Dispersion Studies on the System La$_2$O$_3$/γ-Al$_2$O$_3$

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According to the literature and earlier studies in this laboratory, lanthanum oxide appears to be the best of the known additives for inhibiting the sintering of high-surface-area aluminas. The substrates of the present studies were largely γ-alumina, with minor components of transition aluminas, σ-alumina, and possibly θ-alumina. Alumina samples with different lanthanum concentrations, produced by impregnation with aqueous lanthanum nitrate, followed by calcination at various temperatures, were studied by chemisorption of carbon dioxide, Auger electron spectroscopy, Raman spectroscopy, and by X-ray powder diffraction (XRD). All results are consistent with the following description: Up to a concentration of 8.5 μmol La/m^2, the lanthana is in the form of a two-dimensional overlayer, invisible by XRD or Raman spectroscopy. For greater lanthana concentrations, the excess lanthana forms crystalline oxides, detectable by XRD. In samples calcined to 650°C, this crystalline phase is cubic lanthanum oxide. After calcination at 800°C, the lanthana reacts to form the lanthanum aluminate LaAlO$_3$. © 1989 Academic Press, Inc.

INTRODUCTION

Lanthanum oxide appears to be the best-known inhibitor against loss of surface area in γ-alumina and in other transition aluminas. Schaper and Van Reijen (*1*) found La$_2$O$_3$ to work better than MgO, Cr$_2$O$_3$, or ZrO$_2$. Gandhi (*2*) determined the ranking La$_2$O$_3$ > BaO > CeO$_2$ for effectiveness in preventing sintering in γ-alumina, as measured by loss of surface area. Schaper *et al.* (*3, 4*) investigated the mechanism of sintering in pure and lanthana-doped γ-alumina, at 600–1100°C. They concluded that the mechanism is one of surface diffusion and that there is always a profound loss of surface area *before* the final transition to α-alumina takes place. To explain this, they suggest that α-alumina can nucleate easily only in the recrystallized necks between transition-alumina crystals.

Since X-ray diffraction (XRD) showed no lanthanum-containing phases, they investigated the structure of La$_2$O$_3$/γ-Al$_2$O$_3$ by doping the lanthana with 1% gadolinia, which is paramagnetic. These samples produced an EPR spectrum very similar to the EPR spectrum of 1% Gd in LaAlO$_3$. In dis-

cussing this finding (*3*), they speak somewhat vaguely of "a lanthanum aluminate compound on the alumina surface, forming impassable blocks" to surface diffusion. Since the effectiveness of lanthana addition saturates below the estimated concentration corresponding to a La$_2$O$_3$ monolayer, these "blocks" must either be extremely tiny blocks of three-dimensional (3D) lanthanum aluminate, in order to be spaced closely enough to influence surface diffusion rates, or, perhaps the quoted authors feel that they are dealing with a two-dimensional (2D) lanthanum aluminate surface compound in which, coincidentally, substitutional gadolinium ions give the same EPR spectrum as they do in LaAlO$_3$. We shall suggest another possibility under Discussion.

For completeness, it should be mentioned that Schaper *et al.* (*5*) also tested the effectiveness of lanthana as a sintering inhibitor for γ-alumina under 12 atm of steam, at 840°C. Lanthana had some effectiveness under these conditions, as well. However, the effect had not yet saturated at 5 mole% La$_2$O$_3$, the highest concentration tested, and the final surface area at this

concentration was only 30 m²/g. Thus, the concentration of lanthana per unit surface was much larger than that in the previous "dry" experiments. After steam sintering, XRD showed $LaAlO_3$ phase, even at 1 mole%. This is not surprising, considering the high concentrations reached, per unit area, due to massive sintering. We do not feel that these XRD findings necessarily support the concept of tiny, 3D blocks of $LaAlO_3$ for the case of the dry experiments, considering their much lower surface concentration ranges, and possibly quite different sintering mechanisms.

