

Electron-Transfer at Alumina Surfaces

4. Reduction of Iodine

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The reduction of iodine to iodide ion occurs readily on the surface of partially dehydrated catalytic aluminas and silica-aluminas. An increase in the alumina content of the latter results in an increase in reducing activity. Replacement of the hydroxyl ion on the alumina surface by the fluoride ion decreases the reducing power. Two different surface sites are responsible for the reducing properties. For alumina samples dehydrated at low temperatures ($<400^{\circ}\text{C}$) the reducing site appears to be the hydroxyl ion, whereas at higher activation temperatures a defect site involving oxide ions probably acts as the electron donor. These findings concur with those reported from an earlier study of the reduction of tetracyanoethylene on the alumina surface.

INTRODUCTION

The surface of an alumina catalyst, when suitably activated, possesses both oxidizing and reducing properties (1), the same surface oxidizing suitable hydrocarbons to the corresponding cation radical and at the same time reducing a range of aromatic nitrocompounds to anion radicals. The present paper reports an investigation of the reduction of iodine to iodide ion at the surface of a number of alumina catalysts and forms part of a general study of the redox properties of alumina-containing catalysts (2-4).

EXPERIMENTAL METHODS

The aluminum oxide-hydroxide (boehmite) (5) and aluminum trihydroxide (97% gibbsite, 3% bayerite) (2) have been described previously. Fluorided aluminas were prepared by digesting boehmite samples with aqueous solutions of ammonium hydrogen fluoride at 20°C ; the samples were washed in water and dried at 120°C before further activation. A series of alumina catalysts that contained various percentages of silica was prepared by the hydrolysis of mixtures of aluminum isopropoxide and tetraethyl orthosilicate. Activa-

tion of catalyst samples involved heating in flowing oxygen for 30 min and subsequently in air for 4 hr at temperatures between 100 and 1100°C in an electric muffle furnace, followed by cooling at 10^{-2} mm Hg over phosphoric oxide for 30 min. Iodine from Koch-Light Laboratories Ltd., was used without further purification. Benzene (A.R.) was stored over active silica-alumina and filtered before use.

Reduction of iodine was studied at room temperature using 50-ml flasks fitted with ground-glass stoppers. Activated samples of catalyst (~ 0.5 g, weighed accurately by difference, all transfers being carried out in an atmosphere of dry nitrogen) were added to the flasks containing 6 ml of iodine solution (prepared by mixing known volumes of a stock solution of iodine in benzene with additional solvent). After a known time interval 10 ml of a 0.1 M aqueous solution of potassium iodide were added to the iodine + catalyst system for a dual purpose: unreacted iodine was desorbed from the oxide surface, and most of the iodine in solution entered the aqueous layer. The iodine was estimated by titration with standard sodium thio-sulfate solution using starch as indicator.

RESULTS

Reduction of Iodine by Alumina

When partially dehydrated samples of boehmite were brought into contact with dilute solutions of iodine in benzene ($\sim 10^{-4} M$), the red color faded from the supernatant solution but the catalyst surface remained white. With more concentrated iodine solutions ($\sim 6 \times 10^{-3} M$), a noticeable lightening occurred in the color of the solution and the surface of the solid acquired a yellow/orange coloration. On the addition of water the color of the catalyst reverted to white. The amount of iodine reduced at room temperature ($\sim 20^\circ C$) by a boehmite sample that had been dehydrated at $600^\circ C$ is shown as a function of contact time in Fig. 1. Saturation was reached after about 6 hr; with an initial iodine concentration of $6.2 \times 10^{-3} M$, $\sim 2.3 \times 10^{19}$ atoms of iodine were reduced/g of catalyst in this period of time. The effect of variation in the iodine concentration of the supernatant solution on the amount of iodine that was reduced by boehmite activated at $600^\circ C$ is shown in Fig. 2. The amount increased with increase in the concentration of the solution up to $\sim 0.03 M$, and above this concentration remained constant.

