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# Effects of Preparation Variables of Supported-Cobalt Catalysts on the Selective Hydrogenation of $\alpha,\beta$-Unsaturated Aldehydes

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The effects of starting salts, supports, added amount of $Na_2CO_3$, and other precipitation variables on catalytic properties of supported cobalt catalysts were studied for the hydrogenation of cinnamaldehyde and crotonaldehyde by using TGA, XRD, and XPS. The catalysts prepared from cobalt chloride always exhibited high selectivities to unsaturated alcohols irrespective of the support employed. The amount of surface chlorine remaining after $H_2$-reduction of the $Co/SiO_2$ precursors prepared from cobalt chloride decreased with increasing amount of $Na_2CO_3$ added as the precipitant, and both activity and selectivity reached maxima at around $Cl/Co = 0.2$ in the catalyst surface. The enhanced selectivity of the catalyst prepared from cobalt chloride was explained by the effects of residual chlorine both in the $H_2$-reduction stage and in the reaction stage; the former leads to a favorable crystallite size distribution (CSD) of cobalt and the latter depresses the hydrogenation of $C{=}C$ double bond. The difference in activities and selectivities of various supported catalysts prepared from cobalt nitrate was discussed based on the difference in the strength of metal-support interaction which leads to different CSDs of cobalt in these catalysts. © 1990 Academic Press, Inc.

## INTRODUCTION

Catalytic hydrogenation of $\alpha,\beta$-unsaturated aldehydes to give unsaturated alcohols is a more difficult problem than the hydrogenation producing saturated aldehydes or saturated alcohols. Various platinum metals have been used for decades, but reports on Ni or Co catalysts are limited (*1–4*). Nickel catalysts are known to catalyze the reduction to saturated aldehydes, whereas Co catalysts are suitable for selective reduction to unsaturated alcohols (*5, 6*). We have studied the structure sensitivity of this reaction by using uniformly dispersed Co–$SiO_2$ catalysts prepared by the reduction of cobalt–chrysotile, $Co_3(OH)_4Si_2O_5$, and found that the selectivity for unsaturated alcohols increases with increasing size of cobalt crystallites in the catalyst (*7*). Satisfactorily high selectivities to unsaturated alcohols were obtained with catalysts having relatively large sizes of Co crystallites. However, the reaction rates were low because of the small surface areas of Co metal in such selective catalysts. Recently we have found that a $Co/SiO_2$ catalyst prepared by a precipitation method from cobalt chloride under appropriate conditions exhibits both high activities and selectivities for the hydrogenation of cinnamaldehyde and crotonaldehyde to corresponding unsaturated alcohols: selectivities of 96 and 84%, respectively, at 50–90% conversion (*8*). In the present study, we examined the effect of chlorine remaining on the surface of this improved catalyst, as well as the effects of the support and the other preparation variables, on the activity and selectivity in this reaction under mild reaction conditions.

## EXPERIMENTAL

### *Catalyst Preparation*

Catalyst precursors (Co : support = 1 : 1 by weight unless otherwise noted) were prepared by a precipitation method with sodium carbonate by using cobalt chloride or nitrate as the starting salt. The typical proce-

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dure to prepare a $SiO_2$-supported precursor was as follows: A solution (25 ml) of $Na_2CO_3$ in hot water was added to an aqueous suspension (50 ml) containing 2.0 g of $SiO_2$ (Silica gel no. 1, Nakarai Chemicals, 600 $m^2g^{-1}$) and cobalt(II) chloride (34 mmol, Co = 2.0 g) at 90–93°C with vigorous stirring and aged for 1 h, followed by washing three times with hot water and drying at 120°C for 44 h (this procedure is called severe conditions here). The detailed operations are identical to those described for the preparation of $SiO_2$-supported basic nickel carbonate (*9*). With other supports, precipitation was carried out at 75°C by using cobalt nitrate and the precipitate was aged for 15 min, and washed and dried at 110°C for 20 h (this procedure is called standard conditions here). One gram of a dried precursor was reduced in a hydrogen flow of 8 liter $h^{-1}$ at 400°C for 2 h to give silica-supported catalysts and at 350°C for 1 h to give the other catalysts unless otherwise noted.

### *Hydrogenation*

Crotonaldehyde or cinnamaldehyde, dried and distilled before use, was hydrogenated usually in ethanol (0.2–1.0 *M*) with a freshly reduced catalyst at 30°C under a hydrogen pressure of 1 MPa by using a pressure-resistant glass autoclave equipped with a magnetic stirring system. The stirring speed was high enough so that the hydrogenation rates were independent of mass transfer. The initial hydrogenation rate ($r_0$) was obtained from the conversion of the reactant measured by gas–liquid chromatography. The selectivities at different conversions were determined as the molar percentages of unsaturated alcohol in all the products and extrapolated to find the initial selectivity ($S_0$).

