals are usually prepared as amorphous precipitates. Zirconium phosphonates are solid materials, typically synthesized in amorphous forms under aqueous conditions by the reaction of a soluble salt of a tetravalent metal and an organophosphoric acid: However, it is possible to synthesize many of them as crystalline compounds. The potential applications of crystalline zirconium phosphonates have significant recent interest. Depending on the alkyl group, different

applications for these materials in the fields of chromatographic separation, photochemistry, fuel cells, and catalysis are expected. In the case of zirconium phosphates, with the general formula $\text{Zr}(\text{O}_3\text{POH})_2 \cdot n\text{H}_2\text{O}$, the most extensively investigated crystalline zirconium phosphate is an a layered acid salt [1]. $\alpha\text{-Zr}(\text{O}_3\text{POH})_2 \cdot \text{H}_2\text{O}$ crystallizes in the monoclinic system, as assigned by Troup and Clearfield from their single crystal work [2]. For the zirconium phosphonates, however, the two-dimensional tetravalent metal plane has a structure essentially similar to the zirconium phosphate structure; substituted for hydroxyl groups are the desired organic functional groups, oriented away from the basal surfaces in a bilayered fashion in the interlayer region [3]. Therefore, zirconium phosphonate materials can act as a series of modified layered

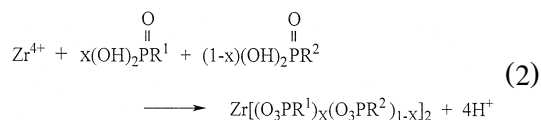
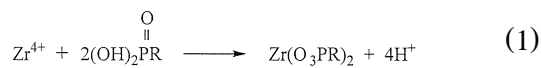
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compounds, and can become accessible for reactant molecules of catalysis. We have reported the preparation and characterization of two-dimensional single component zirconium phosphonates [4]. The acidic function of single zirconium phosphonate showed rather poor catalytic activities for esterification of acetic acid and hydrolysis of ethyl acetate, except over $\text{Zr}(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_2$. In addition, over $\text{Zr}(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_2$ catalyst, the reaction proceeds as a homogeneous reaction (soluble to water or polar molecules), even though the catalytic activity is higher than those of other acidic zirconium phosphonates. In this study, to overcome the problem of water solubility, and/or to improve hydrophobic properties, a second function, $\text{Zr}[(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_x(\text{O}_3\text{PC}_{12}\text{H}_{25})_{1-x}]_2$, was introduced to achieve a catalytic advantage in certain applications. The objective of this study is to explore the role of a second phosphonate function in the single crystal phase in the catalytic performance of acidic function ($-\text{CH}_2\text{SO}_3\text{H}$) and hydrophobic function ($-\text{C}_{12}\text{H}_{25}$) of zirconium phosphonates, and to learn how to exploit this second function to achieve a catalytic advantage in certain applications.

2. Experimental methods

2.1. Preparation of zirconium phosphonates

Addition of a water-soluble Zr(IV) salt to organo-phosphoric acid results in the precipitation of a gelatinous amorphous precipitate. Several types of zirconium phosphonates, $\text{Zr}(\text{O}_3\text{PR})_2$, either in single component (Eq. (1)), such as one kind of R, or in composite zirconium phosphonates (Eq. (2)), such as two different R's, were prepared (pendant type): here R^1 could be $-\text{CH}_2\text{SO}_3\text{H}$ as acidic functional group and R^2 could be $-\text{C}_{12}\text{H}_{25}$ as hydrophobic functional group.



Most of the zirconium phosphonate derivatives were obtained by the addition of aqueous solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (1.17 M) to the (organo) phosphonate reagent, $(\text{HO})_2\text{P}(\text{O})\text{R}$, (R^1 : $-\text{CH}_2\text{SO}_3\text{H}$ and/or R^2 : $-\text{C}_{12}\text{H}_{25}$, 0.75 M, $[\text{R}]/[\text{Zr}] = 2-10$) to yield small particle, amorphous zirconium phosphonates.

For the crystallization process, the amorphous zirconium phosphonate was treated with HF solution. The use of HF as a complexing reagent to inhibit release of free Zr^{4+} had a considerable effect on increasing crystallinity and particle size. The zirconium fluoro-complexes were decomposed slowly by removing the hydrofluoric acid in the presence of phosphonic acid. The crystallinity of composite zirconium phosphonates increased with increasing concentrations of HF. However, some phase segregation of each function was observed when HF concentrations, $[\text{F}]/[\text{Zr}]$, exceeded 9. For the crystallization, amorphous zirconium phosphonates were usually treated with HF solution ($[\text{F}]/[\text{Zr}] = 6$ or 8) at 333 K [5].

