Rare earth stabilization of mesoporous alumina molecular sieves assembled through an N°I° pathway

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The incorporation of 1.0–5.0 mol% Ce^{3+} or La^{3+} ions in MSU-X alumina molecular sieves, prepared through an N°I° assembly pathway, dramatically improves their thermal stability without altering the mesopore size or the wormhole channel motif.

Following the supramolecular assembly of M41S mesoporous molecular sieves in 1992,[1] there have been relatively few reports of mesostructured aluminas. Davis and coworkers[2] have prepared porous aluminas (*ca.* 20 Å pore diameters) by the hydrolysis of aluminium alkoxides in the presence of a carboxylate surfactant as the structure director. The assembly pathway involved S–I complexation reaction between the surfactant (S) and the inorganic reagent (I), as judged by the presence of IR bands characteristic of chelating carboxylate groups. Yada *et al.*[3] reported the preparation of hexagonal alumina mesostructures by electrostatic S^-I^+ assembly of dodecyl sulfate surfactants and aluminium nitrate. However, the mesostructures were not stable to surfactant removal. In contrast, we have obtained mesoporous alumina molecular sieves, denoted MSU-X, by N°I° assembly of electrically neutral polyethylene oxide surfactants (N°) and an aluminium alkoxide as the inorganic precursor (I°).[4,5] These materials exhibited wormhole channel motifs and BJH pore diameters that can be extended beyond 100 Å, depending on the surfactant size.

One limitation of MSU-X alumina molecular sieves is the loss of surface area and porosity when they are heated above 500 °C. The potential applications of these materials in catalysis and other materials areas could be greatly extended by improving their thermal stability. One possible approach to improving the thermal stability of a metastable alumina is to dope the oxide framework with rare earth cations. For instance, the incorporation of rare earths into γ-alumina (pseudoboehmite) and other transition aluminas is known to stabilize these metastable phases against sintering and conversion to α-alumina (corundum). Two stabilization mechanisms have been proposed, namely, the formation of a surface rare earth aluminate phase[6] and the simple replacement of Al^{3+} by rare earth ions in the pseudoboemite structure, which reduces the lability of the oxide matrix.[7] Analogous mechanisms might also be effective in stabilizing the non-crystalline (amorphous) framework walls of MSU-X alumina molecular sieves against collapse at elevated temperatures. In the present work, we demonstrate that MSU-X aluminas indeed are stabilized by doping with rare earth metal ions.

The incorporation of Ce^{3+} or La^{3+} into MSU-X aluminas was accomplished by first dissolving the corresponding rare earth nitrate in a solution of the non-ionic surfactant in warm butanol. The solution was cooled to room temperature and then aluminium *sec*-butoxide was added with stirring. After an additional 1 h of stirring at ambient temperature, a dilute solution of water in *sec*-butanol was added dropwise. The reaction vessel was then placed in a reciprocating shaker bath at 45 °C for a period of 40 h. Recovery of the as-synthesized reaction products was achieved by filtration and air drying.

The molar compositions of the above reaction mixtures were as follows:

$$0.05\ Ce^{3+}\ (\text{or}\ 0.01\ La^{3+}) : 1.0\ Al(Bu^sO)_3 : 0.40\ \text{Tergitol}$$
$$(\text{or}\ 0.20\ \text{Pluronic}) : 3.0\ H_2O : 15.5\ Bu^sOH$$

where the non-ionic surfactants are Tergitol® 15-S-12 (Union Carbide) with the formula $C_{15}H_{33}E_{12}OH$ (E is a polyethylene oxide segment) and Pluronic® P65 or P123 (BASF) block copolymers with the respective compositions $E_{19}P_{30}E_{19}$ and $E_{20}P_{69}E_{20}$ (P is a isopropylene oxide segment).

