

ZIRCONIUM PHOSPHONATES LAYERED STRUCTURE CATALYSTS WITH ORGANIC ACID PENDANTS

1. PREPARATION AND PHYSICAL PROPERTIES

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Abstract—Zirconium phosphonates layered structure (ZPLS) materials with various organic pendant groups have been synthesized. Their physical properties were investigated by means of SEM, BET, XRD, TGA/DTA and FT-IR. These properties, crystallinity in particular, depended strongly on preparation conditions and the nature of the pendant. In general, samples with a sulfonic acid pendant were not as crystalline as the carboxylic acid analogs. Crystalline samples exhibited a plate-like morphology as commonly observed for layered structure materials. Interlayer spacing of these materials was roughly proportional to the size of the pendant. In comparison with a conventional cation exchanged resin (Amberlyst 15), the layered structures with a sulfonic acid pendant showed similar IR characteristics, but much better thermal stability.

INTRODUCTION

Solid acid catalysts have conferred profound impacts on chemical industry and petroleum processing. Most famous are zeolites which were first synthesized by Union Carbide in 1959 [1]. With high activity and unique molecular sieving effects, zeolite catalysts have enjoyed wide industrial applications such as cracking, alkylation and isomerization. Applications of zeolite, however, are limited to reactions occurring at relatively high temperatures because their acidity is not high enough to promote reactions at low temperatures. Cation-exchanged polystyrene sulfonic acid resins are more suitable for low temperature applications [2]. However, they are not thermally stable above 150°C. A perfluorinated ion-exchange resin (Nafion) is a solid superacid, yet unstable above 190°C [3]. Hence, it has been desired to find a new solid acid catalyst usable at temperatures of 200-400°C.

Zirconium phosphonates layered structure (ZPLS) materials could be a candidate for the purpose [4-7]. These materials combine many of the properties of inorganic metal oxides with the organic functionality characteristic of the functionalized polymeric resins. Like acid resins, they can be modified with various

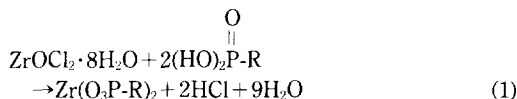
functional groups and yet are thermally more stable than the resins due to the inorganic backbones. Despite of substantial amount of work reported in the literature for these materials [4-7], there are only a few examples of zirconium phosphonates containing acid pendant groups [8-10]. This work is concerned with the synthesis and characterization of the materials especially with pendant sulfonic acid groups. The properties of these materials are compared with two related materials; a cation exchanged sulfonic acid resin (Amberlyst 15, Rohm and Haas) and α -zirconium phosphate (α -ZrP). A companion paper [11] deals with catalytic properties of these materials.

EXPERIMENTAL

1. Sample Preparation

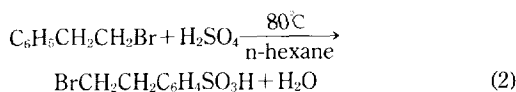
Synthesis of zirconium phosphonates is performed under reflux conditions in a 250 ml round bottom flask fitted with a Dean-Stark trap, reflux condenser, magnetic stirrer and a N₂ purge line. The reaction temperature was maintained by a heated silicon oil bath surrounding the reactor and a temperature controller. Typically, the reactions involve simple mathematical precipitation by Eq. (1) from aqueous solution containing a zirconium salt and an appropriate phosphonic acid at 100°C under N₂ purge [5,6].

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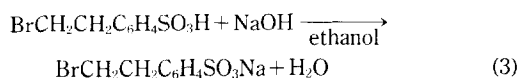


where R represents an organic radical. Zirconium phosphate (R=OH) (α -ZrP) was employed as a reference material and prepared by the same procedure. The precipitates formed very small particle white flocks immediately. However, the reflux was continued for 20 h for digestion of the products ("Ostwald ripening"). The products were washed three times with distilled water, acetone and ether, in the sequence, and then dried at 110°C for 4 h to obtain solid powders.

