

Ferromagnetic Resonance Investigation of Nitrogen Adsorption on Nickel

On the basis of adsorption isotherm measurements several investigators have shown the possibility of nitrogen chemisorption on nickel at low temperatures (1, 2, 3). Others have concluded that nitrogen chemisorption does not occur on nickel film at room temperature (4-7). Electrical conductivity (8, 9) and surface potential (3, 10) measurements show that changes observed do not exceed the effect produced by physical adsorption. One of the authors of this article noted only slight influence of nitrogen adsorption on the magnetization of nickel (11, 12).

Eischens and Jacknow (13) ascribe the infrared band at 2202 cm^{-1} , when nitrogen is adsorbed on nickel, to chemisorbed molecular nitrogen. In recent work van Hardeveld and van Montfoort (14) showed that this band is due to the nitrogen Raman band at 2331 cm^{-1} which shifts under the influence of the Stark effect and which can be observed because of the strong polarizing field of special sites present in nickel particles with a diameter of between 15 and 70 \AA .

In the present work we investigated nitrogen adsorption on nickel by EPR. Use of this technique permits measurement of possible changes in the magnetization of the very small particles of nickel which are active in nitrogen adsorption (14). The EPR method is of far greater sensitivity than the low-frequency permeameter (11, 12). The EPR spectra were recorded with a Varian V-4502 x-band spectrometer with 100-kc/sec field modulation and variable temperature accessory. A suitable high-vacuum device and "quick-disconnect coupling" of the waveguide permitted reduction of the samples *in situ* and a final vacuum of the order of 10^{-6} mm Hg . Use of West-Glass greaseless high-vacuum stop-cocks and a trap cooled with liquid nitrogen eliminated any influence of mercury

and grease vapors. Nine percent nickel catalyst was prepared by homogeneous hydrolysis of $\text{Ni}(\text{NO}_3)_2$ on Davison silica gel according to the method described in ref. (15). The catalysts were reduced for 20 hr at 400°C and evacuated for 4 hr at 360°C . Palladium-diffused hydrogen, and research grade nitrogen (Air Reduction Sales Co.) containing only 3 ppm argon were used. The partial pressure of oxygen impurity in these gases was such as to have a negligible effect on the magnetization, even if completely sorbed by the nickel.

Figures 1 and 2 show the line shapes

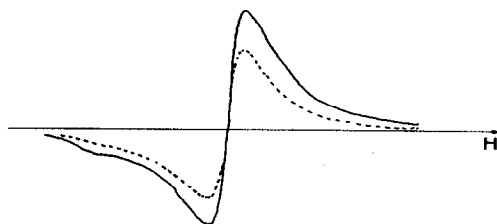


FIG. 1. EPR signal from Ni-SiO₂ catalyst at 25°C ; ———, evacuated; - - - - -, treated with hydrogen (hydrogen pressure 450 mm Hg). The peak-to-peak line width is 550 ± 20 gauss; g value is 2.22.

of FMR signals before and after adsorption of hydrogen and nitrogen. In a typical case of hydrogen adsorption, the magnetization decreased 27%. Nitrogen adsorption causes no more than 1.5% decrease of magnetization up to 350 mm nitrogen pressure. Nitrogen adsorption at -80°C shows the same order of change. Adsorption of nitrogen on the nickel sample with higher nickel content and larger particle size does not show any detectable change of magnetization.

The results of ferromagnetic resonance investigation of nitrogen adsorption on nickel do not give evidence for extensive electronic interaction between the nitrogen and the nickel surface such as would be

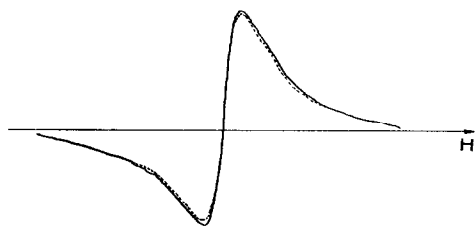


FIG. 2. EPR signal from Ni-SiO₂ catalyst at 25°C; _____, evacuated; _____, treated with nitrogen (nitrogen pressure 350 mm Hg). The peak-to-peak line width is 530 ± 20 gauss; g value is 2.22.

expected for true chemisorption. These results are in agreement with conclusions made on the basis of low-field measurements (11). They confirm van Hardeveld and van Montfoort's (14) findings concerning the relation between catalyst structure and its ability for nitrogen adsorption, and they show that physical adsorption of nitrogen on nickel (11, 14) under these conditions is the more probable.

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A. A. ANDREEV*
P. W. SELWOOD

Department of Chemistry
University of California
Santa Barbara, California
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* Present address: Institute of Organic Chemistry, Bulgarian Academy of Science, Sofia, Bulgaria.