2.2. Characterization of zirconium phosphonates

The experimental procedures of TGA, XRD, and measurement of ion-exchange capacity have been described in detail elsewhere [6]. The interlayer d-spacing from XRD pattern was determined by the angle of (001) reflection.

^{31}P - and ^{13}C -MASNMR spectroscopy: High-resolution solid-state MASNMR spectra were obtained on a Fourier Transform pulsed NMR

spectrometer (JEOL, JNM-GX270) equipped with a CP/MAS unit (JEOL, NM-GSH27MU). All ^{31}P -NMR spectra combined with cross polarization (CP) and/or with magic angle spinning (MAS) at 109.38 MHz were measured with high-power proton decoupling during data acquisition [7]. The ^{13}C -MASNMR spectra were obtained at 67.94 MHz with CP and proton decoupling. Sample spinning speeds, determined from the side-band spacing in spinning spectra, were 3.6 to 4.0 kHz. ^{31}P and ^{13}C chemical shifts were determined by phosphoric acid and TMS, respectively, and its resonance frequency was observed in the absence of spinning.

2.2.1. Catalytic reactions

The catalytic activities of esterification of acetic acid with ethanol at 343 K were measured. 250 mg of catalyst was suspended in ethanol solution of acetic acid or aqueous solution of ethyl acetate, and the reaction rates were measured by GC (PORAPAK Q, 2-m).

2.2.2. Adsorption measurements

Chemisorption of base molecules on acidic zirconium phosphonate was confirmed by micro-calorimetry. High-temperature micro-calorimetry of NH_3 on zirconium phosphonate sample was obtained by the calorimeter (HAC-450G, Tokyo Rikou). Each sample (1 g) was charged into the calorimeter, and evacuated at 373 K for 4 h. NH_3 (15 mmol g^{-1}) was admitted dose by dose at 373 K.

3. Results and discussion

3.1. Preparation and structure of zirconium phosphonates

The structure of a zirconium phosphonate, $\text{Zr}(\text{O}_3\text{PR})_2$ (R: organic group), comprises a metal phosphate core layer with pendant organic groups attached to this core and normal to the

plane of the layer. Compounds of the type $\text{Zr}(\text{O}_3\text{PR})_2$ with lamellar a-type structures are prepared by simply replacing phosphoric acid with phosphonic acid or organophosphonic acid [6]. Elemental analysis results were in fairly good agreement with values calculated from the theoretical chemical formulae. The Zr atoms in zirconium phosphonates lie very nearly in a plane and are bridged by phosphorus tetrahedra. These tetrahedra are situated alternately above and below the Zr atom plane. Thus, each phosphonate R group in $\text{Zr}(\text{O}_3\text{PR})_2$ is directed into the interlayer space. In intercalated zirconium phosphates and phosphonates, guest molecules are accommodated in the interlayer region, and such materials do not usually have any porosity. The use of solid state, magic-angle spinning NMR is a recent development for characterizing layered compounds [7]. In particular, ^{13}C - and ^{31}P -MASNMR spectra are very informative for characterizing the micro environments of phosphonates, which cannot be established by XRD.

The MASNMR spectra of $\text{Zr}(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_2$, and $\text{Zr}(\text{O}_3\text{PC}_{12}\text{H}_{25})_2$ (single zirconium phosphonates) and $\text{Zr}[(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_{0.5}(\text{O}_3\text{PC}_{12}\text{H}_{25})_{0.5}]_2$ (composite zirconium phosphonates) are shown in Figs. 1 and 2. In the case of ^{31}P -MASNMR spectra (Fig. 1) of a single zirconium phosphonate, the chemical shifts represent a single resonance line: $\text{Zr}(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_2$ at -8.7 ppm (Fig. 1C), and $\text{Zr}(\text{O}_3\text{PC}_{12}\text{H}_{25})_2$ at 7.5 ppm (Fig. 1A). This indicates the presence of only one kind of phosphorus environment between each pair of layers. For ^{31}P -MASNMR spectra of composite $\text{Zr}[(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_X(\text{O}_3\text{PC}_{12}\text{H}_{25})_{1-X}]_2$ (Fig. 1B), however, two identical resonance lines are observed: -8.7 ppm for phosphorous of $\text{P}-\text{CH}_2\text{SO}_3\text{H}$ and 7.5 ppm for phosphorous of $\text{P}-\text{C}_{12}\text{H}_{25}$. The relative intensity of the resonance lines varies as a function of the X value. ^{13}C -CP/MASNMR spectra of composite zirconium phosphonate compounds (Fig. 2B) show the same resonance lines as spectra of single zirconium dodecyl phosphonate, $\text{Zr}(\text{O}_3\text{PC}_{12}\text{H}_{25})_2$ (Fig. 2A). The major resonance line, which is attributed to the methyl-

