

Highly Porous Zirconium Aryldiphosphonates and Their Conversion to Strong Bronsted Acids

Abraham Clearfield,¹ Zhike Wang, and Paul Bellinghausen

Department of Chemistry, Texas A&M University, College Station, Texas 77842-3012

Received November 1, 2001; in revised form February 14, 2002; accepted March 1, 2002

IN HONOR OF PROFESSOR GALEN STUCKY ON THE OCCASION OF HIS 65TH BIRTHDAY

Porous inorganic–organic hybrids have been prepared by the reaction of 4,4'-biphenylbis(phosphonic acid) with Zr(IV) in organic solvents. The resultant products consist of α -zirconium phosphate-type layers crosslinked by biphenyl pillars. By using an excess of Zr in the synthesis, surface areas of $\sim 400 \text{ m}^2/\text{g}$ have been obtained and the pores can be controlled to be the micro-type with diameters of 10–20 Å and a relatively narrow pore size distribution. The aromatic rings are readily sulfonated by SO_3 under pressure to produce very strong Bronsted acid catalysts. An NMR procedure, utilizing the shift of the carbonyl carbon of acetone-2-¹³C sorbed onto the sulfonated products, indicated an acid strength for the Bronsted acid sites equal to that of 100% sulfuric acid. Unpillared $\text{Zr}(\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{H})_2$ has a somewhat lower acid strength, but still has a higher acid strength than zeolites HX and HY. The particles of this layered acid exfoliate in water and light-scattering data show that they are in 5 nm size range. They also exhibit high proton conductivity as solid membranes. These sulfonated materials have a potential as strong acid catalysts for a variety of reactions at a low temperature. © 2002 Elsevier Science (USA)

Key Words: organic–inorganic hybrids; micro-porous materials; strong Bronsted acids.

INTRODUCTION

Oftentimes, one begins a line of research that follows naturally from the previous research without realizing the full implications of its importance. Such is the case with our work in metal phosphonate chemistry. In the beginning, gels were refluxed in strong H_3PO_4 and crystallized into what later came to be known as α -zirconium phosphate (α -ZrP), $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (1). This compound has a clay-like structure in which the ZrO_6 octahedra are sandwiched between layers of phosphate tetrahedra (2). In this compound, the tetrahedra are inverted relative to the positioning of the silicate ions in clays. That is, three of the phosphate oxygens

bridge three different zirconium atoms and the –OH group points to the interlamellar space. The protons of these P–OH groups are the source of the compound's ion exchange properties (3–5).

In 1978, Alberti *et al.* (6) prepared the first zirconium phosphonate compounds. Later, we solved the structure of the phenyl derivative using a sample prepared by Alberti (7) (Fig. 1). Essentially, the structure is the same as that of α -ZrP with the phenyl group replacing the OH group. This similarity and our deep involvement in Group 4 and 14 families of phosphates (8) led us to develop a research project in metal phosphonate chemistry. The fascination with metal phosphonates stems from the fact that almost any organic group may be converted into a phosphonic acid by well-known reactions and that these acids can be used to design a variety of structure types. Examples will be provided in what follows, but we shall confine ourselves to describe porous phosphonates, and their use as catalysts.

Background to Porous Materials of the Zirconium Phosphonate Type

Prior to the discovery of mesoporous silicas by Kresge *et al.* (9), there was a concerted effort to prepare zeolites with larger pore openings, so as to be able to effect catalytic reactions of large molecules within the pores. A detailed description of this effort is provided by Davis (10). Concurrent with this effort was the program to convert clay minerals, particularly smectites, into three-dimensional open porous materials by a process termed “pillaring.” Briefly, the procedure consists of swelling the clay in water and then exchanging an inorganic polymer, such as $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ between the layers (11, 12). Upon heating above 500°C, the pillars bond to the layers as permanent oxide pillars, holding the layers apart. In the process, intersecting tunnels are formed, imparting porosity to the system. An extensive literature on this subject exists for which the indicated references provide a good overview (11–15).

¹ To whom correspondence should be addressed. Fax: (979) 845-2370. E-mail: clearfield@mail.chem.tamu.edu.

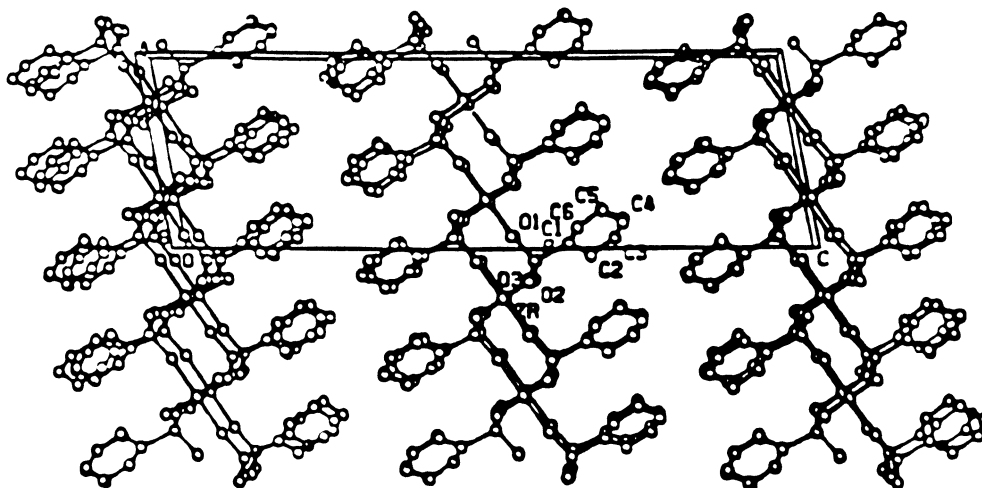


FIG. 1. Schematic representation of the structure of zirconium phenylphosphonate as viewed down the *b*-axis direction.

