Inorg. Chem. 1988, 27, 766-767

Cation Replacement in α-$LiAlO_2$

Sir:

Ion exchange is a low-temperature technique that can be used to obtain new solid-state compounds and metastable structures that cannot be prepared by conventional solid-state syntheses.[1] If the incoming species is a proton or a proton accompanied by water and the substrate is a metal oxide, then the product is in effect an oxide hydroxide or a hydrous oxide, respectively. Subsequent dehydration and/or dehydroxylation will result in an anhydrous oxide. For example, complete proton exchange of the layered oxide $K_2Ti_4O_9$ results in $H_2Ti_4O_9 \cdot xH_2O$ ($x \leq 2$), and by controlled dehydration/dehydroxylation a new polymorph of TiO_2 results.[2]

Ion-replacement reactions are not limited to channel or layered structures, as evidenced by the synthesis of HMO_3 (M = Nb^{5+}, Ta^{5+}) from $LiMO_3$.[3] $LiMO_3$ (M = Nb^{5+}, Ta^{5+}) lacks an open framework, hence there is no apparent ionic interdiffusion pathway. The reaction is believed to proceed by ionic diffusion in the solid phase because a solution phase dissolution–reprecipitation mechanism has been experimentally ruled out.[4] This novel reaction prompted our investigation into other mixed-metal oxides that would exhibit similar reactivity.

We are studying the Li^+ ion–proton-exchange behavior of mixed-metal oxides with the composition $LiMO_2$, where M is a trivalent cation. Where both cations adopt octahedral coordination, one of three superstructures of NaCl (rock salt) will generally result.[5] If the cations are completely disordered, cubic symmetry ($Fm\bar{3}m$) is retained, as in α-$LiFeO_2$. The α-$NaFeO_2$ structure occurs when the monovalent and trivalent cations order in alternating close-packed layers between oxide ion layers to form a rhombohedral structure ($R\bar{3}m$). Where each plane contains both cations, they generally order into zigzag chains where each cation has two like and four unlike near-neighbor cations within the plane, forming a tetragonal structure ($I4_1/amd$) as in γ-$LiFeO_2$. More bonding arrangements exist if both cations are not octahedrally coordinated.

In this communication we report on the reaction of α-$LiAlO_2$ (α-$NaFeO_2$ structure) with molten benzoic acid to form the compound $Li_{1-x}H_xAlO_2$ ($x \geq 0.95$). Upon reaction, the rhombohedral unit cell of α-$LiAlO_2$ ($c_H/2a_H = 2.54$) changes to a cubic unit cell ($c_H/2a_H = 2.45$). This change, along with X-ray powder diffraction peak intensities, leads us to propose a model for $Li_{1-x}H_xAlO_2$ based on a cubic spinel structure.

Preparation of α-$LiAlO_2$. The original synthesis of α-$LiAlO_2$ reported that α-Al_2O_3 and Li_2CO_3, when reacted at 600 °C, formed α-$LiAlO_2$.[6] Our experience has been that mixtures of the α- and γ-polymorphs of $LiAlO_2$ are formed when α-Al_2O_3 is used as a reactant. Boehmite (AlO(OH)) was found to react with a stoichiometric amount of Li_2CO_3 at 600 °C to yield polycrystalline α-$LiAlO_2$, based on X-ray powder diffraction.

Preparation of $Li_{1-x}H_xAlO_2$. A typical reaction used 1.5 g of α-$LiAlO_2$ and 75 g of benzoic acid. The mixture was heated to 200 °C in a covered flask for 36 h. The molten benzoic acid (mp 121 °C) was kept well stirred and then decanted upon termination of the experiment. The solid product and acid residue were cooled, and the lithium benzoate coproduct and unreacted acid were removed with three 100-mL portions of methanol and one 100-mL portion of hot (95 °C) water. The product was dried at 105 °C in a forced-convection drying oven and stored in a desiccator.

Characterization. X-ray Powder Diffraction (XRD). Powder diffraction patterns were recorded with Cu Kα radiation (λ = 1.5418 Å) and a Ni filter on a Rigaku Geigerflex diffractometer. KCl was used as an internal standard in lattice parameter determinations. The lithium content of $Li_{1-x}H_xAlO_2$ was determined by calcination at 1100 °C, followed by comparison of the peak intensities of the resulting mixture of $LiAl_5O_8$ and α-Al_2O_3 to standards of known $LiAl_5O_8$:α-Al_2O_3 ratios.

