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A New and Industrially Favorable Method for Synthesizing Sandia Octahedral Molecular Sieve (SOMS-1) $Na_2Nb_{1.6}Ti_{0.4}O_{5.6}(OH)_{0.4}\cdot H_2O$: Synthesis, Structure, and Scale-up

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In the past decades, microporous framework materials composed of octahedral units (such as [TiO_6]) have attracted much attention owing to their unique properties compared to those for conventional zeolitic phases whose frameworks consist of [SiO_4] and [AlO_4] tetrahedra.[1,2] More recently, a new class of octahedral microporous phases has been synthesized with the compositions $Na_2Nb_{2-x}M_xO_{6-x}(OH)_x\cdot H_2O$ ($M = Ti, Zr$; $0 < x \leq 0.4$) using hydrothermal methods.[3−5] These phases, named Sandia Octahedral Molecular Sieves (SOMS), possess a framework structure composed of layers of edge-sharing [NaO_6] octahedra interleaved with double chains of edge-sharing, disordered, and distorted [NbO_6]/[MO_6] (see Figure 1). The third structural unit, square planar sodium, resides in the channels. This structure is unusual in the sense that Na, which is typically an extraframework cation, also participates in the formation of the framework. Ion exchange experiments show that the SOMS phases are highly selective for large alkaline earth cations over alkali cations. For example, the distribution coefficient (K_d), which is defined as the ratio of cation adsorbed onto the ion exchanger to the cation remaining in the solution, for the $Na_2Nb_{0.6}Ti_{0.4}O_{5.6}(OH)_{0.4}\cdot H_2O$ phase is about 10^5 for Sr^{2+}, but only 95 for K^+ in neutral solutions containing no competitive cations.[3] Hence, these materials can potentially be used for separation of radioactive ^{90}Sr from aqueous nuclear wastes and contaminated groundwater. Moreover, upon heating, the Sr-exchanged SOMS phases dehydrate and convert to thermally stable and chemically durable perovskites.[4] Thus, these perovskites may serve as permanent ceramic host structures for ^{90}Sr in radioactive waste management.

The potential for large-scale and industrial applications of both the molecular sieve phase and the heat-treated perovskite phase necessitate the synthesis and production via low-cost, easily scaleable routes. To achieve this goal, novel synthetic routes utilizing the more plentiful and less costly oxide starting materials needed to be explored, rather than the original air-sensitive alkoxide reagents which required special handling. To that end, we present here a new oxide-based synthesis of the SOMS class of materials, characterization of the pure products, and the procedures for lab-bench product scale-up. We estimate a 500-fold decrease in reagent costs based on our earlier reported procedures.[6]

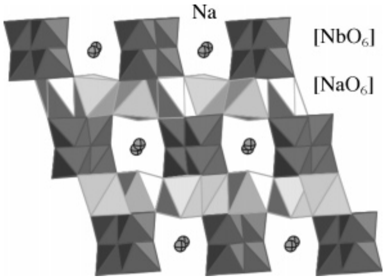

Figure 1. SOMS: Sandia Octahedral Molecular Sieves ($Na_2Nb_{2-x}M^{4+}{}_xO_{6-x}(OH)_x\cdot H_2O$) framework.[3,4] Water molecules excluded from channels for ease of viewing.

Sample Synthesis (23 mL Reactor). $Na_2Nb_{1.6}Ti_{0.4}O_{5.6}(OH)_{0.4}\cdot H_2O$ (SOMS-1) was synthesized using air-stable oxide reactants. In a typical reaction, 0.53 g of Nb_2O_5 and 0.08 g of TiO_2 were mixed in a mortar and pestle using ethanol as a wetting/mixing agent. The mixture was allowed to air-dry before adding 2.03 g of NaOH. The reactants were re-ground. The powder was placed then in a Ni-crucible and heated at 400 °C for 1 h. After cooling, the resultant solid (in pellet form) was placed in a Teflon liner with 10 g of deionized water. The liner was placed into a 23 mL Parr autoclave, which was placed in an oven at 170 °C for 103 h. After cooling, the product is recovered by filtration. Powder X-ray diffraction of the powder crystalline sample confirmed that the $Na_2Nb_{1.6}Ti_{0.4}O_{5.6}(OH)_{0.4}\cdot H_2O$ phase had been synthesized.