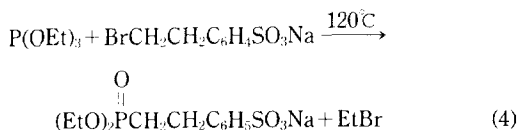
The sulfonic phosphonic acids, required precursors for the preparation of zirconium phosphonates with a sulfonic acid pendants, are not commercially available and hence were synthesized in this study. In the case of 2-sulfophenyl ethyl phosphonic acid, for example, was synthesized by the following sequence of reactions:



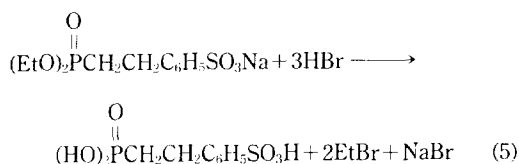
After 3 h of reflux, the bromosulfonic acid was extracted from the two phase mixture and then reacted in ethanolic NaOH.



The 2-sulfophenyl ethyl bromide sodium salt was obtained as white solids after filtration of the reaction product and drying. Phosphonation was carried out via an Arbusov reaction [12] with triethylphosphite in *N,N*-dimethyl formamide solvent.



The progress of the reaction could be monitored by measuring produced ethyl bromide in the Dean-Stark column. Acid hydrolysis with aqueous HBr yielded the desired precursor phosphonic acid.



The desired zirconium bis(2-sulfophenyl ethyl phosphonate) was prepared from this phosphonic acid in the same manner as in Eq. (1). In the case of zirconium bis(2-sulfophenyl propyl phosphonate), two samples were prepared under extreme conditions in order to control the crystallinity. In one case, the ripening step was omitted to obtain a highly noncrystalline sample. In the other case, the sample was prepared with HF added in the precipitation step and ripening continued for 48 h to increase the crystallinity of the product.

2. Sample Characterization

The prepared ZPLS materials were characterized by several physical methods. The powder X-ray diffraction (XRD) patterns were obtained with $\text{CuK}\alpha$ radiation on a Rigaku Dmax-B diffractometer. The reflections at low 2θ values denote the interlayer spacings d according to the Bragg equation $n\lambda = 2d \sin\theta$, where λ is the wavelength of X-ray radiation and θ is the Bragg angle. The specific surface areas were measured by the N_2 BET method on a Micromeritics Accusorb 2100E for samples evacuated at 200°C for 2 h. Thermogravimetric and differential thermal analysis (TGA/DTA) was performed on a Perkin-Elmer 1700 system at a heating rate of 0.33 Ks⁻¹ in flowing N_2 . The scanning electron micrographs (SEM) were obtained on Cambridge Stereoscan 250 Mk3. The infrared (IR) measurements were made with a Perkin-Elmer 1800 FT-IR spectrometer on self-supporting disk samples. The disks were prepared by compressing the powders of the ZPLS (3 wt%) and KBr under 6×10^3 kg cm⁻³. The reported spectra are averages of 16 scans with a spectral resolution of 4 cm⁻¹.

RESULTS

1. Texture and Structure

Table 1 compares the BET surface areas of prepared ZPLS. If prepared under the same precipitation

Table 1. Specific surface areas by the BET method

Material	Surface area m ² g ⁻¹
Zr(O ₃ POH) ₂	7.3
Zr(O ₃ PCH ₂ COOH) ₂	22.8
Zr(O ₃ PCH ₂ CH ₂ COOH) ₂	40.6
Zr(O ₃ PC ₆ H ₅) ₂	64.8
Zr(O ₃ PCH ₂ CH ₂ SO ₃ H) ₂	137.1
Zr(O ₃ PCH ₂ CH ₂ C ₆ H ₄ SO ₃ H) ₂	143.2
Zr(O ₃ PCH ₂ CH ₂ CH ₂ C ₆ H ₄ SO ₃ H) ₂	156.7
Zr(O ₃ PCH ₂ CH ₂ CH ₂ C ₆ H ₄ SO ₃ H) ₂ /HF	6.0

