

## ZIRCONIUM PHOSPHONATES LAYERED STRUCTURE CATALYSTS WITH ORGANIC ACID PENDANTS 2. CATALYTIC PROPERTIES

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**Abstract**—Catalytic properties of Zirconium phosphonates layered structure (ZPLS) catalysts with organic sulfonic acid pendant groups have been studied. The NaOH titration demonstrated the presence of sulfonic acid groups. The ZPLS contained acid sites per weight similar to or slightly less than those for cation exchanged resins. The hydrolysis of ethyl acetate and the esterification of acetic acid with ethanol were studied as test reactions. Accessibility of the reactants to the acid sites present in the interlayer spacing of ZPLS was a determining factor for the activity. Thus the activity depended on the ease of swelling and particle size of the ZPLS.

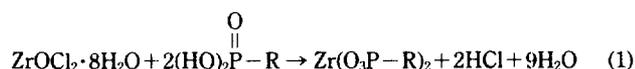
*Key words:* Zirconium Phosphonates Layered Structure, Organic Acid Pendants, NaOH Titration, Acid Catalysis, Hydrolysis, Esterification

### INTRODUCTION

Zirconium phosphonates layered structure (ZPLS) materials combine many of the properties of inorganic metal oxides with the organic functionality characteristic of the functionalized polymeric resins [Alberti et al., 1978; DiGiacomo and Dines, 1982; Dines and DiGiacomo, 1980; Dines and Griffith, 1982; King et al., 1991; Wan et al., 1986; Yang and Clearfield, 1987]. 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. Our previous work [Nam et al. 1993] was concerned with the synthesis and characterization of the materials especially with pendant sulfonic acid groups. The properties of these materials were compared with two related materials; a cation exchanged sulfonic acid resins and  $\alpha$ -zirconium phosphate. This paper reports catalytic properties of these materials. The quantity of acid sites contained in the catalysts was measured by the titration with aqueous NaOH. The hydrolysis of ethyl acetate and the esterification of acetic acid with ethanol were studied as test reactions.

### EXPERIMENTAL

Detailed procedure for the synthesis of zirconium phosphonates has been described in the previous paper [Nam et al., 1993]. Typically, the reactions involve simple precipitation by Eq. (1) from aqueous solution containing a zirconium salt and an appropriate phosphonic acid at 100°C under N<sub>2</sub> purge.



The precipitates of the reaction (1) 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. In this way, three types of zirconium phosphonates were obtained with R = CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>, and CH<sub>2</sub>CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>. 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. Ion exchange resins, Amberlyst 15 and Amberlite IR-120 were purchased from Rohm and Hass.

The prepared ZPLS materials were characterized by powder X-ray diffraction (XRD), specific surface area measurements by the N<sub>2</sub> BET method, thermogravimetric and differential thermal analysis (TGA/DTA), the scanning electron micrographs (SEM) and infrared (IR) measurements [Nam et al., 1993]. For NaOH titration, 0.05 g of a sample is dispersed in 125 ml distilled water. The suspension, while stirring, was titrated with a 0.1 N NaOH solution and a pH meter.

Catalytic reactions were performed under reflux conditions in a 50 ml round bottom flask equipped with a magnetic stirrer and a hot plate. Reaction mixture was sampled during the reaction and analyzed with a gas chromatograph (HP 5890). For the esterification, 0.1 mol of acetic acid (99.7%, Aldrich) and 1 mol of ethanol (99.9%, James Burrough) were reacted at 120°C. For hydrolysis, 0.1 mol of ethyl acetate (99.9%, Aldrich) and 1 mol of water were reacted at 110°C.

### RESULTS AND DISCUSSION

A list of catalysts employed in the present study and their characteristics are summarized in Table 1. All the catalysts except for zirconium bis(2-sulfophenyl propyl phosphonate) treated with HF [denoted as Zr(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H)<sub>2</sub>/HF hereafter] were highly amorphous with surface areas close to 140 m<sup>2</sup>g<sup>-1</sup>. In contrast, Zr(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H)<sub>2</sub>/HF showed a high crystalli-

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**Table 1. Characteristics of catalysts**

Catalyst	Surface area/m <sup>2</sup> g <sup>-1</sup>	Acid site density <sup>a</sup> /meq g <sup>-1</sup>
Zr(O <sub>3</sub> PCH <sub>2</sub> CH <sub>2</sub> SO <sub>3</sub> H) <sub>2</sub>	137.1	4.3
Zr(O <sub>3</sub> PCH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> H) <sub>2</sub>	143.2	3.2
Zr(O <sub>3</sub> PCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> H) <sub>2</sub>	156.7	3.1
Zr(O <sub>3</sub> PCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> H) <sub>2</sub> /HF	6.0	3.1
Amberlyst 15	54.8	4.8
Amberlite IR-120	<0.1	4.6

<sup>a</sup>The values for ZPLS were calculated from molecular formulas. The values for resins were supplied by the manufacture.

nity as evidenced by enhanced XRD intensity [Nam et al., 1993] and a BET surface area of 6 m<sup>2</sup>g<sup>-1</sup>. Amberlyst 15 is a so-called 'macroporous' type polystyrene sulfonic acid resin partially cross-linked with divinylbenzene. It has the pores, most of which are greater than 6 nm in diameter. On the other hand, Amberlite IR-120 is a gel-type and nonporous.

