Selective Reduction of Acrolein to Allyl Alcohol by a Vapor Phase Hydrogen Transfer Reaction

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Selective reduction of acrolein to allyl alcohol has been achieved by a vapor phase hydrogen transfer reaction using isopropyl alcohol as a hydrogen donor. It was found that the preferred catalyst was 50 weight % zinc oxide-magnesium oxide catalyst prepared by calcining a mixture of zinc nitrate and magnesium oxide at 500°C. The optimum conditions were found to be as follows; reaction temperature, near 200°C, total feed rate, 45 moles/l. of catalyst/hr., feed ratio of isopropyl alcohol per acrolein, 10 moles. Under these conditions, the yields of allyl alcohol of 80–65% at 80–90% conversion of acrolein were obtained.

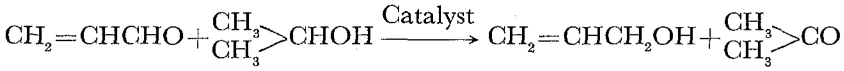
INTRODUCTION

Acrolein has two reactive functional groups, one is carbonyl group and the other is carbon-carbon double bond. Selective reduction of acrolein to allyl alcohol has been studied by several investigators. The reaction was generally carried out by the following two methods:

(1) the Meerwein-Ponndorf-Verley reduction[1–3],

(2) vapor phase hydrogen transfer reaction with various metal oxide catalysts using an alcohol as a hydrogen donor[4–11].

The liquid phase reaction has some technical difficulties owing to the polymerization of acrolein especially at high conversion. Therefore, in the present work, the more promising vapor phase reaction has been studied to find an effective catalyst and favorable reaction conditions.



$$CH_2{=}CHCHO+\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CHOH \xrightarrow{\text{Catalyst}} CH_2{=}CHCH_2OH+\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CO$$

EXPERIMENTAL

Materials. The commercial acrolein and isopropyl alcohol were fractionated and found to be pure gas chromatographically.

Catalysts. Metal oxides and metal nitrates were commercial materials.

The mixed catalysts consisting of two kinds of oxides were prepared by following ways: (1) mixing two kinds of oxides in water and drying up (2) drying up an aqueous solution containing two kinds of nitrates (3) drying up an aqueous solution of a nitrate containing the other oxide. These catalysts were calcined at 500°C for 4 hours.

The most suitable catalyst was prepared as follows. A solution of 730 g. of zinc nitrate in 400 ml. of water containing 200 g. of magnesium oxide was dried up with

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stirring and was calcined at 500°C for 4 hours.

All catalysts thus obtained were made in tablets, 8 mm. in diameter and 3 mm. in thickness.

About 20 ml. of the fresh catalyst was used for each experiment.

Apparatus and Procedure. The apparatus is shown in Fig. 1.

About 20 ml. of the catalyst was placed in a quarz tube 50 cm. long and 1.5 cm. inside diameter. The tube was heated in an electric furnace 30 cm. long and was maintained at a constant temperature during the reaction. The reaction temperature was measured by thermocouples tied to the outside wall of the tube. A mixture of acrolein and isopropyl alcohol was passed over a catalyst under atmospheric pressure. Reaction products were collected in a trap cooled by ice water, weighed and subjected to analysis.

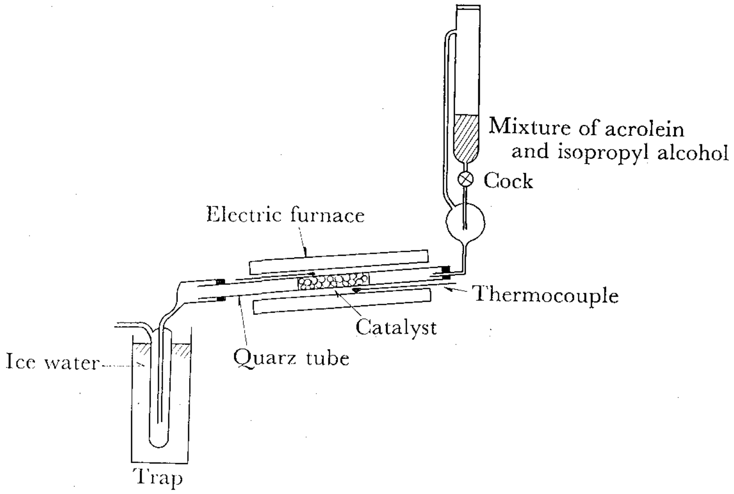

Fig. 1. Apparatus.

