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Studies of Alumina I. Reaction with Hydrogen at Elevated Temperatures

S. W. WELLER AND A. A. MONTAGNA*

Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14214

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The reaction of H_2 with η- and γ-Al_2O_3 has been studied at 200, 450, and 550°C in a closed, circulating system equipped with an in-line cold trap. The samples were pretreated in flowing H_2 and subsequent evacuation at 550°C. Hydrogen uptake does not depend on the presence of chloride, introduced by impregnation, nor is it a function of transition metal impurities. Uptake at 200°C, though slow, tends to reach a limiting value that increases with successive pretreatments in H_2 at 550°C; pretreatment in He at 550°C does not produce sites active for H_2 adsorption at 200°C. Uptake of H_2 at 450 and 550°C continues at a slow and almost constant rate for a period of at least two days. The total uptake in this period corresponds to surface coverage less than 1%, if it is considered as chemisorption; or to the production of $Al_2O_{2.998}$, if it is considered as reduction leading to the production of nonstoichiometric alumina. The results are consistent with the occurrence of a surface reduction, e.g., Al_2O_3 (surf) + H_2 (g) = 2AlO (surf) + H_2O (g), at 450–550°C. The rate of H_2 uptake at high temperatures may be limited by the dissociative adsorption of H_2 and may occur more rapidly in the presence of Pt.

INTRODUCTION

The intermediate oxides (γ, η) of aluminum are perhaps the most commonly used catalyst supports. Our general understanding of alumina has progressed only slowly from the initial conception that its function was that of a chemically inert, thermally stable, high surface area support that was supposed to keep the active ingredient in a well-dispersed condition. The fact that alumina could be catalytically active for olefin hydrogenation and hydrogen–deuterium exchange was pointed out by Holm and Blue (*1*) in 1951 and was developed in detail by Weller and Hindin (*2–5*). In 1956, it was noted that the origin of this catalytic activity was probably the defect structure resulting from surface dehydroxylation at elevated temperatures (*2*). Relatively recently, more detailed models of the defect surface have been proposed by Peri (*6*), largely on the basis of ir studies, and by King and Benson (*7*), who were interested in the polarization of hydrogen isotopes on an alumina surface. All of these models proposed a defect surface consisting of Al^{3+}, O^{2-}, and OH^- ions.

The preparation and properties of a nonstoichiometric, "black" alumina by pumping of specially prepared, amorphous aluminas at 450–800°C, or by compressing of nonporous alumina in a die, have been reported in a series of papers by Teichner *et al.* (*8, 9*). These results have been confirmed and somewhat extended by Literat (*10, 11*). Very recently, French and Somorjai (*12*) have reported that an oxygen-deficient surface structure is produced in the (0001) face of single crystal α-alumina by evacuation above 1250°C. Also relevant to the question of nonstoichiometric alumina are the observations (a) by

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* Present address: Gulf Research and Development Co., P. O. Drawer 2038, Pittsburgh, Pa. 15230.

Bortner and Parravano (*13*) that a small amount of H_2 is formed when alumina, previously treated with H_2 and pumped at elevated temperature, is contacted with water vapor; and (b) by Khoobiar *et al.* (*14*) that η-alumina becomes an n-type semiconductor on exposure to (static) H_2 at 600°C.

Very few systematic studies have been reported previously on the chemisorption of hydrogen on alumina at elevated temperatures. In a classic paper, Taylor (*15*) observed that on alumina prepared by 400°C calcination of the hydroxide, there was no measurable adsorption of H_2 below 400°C at a pressure of 650 mm. However, at 445°C a slow adsorption occurred, leading to a total uptake of 0.07 cm^3 (STP) H_2/g in 3 hr; at 525°C the rate of adsorption was greater, with a total uptake of 0.12 cm^3 (STP)/g in 1 hr. Taylor stated, without giving data, that the adsorption was reversible, the H_2 being removable by evacuation at a higher temperature. He also stated that no water was formed by reduction of the oxide. (This is somewhat strange, since it is now known that the residual surface hydroxyl groups on alumina calcined at 400°C can be removed as water by evacuation at higher temperatures.) The surface area of Taylor's sample is not known.

