and $-150°C$ are shown in the upper curves in Fig. 1. The transmission of the bare sample at the same temperature, measured just before the gas admission, is shown in the respective lower curves.

The peak of the band is at 2202 cm$^{-1}$, as Eischens reported, but this was true with the samples for which the evacuation subsequent to the reduction was made at 370°C for 30 min. When it was made at 370°C for 2 hr, the peak appeared at 2220 cm$^{-1}$ and the band was smaller than shown in Fig. 1. These facts are in harmony with another datum of Hardeveld, by which he suggested that the adsorbed nitrogen is a special unstable species. It is clear that the hydrogen was more thoroughly removed by the latter evacuation conditions (the vac-uum attained finally was higher though of the same order of $10^{-6}$ mm Hg in either case), but it is also conceivable that the longer evacuation time might mean greater possibility of contamination of the surface.

REFERENCE

1. EISCHENS, R. P., AND JACKNOW, J., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* 1, 627 (North-Holland Publ. Co., Amsterdam, 1965).

TOSHIKO NAKATA
SANJURO MATSUSHITA

*Faculty of Science*
*Hokkaido University*
*Sapporo, Japan*
  *Received July 12, 1965*

# Oxidation of Potassium Iodide by Silica-Alumina Catalysts

The oxidizing properties of activated silica-alumina catalysts have been demonstrated in various ways in recent years. Thus the application of the ESR technique has revealed that adsorption of several aromatic compounds involves electron transfer to active sites in the surfaces of such oxides (1–4) and several estimates of the population of these sites have been made (5, 6, 7). This property of silica-alumina was soon shown to be largely due to the presence of active oxygen atoms which are either chemisorbed on the surface or are part of its structure. Fogo (8) found that water was produced on treating silica-alumina at 500°C with hydrogen and some 90% of activity for cation-radical formation from polynuclear aromatic hydrocarbons was eliminated. This result was quickly confirmed by other workers (6, 7). Hirschler and Hudson (9) have also provided evidence that during adsorption of triphenylmethane oxygen atoms abstract hydrogen and that triphenylmethanol may be desorbed from the surface. Oxygen-containing products are also found when 1,1-diphenylethylene is allowed to adsorb and react on activated silica-alumina (10) and unpublished work from this laboratory indicates that oxygen atoms in the surface are also involved in hydrogen abstraction during formation of lavender-colored polymeric complexes from n-butenes (3). In the latter case involatile unsaturated ketones are detected among the desorbed products.

While the oxidizing action of silica-alumina is therefore clearly proven, so far the sites responsible have only been investigated using organic agents which are either adsorbed from the vapor phase or from nonaqueous solvents. It seemed to us that it might be worthwhile studying the interaction of silica-alumina and inorganic redox systems in aqueous solution. We now wish to report that when activated catalyst is added to fairly concentrated aqueous solutions of potassium iodide at room temperature iodine is liberated. This reaction may be used as a basis for a simple titration method of estimating the surface density and strength of oxidizing centers in such catalysts.

Samples of catalyst ($\sim$1 g) were heated

in oxygen at 500°C for 1 hr, cooled to room temperature in a desiccator, weighed in stoppered tubes, and then added to 25 ml portions of $N/10$ KI solution in stoppered titrating flasks. The flasks were stored in the dark and after suitable intervals the liberated iodine was titrated with $N/10^4$ sodium thiosulfate, using starch as indicator. Results are reported in Table 1 for a

TABLE 1

ESTIMATION OF OXIDIZING CENTERS IN SILICA-ALUMINA CATALYST (10%) USING IODINE TITRATION METHOD

| Time (min) | Titer/g (ml of $N/10^4$ thiosulfate) | Sites/cm$^2$ × 10$^{-11}$ |
|---|---|---|
| 10 | 10.0 | 2.4 |
| 100 | 12.7 | 3.1 |
| 1075 | 14.7 | 3.5 |
| 1115 | 15.9 | 3.8 |
| 1330 | 16.0 | 3.8 |
| 2640 | 21.0 | 5.0 |
| 4080 | 26.6 | 6.4 |
| 4400 | 21.5 | 5.1 |
| 5840 | 25.4 | 6.1 |
| 8330 | 30.0 | 7.2 |
| 10080 | 38.3 | 9.2 |
| 10080[a] | 10.0 | 2.4 |

[a] 25% catalyst.

series of titrations using a catalyst (I.C.I., Billingham) which contained 10% alumina and had a surface area of 250 m$^2$/g. In all cases immediate liberation of iodine upon addition of catalyst took place, followed by a slow increase in iodine concentration over prolonged periods. Control experiments, carried out simultaneously, showed that the reaction did not occur when the catalyst was absent. A catalyst containing 25% alumina was also tested but did not liberate iodine immediately, although a very slow reaction was observed over a period of 1 week.

