# Hydrogenation of Propionaldehyde by Nickel Catalysts Supported on $Al_2O_3$, $SiO_2$, $TiO_2$, $Ta_2O_5$, and $Nb_2O_5$

Masaki FUNAKOSHI* and Hakuai INOUE
Department of Chemical Engineering, Faculty of Engineering,
The University of Tokyo,
Hongo 7-3-1, Bunkyo-ku, Tokyo 113

The hydrogenation of propionaldehyde with various nickel catalysts was studied kinetically for a wide range of reaction conditions. The catalysts were supported on $Al_2O_3$, $SiO_2$, $TiO_2$, $Ta_2O_5$, and $Nb_2O_5$. The reaction rates were well correlated with the irreversibly adsorbed hydrogen uptakes. A detailed analysis concluded that this reaction was structure-insensitive under all reaction conditions tested.

In recent studies of supported metal catalysts, considerable attention has been paid to the influence of supports and of metal dispersion on catalytic activities and selectivities.[1-6] The mechanism of the strong interaction between metals and supports was clarified gradually and information about structure-sensitive and/or -insensitive reactions has been accumulated.[7-9]

Hydrogenations of hydrocarbons are said to be structure-insensitive reactions, and the rates seem to be determined mainly by the catalyst metal and its surface area. Therefore, these reactions may be considered suitable for quantitative treatment of supported metal catalysts. But rather few reactants have yet been tested, and it is necessary to examine many other reactants more widely.

In this study, the reaction kinetics of propionaldehyde hydrogenation with nickel catalysts that were prepared by different methods was measured. The main differences in preparation concerned the supports and the metal loadings. Metal dispersions were calculated from the amount of irreversibly adsorbed hydrogen measured by the pulse flow technique at room temperature. Table 1 shows characteristics of the catalysts used.

The first three catalysts were supplied from the Committee in Reference Catalysis, Catalysis Society of Japan. Metal loadings of other catalysts were determined by the I.C.P. method.

The reaction was carried out with a conventional flow-type micro-reactor using 10 to 100 mg of the catalysts. The differential reaction conditions were kept for all experiments. The product and the unconverted reactant gases

Table 1. List of catalysts used

| Mark | Metal content wt% | Pretreatment gas | Pretreatment temp K | Pretreatment time h | Hydrogen uptake ml g-cat.$^{-1}$ | Dispersion |
|---|---|---|---|---|---|---|
| J.R.C.-A4-30Ni | 26.2 | $H_2$ | 813 | 2 | 3.97 | 0.079 |
| -A4- 5Ni | 5.0 | $H_2$ | 813 | 2 | 0.53 | 0.056 |
| -S3- 5Ni | 5.0 | $H_2$ | 813 | 2 | 0.30 | 0.031 |
| 10 %-Ni/SiO$_2$ | 6.4 | $H_2$ | 673 | 0.25 | 1.53 | 0.125 |
| 1 %-Ni/SiO$_2$ | 0.79 | $H_2$ | 673 | 0.25 | 0.23 | 0.153 |
| 0.5%-Ni/SiO$_2$ | 0.39 | $H_2$ | 673 | 0.25 | 0.12 | 0.161 |
| 10 %-Ni/TiO$_2$ | 8.8 | $H_2$ | 813 | 2 | 0.19 | 0.011 |
| 10 %-Ni/Nb$_2$O$_5$ | 9.9 | $H_2$ | 813 | 2 | - | - |
| 10 %-Ni/Ta$_2$O$_5$ | 8.7 | $H_2$ | 813 | 2 | 0.19 | 0.011 |

were analyzed by gas chromatograph.   The reaction temperature ranged from room temperature ( 36 °C ) to 250 °C.   The reactant concentrations were varied from $0.18 \times 10^{-6}$ to $3.8 \times 10^{-6}$ mol/cm$^3$ for propionaldehyde and from $0.52 \times 10^{-5}$ to $4.0 \times 10^{-5}$ mol/cm$^3$ for hydrogen. Helium was used as the diluent gas. The total pressure was 1 atmosphere. At higher reaction temperatures, the propionaldehyde concentration was set below $1 \times 10^{-6}$ mol/cm$^3$. The main product was propyl alcohol, and by-products were negligible under all reaction conditions used.

