Characterization of the $Li_{1-x}H_xAlO_2$ system; $0.00 \leqslant x \leqslant 0.90$

D.C. Tomczak, S.H. Thong and K.R. Poeppelmeier

Department of Chemistry and Ipatieff Catalytic Laboratory, Northwestern University, Evanston, IL 60208, U.S.A.

The mechanism of cation replacement in the $Li_{1-x}H_xAlO_2$; $0.00 \leqslant x \leqslant 0.90$ system was investigated with XRD. Examination of the peak position and intensity associated with the 018 and 110 Bragg reflections ($R\bar{3}m$) in a series of partially replaced samples showed that the cation replacement process proceeded by a two phase mechanism. Catalytic characterization of $\alpha LiAlO_2$ with the 2-propanol probe reaction revealed the formation of the condensation products methyl-cyclopentene, 4-methyl-2-pentanone, and 4-methyl-2-pentanol. These products were seen in addition to propylene and acetone. Catalytic characterization of $Li_{1-x}H_xAlO_2$; $x = 0.90$ with 2-propanol showed a significant decrease in condensation activity and no change in the propylene/acetone ratio relative to $\alpha LiAlO_2$. This suggests that the decrease in the amount of lithium eliminated the basic sites necessary for the condensation reactions.

Keywords: Catalysis by $Li_{1-x}HAlO_2$; structure of $Li_{1-x}HAlO_2$ catalyst; reactions of 2-propanol on $Li_{1-x}HAlO_2$

1. Introduction

Low temperature synthetic techniques are ideally suited for catalysts because they allow for greater control of the morphological and the chemical properties: surface area, pore size, and acidity/basicity. Mild "chimie douce" [1,2] conditions are desirable in solid state synthesis because they reduce the degree of sample sintering, and they allow for the isolation and synthesis of low temperature phases. The synthesis of "$HAlO_2$", a highly hydrated γ-alumina, occurs when $\alpha LiAlO_2$, is reacted with molten lauric ($CH_3(CH_2)_{10}CO_2H$) or benzoic [3] (Ph-CO_2H) acid at a temperature of 220 °C. The product, $Li_{1-x}H_xAlO_2$; $x = 0.90$, retains the morphological characteristics (no microporosity and a SA approximately equal to 40 m^2/g) of its parent material but undergoes an irreversible structural change from the rock-salt to spinel structure. The fact that the material undergoes a structural change is the reason that this synthetic method is called "cation replacement " and not cation exchange. Partially

replaced samples are obtained by reducing the reaction time and temperature. The nearly fully replaced sample ($x = 0.90$) is a novel AlO(OH) precursor to γ-alumina. Calcination produces a dehydrated γ-alumina like spinel phase which contains approximately a 1:10 mole ratio of lithium to aluminum. The calcined material has a larger SA than the parent compound and has a small amount of microporosity.

This paper discusses the cation replacement mechanism and the catalytic properties of the $Li_{1-x}H_xAlO_2$ system; $0.00 \leqslant x \leqslant 0.90$. X-ray powder diffraction was used to probe the mechanistic aspects of the cation replacement process. Since small amounts of the lithium are difficult to detect by surface chemistry analytical techniques, knowledge regarding the mechanism is important in determining the environment of the lithium cation in the structure and understanding the catalytic chemistry. Examination of the catalytic properties focuses on the characterization of the acidic and basic sites with a probe reaction. 2-propanol is an ideal probe reaction molecule because it allows for the simultaneous analysis of both the acidic and the basic sites. The conversion of 2-propanol over acidic sites produces propylene, and the conversion over basic sites produces acetone. In addition to these compounds, we report the occurrence of significant amounts of 4-methyl-2-pentanol (4M2POL) and 1 or 4 methyl-cyclopentene (MCP) with trace amounts of 4-methyl-2-pentanone (4M2PONE). The condensation to form MCP and 4M2POL has not been reported in the literature.

2. Experimental

SYNTHESIS

$\alpha LiAlO_2$ for the catalytic studies was prepared by reacting stoichiometric amounts of gelatinous boehmite ($(AlO(OH) \cdot n\ H_2O$) Kaiser Chemical) and Li_2CO_3 (99% Aldrich Chemical) at 600°C for a period of 2–3 days in an ambient air muffle furnace [3]. Higher crystalline samples for cation replacement mechanistic studies were prepared by running the reaction at 675°C for 26 hours. Samples were characterized by XRD and BET SA analysis.