The 10% catalyst samples which had been in KI solution over periods up to 1 day were filtered off, washed with distilled water, dried, and reactivated. When these samples were again added to $N/10$ KI solution iodine was not formed immediately, and after 1 week the titers were less than those obtained previously by 10–15 ml of

thiosulfate solution. This result shows that those sites in the fresh catalyst which had oxidized iodide ions had been quantitatively eliminated.

When catalyst was added to $N/10$ KCl solution for 5 min before adding $N/10$ KI solution there was no immediate appearance of iodine, but addition of a second sample to a mixed solution gave the same titer after 10 min as that obtained previously when chloride ions were absent.

An attempt was made in the following way to estimate the amount of iodine ions adsorbed by catalyst from solution. Two samples of catalyst were allowed to equilibrate with 25-ml portions of $N/100$ KI solution. After 3 hr, 10-ml portions of these solutions were pipetted into excess concentrated hydrochloric acid solution and titrated with $0.0027\,M$ potassium iodate using the violet color of free iodine in a few milliliters of carbon tetrachloride as indicator. The number of iodide ions adsorbed under these conditions was $4.5 \pm 0.2 \times 10^{12}$/cm$^2$.

The number of oxidizing centers per square centimeter which react immediately with iodide ions agrees very well with the maximum surface concentration of anthracene (5) or perylene (11) cations which can be obtained with the same catalyst. Moreover the absence of rapid reaction initially with the 25% catalyst shows that the method is selective for those sites of high oxidizing power above a certain critical strength. This observation that 10% catalyst has sites of higher acid strength than 25% catalyst has also been made by Hirschler (12) using the method of titrating with $n$-butylamine in the presence of various indicators of different pK values. Although Hirschler (12) concluded that these sites were of the Bronsted type it seems unlikely that protons play any role in assisting the oxidation of iodide ions. It may be possible that the sites are not simply either Bronsted or Lewis but exhibit both protonic activity and oxidizing properties, depending on the adsorbate.

The results provide conclusive evidence that salts interact strongly and directly with the oxidizing centers in these cata-

lysts, the anion competing successfully with water for adsorption. The following reaction scheme is proposed:

$$K^+I^- + \qquad K^+I^- \qquad K^+ + I$$
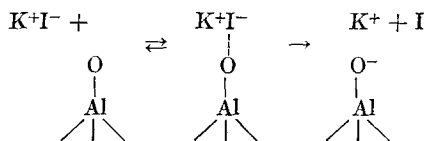


The second stage in this scheme is not readily reversed since used catalyst samples, when reactivated, had lost their ability to liberate iodine immediately. Flockhart and Pink (11) have also found that treating silica-alumina with salts reduces their activity for forming cation-radicals from perylene. It is interesting to note, however, that only a small portion of all the iodine ions taken up by the catalyst are oxidized, even after immersion in solutions for 1 week, and thus most of the adsorption is reversible.

REFERENCES

1. ROONEY, J. J., AND PINK, R. C., *Proc. Chem. Soc. (London)*, p. 70 (1961).

2. BROUWER, D. M., *Chem. and Ind.*, p. 177 (1961).

3. LEFTIN, H. P., AND HOBSON, M. C., JR., *Advan. Catalysis* 14, 115 (1964).

4. TERENIN, A., *Advan. Catalysis* 15, 227 (1965).

5. ROONEY, J. J., AND PINK, R. C., *Trans. Faraday Soc.* 58, 1632 (1962).

6. HALL, W. K., *J. Catalysis* 1, 53 (1962).

7. BROUWER, D. M., *J. Catalysis* 1, 372 (1962).

8. FOGO, J. K., *J. Phys. Chem.* 65, 1919 (1964).

9. HIRSCHLER, A. E., AND HUDSON, J. O., *J. Catalysis* 3, 239 (1964).

10. ROONEY, J. J., AND HATHAWAY, B. J., *J. Catalysis* 3, 447 (1964).

11. FLOCKHART, B. D., AND PINK, R. C., *J. Catalysis* 4, 90 (1965).

12. HIRSCHLER, A. E., *J. Catalysis* 2, 428 (1963).

S. D. MELLOR
J. J. ROONEY
P. B. WELLS

*Chemistry Department*
*The University*
*Hull, England*