### *Analysis*

Thermogravimetric analyses (TGA) of catalyst precursors were carried out with a Shimadzu DT-30 thermal analyzer by heating in a stream of hydrogen to 1000°C at a rate of 10°C $min^{-1}$. The extent of reduction of a resulting catalyst was estimated from the weight loss in the range above 200°C by assuming that the reduction was complete at 1000°C. The weight loss in the range of 200–1000°C was found to be very close to, but more reliable than, the theoretical weight loss for the reduction of anhydrous basic cobalt carbonate to cobalt metal; the composition of silica-supported basic cobalt carbonate varies with the preparation conditions as mentioned below.

Powder X-ray diffraction (XRD) patterns of the reduced catalysts were measured using a Shimadzu VD-1 diffractometer with Cu$K\alpha$ radiation. The mean crystallite size ($D_c$) of Co in the reduced catalyst was calculated mainly from the half-maximum breadth of the (111) peak of fcc Co metal ($\beta$-Co) after correction for instrumental broadening (*10*). For comparison, hydrogen adsorption measurements were performed at around 25°C after evacuation of the reduced samples at 200°C for at least 30 min to less than $5 \times 10^{-5}$ Torr according to the method of Reuel and Bartholomew (*11*).

X-ray photoelectron spectra of $Co/SiO_2$ catalysts were measured using a Hitachi 507 photoelectron spectrometer with Al$K\alpha$ radiation. The atomic ratios of residual chlorine to cobalt in the catalyst surface were estimated from the area intensities of Co $2P_{1/2}$ and Cl $2P$ peaks after correction for atomic sensitivities which were obtained by measuring the spectra for $CoCl_2$. The detailed procedures were reported elsewhere (*12*).

## RESULTS AND DISCUSSION

### *Effects of Precipitation Conditions and Cobalt Salts*

Preliminary experiments showed that the composition and reducibility of precipitated precursors of $Co/SiO_2$ catalysts, namely, silica-supported basic cobalt carbonate, vary with the change in the precipitation conditions similarly to the case of $Ni/SiO_2$ catalysts (*13*). The reducibility of the precursor, and hence the crystallite size of cobalt in the reduced catalyst, decreased with an increase in the precipitation temperature

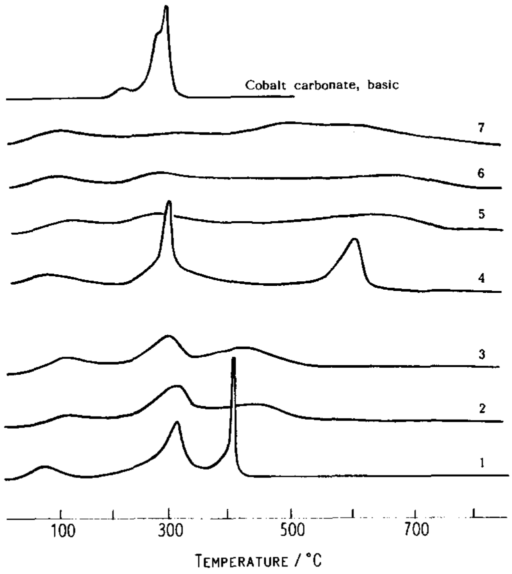

FIG. 1. DTG-in-$H_2$ profiles of the $Co/SiO_2$ precursors prepared from different cobalt salts following standard or severe conditions. Sample numbers as in Table 1.

probably because of the increasing metal-support interaction (*7*). However, the effects of other factors in preparation on the properties of cobalt precursors were more complicated than those in the preparation of $Ni/SiO_2$ catalysts. Mild conditions often led to incomplete precipitation of cobalt species. Therefore, in this work, precipitation was carried out under relatively severe conditions.

Figure 1 shows the reduction behavior of the $Co/SiO_2$ precursors prepared from different cobalt salts following standard (nos. 1–3) and severe (nos. 4–7) conditions. The differential thermogravimetric (DTG) peak around 300°C corresponds to the weight loss due to the decomposition and reduction of basic cobalt carbonate without metal-support interaction. The broad peak extending from 350 to 500°C for the precursor prepared from cobalt nitrate or acetate is attributable to the reduction of cobalt species having interaction with the support, although the nature of the interaction remains unknown. Reuel and Bartholomew suggested the formation of surface cobalt spinels or silicates for the $Co/SiO_2$ catalyst prepared by controlled-pH precipitation as a consequence of more uniform and intimate interaction of the cobalt with the support (*11*). Cobalt chrysotile, a kind of cobalt silicate, is reduced in the temperature range from 400 to 700°C as we reported previously (*7*). As can be seen from Fig. 1, severe conditions of precipitation and the use of excess $Na_2CO_3$ resulted in a decrease in the fraction of the cobalt species without support interaction and also in a shift of the second reduction peak to a higher temperature. These observations indicate that the severer precipitation conditions cause the stronger metal-support interaction as expected from the previous results for precipitated $Ni/SiO_2$ catalysts (*13*).