$Li_{1-x}H_xAlO_2$ $x = 0.90$ was synthesized by stirring $\alpha LiAlO_2$ in a 5 to 10 molar excess of lauric acid ($CH_3(CH_2)_{10}CO_2H$ for a period of 40 hours at 220°C in a flow of N_2 (for $x = 0.49$ $T = 190$°C for 36 hours). The lauric acid was removed by decanting followed by washing of the solid with acetone. The lithium-laurate salt was removed from the product mixture by washing it with 8M HNO_3 and then acetone. Samples were characterized by the previously mentioned methods plus FTIR, TGA, and AA. FTIR was used as a check for lithium laurate impurity, and TGA and AA were used to determine the degree of cation replacement.

CHARACTERIZATION

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku Geigerflex diffractometer using CuK_α radiation ($\lambda = 1.5418$ Å) radiation with a Ni filter.

Surface area (BET method) studies were conducted on an Omicron Omnisorp 360 instrument using N_2 as the adsorbate gas.

Catalytic studies were done using a continuous flow fixed bed reactor system. He was bubbled through a saturator containing 2-propanol (Aldrich Chemical 99.9%) at a rate of 20 cc/min. The temperature of the saturator was maintained at 39 ± 0.5°C which gave a 50–60 torr partial pressure of 2-propanol. 1.0 cc of 30–40 meshed sample was charged to the glass reactor vessel for each run. Chemical analysis of the product stream was performed with a gas chromatograph HP 5840A) equipped with a 20 ft. 10% Carbowax 20M column and a TC detector. Product stream condensation in a liquid N_2 trap followed by GC/MS analysis (performed by the Analytical Services Laboratory of Northwestern University) was used in the positive identification of the C6 products.

3. Results and discussion

An understanding of the cation replacement mechanism was achieved through an XRD analysis of the shifts and changes in the intensity of the 018 and 110 Bragg reflections of the rhombohedral system. $\alpha LiAlO_2$ is rhombohedral (space group $R\bar{3}m$) [4] with hexagonal unit cell parameters of $a_H = 2.8034(3)$ Å and $c_H = 14.228(2)$ Å. $Li_{1-x}H_xAlO_2$ ($x = 0.90$) ($HAlO_2$) is modeled as a pseudo-spinel cubic structure (space group $Fd\bar{3}m$) [3,5] with a unit cell parameter of $a_c = 7.986(4)$ Å. Fig. 1 shows the relationship between the model for $HAlO_2$ developed by Thong [5] and the ideal spinel structure. Similarities in the XRD patterns of the two samples are due to only small differences in the structures (see fig. 2). Elongation along the 111 direction of the cubic system produces what is known as rhombohedral distortion of a cubic unit cell. If the cation replacement process was to proceed via a solid solution mechanism, the 110 and 018 reflections of the rhombohedral system would smoothly coalesce to the 440 reflection of the cubic system found in the product. Equimolar amounts of sample with varying degrees of replacement were pressed into 13 mm diameter pellets. Samples analyzed in the study had the following degrees of exchange: $x = 0.00$, $x = 0.26$, $x = 0.49$, $x = 0.64$, and $x = 0.90$. For reason of clarity, only three XRD patterns are displayed in fig. 3. It is quite evident from these results that the 018 and 110 reflections do not coalesce. The two reflections of $\alpha LiAlO_2$ decrease in intensity as the degree of replacement increases and the 440 reflection of $HAlO_2$ grows in. This evidence suggests that the cation replacement process proceeds by a two-phase mechanism.