Some fifteen years later, Russell and Stokes (*16*) largely confirmed Taylor's results; their extended study, on aluminas of surface area from 38 to 193 m^2/g, covered the temperature range 400–900°C, and the pressure range 9–620 mm. They reported equilibrium H_2 sorptions in the range 0.05–0.2 cm^3 (STP)/g, but *increasing* with *decreasing* temperature, and varying approximately as $p_{H_2}^{1/4}$. Moreover, they observed that (a) equilibrium is reached slowly even at 900°C and is difficult to reproduce; (b) there is evidence of an irreversible H_2 reaction; and (c) the sorption does not correlate with surface area or impurity content of the alumina. Their data also indicate that H_2 adsorption under fixed conditions increases as the temperature of preevacuation is increased.

More recently, Gruber (*18*) has deduced the existence of two types of H_2 adsorption from adsorption isobars on an η-alumina of area 210 m^2/g. "Type A" adsorption, in the 300–500°C range, increases with increasing temperature; "Type B," in the 140–300°C range, decreased with increasing temperature. The equilibrium H_2 adsorption reached 0.14 cm^3 (STP)/g at 150 and 500°C.

This paper describes a study of the interaction of H_2 with high-area aluminas at 200–550°C, in a closed, circulating gas system equipped with an in-line cold trap. The results are consistent with the idea that a surface reaction, which may be written schematically as $Al_2O_3\ (surf) + H_2\ (g) = 2AlO\ (surf) + H_2O\ (g)$, can occur reversibly at elevated temperatures, and at H_2 and H_2O partial pressures such that the corresponding bulk reaction is thermodynamically impossible.

EXPERIMENTAL

The sample of Houdry η-alumina, the method of chloride impregnation, the methods of gas purification, and the adsorption system have been described in a preceding paper (*17*). Matheson "ultra high purity" hydrogen was further purified by passage through heated Pd-Al_2O_3, a type 4A molecular sieve column, and a liquid N_2 trap. During a test, continuous recirculation of the H_2 through the sample and an in-line cold trap (usually at −78°C.) provided a means to control the p_{H_2O}/p_{H_2} ratio at a constant, low level. A sample of high purity γ-alumina was obtained through the courtesy of Dr. J. F. Roth of the Monsanto Co. Its characterization has also been given previously (*19*). All samples were ground and sieved to 35–45 mesh.

The alumina samples were pretreated by successively (a) heating in flowing H_2 from 25 to 450°C in 2 hr and holding at 450°C for ½ hr, (b) heating (flowing H_2) from 450 to 550°C in ½ hr and holding at 550°C for 1 hr, and (c) evacuating at 550°C for 2 hr. When the subsequent adsorption experiment was at a lower temperature, the sample was cooled to the desired temperature under continuous evacuation. Helium dead space was measured at test temperature

TABLE 1
SUMMARY OF PRETREATMENTS

Test	Sample	Weight (g)	Cl$^-$ (wt %)	Pretreatment
1	C-2 (η)	9.7	0.56	Standard 550°C pretreatment
2	C-2 (η)	9.7	0.56	Addtl. std. 550°C pretreatment
3	C-2 (η)	9.7	0.56	Evacuation at 200°C, 2 hr
4	C-2 (η)	9.7	0.56	Addtl. std. 550°C pretreatment
5	C-2 (η)	9.7	0.56	Evacuation at 450°C, 2 hr
6	C-2 (η)	9.7	0.56	Evacuation at 450°C, 2 hr
7	C-2 (η)	9.7	0.56	Evacuation at 550°C, 2 hr
8	C-2 (η)	9.7	0.56	Evacuation at 550°C, 2 hr
9	C-3 (η)	10.6	0.01	Standard 550°C pretreatment
10	C-3 (η)	10.6	0.01	Evacuation at 550°C, 2 hr
11	C-3 (η)	10.6	0.01	Evacuation at 550°C, 2 hr
12	C-5 (η)	9.8	0.01	Standard 550°C pretreatment
13	C-6 (η)	5.1	0.01	Standard 550°C pretreatment
14a	C-7 (η)	5.1	0.01	Standard 550°C pretreatment
14b	C-7 (η)	5.1	0.01	Evacuation at 550°C, 5 min
15	C-8 (η)	9.4	0.01	Standard 550°C pretreatment, but with He in place of H_2
16	G-1 (γ)	5.0	.00	Standard 550°C pretreatment
17	G-1 (γ)	5.0	.00	Evacuation at 550°C, 1 hr

