Selective Reduction of α-Chloroketone to α-Chloroalcohol Using Hydrogen Transfer from Alcohol over Metal Oxide Catalysts

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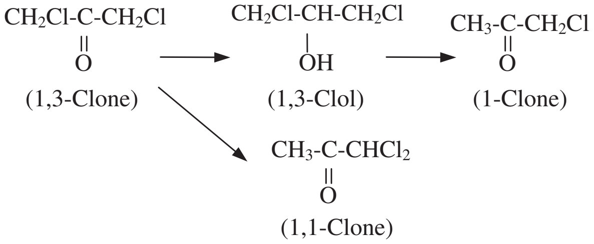
The carbonyl group of 1,3-dichloro-2-propanone was reduced selectively through hydrogen transfer from 2-butanol over MgO, $SiO_2 \cdot Al_2O_3$, Al_2O_3, and ZrO_2. It is suggested that the reaction is promoted by either base or acid site of the catalysts.

α-Chloroalcohols are useful compounds as intermediates in fine chemical synthesis. One of the methods to obtain α-chloroalcohols is the reduction of α-chloroketones or α-chloroaldehydes. However, the selective reduction of carbonyl group is not so easy because the hydrodechlorination takes place simultaneously. 1,3-Dichloro-2-propanol (1,3-Clol) is a potential intermediate to produce epichlorohydrin that is a raw material for epoxy resin, synthetic rubber, etc. The reduction of 1,3-dichloro-2-propanone (1,3-Clone) to 1,3-Clol has been claimed in two patents,[1,2] so far. One is the hydrogen reduction using ruthenium complex catalyst,[1] and the other is the reduction by hydrogen transfer from 2-propanol using aluminum triisopropoxide as a catalyst.[2] They still have problems for practical application. The ruthenium complex is expensive and is synthesized by complicated procedures. Aluminum triisopropoxide is readily decomposed by a trace amount of water present in the reactant as an impurity. Recently, we have found that the Guerbet reaction, a condensation reaction between alcohols to form longer chain alcohols, proceeds in the gas phase over solid base catalysts including MgO[3,4] and alkali salt supported on zeolite,[5] and the fast hydrogen transfer from alcohol to unsaturated carbonyl intermediate is responsible for the formation of saturated alcohol.[4] The finding led us to try the reduction of 1,3-Clone into 1,3-Clol by using hydrogen transfer from alcohol over metal oxide catalysts.

MgO catalyst was obtained by decomposing $Mg(OH)_2$ in a nitrogen stream at 450 °C for 2 h. The detailed procedure was mentioned in our previous papers.[3,4] CaO was prepared similarly, but the decomposition of hydroxide was performed at 600 °C. Cs-exchanged X-zeolite (CsX) was prepared from NaX by an ion-exchange method using aqueous solution of CsCl. CsX-supported Cesium carbonate (Cs_2CO_3/CsX) and alumina-supported potassium carbonate (K_2CO_3/Al_2O_3) were prepared by an impregnation method. The other oxide catalysts were used as purchased. The reaction was performed in a gas phase continuous flow reactor under atmospheric pressure. The reaction mixture of 1,3-Clone, 2-butanol, and cyclohexane (internal standard) was fed into a N_2 carrier gas using a syringe pump. Feed gas composition was 1,3-Clone:2-butanol:cyclohexane:N_2 = 0.1:5:0.1:50, and the total flow rate was 55 mL min^{-1}. The catalyst was heat-treated in a nitrogen stream at 450 or 600 °C for 2 h before the reaction. Products were identified and analyzed quantitatively by GC–MS and GC–FID, respectively.

All the catalysts were deactivated in the initial stage of reaction and showed stable activities after 6 h of time on stream. The stable activities are summarized in the following tables. The results of the reaction over MgO are shown in Table 1. In every run, the products that originated from 2-butanol were 2-butanone and a small amount of butenes. When the reaction was conducted at 150 °C with 1 g catalyst (Run 1), 1,3-Clone was reduced to 1,3-Clol at ca. 90% selectivity. The hydrodechlorination product, 1-chloro-2-propanone (1-Clone), and Cl rearrangement product, 1,1-dichloro-2-propanone (1,1-Clone) were also formed at ca. 8 and 2% selectivities, respectively. Besides the products shown in the table, trace amounts of 1-chloro-2-propanol and acetone were detected. Increasing to twice the catalyst amount (Run 2), the conversion increased from 24 to 80%, while the selectivity of 1,3-Clol decreased to 68% and that of 1-Clone increased to 23%. The facts suggest that 1-Clone was formed by successive HCl elimination from 1,3-Clol. The selectivity of 1,1-Clone did not change appreciably with the catalyst amount (Runs 1–3), but increased remarkably when the reaction temperature was raised to 250 °C (Runs 3–5). It is likely that the carbonyl reduction and the Cl rearrangement proceed concurrently and the latter activation energy is higher than the others. The reaction path to form the observed products can be written as follows:



Scheme 1.

