Chem. Mater. **2006,** *18,* 2781−2783 2781

Preparation, Characterizaton, and Catalytic Aerobic Oxidation by a Vanadium Phosphonate Mesoporous Material Constructed from a Dendritic Tetraphosphonate

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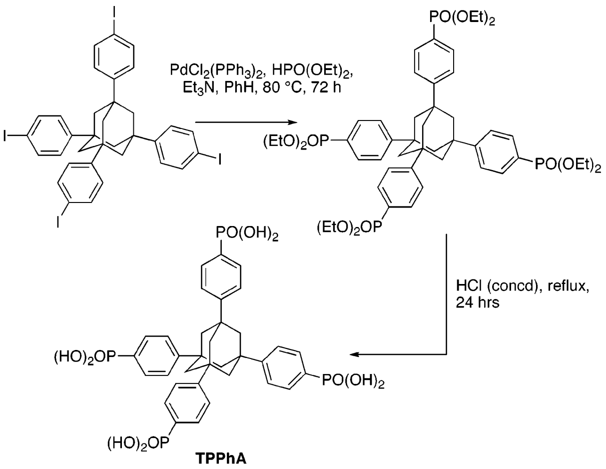
Received February 12, 2006
Revised Manuscript Received April 30, 2006

Metal organophosphonate materials are a prominent class of organic−inorganic hybrid materials.[1] They have gained increasing research interest as a result of their potential applications as sorbents, ion exchangers,[2] ionic conductors,[3] and catalysts.[4] Among all known metal organophosphonates, layered structures are predominant wherein aryl- or alkylphosphonate molecules are coordinated to the metal oxide layers with aryl or alkyl functional groups situated in the interlamellar space.[1a,5] The use of aryl biphosphonic acids gives rise to the formation of so-called pillared layered metal phosphonates.[1b,6] Alteration of the aryl biphosphonic acid pillars with smaller functions such as phosphoric, phosphorus, or methylphosphonic acids led to an increase in the surface area of the resulted hybrid materials due to the formation of pores.[1c,7] Moreover, this increase in porosity allows the metal centers of the metal phosphonate to be accessible to the adsorbed molecules, which can be particularly useful for catalysis.

Over the course of our research aimed at the development of new oxidation catalysts, our attention was drawn to vanadyl organophosphonates. This type of hybrid material is known mainly in two structural variants, namely, lamellar and tubular structures.[5b,8] Layered vanadyl organophosphonates evince an ability to intercalate alcohols and amines by coordination to the vanadium metal center.[9] However, their application to catalysis has been limited to their use as precursors for the vanadium phosphorus oxide catalysts.[10] We thought that the use of tetraphosphonic acid with an extended tetrahedral symmetry, as an example of a polytopic organic building block, could impede the close-packed arrangement of organic molecules in a metal−organic framework. Such an arrangement will permit pore formation and does not require "dilution" with additional building blocks. In addition, it allows interaction of the metal center with a substrate molecule. We have used such principles in the recent past to prepare similar titanium phosphonate materials.[11]

Scheme 1. Synthesis of the Tetradehdral Core, TPPhA



Thus, we now report on the synthesis of a new vanadium phosphonate material prepared by the non-hydrolytic condensation of a vanadium(V) alkoxide with an arylphosphonic acid, tetrakis-1,3,5,7-(4-phosphonatophenyl)adamantane (TPPhA), that has an extended and rigid tetrahedral configuration, Scheme 1. After the structural characterization by electron microscopy and sorption measurements, we further show that the vanadium phosphonate (TPPhA-V), is able to catalyze oxidation of benzylic alcohols under aerobic conditions.

Addition of 4 equiv of neat $V(O)(i\text{-}PrO)_3$ to 1 equiv of TPPhA dissolved in dry dimethylsulfoxide (DMSO) gave a green gel which was separated from the solvent by centrifugation; the residual DMSO was removed by thorough washing with H_2O, EtOH, and Et_2O and drying. The material obtained, TPPhA-V, was insoluble in all organic solvents and water. The elemental analysis of TPPhA-V, by energy-dispersive X-ray spectroscopy, provides a mean V/P ratio of 1:1. In addition, conventional elemental analysis gave C/H/P ratios, and thermogravimetric determination of

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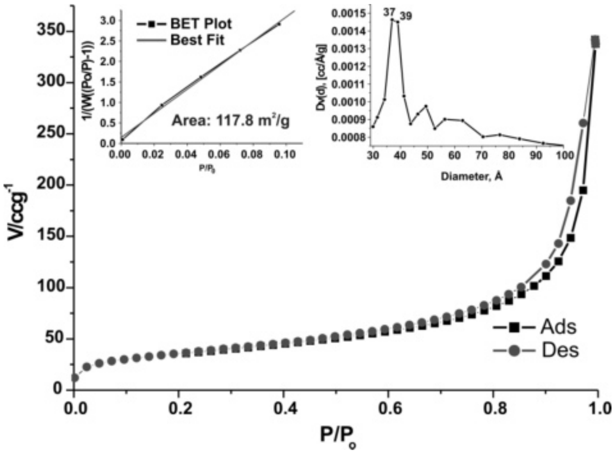

Figure 1. N_2 sorption isotherm for TPPhA-V related BET and BJH plots.

