JOURNAL OF SOLID STATE CHEMISTRY 107, 497–502 (1993)

Synthesis and Structural Analysis of Pure and Mixed Zirconium Phosphonates, $Zr(O_3PR)_x(O_3PR')_{2-x}$

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Received January 19, 1993; accepted April 20, 1993

Several zirconium phosphonates, $Zr(O_3PR)_2$ (R = $(CH_2)_3COOH$, $CH_2C_6H_5$, $(CH_2)_2Cl$, $CH{=}CH_2$, $(CH_2)_2CH{=}CH_2$), containing reactive functional groups were synthesized and structurally characterized. There were found to be nonreactive toward incorporation of small molecules and ions from solution. In an effort to synthesize microporous phosphonates, mixed phosphonates of composition $Zr(O_3PCH_2C_6H_5)_x(O_3PCH_3)_{2-x}$ and $Zr(O_3P(CH_2)_3COOH)_x(O_3POH)_{2-x}$ were prepared, varying x from 0 to 2. The interlayer spacings of the benzyl/methyl derivatives indicated a random distribution of the alkyl moieties throughout the interlayer galleries, resulting in relatively porous materials. The observed interlayer spacings of the 3-carboxypropyl/hydroxyl materials indicated products in which the alkyl groups were segregated, resulting in less porosity. A structural model for porous and nonporous materials is discussed.

Introduction

Due to its layered structure and ion exchange capability (*1*), α-zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP), has proven to be a versatile solid host compound (*2*). α-ZrP can mimic reactions of zeolites and other microporous solids, with the advantage of expandable pore size, in one dimension, due to weak interlayer interactions (*3*). Like many zeolite systems, the zirconium phosphate framework is relatively resistant to chemical attack and maintains its lamellar structure to temperatures in excess of 300°C (*4*).

More recently, interest in layered phosphonates, such as $Zr(O_3PR)_2 \cdot xH_2O$ (R = OC_2H_5, CH_2CHCH_2, C_6H_5, etc.), has risen due to their microporous nature (*5, 6*). While such phosphonates generally lack ion-exchange properties, the solids can be synthesized using a wide variety of organic pendant groups and porous products can result by coprecipitating solids from reaction mixtures containing combinations of two or more organophosphonic acids which are mismatched in size (*7, 8*). This synthetic aspect can potentially be exploited to tailor the pore dimensions of the resulting materials in an effort to design new heterogeneous catalysts, separation materials, and molecular sieves (*9, 10*).

Of interest in the study of the mixed phosphonates is the arrangement of the organic groups in the solid. In order to achieve a material of significant porosity, the mismatched pendant groups must arrange themselves in a random fashion throughout the microcrystals (Fig. 1a). If the mismatched groups tend to segregate into a "staged" structure (Fig. 1b), then the resulting solid is expected to have properties closer to those of a physical mixture of two pure organophosphonates.

Once a combination of organic substituents is found which produces a porous solid, then the average dimensions of the pores parallel to the zirconium layers can be ad-