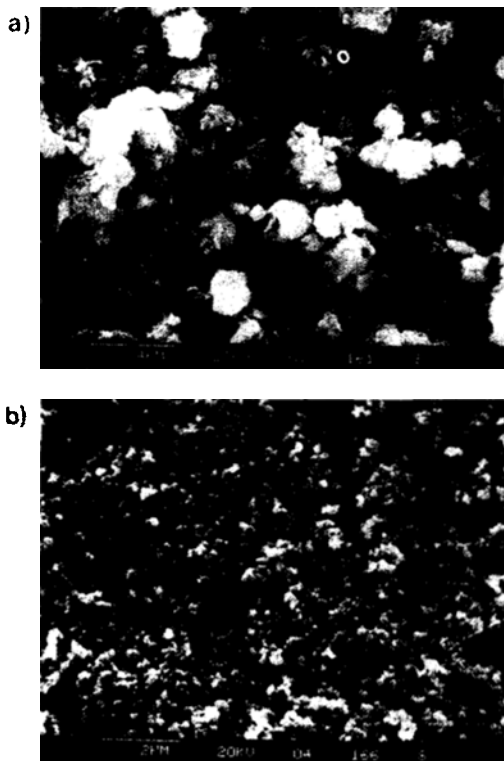


Fig. 1. Scanning electron micrographs of α -ZrP (a) and $Zr(O_3PCH_2CH_2COOH)_2$ (b).

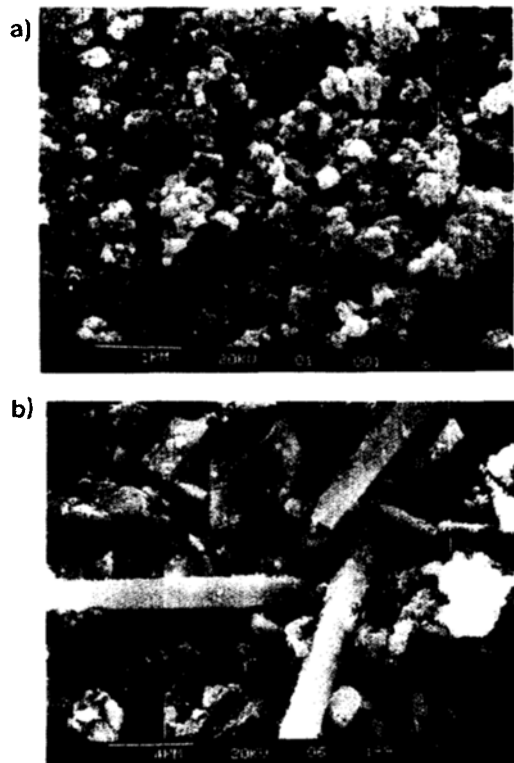


Fig. 2. Scanning electron micrographs of $Zr(O_3PCH_2CH_2CH_2C_6H_4SO_3H)_2$ (a) and $Zr(O_3PCH_2CH_2CH_2C_6H_4SO_3H)_2/HF$ (b).

conditions, the surface area increased as the size of the pendant group increased. The ZPLS containing sulfonic acid group showed particularly high surface areas. A dramatic effect was observed when 3 moles of HF per mole of Zr^{4+} were added to the solution of precipitation reaction [Eq. (1)]. The resulting product denoted as $Zr(O_3PCH_2CH_2CH_2C_6H_4SO_3H)_2/HF$ showed a BET area of only $6 \text{ m}^2 \text{ g}^{-1}$ compared to $157 \text{ m}^2 \text{ g}^{-1}$ without HF. This role of HF has been known as a sequesterant to inhibit release of free Zr^{4+} to solution and enhance the crystallinity and particle size [13].