with the magnetic circulating pump on. In the experiments at 450 and 550°C, a H_2–He mixture was employed in order to obtain better pumping efficiency. The partial pressure of H_2 was typically in the range 5–15 cm Hg.

RESULTS AND DISCUSSION

Since the sample pretreatment appears to be a key parameter, the pretreatments employed in the various tests are summarized in Table 1.

Figure 1 shows the time dependence for chemisorption (net, not cumulative) at 200°C after standard pretreatment at 550°C. Tests 1–4 were consecutive runs on a single sample of prechlorided η-Al_2O_3 (Sample C-2); test 9 was on an unchlorided sample (C-3). Sample C-2 was retreated with H_2 at 550°C and evacuated at

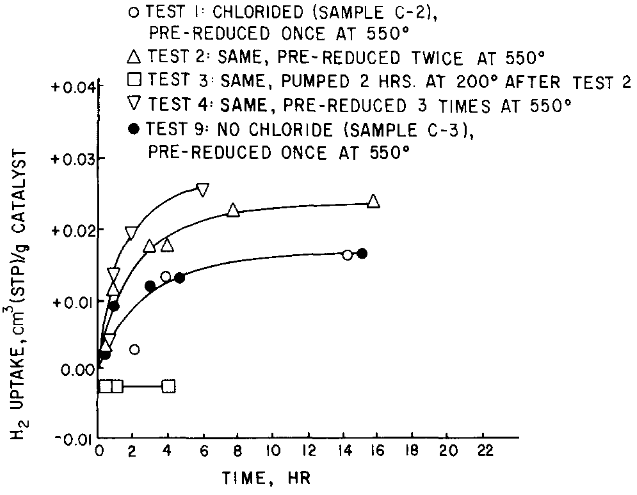

FIG. 1. Time dependence of H_2 uptake by η-Al_2O_3 at 200°C.

550°C prior to Test 2 and prior to Test 4. However, it was evacuated only at 200°C prior to Test 3.

Most of the H_2 adsorption at 200°C occurs in the first 6 hr, and it tends to level off in the next 10 hr. It is noteworthy that the net amount of adsorption increases with progressive 550°C pretreatments (Tests 1, 2, and 4). The low net adsorption in Test 3 indicates that evacuation at 200°C is insufficient to remove H_2 adsorbed at 200°C.

Test 9, on a separate sample of nonchlorided η-Al_2O_3, essentially duplicated Run 1. This implies that the H_2 chemisorption is not related to the presence of chloride.

The fact that increased adsorption at 200°C resulted from progressive 550°C pretreatments (Tests 1, 2, 4 in Fig. 1) raised the question whether the increased number of adsorption sites was the consequence of exposure to H_2 at 550°C, or simply of progressive dehydroxylation ("dehydration") of the surface. To answer this question, Test 15, Table 1 was conducted on a fresh sample of η-Al_2O_3. The pretreatment at 550°C was standard, except that flowing He was used instead of H_2. Subsequent exposure to H_2 at 200°C resulted in the very low uptake of 0.002_6 cm^3 (STP)/g after 17 hr. This is much less than the value of 0.017 cm^3 (STP)/g observed under comparable conditions in Tests 1 and 9, which were carried out with H_2 pretreatment. The implication is that the capacity to adsorb H_2 at 200°C is the result largely of surface reduction, not dehydration, during the pretreatment at 550°C. This question is again treated in the following discussion of the H_2 uptake at higher temperatures.

The time dependence for H_2 uptake at 450 and 550°C is quite different from that at 200°C, as Figs. 2 and 3 show. At these temperatures there is no evidence of leveling off even after 44 hr (Test 10, Fig. 3).