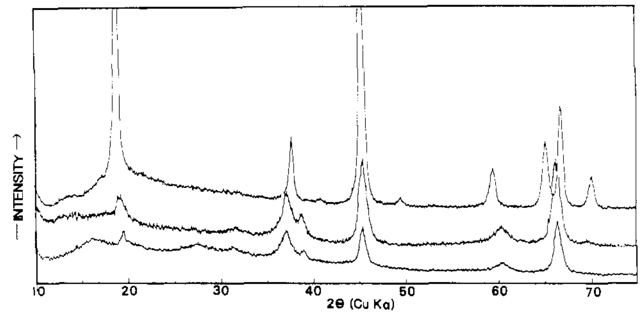

Figure 1. Powder X-ray diffraction spectra: (a) α-$LiAlO_2$ (top); (b) $Li_{1-x}H_xAlO_2$; $x \geq 0.95$ (middle); (c) $Li_{1-x}H_xAlO_2$ (bottom) after calcination at 500 °C.

Thermogravimetric Analysis (TGA). Thermogravimetric measurements were performed with a Du Pont 9900 thermal analysis system. Thermograms were recorded at a heating rate of 5 °C/min under a 50 cm^3/min flow of dry air.

Infrared Spectroscopy (IR). Infrared spectra were collected on a Perkin-Elmer Model 283 spectrophotometer with a pressed KBr pellet.

Atomic Absorption Spectroscopy (AA). A Hitachi Model 180-80 atomic absorption spectrometer was used for quantitative metal analysis. Lithium was analyzed in an air–acetylene flame and aluminum analyzed in a nitrous oxide–acetylene flame.

Results and Discussion. The composition $Li_{1-x}H_xAlO_2$ (x = 0.96 ± 0.02%) has been determined by quantitative X-ray diffraction based on the fraction of $LiAl_5O_8$ in α-Al_2O_3 after calcination at 1100 °C. Consistent with the diffraction measurement was the amount of lithium recovered in the benzoic acid melt, determined by atomic absorption to be 95 ± 5% of the lithium in the starting material (α-$LiAlO_2$). It was necessary to wash the product with methanol and hot water to obtain a clean product for TGA analysis. Repeated washing with methanol would not remove all of the benzoate detectable by IR adsorption bands at 1605, 1563, and 1433 cm^{-1}. The hot water removed the last traces of strongly adsorbed benzoate species. TGA of the product gave a weight loss of 14.1% upon dehydroxylation to 900°C, compared to an expected weight loss of 14.2% for x = 0.95.

The yield of the recovered product was 92 ± 3% determined by the weight of recovered solid. The loss of product was due to partial dissolution during reaction. Benzoic acid was chosen as a proton source because its use minimized dissolution (compared to other acids tried) and its high boiling point (249 °C) enabled reaction temperatures of over 200 °C to be used to facilitate diffusion in the solid. The aluminum benzoate recovered in the benzoic acid melt was 7 ± 2% of the initial starting material. This result is in contrast to the complete dissolution of boehmite (AlO(OH)) and formation of aluminum benzoate that we have observed in molten benzoic acid. The β an γ forms[7] of $LiAlO_2$ do not react or dissolve under identical conditions. These results indicate that proton exchange in α-$LiAlO_2$ proceeds by an interdiffusion pathway.

The X-ray diffraction powder patterns of the starting material (α-$LiAlO_2$), the ion-exchange product ($Li_{1-x}H_xAlO_2$), and the product obtained after calcination (450 °C for 3 h) are shown for comparison in Figure 1. The Al^{3+}–O^{2-} layer–layer separation (ionic radii[8] O^{2-} = 1.40 Å and Al^{3+} = 0.535 Å) of ≈2.0 Å is a prominent Bragg peak in all three patterns. Their diffraction patterns maintain similarities because all samples have a cubic close-packed oxide ion lattice. The structure[6] of α-$LiAlO_2$ is

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0020-1669/88/1327-0766$01.50/0

