A Template-Free, Combustion-Chemical Route to Macroporous Nickel Monoliths Displaying a Hierarchy of Pore Sizes

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Recently, we demonstrated a very general route to monolithic macroporous materials prepared without the use of templates (Rajamathi et al. *J. Mater. Chem.* **2001**, *11*, 2489). The route involves finding a precursor containing two metals, A and B, whose oxides are largely immiscible. Firing of the precursor followed by suitable sintering results in a monolith from which one of the oxide phases can be chemically leached out to yield a macroporous mass of the other oxide phase. The metals A and B that we employed in the demonstration were Ni and Zn. From the NiO−ZnO monolith that was obtained by decomposing the precursor, ZnO could be leached out at high pH to yield macroporous NiO. In the present work, we show that combustion-chemical (also called self-propagating) decomposition of a mixture of Ni and Zn nitrates with urea as a fuel yields an intimate mixture of the oxides that can be sintered and leached with alkali to form a macroporous NiO monolith. The new process that we present here thereby avoids the need for a crystalline single-source precursor. A novel and unanticipated aspect of the present work is that the combination of high temperatures and rapid quenching associated with combustion synthesis results in an intimate mixture of wurtzite ZnO and the metastable rock-salt $Ni_{1-x}Zn_xO$ where x is about 0.3. Leaching this monolith with alkali gives a macroporous mass of rock-salt $Ni_{1-x}Zn_xO$, which upon reduction in H_2/Ar forms macroporous Ni and ZnO. There are thus two stages in the process that lead to two modes of pore formation. The first is associated with leaching of ZnO by alkali. The second is associated with the reduction of porous $Ni_{1-x}Zn_xO$ to give porous Ni and ZnO.

Introduction

Apart from the many applications of macroporous materials, the imperative to make them is also drawn from the desire of materials chemists to pattern materials at increasingly larger length scales. The use of surfactants as templates in the preparation of porous materials, as exemplified by organic amines in the preparation of microporous (zeolitic) materials such as ZSM-5,[1] of surfactant assemblies in the preparation of mesoporous materials such as MCM-41[2] and of block copolymer surfactants in the preparation of materials with pore sizes ranging in the hundreds of Ångströms[3] are well-documented. In recent years, in the quest for increasingly larger pore sizes, all these have yielded ground to ordered emulsion[4] or colloidal superlattice templates.[5] However, as pore sizes increase, so does the difficulty in ordering pores. The use of highly ordered echinoid bioskeletons, a naturally formed macroporous material, as templates for forming macroporous monoliths has been recently suggested.[6]

Preparing porous inorganic materials without templates, or at least without the intermediation of ordered arrays of surfactants, emulsions, or colloids, is a challenge. This is despite the fact that the materials so formed may not possess ordered pores. The preparation of Raney nickel catalysts by the leaching of aluminum from Ni−Al alloys is a well-known example of the preparation of porous materials by leaching.[7] In the Raney nickel case, the leaching is reactive, evolving a great deal of hydrogen which assists in catalytic hydrogenation—the principal use. Recently, it was dem-

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onstrated that the leaching of silver from Au−Ag alloys gives nanoporous materials.[8] Materials with one-dimensional macropores can be prepared by electrochemical etching.[9] Grimes and co-workers[10] have demonstrated that Bénard-Marangoni convection patterns, observed when thin layers of a fluid are allowed to evaporate under a thermal gradient, can be used in the preparation of films of porous inorganic materials. Suzuki, Morgan, and Ohji[11] have used the reactive decomposition of dolomite $CaMg(CO_3)_2$ in the presence of ZrO_2, followed by leaching of MgO, to prepare porous $CaZrO_3$. Alumina and titania are miscible in the molten state but phase-separate upon solidification. By directional cooling of $Al_2O_3-TiO_2$ eutectics followed by the leaching of Al_2O_3, directionally porous TiO_2 monoliths have been prepared.[12]