The sharp and strong peak observed at around 420°C for the precursor prepared from cobalt chloride under standard conditions indicates the abrupt reduction of residual chloride (*14*), which facilitates the reduc-

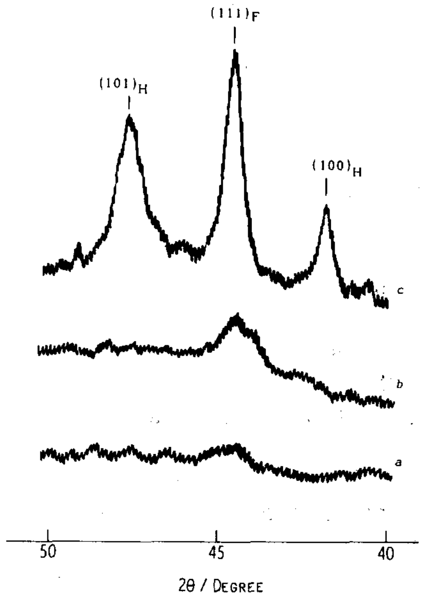

FIG. 2. X-ray diffraction patterns of the $Co/SiO_2$ catalysts prepared under standard conditions from (a) cobalt acetate (precursor 3), (b) cobalt nitrate (precursor 2), and (c) cobalt chloride (precursor 1), and $H_2$-reduced at 400°C for 2 h.

TABLE 1

Effects of Starting Cobalt Salt on the Properties of Co/$SiO_2$ Catalysts for the Hydrogenation of Cinnamaldehyde[a]

| Precursor number | Co Salt | Alkali[b] | Preparation conditions[c] | Reduction degree (%) | $D_c$[d] (nm) | $H_2$ uptake[e] (mol·g$^{-1}$) | $S_0$[f] (%) | $S_{50}$[g] (%) | $r_0$[h] (mmol · min$^{-1}$g$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Chloride | 1.0 | Standard | 99.9 | 18 | 18.0 | 94 | 93 | $4.1 \times 10^{-2}$ |
| 2 | Nitrate | 1.0 | Standard | 87.0 | 7 | 202 | 81 | 77 | $4.5 \times 10^{-1}$ |
| 3 | Acetate | 1.0 | Standard | 67.8 | <4 | 149 | 76 | 68 | $2.2 \times 10^{-1}$ |
| 4 | Chloride | 1.1 | Severe | 79.6 | 7–9 | 9.8 | 98 | 96 | $1.2 \times 10^{-1}$ |
| 5 | Nitrate | 1.1 | Severe | 46.3 | 6 | 32.9 | 78 | 71 | $8.3 \times 10^{-2}$ |
| 6 | Acetate | 1.1 | Severe | 48.9 | 4–5 | 41.7 | 80 | 59 | $8.8 \times 10^{-2}$ |
| 7 | Sulfate | 1.1 | Severe | 50.0 | *i* | 32.7 | 70 | — | $5.2 \times 10^{-3}$ |

[a] Cinnamaldehyde in ethanol (0.2 *M*) was hydrogenated at 30°C under 1.0 MPa of hydrogen.

[b] Molar ratio of $Na_2CO_3$ to Co salt.

[c] See text.

[d] Mean crystallite size of cobalt determined by X-ray diffraction line broadening.

[e] Irreversible $H_2$ uptake at 25°C per gram of catalyst.

[f] Initial selectivity to cinnamyl alcohol.

[g] Selectivity to cinnamyl alcohol at 50% conversion.

[h] Initial reaction rate.

[i] XRD peak was not detected.

tion of the cobalt species interacting with support and results in the formation of large crystallites of cobalt metal in the reduced catalyst as shown in Fig. 2. When the crystallite size was small, a hexagonal close pack (hcp) structure was not observed even at temperatures below 450°C in agreement with the results of previous investigators (*11, 15, 16*). Among the catalysts examined here, only those prepared from cobalt chloride showed both hcp and fcc sructures in XRD patterns.

Table 1 lists the catalytic properties in the hydrogenation of cinnamaldehyde of various Co/$SiO_2$ catalysts prepared by using different cobalt salts under standard (nos. 1–3) or severe (nos. 4–7) conditions. The catalyst prepared from cobalt chloride under standard conditions (no. 1) had a large value of $D_c$ and exhibited a high selectivity but low activity as we reported previously (*7*). It is noteworthy that the catalyst prepared from cobalt chloride under severe conditions with 10 mol% excess $Na_2CO_3$ (no. 4) showed an even higher selectivity than the catalyst prepared under standard conditions (no. 1), although the mean crystallite size of cobalt in the former catalyst was considerably decreased and hence the activity was relatively high. The specific activity of this improved catalyst is of the order for Raney cobalt catalyst having a selectivity as low as 73% under the same reaction conditions (*8*). With the catalysts prepared from other cobalt salts, severer conditions in the preparation resulted in the catalysts with lower activities and selectivities as expected from the lower reducibility and the smaller $D_c$ values of these catalysts. The use of cobalt sulfate led to an almost inactive catalyst with a very low selectivity probably because of the detrimental effect of remaining sulfur.

