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Aldol Addition of Butyraldehyde over Solid Base Catalysts

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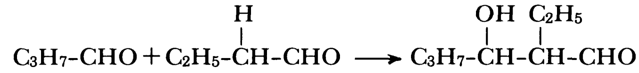
Synopsis. Aldol addition of butyraldehyde was investigated on alkaline earth oxides, zirconium oxide, and lanthanum oxide to compare the active site and mechanism with those for aldol addition of acetone. It is found that the active site is the surface O^{2-} and the rate-determining step is α-H abstraction.

Aldol type reaction of butyraldehyde as shown below is one of the most important reactions in organic chemistry and has been extensively studied for fundamental understanding.



$$C_3H_7\text{-}CHO + C_2H_5\text{-}\overset{H}{C}H\text{-}CHO \longrightarrow C_3H_7\text{-}\overset{OH}{C}H\text{-}\overset{C_2H_5}{C}H\text{-}CHO$$

Many investigations for industrial application of catalysts to aldol addition of ketones and aldehydes were made. Although practical catalysts developed in industry are mostly heterogeneous, the fundamental studies are made primarily in homogeneous system. Recently, we studied aldol addition of acetone over several kinds of solid base catalysts, and found that the active sites for this reaction are surface basic OH groups, and that the rate-determining step is the formation of a new C-C bond between two acetone molecules rather than the abstraction of an α-H^+ ion from acetone.[1-3]

In this work, we studied aldol addition of butyraldehyde over solid base catalysts, and found that the active sites and the rate-determining step for butyraldehyde are different from those for acetone.

Experimental

Catalyst Preparation: Magnesium oxide was prepared from commercial MgO(Merck) as follows. The commercial MgO powder was added into distilled water and stirred at room temperature for 24 h followed by being dried in an oven at 100 °C for 24 h to form hydroxide. Starting material for CaO was $Ca(OH)_2$. Calcium hydroxide was also treated in distilled water in the same way as MgO. The hydroxides of magnesium and calcium were heated at various temperatures in a vacuum to form the oxides before use. Zirconium oxide and La_2O_3 were prepared from aqueous solutions of $ZrOCl_2$ and $La(NO_3)_3$, respectively, by hydrolysis with aqueous ammonia. Strontium oxide was obtained by evacuating $SrCO_3$ at high temperatures.

Reaction Procedures: Reaction was carried out in a H-type batch reactor at 0 °C as described in a previous paper.[1] The two branches were separated by a breakable seal. The catalyst sample was able to be treated in one side and the reactant in another side. One gram of reactant and 50 mg of catalyst were used as a standard procedure. Reactant was admitted to the side of catalyst by breaking the breakable seal and transferring reactant to catalyst side by cooling this side to liquid nitrogen temperature. Reaction was started by rapid melting of the reactant at reaction temperature of 0 °C. In some poisoning experiments, poison was admitted into the reactor before reaction. Products were analyzed by GLC.

Results

The main products were a dimer (namely 2-ethyl-3-hydroxyhexanal) and a trimer. The formation of the trimer was confirmed by field-ionization mass spectrometry, although its exact structure was not clear. Besides dimer and trimer, 2-ethyl-2-hexenal formed by dehydration of dimer was obtained less than 3% of the total products. The activities of several kinds of catalysts for aldol addition of butyraldehyde are summarized in Table 1. Zirconium oxide and La_2O_3 had low activities, while MgO, CaO, and SrO showed high activities. As the specific surface areas were in the order of $MgO > CaO \gg SrO$ (about a ratio 25 : 10 : 1,[1] the order for the activities upon unit surface area basis is $SrO > CaO > MgO \gg La_2O_3 > ZrO_2$. The activities of La_2O_3 and ZrO_2 for aldol addition of acetone were comparable to that of MgO. Considering the strength of basic site being the order $MgO > La_2O_3 > ZrO_2$, the activity dependency on the basic strength is higher for butyraldehyde than for acetone.

Relation between the ratio of dimer to trimer and conversion was examined with MgO and CaO by changing the reaction time although the results are not presented. The ratio with MgO declined slightly from 7.1 to 5.0 over the range of conversion from 7.8 to 84.4, while the ratio with CaO kept near an unchanged value of ca. 0.7 over a similar range of conversion as that with MgO. Variations of activity and selectivity with pretreatment temperature of MgO are shown in Fig. 1. Maximum of conversion ap-

Table 1. Activities of Various Catalysts for Aldol Addition of Butyraldehyde

Cat.	Pretreatment temp./°C	Reaction time/h	Conversion /%	Selectivity to 2EHA[a]/%	Dimer/Trimer
ZrO_2	600	2	0.9	—	—
La_2O_3	600	1	3.2	—	1.3
MgO	600	1	35.0	1.7	5.0
CaO	600	1	41.1	2.8	0.7
SrO	800	1	41.7	1.3	2.2

a) 2EHA: 2-ethyl-2-hexenal.

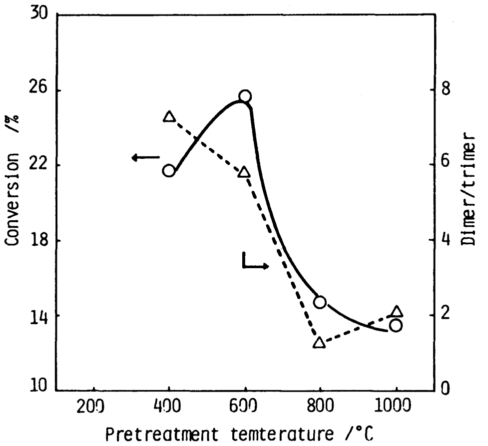


Fig. 1. Pretreatment temperature dependences of activity for aldol addition of butyraldehyde and of ratio of dimer to trimer in the reaction over MgO.

peared around the pretreatment temperature of 600 °C. The ratio of dimer to trimer decreased monotonously as the pretreatment temperature increased.