Inspired by the possibility of decomposition followed by selective leaching as a route to porous materials, we have evolved a rather general scheme[13] wherein we start with two metals A and B that do not form any oxide phase A_xB_yO or solid solution. There are many such pairs of metals in the periodic table that can be found by a simple perusal of the powder diffraction database. By looking out for a crystalline single-source precursor that contains the two metals $[Ni_3Zn_2(OH)_8(CH_3COO)_2 \cdot 2H_2O$ in the case of the Ni−Zn pair,[13] or dolomite $CaMg(CO_3)_2$ in the case of the Ca−Mg pair[11]] one then needs only to press pellets, decompose, sinter, and leach one phase suitably to form a macroporous monolith of the other phase. In the earlier work, we demonstrated that macroporous NiO monoliths can be made by such a process and the monoliths could be reduced to Ni metal with retention of the pore structure. The essential philosophy behind the work is to obtain a sintered mass of two intimately mixed phases from which one can be leached.

It has occurred to us that there are alternate routes to preparing intimately mixed two-phase oxide composites. One of them is combustion synthesis, also referred to as self-propagating high-temperature synthesis.[14] This is a well-known technique for the preparation of ceramic and other advanced materials. It involves the combination of two species that react exothermically, the heat evolved often helping the crystallization and sintering of the product. A dramatic and well-known example is the reaction of Na_2S with $MoCl_5$ to form MoS_2.[15] In the present work, we prepare intimately mixed powders of NiO and ZnO using a simple combustion synthetic route. Sintering the powders and then leaching out the ZnO with alkali results in a macroporous monolith that can be further reduced to porous Ni. An intriguing twist to the entire process is provided by the dissolution of some Zn in the NiO. Since ZnO is not reduced under the same conditions that NiO is, heating the porous Zn-containing NiO under H_2/Ar results in a mixture of Ni metal and small ZnO particles. The ZnO that comes out at this stage results in a new level of porosity. Our reasons for using NiO and Ni as the phases of choice for illustrating this new scheme for preparing macroporous materials has to do with the many uses of porous NiO/Ni in catalysis and electrochemistry.[16]

Experimental Section

The metal nitrates $[Ni(NO_3)_2 \cdot 6H_2O$ (5.81 g, 0.02 mol) and $Zn(NO_3)_2 \cdot 6H_2O$ (5.95 g, 0.02 mol)] were taken with urea (4.00 g, 0.02 mol) in 4 cm^3 of water, forming a clear solution. This solution was divided into three portions. Each portion was taken in a dense, sintered alumina crucible and placed in a preheated electric Bunsen burner (≈923 K). The solution quickly evaporated to dryness and an extremely vigorous and rapid reaction took place, forming a black powder with the evolution of large volumes of smoke. (Caution: This reaction should be performed only with suitable shielding in an open area such as a large hood.) In this reaction, the nitrate ions act as the oxidant and urea the reductant or fuel. The heat generated by the combustion of the urea provides the driving force for the formation of the oxides. The powders formed are rather dense and, as a result, do not disperse very much, but remain in the crucible. They were collected and pressed into cylindrical pellets measuring 10 mm in diameter and 2−3 mm in height. The pellets were sintered at 1273 K for 24 h. The first stage of leaching by alkali involved placing a pellet in 25 mL of 4 M NaOH at 338 K for 2 days, with the supernatant solution being replaced after 1 day. After the leaching, the pellet was washed by soaking in deionized water for 2 days with periodic replacement of the water. The pellet was removed and dried for further characterization, and for reduction in flowing 15% H_2/Ar at 773 K for 3 h. A final removal of the ZnO from the reduced Ni pellet was also achieved using the same 4 M NaOH leaching procedure. At none of the stages in the process is the integrity of the pellet(s) compromised.

After each stage of (i) sintering, (ii) leaching with 4 M NaOH, (iii) reduction in H_2/Ar, and (iv) leaching the reduced product with 4 M NaOH, the samples were studied by powder X-ray diffraction (reflection $\theta-2\theta$ geometry on a Siemens D5005 diffractometer, Cu Kα radiation, 2°/min scan rate, data rebinned into 0.02° steps) and by scanning electron microscopy and energy-dispersive analysis of X-rays (JEOL JSM 5600 LV, samples mounted on brass stubs using conducting carbon tape and sputter-coated with gold, secondary electron imaging).