Although Reuel and Bartholomew (*11*) recommended $H_2$ adsorption for measurement of cobalt crystallite size in Co/$SiO_2$, Co/$Al_2O_3$, and Co/C catalysts, they also reported that less than one monolayer coverage of $H_2$ occurred on Co/$TiO_2$. Moreover, the $H_2$ uptake on the Co/$SiO_2$ catalyst containing residual chlorine was considerably depressed as shown in Table 1, similarly to the case of Cl-containing nickel surfaces (*14*,

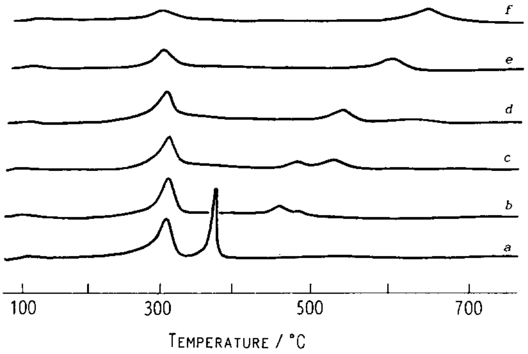

FIG. 3. DTG-in-$H_2$ profiles of the Co/$SiO_2$ precursors prepared under severe conditions from cobalt chloride by using different amounts of $Na_2CO_3$: the molar ratios of $Na_2CO_3$ to cobalt chloride are (a) 1.0, (b) 1.045, (c) 1.05, (d) 1.07, (e) 1.1, and (f) 1.2.

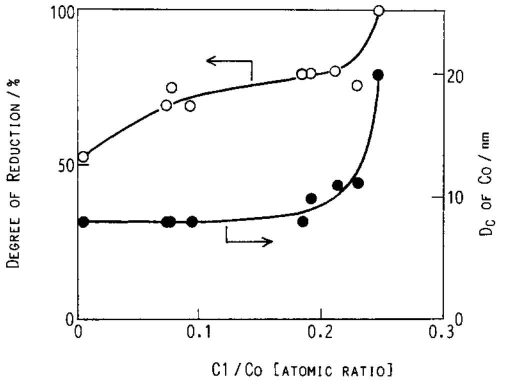

FIG. 4. Dependence of the degree of reduction (○) and the mean crystallite size of Co (●) in Co/$SiO_2$ catalysts on the amount of surface residual chlorine.

17). The significantly small amounts of $H_2$ uptake on the catalysts prepared under severe conditions are probably attributed to the low extents of reduction. It was reported that $H_2$ adsorption on cobalt was highly activated and was kinetically limited by the extent of reduction (*11*). Surface migration of oxygen from unreduced cobalt oxides may be conceivable during evacuation prior to the $H_2$ adsorption measurement. Therefore, we estimated the $D_c$ values for all the catalysts examined here from X-ray line broadening.

It is well known that the chloride ion remaining in the precursor is difficult to be removed during $H_2$-reduction. The amount of the residual chlorine in a precursor is considered to depend on the amount of alkali used in the precipitation. Therefore, we next examined the effects of the amount of added alkali on the properties of resultant catalysts in detail.

### *Effect of the Amount of Added $Na_2CO_3$*

Figure 3 shows the effect of the amount of $Na_2CO_3$, used in the precipitation under severe conditions described above, on the reduction behavior of dried precursors. The increase in the amount of added $Na_2CO_3$ led to the disappearance of the sharp peak around 400°C together with the decrease of the main peak around 300°C and with the shift of the second broad peak to a higher temperature. This means that the amount of cobalt chloride remaining in the precursor decreases and the interaction of the precipitated cobalt species with the support becomes stronger with increasing amount of added $Na_2CO_3$, leading to a change in the property of the reduced catalyst.

The XPS measurements showed that the amount of residual chlorine in the surface of reduced catalysts decreased almost linearly

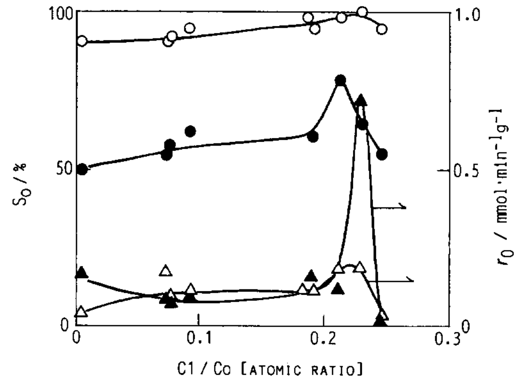

FIG. 5. Dependence of the catalytic properties of Co/$SiO_2$ catalysts on the amount of surface residual chlorine: ○ and △, initial selectivity and activity for the hydrogenation of cinnamaldehyde; ● and ▲, those for crotonaldehyde.