The variability of the data in Fig. 2 makes it difficult to establish a significant difference between uptake at 450 (Tests 5 and 6) and at 550°C (Tests 7 and 8) on a sample of chlorided alumina. It is possible that the spread is partly due to run-to-run variations in the efficiency of the circulating

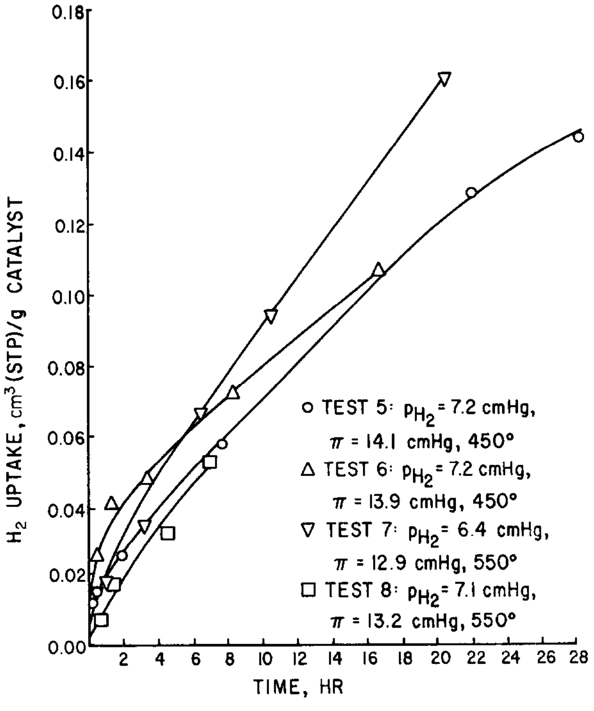

FIG. 2. Time dependence of H_2 uptake by chlorided η-Al_2O_3 at 450 and 550°C.

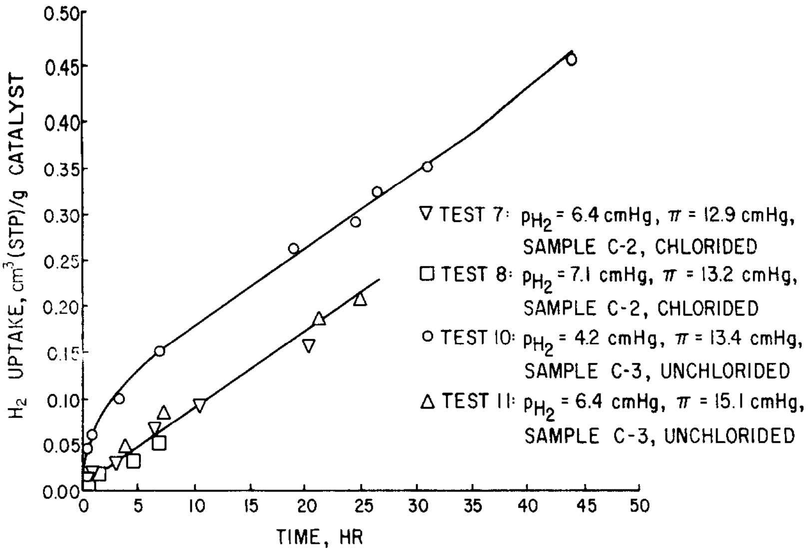

FIG. 3. Time dependence of H_2 uptake by chlorided and unchlorided η-Al_2O_3 at 550°C.

pump (cf. the discussion of Test 10, below).

Tests 7, 8, and 11 in Fig. 3 indicate the absence of any chloride effect on the H_2 uptake at 550°C. The tenacity of the chloride bonding is attested by the fact that wet analysis of Sample C-2 discharged after Test 8 showed $0.56 \pm 0.02\%$ Cl^-, compared with the nominal 0.55% as prepared.