Results and Discussion

Figure 1 shows the scheme employed in the present work to prepare macroporous Ni monoliths. Starting from the aqueous solution "a" of the metal nitrates, evaporation and combustion synthesis results in the powder "b" that is collected, pelletized, and sintered to form the monolith "c". The monolith is expected to comprise NiO and ZnO particles, with the method of preparation ensuring that the particles are intimately dispersed. The ZnO particles in this pellet (white) can be leached in alkali to form the porous NiO monolith "d". The NiO pellet can then be reduced in H_2/Ar to form the Ni monolith "e". As shall be seen presently, this

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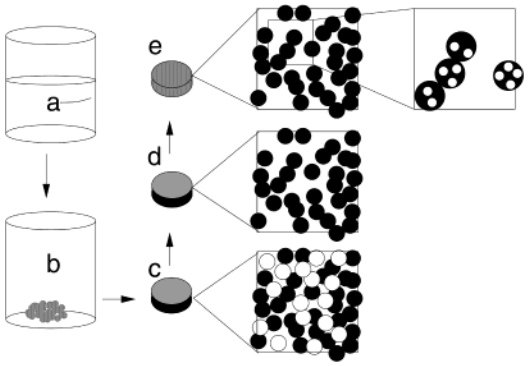

Figure 1. Scheme for the generation of macroporous materials starting with the combustion synthetic preparation of an intimate mixture of two metal oxides. Starting from Ni^{II} and Zn^{II} nitrates in solution with urea as the fuel "a", combustion synthesis yields an intimate mixture of the oxides "b", which is sintered to form the monolith "c". The wurtzite ZnO in monolith can be leached by alkali to yield a macroporous oxide "d". Reduction of "d" should yield macroporous Ni metal "e", but closer examination reveals that, in addition, ZnO is thrown out of "d" on reduction, giving rise to another level of porosity.

monolith turns out to also contain ZnO particles arising from the reaction

$$Ni_{1-x}Zn_xO \xrightarrow{H_2/Ar,\ 773\ K} (1-x)Ni + xZnO \qquad (1)$$

The ZnO particles which are thrown out of the Ni matrix result, inadvertently, in another, smaller level of porosity.

In the rest of this section, we shall present, in detail, the different steps in the scheme and the accompanying evidence.

Figure 2 shows X-ray diffraction profiles of the sintered pellet [panel (a)] and the pellet after leaching [panel (b)], along with respective two- or one-phase Rietveld fits and difference profiles. Vertical lines at the top of the figures indicate the expected peak positions for rock-salt NiO and wurtzite ZnO. No other phases were detected in the sintered pellet. The XND Rietveld code was employed for the refinements.[17] Quantitative phase analysis using Rietveld scale factors followed procedures outlined in the manual of the FullProf Rietveld code.[18] The Brindley microabsorption factors,[19] which are important in performing the phase analysis accurately, were ignored as the two phases, NiO and ZnO, have very similar formula weights and are not expected to differ very much in the extent to which they absorb X-rays.

From the two-phase Rietveld fit of the sintered sample shown in Figure 2a, we found that cell parameters [unit cell volume = 47.57(1) Å^3] of the wurtzite ZnO component refined closely to that reported for pure ZnO (unit cell volume = 47.62 Å^3 from the JCPDS database card no. 36-145). The differences in the two unit cell volumes are about 0.1%. This suggested a relatively pure wurtzite fraction in the two-phase pellet. The presence of Ni