Xie et al. (6) investigated the structure of the dispersion of La_2O_3/γ-Al_2O_3 by XRD only. In effect, they looked for the disappearance of La_2O_3 lines with decreasing La_2O_3 concentrations. At the concentration where the La_2O_3 crystalline phase was no longer visible, either from direct observation or from careful extrapolation from higher concentrations, they considered the lanthana to be present in the form of a two-dimensional monolayer on top of the alumina. Their value for the saturated monolayer is 17.2 μmole La/m², along with 25.8 μmole/m² associated oxide ions, assuming the formula La_2O_3. As the authors point out, this oxide concentration alone is large enough to amount to a trigonal close-packed layer of oxygen ions blanketing all substrate surfaces, with the La^{3+} ions having to be placed on top of the blanket of oxygen ions. This amounts to enclosing the whole substrate crystal with a dipole layer whose dipole vector points toward the substrate surface everywhere, a situation which is not considered to be energetically feasible (7). Another way of putting it is that there would be patches of oxide ions sitting upon oxygen ions of the substrate, without any cementing cations in between.

It is also difficult to believe that such a uniform, close-packed oxide layer can constitute a coincident 2D lattice, relative to all the (hkl) substrate surfaces which it covers. A high degree of coincidence, we believe, is absolutely necessary for the formation of a low-energy ionic overlayer upon an ionic substrate. Otherwise, an overlayer ion, randomly placed relative to the substrate lattice, would as often be coordinated to substrate ions of the same charge as to those of opposite charge. The net energy of coherence would be only a weak van der Waals effect. This should result in a great driving force for dewetting, i.e., agglomeration, of the overlayer into equi-axed, 3D crystals of its own preferred phase. The resulting lowering of the energy would then comprise the difference between the lattice energies of the new crystal and those of the 2D overlayer, less the small van der Waals adhesion mentioned above. Since the 2D layer has only lateral interactions, i.e., its atoms are poorly coordinated, its lattice energy must surely be much lower that that of a 3D structure. Such considerations suggest that a 2D overlayer can be stable only if it strongly adheres to the substrate and/or if the alternatively available 3D structure has a relatively small lattice energy.

The XRD method used by Xie et al. is likely to lead to an exaggerated value for the concentration of the assumed monolayer. Even in the absence of such a monolayer, there exists a threshold volume fraction for a minority crystalline phase below which it is not detectable by XRD, being lost in the incoherent scattering background from majority phases. This threshold value will be added to the concentration of the 2D layer according to the assumptions made by Xie et al. Even extrapolation toward the abscissa from higher concentrations cannot eliminate this problem, because of inherent nonlinearities.

We also propose a 2D overlayer of lanthana over γ-alumina, but our value for the saturation of this layer is almost exactly one-half of the value reported by Xie et al. We have studied this layer by CO_2 chemisorption and by Auger electron spectroscopy (AES).

According to the phase diagram of lanthana–alumina, one should see the "La–β-alumina" phase, sometimes called "lan-

thanum hexaaluminate,'' of nominal composition $La_2O_3 \cdot 11Al_2O_3$, in dilute lanthana–alumina mixtures. That phase is difficult to nucleate and is normally prepared at temperatures of about 1400°C (8), although Matsudo et al. (9) were able to produce the phase by coprecipitation methods at temperatures as low as 1000°C. It appears that in samples produced by impregnation with aqueous lanthanum nitrate, the crystalline phase that develops, beyond the postulated 2D layer saturation, is cubic La_2O_3 below about 700°C and $LaAlO_3$ between about 800°C and at least 1000°C. (The latter, of course, remains stable at much higher temperatures, at sufficiently high concentrations.)

EXPERIMENTAL

Sample Preparation

DeGussa Alumina C was the substrate used for the chemisorption samples. Because of the fluffiness of this alumina, it was first made into a thick aqueous slurry and then dried and calcined for 16 hr at 900°C. The resulting agglomerates were crushed and sieved. Granules in the 0.5–1.0 mm range were used for impregnation. Lanthanum nitrate, about 99⁺% pure, was obtained from Molycorp Corp. Impregnation was performed with aqueous lanthanum nitrate solutions by the incipient wetness method, which permits predetermination of the final sample concentration. The most concentrated stock solution was analyzed by an inductively coupled plasma (ICP) atomic emission spectrometer. No further chemical analyses were carried out. After impregnation, the moist samples were kept in sealed containers for 20 hr to encourage rehomogenization in the conceivable event of fractional adsorption during impregnation. They were then dried for 1 hr at 120°C, followed by a 4-hr calcination at 800°C. This temperature was chosen because Bernal et al. (10) report that it takes temperatures of 700–800°C to remove the last traces of CO_2 from lanthanum oxide that has been exposed to ambient air.