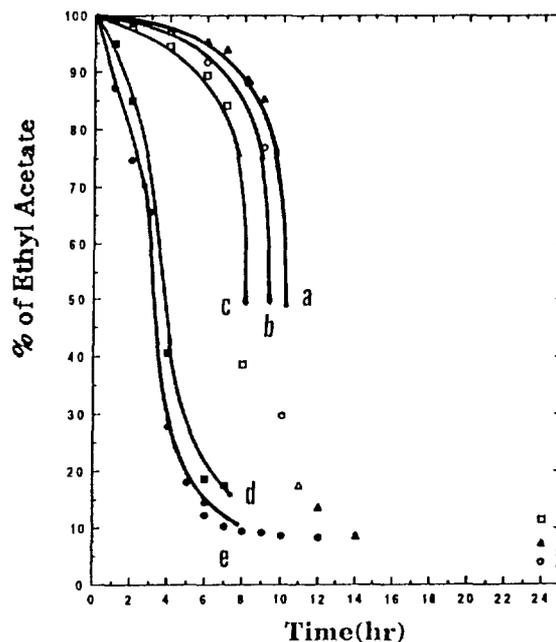
The theoretical densities of acid sites in Table 1 were calculated for ZPLS from their molecular formulas. The data for resins were provided by the manufacture. In the NaOH titration, the pH value shows a jump if all acid sites are titrated by NaOH. Amberlyst-15 shows a typical titration curve with a S-shape. From the accumulated amount of NaOH used up to the jump, the amount of acid in the sample was calculated to be 4.82 meq g<sup>-1</sup>. This is the same value as the one provided by the manufacturer (Table 1). The curve for Zr(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H)<sub>2</sub>/HF shows a different shape. It appears to have two S-curves. The amount of acid calculated from the upper curve with bigger pH jump was 9.01 meq g<sup>-1</sup>. The titration curves for other ZPLS were very complex. However, it was evident that the acid site densities in these catalysts were similar to or less than the value for Amberlyst 15. This is in agreement with the predictions in Table 1. However, the measured value for Zr(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H)<sub>2</sub>/HF was greater by a factor of 3 than the predicted value.

The NaOH titration indicates the presence of a strong Brønsted acid sites. Thus it demonstrates the definitive presence of sulfonic acid group as discussed previously [Nam et al., 1993]. The abnormally high value for Zr(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H)<sub>2</sub>/HF must be due to the presence of HF used during the preparation step. Complex shapes of titration curves are most likely due to two reasons: accessibility of sulfonic acid groups between the layers and hydrolysis of ZPLS during titration [DiGiacomo and Dines, 1982]. The magnitude of the latter correlated with the relative crystallinity of the product. In the more crystalline sample, the hydrolysis is less pronounced than in the less crystalline material. Because of these complications, the NaOH titration does not provide the definite number of acid sites in the sample. Yet, a rough value or the range of the values is still very useful. According to the titration, ZPLS employed in this study contain the amounts of acid sites close to the theoretical values. The values per weight are slightly less than those for cation exchange resins.

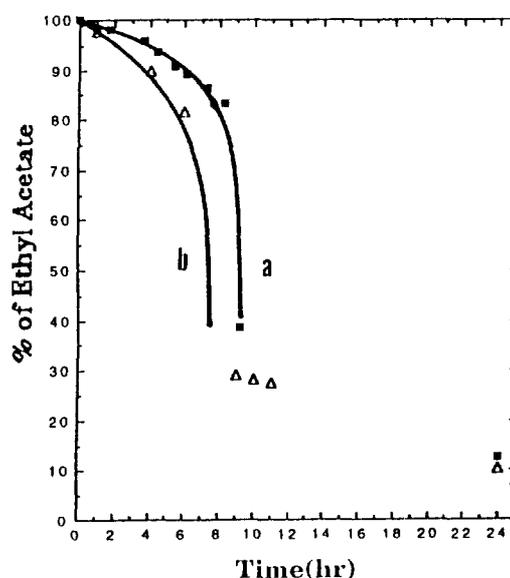
Two typical acid-catalyzed reactions were employed as test reactions.