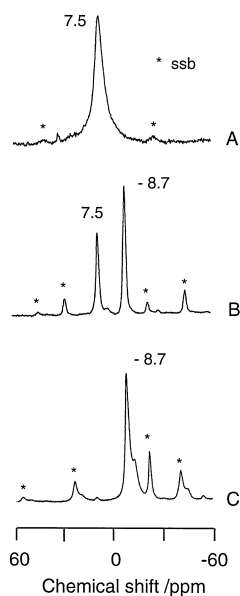


Fig. 1. ^{31}P -MASNMR spectra of single and composite zirconium phosphonates: (A) $\text{Zr}(\text{O}_3\text{PC}_{12}\text{H}_{25})_2$, (B) $\text{Zr}[(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_{0.5}(\text{O}_3\text{PC}_{12}\text{H}_{25})_{0.5}]_2$, (C) $\text{Zr}(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_2$.

ene carbons, is observed at 34 ppm from TMS. The other two lines in ^{13}C -CP/MASNMR spectrum are attributed to the carbon of $\text{P}-\text{CH}_2-$ at 25 ppm and to the terminal methyl carbon at 15 ppm [8]. On the other hand, ^{13}C -CP/MASNMR spectrum of single $\text{Zr}(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_2$ shows only one resonance line at 49 ppm, which is attributed to the carbon of $\text{P}-\text{CH}_2\text{SO}_3\text{H}$.

In addition to single component zirconium phosphonate derivatives, layered structures with multiple functionality can be prepared by incorporating more than one phosphonic acid during the preparation. The syntheses of derivatives of composite zirconium phosphonates with the general formula, $\text{Zr}[(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_X(\text{O}_3\text{PC}_{12}\text{H}_{25})_{1-X}]_2$, are effected by precipitating a mixture of two phosphonic acids with a zirconium salt in the presence of HF. Many other zirconium phosphonate derivatives may be prepared easily by using other mixtures of phosphonic acids. Because of the large variety of possible compositions of the two functional groups, the composite compounds should ex-

hibit a broad range of applications in ion-exchange, adsorption, intercalation, and catalysis.

The layer separation (interlayer d-spacing) of each crystalline zirconium phosphonate was determined from the first reflection line of the XRD pattern. Diffraction data confirmed from the expected correlation of interlayer spacing with the size of the pendant organic group. Solid products consisting of layered sheets with ordered arrays of the pendant organic groups on both sides of the layer were obtained with most phosphonic acids [6]. The interlayer d-spacing of composite zirconium phosphonates depended on the bulkier functional groups. Fig. 3 shows the interlayer d-spacing and ion-exchange capacities of composite $\text{Zr}[(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_X(\text{O}_3\text{PC}_{12}\text{H}_{25})_{1-X}]_2$ as a function of X . The XRD patterns also did not show any segregation, regardless of the concentration of each component. In addition to the interlayer d-spacing, values determined from (001) reflection showed constant (3.24 nm) values similar to

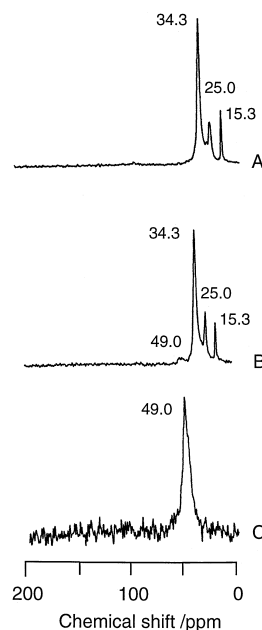


Fig. 2. ^{13}C -CP/MASNMR spectra of single and composite zirconium phosphonates: (A) $\text{Zr}(\text{O}_3\text{PC}_{12}\text{H}_{25})_2$, (B) $\text{Zr}[(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_{0.5}(\text{O}_3\text{PC}_{12}\text{H}_{25})_{0.5}]_2$, (C) $\text{Zr}(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_2$.

