of indium hydroxide and tin hydroxide in the presence of these polymers; this seems to be due to too strong interaction of these polymer with the metal hydroxides. Poly(acrylamide) is known to serve as coagulant of colloidal materials.[10]

The smoothness and transparency of the ITO film depended on the amount of added polymer, and the best results were obtaied at the concentration shown in the third column of Table I. Addition of larger amounts of the polymer caused an increase in the amont of volatile component during the heat treatment and hindered formation of the homogeneous ITO thin film. As shown in Table I, addition of less amount of poly(vinyl alcohol) was enough when the molecular weight of the polymer increased.

The present ITO film on the glass substrate can be prepared with good reproducibility. Due to the simplicity of the process to form the ITO film from simple compounds, the present process will serve as useful method for the preparation of the electrically conducting ITO thin films with large area.

Registry No. ITO, 50926-11-9; indium hydroxide, 20661-21-6; tin hydroxide, 12054-72-7; poly(vinyl alcohol), 9002-89-5; poly(2-vinylpyrrolidone), 9003-39-8; hydroxypropylcellulose, 9004-64-2.

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[10] Japan Analytical Chemistry Association, *Handbook of Polymer Analysis*; Asakura Syoten, 1962; p 443.

Crystal Structure of a New Lead Zinc Acetate Alkoxide, $Pb_2Zn_2(C_2H_3O_2)_4(C_3H_7O_2)_4$

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Sol–gel processing is a popular and versatile method for the preparation of glasses and ceramics in monolithic shapes, fine powders, fibers, and thin layers.[1] The first step in polymeric sol–gel processing is the synthesis of a solution containing the requisite metal cations. Commonly, the solution is comprised of metal alkoxides ($M(OR)_x$) in an alcohol solvent. Addition of water to an alkoxide solution results in hydrolysis followed by condensation reactions, network formation, and the eventual development of a continuous polymeric gel. The heterometallic alkoxides can be viewed as molecular precursors or "building blocks" for the development of gel networks and the synthesis of ceramic materials. While many alkoxides have been synthesized and used successfully in sol–gel processing, some metal alkoxides have low solubility, are difficult to prepare, and are not stable with time.[2] Consequently, the exclusive use of alkoxides for multicomponent sol–gel solutions is sometimes not possible, and often alternative precursors are necessary, especially for specific components.

Metal acetates are often used in combination with alkoxides in sol–gel systems due to their solubility, convenience, and thermolysis behavior. The formation of heterometallic species by the reaction of acetates with alkoxides has been reported,[3–5] and as will be described in the present research, metal acetates can react in alcohol to form a different type of precursor, a heterometallic acetate alkoxide. The structure and composition of precursors formed in solution should be characterized so as to obtain a better understanding of the hydrolysis and gelation reactions and for the control of final properties in the gel and the resulting ceramic. To this end, structural investigations of precursors isolated in single-crystal form provide valuable information.

In this report, the preparation and crystal structure of a heterometallic acetate alkoxide, $Pb_2Zn_2(C_2H_3O_2)_4(C_3H_7O_2)_4$, are described. Single crystals were isolated from a lead zinc acetate based precursor solution used for the sol–gel processing of lead zinc niobate, $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN),[6] a useful electrical ceramic. The sol–gel process is of interest for the fabrication of improved ceramic devices from chemically derived powders and for the spin-casting of thin layers from sol–gel precursor solutions. To prepare a multicomponent PZN solution, however, alternative precursors are necessary. Because lead and zinc alkoxides are difficult to synthesize and not commercially available, a lead zinc acetate based precursor has been developed. Used in combination with niobium alkoxide, the new precursor allows for the synthesis of a PZN solution and the subsequent preparation of ceramic powders and thin layers by sol–gel processing.[6]