TABLE 2

Effect of Chloride Addition on the Hydrogenation of Cinnamaldehyde over $Co/SiO_2$ Catalyst[a]

| Run no. | Method of Cl addition | $D_c$[b] (nm) | $S_0$[c] (%) | $S_{50}$[d] (%) | $r_0$[e] (mmol · $min^{-1}g^{-1}$) |
|---|---|---|---|---|---|
| 1 | Without Cl addition | 6 | 78 | 71 | $8.3 \times 10^{-2}$ |
| 2 | 0.1 mmol of HCl added to the solvent | | 83 | 63 | $7.5 \times 10^{-2}$ |
| 3 | 0.3 mmol of HCl added to the solvent | 4–5 | 87 | <60 | $4.8 \times 10^{-2}$ |
| 4 | 0.15 mmol of $CoCl_2$ added to the solvent | 6 | 88 | <42 | $3.3 \times 10^{-2}$ |
| 5 | 0.3 mmol of $CoCl_2$ added to the solvent | 6 | 89 | <33 | $2.7 \times 10^{-2}$ |
| 6 | The precursor reduced by HCl-containing (1%) hydrogen at 400°C for 30 min followed by $H_2$ reduction at 400°C for 70 min | 15 | ~100 | 75 | $5.8 \times 10^{-2}$ |

[a] The precursor prepared from cobalt nitrate (no. 5 in Table 1) was used.

[b] Mean crystallite size of cobalt measured for the catalysts after reaction.

[c] Initial selectivity to cinnamyl alcohol.

[d] Selectivity to cinnamyl alcohol at 50% conversion.

[e] Initial reaction rate.

with increasing amount of added $Na_2CO_3$ and became negligibly small when 20 mol% excess of $Na_2CO_3$ was added.

Figures 4 and 5 show the dependence of the physical and catalytic properties on the atomic ratio of residual chlorine to cobalt in the catalyst surface. The reducibility of the precursor and the mean crystallite size of cobalt in the reduced catalyst decreased with increasing amount of added alkali, that is, with decreasing amount of surface chlorine, as expected above from the results of TG measurements. On the other hand, both selectivity and activity of these catalysts in the hydrogenation of cinnamaldehyde and crotonaldehyde had maximum values at around Cl/Co = 0.22. The presence of a small amount of chlorine in the precursor will facilitate the reduction of cobalt species interacting with support as can be seen from Fig. 3 and increase the size of the smaller crystallites, resulting in a homogeneous crystallite size of cobalt during $H_2$-reduction in analogy with the reduction of Cl-promoted $Ni/SiO_2$ precursors (*14*). This explains the increase in the selectivity in the range of $Cl/Co < 0.2$ without the apparent increase in the value of $D_c$ shown in Fig. 4. A too large amount of residual chlorine is undesirable because it leads to an inactive catalyst with very large sizes of cobalt crystallites and also because it blocks the surface and inhibits the selective hydrogenation.

### *Effect of Chlorine in the Reaction*

Hotta and Kubomatsu (*5*) reported an enhanced selectivity of Raney cobalt catalyst modified with metal chlorides by adding them to the reaction mixture. Accordingly, not only the effect of the residual chlorine on the reduction stage, i.e., on the CSD of cobalt in the catalyst, but also the effect of surface chlorine in the reduced catalyst on the reaction stage should be considered as the origin of the high selectivity.

A $Co/SiO_2$ catalyst prepared from cobalt nitrate, having relatively low selectivity, was used to examine the effect of chlorides added to the solvent at the reaction stage. As shown in Table 2, the addition of hydrogen chloride or cobalt chloride increased the initial selectivity to a certain extent, whereas the selectivity at 50% conversion was lower than that for the reaction without chloride addition. On the other hand, the catalyst reduced in a stream of HCl-containing hydrogen exhibited an extremely high initial selectivity. Therefore, the enhanced selectivity of the catalyst prepared from cobalt chloride cannot be attributed only to the

TABLE 3

Comparison of Individual Hydrogenation Rates[a] of C=C and C=O Double Bonds over $Co/SiO_2$ Catalysts with and without Residual Chlorine

| Catalyst | $r(C{=}C)^b$ (mmol · $min^{-1}g^{-1}$) | $r(C{=}O)^c$ (mmol · $min^{-1}g^{-1}$) | $r(C{=}C)/r(C{=}O)$ |
|---|---|---|---|
| Prepared from cobalt nitrate (no. 2 in Table 1) | 2.8 | 0.18 | 15.5 |
| Prepared from cobalt chloride (no. 4 in Table 1) | 0.041 | 0.082 | 0.5 |

[a] Hydrogenation was carried out in ethanol at 30°C under 0.1 MPa of $H_2$.

[b] Initial hydrogenation rate for cinnamyl alcohol.

[c] Initial hydrogenation rate for phenyl propionaldehyde.

action of the chloride ion on the reaction stage, but the effect of the residual chloride during $H_2$-reduction is also important; the favorable CSD of cobalt as a result of the latter effect is intrinsic and may not change so much during reaction, while the adsorbed chlorine may desorb and become ineffective as the reaction proceeds.