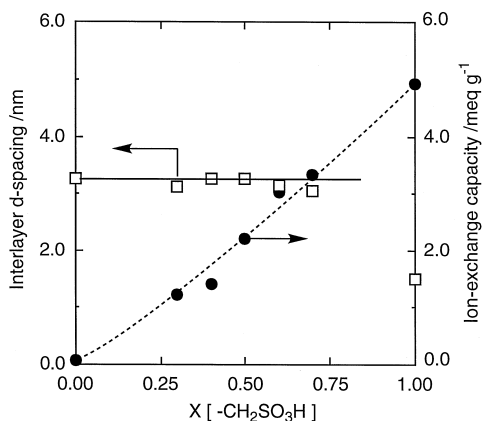


Fig. 3. Interlayer d-spacing and ion-exchange capacity of single and composite $\text{Zr}[(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_X(\text{O}_3\text{PC}_{12}\text{H}_{25})_{1-X}]_2$ as a function of X .

that of single zirconium dodecyl phosphonate, $\text{Zr}(\text{O}_3\text{PC}_{12}\text{H}_{25})_2$. Ion-exchange capacities increased with increasing concentration of X value, in direct proportion to the number of acid hydrogens in the replacing groups; this is shown by the dashed curve in Fig. 3. The results suggest that n -alkyl groups are distributed uniformly between each pair of Zr atom planes and that the interlayer d-spacings are obeyed the bulkiness of n -alkyl groups, and that two functional groups (R^1 : $-\text{CH}_2\text{SO}_3\text{H}$ and R^2 : $-\text{C}_{12}\text{H}_{25}$) are present in the single-crystal phase of zirconium atom plane.

3.2. Adsorption and catalytic activity over composite zirconium phosphonates

Adsorption values of NH_3 over composite $\text{Zr}[(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_X(\text{O}_3\text{PC}_{12}\text{H}_{25})_{1-X}]_2$ as a function of X have been measured by high-temperature micro-calorimetry; the results are shown in Fig. 4. We preferred the temperature at 373 K for calorimetry measurements in order to avoid physisorption of NH_3 . All micro-calorimetric curves decreased with increasing coverage of NH_3 on zirconium phosphonates. The initial heat of adsorption of composite zirconium phosphonate was around 120 kJ mol^{-1} ,

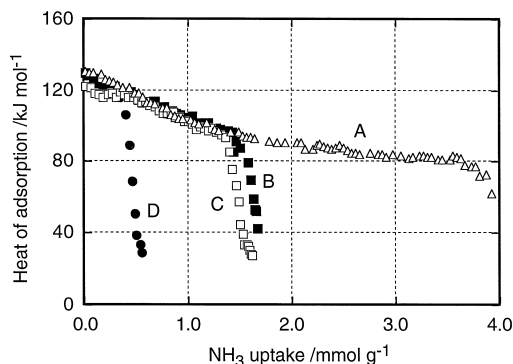


Fig. 4. High-temperature microcalorimetry of NH_3 on single and composite $\text{Zr}[(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_X(\text{O}_3\text{PC}_{12}\text{H}_{25})_{1-X}]_2$: (A) $\text{Zr}(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_2$, (B) $\text{Zr}[(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_{0.6}(\text{O}_3\text{PC}_{12}\text{H}_{25})_{0.4}]_2$, (C) $\text{Zr}[(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_{0.5}(\text{O}_3\text{PC}_{12}\text{H}_{25})_{0.5}]_2$, (D) $\text{Zr}[(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_{0.4}(\text{O}_3\text{PC}_{12}\text{H}_{25})_{0.6}]_2$.

regardless the value of X . The results suggest that the acid strength of $\text{Zr}[(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_X(\text{O}_3\text{PC}_{12}\text{H}_{25})_{1-X}]_2$ was stronger than that of the protonic form of several zeolites [9]. In addition, the acid amounts of stronger acidic sites are decreasing with decreasing number of X .

