The Nature of the Urushibara Nickel Catalyst as Revealed by Electron Diffraction

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Nickel catalyst prepared by Urushibara and his coworkers[1] has been studied by electron diffraction. Electron waves of two energies, one relatively hard and another soft were alternately used here in order to investigate the surfaces of catalyst particles[2]. The harder electrons (wavelength, about 0.02 Å) were able to penetrate thick particles (thickness, about 5000 Å)[3]. On the other hand, the softer electrons (wavelength, about 0.05 Å) could graze only the surfaces of the particles.

Metallic nickel was deposited onto zinc dust from a nickel chloride solution. The composite powder of Zinc-Nickel was treated with an acetic acid solution in order to dissolve zinc *partially* and *appropriately*[1]. Ten grams of zinc dust and 3 cc. of distilled water were placed in a round flask of 10 cc. capacity and heated on a boiling waterbath. Ten cc. of an aqueous solution containing 4.04 g. of nickel chloride, $NiCl_2 \cdot 6H_2O$, were boiled and added to the zinc dust by means of a pipet, in a few seconds time accompanied by rapid stirring. The precipitate was collected on a glass filter by suction, washed with a small quantity of hot distilled water and quickly transferred into 160 cc. of 13% acetic acid. When the generation of hydrogen gas subsided, the product was filtered with a glass filter and washed with distilled water (50–60°C) and finally with alcohol.

A sample of the powder gave a diffraction pattern of Fig. 1 with the harder electrons (wavelength, 0.0284 Å). The positions and the intensities of the diffraction rings observed in Fig. 1 are illustrated in Fig. 2. In the diffraction pattern obtained, there are found diffraction rings corresponding to nickel, zinc oxide and zinc. The diffraction rings characteristic of nickel are quite diffuse, whereas those of zinc oxide and of zinc are comparatively sharp. It was impossible to observe nickel in this crystalline state by means of X-ray diffraction.

1) Y. Urushibara S. Nishimura and H. Uehara, This Bulletin, 28, 446 (1955).
2) S. Yamaguchi, *Z. phys. Chem. N.F.*, 7, 115 (1956).
3) S. Yamaguchi, *J. Appl. Phys.*, 25, 811 (1954).

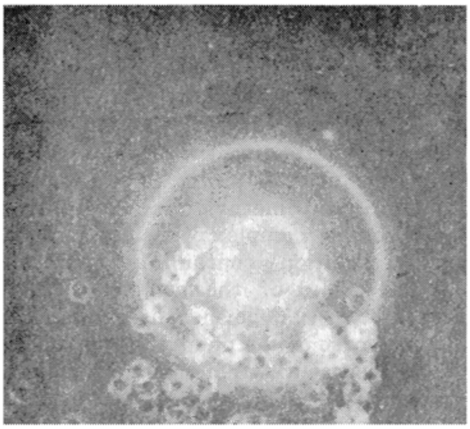

Fig. 1. An electron diffraction pattern of the Urushibara nickel catalyst.
The diffraction rings corresponding to nickel, zinc oxide and zinc. Nickel crystallites are very fine, whereas zinc and zinc oxide are granular. Wavelength, 0.0284 Å. Camera length, 495 mm. Positive enlarged 2.3 times.

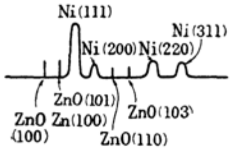

Fig. 2. Positions and the intensities of the diffraction rings are illustrated here.

The same spot in the specimen as in Fig. 1 was observed with the softer electrons (wavelength, 0.0490 Å). A diffraction pattern of Fig. 3 was then obtained. In Fig. 3, diffuseness of the rings from nickel seems to be greater than would be expected from the electron wavelength applied (0.0490 Å). This implies that the surfaces of the nickel particles are nearly amorphous. As a matter of fact, there is no indication of refraction in the diffraction rings of Fig. 3, as well

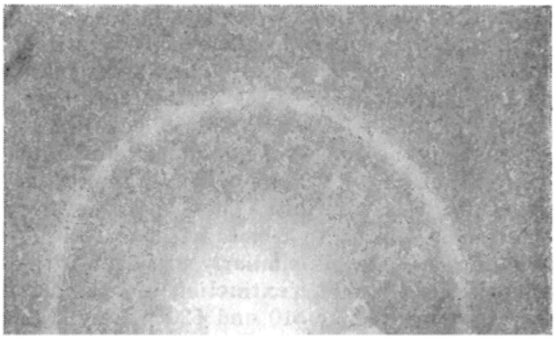

Fig. 3. Diffraction pattern from the same spot of the specimen as for Fig. 1.
Very diffuse rings from nickel are found. Wavelength, 0.0490 Å. Camera length, 495 mm. Positive enlarged 2.3 times.

those of Fig. 1. The nickel in the Urushibara catalyst thus exists in a state of *crystallites*, and is *not crystals.*

The Urushibara catalyst is composed of nickel, zinc and zinc oxide, as is demonstrated in Figs. 1 and 2. The coexistence of zinc, zinc oxide and nickel implies that zinc not only plays the part of a carrier, but also protects nickel from oxidation. This is because of galvanic relation between zinc and nickel (formation of local cells). As long as metallic zinc exists in the catalyst, nickel can survive as active centres. This is the case with the Raney nickel catalyst. Zinc found in the Urushibara catalyst corresponds to the aluminum of the Raney catalyst.

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