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STUDY OF CATALYSIS FOR MAKING ALCOHOL FROM ACROLEIN AND ISOPROPYL ALCOHO

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ABSTRACT

The vapor phase hydrogen trancefer reaction between acrolein and isopropyl alcohol has been investigated over Ag_2O-Cao catalyst. A high selectivity of allyl alcohol was obtained at 88.7% with conversion of 75.4%.

INTRODUCTION

In general, it is difficult to obtain a high selectivity of the corresponding unsaturated alcohol from the hydrogenation of α, β-unsaturated compounds. There are a number of literatures to these reactions[1] but allyl alcohol selectivity is not so high and about around 50 %.[2] Recently, Shimasakiet al have reported to obtain effectively the corresponding allylic alcohols from the vapor phase hydrogen trancefer reaction between α, β-unsaturated carbonyl compounds and alcohols over B_2O_3-MgO catalyst.[3] The author has investigated the vapor phase hydrogen trancefer reaction between acrolein and isopropyl alcohol over metal oxide catalysts and examined relations between activity and selectivity to allyl alcohol.

EXPERIMENTAL

Ag_2O-CaO catalyst was prepared from a mixed solution of silver nitrate, calucium nitrate and an aqueous solution of 6 N soldium hydroxide at pH 12. Then, the gel obtained was washed, dried at 110℃ for 12 h and thereafter calcined at 600℃ for 4 h. by the same method, other metal oxide cata-lysts were prepared and crushed in a particles of 20-40 mesh. The vapor phase hydrogen trancefer reaction was carried out in a conventional fixed bed flow system at atmospheric pressure, using pyrex glass reactor(16ϕ×300 ㎜) immersed in a heating sand bath of fluid bed. A reactant was introduced by a microfeeder. Reaction products were traped in a dry icemethanol and analyzed by gaschromatography(TCD, PEG 6000, 110℃)

RESULTS AND DISCUSSION

The vapor phase hydrogen trancefer reaction between acrolein and isopropyl alcohol was examined at 270℃, using various kinds of metal oxide catalysts of 2.0 g under a gas feed velocity(acrolein : isopropyl alcohol : nitrogen=1 : 4.3 : 89, vol. ratio), S.V 2535 h^{-1}. Results were shown in Table 1. In initial activity, a high conversion was obtained at

around 92%-99% on alkaline earth metal oxide catalysts(CaO, MgO) or dual function catalysts (Ag_2O-CaO, B_2O_3-MgO), but initial selectivities on above catalysts were not very high values of 45.6%-97.6%, MgO or ZnO catalyst bringed about a minor dehydration on initial activity. On the other hand, activities and selectivities on above catalysts of reaction time 1 h were around 17.3%-75.4 % and 88.)%-96.9%, respectively and the selectivity showed a high value than initial selectivity.

Here, compared the activity and selectivity, Ag_2O-CaO (Ag_2O_3 wt%) and B_2O_3-MgO (B : Mg=2 : 100, atomic ratio) catalyst are leaded to all other catalysts and allyl alcohol yields of the former and the latter were 66.9 % and 51.5%, respectively. Therefore, it was found that Ag_2O-CaO catalyst was superior to B_2O_3-MgO catalyst on the activity and

Table 1. Hydrogen Transfer Reaction between Acrolein and Isopropyl Alcohol over Varios Kinds of Metal Oxide Catalysts

	Initial Activity	Initial Selectivity	Activity /mol%	Selectivity /%	Unknown
MgO	92.2	76.8	65.1	88.0	-
CaO	91.8	76.1	71.6	88.6	-
ZnO	39.8	94.1	20.5	88.7	-
Mn_2O_3	55.3	97.6	17.3	96.9	-
Fe_2O_3	83.1	73.0	36.9	87.2	large
TiO_2	75.6	65.7	44.0	84.6	large
B_2O_3-MgO	99.8	45.6	53.5	95.5	-
Ag_2O-CaO	99.0	68.9	75.4	88.7	-

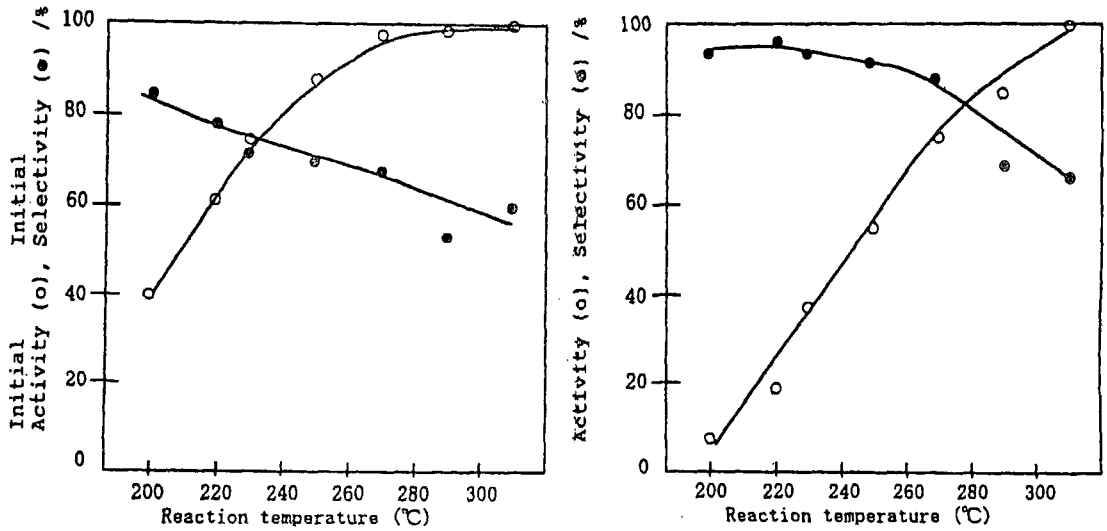
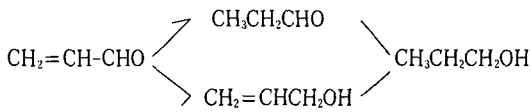


Fig. 1 Activity and selectivity for the hydrogen trancefer reaction of acrolein and isopropyl alcohol over Ag_2O-CaO catalyst vursus changes of reaction temperature

selectivity for hydrogen transfer reaction between acrolein and isopropyl alcohol. Next, relationships between activity, selectivity and reactin temperature on the hydrogen transfer reaction of acrolein and isopropyl alcohol over Ag_2O-CaO catalyst is shown in Fig. 1.

