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The Effect of Reactor Irradiation upon Hydrogen Adsorption by an Alumina Catalyst*

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Hydrogen adsorption experiments were carried out on unirradiated and reactor-irradiated samples of gamma alumina (γ-Al_2O_3) in an effort to interpret the known enhancement by radiation of the catalytic activity of this material. The specific surface area of 85 m^2/g was not changed by irradiation, but the shapes of the hydrogen adsorption isotherms were altered. The observed monolayer capacity for hydrogen indicates that hydrogen atoms are adsorbed (at 78°K) in one-to-one correspondence with the oxygen ions in the alumina surface. Nitrogen contamination, which is not removed by outgassing at 300°C, has been detected. It is displaced systematically as hydrogen is adsorbed at 78°K. Reactor irradiation appears to enhance this nitrogen release phenomenon.

INTRODUCTION

The high specific surface area forms of alumina are extensively used in heterogeneous catalysis. Enhancements have been reported in the catalytic activities of this material after exposure to reactor or gamma radiations. These enhancements were for reactions involving hydrogen, i.e., hydrogen–deuterium exchange (*1*) and *ortho–para* hydrogen conversion (*2*). This suggests that there is a change in the manner in which hydrogen is adsorbed and desorbed from this material. In some preliminary work (*3–5*) the authors found substantial differences in the adsorption of hydrogen on virgin and irradiated gamma alumina. These investigations have been extended and the results are given in this paper.

Changes in catalytic and gas-adsorbing properties are to be expected if the surface of a solid is altered by exposure to radiation. There is a severe limitation on the choice of physical properties useful as indices of radiation damage to a surface. Electrical resistivity, mechanical measurements, or optical absorption, useful in studying bulk effects, are not readily applied to a few atomic planes. Direct observation of surface effects with the field ion microscope of Muller (*6*) is possible, but is limited to a few substances. Young (*7*) has used adsorption of krypton on alpha alumina to reveal an increase in the number of highly active adsorption sites after exposure of this material to reactor irradiation. Gas adsorption can, therefore, be used to detect surface damage, although the interpretation of results is usually not simple.

EXPERIMENTAL PROCEDURE

The material used in these experiments was Linde Alumina Type B, reported to consist chiefly of gamma alumina particles of about 80 Å, although a few relatively large (3500 Å) alpha alumina grains are also present (*8*). Electron diffraction results correspond to the gamma structure (*9*). It is

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known that complex changes occur in gamma alumina if it is exposed to an increasing sequence of temperatures above 300°C. After such treatment, reduction in surface area (largely due to sintering), crystallographic changes, and loss of some residual water all take place (*10*). Moreover, infrared studies (*11*) have shown that OH groups are bound to the surface and that the details of this binding are sensitive to sample history. It is hardly surprising that observed catalytic activities vary greatly with the particular method used in calcining and otherwise preparing samples. To simplify correlation of the present gas adsorption results with the catalytic properties reported by others, temperatures in excess of 300°C were avoided during outgassing of samples. The specific surface areas of samples were then found to be constant and great enough to be characteristic of a catalytically active substance.

After evacuation to pressures of 10^{-5} mm Hg at room temperature or at 300°C, the specific surface areas of samples were determined by nitrogen adsorption at 78°K by the BET method of analysis. Hydrogen adsorption isotherms at 78°K were obtained by admitting known quantities of the gas into a constant-volume apparatus containing a sample and measuring the pressures after attainment of equilibrium. The ampoules containing the samples were then evacuated, sealed off, and irradiated to doses of $\sim 10^{18}$ neutrons/cm^2 at 50°C in the Brookhaven Graphite Research Reactor. The seals of the samples were broken under vacuum by means of magnetically operated hammers to facilitate the measurement of adsorption characteristics on irradiated samples without any intervening exposure to the atmosphere. After again degassing, measurements of nitrogen or hydrogen adsorption were repeated.

