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# Influence of Residual Chloride Ions in Alumina-Supported Cobalt Catalysts on Catalytic Activity in Ketone and Aldehyde Hydrogenation

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The influence of residual chloride ions on the catalytic activity of $Co/Al_2O_3$ was investigated for liquid-phase hydrogenation of ketones and aldehydes using $Cl^-$-free and $Cl^-$-containing catalysts. The $Cl^-$-free catalyst showed high activity for hydrogenation of both, whereas the $Cl^-$-containing catalysts showed very low activity for ketone hydrogenation.

Catalytic hydrogenation of aldehydes and ketones to form alcohols, using molecular hydrogen and heterogeneous catalysts, is a key reaction in the production of fine chemicals. Supported metal catalysts have been widely studied for this reaction;[1,2] in particular, supported Pt catalysts have been the subject of extensive study in spite of the high relative cost of the metal. In addition, cobalt catalysts have been investigated for hydrogenation because when these catalysts are used, carbonyl groups are hydrogenated preferentially over carbon–carbon double bonds. In particular, the hydrogenation reaction of (*E*)-2-butenal (crotonaldehyde) using supported cobalt catalysts has been the subject of a number of investigations,[3–17] because it is difficult to obtain the unsaturated alcohol in high yield when metal catalysts are used. We recently found that alumina-supported cobalt catalyst prepared by a precipitation method using dichlorocobalt hexahydrate and potassium hydroxide as a precipitant shows high activity for selective hydrogenation of $\alpha,\beta$-unsaturated aldehydes to the corresponding unsaturated alcohols,[6] and that addition of chloride ions to the reaction media results in a significant increase in the rate of carbonyl-group hydrogenation compared to that obtained for $Cl^-$-free $Co/Al_2O_3$ catalyst.[15]

Compared with aldehyde hydrogenation over supported cobalt catalysts, the study of ketone hydrogenation has been quite limited; reports include hydrogenation of acetone over CoB,[18] Co/ZnO,[19] $Co/Al_2O_3$,[20,21] $Co/TiO_2$,[20] and $Co/SiO_2$,[22] and hydrogenation of cyclohexanone derivatives,[23] substituted acetophenones,[24] and enones[25] over Raney Co catalysts.

In this work, we investigate the influence of residual chloride ions on catalytic activity in ketone and aldehyde hydrogenation; in addition, we report the results of hydrogenation reactions of various ketones over alumina-supported cobalt catalysts.

## Experimental

Chloride ion-free catalyst, $Co/Al_2O_3$ ($NO_3$-I), was prepared by a conventional impregnation method using $Al_2O_3$ (AEROXIDE® Alu-C, surface area: $110\,m^2\,g^{-1}$) and $Co(NO_3)_2\cdot6H_2O$ aqueous solution. The resultant sample was dried at 400 K overnight and then calcined at 673 K for 5 h in air to prepare a catalyst precursor. The precursor was reduced at 773 K for 3 h in $H_2$ flow before being used in the hydrogenation reaction. The catalyst prepared in the presence of chloride ions, $Co/Al_2O_3$ (Cl-P), was formed by a precipitation method using $Al_2O_3$, an aqueous solution of $CoCl_2\cdot6H_2O$, and KOH as a precipitant, according to the method described in a previous paper.[6] After the reduction, the characteristic peaks derived from metallic cobalt were observed in the XRD profiles of both catalysts.

The amounts of cobalt metal supported on the catalysts were determined quantitatively using an inductively coupled plasma/atomic emission spectrometer (Leeman Labs, JICP-PS1000UV). The metal loadings of $Co/Al_2O_3$ ($NO_3$-I) and $Co/Al_2O_3$ (Cl-P) were 42.1 and 41.2 wt %, respectively. An XRF spectrometer (Philips, PW2400) was used for quantitative analysis of potassium and chloride ions in the catalysts. The data obtained were compensated using calibration factors determined by measurement of standard samples.

