Formation of Small Cobalt Clusters from CoNaY by Reduction with H_2 and Consecutive H_2-O_2 Treatments

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(Received May 11, 1990)

In order to raise the degree of reduction and promote the formation of zerovalent cobalt clusters, repetitive treatments of CoNaY with hydrogen and oxygen were carried out. The intensity of FMR (ferromagnetic resonance) band of CoNaY reduced for 36 h at 773 K with intermittent oxygen treatments was twice as much as that of CoNaY reduced only with hydrogen. This fact meant that reduction of CoNaY with H_2-O_2 treatments favored to produce zerovalent cluster due to the increase in the mobility of Co^{2+} ions in CoNaY. The size of clusters is so small that such conventional methods as hydrogen chemisorption, X-ray diffraction, and TEM can not detect the quantity of zerovalent cobalt clusters. FMR spectroscopy, H_2-consumption measurement, and catalytic probe reaction method were used to measure the degree of reduction and were correlated well with one another.

During the last decade, the properties of small metal cluster have become of increasing interest to physics and physical chemistry of catalysts.[1-3] The prospect of catalytic applications has motivated a large body of research about the preparation of well-defined metal clusters and their characterization to find out the electronic and structural properties in the range of size less than 1 nm. However, the physicochemical properties of supported small metal clusters of size less than 1 nm have not been studied extensively. The major obstacles are the preparation of supported small metal clusters showing stability toward agglomerization and reactant accessibility to the supported metal clusters of very small size. Ag, Cu, Ni, Pt, Pd, and Ru ions exchanged with NaY were easily reduced with hydrogen below 773 K.[4-6] However, these metals were found to migrate to the exterior surface of the zeolite to form clusters of size larger than 1 nm in diameter during reduction. In the case of cobalt, although it was very difficult to reduce cobalt ions exchanged in zeolite even at 773 K, reduced cobalt clusters remained inside zeolite pores.[1,9] This material is adequate to study the catalytic properties of small clusters of size less than 1 nm. Hence, our aim is to find out the method to increase the degree of reduction of cobalt ions in CoNaY to produce more cobalt metal clusters in CoNaY.

Many investigators reported that oxidation–reduction treatments of metal surface can change their catalytic properties in various catalytic reactions.[10-19] This phenomenon was explained based on the surface cleaning by O_2 treatment,[10] the possible promoting influence of oxygen remaining in chemisorbed state on the sub-surface region of metals,[11,12] or the increase in the surface area due to the repeated oxidation and reduction.[13] Amariglio et al.[14-16] recently reported that catalytic activities of cobalt ribbon in CO_2 methanation reaction was largely dependent on various oxidation–reduction treatments due to the significant rearrangement of the surface indicated by AES(Auger electron spectroscopy) and electron microscopy. This rearrangement was ascribed to the increase in the mobility of cobalt atom during oxidation cycles. These studies on the effects of H_2-O_2 suggested that repeated oxidation and reduction of CoNaY might increase the degree of reduction of Co^{2+} in CoNaY. The degree of reduction was measured with FMR which can detect the small amounts of zerovalent cobalt clusters of size less than 1 nm as well as paramagnetic cobalt ions in CoNaY. This FMR result was compared with the results of static H_2-consumption measurement and CO hydrogenation probe reaction.

Experimental

Preparation of Cobalt-Exchanged NaY (CoNaY). NaY zeolite (Strem Chem. Inc.) was used for cobalt ion-exchange. It was pretreated with 0.1 M of NaCl aqueous solution (1 M= 1 mol dm^{-3}) to remove sodium deficiency in NaY. Chloride ions were completely removed by washing with deionized water until AgCl was not precipitated when $AgNO_3$ was added to the spent deionized water. The detailed procedures are described elsewhere.[20] The cobalt loadings of CoNaY were found to be 5.4 wt%. This sample will be abbreviated as Co-IE-5.4 in the following text.

Measurement of H_2-Consumption during the Reduction of CoNaY. The amount of hydrogen consumed at 773 K was measured using chemisorption apparatus to estimate the degree of reduction of Co-IE-5.4 with reduction time. One gram of Co-IE-5.4 was dehydrated under 1.2×10^{-5} Torr (1 Torr=133.322 Pa) at 773 K for 2 h to remove physisorbed water and part of hydroxyl groups on the surface of the zeolite. After dehydration, known volume of H_2 purified with oxytrap and molecular sieve column was introduced to the chemisorption cell. The pressure changes inside the cell during the reduction of CoNaY at 773 K were recorded

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with MKS Baratron Pressure Guage (Model 170 series). After 20 h of reduction of CoNaY at 773 K, the pressure change with time was insignificant. Total amount of hydrogen either consumed in the reduction of CoNaY, adsorbed on zeolite, or adsorbed on the cobalt clusters reduced at 773 K was calculated from the pressure changes in the cell. In order to find out the exact amount of H_2 only consumed for the reduction of CoNaY, the reduced CoNaY was evacuated to 10^{-5} Torr at 773 K to remove H_2 either physisorbed on zeolite or chemisorbed on the reduced cobalt clusters. And then known volume of H_2 was introduced again into the cell. Because the reduction of CoNaY was completed in the first treatment of hydrogen, the pressure changes in this second treatment are due to the hydrogen adsorbed on zeolite and cobalt clusters. The difference between the amount of first hydrogen consumption and that of second hydrogen consumption indicated the amount of hydrogen consumed for the reduction of CoNaY at 773 K.