The morphology of ZPLS was observed by SEM. Representative micrographs are shown in Figs. 1 and 2. The α -ZrP (Fig. 1a) appeared as grainy chunks where individual particles or their aggregates were hardly seen. The carboxylic acid and phenyl ZPLS indicated distinct aggregates of particles as shown typically in Fig. 1b for $Zr(O_3PCH_2CH_2COOH)_2$. The sulfonic acid ZPLS (Fig. 2a) showed again the grainy chunks like α -ZrP, yet in much reduced sizes. However, if the same material was ripened for extended period with HF, large crystals of ZPLS were formed as shown

in Fig. 2b. The crystals assumed a plate-like morphology with approximate sizes of $0.5 \mu\text{m} \times 2 \mu\text{m} \times 10 \mu\text{m}$. This is the morphology commonly observed for layered structure materials. Since only a weak van der Waals force connects each layer, this is the direction that a crystal is most easily cleaved.

Powder XRD has been proved to be one of the most useful techniques in the characterization of layered structure materials. The sharpness of the reflections represents the crystallinity and a reflection at a low 2θ value gives interlayer spacing by the Bragg equation. The XRD pattern of α -ZrP in Fig. 3a is in agreement with reported XRD patterns for the material [14]. The first three peaks could be assigned to be (002), (110), and (112) reflections of $P2_1/n$ symmetry. Other expected reflections of (202) and (604) appears to be unresolved with (110) and (112) reflections, respectively. From the angle of (002) reflection, an interlayer spacing of 7.6 \AA was calculated. This value is also in agreement with the reported value [14].

Figures 3b-d shows XRD patterns for carboxylic acid and phenyl ZPLS. These materials appeared in

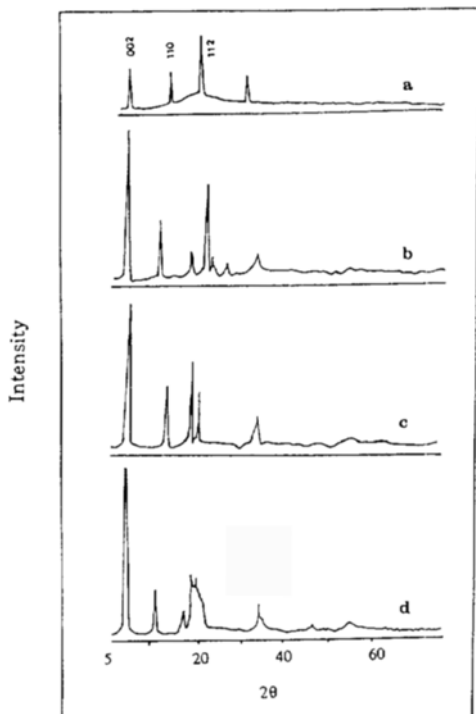


Fig. 3. Powder XRD patterns of α -ZrP (a), $Zr(O_3PCH_2COOH)_2$ (b), $Zr(O_3PCH_2COOH)_2$ (c), and $Zr(O_3PC_6H_5)_2$ (d).

