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Independent Effect of Particle Size and Reduction Extent on CO Hydrogenation over Alumina-Supported Cobalt Catalyst

INTRODUCTION

The catalytic hydrogenation of carbon monoxide on cobalt catalysts has been known to be affected by two factors: the cobalt loading (or the size of cobalt particle) (*1*, *2*) and the extent of reduction (*3*, *4*). Independent investigations of the effects of the two factors on CO hydrogenation, however, were rarely attempted because the changes in the cobalt loadings in supported cobalt catalysts were accompanied inevitably by changes in the extent of reduction, i.e., higher extent of reduction for higher cobalt loading.

Bartholomew and co-workers (*1*, *2*) observed the increasing CO hydrogenation activity with increasing cobalt loading (or particle size) in supported catalysts, but the resultant changes in activity might have also resulted from the changes in the extent of reduction. The effect of the extent of reduction on CO hydrogenation activity was performed on cobalt foil by Palmer and Vroom (*3*), who found that the poorly reduced cobalt catalysts were about two orders of magnitude more active than well-reduced ones.

In this study, CO hydrogenation was performed on partially reduced alumina-supported cobalt catalysts having different cobalt loadings (or particle sizes) with different extents of reduction, and experiments were carried out to delineate their independent effects on CO hydrogenation.

EXPERIMENTAL

Powders of γ-Al_2O_3 were provided by Strem Chemicals and had a mean diameter of 74 μm. Hydrogen and helium (Matheson, 99.999%) were further purified by using Deoxo catalyst followed by a molecular sieve trap. Carbon monoxide (Takachiho, 99.95%) was passed through a molecular sieve trap for the removal of water and metal carbonyl.

Alumina-supported cobalt catalysts were prepared by the incipient wetness method. After the pores of alumina were filled with an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (Aldrich, 99.9%) to an appropriate cobalt loading, the catalysts were dried overnight in air at 90°C. Following calcination with oxygen at 500°C for 24 h, the catalysts were reduced with hydrogen by heating of the catalysts linearly at 5°C/min to the reduction temperature (300–525°C) and maintaining the temperature for a desired time.

All the catalysts used in the present study will be abbreviated by the symbols (cobalt loading, wt%)-(alumina support, A)-(reduction temperature, °C)-(reduction time, h). The symbol "5-A-500-10," for example, denotes 5 wt% Co/γ-Al_2O_3 catalyst which was reduced with hydrogen at 500°C for 10 h.

The adsorption isotherms were measured at 25°C in a conventional Pyrex glass volumetric adsorption apparatus. The gas uptakes were obtained by extrapolating the straight portion of the isotherms to zero pressure and the irreversible uptakes were determined by the difference between the total and the reversible uptakes. The extent of reduction was measured by oxygen titration at 400°C according to the method of Batholomew and Farrauto (*5*) where the reduced cobalt metal is assumed to react with oxygen to Co_3O_4 (*6*). The dispersion of cobalt particle was calculated from the total

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TABLE 1

Chemisorption Data for the Alumina-Supported Cobalt Catalysts with Cobalt Loading and Reduction Extent

Catalyst	Extent of reduction[a] (%)	Total H_2 uptake[b] (μmole/g cat.)	$\left(\frac{CO}{H}\right)_{irr.}$[c]	Dispersion[d] (%)
2-A-500-10	48.6	3.5	2.3	7.6
5-A-500-10	52.5	8.7	1.5	5.1
10-A-500-10	56.6	15.7	1.1	3.9
20-A-500-10	74.4	19.4	0.9	1.5
10-A-300-0.7	7.9	0.5	15.7	0.9
10-A-300-4	15.8	1.1	8.9	1.0
10-A-350-4	17.2	1.4	6.0	1.5
10-A-400-4	19.5	4.1	1.9	2.8
10-A-450-4	22.5	6.3	1.1	4.0
10-A-500-4	35.7	9.1	1.1	4.0
10-A-525-4	48.6	13.2	1.1	4.0
10-A-500-10	56.6	15.7	1.1	4.0
10-A-500-22	62.8	18.8	1.1	4.0

[a] Reduction extent calculated from O_2 titration at 400°C, assuming formation of Co_3O_4 (*6*).