The lanthanum oxide used for chemisorption was Alfa Products (Morton Thiokol Corp.) ''ultrapure'' grade. Polycrystalline $LaAlO_3$ was made by coprecipitating with ammonia, at pH 9, a solution of 0.1 M aluminum nitrate and 0.1 M lanthanum nitrate. The dried precipitate was ground, mixed with 3% Carbowax 600 binder, pressed isostatically at 45 kpsi, and calcined at 900°C for 20 hr. It was nevertheless found by XRD to be phase-impure, with a La_2O_3 component estimated to be about 10%.

The AES samples were impregnated disks, also derived from DeGussa Alumina C, agglomerated, and calcined 6 hr at 700°C. After crushing and sieving, the −35-mesh (<0.5-mm granules) portion was dry-pressed at 20 kpsi in a 1.27-cm-diameter steel die. Most disks were about 2 mm thick. Although mechanically weak, they were sufficiently coherent to be clamped onto an instrument stage. Their BET surface area was 112 m²/g, measured by N_2 adsorption. We assume 16.2 and 16.9 Å² for the areas of the N_2 molecule and the Ar atom (11), respectively, in all our BET measurements. Other literature references place the Ar area in the 13.8–14.6 Å² range. However, several independent comparisons of BET measurements on catalysts supported on γ-alumina in our laboratory have shown that the higher value derived by Pickering and Eckstrom (11) yields the best agreement with nitrogen adsorption, if a nitrogen area of 16.2 Å² is assumed. The disks were impregnated with aqueous lanthanum nitrate, by the method of incipient wetness, as described above for the case of granules. It was attempted to produce a series of eight disks, each with twice the concentration of the preceding one, establishing the series 0.5, 1.0, 2.0, . . . , 64.0 μmole La^{3+}/m^2. Due to the finite concentration of the stock solution, the last three samples had to be impregnated several times, to reach desired concentrations. The lanthanum nitrate was converted to oxide by a 2-hr calcination at 630°C, between suc-

cessive impregnations. The final calcination was for 5 hr at 630°C for all samples. In the case of successive impregnations, it was assumed that the sample would absorb the same volume of solution each time. The BET area of these disks was not remeasured after impregnation because of their mechanical delicacy. The original alumina area of 112 m^2/g was therefore assumed for the concentration calculations.

Sample preparation in two different batches was the result of planning of the CO_2 chemisorption measurements *after* the AES experiments were already in progress. As prepared, the impregnated disks used for AES measurements were not suited for chemisorption.

Procedures

CO_2 chemisorption experiments were carried out at room temperature on a Cahn-type RG microbalance. Before each run, the sample was reheated to 800°C under vacuum for about 0.5 hr, and cooled back to ambient as quickly as possible by admitting some helium as a heat transfer gas. After reevacuation, CO_2 was admitted at various pressures. After each increase in CO_2 pressure, the sample weight took a fast initial jump upward and then approached a straight line, with nonzero slope, in about 10 min. This slope was attributed to moisture absorption. The apparatus contained residual water vapor in the 10^{-5}–10^{-4} Torr range. The linear increases, between steps, were therefore ignored. In effect, we were measuring only the fast portion of the chemisorption, limited to the first 10 min of uptake. A single experiment in a volumetric apparatus demonstrated that the fast chemisorption is followed by a very slow tail of continuing adsorption, which was necessarily ignored in the gravimetric apparatus. After measurement of the incremental CO_2 uptake at several increasing pressures, the apparatus was evacuated for about 1 hr, and the CO_2 adsorption experiments were repeated. This second set of weight gain vs CO_2 pressure data was considered to be

"reversible" chemisorptions. The original set is the "total" chemisorption points, and the differences between the two curves are considered to be the "irreversible" chemisorption values. The irreversible points form a good straight line vs pressure, with a small positive slope. The zero-pressure intercept of this line is the value listed in Table 1 and Fig. 1. After the CO_2 chemisorption measurements, a BET measurement was carried out with Ar at 77 K, after first reheating the sample to 800°C. Helium again was used as a heat transfer gas to help cool the sample to 77 K.