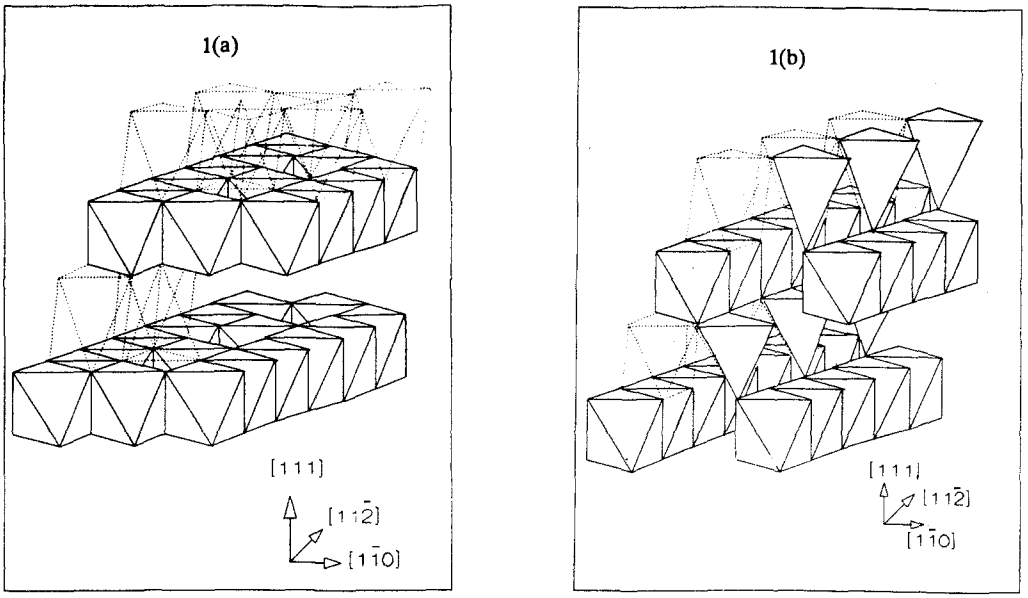

Fig. 1. (a) Ideal spinel structure with the A layers in solid lines and the B layers in dashed lines. Fig. 1(b) Model of $HAlO_2$ illustrating ordering of the cation vacancies with 25% of the aluminum atoms in tetrahedral coordination [5].

Catalytic characterization of the $Li_{1-x}H_xAlO_2$; $0.00 \leqslant x \leqslant 0.90$ system was limited to the two end members ($x = 0.00$ and $x = 0.90$) because this allowed for the study of single phase materials where a maximum in basicity and acidity,

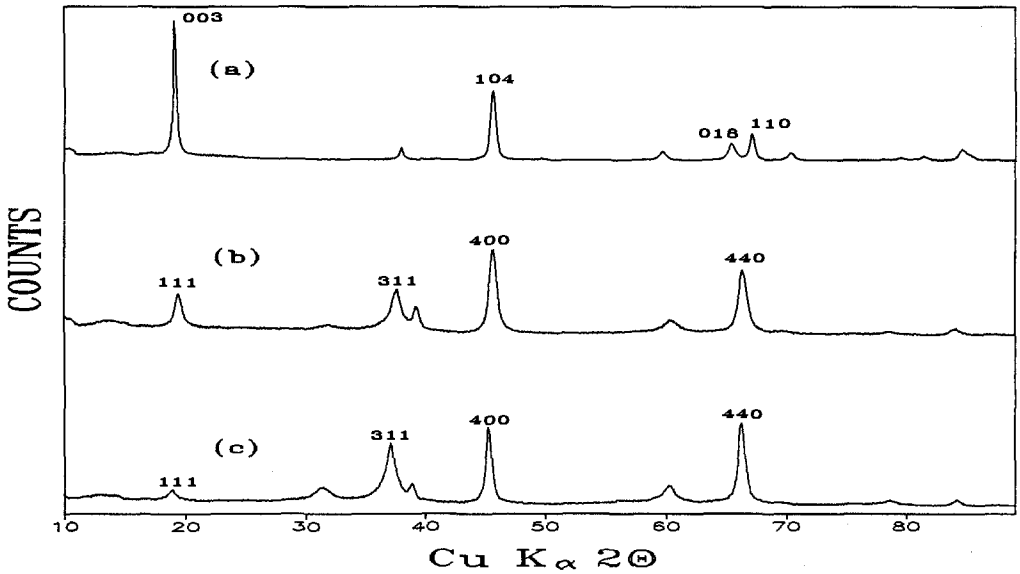

Fig. 2. X-ray powder diffraction patterns of (a) $\alpha LiAlO_2$ made at 675°C, (b) $HAlO_2$, and (c) $HAlO_2$ after 10 hrs of calcination at 500°C.