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0022-4596/93 $5.00

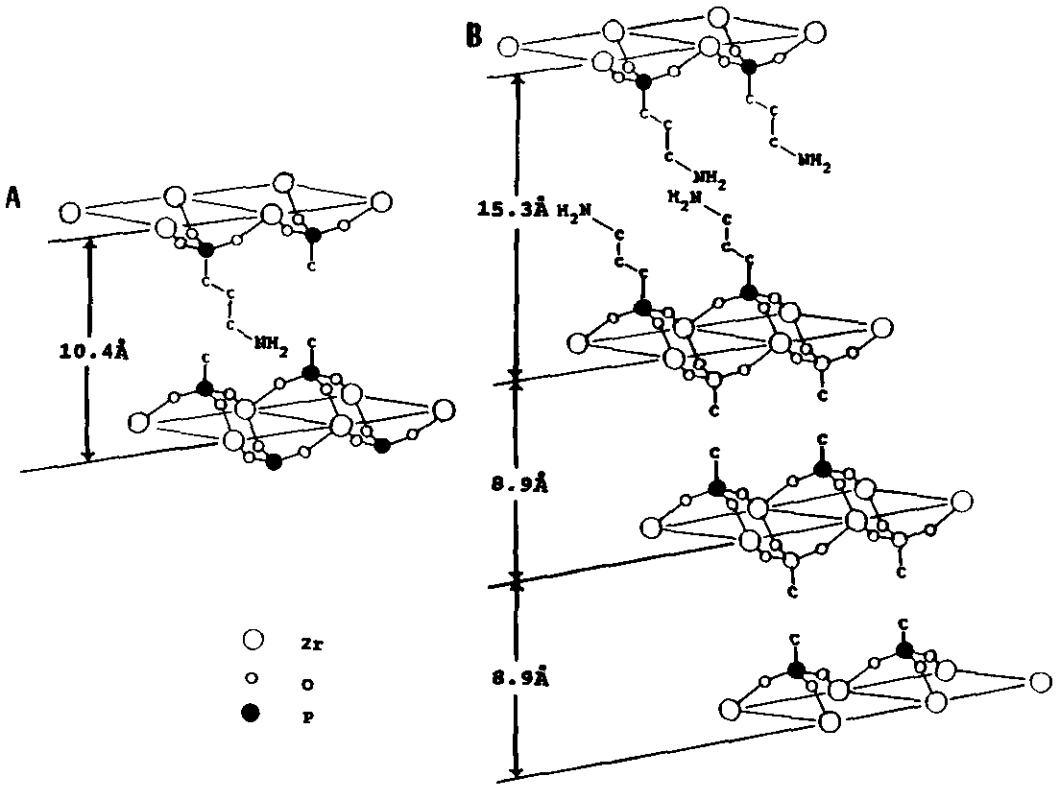

FIG. 1. (A) Gross structure of a mixed phosphonate with organic groups arranged randomly in the interlayer galleries. (B) Gross structure of a mixed phosphonate with a staged structure, showing segregation of similar organic groups.

justed by adjusting the stoichiometry of the coprecipitated solid. The perpendicular dimension depends on the degree of size mismatch between the pendant organic groups (Fig. 2). With this synthetic strategy, families of materials with high internal surface areas and tunable pore sizes are possible.

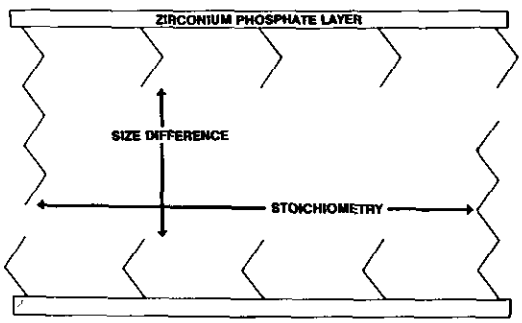

FIG. 2. Schematic diagram showing the relationship of organic group size mismatch and stoichiometry to pore dimensions in mixed phosphonates.

In this work, we report the synthesis of a variety of new pure and mixed zirconium phosphonates and the examination of their gross structures. We are particularly interested in these parameters for their impact upon potential exploitation of these solids as hosts for ions and neutral species from solution, and thus as a new generation of catalysts and catalytic support materials.

Experimental

Synthesis

Zirconium benzylphosphonate, Zr(O$_3$*PCH*$_2$*C*$_6$*H*$_5$*)*$_2$ *(ZrP(bz)*$_2$*)*. Benzylphosphonic acid anilinium salt (11), 0.174 g (0.66 mmol), was dissolved in 4 ml of water. To this solu-

tion, a solution of 0.106 g (0.33 mmol) $ZrOCl_2 \cdot 8H_2O$ (Aldrich) in 1.0 ml water was added dropwise with constant stirring at 20°C. Following formation of a colorless gel, 2.4 ml of 0.55 *M* HF solution was added and the resulting suspension was refluxed for 36 hr under N_2. The solid product was gravity filtered, washed with water, acetone, and diethyl ether, then air dried.

Zirconium 2-chloroethylphosphonate, $Zr(O_3PCH_2CH_2Cl)_2$. 2-Chloroethylphosphonic acid (Aldrich), 0.20 g (1.4 mmol), was dissolved in 1.0 ml water. To this solution, a solution of 0.214 g (0.66 mmol) $ZrOCl_2 \cdot 8H_2O$ in 1.0 ml water was added dropwise with constant stirring. The colorless gel was diluted with 10 ml of water, then 2.6 ml of 0.55 *M* HF solution was added, and the resulting suspension was refluxed for 20 hr. The solid product was filtered, washed, and dried as above.

Zirconium vinylphosphonate, $Zr(O_3PCHCH_2)_2$. Vinylphosphonic acid anilinium salt (*11*), 0.18 g (0.89 mmol), was dissolved in 2 ml water. To this solution, a solution of 0.15 g (0.46 mmol) $ZrOCl_2 \cdot 8H_2O$ in 1.0 ml water was added dropwise with constant stirring. The colorless gel was diluted with 2 ml water, then 3.4 ml of 0.55 *M* HF solution was added and the resulting suspension was refluxed for 18 hr. The solid product was filtered, washed, and dried as above.