To prepare a Pb, Zn precursor solution, $Pb(C_2H_3O_2)_2\cdot 3H_2O$ and $Zn(C_2H_3O_2)_2\cdot 2H_2O$ were combined in a 3:1 molar ratio, dissolved in 2-methoxyethanol (HPLC grade, 8 mol of alcohol/mol of Pb), and heated. Volatiles were removed by distillation until the temperature of condensing vapors reached 124 °C, the boiling point of 2-methoxyethanol. The solution was then diluted with 2-methoxyethanol, and the distillation repeated twice. The distillation procedure was necessary to remove water from the Pb, Zn precursor solution, which was subsequently combined with a water-sensitive niobium alkoxide. During the final distillation, the Pb, Zn precursor solution was concentrated to approximately 3 M, based on Pb content.[7] Small cube-shaped crystals formed at room temperature within 24 h. After 96 h, the crystals grew to between 1 and 10 mm. Chemical analysis indicated the formation of $Pb_2Zn_2(C_2H_3O_2)_4(C_3H_7O_2)_4$ (anal. found Pb, 0.406, Zn, 0.127, C, 0.214, H, 0.0361; calcd Pb, 0.383, Zn, 0.121, C, 0.222, H, 0.0370). The $Pb_2Zn_2(C_2H_3O_2)_4(C_3H_7O_2)_4$ crystals could be redissolved in 2-methoxyethanol[8] and were air and water sensitive.

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[1] Brinker, C. J.; Scherer, G. W. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*; Academic Press: New York, 1990 and references cited therein.

[2] Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: New York, 1978.

[3] Budd, K. D. Structure Evolution in Sol-Gel Derived Lead Titanate-Based Materials, and Application to the Processing of Dielectric Thin Layers. Ph.D. Thesis, University of Illinois, Urbana, IL, 1985.

[4] Thomas, I. M. *Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics, and Specialty Shapes*; Klein, L. C., Ed.; Noyes Publications: Park Ridge, NJ, 1988; p 2.

[5] Ramamurthi, S. D.; Payne, D. A. *J. Am. Ceram. Soc.* **1990**, *73*, 2547.

[6] Francis, L. F.; Payne, D. A. *Proc. 7th IEEE Inter. Sym. Appl. Ferro., ISAF '90*, submitted July 1990.

[7] For preparation of PZN alkoxide based solution, the concentration of the Pb, Zn precursor solution is ~1 M, and crystals do not form.

[8] The crystals were soluble in 2-methoxyethanol, but a precipatate eventually formed in solutions with higher concentrations (>0.5 M).

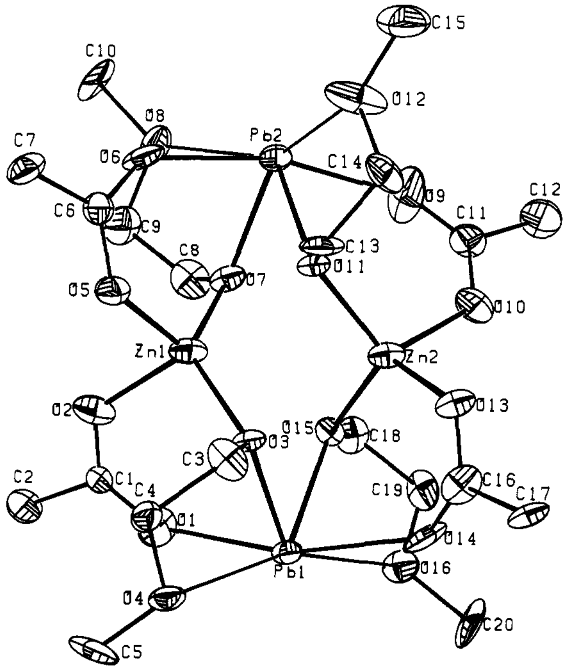

Figure 1. ORTEP plot (35% probability ellipsoids) of $Pb_2Zn_2(C_2H_3O_2)_4(C_3H_7O_2)_4$.