FMR Study. FMR spectra were recorded with Varian E-4 ESR (electron spin resonance) spectrometer equipped with a temperature controller to record the FMR spectra in the range of temperature from 153 K to 573 K. The spectrometer was operated in the X-band microwave frequency (9.115 GHz) with a modulation frequency of 100 kHz. An in situ FMR cell to pretreat CoNaY without contact of air reported elsewhere was used.[20] 0.3 g of Co-IE-5.4 was dehydrated under 1.2×10^{-5} Torr at 773 K for 1 h to avoid the complication of water vapor during the pretreatment at 773 K. This dehydrated sample was reduced in 60 ml min^{-1} flow of hydrogen then oxidized in 40 ml min^{-1} flow of oxygen at 773 K. This procedure was repeated. After this pretreatment, sample was evacuated to 10^{-5} Torr for 1 h at 773 K to remove chemisorbed H_2 or O_2 and lowered to 298 K under vacuum. Then the sample was transferred to quartz ESR tube attached to the in situ FMR cell. This ESR tube (o.d.: 4 mm) was placed in the cavity of the ESR spectrometer to record FMR spectra.

CO Hydrogenation Reaction. CO hydrogenation reaction was carried out at 1 atm in a differential flow tubular reactor. Carbon monoxide (Research grade, 99.95%, Takachiho, Japan) and hydrogen (99.995% purity) prepared with electrolysis (Teledyne Electro Cell hydrogen gas generator, Model MG 251) were further purified with oxytrap and molecular sieve trap. Oxygen (UHP, 99.99%, Matheson, USA) was used for oxidation of catalyst. Small amount of iron carbonyl was removed by decomposing it above 623 K in the preheating zone. The flow rates of CO and H_2 were controlled with fine metering valve and mass flow meter (Brooks Inc., Model 5841). Reaction temperature was controlled with digital programmable controller with microprocessor (PID type controller, RKC Instrument Inc. Model Rex-100). Reaction products were analyzed with a gas chromatograph (Hewlett-Packard, Model 5840A) equipped with porapak Q column (0.32 cm diameter, 1.83 m long). 0.2 g CoNaY was introduced to the reactor and pretreated with 60 ml min^{-1} of hydrogen flow at 523 K for 30 min. Temperature was raised slowly to the desired reduction or oxidation temperature (10 °C min^{-1}). After reduction-oxidation pretreatments, temperature was set at the reaction temperature under 20 ml min^{-1} of hydrogen flow. CO hydrogenation reaction was initiated by introducing 10 ml min^{-1} of carbon monoxide.

Results

Measurement of the Degree of Reduction. The amount of H_2-consumption during the reduction of Co-IE-5.4 was measured to estimate the degree of reduction of Co-IE-5.4. The amount of cobalt clusters was calculated from the amount of H_2 consumed in reducing Co^{2+} ions to Co metal clusters ($Co^{2+}+H_2\rightarrow Co+2H^+$). Figure 1(A) showed total amount of

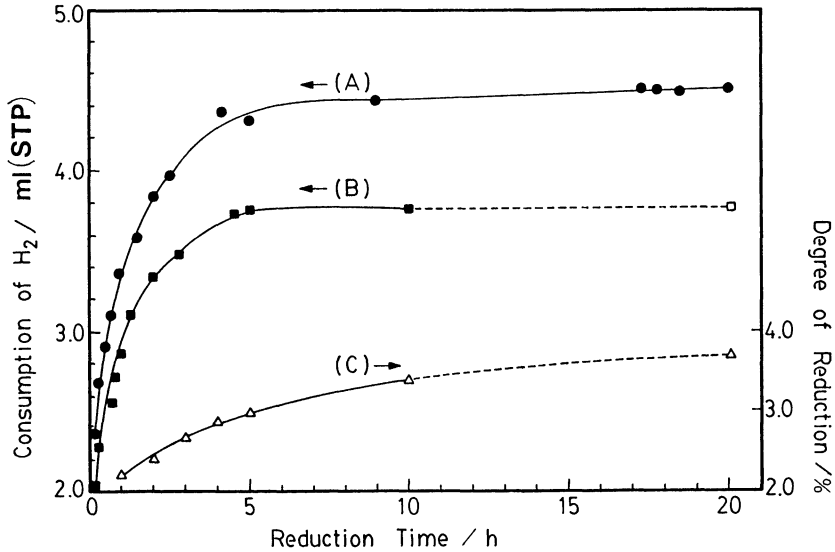

Fig. 1. H_2-consumption and % degree of reduction measured at 773 K as a function of reduction time. (A): total amount of H_2-consumption, (B): amount of H_2 adsorbed either on zeolite or reduced cobalt cluster at 773 K, (C): amount of H_2 consumed only for the reduction.

