Macroporous materials from crystalline single-source precursors through decomposition followed by selective leaching

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There are a number of pairs of elements A and B in the periodic table that do not form binary oxides A_xB_yO. We have used this fact to seek out crystalline precursors containing such metals that can be decomposed at elevated temperatures to form intimate mixtures of the individual oxides, A_xO and B_yO. Selective leaching of one of these oxide components from the monolithic mixture results in a macroporous material. We demonstrate this scheme by decomposing a hydroxy double salt containing Ni and Zn. The ZnO from the decomposition product can be leached out, leaving behind a macroporous NiO monolith that can be further reduced to yield porous metallic Ni.

Introduction

Porous solids are of interest due to their potential application as sorbents,[1] catalysts and catalyst supports,[2] filters,[3] light-weight structural materials[4] and in photonic band gap applications.[5] While microporous solids such as zeolites have perfectly defined pores of the order of a few Å and are crystalline solids,[6] mesoporous solids with pore sizes in the range of 10–100 Å comprise non-crystalline walls enclosing relatively monodisperse pores which are ordered on a lattice.[7] Mesoporous solids are prepared using complex surfactant assemblies as templates. Attention has also been focussed on macroporous solids with pore sizes in the range 1000 Å to a few mm. These are usually prepared by physically holding together small crystallites, with an organic binder for example, in such a manner that the particles do not pack densely. When this composite is calcined, the organic binder burns away leaving behind connected pores in an inorganic network.[8]

An interesting new approach to highly ordered macroporous materials has recently emerged that starts from carefully prepared ordered arrays of oil droplets in water. The hydrolysis of metal alkoxides in the aqueous part of this ordered structure results in a periodic macroporous inorganic network.[9] Following this work, a number of authors have reported the use of crystalline arrays of polystyrene or silica spheres—so-called colloidal crystals. The voids in these colloidal crystals are filled with inorganic materials (metals, oxides, etc.) and then the colloidal template is removed in a "lost-wax" process either by dissolution or calcination, leaving behind a periodic macroporous structure. Macroporous materials made in this manner include SiO_2, TiO_2, ZrO_2 and some zeolites,[10] polymers,[11] semiconductor chalcogenides,[12] and metals.[13] These have recently been reviewed.[14]

Other templating methods have also been employed to obtain macroporous solids. For example, echinoid skeletal plates (the skeletal plates of sea-urchins) have been used as templates to make periodic macroporous gold structures.[15]

It must be noted that in all these routes, the template must be preformed (a colloidal crystal, an emulsion or a pre-existing macroporous structure) or involve some physical process (the mixing of a binder with an inorganic material). Here we describe a novel one-pot route to macroporous solids, starting from a crystalline compound or solid solution comprising two metallic elements. We chose our system and reaction conditions in such a way that we are able to obtain, through decomposition of the precursor, a composite comprising a random distribution of small particles of two daughter phases; one of the new phases is then selectively dissolved, leaving behind the other phase in a macroporous structure. Moreover, the fact that two immiscible phases are formed will tend to inhibit grain growth so that very high surface area and open porosity can be achieved. Fig. 1 displays an illustration of this scheme. In a sense, the manner in which one precursor decomposes into two is reminiscent of spinodal decompositions of binary mixtures in the temperature–composition plane. We have chosen to work with a Ni compound because of the applications of NiO in catalysis[16] and of porous Ni in electrochemistry.[17] Perusal of the JCPDS database suggests that there is no known crystalline binary oxide that contains both Ni and Zn. Since ZnO is well known to be soluble in alkaline media, and since hydroxy double salts of Ni and Zn are known, the compound $Ni_3Zn_2(OH)_8(CH_3COO)_2 \cdot 2H_2O$[18] suggested itself as a precursor.

