Porous Materials

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Hydrogen Storage in a Highly Porous Solid Derived from γ-Zirconium Phosphate**

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The clean production of hydrogen by renewable power sources will make this element the energy vector of the future.[1] However, the handling of this tiny molecule poses extraordinary problems, especially in vehicles, because of the enormous volume occupied by this gas under normal conditions (ca. 12 $\mathrm{L\,g^{-1}}$). Efficient hydrogen storage is thus paramount for the safe application of this technology. One approach to accomplish this goal involves its physisorption in porous solid materials, where the packing of hydrogen molecules must be as dense as possible so as to achieve the maximum volumetric density with the lowest feasible amount of additional material. The number of reports on this topic is vast[2] but, to the best of our knowledge, organic–inorganic layered structures have never been tried for this purpose.

The layered salts of zirconium phosphate (ZrP) readily yield pillared scaffolds.[3] We have shown in previous studies that the surface phosphate groups in γ-ZrP layers are amenable to sequential replacement by phosphonates and hypophosphite which leads to drastic changes in the porosity.[4]

We describe herein the incorporation of rigid 4,4″-terphenyldiphosphonate into γ-ZrP and an attempt to further exchange the residual surface phosphate groups with hypophosphite, in the hope that the resultant nonpolar material would be highly porous and able to store reasonable levels of hydrogen gas.

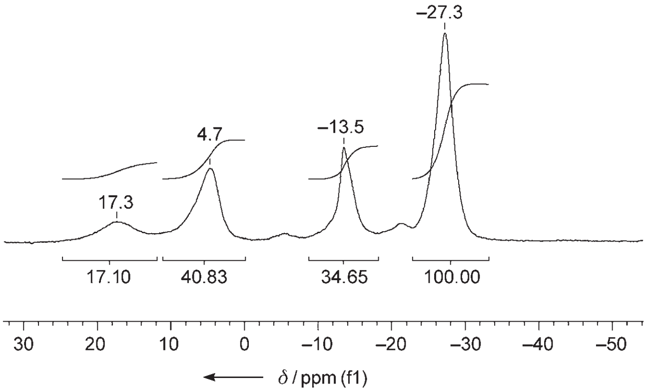

Figure 1. Solid-state MAS (10 kHz) ^{31}P NMR spectrum of material **I**.

The exchange reaction with 4,4″-terphenyldiphosphonic acid led to material **I**, the solid-state MAS (10 kHz) ^{31}P NMR spectrum of which is shown in Figure 1 (relaxation delay 20 s; internal phosphates: $\delta = -27.4$ ppm, remaining surface ones: $\delta = -13.5$ ppm, phosphonate groups: $\delta = 4.4$ and 17.3 ppm).

The presence of two resonances for the phosphonate groups may indicate that some of the diphosphonates do not form pillars but are bonded only by one end to the inorganic layers.[5] The relative integrals (100:35:41:17) and thermogravimetric analysis (TGA) allowed for the calculation of the molecular formula as $\mathrm{Zr(PO_4)(H_2PO_4)_{0.35}[HO_3P(C_{18}H_{14}P_2O_6)PO_3H]_{0.20}[HO_3P(C_{18}H_{14}P_2O_6)PO_3H_2]_{0.17}\cdot 1.4\,H_2O}$, which is in very good accordance with the elemental analysis (calcd: C 20.6, H 2.3; found: C 20.0, H 2.6). Therefore, 65% of the surface phosphate groups were replaced by phosphonates, which is in reasonable agreement with the estimated maximum possible exchange considering the available area surrounding each phosphate group (0.36 $\mathrm{nm^2}$) and the cross-section of the phenyl groups (0.44 $\mathrm{nm^2}$). Powder X-ray diffraction studies showed an interlayer distance of 2.43 nm (Figure 2), which corresponds to an inclination of the 4,4″-terphenyl pillars of about 14° with respect to the axis perpendicular to the layers.

BET analysis of material **I** showed a moderate specific area (90 $\mathrm{m^2\,g^{-1}}$). Treatment of material **I** with hypophosphorous acid gave material **II**. This material had a similar carbon (20.7%) and hydrogen content (2.6%) as material **I**, thus showing that the reaction with hypophosphite did not involve loss of terphenyldiphosphonate. However, the interlayer distance, as well as the crystallinity, of the sample was

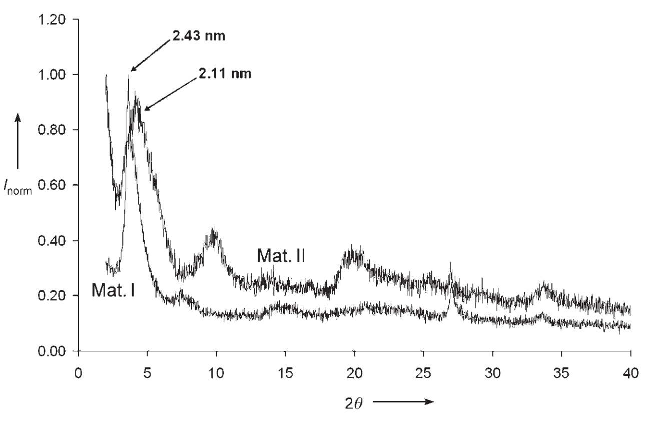

Figure 2. Powder XRD spectra of materials **I** and **II**.