hydrogen consumed as a function of reduction time at 773 K. Total consumption of H_2 increased rapidly up to 1 h followed with a slow increase. The amount of H_2-consumption was very small after 3 h and negligible after 25 h. This sample was evacuated at 10^{-5} Torr and 773 K for 30 min, then the experiment was repeated to measure the amount of reversible adsorption (Fig. 1(B)). By subtracting the amount of H_2 reversibly adsorbed from total amount of H_2 consumed, the amount of H_2-consumption to reduce Co^{2+} ions to Co metal clusters was calculated. Percent degree of reduction was calculated from this value as shown in Fig. 1(C). The degree of reduction is 3.8% after 20 h of reduction at 773 K. Lee and Ihm[21] measured the degree of reduction with the method developed by Jacobs et al.[22] Their value is almost twice as much as ours, because the amount of H_2 consumption by Jacobs' method included H_2 physisorbed on zeolite or chemisorbed on cobalt clusters formed during reduction.

The general static method of H_2-chemisorption at room temperature with this reduced Co-IE-5.4 did not give any reproducible results either because the amount of zerovalent cobalt clusters (0.2 wt%) is too small or because H_2 chemisorption is suppressed on the cobalt clusters of size less than 1.3 nm in NaY.

FMR Study on the Formation of Cobalt Clusters on CoNaY. FMR spectra of Co-IE-5.4 reduced only with hydrogen at 773 K are shown in Fig. 2. An FMR band of weak intensity appeared overlapped with a weak EPR (electron paramagnetic resonance) band of Co^{2+} (g=2.007) after 1 h of reduction (Fig. 2(A)). A broad and asymmetric band appeared after reduction of Co-IE-5.4 with H_2 for 6 h (see Fig. 2(B)). The temperature dependence of this FMR spectrum is shown in Fig. 3. The FMR band of Fig. 2(B) was deconvoluted based on the assumption that the band is composed of two bands, i.e., broad band (I) of Gaussian type and narrow band (II) of Lorenzian type. Computer simulation with adequate g-values, band widths, and band heights of bands (I) and (II) gives the amount of contribution of bands (I) and (II) to total bands as shown in Table 1. A symmetric and broad band (band (I)) appeared (g=2.278, ΔH_{pp}, peak-to-peak band width=900 G) at the FMR recording temperature of 303 K (Fig. 3). A sharp band (band (II)) started to appear (g=2.132, ΔH_{pp}=330 G) at the FMR recording temperature of 423 K, which was superimposed with band (I). Because of appearance of band (II) the whole FMR band became asymmetric, which was more pronounced at 523 K. FMR spectra of Co-IE-5.4 became symmetric and ΔH_{pp} decreased as the reduction time increased as shown in Figs. 2(C) and 2(D).

It was expected that as the reduction time increased, the size of cobalt clusters must increase, which should be reflected in the increase in ΔH_{pp}. However, the opposite phenomenon was observed. At the initial stage of reduction for 1 h, a broad FMR of weak intensity appeared (Fig. 2(A)). The intensity of this broad band increased rapidly during the reduction for 6 h. Cobalt ions located in the sodalite and the

