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SELECTIVE HYDROGENATION OF ACROLEIN BY NICKEL-TITANIUM ALLOY CATALYSTS

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$Ni_{28}Ti_{72}$ alloy catalyst was found to have a high selectivity for the hydrogenation of acrolein to propionaldehyde. However, both the carbon-carbon double bond and the formyl group were hydrogenated by supported nickel or nickel ultra-fine particles, leading to the simultaneous production of 1-propanol together with propionaldehyde. The retardation of the formyl group hydrogenation by alloying has been suggested to be caused by the electronic effect.

Since Sinfelt reported the effect of alloying on the hydrogenolysis of ethane,$^{1)}$ its important role on activity and selectivity of certain reactions has been clarified. This effect influences different reactions in different ways.$^{2,3)}$ For instance, hydrogenation is influenced to a lesser extent than hydrogenolysis. However, in the same kind of reaction, the degree of the effect can change for different functional groups. Then the authors expected that by applying this effect to a parallel consecutive reaction system including a reactant which has different functional groups, it would be possible to increase the selectivity of the main reaction.

As an unsaturated aldehyde has two different functional groups, i.e., a carbon-carbon double bond and a formyl group, and its hydrogenation proceeds through a parallel consecutive reaction system, the hydrogenation of the unsaturated aldehyde is an attractive target for the alloying effect.

Nickel is a very active catalyst in hydrogenation, so for hydrogenation of an unsaturated aldehyde carbon-carbon double bond and formyl group can be hydrogenated at the same time to give a saturated alcohol. Noller and Lin reported the production of both butyraldehyde and 1-butanol in the hydrogenation of crotonaldehyde over alumina supported nickel catalysts.$^{4)}$ While over palladium the reduction stops spontaneously with the formation of the saturated aldehyde.$^{5)}$

In this work nickel catalysts alloyed with titanium were found to have the same character as palladium for the hydrogenation of acrolein, namely it favored the hydrogenation of the carbon-carbon double bond against that of the formyl group, resulting in the production of propionaldehyde exclusively.

$Ni_{28}Ti_{72}$ amorphous alloy was used as a catalyst. Other two catalysts, i.e., nickel ultra-fine particles (supplied by ULVAC co. Ltd.) and alumina supported nickel (J.R.C.-A4-30Ni in Japanese Reference Catalysts) , were also used as standards. Nickel ultra-fine particles and alumina supported nickel were prepared by the physical vapor deposition method [6,7] and by the precipitation technique respectively.[8] The $Ni_{28}Ti_{72}$ alloy was covered with a titanium oxide layer and was inactive even with hydrogen treatment at 300 °C. It was washed either hydrofluoric acid solution or sodium hydroxide solution for pretreatment. The other two catalysts were reduced in hydrogen flow at 200 °C before use.

A conventional flow system was used and each product was analyzed by gaschromatography. The metal surface areas of the catalysts were measured by the carbon monoxide adsorption method for alumina supported nickel catalyst and by the BET method for other two catalysts.

The experimental results are shown in Figs. 1 and 2. In Fig. 1, the Arrhenius plots of the acrolein consumption rate for the catalysts used are shown. The rates normalized by the metal surface area at the same reaction temperature were almost the same for all catalysts for which an activation energy of 32.8 kJ/mol was obtained. In Fig. 2, the conversion to each component against reaction temperature for each catalyst is shown. In the product gas, allyl alcohol could not be detected and hydrocarbons did not exceed 3% of the total products. From these figures, it is clear that in the case of non-alloyed nickel catalyst, both the carbon-carbon double bond and the formyl group were hydrogenated. On the other hand, $Ni_{28}Ti_{72}$ alloy catalyzed the hydrogenation of carbon-carbon double bond but retarded the hydrogenation of formyl group. Moreover, the reaction with crystallized $Ni_{28}Ti_{72}$ alloy obtained by its treatment in hydrogen at 500 °C showed the same results as in the case of amorphous catalyst. This indicates the retardation of the hydrogenation of formyl group is due to the alloying effect and not because of de-crystallization of the catalyst. The hydrogenation of propionaldehyde over the alloy catalyst was also tested. Up to the reaction temperature of 200 °C, no 1-propanol formation by the reduction of propionaldehyde was observed.

