New families of supermicroporous metal oxides: the link between zeolites and mesoporous materials

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Sol–gel hydrolysis reactions in propanol of two or more metal acetates or alkoxides in *n*-alkylamines have been found to yield porous mixed oxides with the presence of pores largely in the 10–20 Å region.

Intense research activity in the synthesis, structural elucidation and properties of mesoporous materials has resulted from the discovery of MCM-41 type mesoporous molecular sieves.[1,2] By using surfactants with moderately long alkyl chain lengths, pores in the 20–100 Å range are routinely obtained.[3] The literature is now quite extensive and many new synthetic procedures have been described. The well known zeolites are more highly crystalline than the mesoporous materials, but are limited to about 10 Å useful pore size.[4] Our goal was to fill the gap between the two types of porous materials by synthesizing oxides with pores in the 10–20 Å range. Here we report the synthesis of a family of mixed oxides with supermicropores largely in the 10–20 Å range using a sol–gel procedure with propanol as the solvent.

Maier *et al.*[5] prepared amorphous titania–silica from their alkoxide solutions in ethanol by acid hydrolysis, giving an average pore size of 7 Å. Ying[6] has reported the synthesis of porous niobium oxide with pore sizes below 20 Å. The procedure involved use of diamines as templates in ethanolic solutions of niobium ethoxide, subjected to hydrothermal treatment. In another procedure[7] adamantanamine was used as a template in ethanol to produce high surface area silica (737 m^2 g^{-1}) with pores in the 13–17 Å range. Ying[8] also reported the preparation of mixed zirconia–silica catalysts using cetyltrimethylammonium bromide (CTAB) as the template. Precipitation was effected by aqueous HCl hydrolysis. Several of these preparations exhibited pore dimensions in the order of 16 Å. Our procedure is very general, applicable to a wide range of mixed oxides.

We will illustrate our findings with examples from several systems we have studied. The inorganic precursors are most often metal acetates and the surfactant hexylamine or octylamine, although other amines may be used. The reactions are carried out in propanol–water mixtures in the presence of hexylamine. The general procedure is to add the metal acetates to propanol and stir until the solid is uniformly distributed. Then hexylamine is added and the mixture stirred overnight to achieve a homogeneous solution or a thixatropic gel. Then $(NH_4)_2HPO_4$ may or may not be added, followed by a water–propanol mixture, followed by refluxing for 3 d. The solid is collected by centrifuging, washed thoroughly with 95% ethanol and dried at 55 °C. Similar experiments were carried out where the mixture was treated hydrothermally at temperatures between 120–170 °C for different lengths of time.

The mixtures contain a substrate oxide which, in the cases described, are either zirconia, titania, silica or silica–alumina, together with a transition metal oxide. Tetraethyl orthosilicate (TEOS) is used as the source of silica, and aluminium tri-*sec*-butoxide as the source of aluminium.

A mixture of basic acetates of chromium, $(CH_3CO_2)_7Cr_3(OH)_2$ and zirconium, $Zr(OH)_{2.64}(CH_3COO)_{1.36}$ were dispersed in propanol and treated as indicated above. The ratio of reactants Zr : Cr : P was 1.0 : 1.81 : 0.59 at concentrations in propanol of 0.0628 : 0.114 : 0.043 M. One sample was refluxed and another treated hydrothermally at 170 °C, both for 3 d.† The yield of product for the hydrothermal sample (identified as **98b**) was 75% Cr and 86% Zr. Yields for the refluxed sample (identified as **98a**) were lower—68% Cr and 80% Zr. In both samples the amount of hexylamine used corresponded to 0.92 moles per mole of acetate group. In a subsequent experiment the amount of amine was increased to three moles of amine per mole of hydrolysable acetate. In this case the yields were higher (89% Cr, 98% Zr). Reduction of amine to 0.46 moles per mole of acetate lowered the yields considerably (25%). The amount of amine incorporated into the precipitated oxide mix depended upon the amount added—being approximately 9% for the least and 21.2% for the highest amount utilized. The total phosphate added in the synthesis was only 0.265 mol per mol of metal which was added to increase the stability of the oxide mixture. However, subsequent preparations could be stabilized to the same extent without phosphate additions by adjusting the preparation method.