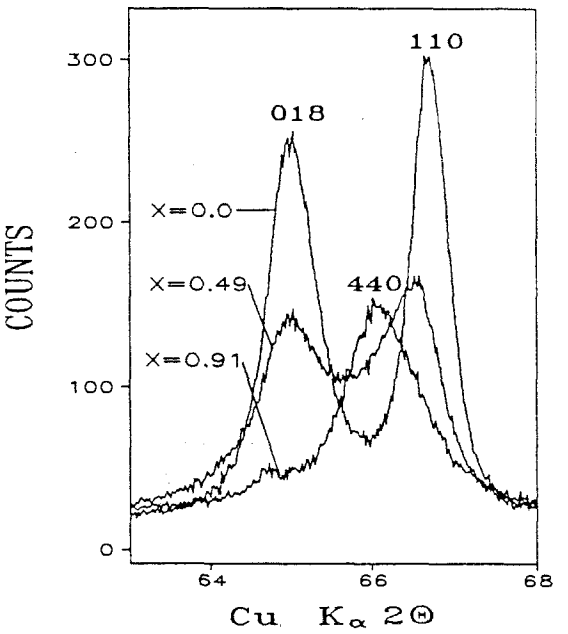

Fig. 3. 018 and 110 reflections of the rhombohedral system and the 440 reflection of the cubic system for three samples where $x = 0.00$, 0.49, and 0.90 for $Li_{1-x}H_xAlO_2$.

respectively, would be expected. The product distribution from the conversion of 2-propanol on $\alpha LiAlO_2$ (BET SA = 43 m^2/g with no microporosity) gives insight into the nature of the active sites. Formation of propylene is widely accepted as an identifier of both acidic and basic sites [6]. Both sites are necessary for the dehydration of a secondary alcohol like 2-propanol. 2-propanol dehydrogenation to form acetone is viewed as a base catalyzed process [7]. The basic sites in mixed metal oxides are those oxide surface species capable of donating electron density because of strongly electropositive cations like Li^+. The condensation product 4M2PONE is formed as a result of acidic and basic sites working in tandem or in succession during the reaction. There are binary oxides and some mixed metal oxides with active acidic and basic sites [8–11], but very few show activity towards this type of condensation chemistry [12–14]. In the literature, the accepted mechanism for 4M2PONE formation involves the condensation of two acetone molecules to form mesityl oxide (4-methyl-3-penten-2-one) which undergoes catalytic hydrogenation of the C=C group with H_2 from 2-propanol dehydrogenation [14]. It is interesting to note that 4M2POL is more prevalent than 4M2PONE (see table 1) which indicates that an additional reaction pathway occurs on $\alpha LiAlO_2$.

A possible mechanism for the formation of 4M2POL can be developed from alcohol/ketone H-exchange chemistry. It is unusual in condensation reactions involving acetone, formed in situ, that an OH monofunctional product like

Table 1

Temp (°C)	Acetone (%)	Propylene (%)	MCP (%)	4-M-2-P-ol (%)	4-M-2-P-on (%)	Conversion (%)
250	0.00	0.8	0.4	0.1	0.00	1.8
275	0.5	1.7	0.9	0.5	0.00	5.0
300	2.2	4.2	2.0	1.8	0.3	14.6

Percentages are in mole percents.
Conversion = [1 − ((IPA)/(IPA + Ace + Prop + (2 × (MCP + 4M2POL + 4M2PONE))))] × 100.

4M2POL is formed. A reasonable mechanism for the formation of 4M2POL may involve the reduction of 4M2PONE with 2-propanol. Ketone reduction can occur via a base catalyzed H-exchange with an alcohol molecule adsorbed on a nearby active site [7]. The first step in this possible mechanism involves the heterolytic cleavage of the alcohol O-H bond to form the alkoxide. This step is followed by an α-hydrogen transfer (H^-) from the alkoxide to the adsorbed ketone. This newly formed alkoxide acquires an H^+ from an acid site and desorbs as an alcohol. Additional research is needed to confirm the relevance of this mechanism.