AES analysis was carried out by a scanning Auger microprobe (Physical Electronics Model 545). All samples were loaded on the same carousel. Because of their hygroscopic nature, they were outgassed for several days in the analysis chamber. During analysis, the background pressure had stabilized at 6×10^{-10} Torr, and all samples were analyzed under the same conditions. A relatively low electron beam current of 200 nA was used, and the beam was defocused to a diameter of about 240 μm to avoid charging artifacts and electron beam effects. A modulation voltage of 3 eV was used to acquire spectra in the derivative mode. Survey spectra showed the presence of lanthanum, aluminum, and oxygen, as
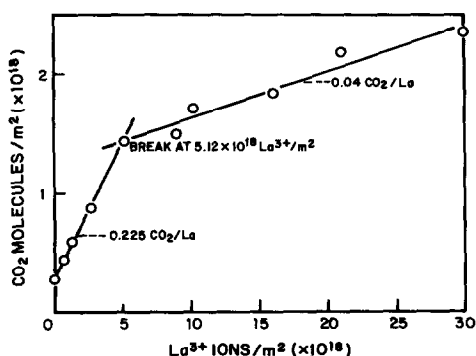

FIG. 1. Carbon dioxide chemisorption [molecules/ $m^2(\times 10^{18})$] versus lanthanum ion concentration [La^{3+} ions/$m^2(\times 10^{18})$]. Units recalculated from Table 1.

TABLE 1

Sample No.	$\dfrac{\text{g La}}{\text{g Al}_2\text{O}_3}$	$\dfrac{\text{mg CO}_2}{\text{g sample}}$	Ar BET (m^2/g)	$\dfrac{\text{m}^2\,^a}{\text{g Al}_2\text{O}_3}$	$\dfrac{\mu\text{mole La}^a}{\text{m}^2}$	$\dfrac{\mu\text{mole CO}_2}{\text{m}^2}$
1	0.0136	2.98	91.7	93.1	1.05	0.739
2	0.0273	3.91	87.9	90.8	2.16	1.011
3	0.0545	5.34	83.7	89.0	4.41	1.45
4	0.101	8.08	76.5	85.6	8.50	2.40
5	0.162	7.90^b	72.2^b	85.9	13.54	2.49
6	0.202	8.72^b	69.8^b	86.4	16.83	2.84
7	0.302	8.19	60.7	82.1	26.46	3.07
8	0.404	9.08	56.7	83.5	34.80	3.64
9	0.505	7.94	46.0	73.2	49.62	3.92
γ-Al$_2$O$_3$		1.75	85.9	85.9		0.46
La$_2$O$_3$		0.55	0.8			15.4
LaAlO$_3$^{c}		1.27	9.24			3.12

^{a} Each La is assumed to add mass according to formula LaO$_{1.5}$.

^{b} Average of two measurments.

^{c} Phase-impure, with a La$_2$O$_3$ component.

expected, as well as small amounts of adventitious carbon and chlorine.

RESULTS

Chemisorption

The results of the carbon dioxide chemisorption experiments are presented in Fig. 1 and Table 1. The first four columns of the latter are essentially raw data. Column 2, the ratio of grams of lanthanum ions to grams of alumina, is obtained from the impregnation calculations. Columns 3 and 4 were measured in the microbalance. In column 4 the BET areas per gram of *sample* decrease substantially for the more concentrated samples. However, this decrease is largely due to the large added mass of the lanthanum. This is illustrated by column 5, the areas per gram of *alumina* in the samples. These were calculated by subtracting the mass contributed by lanthanum, assumed to be in the form of La$_2$O$_3$, from the total sample mass. The same assumption was used in calculating the La surface densities of column 6 from columns 2 and 4.

The specific CO$_2$ adsorption (column 7) is plotted vs the lanthanum surface concentration (column 6) in Fig. 1. The points fall on two straight lines, with an intersection at

5.12 × 10^{18} La ions/m^2 (= 8.5 μmole/m^2). Below this value, the slope suggests that about one CO$_2$ molecule is adsorbed for every 4 La ions. Beyond the intersection, the slope is only about one CO$_2$ for every 25 additional La ions. Note that unimpregnated γ-alumina chemisorbs a small quantity of CO$_2$, but not enough to interfere with the precision of the other measurements.

