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A HIGHLY ACTIVE NICKEL OXIDE CATALYST FOR ETHYLENE HYDROGENATION

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A nickel oxide catalyst prepared by homogeneous precipitation with urea followed by decomposition in vacuo shows an extraordinarily high activity in ethylene hydrogenation. An evidence is given to indicate that the generation of active sites is associated with a partial reduction of oxide by the precipitant, urea, remained in the oxide.

It has been known that the catalytic activity of a catalyst is profoundly affected by the method of catalyst preparation or the condition of pretreatment. Nickel oxide is known to be activated as a catalyst for olefin hydrogenation by evacuation at around 400°C, while the known activity is not very high$^{1)}$. We have found that an unusually active nickel oxide can be obtained when it is prepared by a homogeneous precipitation method using urea as the precipitant. Thus the mechanism of activation of nickel oxide has been qualitatively examined and reported in this communication.

The catalyst sample was prepared as follows; a aqueous solution of nickel nitrate and urea was heated to about 90°C with stirring for 20 hrs. The precipitation could be observed at about 1 hr of heating time. The precipitate was washed with water repeatedly 20 times and dried in air at 85°C. The catalyst precursor was stored in a desiccator. The catalyst was prepared from the precursor by decomposing it in vacuo in the reactor. Series of runs were made using the same batch of the catalyst precursor taking about 30 to 70 mg of fresh sample for each run. The rate of ethylene hydrogenation was determined in a closed circulating system. Since the catalytic activity for ethylene hydrogenation was very high, the reaction temperature was lowered to -78°C to obtain measurable rates.

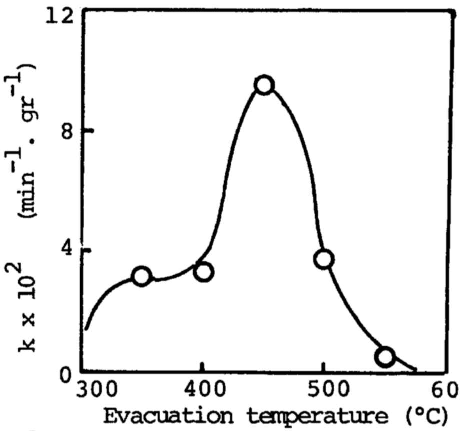

Fig.1 Variation of the activity with evacuation temperature for ethylene hydrogenation at -78°C $P(C_2H_4)$=7.6 cm Hg , $P(H_2)$=8.4 cm Hg

The kinetics of ethylene hydrogenation was found to be first order in hydrogen and zero order in ethylene. Thus the catalytic activity is expressed by the first order rate constant and shown in Fig.1 as a function of the evacuation temperature in the catalyst preparation. A maximum activity is obtained by the evacuation at 450°C.

It is to be noted that the color of the evacuated sample changed from dark brown to black when the evacuation temperature was raised from 300 to 450°C. The decomposition products formed from the catalyst precursor were analyzed by mass spectrometry during the evacuation at temperature between 250 and 550°C, and were found to be largely water and carbon dioxide including trace amounts of nitrogen and ammonia, indicating the presence of urea, the precipitant, in the catalyst precursor. Since such a high activity cannot be obtained by simple dehydration of nickel hydroxide or preformed nickel oxide, it is likely that the active sites are formed by an interaction with urea or its decomposition product. In fact the catalyst evacuated at 300°C exhibits a relatively low activity, while the decomposition of nickel hydroxide is known to proceed at 230°C[2)]. Thus the less active catalyst activated at 300°C was treated with very small amounts of hydrogen at 300°C for 30 min, followed by reevacuation at 300°C for 10 min. All the added hydrogen was consumed within a few minutes accompanying a change in the color of catalyst from dark brown to black. The produced gases were collected in a liquid nitrogen trap and analyzed by mass spectrometry. It was found that the added hydrogen was converted to water accompanied by a simultaneous formation of carbon dioxide. It is clear that the catalyst precursor is partly reduced releasing carbon dioxide, while no metallic phase of nickel was detected by X-ray analysis of the catalyst samples.

The activity of the catalyst thus obtained is shown in Fig.2 as a function of the amount of added hydrogen. The activity increases with the amount of added hydrogen, or the extent of reduction, giving a sharp maximum at a value of 3 cc STP/g. of starting material, which corresponds to 1.4 % reduction on the basis of the amount of hydrogen required for the complete reduction, 221 cc STP/g . Since the excessive reduction causes a drastic decrease in the activity, the activation by the hydrogen treatment cannot be ascribed to a mere formation of metallic nickel, and can be associated with the release of carbon dioxide in addition to the partial reduction of nickel oxide.

Thus the high activity of nickel oxide as obtained by evacuation at around 450°C can be ascribed to the partial reduction by the residual urea. In fact nickel oxide samples prepared by decomposition of nitrate,hydroxide, or carbonate did not show such a characteristic activation when they were partially reduced with hydrogen.

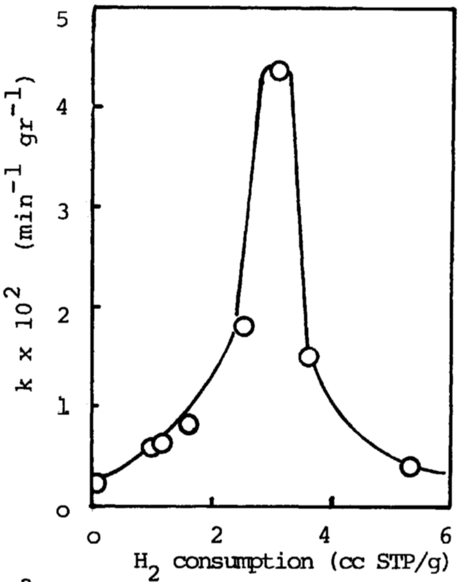

Fig.2 Activity change by hydrogen treatment at 300°C
Reaction temperature; -78°C

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