Essentially all of the N° surfactant could be removed from the alumina mesostructures by extraction with hot ethanol. For convenience, however, the as-synthesized products were freed of surfactant and prepared directly for N_2 adsorption studies in one step by calcining at 500 °C for 6.0 h. Under the calcination conditions the pure alumina mesostructures assembled from the three N° surfactants begin to collapse, as evidenced by a broadening of the one-line diffraction pattern and a decrease in the surface area and pore volume. Upon the introduction of 1–5 mol% rare earth ions, however, the thermal stability of the framework is greatly improved, as judged by substantial increases in surface areas and liquid pore volume (see below).

N_2 adsorption–desorption isotherms for alumina molecular sieves doped with 5.0% Ce^{3+} and 1.0% La^{3+} are shown in Fig. 1. The positions of the pore filling steps in the adsorption curves shift to higher P/P_0 values with increasing surfactant size, as expected for pore structures formed by a supramolecular assembly process. The desorption hystereses signify some

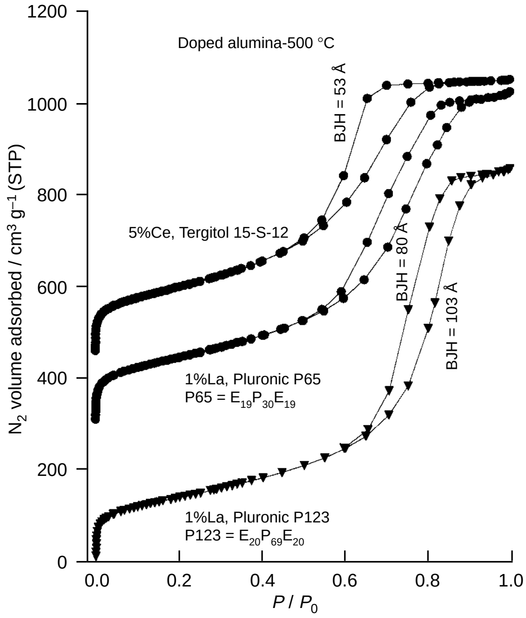

Fig. 1 N_2 adsorption–desorption isotherms of rare earth-stabilized MSU-X alumina molecular sieves assembled in the presence of the non-ionic surfactants Tergitol 15-S-12, Pluronic P65, and Pluronic P123 as structure directors and calcined at 500 °C. The BJH pore sizes obtained from the desorption isotherms are included for comparison.

Table 1 Physical properties of mesoporous MSU-X alumina molecular sieves prepared by N°I° assembly

Surfactant	Rare earth (mol%)	Calcination temp.^{a}/ °C	S_{BET}/ m^2 g^{-1}	BJH pore size/Å	Liquid pore volume/cm^3 g^{-1}	XRD, d/nm
15-S-12	0	500	391	50	0.48	7.8
15-S-12	0	600	267	55	0.31	8.0
15-S-12	5 (Ce)	500	530	53	0.92	8.0
15-S-12	5 (Ce)	600	357	54	0.65	8.0
P65	1 (La)	500	517	80	1.11	> 8.3
P123	1 (La)	500	487	108	1.31	> 10.0

^{a} All the samples were calcined in air for 6 h.