Dines first conceived of producing porous materials by crosslinking the α -zirconium phosphate-type layers using diposphonic acids, $H_2O_3P-R-PO_3H_2$, where *R* may be an alkyl or aryl group (16). The strategy was to choose the crosslinking groups that are tall and then space them such that different size pores would result as indicated in Fig. 2. However, the area subtended by a phosphate group on the α -ZrP layer is 24 \AA^2 (2, 4). Given the fact that an alkyl or aryl group spaced every 5.3 \AA apart on the layer occupies most of the area between pillars, there should be no microporosity. To overcome this restriction, the Dines group used phosphorous acid as a spacer group, together with biphenyl as the *R* group. The idea was to space the biphenyl pillars two or three positions apart, thus creating microporosity. A series of compounds of general composition $Zr(O_3PC_{12}H_8PO_3)_{1-(1/2)x}(HPO_3)_x$ was prepared and indeed, the surface area was found to increase to a maximum at $\sim 50\%$ substitution of phosphite, as shown in Fig. 3 (16). We repeated these experiments using phosphoric acid as a spacer group and found that while the surface areas were high, the distribution of pore sizes was quite large for both the biphenyl and terphenyl derivatives. All these prepara-

tions are amorphous to X rays and produce products with extremely small particle sizes ($\sim 0.06 \mu\text{m}$).

The precipitation can be slowed considerably by complexing the Zr with fluoride ion to form the hexafluozirconate ion, ZrF_6^{2-} . Addition of the phosphonic acid does not precipitate a phosphonate at room temperature. However, heating to above 60°C releases Zr^{4+} allowing the formation of the desired zirconium diposphonate. The precipitated products are partially crystalline from which the interlayer spacings may be derived. The biphenyl pillared product has a spacing of 13.8 \AA and the terphenyl derivative 18.2 \AA . These more crystalline products sometimes exhibited a bimodal pore distribution with diameters of the order of 15 and 40 \AA (17). The pore size was difficult to control and the N_2 BET isotherms indicated a largely mesoporous structure that may arise mainly from interparticle agglomeration.

It should be noted in Fig. 3 that even the 100% pillared product has a high surface area, of the order $300 \text{ m}^2/\text{g}$. The question that begs an answer is how this large surface area is possible without microporosity. Alberti *et al.* (18), concluded that the high surface area arises from the very small particle size of the crosslinked products. They prepared zirconium butanylbis(phosphonate), $Zr[O_3P(CH_2)_4PO_3]$ in both aqueous HF media and in dimethylsulfoxide (DMSO). In both cases, the surface area was of the order $10 \text{ m}^2/\text{g}$. However, when the reactions were carried out in DMSO with 35–40% of the pillars replaced with phosphate groups, high surface areas ($300\text{--}460 \text{ m}^2/\text{g}$) were obtained. The same reaction in which water was the solvent, yielded products with surface areas of $10\text{--}12 \text{ m}^2/\text{g}$. The porosity was in the mesoporous range, generally bimodal clustering in the regions of 2 and 3 nm diameters but covering a range of 1–5 nm (Fig. 4A). The pore structure appeared to be independent of the nature of the pillar. Alberti *et al.* (18) attributed the high surface area to interparticle porosity. They

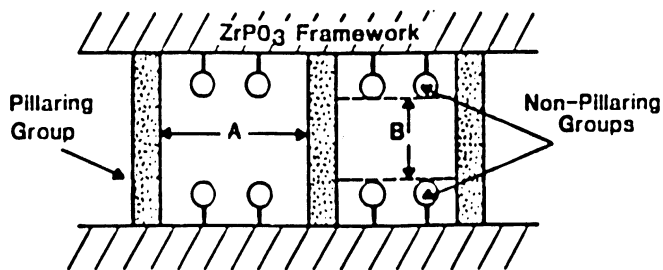


FIG. 2. A cartoon version of the expected effect of using small spacer groups to develop microporosity in organically pillared zirconium phosphonates assuming uniform distribution of the groups (reproduced with permission from Ref. (16)).

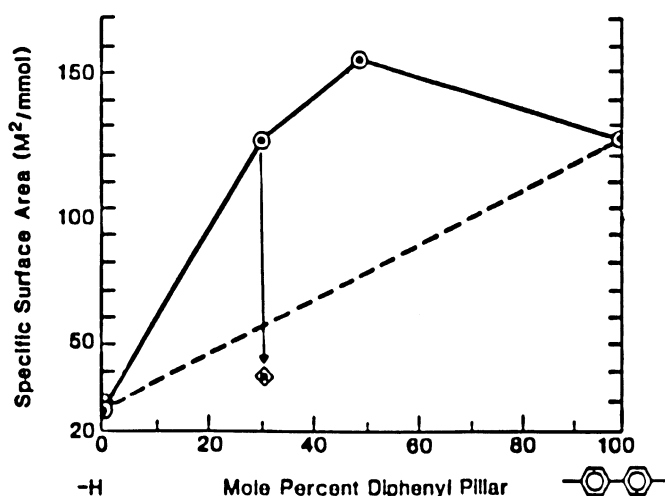


FIG. 3. Variation of the specific surface area of mixed component pillared amorphous zirconium biphenylbis(phosphonate) phosphites. The end members are $\text{O}_3\text{PH}(-\text{H})$ and biphenylbis(phosphonic acid). The point denoted with a diamond corresponds to the surface area after sorption of nonane (reproduced with permission from Ref. (16)).

also prepared, in DMSO as solvent, the benzene diphosphonic acid derivative of Zr in which 40% of the pillars was replaced by phosphite. The BET surface area was $462 \text{ m}^2/\text{g}$, and the pore distribution is shown in Fig. 4B.

Another feature of these compounds is the fact that the P:Zr ratio is often greater than 2. In order to explain the mesoporous nature of these compounds and the high phosphorus content, Alberti *et al.* (18) proposed that the particles consist of very few layers. In the completely exfoliated state, the surface area of the layers is calculated to be $960 \text{ m}^2/\text{g}$. If the pillared product consisted of only two layers per particle, then the surface area would be $480 \text{ m}^2/\text{g}$ and for three layers $360 \text{ m}^2/\text{g}$. These particles are postulated to have a "house of cards" arrangement because of the high residual surface charge and account for the large pore size. Since the particles consist of just a few layers, a large number of diphosphonate groups must exist on the surface. These groups are not terminated by Zr atoms and therefore, the unbonded end must contain two protons increasing the ratio of P to Zr.