As observed Fig. 1, both initial activity and activity increased with an increase of reaction temperature and were obtained in 100% conversion at 315℃. On the other hand, the selectivity decreased with an increase of reaction temperature, especially at above 260℃ and was values in the range of ab. 95% to 65 %. In order to examine relations between activity and selectivity in details, yields of composition products were shown in Fig.2. From the results of Fig. 2, allyl alcohol yield decreased with an increase of reaction temperature, but yield of 1-propanol remarkable increased at avove 270℃ and so, allyl alcohol selectivity decreased. Consequently, the improvement of allyl alcohol yield was adapted for reaction temperature of 270℃.

Generally, the selectivity decreases with an increase of the activity. Therefore, the relation between activity and selctivity was shown in Fig. 3. As observed in Fig. 3, allyl alcohol yield increased with an increase of activity and was an invariable value of ab. 67% in above 75% conversion. On the other hand, allyl alcohol selectivity was an invariable value of ab. 87% in the range of 15% to 75% conversion, and decreased in 60% with the formation of 1-propanol in above 75% conversion. Therefore, the improvement of allyl alcohol yield was agreeded with 75% conversion. Judging from the fact that the formation of propionaldehyde slightly occreded in a low conversion and 1-propanol yield increased with an decrease of allyl alcohol yield in above 75% conversion, the following reaction scheme is considered ;



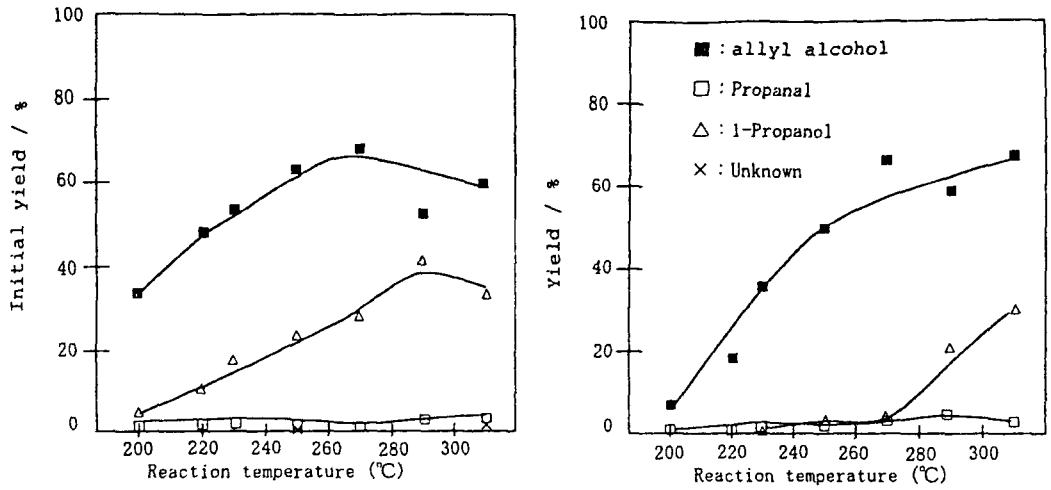


Fig. 2 Yield of reaction product over Ag_2O-CaO catalyst vursus changes of reaction temperature

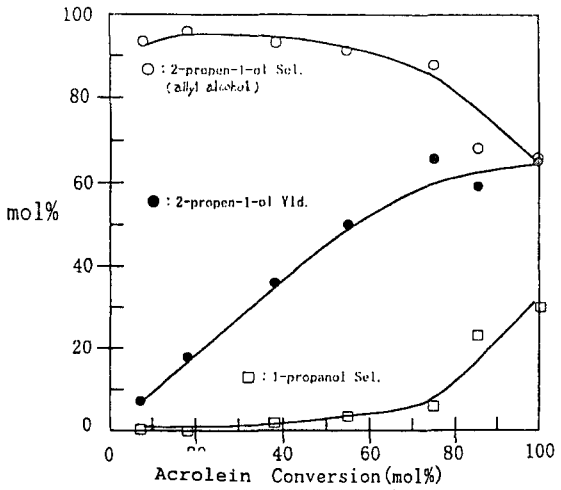


Fig. 3 Relations between activity and selectivity for the reaction over Ag_2O-CaO catalyst

From XRD and XPS measurements of the catalyst, the catalyst was composed of an amorphus silver(1) oxide, a cristalline silver and a cristalline carucium oxide.

CONCLUSSION

The vapor phase hydrogen transfer reaction of acrolein and isopropyl alcohol was examined using Ag_2O(Ag_2O 3wt%)-CaO catalyst at 270℃, 25505^{h-1}(S.V). The catalyst had a high activity and a high selectivity. The activity(conversion) and selectivity were 75.4 % and 88.7%, respectively. Allyl alcohol yield was obtained at 66.9% and superior to yield over B_2O_3-MgO catalyst.

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