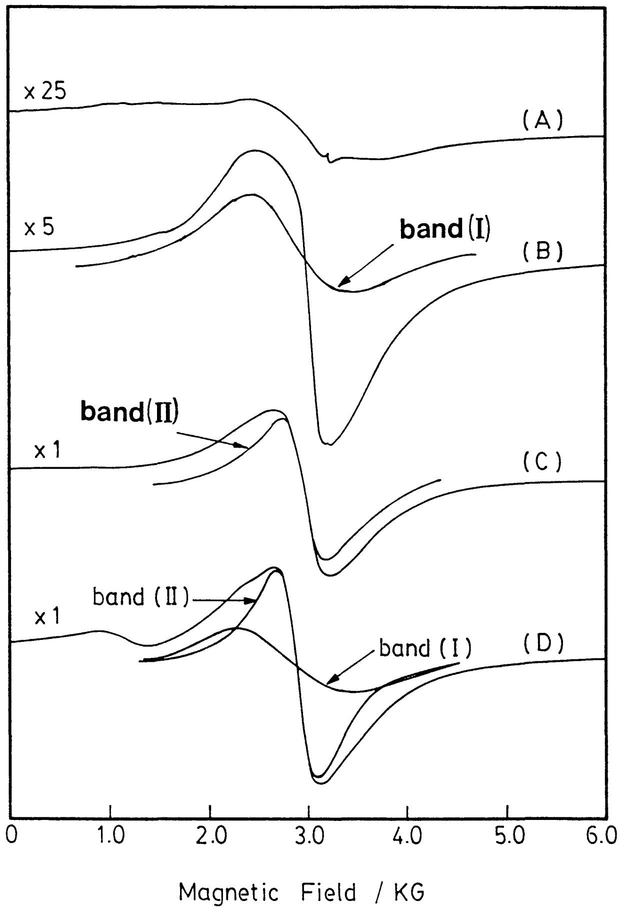

Fig. 2. FMR spectra of Co-IE-5.4 recorded at 523 K reduced with H_2 at 773 K. (A): reduced for 1 h, (B): reduced for 6 h, (C): reduced for 20 h, (D): reduced for 40 h.

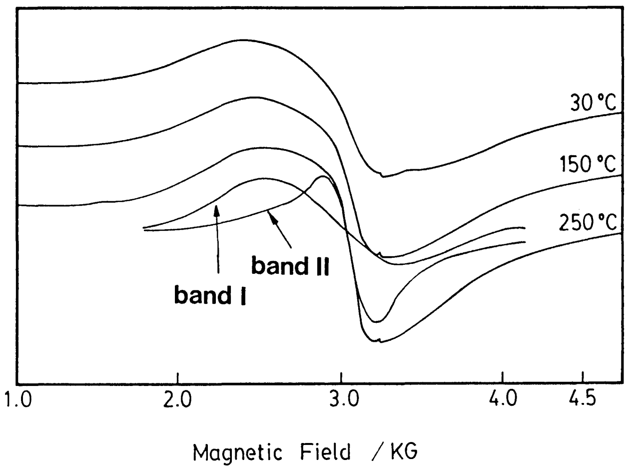

Fig. 3. FMR spectra of Co-IE-5.4 reduced at 773 K for 6 h as a function of recording temperature.

Table 1. Relative Portions of Band(II) in Total FMR Band of CoNaY Reduced with Hydrogen and H_2-O_2 Cycles

Seq. No.	Pret. cond.	Amplitude of total band[a)]	ΔH_{pp} / G	Amplitude of band(II)	Ratio of amplitude of band(II) to that of total band
	R-6	12.4	760	10.6	0.85
	R-20	35.0	600	31.8	0.88
	R-40	45.0	490	43.2	0.96
1	R-3	1.7	825	1.2	0.71
2	O-1-R-5	12.8	840	8.4	0.65
3	O-1-R-12	43.0	900	17.0	0.40
4	O-1-R-15	55.0	880	14.0	0.25

a) Amplitude indicates the height of FMR band (a.u.).

supercage are found to be reduced very slowly.[20)] Hence, the band of Fig. 2(A) and the broad band of Fig. 2(B) must be ascribed to unexchanged cobalt hydroxide remained on the exterior surface or the cobalt ions located on the exterior surface of the zeolite because of their fast reduction rate. However, the amount of this cobalt species was smaller than cobalt ions located inside zeolite pores. Further redution of Co-IE-5.4 produced more cobalt clusters inside zeolite pores, resulting in the increase of the intensity of narrow FMR band (Fig. 2(C)) overlapped with broad band (I) whose intensity is much less than that of narrow band (II) (see Table 1). After reduction for 40 h, ΔH_{pp} was 490 G at 523 K while g-value did not vary much (g=2.20). The intensity of band (II) increased more rapidly than that of band (I) as reduction time increased.

The FMR spectra of Co-IE-5.4 reduced with H_2-O_2 cycles are shown in Fig. 4. The FMR spectrum of Co-IE-5.4 after reduction for 3 h showed two peaks similar to the FMR band of Co-IE-5.4 reduced for 6 h (see Fig. 4(A) and Fig. 2(B)). After oxidation for 1 h and further reduction for 5 h, the intensity of band (I) increased, while the contribution of band (II) superimposed with band (I) decreased as compared with that of Co-IE-5.4 reduced with only H_2 for 6 h (see Fig. 2(B) and Table 1). However, band (II) is clearly present in Fig. 4(B) (g=2.122, ΔH_{pp}=300 G). After repeated pretreatments of H_2-O_2 the shape of FMR band became symmetric without much change in ΔH_{pp} and g-value ($800<\Delta H_{pp}<900$ G and g=2.3). However, the intensity of the band increased.