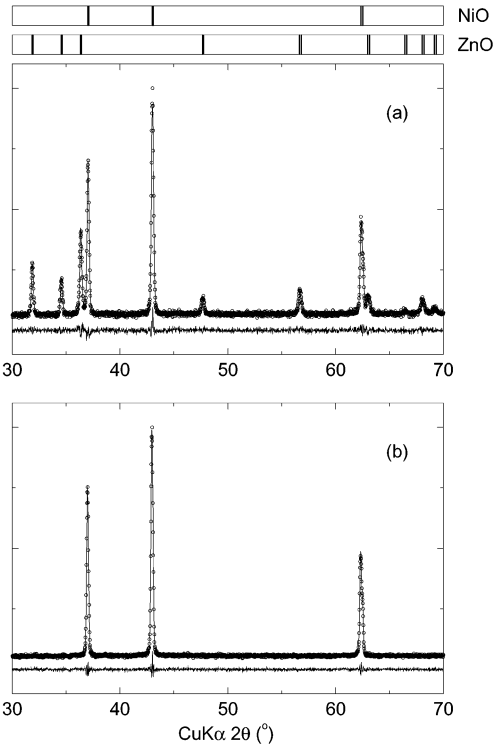

Figure 2. Powder XRD profiles of (a) the sintered mixture of the oxides (corresponding to "c" in Figure 1) and (b) the mixture after the wurtzite ZnO component was leached out (corresponding to "d" in Figure 1). Data points are shown as small circles and the Rietveld fits as solid lines. Difference profiles are also shown. Vertical lines at the top of the figure are the expected peak positions.

substituting for Zn in the wurtzite at the level of even a few percent would be indicated by a significant shrinking of the unit cell volume since the ionic radii of tetrahedral Ni^{2+} (0.55 Å) and Zn^{2+} (0.60 Å) are quite distinct.[20] On the other hand, the rock-salt NiO component possessed refined cell parameters that were significantly larger than reported values—74.71(1) Å^3 as compared with 72.88 Å^3 (JCPDS card no. 47-1049). This suggested that a significant amount of Zn substituted for the smaller Ni in the rock-salt structure—the ionic radii of octahedral Ni^{2+} and Zn^{2+} being 0.69 and 0.74 Å, respectively.[20] Since Zn and Ni differ only by two electrons, it is not possible to refine from X-ray diffraction data the value of x in $Ni_{1-x}Zn_xO$. Quantitative phase analysis from Rietveld scale factors suggested that the molar ratio of rock-salt $Ni_{1-x}Zn_xO$ to ZnO was 71:29.

Alkali leaching of a sintered pellet of the mixtures of rock-salt $Ni_{1-x}Zn_xO$ and wurtzite ZnO resulted in an X-ray diffraction profile that showed no trace of the latter. The cell parameters of $Ni_{1-x}Zn_xO$ for which data and the Rietveld fit are displayed in Figure 2b were unchanged from what was seen in Figure 2a, suggesting that while the alkali leaches away wurtzite ZnO, it leaves x unchanged in the $Ni_{1-x}Zn_xO$. Energy-dispersive analysis of X-rays in the scanning electron microscope (EDAX) suggested atomic ratios of Ni:Zn in the sintered pellet to be 53:47. This is close to the ratio of unity expected from the starting mole ratios of the metal

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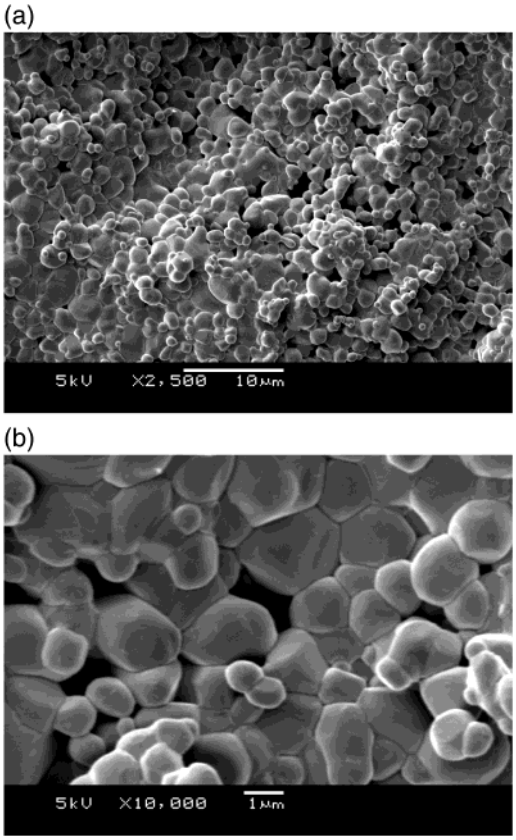

Figure 3. SEM images of the sintered pellet of the two oxide phases corresponding to "c" in Figure 1.