[b] Total H_2 uptake measured at room temperature.

[c] Ratio of irreversible uptake measured at room temperature.

[d] Dispersion calculated from the total hydrogen uptake multiplied with the adsorption activation factor (*7*). The adsorption activation factors for 2, 5, 10, and 20 wt% Co/γ-Al_2O_3 catalysts were assumed to be 2.0, 1.5, 1.3, and 1.0, respectively.

hydrogen uptake multiplied by the activation factor and divided by the extent of reduction (*7*).

Transmission electron microscopy was performed with a JEOL 200CX microscope using 160-keV electrons. About 60 measured points were used to calculate the average value of cobalt particle size.

CO hydrogenation reaction was performed in a differential reactor operating at atmospheric pressure, 250°C, and a H_2/CO ratio of 3. Products were passed through a heated transfer line to a gas chromatograph (Hewlett–Packard 5710A) with TCD and FID detectors connected in series. Products were separated in a 4 ft × $\frac{1}{8}$ in. column packed with Chromosorb 102. The column temperature was held 2 min at 50°C and then heated to 150°C at 16°C/min. The rate reached steady state 1 h after the introduction of the reactant gases and the reaction rates were measured after 2 h for all catalysts.

RESULTS AND DISCUSSION

In Table 1 are listed the chemisorption data for the catalysts which have 2 to 20 wt% cobalt loadings under the same reduction condition (500°C, 10 h) and 10 wt% catalysts with different reduction extents. As reported previously by Reuel and Bartholomew (*7*), with increasing cobalt loading the dispersion and the $(CO/H)_{irr}$ ratio decrease, while the extent of reduction increases. But since it is not well defined whether the changes in $(CO/H)_{irr}$ with cobalt loading are due to the particle size or to the extent of reduction, it is more desirable to investigate the changes in $(CO/H)_{irr}$ with the extent of reduction with constant cobalt particle size. To do this CO and H_2 chemisorption experiments were carried out on

10 wt% Co/γ-Al_2O_3 catalysts having different extents of reduction. The various extents of reduction could be obtained by controlling the reduction temperature and time.

It should be noted that the catalysts used in the present study were a priori calcined with oxygen at 500°C for 24 h and it is believed that all cobalt metals loaded were oxidized to cobalt oxides. The size of the cobalt particles, in which the inner core of cobalt oxide seems to be encapsulated by reduced cobalt metal, is expected not to vary significantly under the milder reduction conditions (lower than 500°C, shorter than 24 h). It was found from the transmission electron micrograph that the cobalt particle sizes of our catalysts varied only slightly with reduction conditions and that the average particle size was about 20 nm (Fig. 1). In other words the average cobalt particle size hardly changes with the extent of reduction at a constant cobalt loading.

On the other hand, the dispersion estimated from hydrogen uptake does not remain constant with reduction extent at the constant loading. The values of $(CO/H)_{irr}$ at low extents of reduction are very high (ranging from 6.0 to 15.7). The dispersion would be underestimated at low extents of reduction if it were calculated from hydrogen uptakes. Hydrogen chemisorption can be said to be highly suppressed on the poorly reduced cobalt particles.