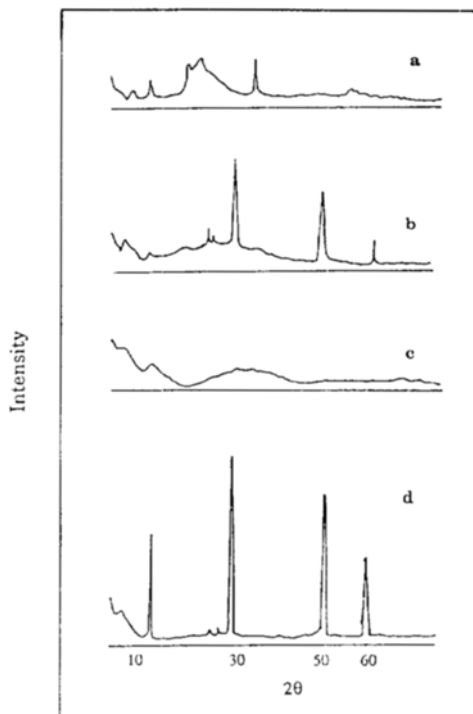


Fig. 4. Powder XRD patterns of $Zr(O_3PCH_2CH_2SO_3H)_2$ (a), $Zr(O_3PCH_2CH_2C_6H_4SO_3H)_2$ (b), $Zr(O_3PCH_2CH_2C_6H_4SO_3H)_2$ (c) and $Zr(O_3PCH_2CH_2CH_2C_6H_4SO_3H)_2/HF$ (d).

good crystalline forms as indicated by sharp XRD peaks. This is also consistent with observations made by SEM. The (002) reflections were the strongest indicating the formation of well-defined layered structures. From these angles, interlayer spacings of 11.4, 12.4, and 14.7 were calculated, which again agreed with reported values [5]. All the XRD patterns of these materials were very similar to each other and to α -ZrP, indicating similar two dimensional structure of each layers.

The XRD patterns of sulfonic acid ZPLS shown in Fig. 4 are much more diffuse, indicating lower crystallinity than those for carboxylic or phenyl counterparts. Low angle reflections, in particular, appeared only as broad shoulders in decreasing backgrounds. Hence, it was difficult to determine the interlayer spacings. Interestingly, the $Zr(O_3PCH_2CH_2CH_2C_6H_4SO_3H)_2/HF$ prepared by an extended ripening with HF in the solution showed significantly enhanced crystallinity on all the reflections other than the low angle reflection. From the positions of these shoulders, the interlayer spacings were calculated anyway and the results were plotted for all the samples in Fig. 5. The x-axis is an arbitrary placement of all the ZPLS prepared in

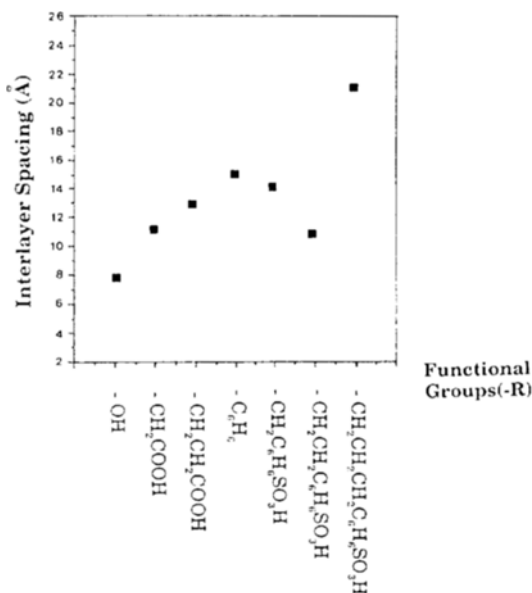


Fig. 5. Dependence of interlayer spacings of ZPLS, $Zr(O_3-P-R)_2$, on their pendant functional groups R.

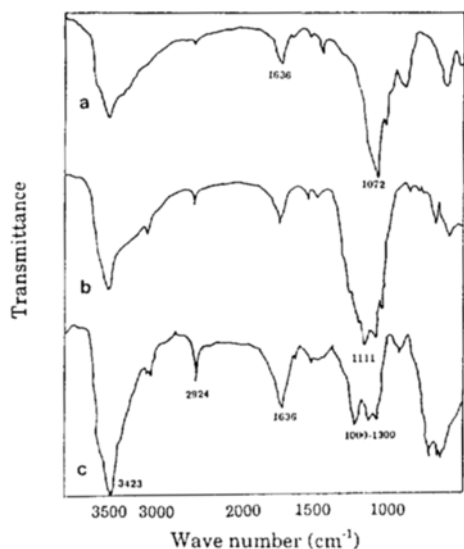


Fig. 6. Infrared spectra of α -ZrP (a), $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H})_2$ (b), and Amberlyst-15 (c).

this study according to the size of their pendant group R. Hence, the absolute scale of x-axis has no meaning here. The plot generally shows that the interlayer spacing increases with increasing size of R. As expected, the deviation from the trend in the plot comes for sulfonic acid ZPLS because of the difficulty involved in the determination of correct positions of low angle reflections for these samples.