As already pointed out, complete degassing is impossible without changing the nature of the powder and it is possible that the extent of adsorbed gas contamination may not be the same for unirradiated and irradiated samples. However, since the samples were irradiated in evacuated ampoules, it is unlikely that the results to be discussed later are caused by accidental differences in outgassing efficiency.

It should also be pointed out that all the data to be reported are for rapid adsorption. By the time a measurement for a data point could be made the process was complete. Therefore, we have no data showing the time needed to reach equilibrium, but the process is certainly complete in a matter of minutes since no time dependence could be observed in these measurements.

EXPERIMENTAL RESULTS

Effect of Irradiation on Specific Surface Area

The specific surface area of the gamma alumina (≈ 85 m^2/g, using 16.2 Å^2 as the area of an adsorbed nitrogen molecule at 78°K) was found to be independent of outgassing temperature between room temperature and 300°C and unaltered by subsequent exposure in a reactor to 10^{18} neutrons/cm^2. The fact that this radiation dose causes no change in specific surface area does not mean that the surface has been unaffected. Changes in the activity of adsorption sites will not affect the values obtained for the surface area, since the BET method measures the number of nitrogen molecules adsorbed in the first monolayer, regardless of the details of the gas–solid interaction. In the case of the material used here, the high specific area is due to small particle size, and, unless sintering occurs or conversely porosity develops as a result of irradiation, no change in specific surface area is to be expected. Evidently such macroscopic changes did not occur in these samples, although they could certainly take place at higher radiation doses. Young (*7*), in about the same dose range, found no change in the specific surface area of alpha alumina.

Effect of Irradiation on Hydrogen Adsorption

The isotherms obtained for hydrogen adsorption on a particular gamma alumina sample (wt, 1.498 g) before and after irradiation are shown in Fig. 1. Irradiation affects not only the amount of adsorption but also the shape of the isotherm. However, the

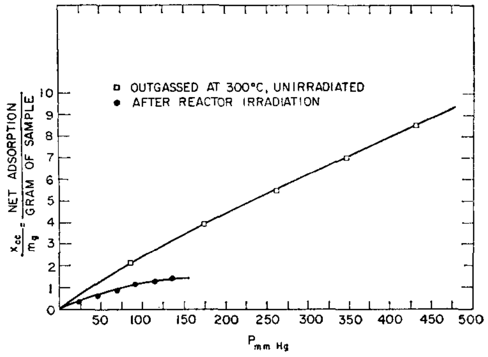

FIG. 1. Specific net adsorption of gas vs. total pressure for hydrogen admitted to gamma alumina powder at 78°K. Data are shown for the same sample before and after reactor irradiation to ~10^{18} neutrons/cm^2 at 50°C. Mass spectrometer analysis was carried out on the gas after the last admission of hydrogen to the irradiated sample (last data point on lower curve).

initial portions on both curves may be fitted by the Langmuir relationship $\Theta = kP/(1 + kP)$, where Θ is coverage, P is pressure, and k is a temperature-dependent constant. The data, therefore, could be analyzed as follows. By algebraic rearrangement the Langmuir equation may be put into the linear form

$$\frac{P}{(x/m)} = \frac{1}{(AB)} + \frac{P}{B}$$

where x is the number of molecules adsorbed at equilibrium on a sample of m grams at pressure P, B is the number of molecules required to complete a monolayer on 1 g of sample, and A is proportional to the ratio of the sticking probability to the evaporation rate. If $P/(x/m)$ is plotted vs. P, the data will fall on a straight line in the Langmuir region and the constants B and A can be calculated from the slope $1/B$ and the intercept $1/AB$.

Figure 2 presents several runs for the same sample as in Fig. 1, but replotted in the linear form. The data for the unirradiated sample follow a straight line up to $P \cong 300$ mm Hg, with $B \cong 24$ cc/g. After adsorption of ~6 cc/g, there is a drastic change in the manner of packing of hydrogen on the alumina surface, as indicated by the abrupt change in slope. After irradiation the behavior of the sample is entirely different. The initial B value is now between 5 and 6 cc/g, or approximately one-quarter of the value for the unirradiated case.