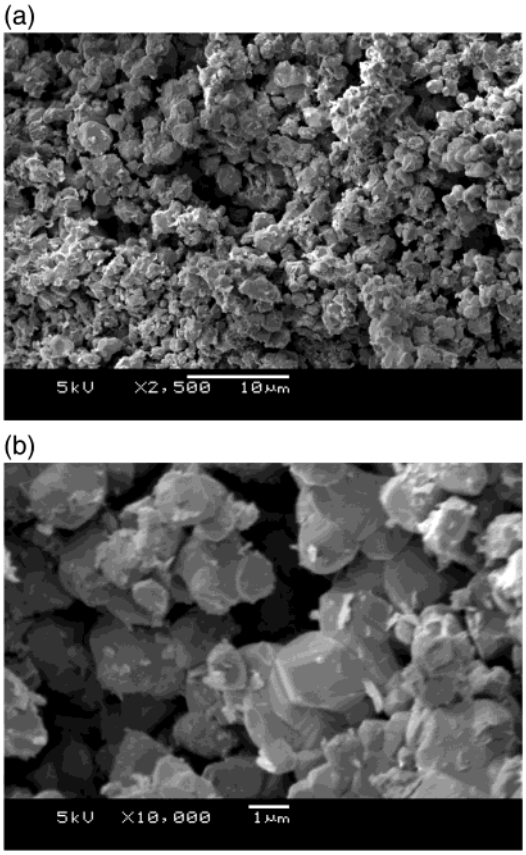

Figure 4. SEM images of the sintered pellet after leaching out the wurtzite ZnO corresponding to "d" in Figure 1.

nitrates. We determine that a value of $x = 0.29$ is consistent with the Rietveld refinement results and the EDAX analysis. We thus have a picture of approximately one-quarter of the total mass of the sintered pellet comprising wurtzite ZnO. This mass should be lost on leaching, as was indeed found from the weight lost by the pellet upon leaching. After leaching of the wurtzite ZnO, EDAX analysis of the pellet gave a Ni:Zn ratio of 72:28.

Panels (a) and (b) of Figure 3 display at different magnifications scanning electron micrographs of cross sections of a sintered pellet of the Ni and Zn oxides. Both rock-salt and wurtzite crystals have similar morphologies. Certainly, even at higher magnifications (Figure 3b), it is difficult to identify two distinct types of crystals. The small difference in the atomic numbers of Ni and Zn make it difficult to use an imaging mode that distinguishes the wurtzite ZnO crystals from the rock-salt $Ni_{1-x}Zn_xO$ crystals. There is some porosity in the sintered pellet, as can be expected of a pressed mass of two different phases that have not been fired for very long and that, too, are well below the melting points.

In Figure 4a,b, we display SEM images of a cross section of the pellet after leaching with alkali, where it is seen that the pellet has developed significant macroporosity. A comparison of the $Ni_{1-x}Zn_xO$ seen in Figure 4a,b with the earlier images of $Ni_{1-x}Zn_xO$ with wurtzite ZnO shown in Figure 3a,b confirms that the morphologies and the distributions of sizes of the two different phases are quite similar. We have analyzed the porosity of leached pellets by digitizing a 2500× magnification image (total image size 52 × 34 μm) into squares that were 1.1 μm on edge. By counting the ratio of squares over pores to the total number of squares, we arrive at a porosity of 24%, close to the estimate obtained from the weight change. It is well-known that, in an analysis such as the one we have made, cross sections are proportional to the volumes.[21]

The leached pellet, upon reduction, results in the formation of Ni and wurtzite ZnO according to eq 1 as testified by the XRD profiles in Figure 5a. X-ray Rietveld analysis suggested an fcc Ni to wurtzite ZnO mole ratio of 77:23. This is not in very good agreement with the earlier estimates of $x = 0.29$ and of the EDAX Ni:Zn ratio of 72:28 in the leached pellet. We attribute the discrepancy to the differences in particle sizes (as suggested by Scherrer broadening of the XRD profiles) and densities of Ni and ZnO in this composite. The ZnO in this reduced pellet can be leached out by alkali once again and this results in pure Ni as seen from XRD profiles in Figure 5b.