The heterometallic acetate alkoxide, $Pb_2Zn_2(C_2H_3O_2)_4(C_3H_7O_2)_4$, crystallizes in an unambiguous monoclinic crystal system.[9] Figure 1 shows the asymmetric unit, with atomic parameters listed in Table I and selected interactions given in Table II (supplementary material; see the paragraph at the end of the paper). The cyclic molecular unit is comprised of four metal atoms, alternating lead and zinc, roughly situated at the corners of a parallelogram. Each metal–metal edge is bridged by acetate and alkoxide ligands alternating above and below the parallelogram plane. The zinc coordination sphere forms an approximate tetrahedron; the mean Zn–O distance is 1.97 (1) Å with no deviations greater than 3σ; however, the range of O–Zn–O angles extends from 94.0 (6)° to 131.2 (5)°. The six-coordinate lead atoms are in grossly distorted octahedra. The distortion is probably due to Pb^{II} lone-pair repulsive interactions, as predicted by valence-shell electron-pair repulsion (VSEPR) theory.[10] There are three distinct Pb–O contacts: Pb–O(alkoxide), 2.26 (1) Å; Pb–O(acetate), 2.48 (2) Å; Pb–O(ether), 2.84 (2) Å. A chain of dimer units is formed roughly parallel to the *a* axis. There are no strong interactions between the extended chains, because they are insulated by aliphatic ligands.

Figure 2 shows the FTIR spectra for the crystals and a solution of crystals in 2-methoxyethanol.[11] The main feature of these spectra is a set of two bands near 1500 cm^{-1}, which can be assigned to the asymmetric (ν_{as}) and symmetric (ν_s) COO^- stretching vibrations of the acetate group.[12] The ν_{as} and ν_s bands appear at ~1574 and ~1410 cm^{-1} for the crystals (A). The frequency difference ($\Delta = \nu_{as} - \nu_s$, 164 cm^{-1}) is characteristic of bidentate acetate ligands, which can be either bridging between two metals or chelating to one metal atom.[12] A bridging configuration is confirmed by the crystal structure. For the crystals in solution (B), the ν_{as} and ν_s bands appear at ~1582 and ~1402 cm^{-1}, and Δ is 180 cm^{-1}. The upward shift in ν_{as} may indicate that the acetate groups are more weakly bound, but Δ is still within the range characteristic of bidentate groups (bridging or chelating). Since Δ is usually smaller for chelating ligands,[13] the acetate groups probably remain in a bridging configuration for the crystals in solution.

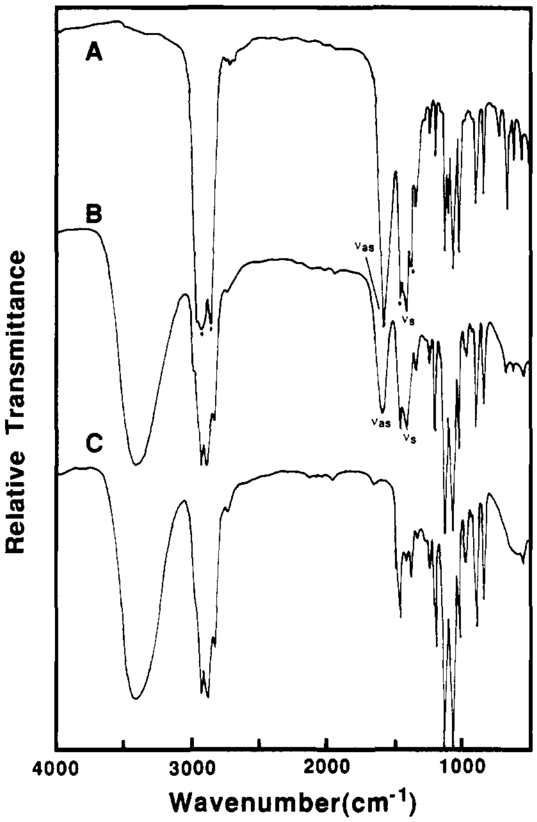

Figure 2. FTIR spectra of (A) crystal powder in mineral oil, (B) crystals dissolved in 2-methoxyethanol, and (C) 2-methoxyethanol. Bands due to mineral-oil are marked by ●.

The crystal structure of $Pb_2Zn_2(C_2H_3O_2)_4(C_3H_7O_2)_4$ demonstrates the formation of a new lead–zinc coordination compound that has important consequences for the preparation of a usable precursor solution. Anhydrous zinc acetate is soluble in 2-methoxyethanol only in the presence of lead. Therefore, the association between lead and zinc through bridging acetate and alkoxide groups allows for the preparation of a soluble precursor suitable for the sol–gel processing of electrical ceramic materials such as PZN. Moreover, the acetate alkoxide represents an alternative precursor for sol–gel processing, and the structure of lead zinc acetate methoxyethoxide is an example of the design of chemical precursors for the molecular building block approach to ceramic synthesis.