Subsequently, it was shown by Alberti *et al.* (19) that the porosity could be altered in the range of 4–14 nm, with surface areas of $230\text{--}400 \text{ m}^2/\text{g}$ and pore volumes of $0.3\text{--}0.7 \text{ cm}^3/\text{g}$ by a choice of solvent and reactant ratios and concentrations.

Our results obtained with 4,4'-biphenylenebis(phosphonic acid) are not in accordance with those of Alberti. We had earlier reported that with this diphosphonic acid, very high surface areas could be attained with no additions of phosphorous or phosphoric acids (20). The pore structure depended upon the solvent system. The compounds prepared in DMSO appeared to be grouped into two categories. Those that were prepared in DMSO diluted with

benzene have relatively low surface areas ($133\text{--}213 \text{ m}^2/\text{g}$) and no micropores. The average pore radius was in the range 4.8–9.0 nm. In contrast, when the synthesis was carried out in concentrated DMSO solutions, the surface areas ranged from 270 to $397 \text{ m}^2/\text{g}$ and there was a significant contribution from the micropores (25–50% of the surface area). The average pore size of these products was in the range 1.1–1.5 nm for the micropores. Finally, the products obtained from the alcohol–water mixtures were high in surface area and had intermediate pore sizes (average 2.4–3.0 nm). These preparations were carried out in considerably more dilute solutions than any of the DMSO preparations because of the low solubility of the biposphonic acid in this medium. Yet, the textural proper-

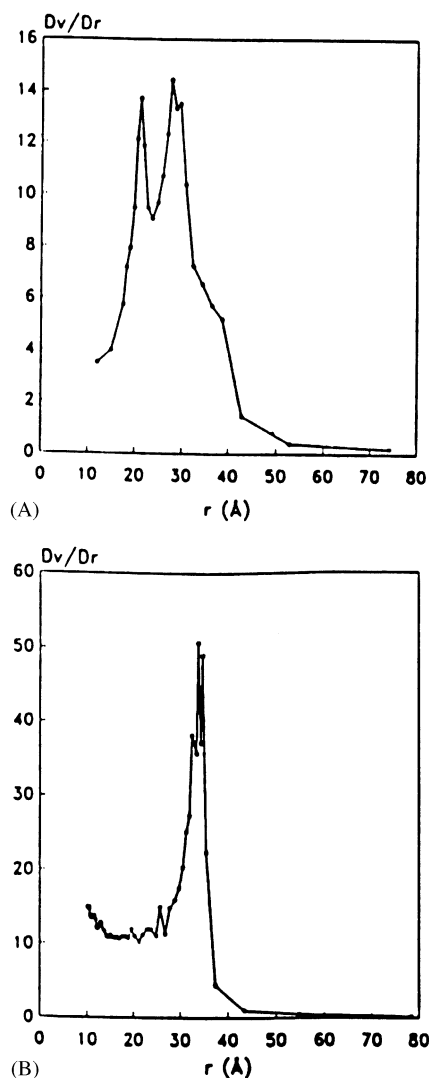


FIG. 4. Pore distribution in zirconium butylenebis(phosphonate) phosphite, $\text{Zr}(\text{O}_3\text{PC}_4\text{H}_8\text{PO}_3)_x(\text{O}_3\text{PH})_{2-2x}$ with $x \cong 0.6$ (top) and pore distribution in zirconium phenylenebis(phosphonate) phosphite, $\text{Zr}(\text{O}_3\text{PC}_6\text{H}_4\text{PO}_3)_x(\text{O}_3\text{PH})_{2-2x}$ with $x \cong 0.6$ (reproduced with permission from Ref. (18)).

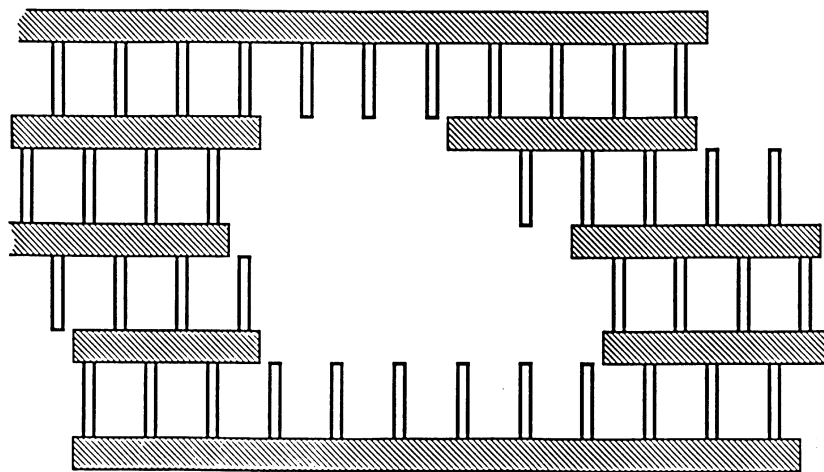


FIG. 5. A schematic drawing of how pores of different sizes may develop in zirconium biphenylenebis(phosphonate), $\text{Zr}(\text{O}_3\text{PC}_{12}\text{H}_8\text{PO}_3)_{1-x/2}(\text{O}_3\text{PC}_{12}\text{H}_8\text{PO}_3\text{H}_2)_x$. The double parallel lines represent the biphenyl pillars and the thick horizontal bars represent the ZrO_3P layers. The pillars bonded to only one layer and capped by a horizontal line at the other end represent unbonded phosphonic acid groups at the horizontal line. Such groups should also be present on the outer surfaces of the particle if an excess of Zr is not used in the synthesis.

ties were intermediate to those prepared in diluted and concentrated DMSO solutions. Thus, it appears that the solvent plays a significant role in determining the textural properties of the end product. Typically BET N_2 sorption-desorption curves for two types of these compounds are shown in Ref. (20).

A theory of micropore and supermicropore (i.e., pores in the 1.0–2.0 nm range) formation in these pillared products must account for the increase in phosphorus to Zr ratio, as well as the internal pore structure. We proposed (20) that the pores result from a coming together of layers of unequal size during particle growth as shown in Fig. 5. This figure is deficient in that the outer surfaces as well as a portion of the inner surfaces would have free phosphonic acid groups. The uneven growth of the layers, one terminating while another bonded to it continues to grow laterally and then binds to another terminated layer, leads to internal micropores. A more quantitative description of these ideas will be published subsequently.