Analysis. Reaction products were analyzed by gas chromatography using the two kinds of columns with hydrogen as a carrier gas at 70°C and flow rate of 40 ml./min.; (1) 30 weight % polyethylene glycol 6000 on C-545 column (5.0 m) for propionaldehyde, acetone, acrolein, and isopropyl alcohol. (2) a combined column of 30 weight % dioctyl phthalate on C-545 (2.5 m) and 30 weight % tricresyl phosphate on C-545 (0.8 m) for isopropyl alcohol, *n*-propyl alcohol, and allyl alcohol.

Cyclohexane was selected as the common internal standard substance.

Gas chromatographic analyses are illustrated in Fig. 2 and Fig. 3.

RESULTS AND DISCUSSION

Catalysts. It was reported that the magnesium oxide and a mixed catalyst consisting of zinc oxide and magnesium oxide were effective[4-8,11].

Although efforts to find out other more effective catalyst were unsuccessful as shown in Table 1, it was observed that the preparative method of the catalyst influ-

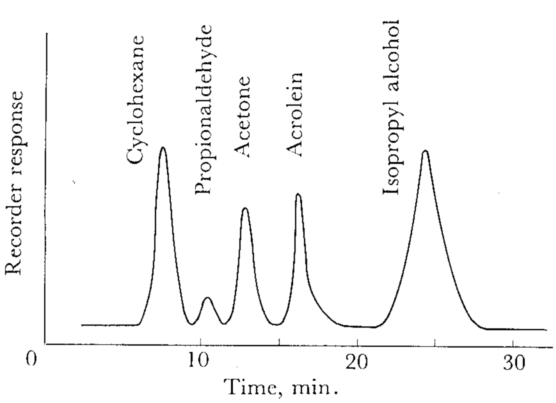

Fig. 2. Chromatogram obtained using 5.0 m. polyethylene glycol 6000.

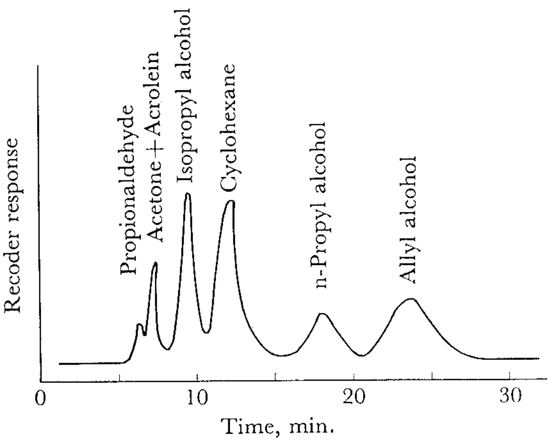

Fig. 3. Chromatogram obtained using the combined column.

Table 1. Experimental conditions and results by various catalysts.

Catalyst	Feed ratio, moles alkohol per acrolein	Feed rate, mol./l./hr.	Temp., °C	Conversion,* %	Yield,** %
MgO	10	45	225	84	50
	10	85	260	85	62
	6	45	325	84	27
	6	85	430	100	20
	2	45	345	63	21
ZnO	10	45	325	52	21
10 wt.% CdO-MgO	10	45	295	91	26
10 wt.% CrO_3-MgO	6	45	335	78	25
10 wt.% Cr-MgO	6	45	350	90	22
25 wt.% Fe_2O_3-MgO	2	45	410	64	11
25 wt.% CuO-MgO	2	45	335	51	10
50 wt.% ZnO-MgO	10	45	285	77	38
	10	85	285	82	30
	6	45	295	81	30
	6	85	360	90	40
50 wt.% ZnO (nitrate)-*** MgO	10	45	185	84	79
	10	85	225	87	70
	6	45	220	80	69
50 wt.% ZnO-MgO (nitrate)	10	45	255	82	66
	6	45	205	56	57
50 wt.% ZnO (nitrate)-MgO (nitrate)	10	45	375	89	41
	10	85	370	76	45
	6	45	350	55	44
50 wt.% CdO (nitrate)-MgO	6	45	270	70	47
	6	85	335	73	42
50 wt.% ZnO (hydroxide)-MgO (hydroxide)	10	45	320	83	47
50 wt.% ZnO (nitrate)-MgO (carbonate)	10	45	425	90	28

* Conversion of fed acrolein. ** Allyl alcohol yield to consumed acrolein.
*** Oxide prepared from nitrate.

enced markedly on its activity and selectivity and 50 weight % zinc oxide-magnesium oxide catalyst prepared from zinc nitrate and magnesium oxide was the most suitable catalyst.