The intensity of FMR band obtained from the double integration of FMR spectrum is proportional to the amount of Co metal clusters reduced from Co-IE-5.4 if the magnetic susceptibility per cobalt atom is constant regardless of size and shape of cobalt clusters. The intensity of FMR band of cobalt clusters reduced from Co-IE-5.4 with H_2 is shown in Fig. 5(A). When Co-IE-5.4 was pretreated with H_2-O_2 repeatedly, the intensity of FMR band increased more rapidly as shown in Fig. 5(B). The intensity of FMR band of Co-IE-5.4 reduced for 36 h at 773 K with intermittent oxygen treatments is twice as much as that of Co-IE-5.4 reduced with H_2 only.

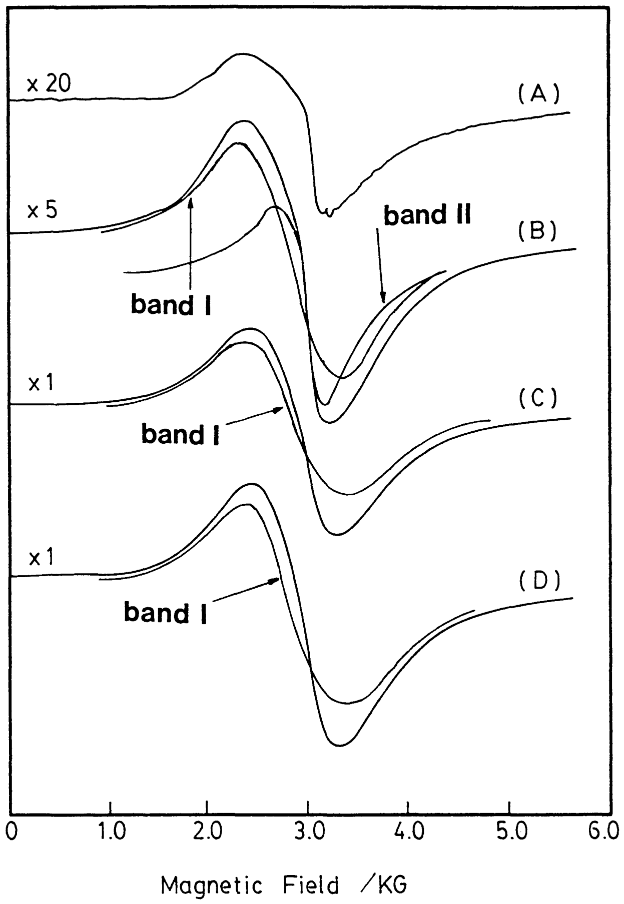

Fig. 4. FMR spectra of Co-IE-5.4 after repetitive pretreatments of H_2-O_2 recorded at 523 K. (A): reduced only for 3 h, (B): oxidized for 1 h and then reduced for 5 h after pretreatment of (A), (C): oxidized for 1 h and then reduced for 12 h after pretreatment of (B), (D): oxidized for 1 h and then reduced for 15 h after pretreatment of (C).

CO Hydrogenation Reaction. Catalytic activities per gram of cobalt of Co-IE-5.4 reduced by either H_2 or cyclic pretreatments of H_2 and O_2 are shown in Figs. 6(A) and (B), respectively. Co-IE-5.4 was pretreated by O_2 at 773 K for 1 h at each point in Fig. 6(B) and purged by helium for 30 min before reduction with

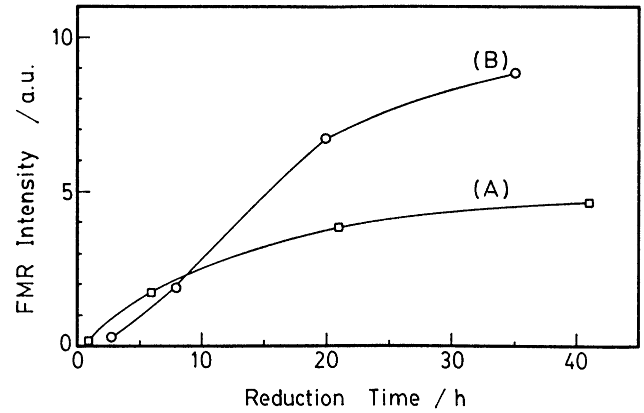

Fig. 5. The intensity of FMR band obtained from double integration of FMR band. (A): as a function of reduction time, (B): as a function of total reduction time. One hour of oxidation was carried out at each point prior to reduction.

H_2. The activities of Co-IE-5.4 reduced by H_2-O_2 treatments were higher by 1.6 times than that of Co-IE-5.4 reduced by only H_2 after 36 h of reduction. In the case of reduction with H_2 only, the pattern of increase in the catalytic activity with reduction time was different from that of increase in the amount of zerovalent cobalt cluster as shown in Figs. 1 and 5. The activity did not increase much up to 25 h of reduction but increased rapidly after 25 h of reduction. In contrast, the catalytic activity of Co-IE-5.4 reduced with H_2-O_2 cycles increased more rapidly than that of Co-IE-5.4 reduced with H_2 only up to 20 h of reduction. After 20 h of reduction, the activity of Co-IE-5.4 reduced with H_2-O_2 cycles increased in the rate similar to that of Co-IE-5.4 reduced with H_2 only.