As interesting as these materials are, what was really desired was a high surface area with a high proportion of micropores with diameters of 1–2 nm. It occurred to us that if an excess of Zr was used in the reaction, then the excess metal would reduce the number of free acid groups and allow a more regular growth of the layers. A number of such reactions have now been carried out as described below. We also report on our own studies with 1,4'-phenylenebis(phosphonic acid) to test the idea that such particles have very few layers.

EXPERIMENTAL

Preparation of Zirconium Phenylenediphosphonates

The general procedure was to react $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Aldrich, reagent grade) with 1,4'-phenylenediphosphonic acid,

$\text{H}_2\text{O}_3\text{P}-\text{C}_6\text{H}_4-\text{PO}_3\text{H}_2$, prepared by an Arbuzov reaction from 1,4-dibromobenzene and triethylphosphite (21). Phosphoric acid (Fisher reagent) was added as a spacer group and HF as a solubilizing agent to improve the crystallinity. Some examples are as follows.

Preparation in Water (53Y-1)

1.0 g (4.20 mmol) of 1,4'-phenylenebis(phosphonic acid) was dissolved in 20 mL of distilled deionized water (ddi) in a plastic beaker. In a separate polyethylene bottle, 0.92 g (2.87 mmol) of zirconyl chloride octahydrate was dissolved in 20 mL of ddi water. 1.65 mL of 48% HF (47.7 mmol) was added to the zirconyl chloride solution. The mouth of the bottle was covered with a parafilm containing a small opening to allow for water evaporation. The bottle was kept in an oil bath at 60°C for 7 days. The collected solid was washed with water and dried at 50°C. Yield 0.82 g, 79%. Found: Zr, 24.97%; P, 20.37%; C 23.99%; H, 1.76; calc. based on $\text{Zr}(\text{O}_3\text{PC}_6\text{H}_4\text{PO}_3)_{0.87}(\text{O}_3\text{PC}_6\text{H}_4\text{PO}_3\text{H}_2)_{0.26} \cdot 0.2\text{H}_2\text{O}$: Zr, 25.35%; P, 19.45%; C, 22.63%; H, 1.52%. ^{31}P : NMR, -5.5 (ZrO_3P) 95%; $+1.5$ ($\text{C}-\text{PO}_3\text{H}_2$) $\sim 5\%$.

Preparation in Ethylalcohol (65W-1A)

0.5 g (2.10 mmol) of 1,4'-phenylenebis(phosphonic acid) and 1.4 g (12.59 mmol) of 85% H_3PO_4 were dissolved in 20 mL of absolute ethylalcohol in a polypropylene vial. 2.98 g (9.25 mmol) of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and 6.4 mL (180 mmol) of 48% HF were added to 20 mL of absolute ethanol in a small polyethylene bottle and shaken until complete solution was realized. This solution was then added to the polypropylene vial, sealed and kept at 75°C for 6 days. The recovered precipitate was washed free of alcohol with ddi

water and dried at 50°C. Yield 2.60 g, 82%. Found: Zr, 26.74%; P, 18.46%; C, 18.66%; H, 1.56%, F, 1.39%. TGA, 3.5% H₂O; Total wt. loss 23.3% to ZrP₂O₇: F. Wt. = 345.4. Zr(O₃PC₆H₄PO₄)_{0.78}(O₃PC₆H₄PO₃H₂)_{0.13}(HPO₄)_{0.2}F_{0.22}·H₂O: Calc. Zr, 26.37%; P, 18.09%; C, 18.96%; H, 1.75%. F, 1.21%; ³¹P NMR: + 2.5 ppm (C-PO₃H₂) ~ 5%; - 5.6 ppm (ZrO₃P), 80%; - 21.5 ppm (HO-PO₃), ~ 15%.

Preparation in DMSO (61W-3)

0.5 g (2.10 mmol) of 1,4'-phenylenebis(phosphonic acid) and 1.45 g (12.58 mmol) of 85% phosphoric acid were dissolved in 20 mL of DMSO contained in a polypropylene vial. A second solution containing 0.68 (2.10 mmol) of ZrOCl₂·8H₂O and 6.4 mL (190 mmol) of 48% HF solution in 20 mL of DMSO was prepared in a polyethylene bottle. After complete dissolution, this solution was added to the polyethylene vial and sealed. The sealed vial was kept at 75°C in an oven for 6 days. The recovered solid was washed free of DMSO with ddi water and dried at 50°C. Yield 0.69 g, 52%. Found: Zr, 25.33%; P, 18.90%; C, 18.18%; H, 1.52%; F, 1.6%. Thermogravimetric analysis (TGA), H₂O 6.42%, Total wt. loss 26.66%. Calc. for Zr(O₃PC₆H₄PO₃)_{0.6}(O₃PC₆H₄PO₃H₂)_{0.3}(HPO₄)_{0.3}F_{0.4}·1.25H₂O:Zr, 25.24%; P, 18.0%; C, 17.95%; H, 1.94%; F, 2.1%. Total wt. loss 26.6%.

Preparation of Zirconium 4,4'-Biphenylenebis(phosphonate) (ZrBPD, 6G)

2.0 mL (mmol) HF was added to 1.0 g (3.08 mmol) of zirconyl chloride in a Teflon pressure vessel containing 40 mL of DMSO. To this solution was added 0.48 g (1.53 mmol) of 4,4'-biphenylenebis(phosphonic acid) dissolved in 40 DMSO. The pressure vessel was kept in an oven at 80°C for 3 days and then cooled to room temperature. The solid was recovered and washed with ddi water until free of chloride ion and dried at 50°C. Yield, 0.54 g, ~ 80%. Product ratio; P:Zr:F, 2.09:1:0.47. ³¹P NMR, - 5.66 ppm (ZrO₃P), + 2.2 ppm(C-PO₃H₂).

