# Hydrogenation of 3-Ethoxy-1-propene Catalyzed by Supported Nickel Catalysts

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**Synopsis** Nickel catalysts supported on different kinds of metal oxides were prepared to search for active catalysts for 3-ethoxy-1-propene hydrogenation. $Ni/ThO_2$ and $Ni/SiO_2-Al_2O_3$ catalysts exhibited high activity and selectivity for 1-ethoxypropane, while Ni/MgO, Ni/CaO, and $Ni/La_2O_3$ catalysts preferentially catalyzed double bond migration to 1-ethoxy-1-propene which undergo hydrogenation with difficulty.

In contrast to extensive studies of hydrogenation of olefins, less attention has been given to hydrogenation of unsaturated compounds containing hetero atoms. We have reported that for the hydrogenation of unsaturated compounds containing nitrogen the activities of nickel catalysts varied considerably with the type of support and the support acted as one function in bifunctional catalysis.[1]

For unsaturated compounds containing oxygen, hydrogenation of allyl alcohols has been studied with heterogeneous catalysts to some extent.[2] However, hydrogenation of allyl ethers has been studied only with Raney Ni[3] and NiB.[4] The present study was undertaken to understand more about hydrogenation of allyl ethers on supported Ni catalysts. Ten kinds of metal oxides were selected as supports for Ni, and used for hydrogenation of 3-ethoxy-1-propene. It was found that the Ni catalysts supported on $ThO_2$ and $SiO_2-Al_2O_3$ were highly active and selective.

Supported Ni catalysts were prepared by an impregnation method. The metal oxides used as support, and their surface areas, were MgO ($84\,m^2/g$), CaO ($16\,m^2/g$), $La_2O_3$ ($43\,m^2/g$), $ThO_2$ ($42\,m^2/g$), $ZrO_2$ ($65\,m^2/g$), $TiO_2$ ($85\,m^2/g$), $Al_2O_3$ ($227\,m^2/g$), $SiO_2$ ($333\,m^2/g$), and $SiO_2-Al_2O_3$ ($278\,m^2/g$). Prior to impregnation, there metal oxides were calcined at 773 K in air for 6 h. The metal oxides were suspended in aqueous nickel nitrate, and the water was evaporated to dryness over a water bath. The nickel nitrate on the metal oxides was then decomposed at 773 K in air for 3 h. Prior to the reaction, the catalysts were reduced with hydrogen at 773 K. The Ni content was 9.1—9.2 wt% for all catalysts except $Ni/Al_2O_3$. The $Ni/Al_2O_3$ contained 10 wt% Ni.

A greaseless closed recirculation reactor was used for carrying out the reaction. A mixture of 1.3 kPa 3-ethoxy-1-propene and 2.6 kPa hydrogen was allowed to react with *ca.* 100 mg of catalyst (24—32 mesh grain) at 273 K or 323 K. The products were analyzed by GLC. Identification was by NMR for separately collected products.

The amount of hydrogen adsorbed on catalysts was measured volumetrically at 273 K. The saturated amounts of hydrogen were calculated by applying the adsorption isotherm to the Langumuir equation for dissociative adsorption.

Time dependences of the composition in the reaction are shown in Fig. 1 for $Ni/Al_2O_3$ and in Fig. 2 for $Ni/ThO_2$ and $Ni/SiO_2-Al_2O_3$. Over $Ni/Al_2O_3$, 3-ethoxy-1-propene underwent both hydrogenation to 1-ethoxypropane and double bond migration to (*E*)- and (*Z*)-1-ethoxy-1-propene when the reaction was carried out at 273 K. 3-Ethoxy-1-propene disappeared after 240 min. As the reaction temperature was raised to 323 K, 1-ethoxy-1-propene underwent appreciable hydrogenation. This feature of the time dependence was commonly observed for all catalysts except for $Ni/SiO_2-Al_2O_3$, though the relative rate of hydrogenation to that of double bond migration varied with the type of catalyst. For instance, over $Ni/La_2O_3$, the double bond migration was very fast as compared with hydrogenation. Over $Ni/ThO_2$, hydrogenation was

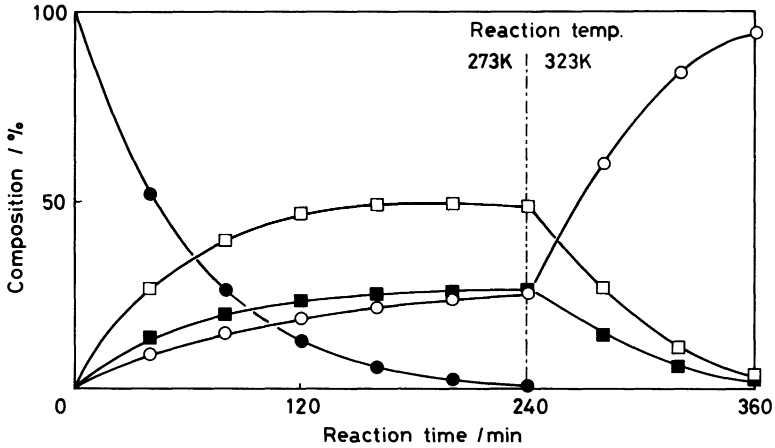

Fig. 1. Time dependence of the composition in the hydrogenation of 3-ethoxy-1-propene over $Ni/Al_2O_3$.
○: 1-Ethoxypropane, ●: 3-Ethoxy-1-propene, □: (*Z*)-1-Ethyoxy-1-propene, ■: (*E*)-1-Ethyoxy-1-propene.