Test 10, Fig. 3, was exceptional in that the total H_2 uptake after 6 hr at 550°C was about 2.5 times that observed in Tests 7, 8, and 11. After 6 hr, however, the rate of incremental H_2 uptake was about the same in all four tests. A possible cause of this difference was the fact that a new circulating pump had been installed prior to the introduction of Sample C-3 and Test 9 (cf. Table 1); visual observation indicated that pumping efficiency was best with a new pump and fell off as the glass walls became eroded. It occurred to us that the extent of H_2 uptake might be dependent on the circulation rate of H_2 through the sample and cold trap. This would be true if the uptake at 450 and 550°C were associated with the reduction of the alumina surface, indicated schematically as:

$$Al_2O_3\ (\text{surf}) + H_2\ (\text{g}) = 2\ AlO\ (\text{surf}) + H_2O\ (\text{g}). \quad (1)$$

Since such a reduction would certainly be reversible near 500°C, the rate of sweeping H_2O out of the particulate sample bed should play a significant role.

The rate of gas circulation was not easily adjustable. However, we could vary the average H_2O vapor concentration in the bed by decreasing the sample size, with the limitation that sufficient sample had to be used to permit reasonable accuracy in the measurement of H_2 uptake. Tests 1–11 had been made on samples of about 10 g (C-2 and C-3, Table 1), with the cold trap at −78°C. Tests 12–14 were then run on separate samples (C-5, C-6, and C-7, Table 1) with the trap at 0°C. The sample weight was 9.8 g in Test 12, and 5.1 g in Tests 13 and 14; the test temperature was 550°C in all cases. Test 14a had a normal pretreatment, but pure He was then circulated instead of H_2–He, during the test. As the end of Test 14a, the He was evacuated for 5 min, and Test 14b was begun by the introduction of H_2–He at 550°C.

Figure 4 shows the time dependence for the H_2 uptake in Tests 12, 13, and 14b. Several points should be noted:

1. Even with the cold trap at 0°C, the rate of H_2 uptake in Test 12 was comparable with that observed in Tests 7, 8, and 11 (Fig. 3), when the trap was at −78°C.
2. Tests 13 and 14b, with smaller (5 g) sample size, showed substantially

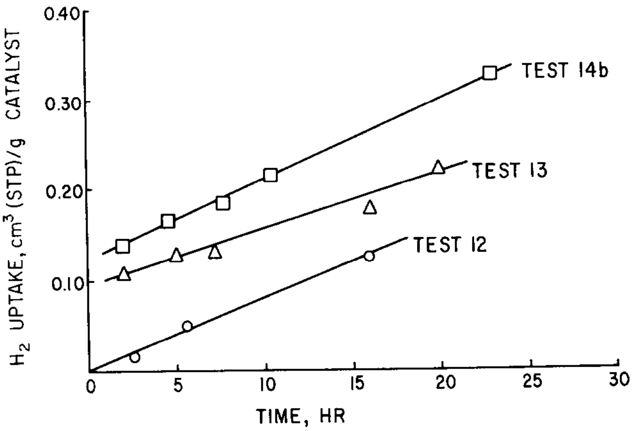

FIG. 4. Effect of sample size on H_2 uptake at 550°C.

higher initial uptakes of H_2, but the rate after 2 hr is indistinguishable from that observed with larger (10 g) samples.

3. The increased initial uptake with 5 g samples could be the result of more efficient surface dehydroxylation during the 550°C pretreatment, rather than the improved gas circulation during the H_2 uptake test proper. This would be consistent with both the higher initial uptake and the unchanged rate after 2 hr. It is also consistent with the fact that a higher initial uptake occurred in Test 14b than in Test 13; Test 14b followed a 21-hr period (Test 14a) in which He was circulated through the sample and cold trap.

Analysis, by emission spectrometry, of the η-Al_2O_3 used in Tests 1–15 indicated a maximum total impurity content of 3350 ppm and a maximum content of transition metals of 150 ppm. Attribution of the 450–550°C H_2 uptake to reaction with the Al_2O_3 surface hinges on ruling out the possibility that it is simply a reaction with transition metal impurities. Tests 16 and 17, Table 1, were carried out to resolve this question. A sample of very pure γ-Al_2O_3 (Monsanto NPB593750), containing <1 ppm iron as the only detectable impurity, was used in these experiments. H_2 uptake was measured at 550°C, the cold trap being at −78°C. Test 16 was performed after standard 550°C pretreatment; after the conclusion of Test 16, the sample was evacuated from 1 hr at 550°C, and Test 17 immediately begun.