Early work by Morgan[19] on the decomposition of dolomite $CaMg(CO_3)_2$ during reactive hot-pressing to yield fine mixtures of MgO and CaO particles, and more recent work by Suzuki et al.[20] on the preparation of porous $MgO/CaZrO_3$ composites by reactive hot-pressing of dolomite with ZrO_2, have led the way in exploiting the decomposition of single-source crystalline precursors into two immiscible (commonly nanophase) components. Superplasticity displayed during the formation of such phases has been studied.[21] Unidirectionally porous oxides have been prepared by Suzuki et al.[22] through the use of eutectic reactions.

Recently, the formation of nanoporous structures on selective chemical leaching of Ag from Ag–Au alloys has been reported,[23] suggesting that, in certain systems, the equivalent of phase segregation can occur concurrently with leaching.
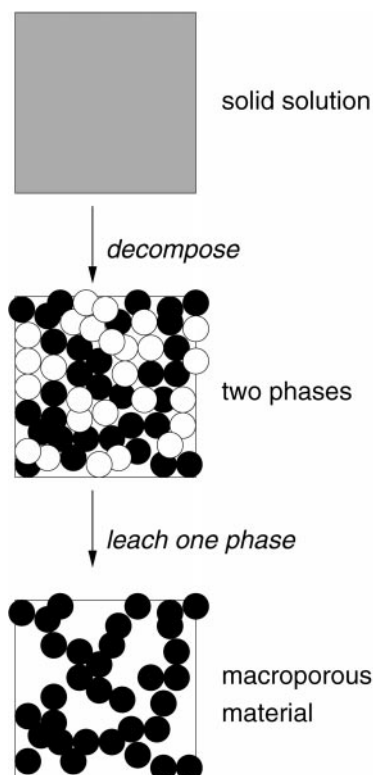
Fig. 1 Scheme showing the decomposition of a monolith comprising a single phase into two immiscible phases from which one can be leached, leaving behind a porous network of the other.

Experimental

Nickel zinc hydroxyacetate, $Ni_3Zn_2(OH)_8(CH_3COO)_2\cdot 2H_2O$ was prepared by a procedure reported by Morioka *et al.*[18] ZnO powder (0.033 mol) was added to 200 ml of an aqueous solution containing 0.050 mol of $Ni(CH_3COO)_2\cdot 6H_2O$ with vigorous stirring. The mixture was then aged at 65 °C for 2 days in an air oven. The green solid obtained was washed free of ions, filtered and dried at 65 °C to constant weight.

About 500 mg of the hydroxyacetate was pressed into a pellet approximately 3 mm thick and 10 mm in diameter. This pellet was heated in air at 400 °C for 6 h to obtain the NiO–ZnO composite. The decomposed pellet was then pressed again, without regrinding, and heated at 1000 °C in air for 24 h. The repressing was necessary to preserve the integrity of the pellet. The resultant sintered pellet was soaked in 4 N NaOH at 65 °C for 2 days to leach out the ZnO. During the repressing/resintering steps, a slight shrinkage of the pellet is observed, but the leaching does not result in any shape change. The NiO pellet obtained by leaching out the ZnO was washed throughly by soaking in deionized water for 2 days, with periodic replacement of water. The dried pellet could be reduced to Ni metal in a $15\%H_2$–Ar atmosphere at 500 °C for 3 h. During each of these stages, the sample was characterized by X-ray diffraction and scanning electron microscopy.

Powder X-ray diffraction (XRD) patterns were obtained on a Siemens D5005 diffractometer operated in reflection geometry. Data were collected with Cu-Kα radiation using a typical continuous scan rate of $2°\ min^{-1}$. Scanning electron micrographs were recorded on a Jeol JSM 5600 LV from samples mounted on brass stubs using conducting carbon tape. The samples were sputter coated with gold to improve conductivity.