The reaction rates of propionaldehyde were analyzed on the basis of the Langmuir-Hinshelwood model. The effects of the supports and the metal dispersion on the reaction rates were analyzed in detail by deriving the reaction equation and its parameters.   The rates obtained for nickel catalysts prepared by different methods were expressed by the same equation:

$$-r_{pi} = k_0 K_1 K_2 C_{pi} C_{H2} / (1 + K_1 C_{pi}) / (1 + \sqrt{K_2 C_{H2}})^2 \quad mol/s/site$$

where $C_{pi}$, $C_{H2}$ are the concentrations of propionaldehyde and hydrogen respectively; $k_0$ is the rate constant. The symbols $K_1$, $K_2$ are the adsorption equilibrium constants of propionaldehyde and hydrogen. This equation can be applied to all reaction temperatures tested.   The parameters in this equation, $k_0$, $K_1$, and $K_2$, were determined for each catalyst using the least-square method. Some of these values are shown in Table 2. All are plotted against reaction temperature in Figs. 1, 2, and 3. The rate constant, $k_0$, is normalized by the hydrogen uptake in Table 1. From the figures it is obvious that the parameters do not depend on the kind of support or the metal dispersion. They depend only on the reaction temperatures, regardless of difference in catalyst preparation method. This fact shows that the reaction, i.e. , the hydrogenation of propionaldehyde with nickel catalysts, is structure-insensitive under all the reaction conditions tested in this study. The temperature dependency of the each parameter is expressed by the following equation.

Table 2. Rate parameters at each reaction temperature

| Mark | Temp = 334 K | | Temp = 385 K | | | Temp = 444 K | | |
|---|---|---|---|---|---|---|---|---|
| | $k_0$ | $K_2$ | $k_0$ | $K_1$ | $K_2$ | $k_0$ | $K_1$ | $K_2$ |
| | $mols^{-1}site^{-1}$ | $cm^3mol^{-1}$ | $mols^{-1}site^{-1}$ | $cm^3mol^{-1}$ | $cm^3mol^{-1}$ | $mols^{-1}site^{-1}$ | $cm^3mol^{-1}$ | $cm^3mol^{-1}$ |
| J.R.C.-A4-30Ni | $9.42 \times 10^{-27}$ | $1.21 \times 10^6$ | $3.75 \times 10^{-25}$ | $2.94 \times 10^6$ | $1.11 \times 10^5$ | - | - | - |
| -A4- 5Ni | - | - | 7.25 " | 6.64 " | 0.96 " | - | - | - |
| -S3- 5Ni | - | - | 2.31 " | 3.12 " | 2.27 " | $2.63 \times 10^{-24}$ | $2.43 \times 10^6$ | $6.02 \times 10^4$ |
| 10 %-Ni/SiO$_2$ | $2.42 \times 10^{-26}$ | $1.43 \times 10^6$ | 6.79 " | 2.05 " | 1.37 " | - | - | - |
| 1 %-Ni/SiO$_2$ | - | - | 8.64 " | 3.14 " | 1.21 " | - | - | - |
| 0.5%-Ni/SiO$_2$ | - | - | - | 3.17 " | - | - | - | - |
| 10 %-Ni/TiO$_2$ | - | - | $4.69 \times 10^{-25}$ | 2.90 " | $1.32 \times 10^5$ | $7.23 \times 10^{-24}$ | $1.36 \times 10^6$ | $5.04 \times 10^4$ |
| 10 %-Ni/Nb$_2$O$_5$ | - | - | - | - | - | - | 1.72 " | 2.75 " |
| 10 %-Ni/Ta$_2$O$_5$ | - | - | $5.14 \times 10^{-25}$ | $3.44 \times 10^6$ | $0.93 \times 10^5$ | - | - | - |
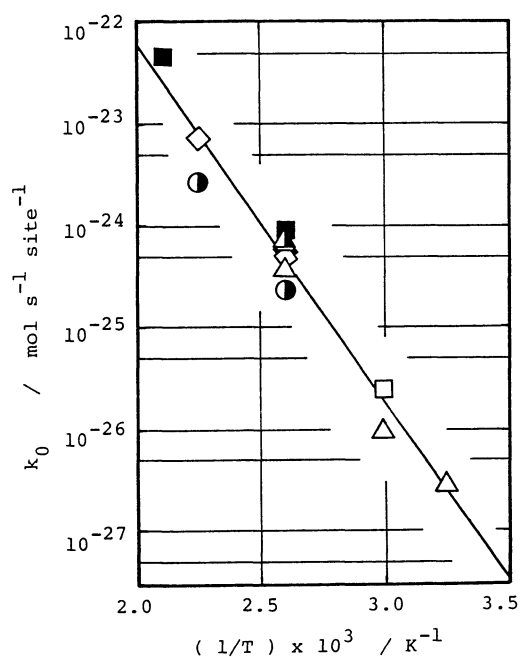