Seven ketones were selected as reactants: 2-butanone, 3-methyl-2-butanone, 3,3-dimethyl-2-butanone, acetophenone, benzophenone, cyclohexanone, and cyclopentanone. To compare the reactivities of ketones and aldehydes, butanal and 2-methylpropanal were also used for hydrogenation. Liquid-phase hydrogenation over $Co/Al_2O_3$ was performed in a stainless-steel autoclave (100 mL) equipped with a mechanical stirrer, a pressure gauge, an inlet valve and a thermocouple. Reactant (3.0 mL), ethanol (solvent, 50 mL), and the reduced catalyst (1.0 g for Tables 1 and 3, and 0.4 g for Figure 1) were placed into the autoclave through the inlet valve under a $H_2$ atmosphere. Hydrogenation was carried out at 1.0 MPa (gauge) and 323 K for 1 h (Tables 1 and 3) or 2 h (Figure 1) without further addition of $H_2$. Products were analyzed by GC (GL Science, TC-WAX capillary column, diameter = 0.25 mm, length = 30 m).

## Results and Discussion

Table 1 shows the results of ketone and aldehyde hydrogenation over $Co/Al_2O_3$ ($NO_3$-I) and $Co/Al_2O_3$ (Cl-P) catalysts. During the reaction, acetal or ketal were formed by condensation of aldehyde or ketone, respectively, with ethanol (solvent) over the acid sites of the support. Especially, acetals and ketals were remarkably formed over $Co/Al_2O_3$ (Cl-P) prepared from $CoCl_2\cdot6H_2O$ as a raw material. Other products were not observed in all experiments.

$Co/Al_2O_3$ ($NO_3$-I) catalyst showed high activity for hydrogenation of all aldehydes and ketones to the corresponding alcohols. The yield of 2-butanol (41.1%) was higher than that of 1-butanol (22.2%) under the same reaction conditions, indicating that hydrogenation of ketones is faster than that of aldehydes. Santori et al. studied gas-phase hydrogenation of 2-butanone and butanal over supported Pt catalysts,[26] and reported

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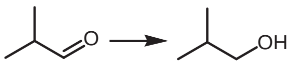
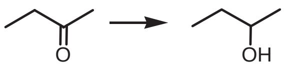
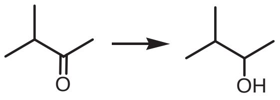
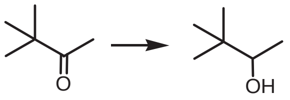
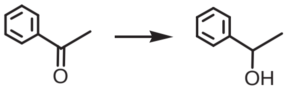
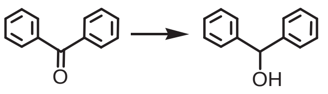
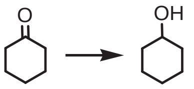
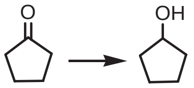
**Table 1.** Hydrogenation of Aldehydes and Ketones Using Cl-Free (Cl-P) or Cl-Containig ($NO_3$-I) $Co/Al_2O_3$ Catalysts

| Reactant → Product | Yield of products/%[a)] Cl-P catalyst | Yield of products/%[a)] $NO_3$-I catalyst |
|---|---|---|
|  | 40.4<br>(3.2) | 22.2<br>(0.5) |
|  | 34.6<br>(4.9) | 24.5<br>(0.2) |
|  | 0.8<br>(3.8) | 41.1<br>(0.1) |
|  | 0.5<br>(1.2) | 33.5<br>(0) |
|  | 0.1<br>(0) | 1.5<br>(0) |
|  | 0.3<br>(0.9) | 28.4<br>(0) |
|  | 0.1<br>(0) | 26.7<br>(0) |
|  | 15.1<br>(38.6) | 56.8<br>(0.4) |
|  | 1.9<br>(9.9) | 39.8<br>(0.6) |

a) The values in the parenthesis represent the yield of acetal or ketal.

that compared with butanal, 2-butanone was more easily hydrogenated to the corresponding alcohol; they explained that the difference in reactivity was attributable to the nature of the adsorbed species.