Since both are equilibrium limited reactions, one reactant (water for reaction 2 and ethanol for reaction 3) was employed in excess.



**Fig. 1. Hydrolysis of ethyl acetate at 110°C with 0.1 mol ethyl acetate and 1 mol water: Zr(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>H)<sub>2</sub> (a), Zr(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H)<sub>2</sub> (b), Zr(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H)<sub>2</sub> (c), Amberlyst-15 (d), and Amberlite IR-120 (e).**



**Fig. 2. Effect of pre-swelling of Zr(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H)<sub>2</sub> before reaction on the hydrolysis of ethyl acetate at 110°C with 0.1 mol ethyl acetate and 1 mol water: (a) without pre-swelling, (b) with pre-swelling at room temperature in water for 10 h.**

The reactions were performed in a batch mode.

Fig. 1 shows change in ethyl acetate concentration with time. If the reaction is controlled solely by reaction kinetics, the curve should show exponential (positive orders) or linear (zeroth order) decrease depending on the reaction orders with respect to ethyl acetate. However, all the curves in Fig. 1, for ZPLS in particular, are of convex shape. This indicates that the reaction is initially hindered by some process. This limitation is relieved once the

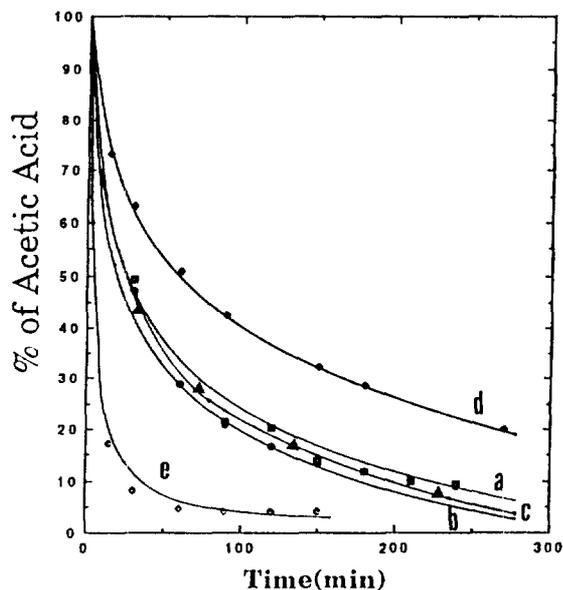


Fig. 3. Esterification of acetic acid at 120°C with 0.1 mol acetic acid and 1 mol ethanol:  $Zr(O_3PCH_2CH_2SO_3H)_2$  (a),  $Zr(O_3PCH_2CH_2C_6H_4SO_3H)_2$  (b),  $Zr(O_3PCH_2CH_2CH_2C_6H_4SO_3H)_2$  (c),  $Zr(O_3PCH_2CH_2CH_2C_6H_4SO_3H)_2/HF$  (d), and Amberlyst 15 (e).

catalysts are swelled and reaction rate are accelerated after some time. Since resins are based on an organic polymer, they swell more rapidly than ZPLS which are based on inorganic zirconium layers. The fact that the two resins with greatly different surface areas show similar activity also indicates that the reaction takes place in a swelled phase. In order to see this swelling effect,  $Zr(O_3PCH_2CH_2CH_2C_6H_4SO_3H)_2$  was swelled in water at room temperature for 10 h. This pre-swelling improved the activity significantly as shown in Fig. 2.

The results of esterification are shown in Fig. 3. In this case, there is no delay in reaction and all catalysts show exponential decrease in acetic acid concentration. It is believed that the reactants used in this reaction ( $CH_3COOH/C_2H_5OH$ ) are more effective than  $CH_3COOC_2H_5/H_2O$  in swelling the ZPLS. Yet, the reactivity of ZPLS still appears to be influenced by mass transfer limitation because  $Zr(O_3PCH_2CH_2CH_2C_6H_4SO_3H)_2$  and  $Zr(O_3PCH_2CH_2CH_2C_6H_4SO_3H)_2/HF$  with the same chemical composition and different crystallinity show substantial difference in activity. The latter with higher crystallinity and large particle size showed lower

activity. For this ZPLS with large particle size, diffusion path of reactants to reach acid sites in the interlayer spacing must be longer.

In conclusion, the NaOH titration confirmed the presence of sulfonic acid pendant in ZPLS although its concentration was difficult to determine because of limited accessibility to the sites and hydrolysis of metal phosphonates. They had similar or less acid site densities than those for cation exchange resins. All ZPLS were active catalysts for hydrolysis and esterification reactions. However, accessibility of the reactants to the acid sites present in the interlayer spacing of ZPLS was a determining factor for the activity. Thus the activity depended on the ease of swelling and particle size of the ZPLS.

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