Figure 5 is the time dependence of H_2 uptake in Tests 16 and 17. Comparison of Figs. 5 and 3 shows that the rate of uptake with the high purity γ-Al_2O_3 was at least as great as with the η-Al_2O_3 sample. The surface areas are not greatly different; 191 m^2/g for the Monsanto γ-Al_2O_3, 235 m^2/g for the Houdry η-Al_2O_3. H_2 uptake at 550°C is therefore a characteristic of the alumina itself and not an impurity phenomenon.

The H_2 uptake may be considered alternately as chemisorption or as reduction of the alumina surface, as represented by Eq. (1). The volumetric determination of uptake does not discriminate between these possibilities.* It is interesting, nevertheless, to ask in either case what fraction of the alumina surface is participating in the reaction with H_2. For convenience, the final H_2 uptakes in Tests 7–14b (η-Al_2O_3) and 16–17 (γ-Al_2O_3) are summarized in Table 2. The uptakes are expressed both as cm^3 (STP) H_2/g and, for the two aluminas, as atoms of H $\times$ 10^{-12}/cm^2 of surface.

It is essential to keep in mind that these numbers represent uptakes over the duration of the individual tests, and not maximum values. The rate of H_2 uptake at

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* Measurement of the H_2O produced, if such a reduction occurs, would permit this discrimination. We are not yet satisfied with our ability to distinguish H_2O produced by reduction (resulting in a nonstoichiometric alumina) from that produced by slow surface dehydroxylation at 550°C. Work is proceeding on this question.

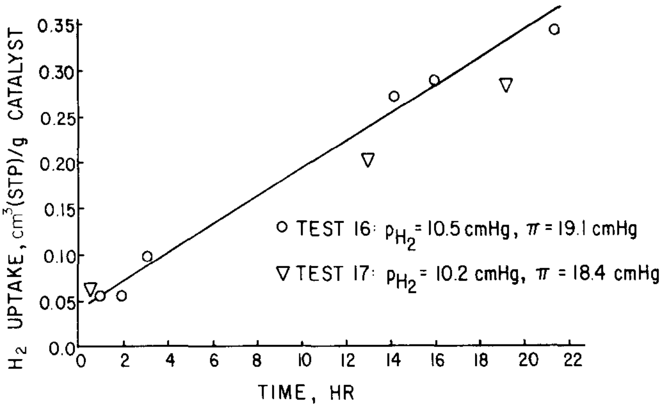

FIG. 5. H_2 uptake by high-purity γ-Al_2O_3 at 550°C.

550°C is almost constant, and there is no indication even in the longest run (43 hr, Test 10) that the rate is falling off with time.

The highest uptakes actually observed were about 10^{13} atoms H/cm^2. From the standpoint of chemisorption, if we assume a surface of close-packed oxide ions and a cross-sectional area of 6.8 Å^2 per oxide ion, this corresponds to a surface coverage of 6.8×10^{-3} H atoms per oxide ion, or less than 1% of the surface.

From the standpoint of reduction according to Eq. (1), two hydrogen atoms are consumed per oxygen removed. The H_2 uptake observed in Test 10, for example, on this basis corresponds to the removal of 2.1×10^{-3} g-atom O per formula weight of Al_2O_3, or to the production of nonstoichiometric alumina of the composition $Al_2O_{2.9979}$. The deviation from stoichiometry is nontrivial, although it is substantially less than that reported by Arghiropolous *et al.* (*8*) who claim the formation of (approximately) $Al_2O_{2.96}$ by evacuation of amorphous or strained aluminas.