Auger Spectroscopy

AES results are summarized in Fig. 2, where the normalized lanthanum Auger peak-to-peak heights are plotted versus lanthanum concentration. The calculated concentrations of the eight samples are 0.46, 0.94, 1.88, 3.76, 7.51, 15.0, 30.0, and 56.3 μmole La/m^2 of initial alumina area, subject to the uncertainties detailed under Experimental. The three curves are for the three lanthanum Auger lines at 625 eV (MNN), 91 eV (NVV), and 71 eV (NVV). The results are similar for all three. There appears to be a break in slope between 8 and 9 μmole La/m^2, similar to the chemisorption results, though the AES result is less precise as reflected by more scatter in the data. The cause for the large deviation of the sample at 30 μmole/m^2 is unknown, but as-
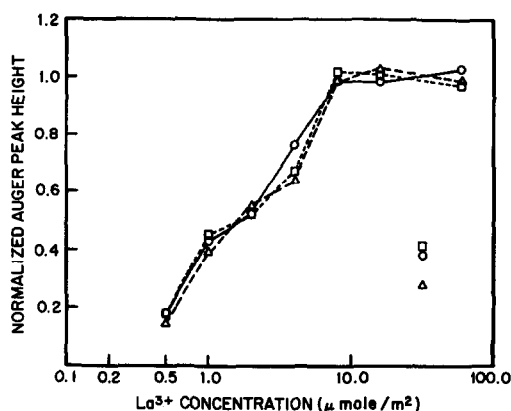
FIG. 2. Normalized peak-to-peak AES response for the three lanthanum AES peaks at 71 (O), 91 (△), and 625 eV (□) versus lanthanum ion concentration in micromoles per square meter.

sumed to be accidental rather than meaningful. The points for this sample were ignored in drawing the curves. An important aspect of the AES results is that the AES samples were calcined at 630°C, only slightly above the temperatures used by Xie *et al.* (*6*) compared to the preparation at 800°C of the chemisorption samples. Interesting and unexplained is the lack of any appreciable slope of the AES response vs concentration in the concentrated region, where the excess lanthanum is in the form of cubic La_2O_3 crystals (as determined by XRD in the case of other, similarly treated samples). A possible speculation was offered by Baird (*12*) of this laboratory: In the process of impregnation, the drying impregnating solution may shrink into the smallest pores by capillarity, where the impregnate will crystallize out upon further drying. The smallest pores are unlikely to be found on the geometrical surface of pressed pellets. Therefore, surface science tools may generally miss some impregnate (i.e., catalyst), when dealing with practical supports.

DISCUSSION

The chemisorption results, Fig. 1, show a sharp break in slope. The dilute region, with a relatively large slope, corresponds to a high dispersion of lanthana. In this region, about one-fourth of a molecule of CO_2 is adsorbed for each lanthanum atom in the sample. In the concentrated region, only 0.04 molecule of CO_2 is adsorbed for each additional lanthanum atom. This is attributed to the presence of relatively large lanthanum aluminate crystals in this region, where most lanthanum ions are subsurface, hence inaccessible to chemisorption. Sample No. 5 (cf. Table 1), the most dilute sample in the concentrated region, shows the presence of $LaAlO_3$ by XRD. By contrast, XRD of sample No. 4 shows only γ-alumina and a small amount of δ-alumina.

It does not seem plausible to us, as suggested by a reviewer of this paper, that the sharp break can be explained by surface heterogeneities. If this were the case, a gently curved plot, especially in the dilute region, would be expected.

The Auger results indicate a break at approximately the same concentration, for samples calcined only to 630°C, where the lanthanum-containing phase in the concentrated range is cubic lanthana, according to XRD. We attribute the high-dispersion region to a two-dimensional overlayer of lanthanum oxide on γ-alumina. One could alternatively consider such a layer as a two-dimensional lanthanum aluminate, or a "surface lanthanum aluminate." We have no explanation for the relatively low stoichiometry (0.25) of CO_2 chemisorption per lanthanum ion in this layer.

