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HIGH CATALYTIC ACTIVITY OF NICKEL SUPPORTED ON BASIC OXIDE FOR HYDROGENATION OF N,N-DIMETHYL-2-PROPENYLAMINE

Hisaya IMAI, Hideshi HATTORI, and Kozo TANABE
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

Various metal oxides were used as supports of Ni catalyst for hydrogenation of N,N-dimethyl-2-propenylamine. In general, the activities of basic oxide-supported Ni catalysts were higher than those of acidic oxide-supported ones. Among the catalysts examined, Ni/MgO exhibited the highest activity.

Hydrogenation of unsaturated compounds containing nitrogen has scarecely been studied over heterogeneous catalyst. Although NiB and borohydride reduced Pd have been reported to be quite active and selective for such hydrogenation,[1,2] poisoning by the reactant and complexities of hydrogenolysis are unavoidable for conventional metal catalysts such as Pt, Pd, and Ni.[3,4]

A selection of materials for supports is crucial in preparation of excellent supported-metal catalysts. We have carried out the hydrogenation of N,N-dimethyl-2-propenylamine over Ni catalysts supported on various metal oxides and found the Ni catalyst supported on basic oxides to be active.

Supported Ni catalysts were prepared by impregnating various metal oxides, which had been calcined at 500°C in air for 5 h, with aqueous $Ni(NO_3)_2$ followed by drying over a water bath and decomposition by heating at 500°C in air for 3 h. Prior to reaction, the catalyst was reduced under a hydrogen stream at 500°C. The content of Ni was 10 % by weight for all catalysts.

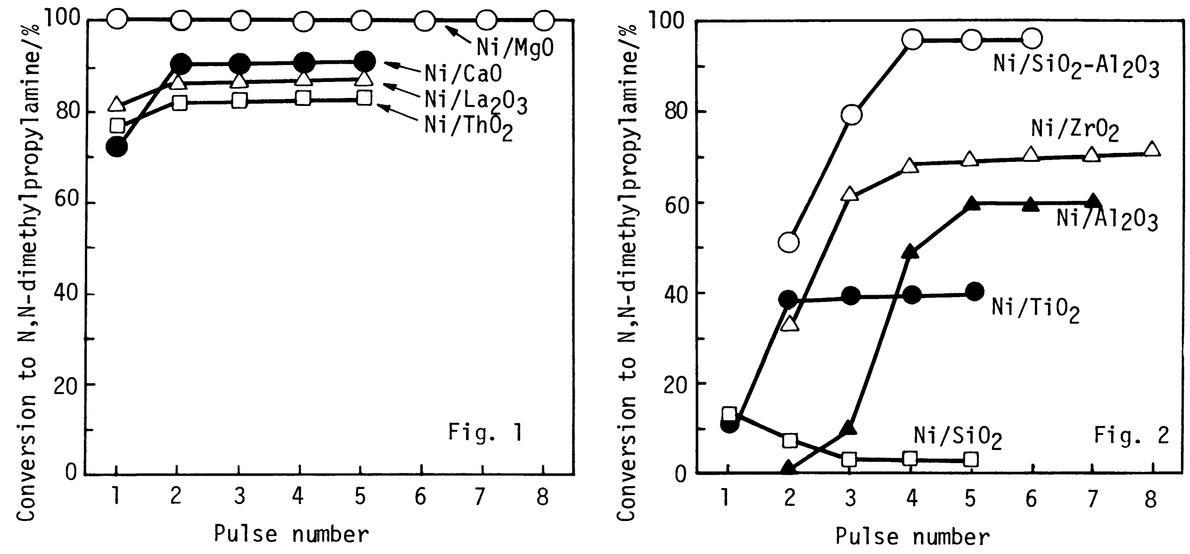
A microcatalytic pulse reactor was employed to carry out the reaction with 30 mg of catalyst at 0°C. N,N-Dimethyl-2-propenylamine (1 μl) was injected into a hydrogen stream (85 ml/min) ahead of the catalyst. Products were collected in a liquid nitrogen trap and then flash evaporated into the gas chromatographic column containing Apiezone L on Chromosorb W treated with KOH.

The percentage conversions of N,N-dimethyl-2-propenylamine are plotted against the pulse number for each catalyst in Figs. 1 and 2. The main product was N,N-dimethylpropylamine. The other products such as propane and dimethylamine which resulted from decomposition were negligibly small. N,N-Dimethyl-1-propenylamine that might result from double bond migration was not detected.

As shown in Figs. 1 and 2, Ni supported on MgO, CaO, La_2O_3, and ThO_2 exhibited high activities from the first pulse. Especially, Ni/MgO gave 100 % conversion. Nickel on SiO_2-Al_2O_3 also showed a high activity after the 4th pulse. Following them, the activities were in the order, $Ni/ZrO_2 > Ni/Al_2O_3 > Ni/TiO_2 > Ni/SiO_2$. With Ni/SiO_2-Al_2O_3, Ni/Al_2O_3, and Ni/ZrO_2, the reactant and products were completely adsorbed on the catalysts at the first pulse. Material balance was not established until the 5th pulse for Ni/SiO_2-Al_2O_3, Ni/Al_2O_3, Ni/ZrO_2, Ni/TiO_2, and Ni/SiO_2.

Since MgO,[5] CaO,[5] La_2O_3,[6] and ZrO_2[7] have basic sites on their surfaces, and Ni supported on these oxides showed high activities, it is suggested that Ni catalyst becomes active when supported on basic oxides, though there is an exception for Ni/SiO_2-Al_2O_3.

There are two possibilities that account for high activities of Ni supported on basic oxides. the reactivity of Ni atoms must depend on the support since it is reported that NiO on MgO is more difficult to be reduced than NiO on Al_2O_3 or SiO_2.[9] Thus, one possibility is that the state



Figs. 1 and 2 Catalytic Activities of Ni Supported on Different Oxides for the Hydrogenation of N,N-Dimethyl-2-propenylamine

of Ni varies with the acid-base properties of a support and Ni on a basic support is in the state that acts better as the active sites. Another possibility is that the support acts as an isomerization catalyst of 2-propenylamine to 1-propenylamine which may undergo hydrogenation over Ni component. Actually, the catalyst mixture containing MgO and Ni/SiO_2 in which MgO was placed just ahead of Ni/SiO_2 gave 100 % conversion. This demonstrates that bifunctional catalysis is operating. Since MgO, CaO, La_2O_3, and ThO_2 are active for double bond migration of 2-propenylamine,[10] bifunctional catalysis seems to be plausible for Ni supported on MgO, CaO, La_2O_3, and ThO_2. However, the differences in the activity among Ni catalysts on different supports, which are inactive for the double bomd migration, suggest that the first possibility mentioned above should also be taken into account.

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