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Liquid-Phase Hydrogenation of Crotonaldehyde over Silver-Manganese Oxide Catalyst

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The liquid-phase hydrogenation of crotonaldehyde has been investigated over silver-manganese oxide catalyst. The selectivity to 2-buten-1-ol was 71.8% at a conversion of crotonaldehyde of 85.1%.

It is difficult to obtain a high yield of the corresponding unsaturated alcohol by the hydrogenation of an α,β-unsaturated aldehyde. A few catalysts suitable for giving a high yield of unsaturated alcohol, i.e, noble metals, Ranney-type alloys, transition metals and Cd-containing alloys have been reported to the present.[1-3] We have prepared silver catalysts which were relatively more abundant and cheaper than noble metal catalysts. Recently, we reported a high yield of 2-buten-1-ol on the liquid-phase hydrogenation of crotonaldehyde over Ag-MnO_2/Al_2O_3·5$AlPO_4$.[4] Here, we wish to report that silver-manganese oxide catalyst gives a high selectivity to 2-buten-1-ol without any supports such as SiO_2 and Al_2O_3. Ag (20 wt%)-MnO_2(80 wt%) catalyst was prepared by coprecipitation method from aqueous solution of sodium hydroxide of 3 molar concentration added to the aqueous solution of the corresponding concentration of metal nitrates. The gel obtained was dried at 110 °C for 12 h and calcined at 500 °C for 3 h.

The reaction was carried out under hydrogen pressure of 50 atm at 130-200 °C for 2 h with a 300 ml autoclave containing 10 ml crotonaldehyde,

Table 1. Conversion of crotonaldehyde and selectivity to 2-buten-1-ol over silver-manganese oxide catalyst in the hydrogenation of crotonaldehyde

Reaction temp /°C	Products (yield / %)				Conversion	Selectivity
	2-Buten-1-ol	Butyraldehyde	1-Butanol	2-Ethyl-2-hexenal	%	%
130	8.9	3.1	0.0	0.0	12.0	74.3
150	29.5	9.4	1.2	0.0	40.1	73.7
160	40.0	11.2	2.6	0.8	54.6	73.4
170	49.0	12.7	3.9	3.0	68.6	71.4
180	61.1	12.3	7.4	4.3	85.1	71.8
190	61.5	11.1	11.1	8.5	92.2	66.7
200	60.1	8.2	15.1	11.9	95.3	63.1

90 ml hexane and 0.5 g of catalyst. The products were analyzed by gas chromatography (TCD), using Carbowax 20 M and carrier gas H_2 (80 ml·min^{-1}).

The conversion of crotonaldehyde and products distribution are summarized in Table 1. The conversion increases with an increase of reaction temperature. The selectivity decreases with increasing reaction temperature.

The selectivity varies only slightly compared to the variation of conversion. The products are composed of large amounts of 2-buten-1-ol, and relatively small amounts of butyraldehyde and other by-products.

The results in Table 1 clearly show that the silver-manganese oxide catalyst is more effective to hydroganate crotonaldehyde to 2-buten-1-ol than to butyraldehyde.

References

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