JOURNAL OF CATALYSIS 56, 297–298 (1978)

The Specific Activity of Supported Nickel and the Hedvall Effect

A recent paper (*1*) has helped to solve a puzzling problem. It has often been observed that the specific activity of finely divided supported nickel may be greater than that of massive nickel under otherwise identical conditions. For example, it has been shown (*2*) that the specific hydrogenolysis rate for ethane over nickel supported on silica–alumina decreases, at constant temperature, with increasing nickel crystallite size. At 540 K the specific rate decreased from 100 to 5 mol hr^{-1} m^{-2} as the crystallite size was increased, by sintering, from under 4 to about 9 nm.

The slow reduction of silica-supported nickel is known (*3*) to yield a catalyst that is ferromagnetic but without a definite Curie point. This effect has been attributed (*4, 5*) to a dependence of Curie point on metal particle size. An attempt to put this in quantitative terms was made (*6, 7*) through the relation $T_c/631 = z/12$ where T_c is the Curie temperature of a particle in which the average number of nearest nickel neighbors is z, and 631 K is the Curie temperature of massive nickel for which the number of neighbors (the coordination number) is 12. Some confidence in the procedure was obtained from the reasonably satisfactory agreement between this method and X-ray linewidth broadening for determining particle diameters and distributions. But later work by various authors cast some doubt on the approach. The magnetic data available were at least equally well interpreted by the concept of superparamagnetism (*8*) although it was shown (*9*) that the "paramagnetic Curie point" is dependent on particle size. This is, of course, not to deny that small particles of nickel may be superparamagnetic.

It has now been shown (*1*) that a significant shift of T_c occurs in nickel–silica catalysts provided that reduction is incomplete and provided that the average nickel particle diameter is not much in excess of 2.5 nm. For a sample containing 4.5% Ni with 50% reduction and an average particle diameter of 2.5 nm, it was found that $T_c = 505 \pm 10$ K. It is obvious that many, if not most, earlier studies on similar catalysts must have been done on samples having Curie points considerably lower than that of massive nickel.

Many reactions over ferromagnetic catalysts show an abnormal increase in rate, the Hedvall effect (*10*), as the temperature is raised through T_c. A large change in rate is not uncommon. For instance, between 628 and 638 K the catalytic decomposition of nitrous oxide over nickel increases by about eightfold (*11*).

It appears from these considerations that the increased specific activity of supported nickel, as compared with that of massive nickel, has a simple explanation. With decreasing crystallite size T_c falls. The reaction under investigation then occurs with the catalyst in the more active paramagnetic phase. But as the crystallite size increases T_c rises. The reaction, at constant temperature, may then occur on the less active ferromagnetic phase.

0021-9517/79/020297-02$02.00/0

REFERENCES

1. Derouane, E. G., Simoens, A., Colin, C., Martin, G. A., Dalmon, J. A., and Védrine, J. C., *J. Catal.* **52**, 50 (1978).
2. Carter, J. L., Cusumano, J. A., and Sinfelt, J. H., *J. Phys. Chem.* **70**, 2257 (1966).
3. Michel, A., *Ann. Chim.* **8**, 317 (1937).
4. Michel, A., and Gallissot, M., *Compt. Rend.* **206**, 1252 (1938).
5. Michel, A., Bernier, R., and LeClerc, *J Chim. Phys.* **47**, 269 (1950).
6. Selwood, P. W., Phillips, T. R., and Adler, S., *J. Amer. Chem. Soc.* **76**, 2281 (1954).
7. Selwood, P. W., Phillips, T. R., and Adler, S., *J. Amer. Chem. Soc.* **77**, 1462 (1955).
8. Selwood, P. W., "Chemisorption and Magnetization," p. 17. Academic Press, New York, 1975.
9. Carter, J. L., and Sinfelt, J. H., *J. Catal.* **10**, 134 (1968).
10. Hedvall, J. A., Hedin, R., and Persson, O., *Z. Phys. Chem.* **B27**, 196 (1934).
11. Hedvall, J. A., *Atti X⁰ Cong. Int. Chim.* **2**, 255 (1938).

PIERCE W. SELWOOD

Department of Chemistry
University of California
Santa Barbara, California 93106

Received June 27, 1978