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(9) Crystal data: colorless, transparent, prismatic, 0.2 × 0.2 × 0.4 mm, monoclinic, $P2_1/c$ (C^5_{2h}); −75 °C, a = 10.820 (6) Å, b = 16.916 (8) Å, c = 17.824 (7) Å, β = 96.58 (4)°, V = 3241 (5) Å^3, Z = 4, ρ_{calc} = 2.217 g/cm^3. Experimental data: Enraf-Nonius CAD4 automated κ-axis diffractometer, graphite monochromator, Mo Kα radiation (λ = 0.71073 Å), $2\theta <$ 48.0° for $-h+k\pm l$, 5688 reflections, 5071 unique data (R_i = 0.024); corrected for anomalous dispersion, absorption (numerical transmission factor range 0.189–0.095), extinction (empirical isotropic parameter, 1.6 (2) × 10^{-8}), Lorentz and polarization effects. Solution: direct methods (SHELXS-86), metal positions deduced from E map. Refinement: least-squares (SHELX-76), 358 variables, 2658 observed data ($I > 2.58\sigma(I)$), R = 0.049 and R_w = 0.050; highest residual density (1.8 e/Å^3) in vicinity of lead atoms.

(10) See, e.g.: Wells, A. F. *Structural Inorganic Chemistry*; Oxford University Press: New York, 1962; p 902. Cotton, F. A.; Wilkinson, G.; Gaus, P. L. *Basic Inorganic Chemistry*; Wiley: New York, 1987; pp 79–92.

(11) Perkin Elmer, Model 1600. The crystal sample was a finely ground crystal powder dispersed in mineral oil and pressed between KBr plates. The solution sample was a 0.5 M solution of crystals in 2-methoxyethanol pressed between KBr plates.

(12) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986; pp 231–33.

(13) Doeff, S.; Henry, M.; Sanchez, C.; Livage, J. *J. Non-Cryst. Solids* 1987, *89*, 206.

Chem. Mater. **1990,** *2,* 647–649

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Supplementary Material Available: Listings of calculated atomic coordinates, anisotropic thermal parameters, and nonessential bond lengths and angles (4 pages); listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

Homogeneous Deposition of Palladium(0) into Sol–Gel-Derived Materials

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Using the sol–gel process,[2] solid oxide ceramic materials can be formed that exhibit numerous technologically important optical, mechanical, and electronic properties.[3] Composite materials containing small metal particles dispersed in an oxide matrix have recently attracted much interest for ceramic modification[3] and for the study of small metal colloidal catalysts.[4] Here we report a trialkoxysilane-promoted method for the homogeneous deposition of metal(0) species into sol–gel-derived materials at ambient temperatures during the sol formation process to generate metal particles approximately 15 Å in size. This method for metal(0) deposition should prove to have numerous applications including (1) ceramic modification, (2) supported heterogeneous catalyst preparation, and (3) third-order ($\chi^{(3)}$) nonlinear optical (NLO) enhancement of conjugated organic molecules in monolithic xerogels (precalcinated material) by surface plasmon enhanced Raman scattering.[5]

Metal(0) incorporation into sol–gel-derived ceramic oxides normally involves a four-step sequence including dissolution of the metal salt and $Si(OR)_4$ in an aqueous/organic solvent (ph < 3 or > 9) to allow for the gel formation, drying of the gel to form the xerogel, calcination in air (≥500 °C), and reduction of the metal salt to metal(0) in a hydrogen atmosphere at 300–900 °C.[6,7] The complete reduction of the metal is imperative to ensure homogeneity of the metal(0) species rather than regions of unreduced metal salts. Since reduction takes place after calcination, reduction occurs in the solid (or inhomogeneous melt), and homogeneity of the *metal(0)* can be difficult to obtain. With solid-phase reactions, metal surface reduction can occur without the uniform reduction of the entire particle.[7] Though this classical process is sufficient for many ceramic needs, the high temperatures required for both calcination and reduction to the metal(0) make the development of a milder approach desirable for the synthesis of xerogels containing metal(0).[8]