Results and discussion

The IR spectrum and XRD pattern of the crystalline precursor, shown in Fig. 2(a) and (b), respectively, confirm that the
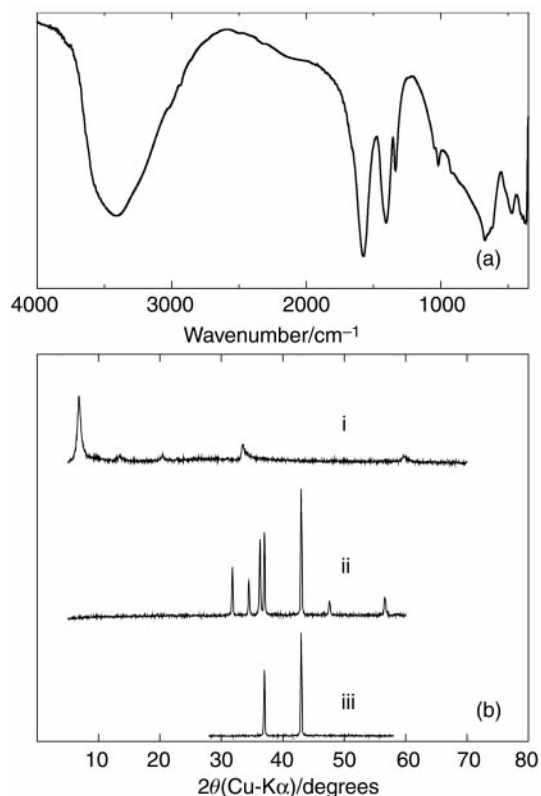

Fig. 2 (a) FTIR spectrum of the starting material, the Ni–Zn hydroxy double salt, $Ni_3Zn_2(OH)_8(CH_3COO)_2\cdot 2H_2O$. (b) Powder XRD patterns of (i) the starting compound, (ii) the decomposition product, comprising a mixture of NiO and ZnO, and (iii) the porous NiO that is left behind when the ZnO is leached out.

compound formed is indeed the layered hydroxyacetate, $Ni_3Zn_2(OH)_8(CH_3COO)_2\cdot 2H_2O$.[18] In the IR spectrum, peaks are observed at 1575, 1400, 1340 and 1020 cm^{-1} due to acetate ions that are held between the inorganic slabs in the structure. The interlayer distance calculated from the first XRD peak (12.9 Å) matches well with what was reported by Morioka *et al.*[18] Thermogravimetry of this compound (not shown here) indicates that it decomposes around 300 °C.

The XRD patterns of a sintered pellet of the decomposed hydroxyacetate and the same pellet after soaking in 4 N NaOH for 2 days at 65 °C are displayed in Fig. 2(b). The decomposition of the hydroxyacetate gives rise to a mixture of NiO and ZnO. This is as expected, since NiO and ZnO are not known to form either a solid solution or a compound. In the XRD pattern of the alkali-leached pellet the peaks due to ZnO have vanished, indicating complete dissolution of ZnO. Weight loss measurements and EDAX corroborate this observation. On reduction with $15\%H_2$–Ar at 500 °C for 3 h, the NiO pellet is completely reduced to Ni metal, as verified by XRD (not shown).

An SEM image of the sintered NiO–ZnO pellet obtained by decomposition of the hydroxyacetate precursor is displayed in in the top panel of Fig. 3. A dense, well-packed surface is observed for this pellet. The middle panel of Fig. 3 shows a micrograph of the pellet after leaching with alkali, and the bottom panel, the same pellet after reduction with H_2–Ar at 500 °C. The leached product shown in the middle panel and the leached/reduced product in the bottom panel possess a large number of connected pores with a typical size of 1 μm.