3,3-Dimethyl-2-butanone, in which hydrogen atoms are substituted by methyl groups at the $\alpha$-position of the carbonyl group, underwent little hydrogenation under the conditions employed, which indicates that steric hindrance around the C=O group strongly affects the rate of hydrogenation. The reactivity order of butanones in the hydrogenation reaction over $Co/Al_2O_3$ ($NO_3$-I) catalyst was 2-butanone > 3-methyl-2-butanone > 3,3-dimethyl-2-butanone. Simoniková et al.[27] investigated the effects of steric hindrance on hydrogenation rate in gas-phase hydrogenation of the above-mentioned butanones over Cu, Rh, and Pt catalyst supported on kieselguhr, and concluded that the equilibrium constant for substrate adsorption on active sites is strongly affected by steric hindrance. The reactivity order obtained in that study is the same as ours.

Aliphatic cyclic ketones cyclohexanone and cyclopentanone also underwent effective hydrogenation over $Co/Al_2O_3$ ($NO_3$-I) catalyst, and cyclohexanone showed the highest reactivity among the reactants used. Compared with aliphatic ketone hydrogenation, hydrogenation of acetophenone and benzophenone, which contain bulky phenyl groups on the carbonyl group, gave relatively high yields of the corresponding alcohols. It was found that the reactivity of aromatic ketones did not depend on the number of bulky phenyl groups, clearly indicating that electrical effects, rather than steric hindrance, play the largest role in determining reactivity.

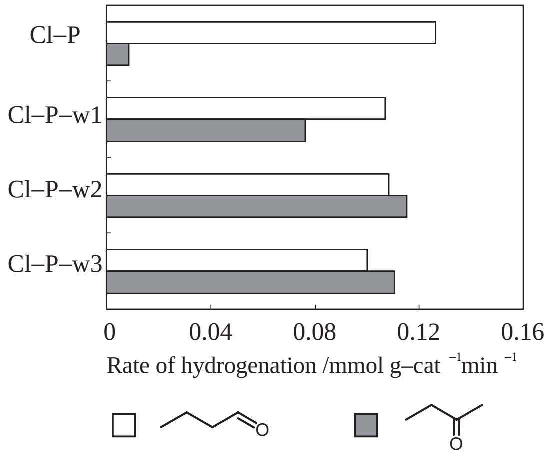


**Figure 1.** Hydrogenation of butylaldehyde and 2-butanone using $NH_3$ aq-washed $Co/Al_2O_3$ (Cl-P).

**Table 2.** Chemical Composition of Original and Washed $Co/Al_2O_3$ Catalysts

| Catalyst | Content/wt % Co[a)] | Content/wt % Cl[b)] | Content/wt % K[b)] | $CO_{ad}$[c)] /µmol g-cat$^{-1}$ |
|---|---|---|---|---|
| Cl-P | 41.2 | 0.76 | <0.01 | 28 |
| Cl-P-w1 | 40.5 | 0.13 | <0.01 | 104 |
| Cl-P-w2 | 40.2 | 0.04 | <0.01 | 114 |
| Cl-P-w3 | 40.3 | 0.04 | <0.01 | 115 |

a) Determined by ICP-AES measurement. b) Determined by XRF measurement. c) The amount of CO chemisorption (amount of surface Co metal).