Selectivities, activities, and TON are shown in Tables 2 and 3. The methane selectivity of Co-IE-5.4 pretreated with only H_2 was lower than that of Co-IE-

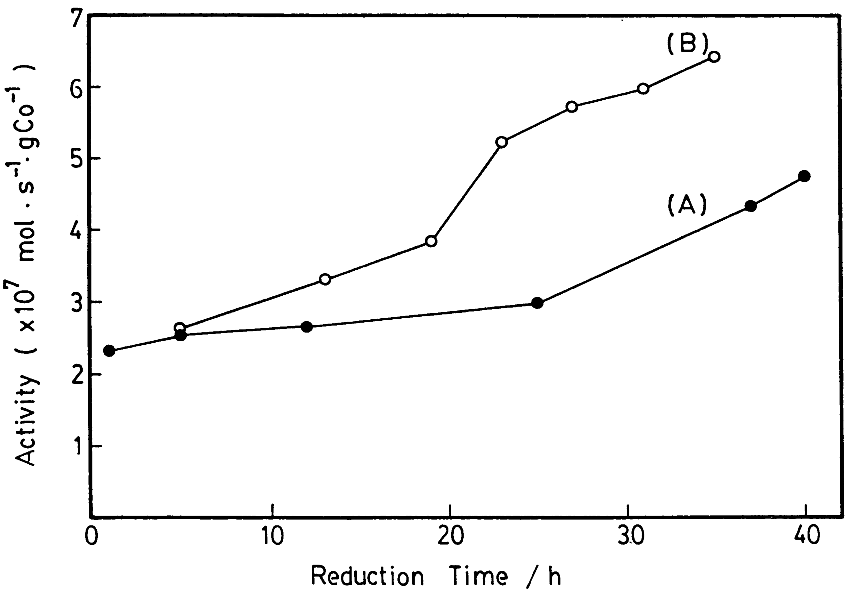

Fig. 6. The catalytic activities of Co-IE-5.4 in CO hydrogenation reaction. (A): as a function of reduction time, (B): as a function of total reduction time. Oxidation was carried out for 1 h at each point prior to reduction.

Table 2. Catalytic Activities and Selectivities of Co-IE-5.4 in CO Hydrogenation Reaction at 723 K as a Function of Reduction Time

Pret. cond.	Activity[b]	Selectivity/mol%			TON[c]
	×10^7 mol s^{-1} (g-Co)$^{-1}$	C_1	C_2	C_3	×10^3 s^{-1}
R-1[a]	2.33	71.0	23.9	5.1	0.01
R-5	2.55	74.4	21.1	4.5	0.50
R-12	2.67	75.2	20.5	4.3	0.46
R-25	2.99	75.2	20.5	4.3	0.48
R-37	4.43	77.6	19.1	3.3	—
R-40	4.78	77.2	19.1	3.7	—

a) R-1 means reduction in H_2 flow (60 ml min^{-1}) for 1 h at 773 K. b) Based on the amount of hydrocarbons produced after 30 min of reaction. c) TON based on the amount of zerovalent cobalt cluster of 100% dispersion measured with H_2 consumption method.

Table 3. Catalytic Activities and Selectivities of Co-IE-5.4 in CO Hydrogenation Reaction at 723 K after Cyclic Pretreatments of H_2-O_2

Sequence No.	Pret. cond.	Activity[b) $\times 10^7$ mol s^{-1} (g-Co)$^{-1}$	Selectivity/mol% C_1	C_2	C_3
1	R-5	2.55	74.4	21.1	4.5
2	O-1-R-8[a)]	3.32	78.4	18.0	3.6
3	O-1-R-6	3.84	78.8	17.8	3.4
4	O-1-R-4	5.25	81.8	15.3	2.9
5	O-1-R-4	5.71	84.1	13.2	2.7
6	O-1-R-4	5.99	84.5	12.9	2.6
7	O-1-R-4	6.41	85.5	12.1	2.4

a) O-1-R-8 means that after experiment of seq. no. 1, Co-IE-5.4 was oxidized at 773 K for 1 h, then reduced at 773 K for 8 h. b) Based on the amount of hydrocarbons produced after 30 min of reaction.

5.4 pretreated H_2-O_2 cycles. In both cases, the activities and selectivities of methane increases with increasing reduction time. Ethane and propane were not produced. Only ethylene and propylene were produced. In contrast, the cobalt clusters of size larger than 2 nm at 723 K in CO hydrogenation reaction produced only methane.