Table 2 summarizes the activities of various catalysts for the reduction of carbonyl group in 1,3-Clone, where the data shown in Table 1 (Run 1) were cited for comparison. Among basic met-

Table 1. Reaction of 1,3-dichloro-2-propanone with 2-butanol over MgO catalyst

Run	Amount[a] /g	Temp.[b] / °C	Conv.[c] /%	Selectivity/%		
				1,3-Clol	1-Clone	1,1-Clone
1	1	150	24.2	89.4	8.3	2.2
2	2	150	80.0	68.0	23.0	2.4
3	0.5	150	10.6	94.4	4.2	1.8
4	0.5	200	28.4	62.6	26.0	9.6
5	0.5	250	63.6	4.4	48.6	46.4

[a]Amount of the catalyst. [b]Reaction temperature. [c]Conversion of 1,3-dichloro-2-propanone.

al oxides, MgO showed the highest activity for the reduction of carbonyl group. CaO showed no activity, although its basicity was thought to be similar to or higher than MgO. The values of conversion over SnO_2 and ZnO were comparable to that over MgO. However, these catalysts did not promote the reduction of carbonyl group appreciably and gave the hydrodechlorination and chlorine rearrangement products, respectively. Although CsX was reported to be active for the carbonyl reduction of citronellal to form citronellol[6] and Cs_2CO_3/CsX showed higher activity for the Guerbet reaction than MgO,[5] both catalysts yielded only a trace amount of 1,3-Clol. K_2CO_3/Al_2O_3, whose strong basicity was reported by Yamaguchi et al.,[7] gave 1,3-Clol at about 60% selectivity which was much lower than the selectivity observed with MgO. SiO_2 used frequently as an inert support was inactive substantially. Over ZrO_2 the value of conversion was twice higher than that over MgO and the selectivity for carbonyl reduction was similar to MgO. The much higher conversions, more than 90%, were obtained with Al_2O_3 and $SiO_2{\cdot}Al_2O_3$, although the amount of catalyst used was a half of MgO. The selectivity of these catalysts for the carbonyl reduction was lower than that of MgO but seemed to be comparable to MgO, considering the high conversion level. However, they had a disadvantage from the standpoint of stoichiometric reduction, because a considerable amount of reductant 2-butanol was consumed by being dehydrated to butenes on their acid sites.

Table 2. Reaction of 1,3-dichloro-2-propanone with 2-butanol over various catalysts (150 °C)

Catalyst	Amount/g	Conv. /%	Sel.[a]/%
MgO	1.0	24.2	89.4
CaO[b]	0.5	≈ 0	tr.
SnO_2[b]	1.0	36.6	2.7
ZnO	1.0	12.8	tr.
CsX	1.0	16.9	tr.
Cs_2CO_3/CsX[c]	0.5	≈ 0	tr.
K_2CO_3/Al_2O_3	1.0	17.7	59.0
SiO_2	0.5	1.8	tr.
ZrO_2	1.0	49.4	85.2
Al_2O_3	0.5	90.9	72.6
$SiO_2{\cdot}Al_2O_3$	0.5	96.0	76.7

[a]Selectivity of 1,3-dichloro-2-propanol. [b]Pretreatment temperature, 600 °C. [c]Reaction temperature, 250 °C.

It is of interest that MgO, ZrO_2, Al_2O_3, and $SiO_2{\cdot}Al_2O_3$ show the high activity and selectivity for the reaction although they are different in their acid-base properties. In order to clarify the role of acid and base sites, poisoning effects of CO_2 and pyridine were studied for the similar and simple reaction, that is, the reduction of acetone with 2-butanol. The reaction was carried out at 150 or 200 °C in the same reactor as used for the reduction of 1,3-Clone loading 0.1 g catalyst.

The effects of CO_2 and pyridine addition into the reaction feed were summarized in Table 3. MgO was most active for the reduction of acetone unlike the order of catalytic activity for the reduction of 1,3-Clone. This suggests that the rate of carbonyl reduction through the hydrogen transfer from alcohol strongly depends on both the acid-base properties of catalyst and the electron density on the carbonyl group, as it will be revealed by the kinetic studies now under way. The reduction of acetone did not take place in the presence of CO_2, indicating the base sites on MgO are indispensable to promote the reaction. In the presence of pyridine, the conversion of acetone decreased gradually from 91 to 60% in 4 h, but the reaction did not stop completely. Pyridine seems to hinder the adsorption of acetone and/or 2-butanol on Lewis acid sites by competitive adsorption. Lewis acid sites might facilitate the formation of surface butoxy species as assumed for the Guerbet reaction over MgO catalyst.[4] The reactions over ZrO_2 and Al_2O_3, which have both base and acid sites, were not poisoned completely by the addition of CO_2 or pyridine. Over $SiO_2{\cdot}Al_2O_3$, 2-propanol and its successive dehydration product propene were formed at 85 and 15% selectivity, respectively. The reaction was stopped substantially by the addition of pyridine.

Although the detailed mechanism is now in investigation, we deduce that either base or acid site promotes the reduction of carbonyl group with alcohol by individually different mechanisms.

Table 3. Effect of CO_2 or pyridine addition in the reaction of acetone with 2-butanol over various catalysts[a]

Catalyst	Additive	Conv.[b]/%	Sel.[c]/%
MgO	None	91.0	100
	CO_2	0.0	—
	pyridine	60.0	100
ZrO_2	None	29.9	100
	CO_2	12.3	100
	pyridine	12.3	100
Al_2O_3	None	24.2	100
	CO_2	12.3	100
	pyridine	5.4	100
$SiO_2{\cdot}Al_2O_3$	None	38.4	85.7
	CO_2	42.3	93.9
	pyridine	0.0	—

[a]Reaction conditions: amount of catalyst, 0.1 g; feed gas composition, acetone : 2-butanol:N_2 = 0.15:1.5:50 (None), acetone:2-butanol:N_2:CO_2 = 0.15:1.5:45:5(CO_2), acetone:2-butanol:N_2:pyridine = 0.15:1.5:50:1.5 (pyridine); total flow rate, 52 mL min^{-1}; reaction temperature, 150 °C (MgO, Al_2O_3, and $SiO_2{\cdot}Al_2O_3$), 200 °C (ZrO_2). [b]Conversion of acetone. [c]Selectivity to 2-propanol.

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