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Selective Hydrogenation of Crotonaldehyde to Crotyl Alcohol on Ag-MnO_2/Al_2O_3·$5AlPO_4$ Catalysts

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The activity and selectivity of Ag-MnO_2/Al_2O_3·$5AlPO_4$ catalysts for the hydrogenation of crotonaldehyde to crotyl alcohol have been investigated in liquid phase. When MnO_2 was added to the catalyst, the activity and selectivity for the reaction were remarkably improved to give the conversion of 100 mol% and the selectivity of 69.5%.

α-β-Unsaturated aldehyde which has both C=C and C=O double bonds is preferentially hydrogenated to saturated aldehyde in most case, followed by the successively hydrogenation to saturated alcohol. On the other hand, unsaturated alcohol formed with the hydrogenation of unsaturated aldehyde undergoes isomerization to saturated aldehyde, and also a partial dehydrogenation, accordingly it is difficult to obtain a high yield of the corresponding unsaturated alcohol by means of the selective hydrogenation of unsaturated aldehyde. A few catalyst suitable for giving a high yield of unsaturated alcohol from the above reaction have been reported up to now. For example, mild hydrogenation catalysts such as noble metal,[1)] transition metal,[2)] Raney-type metal[3)] and catalysts with Cd[4)] have been reported to show a high activity and selectivity for the above reaction. Rylander et al. hydrogenated crotonaldehyde to crotyl alcohol in ethanol over platinium-zinc-iron catalyst in 1963.[5)] Yada et al. reported a yield of 50 mol% of crotyl alcohol at 225-250 °C from crotonaldehyde at 80% conversion.[6)] Vanderspurt hydrogenated acrolein to obtain a high yield of allyl alcohol over Raney-type silver-cadmium catalyst.[7)] Recently, Noller et al. hydrogenated crotonaldehyde to obtain 54 mol% crotyl alcohol of the usual maximum yields over Cu-Ni/Al_2O_3 catalyst in a flow system at 80 °C.[8)]

It was recognized in this study that the $Ag-MnO_2/Al_2O_3\cdot 5AlPO_4$ catalyst for the selective hydrogenation of crotonaldehyde showed a high activity with a yield of 69.5 mol% of crotyl alcohol. This catalyst is superior to the former cases.

The catalyst was prepared by the coprecipitation and impregnation methods according to the following procedure ; 25% ammonium aqueous solution was added to a mixed solution of aluminium nitrate and phosphoric acid at pH=8. The gel precipitates thus obtained were successively impregnated with silver nitrate solution for 15 h, and then vaporized in water bath at 60 °C for 8 h. These materials were dried in air oven at 120 °C for 20 h, and thereafter calcined at 500 °C for 10 h in an electric furnace (Ag-AAP). As the next procedure, Ag-AAP was impregnated with a fixed magnesium nitrate solution. The procedures of vaporizing, drying, and calcinating described above were repeated respectively. As the final catalyst containing of 20 wt% Ag, $Ag-MnO_2/Al_2O_3\cdot 5AlPO_4$ was obtained.

The reaction was carried out by using powder catalyst less than 40 mesh particles. A 300 ml autoclave was employed for carrying out the reaction. A mixture of 10 ml crotonaldehyde and 90 ml hexane was introduced into the autoclave with catalyst of 1.0 g. The reaction was performed at 100-200 °C for 30-180 min under an initial hydrogen pressure of 50 atm. The reaction products were analyzed by gas chromatography with thermal conductivity detector. Column ; Carbowax 20 M (0.6 cm x 2 m) and Reoplex 400 (0.6 cm x 1 m), 80-100 mesh.

The results are summarized in Table 1 and Table 2.

Table 1. Activity and selectivity for the hydrogenation of crotonaldehyde on $Ag-MnO_2/Al_2O_3\cdot 5AlPO_4$ catalyst [a)]

Catalyst	Reaction temp/ °C	Composition product (mol%)				Conversion	Selectivity
		Crotyl alcohol	Butyraldehyde	Butyl alcohol	Rest		
Ag / AAP	130	28.9	26.2	4.1	0	59.8	48.8
	150	38.4	30.2	19.5	0	84.6	41.2
	170	23.0	33.7	21.1	6.5	84.5	27.5
$Ag-MnO_2$/AAP (Mn/Ag = 3)	150	68.5	12.8	16.6	0	97.9	70.0
	170	60.2	3.8	32.3	3.0	99.3	60.6
$Ag-MnO_2$/AAP (Mn/Ag = 5)	150	69.5	9.2	19.0	2.3	100.0	69.5
	170	63.5	10.2	21.0	3.7	98.3	64.6

a) Feed ; crotonaldehyde 10 ml, hexane 90 ml, initial hydrogen pressure 50 atm, reaction time 2 h, catalyst 1.0 g, Mn/Ag ; atomic ratio, AAP ; $Al_2O_3\cdot 5AlPO_4$.