TABLE 1. HYDROGENATION OF 3-ETHOXY-1-PROPENE OVER SUPPORTED Ni CATALYSTS

| Catal. | Weight /mg | Conv. of reactant/% | Composition of products/% | | | | Amount of $H_2$ adsorption $/\times 10^{-5}$ mol $g^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | | 3-ethoxy-1-propene | (*Z*)-1-ethoxy-1-propene | (*E*)-1-ethoxy-1-propene | 1-ethoxy-propane | |
| $Ni/ThO_2$ | 104 | 100 | 0.0 | 0.0 | 0.0 | 100 | 0.9 |
| $Ni/La_2O_3$ | 105 | 100 | 0.0 | 74.8 | 12.3 | 12.9 | 0.6 |
| $Ni/CaO$ | 107 | 100 | 0.0 | 87.4 | 4.2 | 8.4 | 0.1 |
| $Ni/MgO$ | 97 | 100 | 0.0 | 99.3 | 0.7 | 0.0 | 0.0 |
| $Ni/SiO_2$-$Al_2O_3$ | 102 | 100 | 0.0 | 0.0 | 0.0 | 100 | 4.0 |
| $Ni/TiO_2$ | 105 | 9.4 | 90.6 | 0.9 | 0.0 | 8.5 | 0.8 |
| $Ni/ZrO_2$ | 100 | 3.0 | 97.0 | 0.0 | 0.0 | 3.0 | 0.2 |
| $Ni/Al_2O_3$ | 109 | 62.8 | 37.2 | 34.1 | 16.9 | 11.8 | — |
| $Ni/SiO_2$ | 100 | 15.2 | 84.8 | 1.9 | 4.0 | 9.3 | 12.8 |

Reaction temperature; 273 K; reaction time; 60 min.

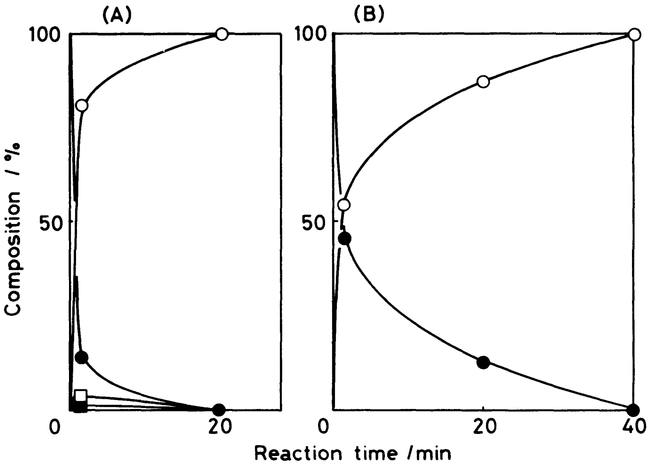

Fig. 2. Time dependences of the composition in the hydrogenation of 3-ethyoxy-1-propene over $Ni/ThO_2$ (A) and $Ni/SiO_2$-$Al_2O_3$ (B).
○: 1-Ethyoxypropane, ●: Ethyoxy-1-propene, □: (*Z*)-1-Ethyoxy-1-propene, ■: (*E*)-1-Ethyoxy-1-propene.

complete in 20 min, and the amount of 1-ethoxy-1-propene formed was very small as shown in Fig. 2(A). The characteristic feature with $Ni/SiO_2$-$Al_2O_3$ is seen in Fig. 2(B); double bond migration to 1-ethoxy-1-propene did not occur.

The composition of the products after 60 min when reactions were carried out at 273 K over *ca.* 100 mg of catalyst samples are summarized in Table 1. Other products such as ethanol and propane were not detected. The amounts of hydrogen adsorbed are also included. The $Ni/ThO_2$ and $Ni/SiO_2$-$Al_2O_3$ exhibited high activity; giving 100% hydrogenated product in 60 min. In particular, the $Ni/ThO_2$ gave 100% hydrogenated product even in 20 min. The hydrogenation activities were low for the catalysts other than $Ni/ThO_2$ and $Ni/SiO_2$-$Al_2O_3$. With $Ni/MgO$, $Ni/CaO$, and $Ni/La_2O_3$, large amounts of 1-ethoxy-1-propene resulted from the double bond migration. 1-Ethoxy-1-propene undergoes hydrogenation at a much slower rate than 3-ethoxy-1-propene does. To obtain a faster hydrogenation rate, catalysts are desirable that do not catalyze the double bond migration of 3-ethoxy-1-propene. The low hydrogenation activities of $Ni/MgO$, $Ni/CaO$, and $Ni/La_2O_3$ are considered to be due to the high activity of the supports for double bond migration.[5]

The active catalysts, $Ni/ThO_2$ and $Ni/SiO_2$-$Al_2O_3$, adsorbed relatively large amount of hydrogen. Although $Ni/SiO_2$ adsorbed large amounts of hydrogen but showed low activity, a capability of adsorption of a large amount of hydrogen may be required for a catalyst to be active for hydrogenation.

## References

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