Zirconium 3-butenylphosphonate, $Zr(O_3P(CH_2)_2CHCH_2)_2$. 3-butenylphosphonic acid anilinium salt (*11*), 0.172 g (0.75 mmol), was dissolved in 4.4 ml water. To this solution, a solution of 0.12 g (0.37 mmol) $ZrOCl_2 \cdot 8H_2O$ in 2 ml water was added dropwise and with constant stirring. Following formation of a colorless gel, 0.7 ml of 2 *M* HF solution was added and the resulting suspension was refluxed for 4 days under N_2. The solid product was filtered, washed, and dried as above.

Zirconium 3-carboxypropylphosphonate, $Zr(O_3P(CH_2)_3COOH)_2$ ($ZrP(bt)_2$) (12), zirconium methylphosphonate, $Zr(O_3PCH_3)_2$ ($ZrP(Me)_2$) (13), and α-zirconium phosphate, $Zr(O_3POH)_2$ (14). These compounds were synthesized by previously published methods.

The stoichiometries reported below are derived from the compositions of the reaction mixtures. Results of elemental analyses are roughly consistent with the reported stoichiometries, but precise and reproducible (±1%) analyses are not available due to sample inhomogeneity and difficulties in digesting and analyzing solid phosphonates.

Zirconium benzylphosphonate methylphosphonate, $Zr(O_3PCH_2C_6H_5)_x(O_3PCH_3)_{2-x}$ ($ZrP(bz)_x(Me)_{2-x}$). For $x = 0.25$, 0.076 g (0.79 mmol) methylphosphonic acid (Aldrich) and 0.030 g (0.11 mmol) benzylphosphonic acid anilinium salt were dissolved in 3 ml water. To this solution, a solution of 0.146 g $ZrOCl_2 \cdot 8H_2O$ in 2 ml water was added dropwise and with constant stirring. Following formation of a colorless gel, 0.9 ml of 2 *M* HF solution was added and the resulting suspension was refluxed for 4 days under N_2. The solid product was filtered, washed, and dried as above. Solid solutions were also prepared with $x = 0.50$, 1.0, and 1.5. For the phase with $x = 0.50$, calculated values for $C_5H_8O_6P_2Zr$ were C, 18.9; H, 2.5: Found values were C, 15.7; H, 2.1. For the phase with $x = 1.5$, calculated values for $C_{11}H_{12}O_6P_2Zr$ were C, 33.5; H, 3.1: Found values were C, 32.5; H, 2.8.

Zirconium 3-carboxypropylphosphonate phosphate, $Zr(O_3P(CH_2)_3COOH)_x(O_3POH)_{2-x}$ ($ZrP(bt)_x(OH)_{2-x}$). For $x = 0.75$, 0.070 g (0.42 mmol) of 4-phosphonobutyric acid (Lancaster) was dissolved in 1.4 ml of 0.5 *M* phosphoric acid. To this solution, a solution of 0.179 g (0.56 mmol) $ZrOCl_2 \cdot 8H_2O$ in 3 ml water was added dropwise with constant stirring. Following formation of a colorless gel, 1.1 ml of 2 *M* HF solution was added and the resulting suspension was refluxed for 12 days under N_2. The solid was filtered, washed, and dried as above. Solid solutions were also prepared with $x = 0.25$, 1.0, and 1.5. For the phase with $x = 1.0$, calculated values for $C_4H_8O_9P_2Zr$ were C, 13.6; H, 2.3: Found values were C, 12.1; H, 2.8. For the phase

TABLE I

INTERLAYER SPACINGS OF PURE ZIRCONIUM PHOSPHONATES, $Zr(O_3PR)_2$

R	Interlayer spacing (Å)[a]
$(CH_2)_3COOH$	14.8
$CH_2C_6H_5$	16.6
$(CH_2)_2Cl$	12.3
$CH{=}CH_2$	10.8
$(CH_2)_2CH{=}CH_2$	13.5
CH_3	8.9
OH	7.6

[a] Interlayer spacings were determined from 00l diffraction lines (l = 1–3).

with x = 1.5, calculated values for $C_6H_{11}O_{9.5}P_2Zr$ were C, 18.5; H, 2.8: Found values were C, 17.0; H, 2.4.