One distinct advantage in preparing xerogels (rather than calcinated materials) containing metal(0) lies in the ability to prepare novel metal(0), oxide-supported, heterogeneous catalysts. Supported metal catalysts that allow simple separation from the reaction products as well as repeated recycling are the most widely used catalytic systems, and the support is definitely instrumental in modifying the activity of the catalytic metal(0).[4b] These are most often prepared by the deposition of metals onto oxide supports followed by calcination and reduction, but the calcinated oxide material may be far less permeable to reactant molecules than the original xerogel.[2,3] For heterogeneous catalysis, metal(0) in the xerogel would allow the support to remain permeable to organic substrates, and unique catalytic activities should be observable. Accordingly, we recently demonstrated the excellent ability of this palladium-containing gel to act as a chemo- and stereo-

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(1) Recipient of an Office of Naval Research, Young Investigator Award (1989–92).

(2) (a) Hench, L. L.; West, J. K. *Chem. Rev.* **1990,** *90,* 33. (b) Hench, L. L.; Orcel, G. *J. Non-Cryst. Solids* **1986,** *82,* 1. Schubert, U.; Rose, K.; Schmidt, H. *J. Non-Cryst. Solids,* **1988,** *105,* 165. Deschler, U.; Kleinschmit, P.; Panster, P., DeVries, R. C. *Angew. Chem., Int. Ed. Engl.* **1986,** *25,* 236. For some of the original work, see: Roy, R. *J. Am. Ceram. Soc.* **1956,** *39,* 145. Roy, R.; Osborn, E. F. *Am. Mineral.* **1954,** *39,* 853.

(3) (a) For a comprehensive survey on the process and applications, see: *Science of Ceramic Chemical Processing*; Hench, L. L.; Ulrich, D. R., Eds.; Wiley: New York, 1986. (b) Also see: Ulrich, D. R. *Chem. Eng. News* **1990,** *68*(1), 28. Hench, L. L. *Mater. Res. Soc Symp. Proc.* **1988,** *125,* 189. Hench, L. L. *NATO ASI Ser., Ser. E* **1985,** *92,* 259. Hench, L. L.; Wang, S. H.; Nogues, J. L. *Proc. SPIE-Int. Soc. Opt. Eng.* **1988,** *878,* 76. Shoup, R. D. U.S. Patent 4,786,618, 1987. Roy, R. A.; Roy, R. *Mater. Res. Bull* **1984,** *19,* 169. Roy, R.; Komarneni, S.; Roy, D. M. *Mater. Res. Soc. Symp. Proc.* **1984,** *32,* 347. Subbanna, G. N.; Rao, C. N. R. *Mater. Res. Bull.* **1986,** *21,* 1465. Meng, G.-Y.; Huggins, R. A. *Mater. Res. Bull.* **1983,** *18,* 581. Uhlmann, D. R. *Bull. Am. Ceram. Soc.* **1983,** *62,* 380. Huynh, T. C. T.; Bleier, A.; Bowden, H. K. *Bull. Am. Ceram. Soc.* **1983,** *62,* 376.