For catalytic esterification of acetic acid in ethanol medium over zirconium phosphonates, the composite materials showed higher catalytic activities than single phosphate, as shown in Fig. 5. It is quite interesting that, no matter how small the proton concentration became, the

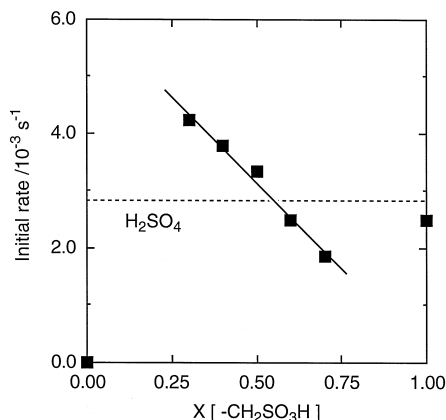


Fig. 5. Catalytic activity for esterification of acetic acid on single and composite $\text{Zr}[(\text{O}_3\text{PCH}_2\text{SO}_3\text{H})_X(\text{O}_3\text{PC}_{12}\text{H}_{25})_{1-X}]_2$ as a function of X .

reaction rate for esterification was enhanced. After introduction of hydrophobic functions ($-C_{12}H_{25}$) to acidic zirconium phosphonate ($-CH_2SO_3H$), composite materials became accessible to any reactant molecule, since the interlayer d-spacing were increased, and these materials improved in hydrophobicity. Thus, the functional groups for catalysis are incorporated in one crystal phase. The findings suggest that the composite compounds may be variety of reactions in aqueous or polar organic solvents. Some of these compounds, such as pendant $Zr[(O_3PCH_2SO_3H)_X(O_3PC_{12}H_{25})_{1-X}]_2$ ($X = 0.2-0.5$), showed much higher catalytic activities for the esterification of acetic acid than sulfonic acid without soluble to the reaction media, the reaction takes place under heterogeneous catalytic system.

4. Conclusions

The idealized structures of composite $Zr[(O_3PCH_2SO_3H)_X(O_3PC_{12}H_{25})_{1-X}]_2$ are illustrated in Fig. 6. In such compounds, which show an α -layered structure similar to that of zirconium phosphate, two different tetrahedral phosphates are bonded to the plane of zirconium atoms. Thus it is of great interest to examine the possibility of obtaining various organic derivatives of zirconium phosphonate in which two or more different functional groups are present in the same compounds. No single crystals for XRD structural determination have yet been obtained. Only speculations on the structure of the composite compounds may be made on the basis of their MASNMR spectra and XRD powder patterns, their chemical behavior, and existing knowledge of the structure of α -zirconium phosphate and its organic derivatives. Diffraction data confirm the expected correlation of interlayer spacing with the size of pendant organic group [8]. Solid products consisting of layered sheets with ordered arrays of the pen-

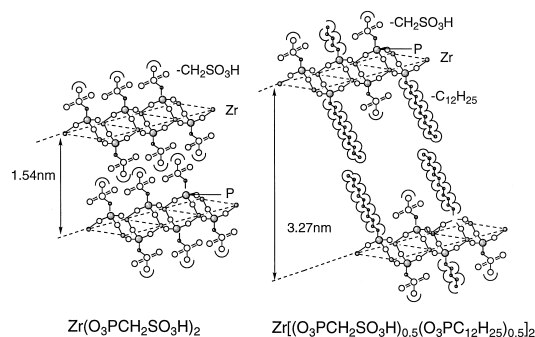


Fig. 6. Idealized structure of $Zr(O_3PCH_2SO_3H)_2$ and $Zr[(O_3PCH_2SO_3H)_{0.5}(O_3PC_{12}H_{25})_{0.5}]_2$.

dant organic groups on both sides of the layer are obtained with most phosphonic acids [9,10].

Because of their layered structure, zirconium phosphonate materials can act as a series of modified surfaces, accessible by introducing organic functional groups. The structure of zirconium phosphonates is similar to that of the zirconium phosphate core layer, with pendant organic groups attached to this core and extending perpendicular to the plane of the layer. The pendant and polar groups of zirconium phosphonates are distributed uniformly between each pair of Zr atom planes and the interlayer d-spacings are obeyed the bulkiness of alkyl groups. The composite zirconium phosphonates show higher catalytic activities for acid catalyzed reactions than that of the corresponding single zirconium phosphonate. After introduction of hydrophobic functions (alkyl groups), the composite zirconium phosphonates become accessible to any reactant molecules and exhibited improved hydrophobic properties.

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