The effect of activation temperature on the activity of alumina for the reduction of iodine is presented in Fig. 3. When 6 ml of $6.2 \times 10^{-3} M$ iodine solution were brought into contact with a 0.5-g sample

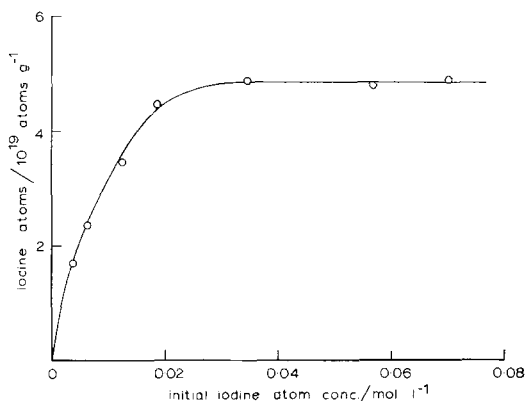


Fig. 2. Amount of iodine reduced by boehmite (dehydrated at $600^\circ C$) after 24 hr as a function of the iodine initially present in the supernatant solution.

of boehmite previously deaerated at $\sim 10^{-5}$ mm Hg for 1 hr at room temperature, the iodine reacted so quickly with the catalyst that in less than 1 hr the color of the supernatant solution had changed from dark red to pale yellow. A sample of gibbsite similarly treated was inactive for the reduction. Whereas the activity curves for boehmite and gibbsite correspond qualitatively at activation temperatures above $\sim 400^\circ C$, markedly different behavior is displayed at lower activation temperatures. In showing two optimum temperatures of activation for the reduction of iodine (280 and $600^\circ C$, approximately), the curve for gibbsite resembles that obtained for the radical-forming ability of this catalyst

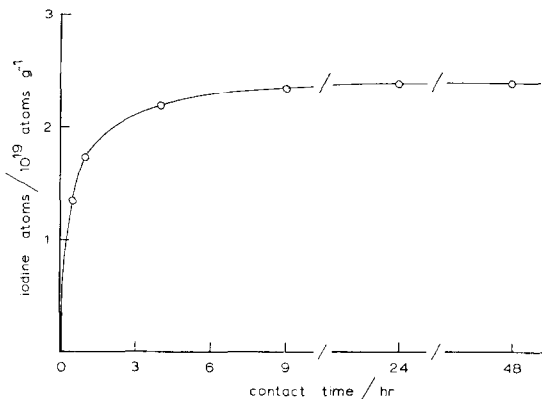


Fig. 1. Amount of iodine reduced by boehmite (dehydrated at $600^\circ C$) as a function of time of contact with an iodine solution initially $6.2 \times 10^{-3} M$.

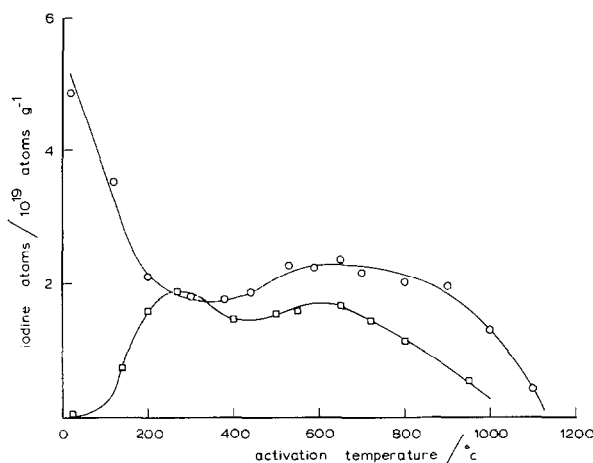


Fig. 3. Amount of iodine reduced after 24 hr as a function of activation temperature: boehmite (○) and gibbsite (□) in contact with an iodine solution initially $6.2 \times 10^{-3} M$.

when the adsorbate was tetracyanoethylene (240 and 750°C) (3). The agreement would probably have been even better if the activation conditions had been similar in the two sets of experiments.

With silica-alumina samples the reducing behavior towards iodine is markedly dependent on the alumina content (Fig. 4). Introduction of even a small amount of silica into alumina results in an appreciable lowering of the reducing activity. Incorporation of fluorine has a similar effect (Fig. 4). The effect of adsorbates on the reducing activity was investigated by the addition of 0.5-g samples of boehmite dehydrated at 700°C to neat benzene and to benzene solutions of perylene ($10^{-3} M$), benzalacetophenone ($8 \times 10^{-4} M$), and *n*-butylamine ($2 \times 10^{-2} M$). After an interval of 24 hr 0.5 ml of 0.2 *M* solution of iodine was added to each of these systems, and after a further 24 hr the amount of iodine was determined. None of these adsorbates had any effect on the reducing power for iodine of alumina. Since a strong ESR signal was obtained from the system containing perylene, iodine was not displacing this adsorbate from the surface.