Table I. Calculated versus Observed X-ray Powder Pattern

hkl	d_{calcd}, Å	I_{calcd}	d_{obsd}, Å	I_{obsd}
111	4.61	37	4.65	34
220	2.83	21	2.84	16
311	2.41	76	2.41	75
222	2.31	27	2.31	23
400	1.998	100	1.992	94
331	1.834	0		
422	1.631	7		
511, 333	1.538	40	1.535	36
440	1.413	94	1.411	100
530	1.351	4		

trigonal ($R\bar{3}m$) with hexagonal lattice parameters $a_H = 2.800$ (1) Å and $c_H = 14.22$ (1) Å or, alternatively, rhombohedral lattice parameters $a_R = (1/3)\ (3(2a_H)^2 + c_H{}^2)^{1/2} = 5.74$ Å and $\alpha = 2$ arcsin $[3/(2(3 + (c_H/2a_H)^2)^{1/2})] = 58.4°$. The doubling of the a_H parameter in the conversion is required by the ordering of the Li^+–Al^{3+} ions into layers perpendicular to c_H.

The powder pattern of the product after ion exchange (Figure 1) can be indexed with an analogous hexagonal cell $a_H = 2.823$ (3) Å and $c_H = 13.82$ (9) Å. However, the ratio $c_H/2a_H$ takes on the special value of 2.45, indicating that the rhombohedral angle α is 60.0° and $a_R = 5.643$ Å. Such a structure is preferentially described by a face-centered cubic lattice with $a_c = 2^{1/2} a_R = 7.981$ Å. These changes suggest that the regular alternation of trivalent (Al^{3+}) and monovalent (Li^+ or H^+) ions is not preserved during the ion exchange. The observed intensities, including the absence of the 200 and 420 reflections, are best fit with a spinel structure model ($Fd\bar{3}m$). The model used placed tetrahedral Al^{3+} on 8(b), octahedral Al^{3+} on 16(c), and O^{2-} on 32(e). The occupancy factor of the cation sites was constrained such that the Al:O ratio was 1:2, requiring that $f = f_{tet} + 2f_{oct} = 2.0$. No distinction was made between oxide and hydroxide anions. The best overall fit of peak intensities ($R = 7.7\%$, Table I) was obtained with the composition $Al_{0.6}(tet)Al_{1.4}(oct)O_2(OH)_2$ and $x = 0.242$ for the oxygen position. The function minimized was $R = 100\sum|I_{obsd} - I_{calcd}|/\sum I_{obsd}$. More studies including ^{27}Al MAS-NMR are under way to characterize this interesting new pseudo aluminum oxide hydroxide.

At 475–500 °C $Li_{1-x}H_xAlO_2$ is converted to a transitional alumina with a diffraction pattern (Figure 1) very similar to that of γ-Al_2O_3.[9] The similarity of this powder pattern to that of the uncalcined material is interesting to note because nearly one-fourth of the oxygen has been lost as H_2O during dehydroxylation. This material has a specific surface area (BET method) of 83.4 m^2/g and a pore volume of 0.28 mL/g.

Attempts have been made to remove 100% of the lithium from α-$LiAlO_2$. Longer reaction times and multiple reactions of $Li_{1-x}H_xAlO_2$ with fresh benzoic acid do not succeed in replacing more lithium from the solid.

The reason for less than full ion replacement is not known. The residual lithium may be a necessary part of the structure of $Li_{1-x}H_xAlO_2$. This seems unlikely since the small mole fraction of lithium would not lend much stability to the lattice as does the sodium in β-alumina ($Na_2O{\cdot}nAl_2O_3$, $n \simeq 11$). The lithium left could be trapped in the interior of relatively large α-$LiAlO_2$ crystallites during the ion-replacement reaction and subsequently be unable to diffuse through the solid product into the acid solution. A third possibility is that the lithium in the product is the result of impurities in the α-$LiAlO_2$ starting material. Because β- and γ-$LiAlO_2$ nucleate under conditions similar to those for α-$LiAlO_2$, as shown by our syntheses and others,[10] and β- and γ-$LiAlO_2$ do not undergo lithium replacement, the lithium in the solid product may arise from small amounts of these impurities that have not been detected by powder X-ray diffraction. The latter two possible explanations for the cause of residual lithium in $Li_{1-x}H_xAlO_2$ would mean that this solid is actually a nonhomogeneous mixture. Future attempts to prepare pure $HAlO_2$ will include careful synthesis of α-$LiAlO_2$, particle size control, and elimination of trace amounts of other polymorphs through the use of high-pressure[11] and salt-imbibition[12] syntheses.

Acknowledgment. This research was sponsored by the Alcoa Foundation and the Materials Research Center at Northwestern University under NSF(DMR) Grant 8520280.

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Received October 30, 1987