Scale-up Process (from 23 mL to 1 gal Reactor). A larger scale version of the novel oxide process for synthesizing $Na_2Nb_{1.6}Ti_{0.4}O_{5.6}\cdot H_2O$ (SOMS-1) was also prepared via a hydrothermal route. Approximately 79.5 g of niobium pentoxide and 12.0 g of titanium dioxide are mixed thoroughly and then combined with 304.5 g of sodium hydroxide (NaOH) pellets. The mixture is loaded into an Fe crucible and fused at 400 °C. After cooling, the resultant solid was placed in a Teflon liner bag with 1500 mL of deionized water; the bag was then sealed. The liner was placed into a 1 gal reactor, surrounded by water, sealed, and autoclaved at 170 °C for 103 h. After cooling, the product is recovered by filtration. Powder X-ray diffraction of the powder crystalline sample verify that the $Na_2Nb_{1.6}Ti_{0.4}O_{5.6}(OH)_{0.4}\cdot H_2O$ phase had been synthesized.

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The scaled-up synthesis focused on SOMS-1 because of its ease of synthesis. Recently published calorimetry studies[7,8] support that this composition is the easiest to synthesize due to its lowest energy of heat of formation with respect to other Ti analogues in the series. However, we propose that this synthetic procedure can easily be translated to the other substituted analogues we have synthesized in this family.[4,5]

This method for making pure SOMS-1 from oxides involves a new hydrothermal process. Originally, air-sensitive and expensive starting materials were used for the synthesis, including hydrolyzed metal (Nb, Ti, Zr) alkoxides. In an effort to make this material more attractive to industrial scale-up (and commercialization), a solid solution of niobium, titanium, and sodium oxides were fused together. This new “intermediate” phase is characterized as a combination of NaOH, $NaOH{\cdot}H_2O$, Na_3NbO_4, TiO_2, and an amorphous phase, as determined by JCPDS phase matching of the XRD powder diffraction file. The “intermediate” phase was placed in a reactor (as a reactant) and treated hydrothermally, resulting in the formation of the metastable SOMS microporous framework structure, instead of the thermodynamically more stable perovskite end product.

In comparison to the traditional method of synthesizing SOMS, the reaction time is comparable.[3,4] The major difference in the procedure is the formation of a stable new oxide “intermediate” phase that combines all the framework elements. During the hydrothermal treatment of the “intermediate” phase, the reaction goes through an unidentified hexaniobate phase (similar to another phase reported earlier[9]) prior to the SOMS framework formation. Ultimately, this hexaniobate phase is temporary, but seems stable because of its presence for 99 h of hydrothermal reaction time. During the final hours of cooking, the structure crystallizes into the microporous SOMS phase. See Figure 2. The details of the structure have been reported elsewhere.[3,4]

Characterization[11] of the 1 gal scale-up version of SOMS-1 included powder X-ray diffraction (XRD), scanning electron microscopy (SEM), thermal analyses, and ion exchange selectivity (K_d[12]). In all characterization comparisons of the scale-up versus the original alkoxide small-scale version, the materials were nearly identical.