Quantitative determination of iodine in the presence of tetracyanoethylene (TCNE) is difficult because of complex formation between the two species. Qual-

itative information on the effect of TCNE on the iodine reducing power of alumina was obtained as follows. Samples of boehmite (~ 0.5 g) dehydrated at 700°C was added to 1-ml quantities of 0.1 *M* benzene solutions of iodine and TCNE contained in separate tubes. Twenty-four hours later 1 ml of 0.1 *M* TCNE solution was added to the alumina + iodine system, and 1 ml of 0.1 *M* iodine solution to the alumina + TCNE system. Observations, which extended over a period of 7 days, showed that the supernatant solution in the latter system was much darker in color. The most likely interpretation of this result is that TCNE had blocked some of the sites active for the reduction of iodine.

The extent of reaction between iodine and alumina is somewhat dependent on the solvent used for the halogen. With hexane as solvent and an initial iodine concentration of $6.0 \times 10^{-3} M$, $\sim 3.1 \times 10^{19}$ atoms of iodine were reduced/g of alumina in 24 hr; the alumina was a sample of boehmite calcined at 600°C. The corresponding value obtained with a $6.2 \times 10^{-3} M$ solution of iodine in benzene was $\sim 2.3 \times 10^{19}$ iodine atoms.

Reaction Product

A solution of iodine in benzene was left in contact with a boehmite sample (activated at 700°C) for 24 hr. The super-

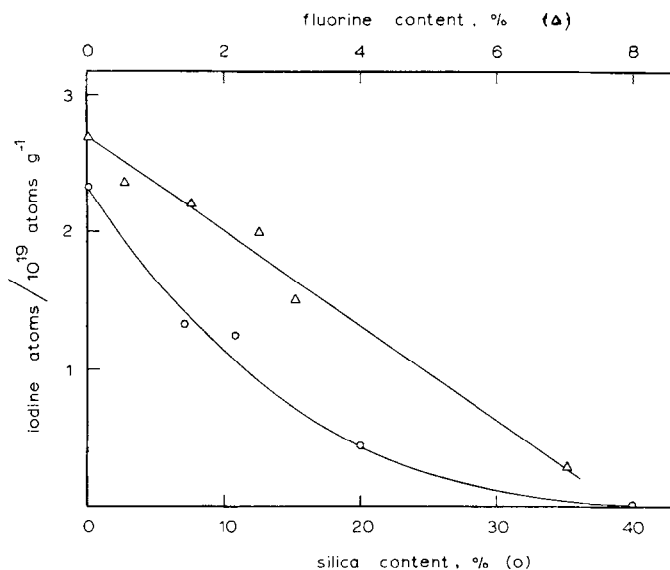


FIG. 4. Amount of iodine reduced by silica-aluminas (dehydrated at 650°C) after 24 hr as a function of the silica content (○). The iodine solution was initially $6.2 \times 10^{-3} M$. Amount of iodine reduced by fluorided aluminas (dehydrated at 175°C) after 24 hr as a function of the fluorine content (△). The iodine solution was initially $6.7 \times 10^{-3} M$.

natant solution was then decanted and the solid was heated at 80°C to remove adsorbed iodine. When 2 ml of water and a few drops of starch solution were added to the solid, no color change occurred. But when a piece of filter paper soaked in the aqueous solution was brought into contact with nitric acid fumes, a dark blue color was produced. This indicated that iodide ion was present in the solution and was being oxidized back to iodine. As further proof of the presence of iodide ion, a few drops of hydrogen peroxide were added to a portion of the aqueous solution + solid; both the catalyst surface and the supernatant solution immediately turned dark blue. To the remaining solution + solid was added ~2 ml of 1 M sulfuric acid solution and a few drops of 0.1 M potassium iodide solution; no blue color appeared which indicated the absence of iodate and iodite ions.