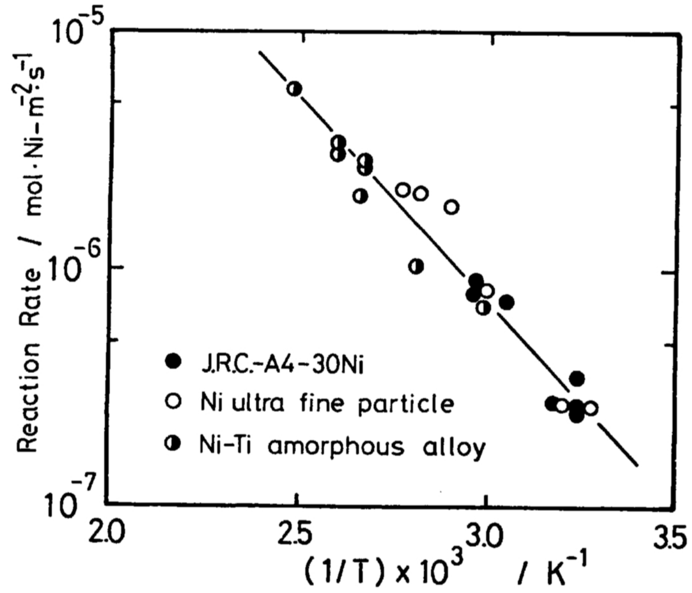
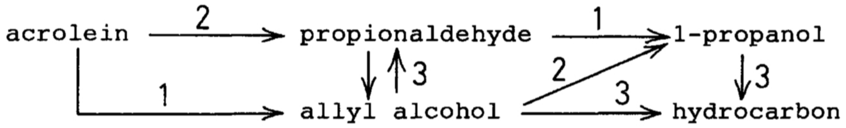


Fig. 1. Arrhenius plots for three different kinds of catalysts.

The scheme of this reaction system is as follows;



1 ; hydrogenation of formyl group
2 ; hydrogenation of carbon-carbon double bond
3 ; hydrogenolysis or isomerization

As little hydrocarbon products were detected, the hydrogenolysis could be considered negligible. The results were not sufficient to rule out the possibility of isomerization, although it could not have been important since no allyl alcohol was observed in the gas phase. Then the hydrogenation of acrolein by nickel catalysts is thought to be a typical parallel consecutive reaction system with the reaction 1 and 2.

Alloying effect has two different effects on the reaction, i.e., the ensemble effect and the ligand effect. The former is a structural effect caused by the dilution of active sites. First we tried to understand the retardation of the formyl group hydrogenation by this effect. A carbon-carbon double bond is more easily hydrogenated than a formyl group.4) Then a carbon-carbon double bond in an acrolein molecule is preferentially adsorbed on a nickel active site. In the case of non-alloyed nickel catalysts, the formyl group of the adsorbed acrolein molecule may reach the surrounding nickel atoms to be hydrogenated to alcohol. 1-propanol, therefore, is produced as well as propionaldehyde. By alloying nickel with titanium the nickel concentration around a nickel atom decreases. When a carbon-carbon double bond is adsorbed on the alloyed nickel,