Sorption–desorption isotherms for the mixed chromia–zirconia oxides were obtained using the N_2 sorption method. The solid samples were heated for 24 h at a number of predetermined temperatures and outgassed for 10 h before the collection of isotherm data. The isotherms for sample **98a** are shown in Fig. 1a and the pore size distribution of the sub-sample heated to 414 °C in Fig. 1b. Up to about 500 °C the isotherms are of type I, indicative of a microporous structure with a narrow pore distribution. This expectation is fulfilled, as shown in Fig. 1b. At about 520 °C the nature of the isotherm changes to a pseudo Type IV, signifying the presence of larger pores. In Table 1 we list the total surface areas for the refluxed and hydrothermally treated samples and their surface areas due to micropores. Surface areas decrease as the temperature of preheating is increased, but the maxima in the pore size distribution curve remains in the 10–20 Å region.

For the hydrothermally prepared sample, the isotherms were all type IV, even for samples preheated at 260 °C or less. The data for

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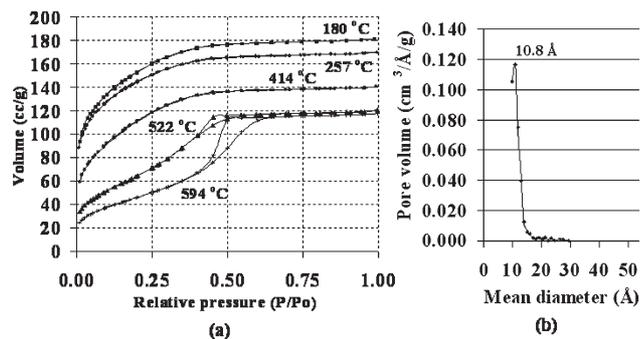
Fig. 1 N$_2$ sorption–desorption isotherms for a chromia–zirconia mixed oxide (**98a**) (a) as a function of temperature and (b) the pore size distribution obtained of the isotherm of the sub-sample of it heated to 414 °C by the MP method.

Table 1 BET and micropore surface areas for chromia–zirconia samples **98a** (refluxed) and **98b** (hydrothermal), calcined at different temperatures.

Calcination temperature/°C	BET surface area/m^2 g^{-1}		t-Method micropore surface area/m^2 g^{-1}		Maximum in pore size distribution curve/Å	
	98a	98b	98a	98b	98a	98b
180	559	630	556	608	8.7	14.4
257	501	555	498	541	9.2	15.6
410	384	365	381	336	9.8	17.1
520	239	277	234	259	12.8	19.1
613	151	173	144	—	16.9	—

the various samples are collected in Table 1 and indeed show that the pores are approximately 6 Å greater, but the maxima in the pore distribution curves are still in the micropore region. A small portion of the pores were also in the 20–30 Å range. The isotherm recorded at 613 °C, in the case of sample **98b**, indicated the loss of any regularity in the pore structure.

X-ray patterns showed that the samples for the most part were completely amorphous. However in some cases, a single peak with a *d*-spacing in the 25–30 Å range was observed. Fig. 2 is a transmission electron micrograph of the mixed Cr$_2$O$_3$–ZrO$_2$ sample heated to 414 °C. The particles are quite small (less than 1μm) and have no regular shape. The pores also do not have a regular arrangement, as do templated mesoporous silicas. Micrographs such as these indicate that the pores are textural,
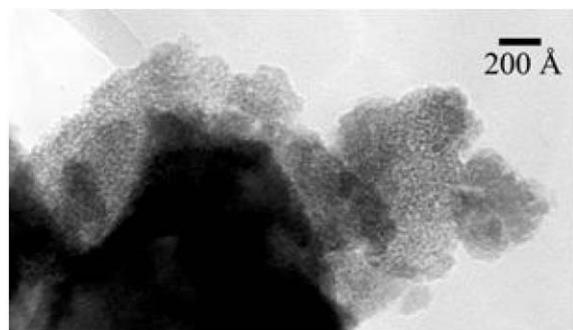
Fig. 2 Electron micrograph of a chromia–zirconia porous solid pre-heated to 414 °C.

that is, formed by the framework with thin walls. For this reason they are not as stable as the mesoporous, templated, more regularly structured oxides. The TGA data for the refluxed sample (**98a**) show that the total weight loss to 850 °C was about 40%. This higher weight loss with respect to the hydrothermal samples resulted from a greater retention of amine and some acetate. The weight loss begins immediately when heating commences, even though the sample was preheated to 60 °C. This low temperature weight loss is undoubtedly due to sorption of water by the micropores during exposure to air. The organic component is predominantly lost below 300 °C, with only an additional 1% lost to 800 °C. We have obtained similar results to those reported here with V$_2$O$_5$–ZrO$_2$, CoO–ZrO$_2$, NiO–ZrO$_2$, CuO–ZrO$_2$ and low loadings (1–3%) of palladium in ZrO$_2$, Cr$_2$O$_3$–TiO$_2$ and CuO–TiO$_2$.