Characterization. X-ray powder diffraction was performed on an Enraf–Nonius FR590 Guinier system, using an internal silicon standard with all samples. Interlayer spacings were determined from 00l (l = 1–3) reflections. Ethanol adsorption measurements were performed by drying the phosphonates at 110°C for 16 hr, then suspending them in 100% ethanol and stirring for 2 hr. Weight uptake was determined after evaporation of ethanol in dry air until weight remained constant. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory.

Results and Discussion

The synthesis and characterization of these layered solids represent an entry into the design of new porous materials with specific structural characteristics and chemical reactivity through rational synthetic strategies. The data on the new compounds, coupled with previous work in this area and on zirconium phosphate (*2*), shed light on the nature of the interlayer environment.

The interlayer spacings of all the pure (single organic moiety) phosphonates are summarized in Table I. The clear relationship between length of the organic substituent and interlayer spacing indicates that all of these solids contain an organic bilayer between zirconium phosphate layers, and that "nesting," or interweaving, of organic groups is not a significant structural consideration. Hydration also does not appear to be a factor in the pure phosphonates containing hydrophobic organic groups. For instance, the interlayer spacing of 16.6 Å for the benzyl derivative, $ZrP(bz)_2$, agrees with the spacing calculated roughly from the sum of the width of a Zr–O–P layer and the length of two benzyl groups placed end to end (*9*).

We have shown (*15*) that phosphonates of the formula $Zr(O_3PR)_2$, synthesized from a single alkyl phosphonic acid, generally display no ion exchange or acid–base reactivity with acids, bases, or metal ions in aqueous solution. Presumably, this stability results from a highly crowded interlayer region which does not permit migration of species into the bulk of microcrystals. The mixed phosphonates are far more amenable to interlamellar chemistry, including anion-exchange, metal coordination, and acid–base reactions. The difficulty of producing single-phase solid solutions (*16*) with nonsegregated short-range structures (*17*) limits the availability of porous phases, and not all combinations of the organic groups in Table I produce a single phase at all compositions. However, recent work has suggested (*8*) that the use of a moderate amount of HF in the crystallization of the mixed phosphonates facilitates formation of the porous product.

In order to determine whether the mixed phosphonates, $Zr(O_3PR)_x(O_3PR')_{2-x}$, adopted a random (Fig. 1a) structure or a staged (Fig. 1b) structure, the X-ray powder results were analyzed to determine the solids' adherence to or deviation from Vegard's Law (*18*), which predicts that the alkyl moieties will pack as efficiently in the mixed phosphonates as in the pure limiting compositions, i.e., that some form of staged configuration will result. In that event, the observed reflection at low angle corre-

sponds to a "weighted average" interlayer spacing, or to the $00n$ reflection for a cell consisting of n layers of Zr ($n = 2/x$). This average interlayer spacing should vary nearly linearly with the composition of the solid solution.

In the random (porous) structure, the interlayer spacing is determined by the length of the longest alkyl group, thus if the long groups are relatively sparse, the interlayer spacing is $(a + b)/2$, where a and b are the interlayer spacings of the pure phosphonates. Ideally, this spacing does not vary as x is varied between 0 and 1. For x greater than 1, the interlayer spacing is equal to that of the pure phosphonate composed of the longest alkyl groups. While the layers are expected to show some flexibility, the longer groups should stand in close enough proximity for $x > 0.1$ to produce rigid layers. Hydration of hydrophilic alkyl groups can cause deviations from this argument, so phases composed of hydrophobic groups are expected to conform most closely to the above reasoning.

Structural analysis of phosphonates with the formula $Zr(O_3PCH_2C_6H_5)_x(O_3PCH_3)_{2-x}$ shows that their interlayer spacings do not obey Vegard's Law, which predicts a constant slope for a plot of unit cell dimension c (interlayer spacing) vs x. Instead, the graph of interlayer spacing vs x shows two plateaus, at 12.4 Å and 16.6 Å (Fig. 3a). This indicates that, for $x < 1$, the larger benzyl groups are acting as well-spaced pillars holding the layers apart. As the benzyl pillars become less scattered, near $x = 1$, a few of them locate opposite each other, leading to the same interlayer spacing as $Zr(O_3PCH_2C_6H_5)_2$. The pillars leave substantial channels between the smaller methyl groups dangling into the gallery, through which species from solution may migrate and eventually reside in intercalation reactions.