Discussion

Reducibility of Co^{2+} Ions in Co-IE-5.4. As shown in Fig. 1(C), 90% of reduction proceeded within 10 h and thereafter reduction proceeded very slowly (H_2-consumption rate=0.06 ml h^{-1}). Co^{2+} ions in CoNaY were reduced rapidly at the initial stage of reduction (H_2-consumption rate=0.46ml h^{-1}). This result suggests that the location of cobalt ions in CoNaY to be reduced determines the rate of reduction. Co^{2+} ions located on the exterior surface of CoNaY or on supercage (site II and site III) are reduced more rapidly than Co^{2+} ions located in sodalite cage (site I′ and site II′), resulting in higher H_2-consumption rate at the initial stage of reduction. Co^{2+} ions located in hexagonal prism (site I) may not be reduced at all. Our sample used in H_2-consumption measurement was dehydrated at 773 K to avoid adverse effect of water vapor on the reduction of Co^{2+} with H_2. During dehydration, Co^{2+} ions were migrated from supercage into either sodalite cage or hexagonal prism.[23-25] Gallezot and Imelik[25] reported through their X-ray diffraction study that 83 and 17% of Co^{2+} ions were located in hexagonal prism and sodalite cage, respectively, when 55% cobalt-changed CoNaY was completely dehydrated. When CoNaY was partially dehydrated, 41, 37, and 22% of Co^{2+} ions were located in hexagonal prism, sodalite cage, and supercage, respectively. The degree of ion-exchange in Co-IE-5.4 is 58%, which is similar to that of the work of Gallezot and Imelik. Our sample has a small amount of Co^{2+} ions located in the supercage which can be reduced rapidly at the initial stage of reduction. Most of Co^{2+} ions located inside sodalite cage and hexagonal prism can not be reduced, resulting in the small degree of reduction (3.8%).

FMR results are also in agreement with H_2-consumption measurement. After 1 h of reduction, band (I) appeared without the appearance of band (II) (Fig. 2(A)). Band (II) was ascribed to the cobalt clusters located in supercage indicated by the narrow ΔH_{pp} and its Lorenzian line shape according to the results of Che et. al.[26] Jacobs et. al.[27] also reported that Lorenzian line shape or Gaussian line shape of FMR band was obtained if the spherical metal particles had a certain particle size distribution and that FMR band of Gaussian line shape was assigned to the population of large particles. The FMR bands of Co-IE-5.4 reduced with H_2 were composed of band (I) of Gaussian line shape and band (II) of Lorenzian line shape estimated by Poole's method.[28] The intensity of band (II) increased with reduction time, suggesting that Co^{2+} ions inside zeolite cage were slowly reduced. The relative portion of band (II) superimposed with band (I) increased with reduction time (see Table I). ΔH_{pp} and g-values of band (II) did not change much with recording temperature (see Fig. 3), which is characteristic of superparamagnetic cobalt particles. Prolonged reduction did not cause ΔH_{pp} of band (II) to be increased indicating that there was no sintering of cobalt clusters. Cobalt clusters are stabilized inside zeolite pores (see Table 1, Figs. 2(B) and 2(D)). Band (I) appeared right after the reduction started. And its contribution to the total FMR band of Co-IE-5.4 reduced for 40 h at 773 K is only 4% (see Table 1). These results indicated that cobalt ions present as a hydroxide form on the exterior surface or in the half sphere of supercage on the exterior surface are reduced to show band (I).

Iton et. al.[3] reported the FMR spectra of cobalt clusters prepared from the reduction of $Co(NH_3)_6^{3+}$-exchanged Y zeolite. High temperature FMR data suggested that a small amount of Co metal particles was produced. ΔH_{pp} of their FMR spectrum of cobalt clusters at FMR recording temperature of 523 K was 600 G, which is larger than that of Co-IE-5.4 reduced with hydrogen for 40 h at 773 K (ΔH_{pp}=490 G). This indicated that the size of cobalt clusters in Co-IE-5.4 is less than that of cobalt clusters reported by Iton et al.[3] Zerger et al.[29] also reported the FMR spectra of cobalt clusters supported on NaX obtained from the decomposition of $Co_2(CO)_8$ with microwave discharge. The ΔH_{pp} of prepared cobalt clusters (30 Å in diameter) was 1050 G at 523 K, which is larger than that of our sample. From these previous results, it can be concluded that the size of cobalt clusters obtained from the reduction of Co-IE-5.4 with H_2 is the smallest and that the size of cobalt clusters is dependent on the preparation method of cobalt clusters, although we failed to measure the size of cobalt clusters in CoNaY with TEM and hydrogen chemisorption method.

Reduction of Co-IE-5.4 Facilitated with H_2–O_2 Treatments. The FMR spectra of Co-IE-5.4 reduced with H_2 with intermittent oxygen treatments are presented in Fig. 4. The relative portion of Lorenzian band (II) in the FMR band decreased as the number of oxygen treatment increased (see Table 1). In addition to the change in line shape of FMR band, the degree of reduction with H_2–O_2 treatment is twice as much as that of reduction with only hydrogen (see Fig. 5).