Our dispersion studies do not absolutely eliminate the possibility of exceedingly small blocks of three-dimensional lanthanum aluminate, proposed by Schaper *et al.* (*3*). If such were the case, however, it would be difficult to explain the sudden change in dispersion which we encounter at surface concentrations exceeding 8.5 μmole La/m^2, a value corresponding to a submonolayer. Furthermore, the extremely large surface energy associated with such microblocks makes this concept inherently unattractive, in our view.

An attempt was made to find a Laser–

Raman spectrum of the postulated 2D over-layer, in the range 100–1000 cm^{-1}. The sample had 5.2 μmole La/m^2 and was calcined at 800°C for 19 hr. A second spectrum of the same sample was taken after further calcination for 17 hr at 1000°C. The two spectra were nearly identical and had no features that could be attributed to the presence of lanthanum. The only observed lines were those due to δ-alumina. They were incorrectly attributed to the 2D over-layer in an earlier oral presentation (13). Much more concentrated samples, calcined at 800°C, showed, in addition to the δ-alumina lines, weak lines of lanthanum aluminate, as well as some unattributed features, particularly a strong, broad line at 360 cm^{-1}.

We cannot account for the EPR results of Ref. (3), described in the Introduction, but we can offer two alternative speculations. (i) The 2D overlayer structure coincidentally produces an EPR line of the same frequency and linewidth as LaAlO₃ crystals, (ii) It is conceivable that even in the dilute range a minor portion of the lanthanum forms lanthanum aluminate in the smallest pores of the substrate, stabilized there by capillarity, and thus coexists with the lanthana overlayer. It might get there during the impregnation process. If it exists, it is below the detectability limit of XRD or Raman. EPR could, however, pick up such a trace quantity of LaAlO₃ if the EPR line from its Gd substitution ions is sharp, while, at the same time, the EPR spectrum from the majority of Gd ions in the overlayer is very broad.

A comment about column 5 of Table 1: This column lists the recalculated BET area per gram of alumina. If the addition of lanthana had no effect on surface area at all, the values in this column would stay constant, but, in fact, they decrease moderately. Let us assume that the pores are coated by a monolayer of lanthana. For an equi-axed pore, the pore area is proportional to d^2, where d is a characteristic diameter. Thus, $\Delta A/A = 2\Delta d/d$. If, typically,

a 50Å-diameter pore is covered by a 3-Å-thick layer, the diameter will be reduced by 12%, and the pore area by 24%. This is a much greater reduction than that seen between sample 1 and sample 4, the latter corresponding to the saturated overlayer. Thus, there is no indication of any profound filling up of pores, judging from these crude approximations.

An attempt was made to determine whether the proposed lanthana overlayer is stable, relative to dewetting and agglomerating into LaAlO₃ crystals. In a mechanical mixture of γ-Al₂O₃ and LaAlO₃, would some of the latter "dissolve" onto the surface of the former to form the desired overlayer at elevated temperatures? A sample of 44 wt% of lanthanum aluminate was ground and mixed with γ-alumina in a mortar. The LaAlO₃ contained some La₂O₃, as mentioned previously. This mixture had a BET area of 56 m^2/g and chemisorbed 1.3 mg CO₂ per gram of sample, using our standard procedures. Exposure for 90 hr at 800°C produced insignificant changes in these quantities. If there were significant spreading of lanthanum species onto the much larger surface area of the γ-alumina, then we would expect a significant increase in CO₂ chemisorption, after heat treatment. An additional 67 hr at 910°C resulted in a BET area of 53 m^2/g and CO₂ chemisorption of 1.18 mg/g. An additional 428 hr at 950°C yielded a BET area of 48 m^2/g and CO₂ chemisorption of 0.67 mg/g. Therefore, there was no evidence of "spreading," whereas the LaAlO₃ component lost about one-half of its ability to chemisorb CO₂, probably due to sintering. The question of absolute stability, relative to agglomeration, therefore remains unresolved.

Our experiments demonstrate a lack of agglomeration, at surface concentrations below 8.5 μmole La/m^2, at 800°C. The sintering experiments of Schaper et al. (3) suggest that the same structure persists at 1100°C as well. We propose that this high degree of metastability, or possibly absolute stability, derives from a substantial

lowering of the surface energies of γ-alumina and of transition aluminas by the lanthana overlayer. This lowers the driving force for sintering and thus is believed to be a major ingredient in the preservation of alumina surface area by lanthana additions.

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