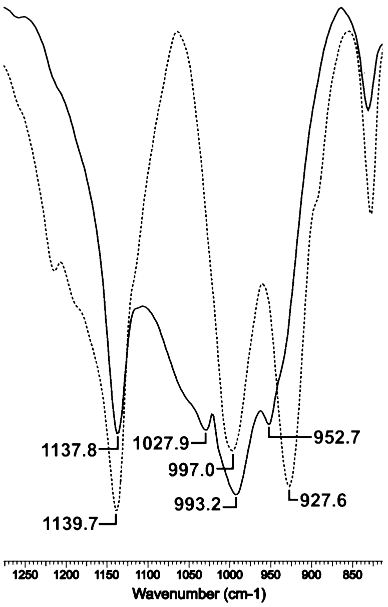

Figure 2. IR spectra of TPPhA (dotted line) and TPPhA-V (full line).

water allowed the prepared material to be formulated as $C_{34}H_{28}O_{16}P_4V_4 \cdot 10H_2O$.

The nitrogen sorption isotherm of TPPhA-V is consistent with a mesoporous material, Figure 1, with a surface area value of 118 m^2 g^{-1}.

The mesopore size distribution curve derived from the desorption branch of the isotherm using the BJH method (Figure 1, inset)[12] showed the main maximum corresponding to a pore diameter of 38−39 Å. Interestingly the pore size is the same as that observed for a similarly prepared titanium phosphonate, but the surface area is considerably lower.[11]

The Fourier transform infrared spectrum, Figure 2, of the dendron alone, TPPhA, shows absorption maxima characteristic for an alkylarylphosphonic acid ($\nu_{\mathrm{C-H(Ar)}}$, 3008; $\nu_{\mathrm{C-H(Alk)}}$, 2921 and 2850; $\nu_{\mathrm{C=C}}$, 1604; $\nu_{\mathrm{P=O}}$, 1139; $\nu_{\mathrm{P-O}}$, 997 and 928 cm^{-1}). Upon formation of the vanadium phosphonate, there are significant changes in the energies of the peaks associated with $\nu_{\mathrm{P-O}}$, and peaks may now be observed at 1028, 993, and 952 cm^{-1} indicating the formation of new P−O−V bonds. Notably, the P═O absorption band remains almost unchanged and points to the likelyhood that the oxygen atom of a P═O fragment does not bind to a vanadium atom. These results together with the elemental analysis suggest that the tetraphosphonic acid molecules are most plausibly connected through ArP(O)$O_2V_2O_2$(O)PAr units.

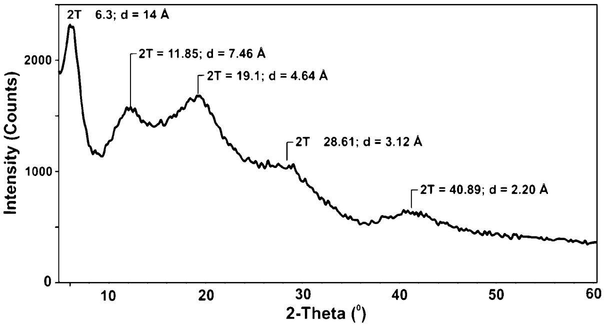

Figure 3. X-ray powder diffraction pattern (Cu Kα) of TPPhA-V.

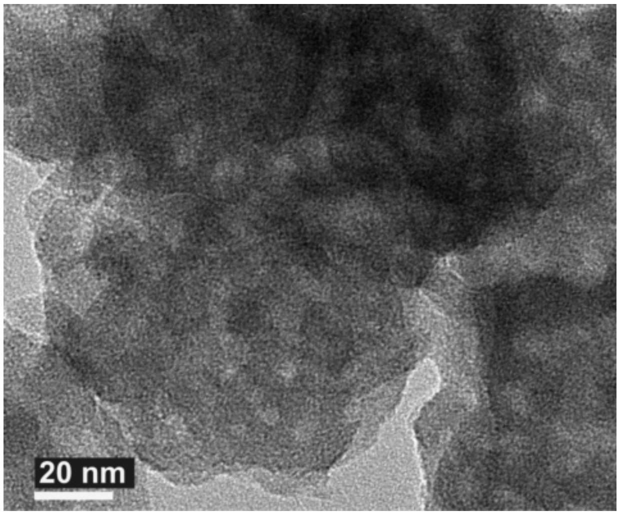

Figure 4. Typical TEM image of TPPhA-V.

The X-ray powder diffraction pattern (Cu Kα) of TPPhA-V, Figure 3, shows one strong and relatively broad peak at a 2θ value of 6.3° (d spacing 14 Å) and four broad low-intensive peaks at $2\theta = 11.85$, 19.1, 28.6, and 40.9° providing some evidence for periodicity in the material. Figure 4 shows a typical transmission electron microscope image of TPPhA-V in which the specimen appears to be granular with small highly contrasting dots situated within a more poorly contrasting substance. Observation of the edges of the specimen indicates that the TPPhA-V has a lamellar structure. Attempts to observe a two-dimensional electron diffraction pattern by means of transmission electron microscopy (TEM) were not successful.

