CHEMISTRY LETTERS, pp. 1615-1618, 1983.

SELECTIVE HYDROGENATION OF ACROLEIN TO ALLYL ALCOHOL CATALYZED BY RANEY-TYPE SILVER-ZINC CATALYST

Yoshinori NAGASE,* Hideshi HATTORI, and Kozo TANABE+
Department of Industrial Chemistry, Faculty of Engineering,
Ibaraki University, Hitachi 316
+ Department of Chemistry, Faculty of Science, Hokkaido University,
Sapporo 060

A Raney-type silver-zinc (1:1 wt. ratio) catalyst was found to exhibit a high activity and selectivity for the hydrogenation of acrolein to allyl alcohol, 70% conversion and 90% selectivity being observed in 90 min at 120 °C. Addition of small amount of Fe^{3+} to the catalyst resulted in an increase in the selectivity to 95% with a slight decrease in activity.

Catalytic hydrogenation of acrolein to allyl alcohol accompanies the formation of the products other than allyl alcohol; propionaldehyde is often formed to a considerable extent by either double bond hydrogenation of acrolein or isomerization of formed allyl alcohol, and propanol is formed by successive hydrogenation. As selective hydrogenation catalyst for acrolein to allyl alcohol, noble metal catalysts,[1,2)] transition metal catalysts,[3-5)] and several kinds of Raney-type catalysts such as Ag-Cd and Zn-Cu have been reported to exhibit high activities and selectivities. In this communication, we wish to report that Raney-type Ag-Zn catalyst showed high activity and selectivity for the selective hydrogenation of acrolein, and that the selectivity could be improved by addition of Fe^{3+} ions to the Ag-Zn catalyst.

The Raney-type Ag-Zn catalyst was prepared as follows. A mixture containing granular Ag, small pieces of Zn and Al plates, and carbon powder was placed in a graphite crucible, and fused at 900 °C for 1 h in an electric furnace. The ratio of the amounts of Ag, Zn, and Al was 1:1:2 in weight. The fused material was

Table 1. Activities and selectivities of different kinds of Raney-type Catalysts for Hydrogenation of Acrolein [a)]

Catalysts	Conversion (mol%)	Distribution of products (mol%)				Selectivity to allyl alcohol (mol%)
		Propionaldehyde	Propanol	Allyl alcohol	Acrolein	
Cu	99.4	68.2	19.2	12.0	0.6	12.1
Zn	88.4	52.9	4.2	31.4	11.6	35.5
Ag	86.9	38.2	6.7	42.0	13.1	48.3
Ag-Zn	69.8	3.3	5.9	60.6	30.2	86.6

a) 120 °C for 2 h.

poured onto a heat-resisting brick. The casting alloy was leached at 60 °C with a 30% NaOH aqueous solution for 1 h. The resulting catalyst was washed with distilled water and then with ethanol. The other Raney-type catalysts were similarly prepared.

A 300 ml-autoclave was employed for carrying out the reaction. A mixture of acrolein (10 ml), ethanol (90 ml) and catalyst (1.0 g) was placed in the autoclave. The reaction was performed at 80-160 °C for 30-180 min under an initial H_2 pressure of 50 atm. The reaction products were analyzed by gas chromatography.

The results are summarized in Table 1. It is shown that the catalytic behavior of the Raney-type Ag-Zn was remarkable in that the selectivity to allyl alcohol was outstandingly high. As compared with the other catalysts the high selectivity of the Raney-type Ag-Zn catalyst was caused primarily by retardation of propionaldehyde formation. The formation of propanol over the Ag-Zn catalyst did not differ from those observed for the Ag and Zn catalyst.

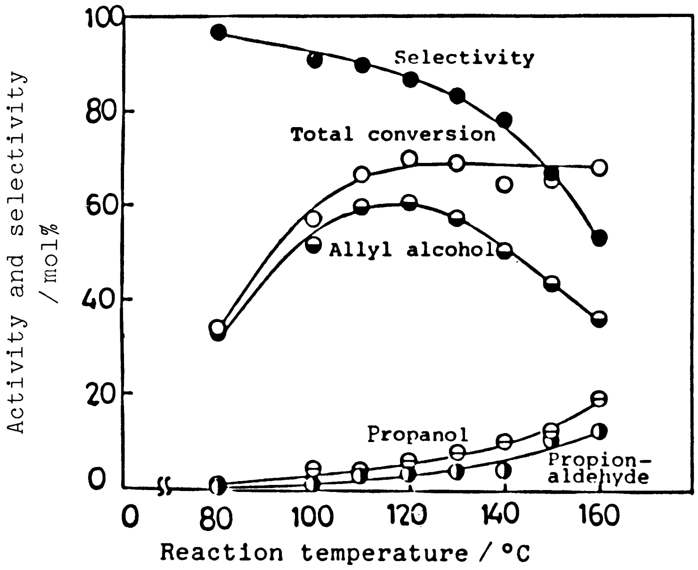

Fig. 1. Effects of the reaction temperature on the activity and selectivity in the hydrogenation of acrolein over Raney-type Ag-Zn Catalyst.