A mixture of nickel acetate and TEOS, to which phosphate was added in the ratio of Si : Ni : P of 1 : 0.5 : 0.43, was refluxed in a mixture of propanol (500 ml) and hexylamine (35.66 g) for 24 h. The isotherm obtained (Fig. 3a) after heating the solid at 252 °C for 24 h and outgassed overnight at 234 °C, yielded a surface area of 508 m^2 g^{-1} of which 485 m^2 g^{-1} in the form of micropores. The micropore distribution curve (Fig. 3b) indicates that micropores are mostly between 10 and 20 Å in diameter with a small volume in the 20 to 27 Å range. The curve maxima was approximately 14 Å. Reheating the sample to 650 °C reduced the surface area to 383 m^2 g^{-1}, of which 92% resulted from micropores, but shifted the maxima in the pore distribution curve to approximately 16 Å. The micropore volumes were 0.227 cm^3 g^{-1} for the sample heated at 252 °C and 0.310 cm^3 g^{-1} for the sample heated to 650 °C. There was only a trace of phosphorus in the solid.

Addition of 4–20 mol% of alumina in the form of aluminium tri-*sec*-butoxide, [Al(OCH(CH$_3$)C$_2$H$_5$)$_3$] produced mixed oxides with much higher surface areas and stabilities. As an example, a mix was prepared where the ratio of Si : Al : Ni : amine was 1 : 0.0455 : 0.250 : 1.622. The corresponding ratio in the product was 1 : 0.0565 : 0.312 : 0.314. The increase in proportion of aluminium and nickel indicates that upwards of 20% of the silicon tetraethoxide remained in solution. The N$_2$ isotherms of the samples heated to different temperatures are shown in Fig. 4a. The surface areas derived from the isotherms are 960, 807 and 317 m^2 g^{-1} for preheating temperatures of 281, 520, and 800 °C respectively. The pore size distribution derived from the 800 °C isotherm is shown in Fig. 4b. An alumina–silica sample of the
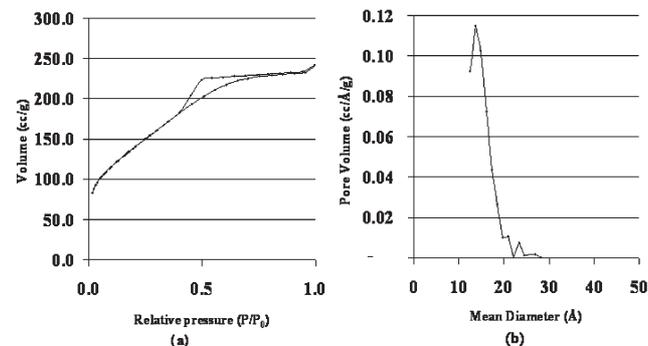
Fig. 3 (a) The N$_2$ sorption–desorption isotherm for NiO–SiO$_2$ preheated to 252 °C. (b) Pore size distribution curve for isotherm (a), as determined by the MP method.
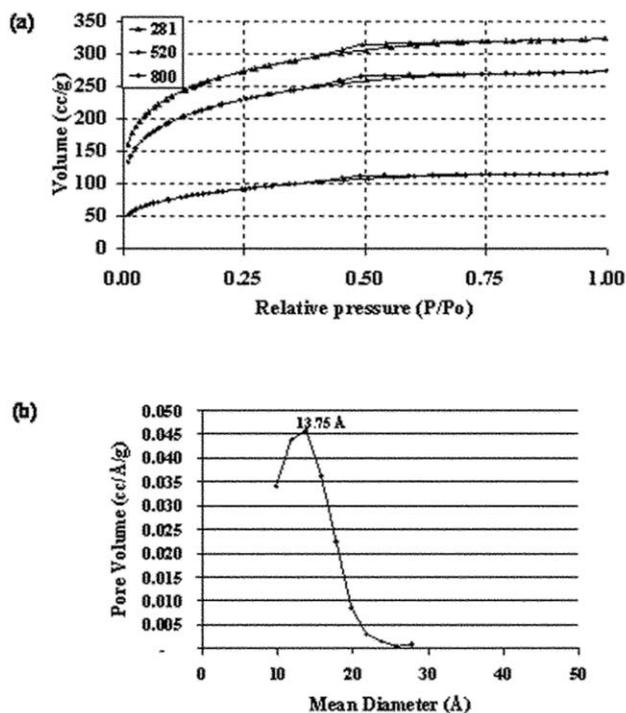
Fig. 4 (a) N_2 sorption–desorption isotherms of single phase silica–alumina nickel oxide preheated at the indicated temperatures. (b) The pore size distribution curve for SiO_2–Al_2O_3–NiO (1 : 0.056 : 0.312) preheated to 800 °C.