The activities of two kinds of $Co/SiO_2$ catalyst with and without residual chlorine, i.e., prepared from cobalt chloride and cobalt nitrate, respectively, having similar size of cobalt crystallites, were compared in the hydrogenation of cinnamyl alcohol (C=C bond) and phenyl propionaldehyde (C=O bond) at 30°C under atomospheric pressure of hydrogen. As shown in Table 3, the hydrogenation of C=C bond on the catalyst prepared from cobalt chloride was strongly depressed compared to the reaction of C=O bond. This directly explains the high selectivity of the $CoCl_2$-originating catalyst in the hydrogenation of unsaturated aldehydes.

In the preceding paper (*7*), we compared the activities of two $Co/SiO_2$ catalysts, having different sizes of cobalt crystallites but prepared from the same source, in the hydrogenation of unsaturated alcohols (C=C bond) and saturated aldehydes (C=O bond). It was shown that, although specific activities for both reactions were depressed on the catalyst with large cobalt crystallites, the relative adsorption strength of unsaturated alcohol was always smaller for the catalyst with larger cobalt crystallites. This explained the higher selectivity of this catalyst in the hydrogenation of $\alpha,\beta$-unsaturated aldehydes to unsaturated alcohols; unsaturated alcohols on larger crystallites are more easily removed and replaced by saturated or unsaturated aldehydes before being hydrogenated to saturated alcohols.

On the basis of these results, the much enhanced selectivity of the catalyst prepared from cobalt chloride and a slight excess of $Na_2CO_3$ can be explained by both effects of residual chlorine: the effect of the surface chlorine on the reaction stage and the effect of chloride remaining in the precursor which leads to a homogeneous crystallite size of cobalt during $H_2$-reduction just as in the case of Cl-promoted $Ni/SiO_2$ catalysts (*14*). Therefore, the increased selectivity of Raney-cobalt catalyst modified with $FeCl_2$, reported by Hotta and Kubomatsu (*5*), appears to be attributable to the chlorine and not necessarily to the iron.

### *Support Effects*

Various supports as listed in Table 4 were examined in the preparation of supported cobalt catalysts following standard conditions. The reduction temperature for each precursor was selected to meet the requirement that the extent of reduction was higher than 90%. As shown in Table 5, all catalysts prepared from cobalt chloride exhibited re-

TABLE 4

Characteristics of Supports Used for Preparation of Cobalt Catalysts

| Support | Notation | Source | Particle size | BET surface area ($m^2g^{-1}$) | Structure |
|---|---|---|---|---|---|
| $TiO_2$ | UFP–TIO | Idemitsu Kosan Co. | 10–30 nm | 100–150 | Amorphous |
| | JRC–TIO-4 | Catalysis Society of Japan | ~21 nm | 150 ± 15 | Anatase |
| | JRC–TIO-3 | Catalysis Society of Japan | 30–50 nm | 40 | Rutile |
| $SiO_2$ | Aerosil-300 | Nippon Aerosil | 7 nm | 300 ± 30 | |
| | Silica gel no. 1 | Nacalai Tesque | 80–250 μm | 600 | |
| $Al_2O_3$ | AKP–G | Sumitomo Chemical Co. | <100 nm | 110–170 | γ-Alumina |
| | A-11 | Sumitomo Chemical Co. | 35–45 μm | 120 | γ-Alumina |
| $ZrO_2$ | NS–0Y | Nippon Shokubai Kagaku Kogyo Co. | 37 nm | 27 | |
| | NS-8Y | | 13 nm | 80 | $Y_2O_3$ 8 mol% |
| C | AC | Wako Pure Chemical Industries | | 1300 | |

TABLE 5

Selective Hydrogenation of Crotonaldehyde on Supported Cobalt Catalysts

| Catalyst | Support | Co Salt[a] | Reduction temp. (°C)/time (h) | $D_c$[b] (nm) | $S_{50}$[c] (%) | $r_0$[d] (mmol · $min^{-1}g^{-1}$) |
|---|---|---|---|---|---|---|
| $Co/TiO_2$ | UFP–TIO | Nitrate | 350/1 | 17 | 15 | $8.1 \times 10^{-1}$ |
| | UFP–TIO | Chloride | 350/1 | 23 | 75 | $6.9 \times 10^{-2}$ |
| | JRC–TIO-4 | Nitrate | 350/1 | 17 | 25 | $2.7 \times 10^{-1}$ |
| | JRC–TIO-4 | Chloride | 350/1 | 31 | 80 | $6.4 \times 10^{-2}$ |
| | JRC–TIO-4 | Nitrate[e] | 350/1 | 10 | 18 | $4.3 \times 10^{-1}$ |
| | JRC–TIO-4 | Nitrate[e] | 500/1 | 12 | 22 | $5.7 \times 10^{-1}$ |
| | JRC–TIO-4 | Nitrate[e] | 700/1 | 13 | 23 | $3.6 \times 10^{-1}$ |
| | JRC–TIO-3 | Nitrate | 350/1 | 25 | 24 | $7.4 \times 10^{-2}$ |
| $Co/SiO_2$ | Aerosil-300 | Nitrate | 500/2 | 5 | 27 | $1.3 \times 10^{-1}$ |
| | Aerosil-300 | Chloride | 500/2 | 10 | 73 | $2.9 \times 10^{-1}$ |
| | Silica gel no. 1 | Nitrate | 400/2 | 8 | 32 | $4.4 \times 10^{-1}$ |
| | Silica gel no. 1 | Chloride | 400/2 | 9 | 80 | $2.7 \times 10^{-1}$ |
| $Co/Al_2O_3$ | AKP–G | Nitrate | 350/1 | 12 | 29 | $1.7 \times 10^{-1}$ |
| | AKP–G | Chloride | 350/1 | 14 | 65 | $7.4 \times 10^{-2}$ |
| | A-11 | Nitrate | 350/1 | 22 | 32 | $1.7 \times 10^{-1}$ |
| | A-11 | Chloride | 350/1 | 29 | 74 | $1.5 \times 10^{-2}$ |
| $Co/ZrO_2$ | NS–OY | Nitrate | 350/1 | 16 | 28 | $3.1 \times 10^{-2}$ |
| | NS-8Y | Nitrate | 350/1 | 20 | 23 | $6.5 \times 10^{-2}$ |
| Co/C | AC | Nitrate | 300/1 | 25 | 24 | $1.0 \times 10^{-1}$ |