In Fig. 2 is plotted the turnover frequency against cobalt loading under the same reduction conditions of 500°C and 10 h. Above a ninefold increase in activity is observed as the metal loading varies from 2 to 20 wt%. A similar result was also observed by Fu and Bartholomew (2) who suggested that it was due to the structure-sensitive nature of CO hydrogenation on supported cobalt catalysts. As metal loading (or dispersion) increases (or decreases), the relative concentrations of the

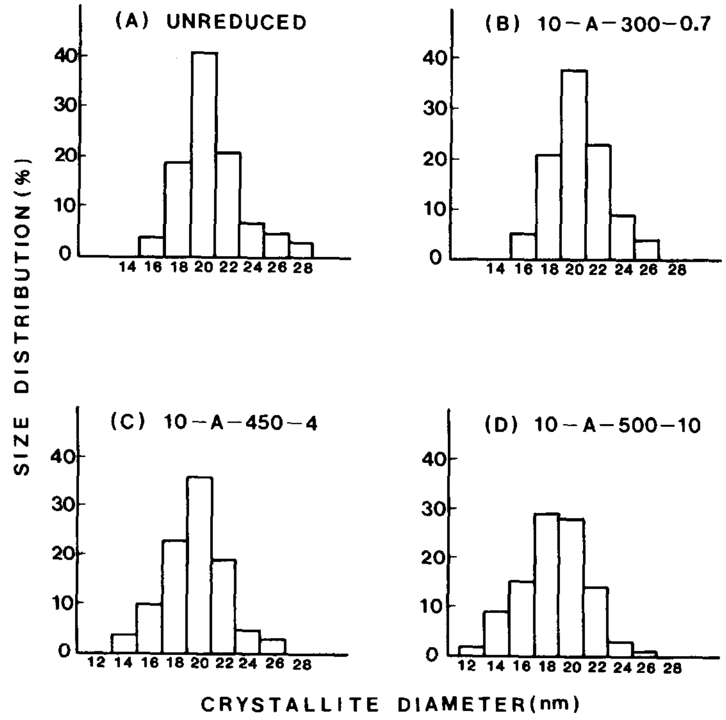

FIG. 1. Histogram of cobalt particle size distribution at constant loading of 10 wt% Co/γ-Al_2O_3.

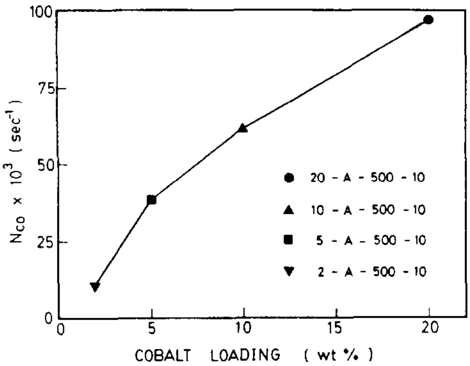

FIG. 2. Changes in turnover frequency with cobalt loading under the same reduction conditions (500°C, 10 h). Reaction conditions: 1 atm, 250°C, $H_2/CO = 3$.

surface sites with lower coordination numbers (for example, planar sites) will increase. Also, Keller and Bell (*8*) suggested that planar sites are the most active for CO hydrogenation. Accordingly, the activity may be the highest for the catalysts having the highest cobalt loading (in this case 20-A-500-10 catalyst). Since different cobalt loadings even under the same reduction conditions show different extents of reduction as shown in Table 1, the activity of CO hydrogenation in Fig. 2 must have been affected by both the size of the cobalt particles and the extent of reduction. It is necessary to discriminate between the effects of two factors.

Since the cobalt particle size for a given metal loading did vary only slightly with reduction conditions, the effect of reduction extent on the activity can be observed over a catalyst with a constant value of cobalt loading. Figure 3 shows that the turnover frequency in CO hydrogenation of the catalysts with 5, 10, and 20% loading shows a maximum reduction extent around 10 to 20%.

The increase in activity with the decrease in reduction extent above 15% in Fig. 3 seems to be attributed to the electronic role of subsurface cobalt oxides. Palmer and Vroom (*3*) proposed for nickel and cobalt foils that significantly higher activities of poorly reduced catalysts are due to the presence of subsurface metal oxides. Sexton and Somorjai (*9*) also reported similar data on rhodium foils. On the other hand, further decreases in the reduction extent resulted in rapid decreases in activity. This does not seem to be due to the role of the subsurface cobalt oxides but to the abundance of stable surface oxides (e.g., spinels). The stable surface oxides, which are known to be highly inactive to CO hydrogenation (*10*), may be abundant in extremely poorly reduced catalysts, thereby resulting in the significantly low activity of those catalysts.

