Evidence for the Activity Difference between Pure and Supported Nickel Catalysts

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In a previous paper,[1] we reported on the difference in catalytic activity between nickel alone and nickel supported on γ-alumina (Ni : $Al_2O_3 = 1:1$ in weight) in the isotopic hydrogen exchange of propene with deuterium oxide. From the infrared and NMR spectroscopic data then obtained, we suggested that vinyl hydrogens are more exchangeable than methyl hydrogens on nickel and that the ratio of the exchangeability of the vinyl group to that of the methyl group was about 3.4, while supported nickel shows the opposite exchangeability (i. e., methyl hydrogens are more exchangeable). By the microwave spectroscopic method,[2-4] this suggestion was not only confirmed quantitatively, but also detailed knowledge could be obtained, as has been reported already.[2,3]

Table I shows the experimental conditions, while Table II shows the subspecies distribution of d_1 determined by the microwave spectroscopic method, as well as the d_y-distribution determined by a mass spectrometer.

TABLE I. EXPERIMENTAL CONDITIONS

No.	Catalyst		Reaction		Sample	
		g.	Temp. °C	Time hr.	C_3H_6	D_2O
					mol. ×10^3	
3513	Ni	1.65	17	25	2.18	10
A9	Ni-Al_2O_3	5.0	$18._6$	354	6.00	18.1

The ϕ values of the two samples are nearly equal, both being ca. eight, so that their d_y-distribution shows the initial stage of the reaction in these cases. By comparing the amount of catalyst (only the weight of nickel) and the reaction time, it may be seen that the exchange rate is markedly decreased, by 7—8 times, if nickel is supported on γ-alumina. Besides, important information was obtained from the difference between the infrared spectra of No. 3513 (Ni) and No. A9 (Ni-Al_2O_3). However, the spectrum of No. 3513 (Ni) is not shown because it is almost identical with that of No. A4, which has already been shown in a previous report.[1] A completely different feature can be seen in the region of the C-D stretching band, suggesting that the catalytic activities of the two catalysts are different.

According to a comparison of the subspecies distribution of the d_1 of No. 3513 with that of No. A9, methine hydrogen is the most exchangeable on nickel (No. 3513), while methyl hydrogens are the most exchangeable on supported nickel (No. A9). The subspecies distribution of d_1 in the product of the catalytic exchange reaction shows some similarity between supported nickel (No. A9) and palladium in that methyl hydrogens became exchangeable to some extent, though methine hydrogen was still more exchanged on supported nickel than on palladium.[2] Such a tendency has been recognized in the exchange reaction of para-xylene with deuterium oxide,[5] though in this system only methyl hydrogens were exchanged on nickel, while both methyl and aromatic hydrogens became exchangeable on palladium and on supported nickel. Such a tendency in the exchangeability with respect to the double bond showed a tendency opposite to that of the present system.

From Table II, it may be seen that the exchangeability of methine hydrogen was larger than that of methylene hydrogen on both catalysts. The result of No. A9 may be interpreted in terms of the existence of two different active sites on supported nickel for this reaction. One of the sites (A), ascribable to nickel, has an activity similar to that of unsupported nickel, and the subspecies distribution of d_1 may, consequently, be similar to that of No. 3513, as is shown in Table II. The other site (B) has an activity similar to that of palladium, and the subspecies distribution of d_1 may become similar to that of palladium.[2] It may, therefore, be concluded that the activity of the A site has no interaction with the γ-alumina and that the activity of the B site may result from the interaction with γ-alumina. The subspecies distribution of d_1 of No. A9 may, therefore, be regarded as a mean value of two different distributions.

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[1] K. Hirota and Y. Hironaka, This Bulletin, **37**, 535 (1964).

[2] K. Hirota, Y. Hironaka and E. Hirota, *Tetrahedoron Letters*, **1964**, 1645.

[3] K. Hirota and Y. Hironaka, *J. Catalysis*, to be published.

[4] Y. Morino and E. Hirota, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **85**, 535 (1964).

[5] K. Hirota and T. Ueda, This Bulletin, **33**, 423 (1960).

TABLE II. DEUTERIUM DISTRIBUTION (%) AND SUBSPECIES DISTRIBUTION OF d_1 (%)

Subspecies	No. A9(Ni-Al_2O_3)	No. 3513(Ni)**	No. 3315(Pd)**
$CH_2DCH=CH_2$	45.3±2.5(15.1)*	22.5±2.7(7.5)*	59.2±2.2(19.7)
t-CH_3 CH=CHD	12.5±1.5	9.5±2.1	16.4±1.5
c-CH_3 CH=CHD	11.3±1.7	9.9±2.2	13.4±2.1
CH_3 CD=CH_2	30.9±2.8	58.1±5.1	16.1±2.4
d_0	$63._6$	$58._4$	$51._3$
d_1	$29._8$	$33._3$	$36._8$
d_2	$5._9$	$7._3$	$10._7$
d_3	—	$1._0$	$1._6$
$\phi=\frac{1}{6}\sum_{y=1}^{6} yd_y$	$7._4$	$8._5$	$10._4$

* Numerals in parenthesis are the ones alloted per one hydrogen atom.

** These data, already published,[2] were shown for the sake of comparison.

Morikawa and Nozaki[6] reported that both free metallic nickel and nickel atoms forming chemical bonds with γ-alumina existed in supported nickel. These states seem to correspond to the two states mentioned above.

The catalytic activity of supported nickel decreased as compared with that of nickel, as has been mentioned already. This decrease in activity may be attributed to the formation of nickel oxide with the oxygen absorbed on γ-alumina, because neither nickel oxide nor γ-alumina could catalyze this reaction. However, since the answers to these problems are not evident, further investigation is necessary on this point.

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[6] K. Morikawa and F. Nozaki, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **64**, 1562 (1961).