The results of poisoning experiments with MgO are summarized in Table 2. Ammonia did not poison the active sites, whereas pyridine, carbon dioxide, and water poisoned to considerable extents. Poisoning effect of water in aldol addition of butyraldehyde is in contrast to a marked promoting effect of water in aldol addition of acetone. The ratio of dimer to trimer was increased by water addition. Addition of acetone to butyraldehyde did not affect the reaction of butyraldehyde at all. Neither aldol addition of acetone nor cross aldol addition between butyraldehyde and acetone occurred.

Discussion

A good correspondence of the order of the activity for aldol addition of butyraldehyde to the basic strength of catalyst indicates that the reaction proceeds on the basic sites. Since the activity dependency on the surface basic property is stronger for butyraldehyde than that for acetone, some differences between the constitutions of active sites for aldol addition of acetone and aldehyde are suggested. Two kinds of basic sites, basic OH groups and the surface O^{2-}, exist on the surface of solid base catalysts. The results of poisoning experiments in aldol additions of butyraldehyde and acetone suggest the relevant sites for each reaction. The poisoning and promoting effects on the aldol additions of butyraldehyde and acetone are compared in Table 3. Marked difference is observed for the effect of water; considerable promoting effect was observed for acetone while poisoning effect for butyraldehyde. If only surface O^{2-} ions were active sites, water and carbon dioxide would have completely poisoned the active sites. Complete poisoning effect with water and carbon dioxide were observed for many other base-catalyzed reactions such as double bond migration of olefin, hydrogenation of 1,3-butadiene, etc.[4)] This is, however, not the observed result for aldol addition of butyraldehyde. The percentage of the activity remaining on addition of water and carbon dioxide is considered to be due to surface OH groups. No promotion effect observed on addition of water is explained by the higher efficiency for the surface O^{2-} ions than for the surface OH groups which may be weaker base than the surface O^{2-}. For aldol addition of acetone, the active sites are the surface OH groups.

Table 2. Preadsorption Effect of Various Additives on Aldol Addition of Butyraldehyde over MgO

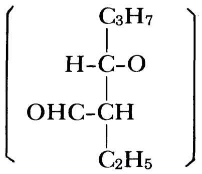
Additives[a)]	Conversion[b)] /%	2-Ethyl-2-hexenal	Ratio of dimer to trimer
None	23.5	0.4	6.6
Pyridine	17.4	0.2	6.9
NH_3	24.5	0.4	6.6
CO_2	15.1	0.2	6.0
H_2O[c)]	14.7	0.3	7.4
H_2O[d)]	4.4	0.3	13.3

a) All molecules adsorbed at room temperature. b) Reaction time: 0.5 hour. c) Amount of H_2O adsorbed was 2.4 mmol/g-cat. d) Amount of H_2O adsorbed was 4.8 mmol/g-cat.

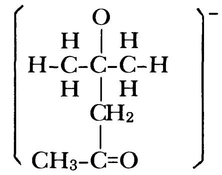
Table 3. Relative Activity with Poison or Promoting Molecules in the Aldol Additions of Butyraldehyde and Acetone

Reactant	Added molecule				
	Ammonia	Pyridine	Water	Carbon dioxide	None
Butyraldehyde	1.04	0.74	0.63	0.64	1.00
Acetone	1.38	1.15	1.69	0.86	1.00

Differences in the activity dependency on basic strength and the efficiency of surface O^{2-} and OH groups between aldol addition of butyraldehyde and acetone are considered to be caused by the difference in rate-determining steps for these reactions. Since the aldehyde is stronger acid than ketone, and the surface OH groups can abstract α-H from acetone, it is plausible that the basic strength of the surface OH groups is sufficient to abstract α-H from both butyraldehyde and acetone. The steric hindrance in the C–C bond formation is thought to be larger for acetone than butyraldehyde as shown below.


$$\left(\begin{array}{c} C_3H_7 \\ | \\ H\text{-}C\text{-}O \\ | \\ OHC\text{-}CH \\ | \\ C_2H_5 \end{array}\right)^-$$

a) Intermediate for butyraldehyde.


$$\left(\begin{array}{c} O \\ H\ |\ H \\ H\text{-}C\text{-}C\text{-}C\text{-}H \\ H\ |\ H \\ CH_2 \\ | \\ CH_3\text{-}C{=}O \end{array}\right)^-$$

b) Intermediate for acetone.

The rate of C–C bond formation between two butyraldehyde molecules is fast as compared to an α-H abstraction, while the C–C bond formation is slower than an α-H abstraction for acetone. Therefore, the rate-determining step is suggested to be an α-H abstraction for butyraldehyde in contrast to C–C bond formation for acetone. The base strength is directly associated with the slow step for butyraldehyde, which causes strong dependency of the activity on the basic strength.

It should be noted that the variation of ratio of dimer to trimer with conversion is very small. Nearly constant values of the ratio indicate that the dimer converts to trimer very slowly. Increase of ratio of dimer to trimer owing to the addition of water as shown in Table 2 is ascribed to the conversion of the surface O^{2-} of strong basic sites into the OH groups of weak basic sites. These results indicate that a stronger basic site facilitates the formation of trimer without desorption of dimer. The fact that the ratio of dimer to trimer obtained with MgO is higher than those for CaO and SrO coincides with the result, although a slightly opposite tendency is observed as comparing CaO with SrO.

References

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