(100) and (111) faces, and it was found that appreciable differences in rates existed between the two faces. These differences depended on both the differences in activity per unit of surface and on the differences in total surface area exposed on the two faces. The rate measurements were correlated with the structure of the surfaces as the surfaces rearranged under the action of the catalytic reaction.

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The Selective Deposition of Carbon on the (111) Face of a Nickel Crystal in the Catalytic Decomposition of Carbon Monoxide[1]

BY HENRY LEIDHEISER, JR., AND ALLAN T. GWATHMEY

Previously reported results[2] have shown that the catalytic reaction of hydrogen and oxygen leads to rearrangement of a copper surface and proceeds at a rate dependent on the crystal face exposed to the reacting gases. Results reported herein give an example of a catalytic process which does not lead to visible rearrangement of the surface initially and which proceeds at a rate dependent on crystal face.

A monocrystalline sphere[3] of nickel, 0.5 in. in diameter, with a shaft, $^3/_{16}$ in. in diameter and $^3/_8$ in. long, on one side was mechanically polished and then electrolytically polished by the method of Hothersall and Hammond[4] in order to give a smooth and strain-free surface. It was heated to 550° in carbon monoxide at a pressure of one atmosphere in an electric furnace provided with a window for continuous observation. After ten hours the pattern shown in Fig. 1 (see insert facing page 1203) began to develop. Black deposits had formed in large areas around the (111) poles but not in areas at the (100) and (110) poles. As the reaction continued the diameter of the (111) areas increased until the deposit covered the entire surface with the exception of a small square at each (100) pole and a narrow band between neighboring (100) poles and running through (110) poles. The photograph shows in a striking manner that the decomposition of carbon monoxide to form carbon on nickel at 550° proceeds at widely different rates on the (100) and (111) faces. The black deposit was readily removable by rubbing with tissue within several hours after it was first observed. As the reaction continued, however, the deposit tenaciously adhered to the surface, and it could not be removed by rubbing.

Evidence summarized by Hofer[5] indicates that when nickel is treated with carbon monoxide above 500° the major product left on the surface is carbon, although the presence of an intermediate carbide is not excluded. In order to obtain a sufficient amount of deposit for analysis, a polycrystalline nickel foil of larger surface area was treated with carbon monoxide under identical conditions as the single crystal. The analysis of the product on the surface was as follows: carbon 88.52 wt. %, nickel 11.01 wt. %. This analysis corresponds to approximately 97.5 atom % carbon and 2.5 atom % nickel.

Results similar to those shown in Fig. 1 were obtained at 550° in mixtures of hydrogen and carbon monoxide when the carbon monoxide was in excess. When the carbon monoxide was present in low concentrations in the neighborhood of 10%, no carbon deposit was observed and rearrangement patterns resulted.

It is interesting that the crystal lattice of graphite may be superimposed on the (111) face of nickel with only slight distortion. No similar match is possible on the (100) or (110) faces of nickel. It should be pointed out, however, that even though the (111) face of copper would give almost as good a match, no carbon deposits were visible after forty-eight hours at 550°.

Information on the deposition of carbon is important in an understanding of the Fischer–Tropsch catalytic process, and the results herein reported indicate the importance of crystal face in reactions of this type.

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[2] Leidheiser and Gwathmey, THIS JOURNAL, **70**, 1200 (1948).

[3] See Gwathmey and Benton, *J. Phys. Chem.*, **44**, 35 (1940), for a description of the technique for growing and machining single crystals.

[4] Hothersall and Hammond, *J. Electrodepositors' Tech. Soc.*, **16**, 83 (1940).

[5] Hofer, U. S. Bur. Mines Rept. Investigations 3770, 39 pp. (1944).