The difficulties of interpreting apparent Langmuir isotherms are well known but all further interpretation will be based on the initial portions of the curves of Figs. 2 and 3

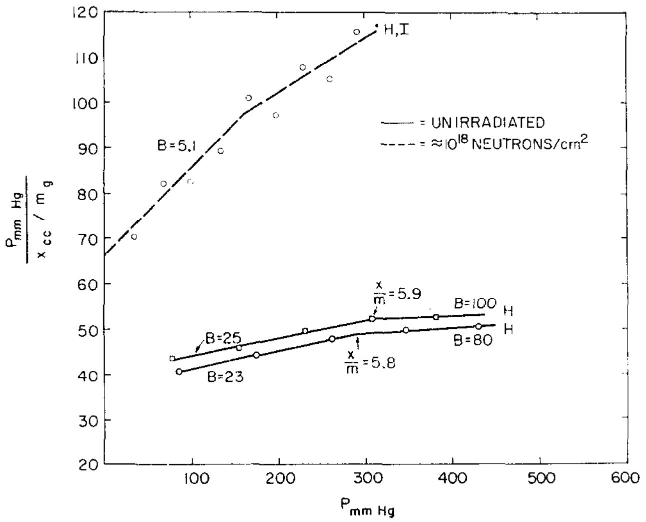

FIG. 2. $P/(x/m)$ vs. P, where x is loss in gas phase, curves for hydrogen adsorption for unirradiated and irradiated alumina. The initial slope of the lower curves indicates a monolayer capacity of ~24 cc/g and changes in slope at ~$x/m = 6$ cc/g.

(i.e., the low-pressure region). The fact that the high-pressure data can also be fitted by a Langmuir plot may well be fortuitous.

Experiments with a large number of samples (see Fig. 3) showed that the amounts of hydrogen adsorbed as well as the shapes of the isotherms varied greatly from sample to sample. Even though the samples used had been subdivided from the same original lots of powder, variations occurred between the unirradiated samples. There were also differences in behavior between various irradiated samples. However, the results are not random; the isotherms indicate that two different modes of adsorption are prevalent, with adsorption on the irradiated samples being characterized by only one of these modes. In Fig. 3 two different unirradiated samples (the solid lines) are shown; each sample was run twice, and the curves for a single sample lie adjacent to one another. Data for several irradiated samples are also shown (the dashed curves). These curves all lie above those obtained for the unirradiated samples. Examination of curves such as those of Fig. 3 reveals that, in general, the results may be divided into the following three cases: unirradiated type 1, with initial $B \cong 24$ cc/g; unirradiated type 2, with initial $B \cong 6$ cc/g; and irradiated samples for which initial B also $\cong 6$ cc/g.

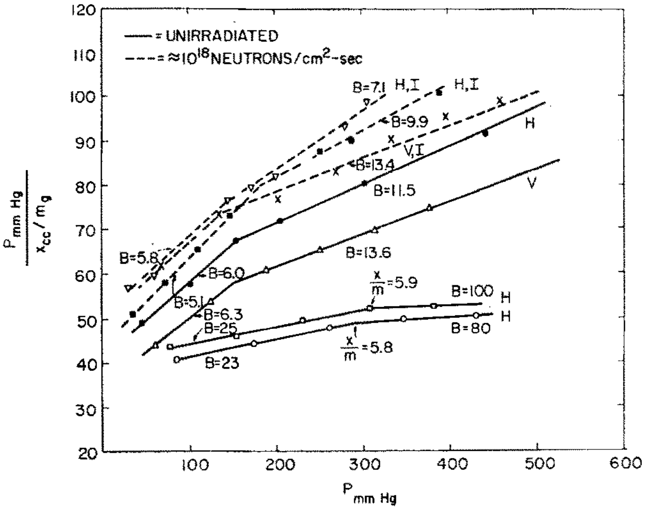

FIG. 3. Plots of $P/(x/m)$ vs. P for unirradiated and reactor-irradiated samples. The two lowest curves represent data for a "clean" sample. The labels **H**, V, and I refer to outgassing at 300°C, outgassing at room temperature, and irradiation to $\sim 10^{18}$ neutrons/cm^2, respectively.