Hydrocarbon product distributions are shown in Table 2. The products are represented as the number of carbon atoms per molecule, and their respective concentrations are listed as weight percents. With increasing cobalt loading the production of higher hydrocarbons increases, while the olefin fraction decreases.

The increasing production of higher hydrocarbons with increasing cobalt loading may be explained by changes in the adsorption strength of carbon-containing intermediates. The increasing strength might result in longer residence times of carbon-containing reaction intermediates on the surface, and the intermediates would propagate more easily to higher hydrocarbons.

The decrease in the olefin fraction with the increase in cobalt loading seems to be

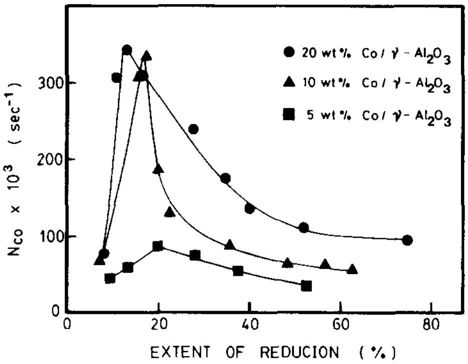

FIG. 3. Changes in turnover frequency with reduction extent. Reaction conditions are the same as those for Fig. 2.

TABLE 2

Changes in Hydrocarbon Product Distribution with Cobalt Loading and Reduction Extent

Catalyst	Reduction extent (%)	Conversion (%)	Production distribution (wt%)					$\frac{C_2^=}{C_2}$	$\frac{C_3^=}{C_2}$
			C_1	C_2	C_3	C_4	C_5		
2-A-500-10	48.6	1.7	68.1	10.4	11.7	8.9	0.9	0.61	0.74
5-A-500-10	52.5	1.7	61.4	12.7	16.5	7.4	2.0	0.32	0.44
10-A-500-10	56.6	1.8	49.6	10.1	18.1	12.4	9.8	0.18	0.31
20-A-500-10	74.4	1.7	41.1	8.1	20.1	18.4	12.3	0.17	0.31
10-A-300-0.7	7.9	1.7	50.6	11.0	20.4	12.1	5.9	0.21	0.39
10-A-300-4	15.7	1.9	50.3	10.6	19.6	11.5	8.0	0.23	0.37
10-A-350-4	17.2	1.8	52.2	10.5	19.3	11.2	6.8	0.20	0.32
10-A-400-4	19.5	1.8	51.4	9.5	19.4	11.1	8.6	0.13	0.36
10-A-450-4	22.5	1.8	49.2	10.6	18.6	11.7	9.9	0.14	0.33
10-A-500-4	35.7	1.9	51.1	9.6	17.8	12.1	9.4	0.21	0.29
10-A-525-4	48.6	1.7	50.4	9.8	18.3	11.8	9.7	0.15	0.33
10-A-500-10	56.6	1.8	49.6	10.1	18.1	12.4	9.8	0.18	0.31
10-A-500-22	62.8	1.9	48.5	10.5	18.7	12.3	10.0	0.16	0.31

[a] Reaction conditions: 1 atm, 250°C, $H_2/CO = 3$.

due to the stronger competition of H_2 against CO for adsorption sites. If the relative concentration of surface hydrogen increases, the secondary hydrogenation of primarily formed olefins to corresponding paraffins results in a decrease in olefin fraction.

Table 2 shows that both the distribution in carbon number and the olefin fraction were hardly affected by the extent of reduction for the 10% loading. Similar results, although not included in this table, were observed for different loadings.

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