Preparation in Mixed Ethanol-DMSO Solvent (II-9)

1.03 g (3.28 mmol) 4,4'-biphenylenebis(phosphonic acid) was dissolved in a mixture of 100 mL ethanol (95%) + 25 mL DMSO. A mixture of 2.172 g ZrOCl₂·8H₂O (6.72 mmol) and 4.24 mL of HF (121 mmol) in 100 mL ethanol was added to the phosphonic acid solution, which was placed inside a Teflon-lined steel pressure vessel and maintained at 80°C for 3 days. The solid precipitate was then recovered by centrifugation, washed free of chloride and fluoride ions and dried at 50°C. Yield, 0.993 g

(70%). Found: Zr, 20.68%; P, 14.20%, F, 1.85%; Total TGA wt. loss 37.04%, H₂O 3.8%. Calc. for Zr(O₃PC₁₂H₈PO₃)_{0.78}(O₃PC₁₂H₈PO₃H₂)_{0.23}F_{0.42}·H₂O: Zr, 21.17%; P, 14.52%; F, 1.85% H₂O, 4.18%.

Sulfonation of Zirconium 4,4'-Biphenylenebis(phosphonic acid)

One gram of ZrBPD was placed into a 100 mL Teflon-lined pressure vessel along with 2 mL of 30% fuming sulfuric acid contained in a 25 mL beaker. The sealed vessel was then kept at 150°C for 6 days. The cooled vessel was opened in a plastic airbag purged with dry N₂ and the sulfonated solid was transferred to a dry vial and sealed with wax and stored in a nitrogen-purged glove box.

Surface Area Measurements

Sorption-desorption isotherms were obtained with a Quantachrome Autosorb-6-automated N₂ gas adsorption unit. The samples (0.2–0.6 g) were preheated at a temperature between 150 and 200°C and then degassed overnight at 250°C under the vacuum on the Quantachrome degasser until a pressure 2 × 10⁻³ Torr was achieved. The isotherms were obtained at 77 K and analyzed by the BET model. The micropore volume was determined by the DeBoer *t*-plot method and the micropore distribution calculated by the MP method.

Analytical and Instrumental

Zirconium and phosphorus analysis was carried out in-house with a Direct Current Plasma (DCP) spectrometer. A weighted portion of the sample was dissolved in 1 mL of 48% HF with heating and then diluted to 200 mL. Aliquots were then removed and diluted to a composition falling well within the standard curves of Zr and P, respectively. Alternatively, these elements and F were determined using a Cameca 5 × 50 electron microprobe at an accelerating voltage of 15 kV and operating with a beam current of 20 mA using a wavelength-dispersive spectrometer. Samples that did not dissolve in HF were heated to 500°C in air for 10 h to destroy the organic. The residue was then dissolved in HF and diluted as before. C, H, S analyses were performed by either Galbraith Labs or Oneida Research. TGA was performed on a TA 950 unit at a heating rate of 3–10°C/min under a flow of air. Solid-state MAS NMR measurements were obtained on a modified Bruker MSL-300 MHz spectrometer operating at 121.5 MHz for ³¹P, 75.4 MHz for ¹³C and 30.42 MHz for ¹⁵N. X-ray powder patterns were obtained on a Seifert-Scintag PAD-V unit with CuKα (λ = 1.5418 Å) at 40 kV and 30 mA.

TABLE 1
Synthesis Conditions and Product Texture for Zirconium Monophenyldiphosphonate

Sample no.	Ratio reactants Zr:PDP ^a :H ₃ PO ₄ :HF	Solvent	Temp (°C) Time (day)	Micropore S.A. (m ² /g)	Mesopore S.A. (m ² /g)
53Y-1	1:1.5:0:16.6	Water	60, 7	2.96	27.2
59Y-1	1:1:8:20	H ₂ O + HCl	90, 6	13.7	14.3
65Y-1	1:0.9:9.25:20	H ₂ O	154, 6	1.5	7.0
65W-1A	1:0.24:1.36:20	C ₂ H ₅ OH	75, 6	14.6	11.1
66Y-1	1:0.78:8:60	C ₂ H ₅ OH + HCl	90, 3	11.2	129
66Y-2	1:0.78:8:60	C ₂ H ₅ OH + HCl	90, 3	65.3	138
61W-3	1:1:6:90	DMSO	75, 6	100	240

^a PDP = 1,4'-phenylenebis(phosphonic acid), H₂O₃PC₆H₄PO₃H₂.

RESULTS

The conditions of synthesis and resultant porosity for the zirconium 4,4'-phenylenebis(phosphonates) are summarized in Table 1. A typical X-ray pattern is shown in Fig. 6. The X-ray pattern for a biphenyl derivative is very similar but with an initial peak at 13.8 Å (20). For the main part, the monophenyl samples had low surface areas and very few regions of micropores. However, samples 66Y-2 and 61W-3 had relatively high surface areas of which a significant portion contained micropores. The highest surface area was obtained for samples synthesized in DMSO. This finding

is consistent with our previous findings for zirconium biphenylene phosphonates (20). The difference in the present study with the biphenylphosphonic acid is that we used an excess of Zr. This change produces very high surface areas, of the order 400 m²/g, but also with more than 90% of the surface area accounted for by micropores in the range of 10–20 Å. A typical N₂ BET isotherm is shown in Fig. 7 and the pore size distribution is shown in Fig. 8.