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reduced (2.11 nm, see Figure 2). More importantly, the solid-state MAS ^{31}P NMR spectrum obtained for **II** was unexpected (Figure 3).

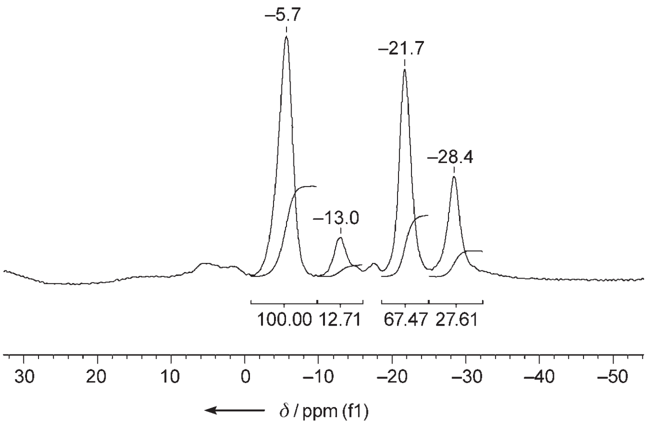

Figure 3. Solid-state MAS (10 kHz) ^{31}P NMR spectrum of material **II**.

In previous cases, the reaction of hypophosphite with pillared γ-ZrP containing nonrigid polyethylenoxadiphosphonates led to the complete elimination of the signal corresponding to the surface phosphate groups (ca. $\delta = -14$ ppm) and the appearance of a new one at about $\delta = 14$ ppm, which corresponds to hypophosphite. However, the latter signal was not observed in material **II**, thus suggesting that hypophosphite was not incorporated into the matrix. In contrast, two new signals were evident at $\delta = -21.7$ and -5.7 ppm, which were assigned to phosphate and phosphonate groups, respectively. The chemical shifts of these signals were compatible with the groups bonding to Zr through three oxygen atoms, that is, corresponding to α-ZrP-type phosphorus instead to the starting γ-ZrP type. However, the signals of lower intensity at $\delta = -28.4$ and -13.0 ppm (Figure 3) are characteristic of the latter phase. It should also be noted that the true α-ZrP phase derived from 4,4''-terphenyldiphosphonic acid bears an interlayer distance of 1.77 nm,[6] which is much shorter than that measured for material **II** (2.11 nm). Therefore, the reaction with hypophosphite was not topotactic, as occurred in the case of pillared γ-ZrP with polyethylenoxadiphosphonates. In turn, a mixed phase was obtained.[7] Interestingly, BET analysis of material **II** gave a specific area of approximately 400 m^{2}g^{-1}. It is thus evident that the hypophosphite treatment produced a much more porous solid, which was worth testing for its capacity to store hydrogen. Figure 4 shows the hydrogen-sorption isotherm of material **II** at 77 K.

It may be seen that hydrogen uptake amounts to 74 cm^3 per gram of material at 650 Torr, which is among the highest reported in the literature for related systems, namely metal–organic frameworks (MOFs).[8] We should also point out that the present work concerning the development of new sorbents for hydrogen and other combustible gases by means of ZrP-derived solid matrices is the first one reported in the literature. Therefore, our successful preliminary findings should constitute an excellent starting point to promote research in the application of layered organic–inorganic salts to this important area. Furthermore, the modular rationale followed in the assembly of these layered materials from discrete, preformed building units provide a set of porous solids with finely tuned structures to elucidate the still unknown properties that nanoporous materials must convey for enhancement of hydrogen storage.

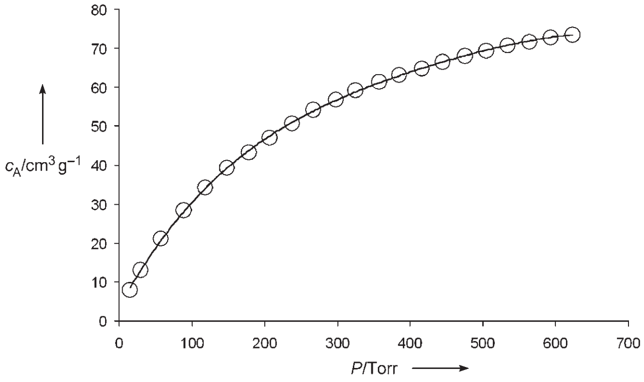

Figure 4. Hydrogen-sorption isotherm at 77 K of material **II**. c_A = concentration absorbed.

Experimental Section

γ-ZrP (0.3 g, 0.94 mmol) was suspended in water/acetone (130 mL, 2:8) and the mixture stirred vigorously and refluxed for 1 h. 4,4''-Terphenyldiphosphonic acid (183 mg, 0.47 mmol) was then dissolved in water/acetone (300 mL, 2:8) and the mixture slowly added at a constant rate of 0.65 mL min^{-1}. The reflux was continued for four days. After a standard work up, a solid was obtained (0.38 g; material **I**). This material was suspended in a 1 M solution of hypophosphorous acid (25 mL) containing a small amount of of 4,4''-terphenyldiphosphonic acid (15 mg), to compensate for possible losses of diphosphonate during the reaction, and the mixture was maintained overnight at 80 °C. After a standard work up, a solid was obtained (material **II**).

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