Growth of Large Buserite Crystals: Precursors for Octahedral Molecular Sieves

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Large buserite crystals that are important in the generation of octahedral molecular sieves are prepared by crystal growth in gels.

Manganese nodules which often contain the minerals todorokite and hollandite are found as deep sea deposits that can include and concentrate ionic species found in sea water. Practically every stable ion of elements of the Periodic Table has been found in such deposits throughout the world.[1] Such materials have been implicated in abiotic formation of organic nitrogen complexes in natural environments,[2] and have been used as oxidation catalysts and adsorbents due to their unusually high surface areas and porous structures.[3,4] Nodules have been used to trace geologic events such as the genesis of hydrothermal crusts,[5] equilibria of isotope exchange,[6] changes in fertility[7] and redox character of the oceans,[8] and as a direct probe of the hydrothermal activity of the ocean floor.[9,10]

We have recently reported[11,12] the synthesis, characterization, and catalytic activity of one-dimensional tunnel-structure materials of manganese oxide that have the structure of todorokite. Synthetic todorokite is an octahedral molecular sieve (OMS) which is designated OMS-1 having a pore size of 6.9 Å. OMS-1 is synthesized *via* hydrothermal alteration of a layered precursor known as buserite. We report here that large 190 µm crystalline aggregates of buserite can be prepared by crystal growth in silica gels. A mechanism of formation of todorkite from buserite is also proposed.

Gel growth of manganese nodules by Momoi *et al.*[13] showed that various morphologies of manganese oxide materials similar to natural manganese nodules could be obtained in agar gels. No well-formed crystalline materials or large crystals were observed in these studies.

Crystal growth in gels[14] was used to prepare large aggregates of buserite. 3 ml of a sodium silicate stock solution of 40% $Na_2Si_3O_7$ and of density 1.4 g ml^{-1} was diluted with 17 ml distilled deionized water and used as the diffusion medium. 10 ml of a solution of 20 ml 1 mol dm^{-3} acetic acid and 1 ml of 0.1 mol dm^{-3} $KMnO_4$ solution was added to the silicate solution to produce homogeneous gels. About 15 ml total acidified gel was placed in test tubes having a 25 mm inside diameter and a length of 8 in. Syneresis[14] occurred with concomitant loss of H_2O and networking of siloxane bonds formed over a 24 h period.

Once the gels had set, varying amounts of a 0.265 mol dm^{-3} $MnCl_2$ solution were added on top of the gel. A very dark interface appeared and diffusion occurred at a rate of 4 mm per day. The sizes of resultant materials range from 80 to 190 µm depending on synthetic conditions. The chemical composition of crystals growing in the lower part of the tube is $K_2Na_2Mn_{14}O_{27}{\cdot}21H_2O$. The size of crystals of layered materials like birnessite and buserite grown from hydrothermal methods[11,12] is significantly smaller (<80 Å) than the 80–190 µm size materials grown in gels as reported here. It is clear from comparison to research of Momoi *et al.*[13] that silica gels allow formation of much larger single phase materials than with agar gels.

The morphologies of the brown–black materials that were extracted from the gels by using tweezers and by washing were octahedral which appeared thirteen days after the addition of the Mn^{2+} solution. Scanning electron microscopy (SEM) photos at low and high magnification are shown in Fig. 1(a) and (b) respectively. An edge of the octahedra is about 100 µm. Layers of material perpendicular to the [111] direction emanate outward from the centre of the crystal. At least 20 individual layers can be counted in these and similar materials.

X-Ray powder diffraction (XRD) experiments with both thin-film and normal powder collimators showed the presence of three major extremely sharp diffraction lines at 10.2, 4.6, and 2.8 Å consistent with buserite, as well as other weaker diffraction peaks. Prolonged exposure of crystals to X-ray (or synchrotron) radiation led to alteration of the crystals to amorphous materials.