The existence of a high level of micropores of uniform size stands in opposition to the hypothesis of Alberti *et al.* (18) in that the particles can be no more than a few layers thick and the porosity is due to interparticle voids. Evidence for the

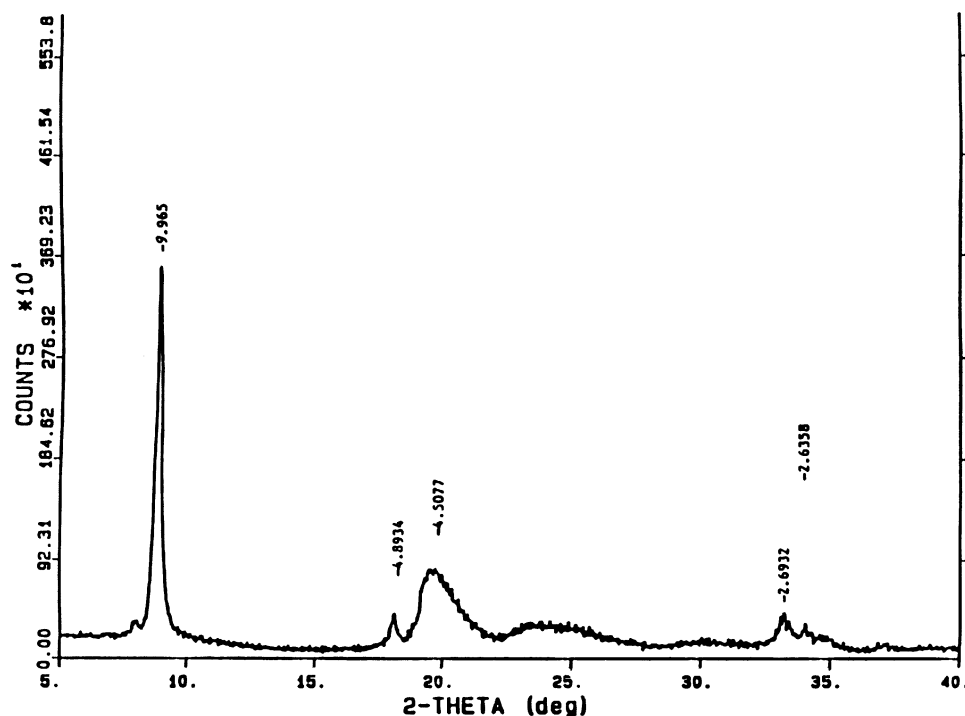


FIG. 6. X-ray powder diffraction pattern (XRPD) of zirconium phenylenebis(phosphonate) Zr(O₃PC₆H₄PO₃) illustrating the narrow (001) reflection at 9.96 Å.

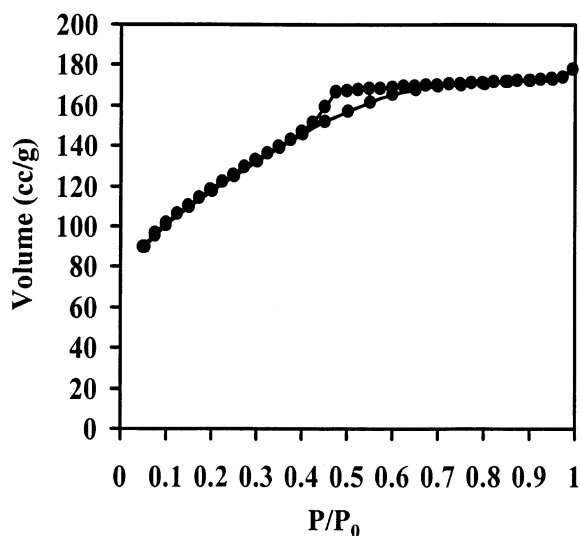


FIG. 7. The sorption-desorption BET N_2 isotherm of $Zr(O_3PC_{12}H_8PO_3)$ prepared in a DMSO- C_2H_5OH mixed solvent. The sample was outgassed at $200^\circ C$ for 10 h, surface area $416 \text{ m}^2/\text{g}$, total pore volume $0.268 \text{ cm}^3/\text{g}$.

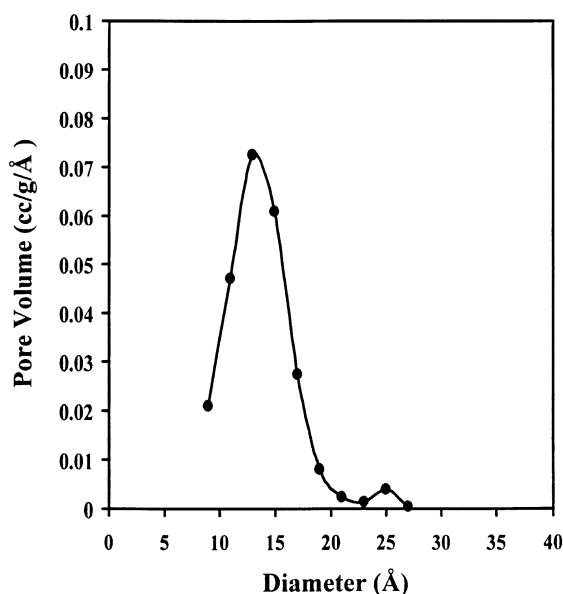


FIG. 8. Micropore distribution of pore diameters (top), based on the isotherm of Fig. 7, determined by the Deboer t -plot method. The maximum is at 13 \AA .

number of layers in a particle may be adduced from the full-width at half-maximum of the (001) reflection. This reflection has a width at half-height of approximately 0.36° (Fig. 6). This value is used in the Sherrer equation in the form

$$t = \frac{0.9 \lambda}{\sqrt{B_s^2 - B_i^2 \cos^2 \theta}}$$

where t is the thickness of the particle, λ the X-ray wavelength, θ the Bragg angle and B_s and B_i are the width at

half-height of the sample and instrument i.e., the instrumental broadening. Without making the correction for instrumental broadening, the calculated value of $t = 220 \text{ \AA}$ or about 22 layers of 10 \AA thickness. The true value would be about double this thickness if instrumental broadening were to be taken into account. A transmission electron micrograph (TEM) of a sample of zirconium, 4,4'-biphenylenebis (phosphonic acid) is shown in Fig. 9. The solid was ground