The isotherms of Fig. 4 may be compared with the linear plots of Fig. 3. The changes in slope of Fig. 3 correspond to the changes in curvature of Fig. 4. Type 1 adsorption is represented by the points falling along the solid line in Fig. 4. As is explained later, this probably results from adsorption on a relatively clean sample, whereas the other data are influenced by nitrogen contamination. Some of this nitrogen is driven into the gas phase when hydrogen is adsorbed, which results in a lowering in the net gas adsorption, i.e., the observations, which consist of measurements of loss of molecules from the gas phase, are reduced when nitrogen is evolved. The runs in Fig. 4 that do not follow the solid curve belong to type 2 adsorption, in which adsorbed hydrogen replaces nitrogen and a reduction in the net adsorption results.

Mass Spectrometer Evidence for Nitrogen Contamination

In Fig. 4 the lowest curve, marked M.S., shows unusually small net adsorption, and therefore substantial nitrogen release was suspected in this case. Consequently, the

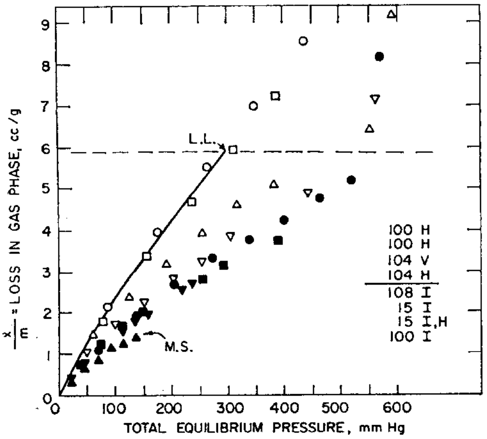

FIG. 4. Specific adsorption vs. total pressure for various alumina samples. The solid line through the open circles and squares indicates that part of the data (unirradiated "clean" sample) that follows Langmuir adsorption with a monolayer capacity of 24 cc/g. Open points are for unirradiated samples, filled points are for samples preirradiated to ~10^{18} neutrons/cm^2. Sample numbers and treatment are indicated: H, heating to 300°C during preliminary outgassing; V, degassed at room temperature; I, reactor irradiated, I,H, reactor irradiated followed by degassing at 300°C. The limit for Langmuir adsorption is indicated by L.L.

gas involved in this run was subjected to mass spectrometer analysis. After the last admission of hydrogen (at 78°K) to the dead volume containing the sample (the last point shown for sample 100-I in Fig. 4) the gas was analyzed and found to consist of 88% hydrogen and 12% nitrogen. Since only hydrogen was admitted, the nitrogen must have been displaced from the sample as the hydrogen was adsorbed. The difference between the known quantity of hydrogen admitted and that remaining in the gas phase as shown by the mass spectrometer, i.e., the *true* hydrogen adsorption, was 4.42 cc/g of sample. The gaseous nitrogen (by the mass spectrometer result) was 3.02 cc/g. The net observed adsorption should therefore be 4.42 − 3.02 = 1.40 cc/g, which is close to the observed net adsorption of 1.39 cc/g.

Chemical Analysis of Linde Alumina Type B

Spectroscopic analysis cited by the manufacturer indicated that the material was relatively free from ordinary impurities, but no estimate of nitrogen content was furnished. Quantitative chemical analysis of a number of fresh samples yielded very variable results, with a typical nitrogen content of 200 ppm. This amount of nitrogen, even if fully released, would not account for the sizable effect observed directly in the mass spectrometer experiment. However, surface nitrogen contamination would probably not show up in the chemical analysis. A simple calculation shows that a monolayer of nitrogen corresponds to 24 000 ppm of nitrogen for the particle size of these samples.