2. IR and Thermal Stability

Figure 6 shows a typical IR spectrum of ZPLS in comparison with those of α -ZrP and Amberlyst 15. The assignment of the IR absorption bands for α -ZrP (Fig. 6a) is well documented [15]. Bands in the region $965\text{--}1120\text{ cm}^{-1}$ represent phosphate vibrations of symmetry group C_{3v} (asymmetric and symmetric stretch) while those at $375\text{--}600\text{ cm}^{-1}$ represent the various bending modes. The broad bands at $3400\text{--}3550\text{ cm}^{-1}$ are assigned to the asymmetric and symmetric water stretching while the one at 1636 cm^{-1} is the bending vibration. Another reference sample Amberlyst 15 (Fig. 6c) showed a number of bands at $1000\text{--}1200\text{ cm}^{-1}$ due to $-\text{SO}_3\text{H}$ group. Bands $2800\text{--}3000\text{ cm}^{-1}$ represent stretching and bending vibrations of alkanes. Intensity of the band at 1636 cm^{-1} increased probably due to the contribution from vibration of benzene rings in the polystyrene-based resin.

All the sulfonic acid ZPLS showed similar IR spectra. The IR spectrum of $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H})_2$ is shown in Fig. 6b as an example. Because of the overlap of the spectral regions for phosphate and sul-

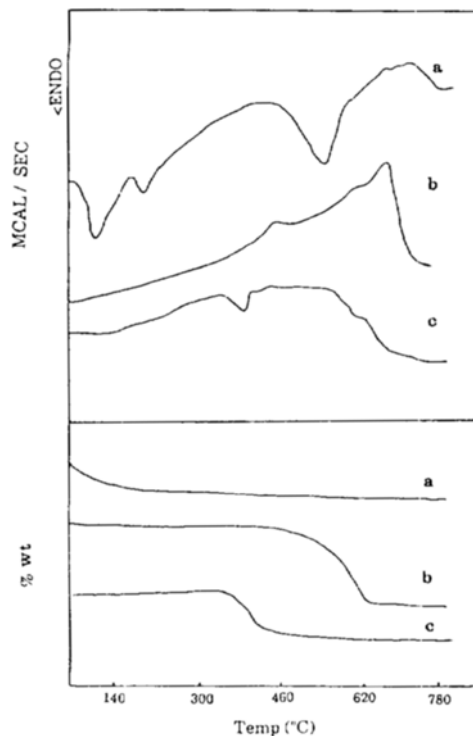


Fig. 7. DTA (top) and TGA (bottom) of α -ZrP (a), $\text{Zr}(\text{O}_3\text{PCH}_2\text{COOH})_2$ (b), and $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H})_2$ (c).

monic acid groups, the bands at $950\text{--}1300\text{ cm}^{-1}$ were complicated. However, it was evident that the IR spectrum of ZPLS contained spectral features of both α -ZrP and Amberlyst 15. The results are consistent with the expected structure of ZPLS in which aryl sulfonic acid groups are attached to inorganic layers of zirconium phosphate.

The thermal stability of ZPLS was investigated by TGA/DTA. As shown in Fig. 7a, DTA curve for α -ZrP showed three endotherms. The first two around 150°C and 230°C are known to be due to phase transitions of α -ZrP to ζ -ZrP and then to η -ZrP, respectively [16]. Removal of hydrated water also takes place as evidenced by the weight loss. The endotherm around 450°C is attributed to another water loss as a result of condensation of monohydrogen phosphate groups to form pyrophosphate [16]. The carboxylic acid ZPLS, $\text{Zr}(\text{O}_3\text{PCH}_2\text{COOH})_2$, showed no change up to 500°C , above which the decomposition of organic pendant appeared to take place. The weight loss of sulfonic acid ZPLS, $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H})_2$, started around 420°C . The thermal behavior of another ZPLS, $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H})_2$, was compared with Amberlyst 15 in Fig.