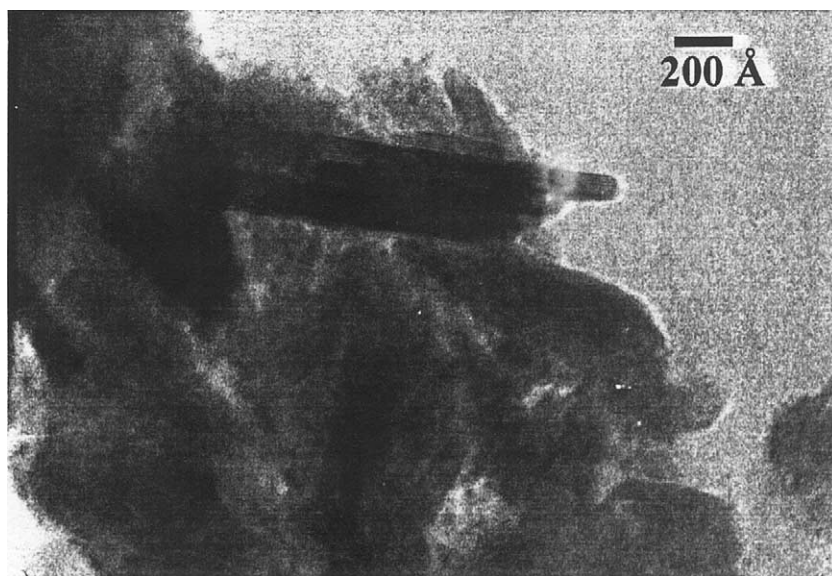


FIG. 9. TEM of zirconium 4,4'-biphenylenebis(phosphonate) prepared in DMSO as solvent.

and sedimented and the smallest particle fraction was chosen for examination. The smallest particle in the upper center has 5 layers and is placed on top of another crystallite with about 7 layers to which it may be bonded. Other particles are larger still so that the surface area, 403 m²/g, largely micropores, cannot be accounted for as interparticle voids.

A number of such reactions have been carried out as described in the experimental section for ZrBPD yielding surface areas in the 350–425 m²/g range. The pore structure changes somewhat with the conditions, but the dv/dr plot always yields maxima in the 1–2 nm range. About 90–95% of the surface area is accounted for as micropores. Sulfonation of these pillared and unpillared aryl zirconium compounds results in strong Bronsted acid materials with interesting properties.

Zirconium Sulphosphonates

Zirconium phenylphosphonate may be sulfonated by reaction with fuming sulfuric acid to obtain $Zr(O_3PC_6H_4SO_3H)_2 \cdot nH_2O$ (22). Isolation of the sulfonated product from liquid fuming sulfuric acid is difficult so that at present, we use SO_3 under pressure to obtain dry powders as described in the Experimental section. The sulfonate swells on standing in air by spontaneous uptake of water vapor. It spontaneously exfoliates in water to yield a colloidal suspension of the particles. Recent light-scattering measurements indicate that 95% of the particles are in the range of 4–5 nm on a side and 1.5 nm thick (23), true nanoparticles. They exhibit high proton conductivity, $2.1 \times 10^{-2} \Omega^{-1} cm^{-1}$ at 25°C and 85% RH (24). The activation energy for conduction as determined for data at 30% RH in the temperature range 285–380 K was 0.28 eV. The titanium analog exhibits even higher conductivities, the value of 85% RH was $1.3 \times 10^{-1} \Omega^{-1} cm^{-1}$.

Catalysis Utilizing Sulfonated Zirconium Phosphonates

One can readily predict that the sulfophenylphosphonates would behave as strong Bronsted acids. We have attempted to assess the acid strength of these materials by the use of NMR techniques as developed by Haw *et al.* (25, 26) applied mainly to zeolites. This method is a variable temperature solid-state NMR approach for the *in situ* study of reactions between a solid acid and a sorbate. The sorbate contains a single carbon atom, highly enriched in ¹³C. This carbon atom exhibits a considerable chemical shift from its normal resonance position upon interaction with the solid acid. They developed a scale of acid strengths based upon chemical shifts of known strong acids and superacids. For example, the chemical shift for acetone-2-¹³C in 100% H_2SO_4 is 244 ppm. Initially, we carried out a similar reaction utilizing a sulfonated zirconium phenyl phosphonate, $Zr(O_3PC_6H_4SO_3H)_2$ mixed with 10% silica and acetone-

TABLE 2
Chemical Shift to Acetone-2-¹³C When Exposed to Different Acid Species (from Ref. (26))

Acid	Shift
$CDCl_3$	205
Ze-HX	215
Ze-HY	220
HZSM-5	223
$H_2SO_4 - 80\%$	~ 235
$H_2SO_4 - 100\%$	244
$AlCl_3$	245
SO_3/H_2SO_4	246
FSO_3H/SbF_5	248
SbF_5	250

2-¹³C (23). This solid had an S.A. of 40 m²/g. The level of acetone loading was 0.30 mmol/g and the observed shift was 237 ppm. Table 2 lists the shifts obtained for several substrates under the same conditions of reaction as determined by Haw *et al.* (25). This chemical shift for the sulfophenylphosphonate of zirconium was found to be equivalent to an acid strength exhibited by 80% H_2SO_4 (Fig. 10). Even at room temperature and this low concentration of acetone on the catalyst, measurable amounts of mesityl oxide (212 and 197 ppm), trimethyl benzene isomers and olefins (132 and 127 ppm) were identified as forming spontaneously.

Sulfonated zirconium biphenyldiphosphonate, sample number II-9, was also examined and the NMR spectrum of ¹³C at low loading is shown in Fig. 11. The chemical shift is

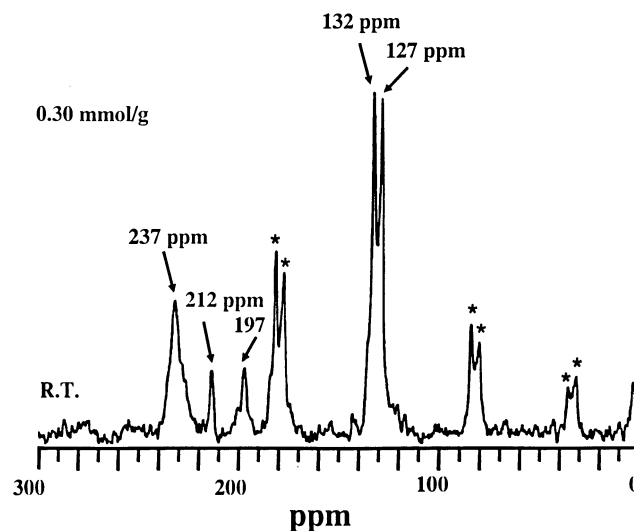


FIG. 10. Solid-state MAS NMR spectrum of acetone-2-¹³C sorbed (0.30 mmol/g) on $Zr(O_3PC_6H_4SO_3H)_2$ at room temperature. The peak at 237 ppm represents the protonated acetone species, the resonances at 212 and 197 ppm are due to mesityl oxide containing two ¹³C sites and those at 132 and 127 ppm may be due to olefinic and aromatic derivatives formed. Starred peaks are spinning side bands.