same composition, but with no Ni^{2+} added, was prepared and heated to 234 °C. The ^{27}Al MAS solid state NMR spectrum showed a chemical shift of 53.8 ppm and the ^{29}Si NMR spectrum comprised chemical shifts of -115.9 and -108.8 ppm. These results indicate that the aluminium is tetrahedrally coordinated and that a significant portion of the silica has an environment that includes one aluminium.

Pinnavaia[9,10] and co-workers have shown that solvents of different polarity have a profound effect on the nature of the porosity of mesoporous silicas in the S°I° synthesis method. They reported that a water–ethanol solvent mix with a high alcohol content yielded a solid that contained almost all framework pores. In contrast, a water rich system gave textural pores majoritarily because of the sub-micron size of the particles. At calcination temperatures below 400 °C the Cr–Zr–P system isotherms are characteristic of framework microporosity with a wormhole structure of short range order, but with no order of the type shown in Pinnavaia's study. Above 450 °C some walls collapse to form larger pores (+ 100 Å) and more textural porosity. Some loss of surface area is due to the appearance of a particle shape reminiscent of crystallization in a fraction of the particles. It is unlikely that the hexylamine formed a micelle because the amount added exceeded the amount required for critical micelle formation. In fact, the role of the amine appears to be as an agent of hydrolysis as well as of pore formation. When the amine is omitted, mostly non-porous structures or mesoporous solids, with

a broad range of pore sizes, are obtained. If 50% less amine is used, incomplete hydrolysis results in low yield of the mixed oxide.[11] Another interesting point is that much of the amine is removed at relatively low temperatures, any residual acetate, is removed by approximately 350 °C—as shown by IR spectroscopy and TGA. Higher temperatures may be required for oxide mixtures which do not contain an oxidizing component. Investigations into the structure of these mixed oxides and their potential role in catalysis is under way.

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Notes and references

† Basic chromium acetate (18.18 g , 0.0301 mol) and basic zirconium acetate $Zr(OH)_{2.64}(OOCCH_3)_{1.36}$ (10.8 g, 0.050 mol) were added to propanol (636 g) and stirred for several hours while hexylamine (26 g, 0.2569 mol) was added dropwise to produce a clear solution. $(NH_4)_2HPO_4$ (3.9 g, 0.0295 mol) was added as a solid and stirred to disperse it uniformly. A mixture of water (145 g) and propanol (206 g) was then added dropwise to the solution of oxides with vigorous stirring, followed by refluxing for 3 d. A second batch was heated at 170 °C hydrothermally for 3 d. Both products were washed with ethanol, then water and dried at 55 °C. Elemental analysis of the hydrothermally treated sample—Found: Zr, 19.06; Cr, 17.54; P, 4.48; C, 11.44; H, 3.90; N, 2.33. $ZrO_2(Cr_2O_3)_{0.807}(P_2O_5)_{0.723}(CH_3(CH_2)_5NH_2)_{0.796}\cdot2.8\ H_2O$ requires Zr, 19.02; Cr, 17.51; P, 4.67; C, 11.97, H 3.69; N, 2.33%. TGA weight loss—Found 27.1%, requires 27.37%. Two steps were observed: water loss from room temperature to 150 °C, $\sim$10% and the organic, $\sim$17% from 150–250 °C.

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