Fig. 1. Arrhenius plot of $k_0$.

| | |
|---|---|
| △ | J.R.C.-A4-30Ni |
| ▲ | -A4- 5Ni |
| ◑ | -S3- 5Ni |
| □ | 10%-Ni/SiO$_2$ |
| ■ | 1%-Ni/SiO$_2$ |
| ◪ | 0.5%-Ni/SiO$_2$ |
| ◇ | 10%-Ni/TiO$_2$ |
| ◈ | 10%-Ni/Nb$_2$O$_5$ |
| ◆ | 10%-Ni/Ta$_2$O$_5$ |
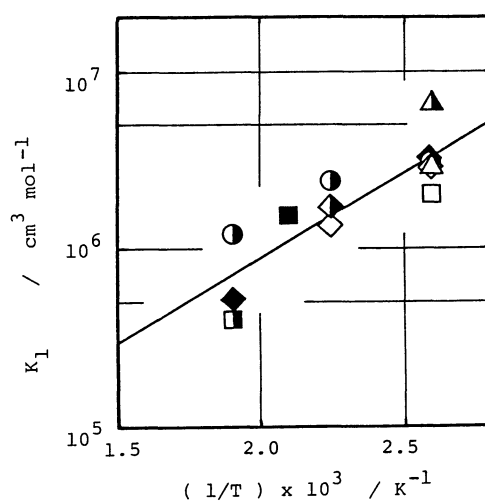


Fig. 2. Arrhenius plot of $K_1$.
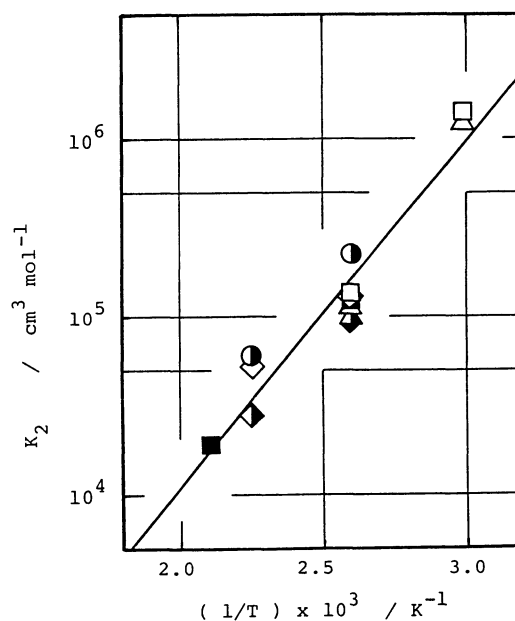


Fig. 3. Arrhenius plot of $K_2$.

$$K_1 = (1.04 \times 10^4) \exp (4.41/RT) \qquad cm^3/mol$$
$$K_2 = (1.54) \qquad\quad \exp (8.82/RT) \qquad "$$
$$k_0 = (6.63 \times 10^{-16}) \exp (-16.1/RT) \qquad mol/s/site$$

Here, the value of the gas constant, R, equals $1.986 \times 10^{-3}$ Kcal/K/mol and T is absolute temperature.

The activation energy and the adsorption heat of hydrogen are comparable to the values in the literature.[10,11] However, the heat of adsorption of propionaldehyde is quite small. This may imply that propionaldehyde does not interact with nickel directly during the reaction. It has become clear, using the LEED analysis, that in the hydrogenation reactions of ethylene and propylene, which are also structure-insensitive, olefine adsorbs onto surface species which are thought to be olefilidine and hydrogen reacts with the adsorbed olefines.[9] In this reaction the same situation may occur.

The structure insensitivity of a certain reaction has rarely been studied kinetically, and not sufficiently even when done.[12-15] It has usually been tested by the reaction rate at a definite reaction condition. In this study various nickel catalysts were tested for the hydrogenation of propionaldehyde over a wide range of reaction conditions. As a result, it was shown that the reaction rates were correlated with the irreversibly adsorbed hydrogen uptakes.

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