DISCUSSION

It is well known that very high temperatures and advanced vacuum techniques are required to free the surfaces of metallic oxides from all traces of original gas. Moreover, gamma alumina possesses surface water which changes to bound hydroxyl groups in a complicated fashion as the temperature is increased (*11*). Any effort to get a "pure" surface would result in a material totally different from those used in catalysis. The character of the surfaces after degassing at room temperature or 300°C for 24 hr at 10^{-5} mm Hg must be regarded as unknown and not necessarily reproducible. The radiation-induced enhancements in the catalytic activity of gamma alumina demonstrated by others and referred to here in the introduction are apparently not due to an increase in surface area, which remains constant at 85 m^2/g.

In our experiments we have found (from the initial slopes of type 1 adsorption isotherms of Fig. 2 and Fig. 3) that 24 cc/g of hydrogen would complete a monolayer, or, if the measured surface area is used, the area occupied by a hydrogen molecule is

$$(85 \times 10^{20})/24 \text{ Å}^2/\text{cc} = 13.2 \text{ Å}^2 \text{ per molecule of } H_2$$

This result is in approximate agreement with the experiments of de Boer *et al.* (*12*) on the chemisorption of water in alumina. These workers showed that water molecules occupy 12.1 Å^2 per molecule of water. They claim that the most probable lattice plane in the surface will be the (111) plane of the spinel lattice, in which each oxygen ion takes in 6.74 Å^2 of surface. Consequently each water molecule in the experiments of de Boer *et al.* is chemisorbed to two oxygen ions in the alumina surface. In the hydrogen case, our experiments indicate that adsorption at low pressures occurs on all available sites and these hydrogen atoms are chemisorbed in association with one oxygen surface ion. At higher pressures, when the coverage is about 6 cc/g, the nature of the adsorption changes. At these pressures more hydrogen is adsorbed than indicated by the simple Langmuir isotherm valid at low pressures.

The remaining curves of Fig. 3 probably reflect contamination with nitrogen. This is suggested by the mass spectrometer analysis of the gas which is in contact with the powder.

From the data of Fig. 4, the differences between the solid line (type 1 adsorption) and the rest of the data are approximately linear with respect to pressure. This observation is difficult to interpret, but one may speculate as follows. Let the hydrogen displace nitrogen from the sample at a constant rate. The released nitrogen will be partly readsorbed on the surface by physical adsorption. The rate of gaseous nitrogen production and destruction may be written as

$$d[N_2]^g/dt = K_1[H_2]^g + K_2[N_2]^s,$$

$$-\,d[N_2]^g/dt = K_3[N_2]^g,$$

where

$[N_2]^g$ = concentration of nitrogen in gas phase,
$[N_2]^s$ = concentration of nitrogen on solid,
$[H_2]^g$ = concentration of hydrogen in gas phase.

Under steady state conditions

$$[N_2]^g = (K_1/K_3)[H_2]^g + (K_2/K_3)[N_2]^s.$$

At low nitrogen pressures the nitrogen adsorption isotherm is approximately linear, giving

$$[N_2]^s = K_4[N_2]^g,$$

and therefore

$$[1 - (K_2K_4/K_3)][N_2]^g = (K_1/K_3)[H_2]^g \quad \text{or} \quad [N_2]^g = K[H_2]^g$$

Thus, this speculation suggests that the major difference between type 1 and type 2 behavior is that in the latter case nitrogen is released. This release of nitrogen is facilitated by prior irradiation of the samples. The unirradiated type 2 samples appear to correspond to various degrees of nitrogen contamination.

The existence of an original layer of adsorbed nitrogen may be of significance for a qualitative understanding of the catalytic properties of gamma alumina. It is known that the unirradiated material has a variable catalytic behavior depending upon the heating and outgassing procedures used. Kohn and Taylor (*1*) report that the choice of degassing technique affects the subsequent radiation enhancement of the material's catalytic activity. Maurin, Ballantine, and Sucher (*2*) obtained no increase in catalytic activity when they irradiated in vacuum, but did obtain an increase when hydrogen was in contact with the alumina during irradiation. This result appears to be in accord with the conclusions reached here, i.e., irradiation in vacuum does not remove the nitrogen contamination but nitrogen is replaceable by hydrogen.

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