Scanning electron microscopy (SEM) examination of the hybrid TPPhA-V material revealed formation of spongelike amorphous material as the only type of the specimen morphology, Figure 5. Dielectric properties of the material did not permit more highly magnified SEM images to be obtained.

Room-temperature electron spin resonance measurement of the TPPhA-V isotropic broad singlet resonance line indicated strong interaction between neighboring vanadium(IV) atoms, as is expected for the ArP(O)$O_2V_2O_2$(O)PAr structural units. Dilution of the sample by a solid-state

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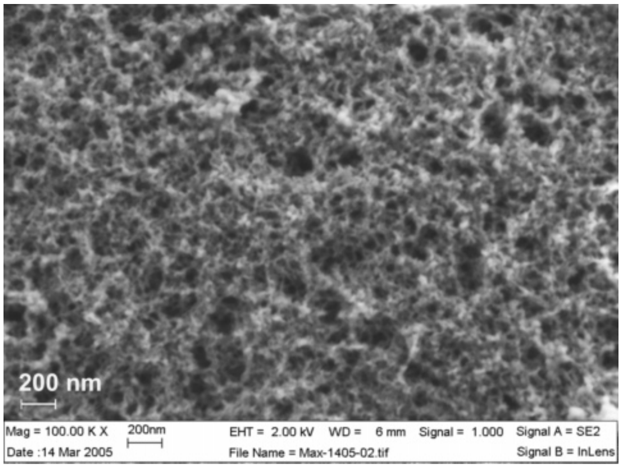


Figure 5. SEM image of TPPhA-V.

reaction, that is, grinding of TPPhA-V with a 10-fold excess of TPPhA gave rise to a material that showed the typical anisotropic V(IV) electron paramagnetic resonance (EPR) spectra with hyperfine splitting. The EPR parameters $g_{\|} = 1.948$ and $A_{\|} = 200-210$ G, and $g_{\perp} = 1.985$ and $A_{\perp} = 75$ G are similar to those observed for V(IV) vanadyl species.[13]

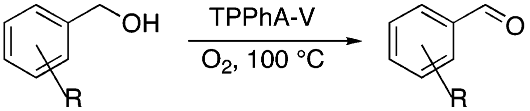
The catalytic properties of the TPPhA-V hybrid material were tested on the aerobic oxidation of benzylic alcohols. As one can conclude from the results collected in Table 1, the oxidation generally proceeded very smoothly with the formation of the corresponding benzylic aldehydes at high conversion and selectivity. Neither benzoic acid, a product of benzaldehyde overoxidation, nor ethers from acid condensation of the benzylic alcohol substrates were found in significant amounts as products in the reaction mixture, Scheme 2.

Table 1. Aerobic Oxidation of Benzylic Alcohol Substrates to the Corresponding Benzylic Aldehydes[a]

substrate	product	conversion, mol %	selectivity, mol %
$PhCH_2OH$	PhCHO	>99	96
4-$MeOPhCH_2OH$	4-MeOPhCHO	>99	98
4-$MePhCH_2OH$	4-MePhCHO	98	96
4-NO_2PhCH_2OH	4-NO_2PhCHO	92	>98
4-CF_3PhCH_2OH	4-CF_3PhCHO	>99	>98
4-pyridylCH_2OH	4-pyridylCHO	98	97
2,4,6-triMeCH_2OH	2,4,6-triMeCHO	56	79[b]

[a] Reaction conditions in a 15 mL glass pressure tube: 1 mmol of benzylic alcohol, 20 mg of TPPhA-V, 1 mL of toluene, O_2 at 2 bar, 100 °C, and 15 h. [b] The byproducts were 7% 2,4,6-trimethylbenzoic acid and 14% unidentified product (possibly 3,5-dimethylphthalide by GC-MS). Analysis was by GC and GC-MS.

Scheme 2. Aerobic Oxidation of Benzylic Alcohols Catalyzed by TPPhA-V



The poorer conversion and lower yield observed for the oxidation of 2,4,6-trimethylbenzyl alcohol compared to the other substrates suggested that the catalyst was shape selective, because there appeared to be little effect on the reactivity and selectivity in the reactions of the other substrates as a function of electron withdrawing (NO_2, CF_3) and electron dontating (MeO, Me) moieties.

We have prepared a new mesoporous vanadium phosphonate catalytic material that is effective for the aerobic oxidation of benzylic alcohol substrates. Some shape selectivity was observed. Future research will emphasize additional catalytic applications and preparation of additional phosphonates with other metals.

Acknowledgment. The research was supported by the Minerva Foundation and the Helen and Martin Kimmel Center for Molecular Design. Ronit Popovitz-Biro and Irakily Ebralidze are thanked for their help with the electron microscopy meausurements. R.N. is the Rebecca and Israel Sieff Professor of Organic Chemistry.

Supporting Information Available: Detailed experimental section (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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