[a] When chloride was used, 10 mol% excess (instead of equimolar) alkali was added.

[b] Mean crystallite size of cobalt determined by X-ray diffraction line broadening.

[c] Selectivity to crotyl alcohol at 50% conversion.

[d] Initial reaction rate at 30°C in ethanol under 1.0 MPa of hydrogen.

[e] Cobalt loading is 17 wt% instead of 50 wt%.

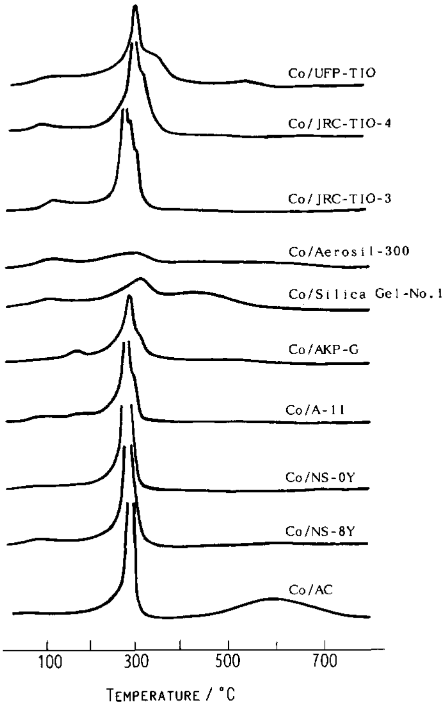

FIG. 6. DTG-in-$H_2$ profiles of various Co catalysts (Co loading = 50 wt%) prepared from cobalt nitrate and the supports listed in Table 4.

markably high selectivities irrespective of the support employed. This is attributable to the effect of remaining chloride as discussed above. Therefore, the catalysts prepared by using cobalt nitrate were compared with each other to examine the support effects. Figure 6 shows the reduction behavior of the precursors of these catalysts. The precursors having sharp reduction peaks at around 300°C, e.g., those supported on JRC-TIO-3, A-11, $ZrO_2$, and AC, are regarded to have large fraction of the cobalt species without metal-support interaction and they resulted in catalysts with relatively large values of $D_c$ and low activities. On the other hand, silica-supported precursors were reduced gradually with increasing temperature and produced catalysts with relatively small $D_c$. As for selectivities of the catalysts prepared by using a given kind of support, the use of ultrafine particles as the support, e.g., Aerosil-300 and AKP-G, always led to a smaller value of $D_c$ and hence to a lower selectivity than those for the catalysts prepared with the support having larger particle sizes. Such effects of the particle size of support were also observed in a structure-sensitive hydrogenation on $Ni/SiO_2$ catalysts (*18*).

With $TiO_2$-supported catalysts, SMSI effects might be expected particularly at higher reduction temperatures which might cause changes in catalytic properties. Vannice and Sen (*19*) recently reported an enhanced activity and selectivity of the $Pt/TiO_2$ catalyst reduced at a relatively high temperature (500°C) in the hydrogenation of crotonaldehyde to crotyl alcohol. An extremely enhanced activity in propene hydrogenation on a $Co/TiO_2$ catalyst, prepared by an alkoxide technique and reduced at 700°C, was reported and explained in terms of the redispersion of metallix cobalt particles caused by the phase transformation of $TiO_2$ from anatase to rutile form (*20*). With these results in mind, we examined the effect of reduction temperature on the properties of 17% $Co/TiO_2$(JRC–TIO-4) catalysts. As shown in Table 5, higher reduction temperatures led to a slightly increased $D_c$ and selectivity ($S_{50}$) but not to an enhanced activity.