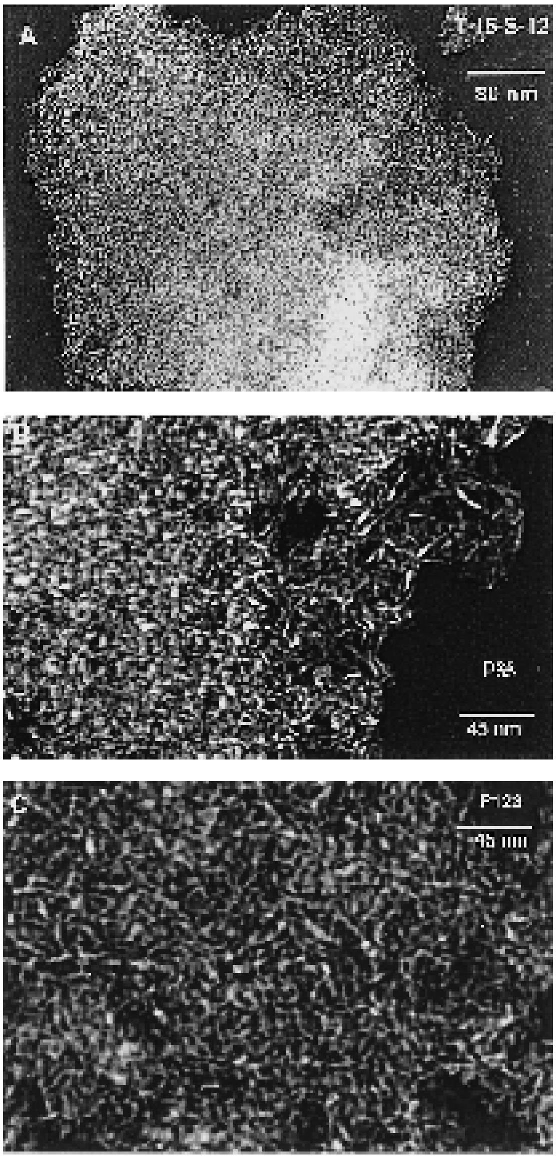

Fig. 2 TEM images of rare earth-stabilized MSU-X alumina molecular sieves assembled from non-ionic surfactants and calcined at 500 °C: (A) 5.0% Ce^{3+}, Tergitol 15-S-12; (B) 1.0% La^{3+}, Pluronic P65; (C) 1.0% La^{3+}, Pluronic P123

degree of pore blocking. These qualitative features of the isotherms also are observed for the pure alumina mesostructures. Furthermore, the doped mesostructures exhibit XRD basal spacings and wormhole TEM images (*cf*., Fig. 2) equivalent to those observed for the pure alumina phases. Therefore, the introduction of the rare earth cations at the 1.0–5.0 mol% level does not alter the N°I° assembly of MSU-X aluminas.

As can be seen from the results provided in Table 1, the incorporation of 5.0 mol% Ce^{3+} in the alumina framework assembled from Tergitol® 15-S-12 results in a 35% increase in the surface area after calcination at 500 or 600 °C. Moreover, the presence of the rare earth nearly doubles the pore volume without changing the average BJH pore size. Thus, the thermal stability of the amorphous framework walls clearly is enhanced without sacrificing the channel size or packing motif. Improved thermal stability also is realized for the La^{3+}-doped mesostructures assembled from Pluronic surfactants, even at the 1 mol% doping levels.

We conclude from the above results that the framework walls of mesoporous MSU-X molecular sieve aluminas are stabilized by the incorporation of rare earth cations. This stabilization effect is general in scope and can be applied over a range of rare earth metal ion loadings to structures assembled from different families of non-ionic polyethylene oxide surfactants. Although the framework walls in MSU-X alumina molecular sieves are amorphous and lack the quasi-crystalline order of transition aluminas, the stabilization mechanisms most likely are related. Thus, rare earth doping also should be effective in stabilizing the amorphous walls of alumina mesostructures assembled through S–I and S$^-$I$^+$ pathways.[2,3]

Based in part on the absence of XRD evidence for the formation of rare earth aluminates upon calcination, we favor a stabilization mechanism in which the lability of the oxide framework is reduced through site substitution of aluminium by rare earth cations. The incorporation of the rare earth cations into the oxide framework occurs during the mesostructure assembly process. We may rule out a doping process in which the rare earth is first incorporated into the mesostructure by complexation to the polar ethylene oxide head groups of the surfactant phase and then subsequently transferred into the framework upon calcination. Rare earth incorporation into the framework occurs even when the surfactant is removed from the mesostructure by solvent extraction under ambient conditions. Thus, the direct incorporation of the rare earth cations into the framework structure is a general feature of the assembly pathway.

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Notes and References

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