Surface Basicity of Boehmite

The basicity of boehmite calcined at various temperatures was measured by titrating the samples suspended in benzene with a benzene solution of 0.1 M acetic

acid, using bromocresol green ($pK_a = 4.6$) as indicator. The following results were obtained: 20°C (calcination temp), 1.05 mmole g⁻¹; 150°C, 0.97; 200°C, 0.83; 240°C, 0.07; 310°C, 0.00.

Reduction of Iodine by Other Oxides

A 1-g sample of calcium oxide was heated in air at 700°C for 4 hr and cooled at 10^{-2} mm Hg over phosphoric oxide for 30 min before being added to 6 ml of $6 \times 10^{-3} M$ iodine solution. Over a period of several hours the surface of the oxide turned an orange color and the red color faded from the supernatant solution. In the presence of moisture the reaction was much faster.

A 0.8-g sample of sodium hydroxide that had been heated at 120°C for 4 hr and evacuated at room temperature for 12 hr at 10^{-2} mm Hg was added to 6 ml of a $9 \times 10^{-2} M$ iodine solution. Within 5 min the red color disappeared from the solution. The surface of the solid assumed a grey color on coming into contact with the iodine solution, but within 1 hr it was again white.

DISCUSSION

In the preceding paper (5) it was shown that, in the presence of a suitably activated silica-alumina catalyst and molecular oxygen, aqueous solutions of iodide ion are oxidized to iodine in a continuing reaction, the oxidizing properties being associated with the Bronsted acidity of the oxide catalyst.

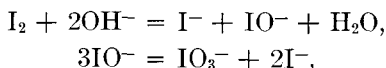
The principal result of the present study is to show that the reverse reaction, the reduction of iodine to iodide ion, occurs equally readily on the surface of an activated alumina. With a boehmite sample activated at 600°C the maximum amount of iodine reduced to iodide corresponded to a concentration of reducing sites of $\sim 2.3 \times 10^{19} \text{ g}^{-1}$ of catalyst, or $\sim 7.0 \times 10^{16} \text{ m}^{-2}$ of surface, when the initial iodine concentration in the supernatant solution was $6.2 \times 10^{-3} \text{ M}$, and the reaction was complete at room temperature in about 6 hr. In comparison, the maximum concentration of anion radicals obtained by the reduction of TCNE was $9.0 \times 10^{18} \text{ g}^{-1}$ of catalyst, when the initial TCNE concentration was 0.10 M. The corresponding values for a gibbsite sample similarly activated were 1.7×10^{19} sites active for iodine reduction and 8.1×10^{18} sites active for TCNE reduction. The finding that the concentration of iodine atoms formed at the surface is a function of the iodine concentration in the supernatant solution (Fig. 2) implies that an adsorption equilibrium is set up between the adsorbate molecules in solution and those held at the surface.

The effect of activation temperature on the reducing power for iodine of several alumina samples is shown in Fig. 3. The results for gibbsite parallel closely the pattern found with TCNE (3). With gibbsite two maxima are observed in the reducing activity-activation temperature plot. This suggests that, as in the reduction of TCNE, the reducing site at low activation temperatures (<400°C) may be the hydroxyl ion, whereas at higher activation temperatures oxide defects are more important as reducing centers. In ac-

cordance with this view, boehmite, the surface of which contains hydroxyl ions, shows reducing activity even when activated by evacuation at room temperature, which removes molecular water from the surface. The variation with temperature of the basicity of the boehmite surface is consistent with the hypothesis that the hydroxyl ion is one of the active reducing centers, as are the results for the reduction of iodine by other oxides. Both forms of alumina show a maximum in activity for the reduction of iodine at around 600°C, corresponding to the optimum activation temperature for the reduction of TCNE at oxide ion defect centers (3).

The experiments with silica-aluminas (Fig. 4) demonstrate clearly that it is the alumina phase which is active for iodine reduction and is further evidence that, at the lower activation temperatures, the hydroxyl ion is the active reducing agent on the surface. Silica itself is inactive as a reducing agent for iodine indicating that the silanol hydroxyl groups are inactive in this respect. Further confirmation for the view that the reducing agent at low activation temperatures is the hydroxyl ion is seen in the effect of replacing OH^- by fluoride (Fig. 4).

The reduction of iodine on the surface of alumina, now reported, is analogous to the reaction in aqueous alkaline solution:



except that in the surface reaction I^- was the only product found. The iodate ion could not be detected in these systems.

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