An examination of the SEM images of the reduced pellet (Figure 6a,b) suggests that porosity is retained. An analysis similar to the one made previously gives a macroporosity of 25%. When examined more closely, however, (Figure 6b), we find the porous Ni structure comprising Ni particles and void at the level of 1 μm has another finer level of porosity that has arisen from the process of reduction. These are fine cavities of the order of 100 nm in the Ni particles, arising presumably, from the ZnO being thrown out of the matrix according to eq 1. This level of porosity is more difficult to quantify

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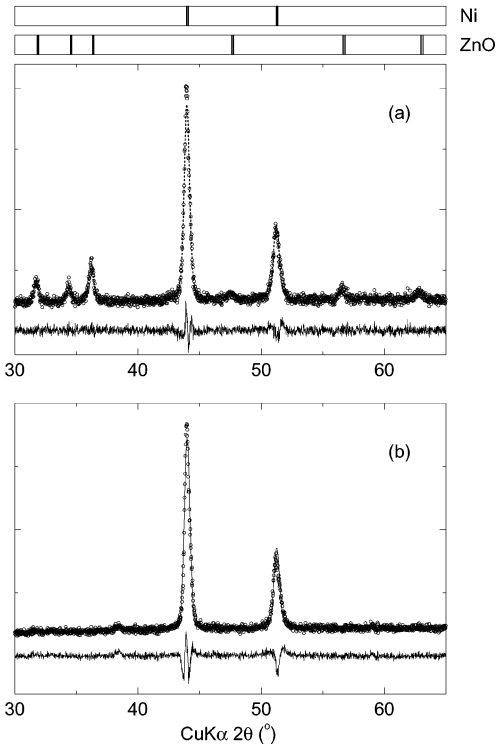

Figure 5. Powder XRD profiles of (a) the reduced pellet (corresponding to "e" in Figure 1) and (b) the reduced pellet after the wurtzite ZnO component was leached out.

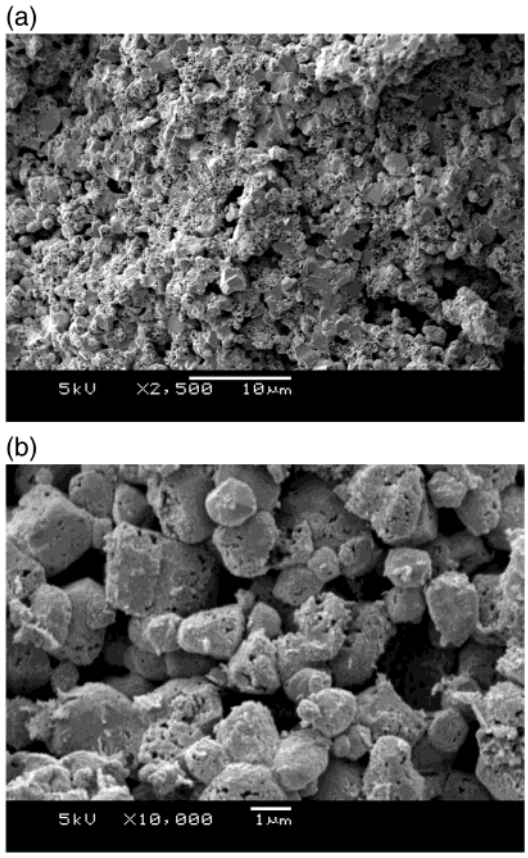

Figure 6. SEM images of the pellet after reduction, corresponding to **e** in Figure 1. An examination of the image in panel (b) shows small cavities in the Ni particles that ensue from the ZnO being thrown out.

and is not expected to be "open" or connected. EDAX analysis of this reduced material suggests a Ni:Zn ratio