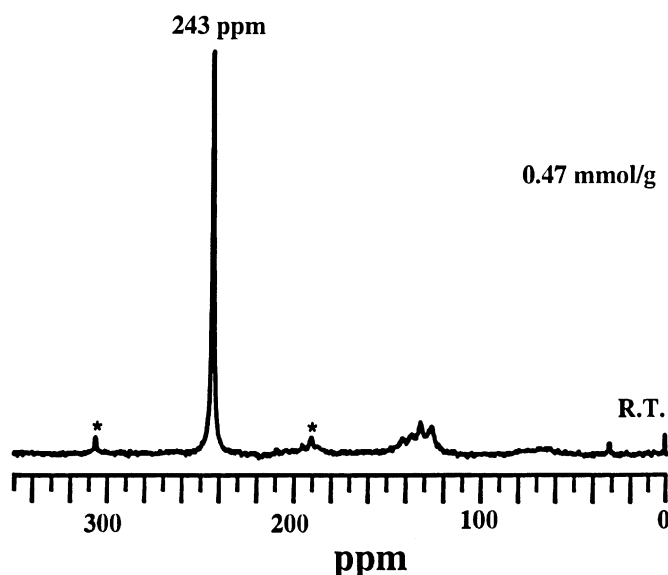


FIG. 11. Solid-state MAS NMR spectrum of acetone-2- ^{13}C sorbed on pillared sulfonated zirconium biphenylenebis(phosphonate) at room temperature at a level of 0.47 mmol/g. The resonance at 243 ppm represents the protonated acetone species and the minor peaks are the same as those shown in Fig. 10 for polymerized acetone derivatives. Starred peaks are spinning side bands.

seen to be 243 ppm, which is closer to the shift of 100% H_2SO_4 . At the level of 0.47 mmol/g, only small amounts of the condensation polymerization products were formed. This is in contrast to the result obtained with the unpillared sulfonated product. However, when the amount of acetone vapor was increased to the saturation point, all the acetone reacted, so the peak at 243 ppm was no longer present as all the acetone was converted to higher molecular weight species and more extensive cracking reaction products. A full report is in preparation (23).

A possible explanation for the greater reactivity of the catalyst with the weaker strength acid groups involves some structural considerations. In $\text{Zr}(\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{H})_2$ we know that the unsulfonated product has the α -ZrP structure (Fig. 1). The phenyl groups are arranged in hexagonal arrays at distances of 5.3 Å apart. In the examined catalyst, every ring was sulfonated. Thus, adjacent sulfonic acid groups are very close together and may exert a synergistic effect on the catalytic reaction. In contrast, in the pillared catalyst, the level of sulfur determined by the analysis corresponded to only half the phenyl rings being sulfonated. That is, only one ring of each biphenyl group contains, on average, one sulfonic acid group. Since the pillars are roughly 15 Å apart, the sulfonic acid groups are too far apart to act synergistically. We shall test this hypothesis by reducing the level of sulfonation of the unpillared catalyst and increase the sulfonation of the biphenyl-pillared product.

Our preliminary results also show that large molecules, such as those obtained by the aldol condensation-polymerization of cyclopentanone, take place in the cavities of the biphenyl-pillared catalyst. Recovery of these products would show that unlike zeolites, where the narrow openings restrict the size of molecules that can be treated catalytically, these sulfonated products may be useful in a number of such reactions involving large molecules. These ideas are being actively pursued.

DISCUSSION

This study had several objectives. One was the synthesis of porous zirconium-phosphate-type organic-inorganic hybrids in which the pores were largely of the micropore size. A second objective was to examine the hypothesis put forward by Alberti *et al.* (18) that the high surface areas of the hybrids are due to interparticle voids, where the extremely small particles built up of less than five years assume a "house of cards" arrangement. This argument is based on the composition of the hybrids, where it is consistently shown that the P/Zr is greater than 2. If there is a large external surface terminated by diphosphonate groups, half of these groups will not be bonded to metal. The formula would then be of the type $\text{Zr}(\text{O}_3\text{P-R-PO}_3)_{1-x}(\text{O}_3\text{P-R-PO}_3\text{H}_2)_{2x}$. Since each surface phosphonate group increases the ratio of phosphorus to zirconium, the external surface area may be deduced from the ratio. However, we have shown that the individual hybrid particles may have much more than five layers, when this hypothesis becomes untenable. Furthermore, several preparations of the ZrBPD hybrid we have made with excess Zr present have 90% or more of the total surface in micropores with maxima in the 1.0–1.9 nm range. It is unlikely that a house of cards arrangement would produce such a regularity.

We have, instead, proposed a model as depicted in Fig. 5. In this model, not only do the diphosphonate groups on the external surface increase the P/Zr ratio, but part of the internal surface also contributes to the increase in this ratio. By using an excess of Zr in the preparations, it is likely that most of the free phosphonate groups are complexed by the excess Zr so that the external surface is now terminated in Zr and is smooth as shown in Fig. 5. Furthermore, our analytical data indeed show that the P/Zr ratio is closer to 2 when excess zirconium is present. The role of fluoride needs to be assessed. It is most likely bonded to Zr and this would eliminate a site on the layer for bonding by phosphonate and thus contribute to the porosity. Whether this presence has an effect on the acid strength also needs to be assessed.

Sulfonation of the phenyl rings converts the hydrophobic pillars to hydrophilic strong Bronsted acids. The acidity is sufficiently high, that acid catalyzed reactions may be carried out at relatively low temperatures. Since the micropores

are larger than 10 Å, these materials may be suitable for reactions involving molecules in the 10–15 Å range.

ACKNOWLEDGMENT

This study was supported with funds supplied by NSF Grant No. DMR-0080040, for which the authors are grateful.

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