(4) (a) Wang, Y.; Liu, H.; Jiang, Y. *J. Chem. Soc., Chem. Commun.* **1989,** 1878. Hirai, H.; Ohtaki, M.; Komiyama, M. *Chem. Lett.* **1986,** 269; **1987,** 149. Li, X.; Liu, H.; Jiang, Y. *J. Mol. Catal.* **1987,** *39,* 55. Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc* **1986,** *108,* 7228. Tamagawa, H.; Oyama, K.; Yamaguchi, T.; Tanaka, H.; Tsuiki, H.; Ueno, A. *J. Chem. Soc., Faraday Trans. 1* **1987,** *83,* 3189. Ueno, A.; Suzuki, H.; Kotera, Y. *J. Chem. Soc., Faraday Trans. 1* **1983,** *79,* 127. Sinfelt, J. H.; Via, G. H. *J. Catal.* **1979,** *56,* 1. de Jongste, H. C.; Ponec, V.; Gault, F. G. *J. Catal.* **1980,** *63,* 395. Jiang, X.-Z.; Stevenson, S. A.; Dumesic, J. A. *J. Catal.* **1985,** *91,* 11. Tauster, S. J.; Fung, S. C.; Garten, R. L. *J. Am. Chem. Soc.* **1978,** *100,* 170. Tauster, S. J.; Fung, S. C. *J. Catal.* **1978,** *55,* 29. Kunimorr, K.; Matsui, S.; Uchijima, T. *J. Catal.* **1984,** *85,* 253. Benson, J. E.; Boudart, M. *J. Catal.* **1965,** *4,* 704. Otero-Scripper, P. H.; Wachter, W. A.; Butt, J. B.; Burwell, R. L., Jr.; Cohen, J. B. *J. Catal.* **1978,** *53,* 414. Anderson, J. R. *Structure of Metallic Catalysts*; Academic Press: New York, 1975. Braunstein, P.; Devenish, R.; Gallezot, P.; Heaton, B. T.; Humphreys, B. J.; Kervennal, J.; Mulley, S.; Ries, M. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 927. Christmann, K.; Ertl, G. *J. Mol. Catal.* **1984,** *25,* 31. Sachtler, W. M. H. *J. Mol. Catal.* **1984,** *25,* 1. b. Sinfelt, J. H. *Sci. Am.* **1985,** *253,* 90. Ponec, V. *Adv. Catal.* **1983,** *32,* 149. (b) Sinfelt, J. H. *Bimet. Clust. Catal.* **1977,** *10,* 15. Guczi, L. *J. Mol. Catal.* **1984,** *25,* 13. Biswas, J.; Bickle, G. M.; Gray, P. G.; Do, D. D.; Barbier, *J. Catal. Rev. Sci. Eng.* **1988,** *30,* 161.

(5) Haus, J. W.; Kalyaniwalla, N.; Inguva, R.; Bloemer, M.; Bowden, C. M. *J. Opt. Soc. Am.* **1989,** *6,* 797. Haus, J. W.; Kalyaniwalla, N.; Inguva, R.; Bowden, C. M. *J. Appl. Phys.* **1989,** *65,* 1420. For an overview of NLO, see: Williams, D. G. *Angew. Chem., Int. Ed. Engl.* **1984,** *23,* 690. *Nonlinear Optical Properties of Organic and Polymeric Materials*; Williams, D. J., Ed.; ACS Symposium Series 233; American Chemical Society: Washington, DC, 1983. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J. S., Eds.; Academic Press: Orlando, FL, 1987. *Organic Materials for Non-Linear Optics*; Hann, R. A., Bloor, D., Eds.; Royal Society of Chemistry: London, 1989. Prasad, P. N. *Mater. Res. Soc. Symp. Proc.* **1988,** *109,* 271. Prasad, P. N.; Perrin, E.; Samoc, M. *J. Chem. Phys.* **1989,** *91,* 2360. Zhao, M.-T., Singh, B. P.; Prasad, P. N. *J. Chem. Phys.* **1988,** *89,* 5535.

(6) For Ni incorporation, see: Tohji, K.; Udagawa, Y.; Tanabe, S.; Ueno, A. *J. Am. Chem. Soc.* **1984,** *106,* 612. For Fe, see: Tanabe, S.; Ida, T.; Suginaga, M.; Ueno, A.; Kotera, Y.; Tohji, K.; Udagawa, Y. *Chem. Lett.* **1984,** 1567. Akiyama, T.; Tanigawa, E.; Ida, T.; Tsuiki, H.; Ueno, A. *Chem. Lett.* **1986,** 723. For Rh incorporation, see: Seiji, T.; Koga, F.; Tanabe, S.; Ueno, A.; Kotera, Y. *Nippon Kagaku Kaishi* **1984,** 998; *Chem. Abstr.* **1984,** *101,* 44044a.

(7) A method was recently described for the deposition of Pd(0) in sol–gel-derived materials by reduction of PdO to Pd(0) after calcination; however, no X-ray determination of the metal oxidation state was presented. Schubert, U.; Amberg-Schwab, S.; Breitscheidel, B. *Chem. Mater.* **1989,** *1,* 576.

(8) The term xerogel is used for materials that can readily absorb and desorb water, unlike the final calcinated glass materials. See ref 2a for a detaled explanation.

0897-4756/90/2802-0647$02.50/0