We have analyzed the distribution of pores by digitizing the micrographs on a two-dimensional grid with a cell resolution of about 1 μm. This allows us to pick out patterns on this scale, ignoring levels in the organization that might be smaller. Such digitization permits the ratio of empty to filled cells to be
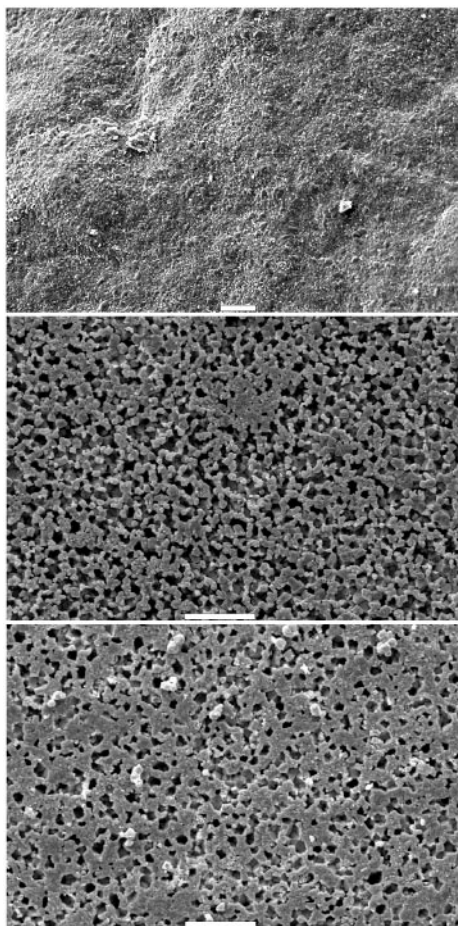
Fig. 3 Top: SE micrograph of a portion of the pellet of the decomposed product displaying a rather dense packing of crystallites. Middle: the pellet after the ZnO component has been leached away as described in the text. Bottom: porous Ni obtained by reducing the porous NiO pellet. The bars are 10 μm.

Fig. 4 SE micrographs of cross-sections of the porous Ni pellet, indicating that the pore structure is preserved through the monolith. The bars are 10 μm (top) and 1 μm (bottom).

and through pressure applied in the process of making the pellets.

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calculated at this cell resolution. It is known that the area of each constituent element in an aggregate (from a random cross-section) is directly proportional to its volume.[24] The volume ratio of the pores can thus be obtained from an analysis of cross-sectional micrographs. For the porous NiO micrograph, we obtain a ratio of void grid cells to total cells of 0.43 suggesting 43% porosity at 1 μm resolution. It must be emphasized that this value is not a measure of the total porosity. For the reduced porous Ni monolith, we similarly obtain a pore volume of 41% suggesting that the process of reduction does not change the pore sizes and their distribution.

One of the problems faced in demonstrating the connected nature of the pores is that on the surface of the pellets, there is some sintering which tends to mask the pores. We have therefore broken the pellet and recorded SE images of the cross-section. Fig. 4 displays these for the Ni pellet at two different magnifications. It is clear from these micrographs that the porous structure propagates throughout the entire material.

To summarize, we present a novel route for preparing monolithic macroporous materials starting from single-source crystalline precursors. The method should have wide applicability and is limited only by the conditions that, for the two metals taken, the corresponding oxide phases should be immiscible, and that it should be possible to leach out one of the oxide phases. It is also necessary that the monoliths should maintain their integrity following decomposition and leaching. In our experience, this is not always possible. Pore sizes could perhaps be controlled through selection of suitable conditions for decomposition, for the growth of the immiscible phases,
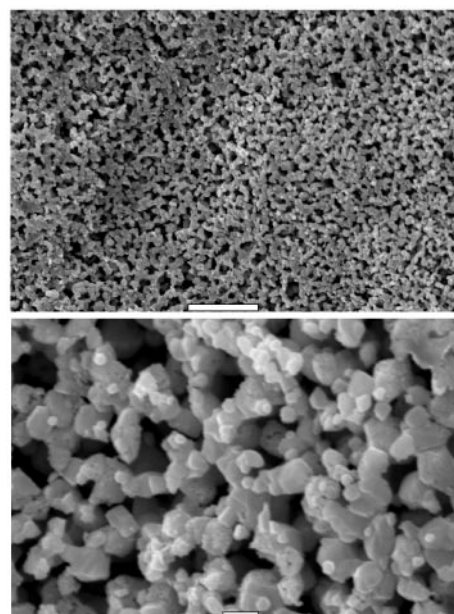
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