With the Raney-type Ag-Zn catalyst, the effects of the reaction temperature on the activity and selectivity were examined, while

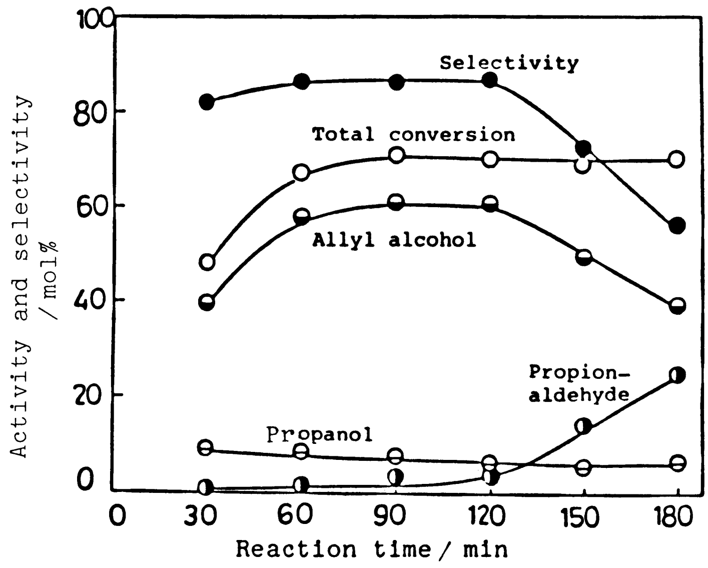

Fig. 2. Effects of the reaction time on the activity and selectivity in the hydrogenation of acrolein over Raney-type Ag-Zn catalyst at 120 °C.

the reaction time was kept constant, 120 min. The results are shown in Fig. 1. The total conversion of acrolein increased with an increase in the reaction temperature over the range 80-120 °C, and became constant. The composition of allyl alcohol went through a maximum at the reaction temperature of 120 °C as the temperature increased. The formations of propionaldehyde and propanol were accelelated by increase in the temperature. As a result, the selectivity to allyl alcohol decreased with an increase in the temperature. These results show that, above 120 °C, the formed allyl alcohol prominently underwent isomerization to propionaldehyde and hydrogenation to propanol. The effects of the reaction time on the activity and selectivity were examined at the reaction temperature of 120 °C, and the results are shown in Fig. 2. The total conversion increased with the time up to 90 min, and became constant value of 70% thereafter. The composition of allyl alcohol increased in the initial period of 90 min, and decreased after 120 min with comcomitant increase in the amount of propionaldehyde. The composition of propanol was almost contant with the reaction time. As a conclusion, to obtain a maximum yield of allyl alcohol, the reaction is desirable to be carried out at 120 °C for 120 min.

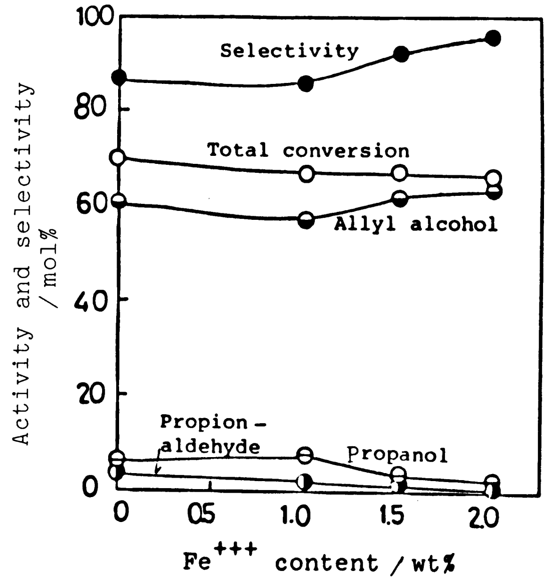

Fig. 3. Effects of Fe^{+++} content in Raney-type Ag-Zn catalyst on the activity and selectivity in the hydrogenation of acrolein at 120 °C for 2 h.

Since it has been reported that

addition of metal salts such as $Cd(NO_3)_2$ and $Fe(NO_3)_3$ to Raney-type catalysts improved the selectivity,[8)] small amounts of Fe^{3+} ions were added to the Ag-Zn catalyst. The addition of Fe^{3+} ions was done by leaching the casting alloy with the 30% NaOH aqueous solution containing a certain amount of $Fe(NO_3)_3$. The amounts of Fe^{3+} ions were adjusted to 1, 1.5, and 2 wt% of the catalyst. The results are shown in Fig. 3. As the amounts of Fe^{3+} ions increased, the selectivity to allyl alcohol increased to 95%, although the total conversion slightly decreased. The effects of addition of Cd^{2+} ions were also examined. By addition of Cd^{2+} ions, the selectivity increased, but a considerable decrease in the total conversion was observed.

The authors thank Mr. Tyuji Okawa of Joyo Industrial Co. for his helpful cooperation to the experimental measurements of this work.

References

1) H. S. Broadbent, G. C. Campbell, W. B. Bartley, and J. H. Johnsons, J. Org. Chem., 24, 1847 (1959).
2) E. N. Bakhanova, A. S. Astakhova, and Kh. A. Brikenshtein, Izv. Akad, Nauk. SSSR, Ser. Khim, 9, 1993 (1972).
3) T. H. Vanderspurt, U.S. Patent 4048110 (1977).
4) L. J. Richard, M. H. Delbert, and S. M. Darrel, U.S. Patent 4292452 (1981).
5) T. H. Vanderspurt, U.S. Patent 4020116 (1977).
6) K. Yamagishi, S. Hamada; H. Arai, and H. Yokoo, Yuki Gosei Kagaku Kyokai-shi 24, 54 (1966).
7) T. H. Vanderspurt, Ann. N. Y. Acad. Sci., 333, 155 (1980).
8) K. Hotta and T. Kubomatsu, Bull. Chem. Soc. Jpn., 42, 1447 (1969).

(Received July 13, 1983)