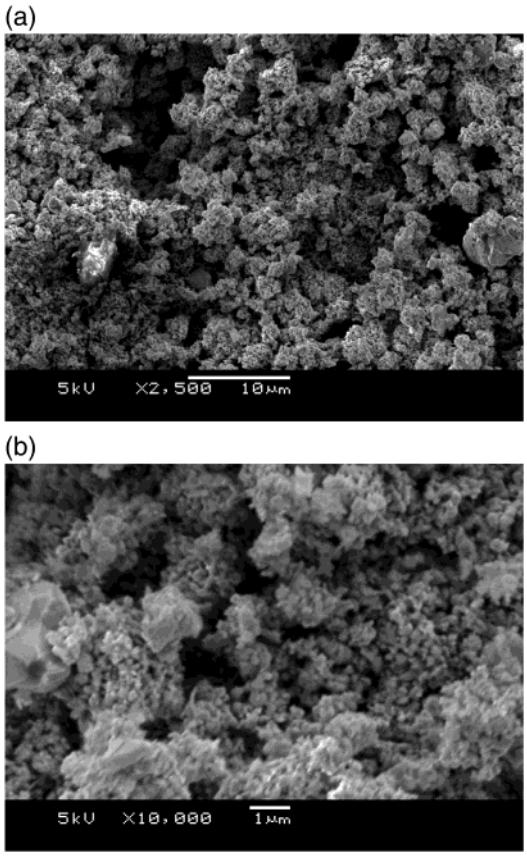

Figure 7. SEM images of the reduced pellet after further removal of wurtzite ZnO by leaching in alkali.

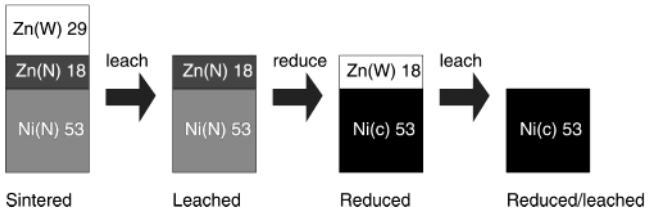

Figure 8. Material balance for Ni and Zn in the different stages of leaching and reduction. "N" refers to the rock-salt phase, "W to the wurtzite phase, and "c" to the fcc phase of Ni metal. The numbers are scaled to a starting mole number of 100. The numbers are those most consistent with EDAX (total atom ratios of Ni:Zn) and Rietveld analysis (relative amounts of different crystallographic phases).

of 69:31, which is close to the estimated value of x in the $Ni_{1-x}Zn_xO$, and also close to the estimate by EDAX of the Ni:Zn ratio in the leached product. When the ZnO particles are removed by further leaching (Figure 7a,b), the structure unexpectedly changes by a surprising degree, while remaining porous. The only reason that we can find for such change is that the ZnO particles assist in some way in holding together the Ni particles and this composite structure collapses when the former is leached out.

Figure 8 is an attempt to summarize the material balance that is most consistent with the relative amounts of Ni and Zn in the different stages of the process of preparing macroporous materials as outlined here. The only discrepancy among the different techniques used arises from the Rietveld estimate of the ratios of fcc Ni to wurtzite ZnO in the reduced product as mentioned earlier.

Conclusions

In this contribution we have demonstrated proof of the concept of a general method for the preparation of macroporous materials through selective leaching of one oxide phase from a mixture of oxide phases. The manner in which we generate the intimately mixed oxide phases differs in the present work from what we have done previously—in earlier work, we generated an intimate mixture of Ni and Zn oxides by decomposing a single-source precursor. It that case, the pores were indeed more uniform than what has been obtained here. However, the significant solubility of Zn in rock-salt NiO at the high temperatures of formation involved here[22] gives rise, after the first leaching, to a porous $Ni_{1-x}Zn_xO$ material that on reduction throws out ZnO and forms an Ni/ZnO composite material. The two stages of Zn removal give rise, therefore, to two levels of porosity. While this has been inadvertent in the present work, we see no reason why two stages of leaching cannot be designed into systems where a hierarchy of pore sizes are desired.

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