It may be possible that an ordered aggregation of layers of buserite along one direction perpendicular to the layers is a primary step in the formation of the 3 × 3 tunnel structure mineral todorokite and in the generation of OMS-1. A

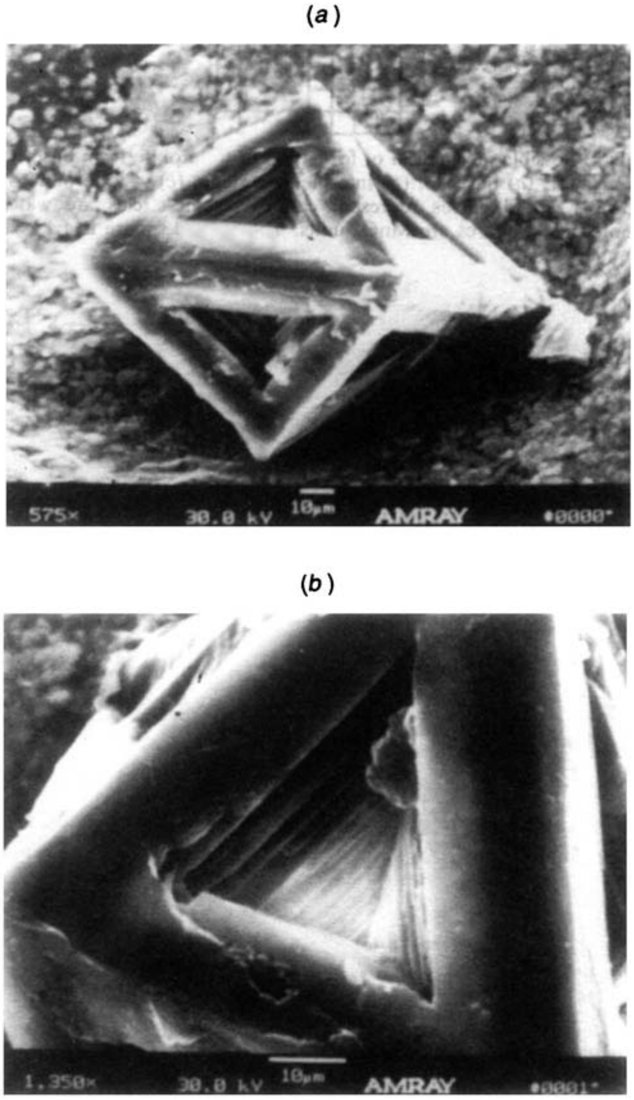

Fig. 1 Scanning electron micrograph of synthetic buserite, (*a*) magnification × 575. (*b*) magnification × 1350

plausible mechanism for such crystal growth is given in Fig. 2. This mechanism is different than that proposed by Usui[15] who suggests a manganite precursor. Separate steps for closing off the layers was not considered in their model.

Such materials that have a large number of layers and an open porous structure along the [111] direction of octahedra would be expected to have unusually high surface areas for a material having overall dimensions ranging from 80 to 190 μm. Potential applications of these materials in the areas of adsorption, catalysis and photochemistry are under way in our laboratories.[16]

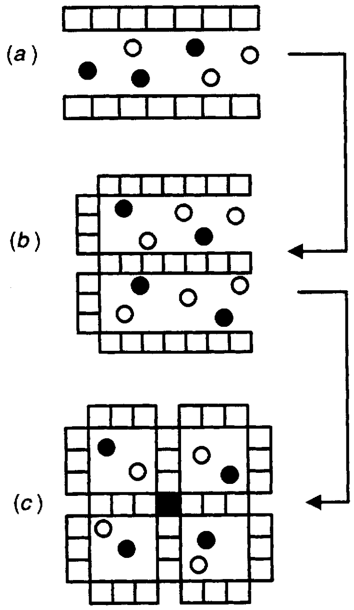

Fig. 2 Possible mechanism of formation of todorokite from buserite Precursor: (*a*) buserite, (*b*) intermediate stage, (*c*) = todorokite or OMS-1. Solid circles represent cations, Open circles are water molecules. Squares are MnO_6 units. The shaded square is a 1 × 1 tunnel.

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