Effect of Temperature. The reaction was carried out over the temperature range 150–450°C.

The temperature near 200°C was found to be suitable for the reaction with 50 weight % zinc oxide-magnesium oxide catalyst prepared from zinc nitrate and magnesium oxide as shown in Fig. 4 and Fig. 5. This temperature was 200°C lower than the value reported previously.[4-8,11]

In order to explain why the low temperature was suitable for the reaction, the decomposition of allyl alcohol was examined. It was ascertained that the extent of decomposition of allyl alcohol was independent upon the feed rate, and allyl alcohol was stable at a temperature of 200–300°C as shown in Fig. 7. At the higher temperature considerable decomposition of allyl alcohol to *n*-propyl alcohol and high boiling materials was observed.

These facts suggest that the optimum temperature is near 200°C for the reaction.

Effect of Feed Rate. Effect of feed rate on conversions of acrolein and yields of allyl alcohol is shown in Fig. 4.

The conversions of acrolein increased with decreasing the feed rate, but the yields of allyl alcohol were hardly affected with varying the feed rate.

Effect of Feed Ratio. Feed ratios of 2, 6, 10, and 15 moles isopropyl alcohol per mole acrolein were examined.

Since the reaction was reversible as described by Ballard[6], the use of a large

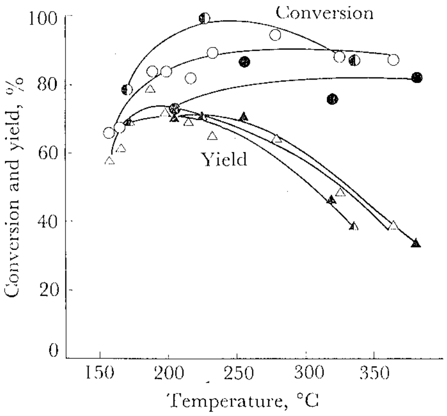

Fig. 4. Effect of feed rate.
50 wt. % ZnO (nitrate)-MgO catalyst.
Circles: conversions.
Triangles: yields.
◐, ◭: Runs at feed rate of 30 mol./l./hr..
○, △: Runs at feed rate of 45 mol./l./hr..
●, ▲: Runs as feed rate of 85 mol./l./hr..

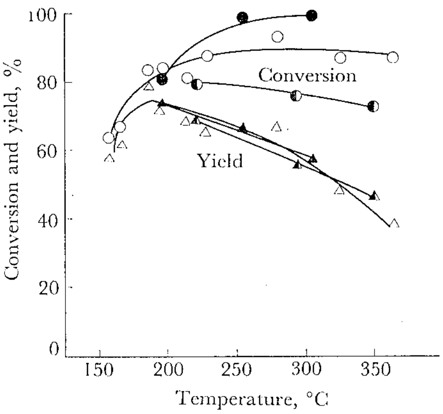

Fig. 5. Effect of feed ratio.
50 wt. % ZnO (nitrate)-MgO catalyst.
Circles: conversions.
Triangles: yields.
◐, ◭: Runs at feed ratio of 6 moles isopropyl alcohol/acrolein.
○, △: Runs at feed ratio of 10 moles isopropyl alcohol/acrolein.
●, ▲: Runs at feed ratio of 15 moles isopropyl alcohol/acrolein.

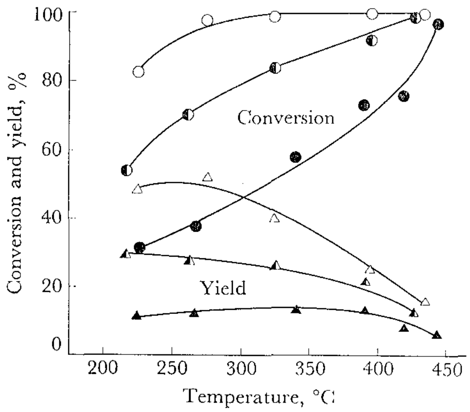

Fig. 6. Effect of feed ratio.
MgO catalyst.
Circles: conversions.
Triangles: yields.
●, ▲: Runs at feed ratio of 2 moles isopropyl alcohol/acrolein.
◐, ◭: Runs at feed ratio of 6 moles isopropyl alcohol/acrolein.
○, △; Runs at feed ratio of 10 moles isopropyl alcohol/acrolein.