The rate of H_2 uptake around 500°C may be limited by the rate at which H_2 is dissociatively adsorbed on the alumina surface. This would be consistent with the almost constant rate, since only a small fraction of the surface is covered (or reduced) during a test. If this assumption is true, the rate of adsorption or reduction on, say, a Pt-Al_2O_3 sample may be much higher than on pure Al_2O_3, since hydrogen atoms could be produced on the platinum and then diffuse to the alumina surface. This

TABLE 2
HYDROGEN UPTAKE AT 550°C

Test	Final p_{H_2} (cm Hg)	Duration of test, hr	Total H_2 uptake (cm^3 (STP) H_2/g)	Total H_2 uptake (10^{-12} atoms H/cm^2)
7	6.4	20	0.16	3.7
8	7.1	7	0.05	1.1
10	4.2	43	0.46	10.5
11	6.4	25	0.21	4.8
12	2.5	16	0.12	2.7
13	4.1	20	0.23	5.2
14b	3.4	22	0.33	7.5
16	10.5	21	0.35	9.8
17	10.2	19	0.29[a]	8.1[a]

[a] Excludes uptake in Test 16.

possibility has been previously suggested (*17*) to account for the high O:Pt ratios observed on O_2 treatment at 525°C of samples prereduced in H_2 at 550°C. We note that a H_2 uptake of 0.46 cm^3 (STP)/g (Test 10) would correspond to a subsequent O_2 uptake of 10.3 μM O_2/g; 0.5 wt % Pt in a catalyst corresponds to 25.5 μ g-atoms Pt/g.

Our samples were not dark at the end of a 550°C test in H_2. Attempts to confirm Literat's report (*10*) of ESR spectra in "black" alumina corresponding to that of a free electron were only occasionally successful on our treated samples, and in at least some of these samples, we believe the spectrum to be an artifact associated with the presence of trace amounts of carbon (*20*). This work will be reported in a later communication. We also plan to look for reduced species, such as Al^{2+}, by comparing the rates of the ortho-para hydrogen conversion and H_2–D_2 exchange at low temperature.

Thermodynamic data for bulk crystalline phases are of little use in predicting the possibility of "surface reduction." The equilibrium constant for the direct dissociation, $\frac{2}{3}$ α-Al_2O_3 (c) = $\frac{4}{3}$ Al (c) + O_2 (g), is about 10^{-59} at 550°C (*21*). Even for the more favorable reaction with H_2, $\frac{1}{3}$ Al_2O_3 (c) + H_2 (g) = $\frac{2}{3}$ Al (c) + H_2O (g), the equilibrium constant at 550°C is only about 1×10^{-17}. Equilibria for reactions involving postulated lower oxides, such as α-Al_2O_3 (c) + H_2 (g) = 2AlO (c) + H_2O (g), cannot be calculated because of the absence of thermodynamic data for any solid lower oxides. Of equal importance is the fact that the energetics for surface species are both unknown and substantially different than for bulk; however, qualitative arguments can be advanced that lower-valent ions will be relatively favored on the surface.*

Although many questions remain concerning the interaction of alumina with hydrogen, the following conclusions may be drawn:

1. The uptake of H_2 at 200–550°C is characteristic of the alumina itself and not of impurities.
2. The uptake is not related to the presence of chloride.
3. The uptake at 200°C, though slow, tends to reach a limiting value that increases with increasing extent of pretreatment at 550°C.
4. The uptake at 200°C is largely on sites produced by exposure to dry H_2 at 550°C, not on sites produced by simple dehydroxylation.
5. Uptake of H_2 at 540–550°C occurs at an almost constant rate for at least two days. The total uptake during this period corresponds to coverage, or reduction, of a small fraction (<1%) of the alumina surface.
6. Whether the uptake at 450–550° is better described as chemisorption or surface reduction is not yet known. If surface reduction is occurring, it is at ratios of p_{H_2O}/p_{H_2} such that the bulk reaction is thermodynamically impossible.

ACKNOWLEDGMENT

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* From calculations of lattice energies, we are attempting to estimate the heat and free energy of formation of a postulated AlO (c), the energy difference between aluminum ions in the surface and those in the crystalline solid, and the energetics for surface AlO on a substrate of Al_2O_3. These calculations will be reported in a subsequent publication.

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