The above observations are in fair agreement with the crystallite-size effect in this reaction (*7*). The structure sensitivity on such relatively large crystallites is not so suprising if we take into account the higher probability for obtaining large cobalt ensembles on larger crystallites, by analogy with the modified $Ni/SiO_2$ catalysts for enantioselective hydrogenation (*21*). However, the relatively high selectivity of the $Co/SiO_2$ catalysts cannot be explained merely in terms of the mean crystallite sizes of cobalt. As previously discussed for a structure-sensitive hydrogenation on supported nickel catalysts (*13, 22*), not only the $D_c$ values but also the CSDs are very important especially when we compare the selectivities of supported catalysts having different nature of metal-support interaction.

Two typical catalysts, $Co/SiO_2$(Silica gel

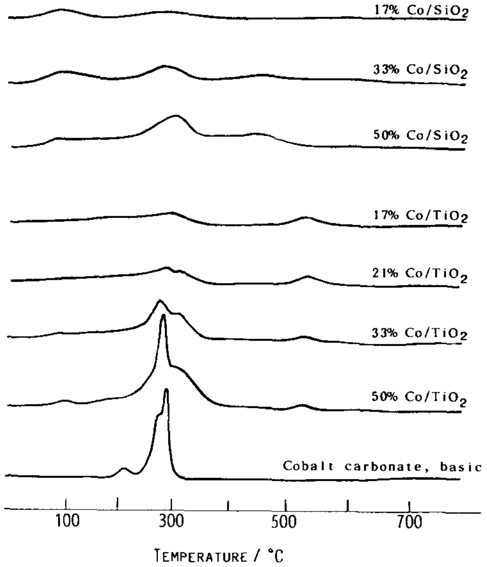

FIG. 7. DTG-in-$H_2$ profiles of $Co/SiO_2$ (Silica gel no. 1) and $Co/TiO_2$ (UFP–TIO) catalysts with different Co loadings.

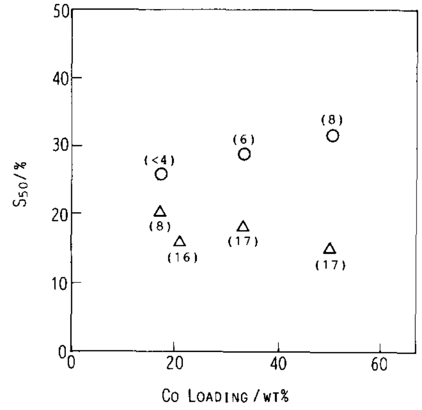

FIG. 8. The selectivities of $Co/SiO_2$ (○) and $Co/TiO_2$ (△) catalysts shown in Fig. 7 for hydrogenation of crotonaldehyde. Figures in parentheses indicate the mean crystallite sizes of Co obtained from X-ray line broadening.

no. 1) and $Co/TiO_2$ (UFP–TIO) were used to examine the effect of CSD. Figure 7 shows the reduction behavior of these catalysts with different cobalt loadings. In the case of $TiO_2$-supported precursors, the increase in the cobalt loading resulted in an increase in the fraction of cobalt species without metal-support interaction, i.e., the species reducible at around 300°C, leading to the predominant formation of large and inactive cobalt crystallites. The remaining part of the cobalt species, having strong interaction with the support, is reduced at higher temperatures and will yield small and active crystallites with low selectivity. The presence of such small crystallites of cobalt explains the relatively low selectivity of $Co/TiO_2$ catalysts in spite of the large $D_c$ as determined by XRD method. On the other hand, the DTG profiles of $Co/SiO_2$ precursors show that all kinds of cobalt species having different strengths of metal-support interaction increase with an increase in cobalt loading homogeneously in the overall temperature range, which will lead to a uniform increase in the size of cobalt crystallites, and hence to an increase in the selectivity, with increasing cobalt loading. As shown in Fig. 8, the experimental results of selectivities for the hydrogenation of crotonaldehyde are consistent with these considerations. The above results strongly suggest that the selectivity of various supported catalysts depends primarily on the crystallite size of cobalt, and that the difference in the CSD of cobalt, resulting from the difference in the strength of metal-support interaction, explains the different selectivities as well as different activities of various supported catalysts other than those prepared from cobalt chloride.

## CONCLUSIONS

1. The catalysts prepared by using cobalt chloride and 10 mol% excess $Na_2CO_3$ exhibit high selectivities to unsaturated alcohols irrespective of the support employed.

2. Both activity and selectivity of $Co/SiO_2$ catalysts prepared from cobalt chloride become maximum at around Cl/Co = 0.2 in the catalyst surface after $H_2$-reduction as determined by XPS measurement.

3. The residual chloride in the catalyst precursor leads to a homogeneous crystallite size of cobalt during $H_2$-reduction by

facilitating the reduction of cobalt species with metal-support interaction, resulting in a high selectivity of the catalyst.

4. The surface chlorine remaining in the catalyst after $H_2$-reduction depresses the hydrogenation of C=C double bond, also leading to an increased selectivity.

5. The difference in activities and selectivities of various supported catalysts prepared from cobalt nitrate and different supports is explained in terms of the difference in CSDs of cobalt in these catalysts as a consequence of the different strength of metal-support interaction.

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