Direct Observation of Catalytic Activity Change in Nickel Metal Deformed in Torsion During Reaction

Eizo Miyazaki, Takakazu Fukushima, Kiyoshi Kawasaki, and Kazuo Nakada
Department of Chemical Engineering, Niigata University, Nagaoka

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There have been many experimental investigations on the role of defect structure in the catalytic activity of metals. Some investigations[1] show that the defect plays an important role in heterogeneous catalysis; others[2] show that the effect of defect is minimal. The former proposal is, however, based mainly on the parallelism between the change in catalytic activities of cold-worked, quenched and irradiated metals during annealing. The purpose of this paper is to show more explicitly the influence of the defect on catalytic activity by a method in which metal was *in situ* cold-worked during reaction.

The main parts of the apparatus consist of a reaction tube and a manometer. In the center of the reaction tube a nickel sheet (0.1 mm thick, 3 mm wide and 130 mm long), washed in acetone and subsequently annealed in hydrogen at 700°C, was fixed to a pyrex glass rod with one end connected to a ground glass joint. The sheet was treated afresh in hydrogen at 600°C in order to remove the oxidized layer on surface before reaction, and the sheet was deformed in torsion during reaction up to a definite number of turns with the aid of the joint. The reaction was followed by continuously recording the total pressure change with a newly-devised glass made manometer.[3] The small surface areas of the catalysts were measured by the BET method using xenon vapor at 78°K.[4] The surface areas before and after deformation in torsion up to 6 turns were 10.1 cm^2 and 13.1 cm^2 per catalyst, respectively. A full description of the apparatus will be given in a later publication.

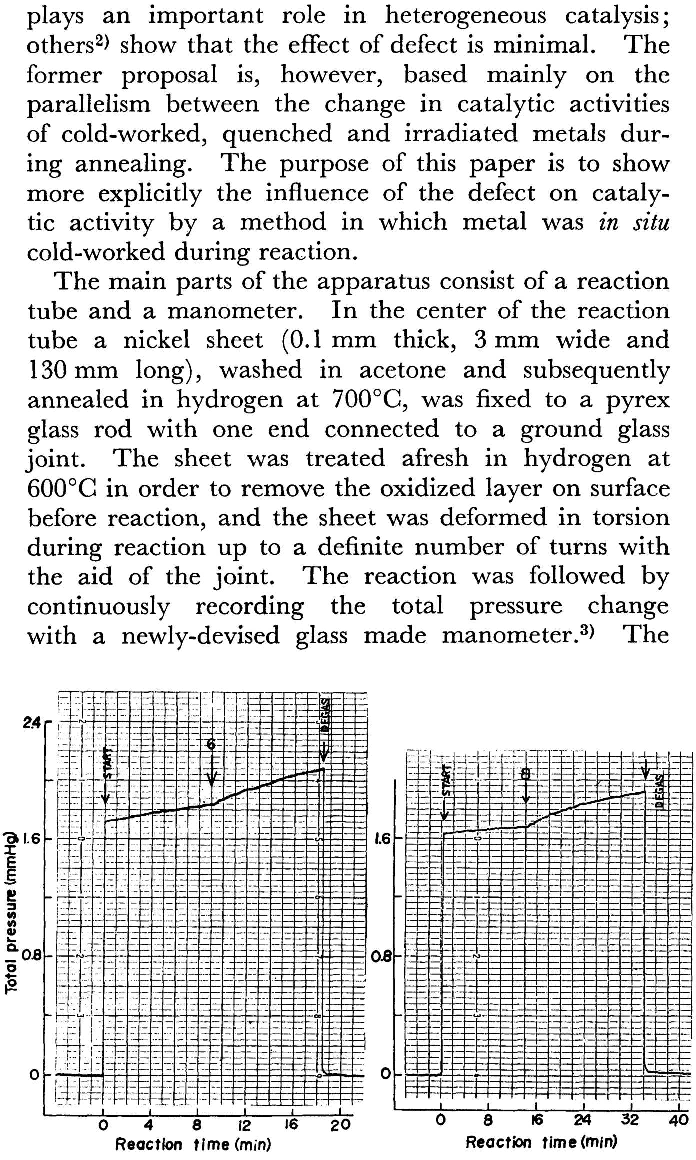

Fig. 1 Fig. 2

Figs. 1 and 2. Changes in total pressure with reaction time at 194°C(Fig. 1) and 182°C (Fig. 2). Deformations in torsion were made at the points given by arrows up to 6 and 8 turns, respectively.

Figure 1 shows a typical curve obtained in the change of total pressure for the decomposition of formaldehyde ($H_2CO=CO+H_2$) over nickel sheet at 194°C, where deformation by torsion was carried out up to 6 turns at the point given by arrow. The discontinuity or sudden increase in total pressure was observed at the point of deformation, *i. e.*, deformation elevated the activity (slope of the curve). A similar result was obtained when the torsion was made up to 8 turns at 182°C as shown in Fig. 2, in which the increase in activity by deformation was found to be more drastic. However, such deformation-induced activities were found to practically disappear after the catalysts were annealed at 400°C. In addition, the reaction was confirmed to be kinetically first order with respect to formaldehyde pressure regardless of deformation range. Integral forms of the first order reaction before and after deformation during reaction are shown respectively as follows: $2.3\log(P_0/P)=kt$ and $2.3\log(P_0'/P)=k'(t-t_0')$, where k and k' are rate constants and P_0 or P_0' is formaldehyde pressure at $t=0$ or $t=t_0'$ (reaction time when deformation was made), respectively. The ratio of k' to k for the case shown in Fig. 1 was 2.1, *i. e.*, the activity was enhanced by 110% due to the deformation in torsion up to 6 turns during formaldehyde decomposition at 194°C. Increase in activity, however, might be due to the increase in surface area accompanying deformation in torsion. The actual surface areas were therefore measured for the catalysts only annealed and deformed in torsion up to 6 turns. The result was 29.8% increase; the residual increase in activity $(110-30=80\%)$ due to the deformation should be therefore attributed to other origins such as lattice imperfections which are known to be produced when nickel is subjected to deformation in torsion.[5] This can be also supported from the result of the annealing effect.

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