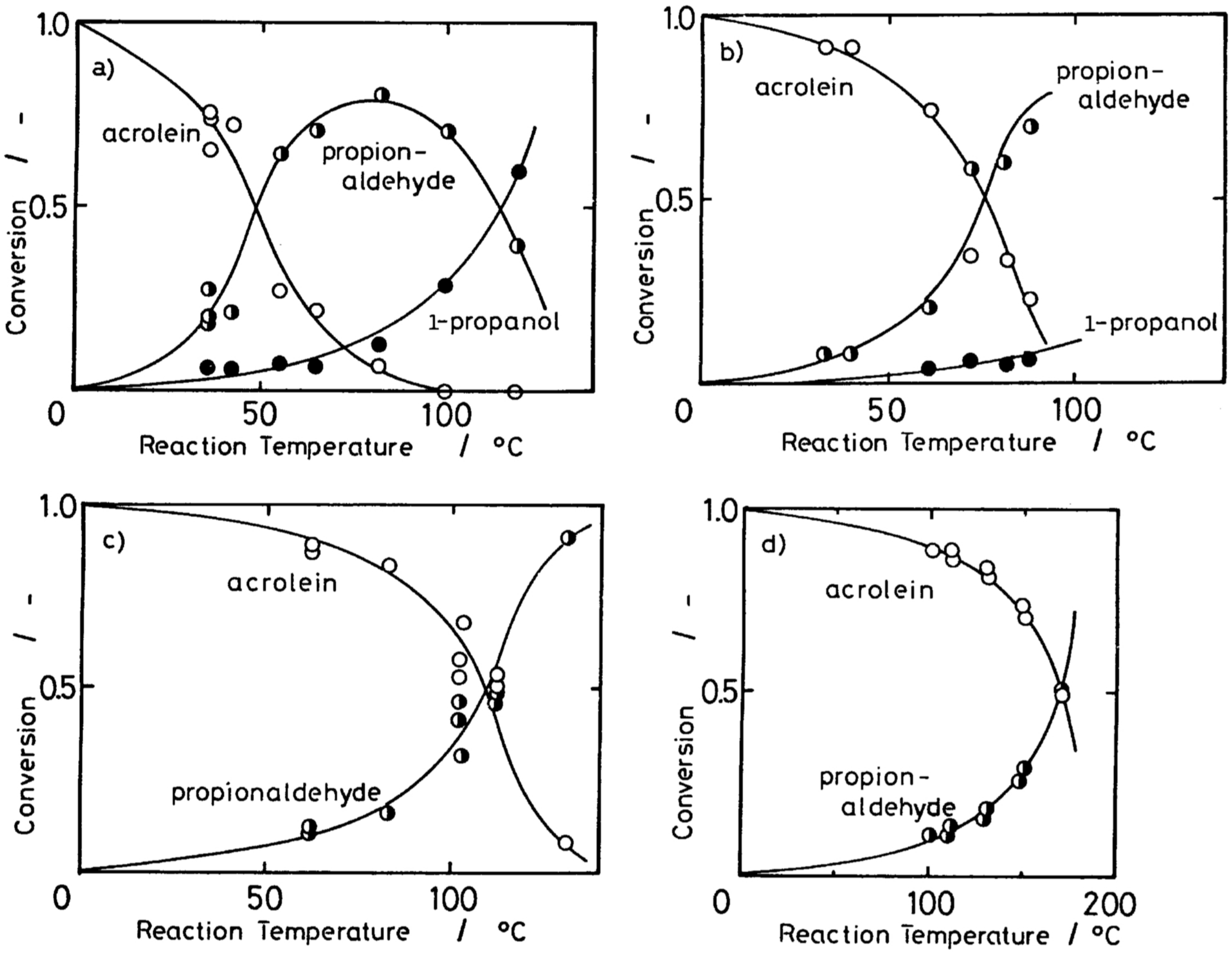


Fig. 2. Effects of the reaction temperature on the conversion to each component for catalysts used.

a); J.R.C.-A4-30Ni b); Ni ultra-fine particles
c); $Ni_{28}Ti_{72}$ amorphous d); $Ni_{28}Ti_{72}$ crystal

the probability of the formyl group of the adsorbed acrolein molecule to reach other nickel atoms will be drastically decreased. This may cause the retardation of the formyl group hydrogenation, which may be the mechanism of the ensemble effect in the hydrogenation of a molecule of two functional groups. If this is true, a saturated aldehyde, e.g., propionaldehyde, must be hydrogenated in the absence of acrolein. The experimental results in Fig. 2-c) are rather contradictory. As shown in this figure, propionaldehyde did not react to saturated alcohol, even when acrolein was almost completely converted at the temperature range around 120 °C. This is quite different from the results of an alumina supported catalyst as shown in Fig. 2-a). Inactivity of the alloyed nickel catalyst in the hydrogenation of propionaldehyde was also confirmed in another experiment as mentioned before. These facts indicate that the retardation of the formyl group hydrogenation is not caused by the ensemble effect.

The ligand effect is an electronic effect. Fischer at al. have reported the shift of the U.P.S. spectrum of adsorbed CO and H_2 on the nickel-titanium alloy.9) Moreover, for the alloys of nickel with various metals, the shift of the binding energy has been observed for core electrons by X.P.S. and valence electrons by U.P.S.10) These information indicate that nickel accepts an electronic effect by its alloying with IVA metals. Then it has been concluded from the present experimental results and the knowledge of the electron spectroscopic analysis mentioned above that the alloying effect on the hydrogenation of acrolein with $Ni_{28}Ti_{72}$ alloy catalysts is an electronic effect.

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References

1) J. H. Sinfelt, J. L. Carter, and D. J. C. Yates, J. catal., 24, 283 (1972).
2) H. Miura, M. Osawa, T. Suzuki, K. Sugiyama, and T. Matsuda, Chem. Lett., 1982, 1803.
3) J. R. H. van Schaik, R. P. Dessing, and V. Ponec, J. Catal., 38, 273 (1975).
4) H. Noller, and W. M. Lin, J. Catal., 85, 25 (1984).
5) P. N. Rylander, " Catalytic hydrogenation over Platinum Metals, " Academic Press, New York (1967), p. 238.
6) M. Noda, S. Shinoda, and Y. Saito, Nippon Kagaku Kaishi, 1984, 1017.
7) S. Kashu, Kagaku Kogaku, 46, 530 (1982).
8) U. Asami, Preprints of 4th Annual Symposium on Reference Catalysts, Tokyo, Dec. 3, 1982.
9) T. E. Fischer, S. R. Kelemen, and R. S. Polizzotti, J. Catal., 69, 345 (1981).
10) P. Oelhafen, " Topics in Applied Physics, " ed by H. Beck et al., Springer Verlag, Berlin (1983), Vol. 53, p. 283.

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