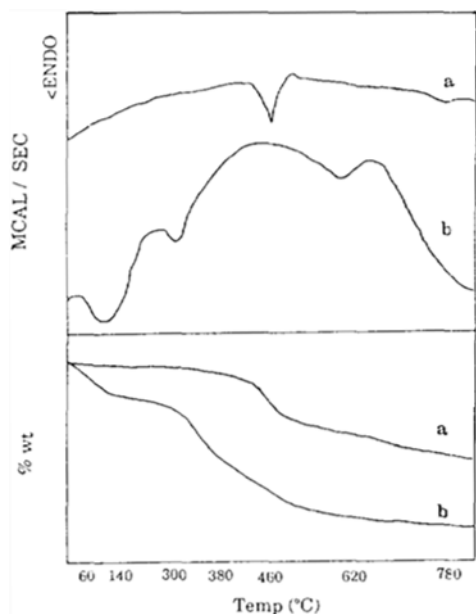


Fig. 8. DTA (top) and TGA (bottom) of $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}_2\text{-CH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H})_2$ (a), and Amberlyst-15 (b).

8. Again, the ZPLS showed weight loss from 420°C while Amberlyst 15 did so from 150°C . All ZPLS materials showed significantly better thermal stability than Amberlyst 15.

DISCUSSION

Zirconium phosphonate layered structures (ZPLS) with organic functional group as pendant have been developed by Alberti et al. [4] and Dines et al. [5, 6], and recently by Clearfield [7]. Despite the substantial amount of work reported in the literature for these materials, there are only a few studies on ZPLS with acid pendant groups and their applications as an ion exchanger or a solid acid catalyst [8-10]. In particular, sulfonic acid ZPLS could serve as an inorganic analog for sulfonic acid ion-exchange polystyrene resins which are widely employed as industrial cation exchangers and acid catalysts. In the present study, we attempted to prepare and characterize sulfonic acid ZPLS. For comparison, we also prepared some other ZPLS including carboxylic acid analogs.

The α -zirconium bis (monohydrogen orthophosphate), $\text{Zr}(\text{O}_3\text{POH})_2 \cdot \text{H}_2\text{O}$, commonly called α -ZrP, forms the structural basis for ZPLS in general. As schematically shown in Fig. 9, the materials assume a two-dimensional layered structure with an octahedral coordination of oxygen around zirconium ion and a tetra-

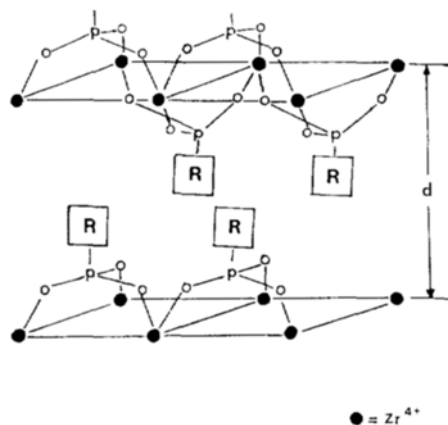


Fig. 9. A schematic representation of ZPLS, $\text{Zr}(\text{O}_3\text{P-R})_2$ with pendant functional groups R.

hedral coordination around phosphorus. Each Zr is connected to a neighboring Zr through an O-P-O linkage and the P is connected to three Zr ions via three oxide linkages with the remaining bond projected perpendicular to the planar inorganic Zr-O-P polymer sheet. On this last P bond, an organic pendant R is attached for ZPLS and -OH for α -ZrP. The ordered stacking of these layers occurs with a fixed interlayer spacing and is responsible for the characteristic low angle XRD reflections. Only van der Waals force is operating between these layers. The lateral spacing within the layer between adjacent P groups in their hexagonal array is 5.3\AA . These leads to an area per site of 24\AA^2 , which represents a cross-sectional limit for pendants. Furthermore, this provides high site densities comparable to those of ion-exchange sulfonic acid resins.