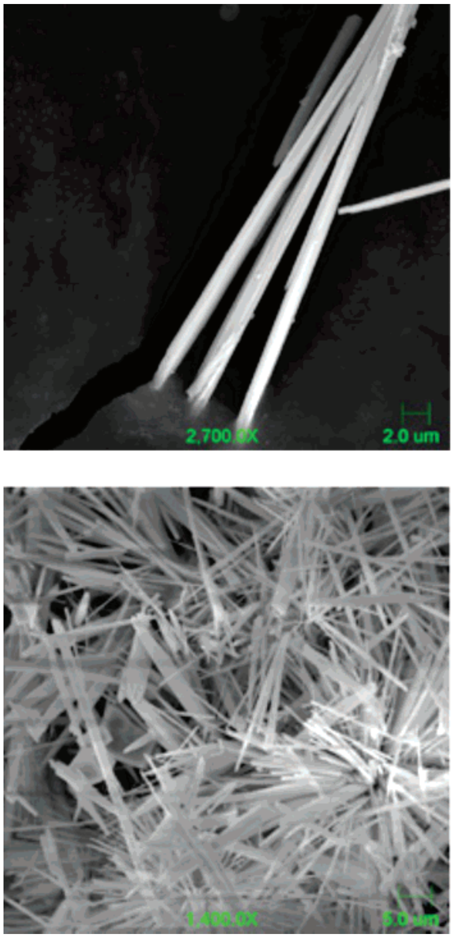

Figure 2. SEM of SOMS-1 from 1 gal of oxide-based scale-up reaction.

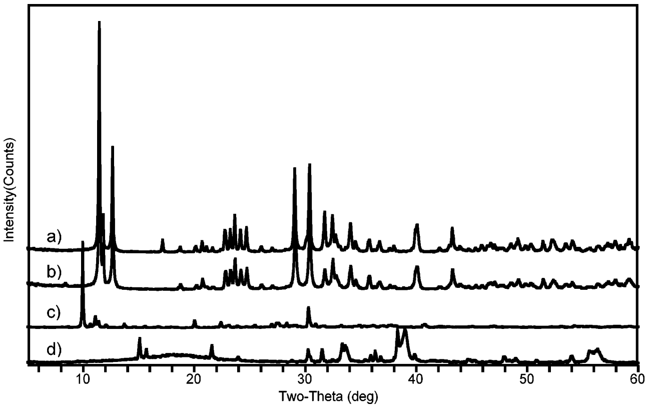

Figure 3. Powder X-ray diffraction (XRD) pattern of SOMS and related materials: (a) SOMS from 23 mL batch; (b) SOMS from 1 gal scale-up (minor impurity seen at 8° and 17°); (c) hexaniobate phase; (d) “intermediate” oxide precursor phase.

The powder XRD pattern in Figure 3 shows the phase match between the alkoxide method[3,4] and the varying larger scale oxide methods. Using SEM, the morphology of the scale-up version of the SOMS-1 was determined to be identical to that of the original material. In both cases, the product is comprised of long thin needles, of approximate size $0.5 \times 20\ \mu m$. As expected from the previous results, the TGA/DTA of the SOMS-1 product also duplicated earlier alkoxide-based synthesis methods. K_d values were collected to determined if the oxide-based SOMS had similar ion exchange abilities to the original alkoxide-based SOMS. K_d measurements for Sr selectivity were repeated four times for reproducibility. The K_d values are 123511, 524761, 204605, and 49889. The average value for the four measurements is

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(11) XRD patterns were recorded at room temperature on a Siemens Kristalloflex D 500 diffractometer (Cu Kα radiation, Ni filter, 40 kV, 30 mA.; $2\theta = 5-60°$, 0.05° step size, and 3 s count time); simultaneous TGA/DTA were performed on a TA Instruments STD 2960 with alumina crucibles and alumina powder reference; SEM was performed on a JEOL JSM-6300V scanning electron microscope with the LINK GEM light-window energy dispersive spectrometer.

(12) K_d (mL/g) = $\{[M_{ix}]/g_{ix}\}/\{[M_{sln}]/mL_{sln}\}$; $[M_{ix}]$ is metal concentration adsorbed onto SOMS, g_{ix} is weight of SOMS (0.25 g), $[M_{sln}]$ is metal concentration in solution, and mL_{sln} is volume of solution (25 mL). 50 ppm solutions were in contact with SOMS at room temperature for 12 h, followed by chemical analyses of the solutions.

224442. There is a large deviation for the samples, but all the K_d values of the scale-up version of SOMS-1 are higher than the previously reported K_d.

In conclusion, we have expanded our knowledge and understanding of the unique class of molecular sieve family known as the SOMS. We are now able to synthesize the material from oxide-based reactants both in small- and large-scale benchtop batches. We are currently expanding the stoichiometry mixtures of this class of ion exchangers by including different octahedral atoms into the framework.

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