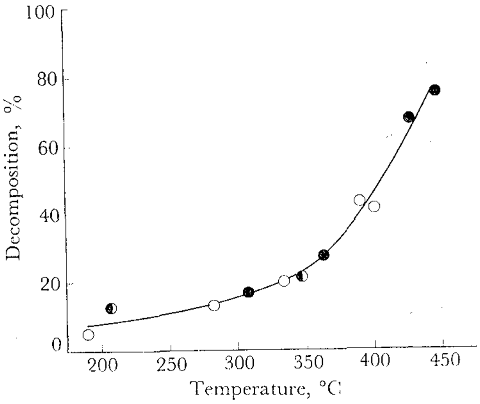

Fig. 7. The decomposition of allyl alcohol.
○: Runs on MgO catalyst, feed rate, 50 mol./l./hr..
●: Runs on MgO catalyst, feed rate, 105 mol./l./hr..
◐: Runs on 50 wt. % ZnO(nitrate)-MgO catalyst, feed rate, 50 mol./l./hr..

amount of isopropyl alcohol to acrolein improved the total yields of allyl alcohol as shown in Fig. 5 and Fig. 6.

By-products. By means of the gas chromatographic analysis, it was ascertained that the reaction yielded a small amount of *n*-propyl alcohol and a smaller amount of propionaldehyde. In addition, the formation of high boiling materials was observed. The amounts of these by-products depended upon the reaction temperature—the higher the temperature, the more the amounts of the by-products.

The Life Time of the Catalyst. No final information was yet available to the life time of the catalyst, but its activity and selectivity decreased remarkably after several uses of the catalyst as shown in Table 2.

Table 2. The life time of the catalyst.
50 wt.% ZnO (nitrate)-MgO catalyst.
Feed ratio, 10 moles isopropyl alcohol/acrolein.
Feed rate, 45 mol./l./hr. (reaction time, 13 min.).
Temperature, 220°C.

Run, No.	Conversion, %	Yield, %	
		to consumed acrolein	to fed acrolein
1	89	65	57
2	71	58	41
3	52	50	26
4	32	59	19
5	49	47	23

REFERENCES

(1) A.L. Wilds, "Organic Reactions", Vol. II, John Wiley & Sons, New York, 1944, p. 178.

(2) N.C. Deno, H.J. Peterson and G.S. Saines, *Chem. Revs.*, **60,** 7 (1960).

(3) S.A. Ballard and E.A. Youngman, U.S. Pat., 2, 991, 305; *Chem. Abstr.*, **55,** 25758 (1961).

(4) S.A. Ballard and H.V. Finch and E.A. Peterson, Brit. Pat., 619,014; *Chem. Abstr.*, **43,** 7497 (1949).

(5) S.A. Ballard, H.V. Finch and E.A. Peterson, U.S. Pat., 2,767,221; *Chem. Abstr.*, **51,** 7399 (1957).

(6) S.A. Ballard, H.V. Finch and D.E. Winkler, "Advances in Catalysis" Vol. IX, Academic Press, New York, 1957, p. 754.

(7) S. Malinovski and T. Kobylinski, *Przemysl Chem.*, **41,** 148 (1962); *Chem. Abstr.*, **57,** 14923 (1962).

(8) S.D. Mekhtiev and O.A. Narimanbekov, *Azerb. Khim. Zh.*, **1963**(4), 77; *Chem. Abstr.*, **61,** 1746 (1964).

(9) J. Newham and R.L. Burwell, Jr., *J. Am. Chem. Soc.*, **86,** 1179 (1964).

(10) S.D. Mekhtiev and O.A. Narimanbekov, *Azerb. Khim. Zh.*, **1964**(1), 31; *Chem. Abstr.*, **63,** 477 (1965).

(11) S.D. Mekhtiev and O.A. Narimanbekov, *Neftekhimiya*, **5**(2), 237 (1965); *Chem. Abstr.*, **63,** 5520 (1965).