As shown in Table 1, the activity and selectivity for the hydrogenation of :rotonaldehyde were examined by using Ag-Al_2O_3·$5AlPO_4$ catalyst. The conversion of :rotonaldehyde was increased with an increase of reaction temperature and the selectivity was decreased. On the other hand, the results of the hydrogenation of acrolein on Ag-Al_2O_3·$5AlPO_4$ catalyst is shown in Table 2.

Table 2. Activity and selectivity for the hydrogenation of acrolein on Ag-MnO_2/Al_2O_3·$5AlPO_4$ catalyst [a)]

Catalyst	Reaction temp /°C	Composition product (mol%) Allyl alcohol	Propion aldehyde	Propanol	Rest	Conver-sion	Selec-tivity
Ag / AAP	130	14.0	21.0	0	0	35.5	40.0
	150	30.2	44.7	0	0	74.9	40.3
	170	37.4	48.4	7.8	3.6	97.3	38.5
Ag-MnO_2/AAP (Mn/Ag = 3)	150	49.6	22.2	18.7	9.3	99.9	49.7
	170	49.5	9.3	35.2	5.1	99.1	49.9
Ag-MnO_2/AAP (Mn/Ag = 5)	150	52.9	17.9	19.1	9.8	99.6	53.1
	170	49.7	12.3	30.3	5.9	98.1	50.6

a) Feed ; acrolein 10 ml, hexane 90 ml, initial hydrogen pressure 50 atm, reaction time 2 h, catalyst 1.0 g, Mn/Ag ; atomic ratio, AAP ; Al_2O_3·$5AlPO_4$.

As shown in Table 2, the reaction had a high conversion, but the selectivity as as low as 40% independently of conversion. However, as these results were un- atisfactory in the selectivity of the reaction, catalyst containing of other metal as researched. Effect of activity and selectivity for the hydrogenation of rotonaldehyde on catalyst containing of Mn added to Ag-Al_2O_3·$5AlPO_4$ is shown in able 1 and Fig. 1. As observed in Table 1 and Table 2, above both reactions on atalysts containing of MnO_2 had a high conversion and selectivity. As shown in ig. 1, Mn addition to the catalyst (Mn/Ag 2-5 atomic ratio) was allowed to ncrease conversion and selectivity. When MnO_2 (Mn/Ag = 5 atomic ratio) was dded to Ag-AAP catalyst, a yield of crotyl alcohol was improved from 34.9 mol% ields of Ag-AAP catalyst to 69.5 mol% at 150 °C. From another preliminaly xperiments, it was thought that MnO_2 addition to the catalyst promoted the ydrogenation of the C=O group of unsaturated aldehyde, and moreover gave a high ield due to inhibit a partial dehydrogenation of unsaturated alcohol.

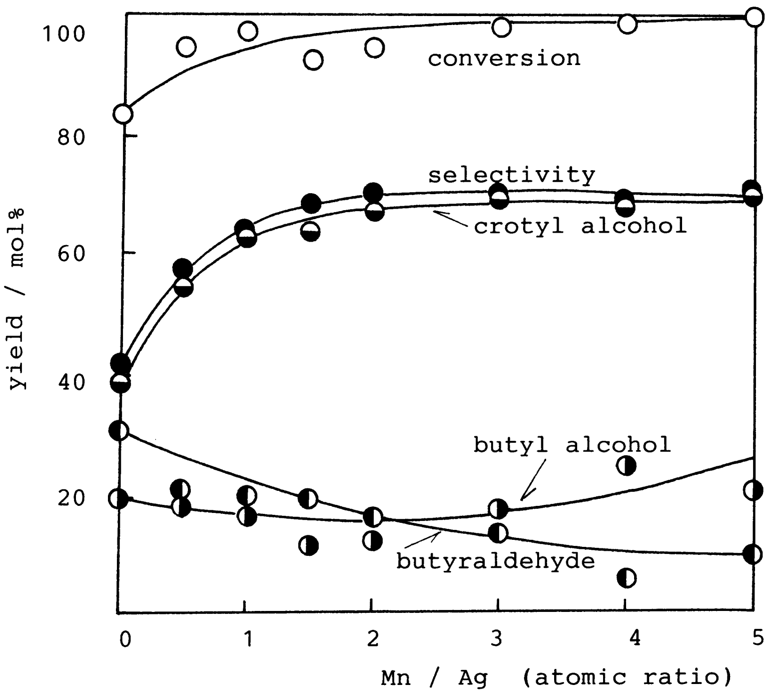

Fig. 1. Effect of activity and selectivity for the hydrogenation of crotonaldehyde on catalyst of Mn added to Ag-$Al_2O_3 \cdot 5AlPO_4$

It was found in this study that Ag-$MnO_2/Al_2O_3 \cdot 5AlPO_4$ catalyst had a high conversion of 100 mol% and selectivity of 69.5% for the above reaction of crotonaldehyde at 150 °C. This result is superior to the usual maximum yields of crotyl alcohol 54 mol%.

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