Carboxylic acid ZPLS, phenyl ZPLS, and α -ZrP synthesized here all behaved as expected for a layered structure material. Thus powder XRD patterns exhibited a prominent series of low angle reflections indicating the presence of well-defined layers. The interlayer spacings calculated from the reflections were consistent with the value expected from the size of the pendant groups. The ideal behavior of these ZPLS is expected because the cross-sectional areas of their pendant groups are less than 24\AA^2 and thus pendants fit nicely into the space allotted for each site by the inorganic Zr-O-P sheets. However, alkyl sulfonic acid groups will essentially fill the whole area and even more severe crowding exists for aryl sulfonic acid ZPLS. The excess size of the pendant group will strain the limits of the stability of these ZPLS. Hence, if prepared under the similar conditions, sulfonic acid ZPLS

are much less crystalline than carboxylic acid counterparts as evidenced by diffuse XRD patterns and SEM images.

Since XRD patterns of sulfonic acid ZPLS do not show clear low-angle reflections corresponding to the interlayer spacing, a question arises if the layered structure with a sulfonic acid pendant was really formed. The IR spectrum indicated the presence of both phosphate group and $-\text{SO}_3\text{H}$. The definitive presence of $-\text{SO}_3\text{H}$ group is also demonstrated by the titration of the acid with aqueous NaOH as discussed in the companion paper [11]. The TGA/DTA behavior of our samples is similar to that of sulfonic acid ZPLS prepared by sulfonation of zirconium phenyl phosphonate [9, 10]. Finally, the crystalline $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4-\text{SO}_3\text{H})/\text{HF}$ showed a well-developed platelet morphology commonly observed for layered structure materials. Taken all these results together, it is believed that layered structures were indeed formed with sulfonic acid pendants. Despite highly diffuse low angle reflections, other XRD reflections of sulfonic acid ZPLS could be strong as shown in Fig. 5. Hence, it appears that well-defined two-dimensional backbones exist in these materials although there is a lack of registry perpendicular to the Zr-O-P sheets.

In order for ZPLS to be used as solid acid catalysts, several attributes should be considered. High density of acid sites discussed above is originated from their structure. Acid strength of sulfonic acid ZPLS should be higher than carboxylic acid analogs and comparable to that of sulfonic acid resins. Specific surface area should be an important consideration. However, meaning for the BET area is not simple for ZPLS. The key question is whether N_2 molecules could intercalate into the interlayer space. As calculated by Dines and Griffith [6], a hypothetical single extended layer, which is accessible for N_2 coverage on both basal surfaces, gives a surface area of $1000 \text{ m}^2 \text{ g}^{-1}$. In the other extreme, micron-sized crystallites with an aspect ratio of 10 will have external surface area of *ca.* $0.1 \text{ m}^2 \text{ g}^{-1}$. The values of surface area listed in Table 1 indicate that our samples belong to neither of these extreme cases. The micron-sized crystallites seen by SEM may be agglomerates of smaller crystallites with size of 10-100 nm, or only a part of interlayer space may contribute. Probably, both effects may be important. Apparent dependence of the surface area on the crystallinity reflects the first effects.

As mentioned, one of the motivation in the study of ZPLS is their thermal stability in comparison with polystyrene-based sulfonic acid resins. This is expected

because ZPLS contain inorganic Zr-O-P layers which should be thermally more stable than all-organic resins. Indeed, as shown in Figs. 7 and 8, ZPLS exhibited excellent thermal stability. Generally, it seems that carboxylic acid ZPLS survive to higher temperatures than sulfonic acid ZPLS. Still, the latter decomposes at temperatures at least 200°C higher than for Amberlyst 15.

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