A possible mechanism for MCP formation can be postulated from the known chemistry of strong bases. As was the case for 4M2PONE and 4M2POL, the C6 parent compound in this mechanism is mesityl oxide. Mesityl oxide can be converted to the corresponding alcohol by the reduction process described above. This corresponding alcohol, 4-methyl-3-penten-2-ol, contains β, γ unsaturation which allows for the possibility of base catalyzed dehydration of the alcohol to form the conjugated diene [15]. In the presence of a strong base, this conjugated diene can undergo ring closure to form MCP [16]. This mechanism is speculation at this point, but would fit the conditions that appear to exist on the surface of $\alpha LiAlO_2$. As in the case of 4M2POL, additional evidence needs to be gathered in the form of positively identified intermediate molecules or pathways which infer the existence of the discussed intermediates.

The conversion of 2-propanol over $HAlO_2$ (calcined 10 hrs at 500°C BET SA = 69 m^2/g, micropore volume = 1.8 E-2 ml/g) gives a product distribution indicative of the acidic character of the lithium doped γ-alumina. The small increase in conversion can be attributed to the increase in SA (see table 2). Through cation replacement, the lithium/aluminum ratio is reduced by a factor

Table 2

Temp (°C)	Time (hrs)	Propylene (%)	Acetone (%)	MCP (%)	Iso-ether (%)	Conversion (%)
300	1.0	11.3	6.4	0.2	0.2	18.5

Percentages are in mole percents. Iso-ether = Di-isopropyl ether.
Conversion = [1 − ((IPA)/(IPA + Ace + Prop + (2 × (MCP + Iso-ether))))] × 100.

of ten, and thus the basicity of the material's surface is reduced. The propylene/acetone ratio is 1.89 for $x = 0.00$ and 1.96 for $x = 0.90$. This lack of variance indicates that the removal of the lithium eliminates those basic sites which are necessary for the formation of mesityl oxide and the subsequent reactions.

4. Conclusion

In conclusion, we have shown through XRD that the cation replacement mechanism in the $Li_{1-x}H_xAlO_2$; $0.00 \leqslant x \leqslant 0.90$ system proceeds by a two phase process. Conversion of 2-propanol to MCP, 4M2PONE, and 4M2POL over $\alpha LiAlO_2$ illustrates the extensive reaction chemistry that can occur on materials with strong basic sites. Catalytic characterization of calcined $HAlO_2$ with 2-propanol showed a loss of condensation activity coupled with no significant change in the propylene acetone ratio compared with $\alpha LiAlO_2$.

Acknowledgments

The authors gratefully acknowledge support from the Department of Energy,contract DE-F605-86ER75295, for the surface area and porosity measurement equipment, and from the National Science Foundation, Solid State Chemistry, contract DMR-8915897, for support on compound precursors to mixed metal oxides. The authors would also like thank Herman Pines for his insightful comments regarding the catalytic results.

References

[1] M. Figlarz, Chem. Scr. 28, No. 1 (1987) 3.
[2] C. Delmas, Y. Borthomieu, C. Faure, A. Delahaye and M. Figlarz, Solid State Ionics 32-33, Pt. 1 (1989) 104.
[3] K.R. Poeppelmeier and D.O. Kipp, Inorg. Chem. 27, No. 5 (1988) 767.
[4] V.H.A. Lehmann and H.Z. Hesselbarth, Anorg. Allg. Chem. 313 (1961) 117.
[5] S.H.K. Thong, Thesis, Northwestern University, 1989.
[6] H. Pines and J. Manassen, Adv. Catal. 16 (1966) 49.
[7] C.L. Kibby and W. Keith Hall, J. Catal. 31 (1973) 65.
[8] A. Eucken and K. Heuer, Z. Physik Chem. 196 (1950) 41.
[9] K. Balasubramanian and V. Krishnasamy, Indian J. Chem. 21A (1982) 813.
[10] I. Udrea and D. Crisan, Rev. Roum. Chim. 20 (1975) 217.
[11] F. Pepe and F.S. Stone, J. Catal. 56 (1979) 160.
[12] B. Viswanathan, N.S. Raman and T.K. Varadarajan, Indian J. Chem. 29A (1990) 1135.
[13] E. Suzuki, S. Idemura and Y. Ono, Chem. Lett. (1987) 1843.

[14] M.P. Sridhar Kumar, B. Viswanathan, C.S. Swamy and V. Srinivasan, Indian J. Chem, 28A (1989) 19.
[15] H. Pines, *Base-Catalyzed Reactions of Hydrocarbons and Related Compounds* (Academic Press, New York, 1977) 544–550.
[16] Ibid. p. 108–116.