The activity of $Co/Al_2O_3$ (Cl-P) catalyst for aldehyde hydrogenation was much higher than that of $Co/Al_2O_3$ ($NO_3$-I), whereas no significant activity was observed for ketone hydrogenation over $Co/Al_2O_3$ (Cl-P), except in the case of hydrogenation of cyclohexanone (Table 1). We previously reported that in the hydrogenation of various $\alpha,\beta$-unsaturated aldehydes to $\alpha,\beta$-unsaturated alcohols, $Co/Al_2O_3$ (Cl-P) acts as an effective catalyst,[6] and that the addition of chloride ions to the reaction media dramatically promotes the formation of alcohols over chloride ion-free $Co/Al_2O_3$ ($NO_3$-I).[15] These results strongly suggest that chloride ions have a significant effect on catalytic activity in the hydrogenation of carbonyl groups. To investigate this, we carried out 2-butanone and butanal hydrogenation using washed catalysts $Co/Al_2O_3$ (Cl-P-w1–w3) prepared by washing the precursor ($Co_3O_4/Al_2O_3$) of the $Co/Al_2O_3$ (Cl-P) catalyst with $NH_3$ aqueous solution ($0.01\,mol\,L^{-1}$) before reduction. The amounts of supported Co metal, residual $Cl^-$ and $K^+$ ions contained in the catalysts are summarized in Table 2.

**Table 3.** Competitive Hydrogenation of Butanal and 2-Butanone over $Co/Al_2O_3$ Catalysts[a)]

| Catalyst | Yield/% | |
|---|---|---|
| | 1-Butanol | 2-Butanol |
| Cl-P | 22.3 (3.5) | 0 (0.1) |
| $NO_3$-I | 16.7 (0.7) | 0 (0) |

a) Mixture of 1-butanal (3.0 mL) and 2-butanone (3.0 mL) was used as the reactant.

Table 2 shows that the residual chloride ions were effectively removed from the catalyst (Cl-P) to less than 6% of the initial value by washing it with $NH_3$ aqueous solution, and the amount of active surface metal increased as the amount of residual $Cl^-$ ions, which prevent CO chemisorption, decreased. In that treatment, cobalt metal was slightly bleached from the catalysts. Potassium ions were completely removed during the catalyst preparation because the amounts in all catalysts were not more than 0.01 wt % (lower limit of detection).

Figure 1 shows the rates of butylaldehyde and 2-butanone hydrogenation using the washed and unwashed catalysts. As shown in Figure 1, the rate of 2-butanone hydrogenation over the washed $Co/Al_2O_3$ catalyst (Cl-P-w1) increased dramatically compared with that for the original catalyst (Cl-P). When hydrogenation was carried out using the twice-washed catalyst (Cl-P-w2), the rate was higher than that obtained using the (Cl-P) or (Cl-P-w1) catalyst. The catalytic activities of these catalysts correspond well to the amounts of residual chloride ions present, as shown in Table 2. By contrast, the rate of butanal hydrogenation gradually decreased as the amount of $Cl^-$ decreased. These results clearly indicate that residual $Cl^-$ acts as a poison in supported cobalt catalysts in ketone hydrogenation, but promotes aldehyde hydrogenation. The latter conclusion is in good agreement with that of our previous work[15] on the promoting effect of $Cl^-$ on catalytic activity of $Cl^-$-free $Co/Al_2O_3$ in selective hydrogenation of $\alpha,\beta$-unsaturated aldehydes.

The competitive hydrogenation of butanal and 2-butanone over $Cl^-$-free $Co/Al_2O_3$ ($NO_3$-I) gave fascinating results (Table 3); only butanal was selectively hydrogenated to corresponding alcohol, even though the reactivity of 2-butanone was nearly equal to that of butanal in the hydrogenation using the $Co/Al_2O_3$ ($NO_3$-I) catalyst. This fact suggested that a ketone molecule was more weakly adsorbed on the metal surface than an aldehyde molecule. From the results in Table 2, the new active sites produced by washing $Co/Al_2O_3$ (Cl-P) with $NH_3$ aqueous solution was 86 μmol g$^{-1}$ and that amount was much lower than the amount of residual $Cl^-$ ions (0.76 wt %, 214 μmol g$^{-1}$). Therefore, the low activity of $Co/Al_2O_3$ (Cl-P) catalyst for ketone hydrogenation is attributed to the blockage of ketone adsorption with residual $Cl^-$ ions.

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