Structural analysis of the family of mixed phosphonates, $Zr(O_3P(CH_2)_3COOH)_x(O_3POH)_{2-x}$, shows that this solid solution adheres more closely to Vegard's Law, with

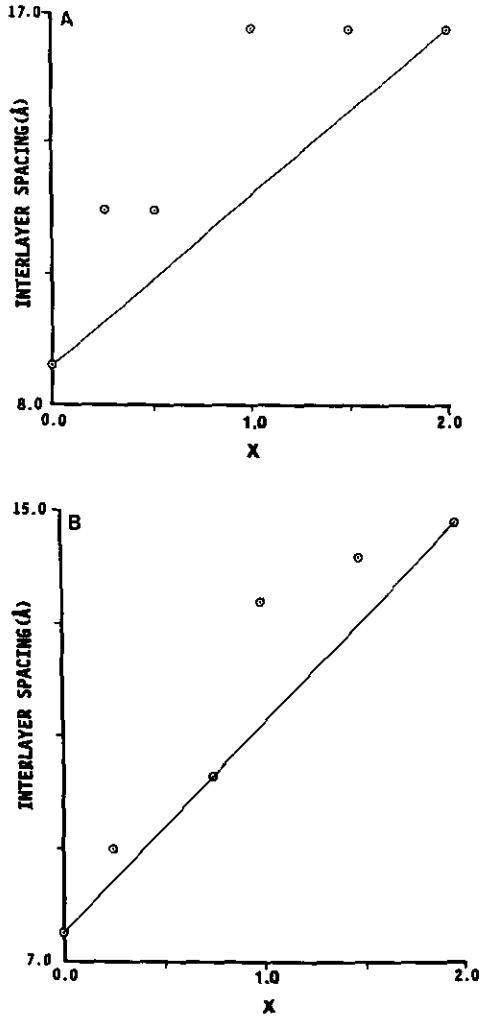

FIG. 3. (A) Plot of interlayer spacing vs x for $Zr(bz)_x(Me)_{2-x}$. (B) Plot of interlayer spacing vs x for $Zr(bt)_x(OH)_{2-x}$.

a steadily increasing average interlayer spacing as x increases from 0.25 to 1.5 (Fig. 3b). At $x = 0.75$, for example, the interlayer spacing predicted on the basis of Vegard's Law matches that observed for the compound, 10.3 Å. The predicted interlayer spacing for the random (porous) arrangement is 11.2 Å. The consistent positive deviation from the linear relationship probably reflects some tendency toward the random arrangement, but it may be due to differences in hydration between the pure and

mixed phosphonates. The positive deviation suggests that even materials of this system may display inclusion chemistry.

Ethanol adsorption by selected mixed phosphonates bears out the prediction of relative porosity based on the structural models above. The most porous of the materials described, $Zr(O_3PCH_2C_6H_5)_{1.0}(O_3PCH_3)_{1.0}$, takes up 6.2% of its weight in ethanol, corresponding to one molecule per Zr atom, despite its nonpolar internal surface. X-ray powder diffraction indicates that the interlayer spacing is unchanged, and the crystallinity of the solid is unaffected. By contrast, $Zr(O_3PCH_2C_6H_5)_{0.2}(O_3PCH_3)_{1.8}$, which is predicted to be somewhat less porous, takes up only 3.2% of its weight in ethanol and $Zr(O_3P(CH_2)_3COOH)_{0.8}(O_3POH)_{1.2}$, which lies on the line predicted from Vegard's Law (Fig. 3b), takes up only 3.6% of its weight in ethanol, presumably by surface adsorption.

The factors which determine whether a particular mixed phosphonate system condenses with porous or more closely packed galleries are not yet known. Clearly, the stronger interactions between the hydrophilic organic groups in $ZrP(bt)_x(OH)_{2-x}$ help to explain the closer adherence of this system to Vegard's Law, despite the presence of a moderate amount of HF in the crystallization mixture. Future experiments will focus on determination of these factors.

Conclusion

The crowded interlayer galleries of pure zirconium phosphonates, $Zr(O_3PR)_2$, are not inclined to include molecular species from surrounding media (*15*), despite relatively weak interlayer interactions. Whether this is a thermodynamic or kinetic result, these solids appear to have little promise for common applications of microporous materials.

Mixed zirconium phosphonates, $Zr(O_3PR)_x(O_3PR')_{2-x}$, however, can crystallize with inefficient interlayer ordering, resulting in porous structures. Solids of this type have great promise as catalysts, catalytic supports, and separation materials. Further work aimed at exploiting both the physical porosity and the chemical reactivity of this interlayer region for these applications is in progress.

Acknowledgments

The authors thank and acknowledge Jessica Wysocki for assistance in repeating syntheses of phosphonates and the donors of the ACS/Petroleum Research Fund (Grant 22359-G3) for funding support.

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