On the Infrared Band of Nitrogen Chemisorbed on Nickel

At the 3rd International Congress on Catalysis, R. P. Eischens made a report on the infrared absorption band of nitrogen chemisorbed on nickel. R. v. Hardeveld objected to Eischens' report and stated that on the basis of his own experimental results Eischens' band could be observed only when the nickel sample was prepared from nickel nitrate through its direct reduction with hydrogen (as Eischens did) and not with the samples prepared in other ways (*1*). The suspicion that the band observed by Eischens could not be regarded as due to an adsorption on the surface of nickel in general appears to have been strengthened by some other questioners, who said that they had perceived no chemisorption of nitrogen on nickel in their respective adsorption experiments. Under these circumstances it is necessary to report the experimental facts which we have that the band observed by Eischens can also be observed with a sample whose preparation is begun with the thermal destruction of nickel nitrate to oxide, as Hardeveld initially did, and moreover, even with a sample prepared from another nickel source.

In infrared studies of nitrogen-on-nickel adsorption we used as the metal source mainly nickel nitrate, but in some cases nickel acetate. In such experiments it has been our usual method to calcine the salt (which is dispersed in Aerosil) into oxide in the air and then reduce it in the observation cell. With either of these salts the band in question has clearly been observed. In this short letter, it suffices to report somewhat in detail only the results obtained with samples from the acetate.

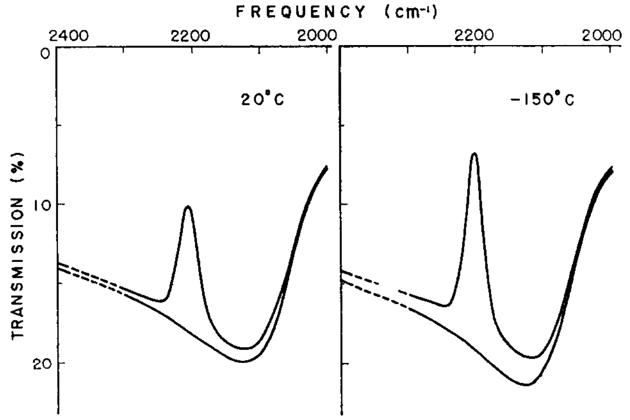

Fig. 1. The infrared absorption of chemisorbed nitrogen observed at 20°C and −150°C with the nickel sample prepared from nickel acetate.

A mixture of aqueous solution of nickel acetate and Aerosil silica was, after being dried, heated in the air at 700°C for 3.5 hr (in the case of nitrate, at 300°C), becoming a powder containing nickel oxide. The powder was pressed into a thin disc and placed in the infrared cell, where the sample was, after being degassed at 350°C, reduced with 99.99%-pure hydrogen at the same temperature. The thickness of the disc was 30 mg/cm^2 after the reduction and it contained 10% nickel. The reduction was by the static method but continued for about 50 hr with the hydrogen renewed frequently. The reduction being complete and hydrogen evacuated, nitrogen was admitted at the pressure of 7 cm Hg. The transmission of this sample was measured at various temperatures; the results obtained at 20°

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 vacuum 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).

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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 (~1 g) were heated