It is clear that H_2–O_2 treatment facilitated the reduction of cobalt ions in Co-IE-5.4. It produced cobalt clusters larger than those produced by H_2-reduction. This result can be explained by the fact that O_2 pretreatment increases the mobility of Co^{2+} ions in CoNaY, resulting in the migration of nonreducible Co^{2+} ions located either in hexagonal prism or in sodalite cage to supercage. Co^{2+} ions in supercage were reduced more easily than Co^{2+} ions in hexagonal prism and sodalite cage. The probability that Co^{2+} ions can migrate to the supercage and the exterior surface of zeolite and collide with the cobalt clusters to form a large cobalt cluster was enhanced during the oxygen treatment at 773 K. The contribution of band (I) to the total FMR band increased with the number of oxygen treatment at 773 K indicating that the cobalt clusters inside supercage migrated out to the exterior surface of zeolite to form larger cobalt clusters. However, the size of cobalt clusters on the exterior surface of zeolite is still in the range of superparamagnetic particles evidenced by the fact that the *g*-value, intensity, ΔH_{pp} and symmetric shape of FMR band of cobalt clusters produced did not change much with the FMR recording temperature.

Catalytic Properties of Small Cobalt Clusters in CoNaY. Many authors showed that TON's in CO hydrogenation reaction increased with decreasing dispersion in the case of Co,[30,31] Ni,[32,33] Ru,[34,35] and Fe.[36] Jung et al.[36] reported that the TON increased more than 20 fold as iron crystallite size increased from about 1 to 10 nm, whereas the activities of gram iron or gram catalyst basis were similar because the low TON's on high dispersion catalysts were compensated by the higher iron surface area. We reported that TON of cobalt clusters (100 nm in diameter) prepared by impregnating aqueous $Co(NO_3)_2 \cdot 6H_2O$ solution to NaY (10 wt% cobalt loading) is 34 s^{-1} and that TON of cobalt clusters prepared by the reduction of Co-IE-5.4 (0.8 nm in diameter by CO chemisorption method) is 0.46×10^{-3} s^{-1} in the CO hydrogenation reaction at 723 K.[20] The TON's of cobalt clusters obtained by the H_2 reduction of Co-IE-5.4 are in the range of order of 10^{-4} s^{-1} in the CO hydrogenation reaction at 723 K (see Tables 2 and 3). We suspected that this small catalytic activity may come from the impurity of metals in NaY produced by H_2 reduction. Hence, we reduced NaY with H_2 in the same manner as the reduction of CoNaY and found out that NaY reduced with H_2 has no catalytic activity in the CO hydrogenation reaction at 723 K. This allows us to conclude that the small catalytic activity of Co-IE-5.4 reduced with H_2 is ascribed to the small cobalt clusters produced. This low catalytic activity must be due to the suppression of hydrogen chemisorption on the small cobalt clusters less than 1.3 nm, which is the approximate size of the supercage in NaY. The appreciable amount of H_2 could not be chemisorbed on cobalt clusters in Co-IE-5.4 at room temperature. However, very small amount of H_2 can be dissociatively chemisorbed at 723 K, because the H_2 chemisorption on cobalt clusters is known to be an activated chemisorption.[37] The appreciable catalytic activity in CO disproportionation reaction at 393 K with small cobalt clusters of Co-IE-5.4[38] indicated that CO is easily dissociatively chemisorbed on the cobalt clusters of sizes less than 1.3 nm at 393 K. These results lead us to conclude that the small catalytic activity of small cobalt clusters in the CO hydrogenation reaction is due to the suppression of H_2 chemisorption. The capability to produce C_2- and C_3-hydrocarbon at the reaction temperature of 723 K also suggests a unique catalytic properties of small cobalt clusters. The suppression of H_2 chemisorption is also evidenced by the formation of C_2- and C_3-olefinic hydrocarbons.

The catalytic activity in CO hydrogenation reaction increased with reduction time as shown in Fig. 6(A). The activity of Co-IE-5.4 increased more rapidly with intermittent O_2 treatments between each reduction steps than with reduction by only H_2. The similar increasing trend of activity with that of FMR intensity means that the increase in the catalytic activity is related to the increase in the amount of cobalt metal clusters reduced from CoNaY whether it is prepared by H_2 only or repetitive H_2–O_2 treatment. This result indicated that the reduction is facilitated by the intermittent O_2 treatment due to the increase in the mobility of Co^{2+}, which is consistent with FMR results.

In summary, small cobalt clusters obtained by the reduction of CoNaY are adequate materials to study the catalytic properties of supported small cobalt clusters of diameters less than 1.3 nm. The reduction was facilitated by the consecutive H_2–O_2 treatment evidenced by FMR and CO hydrogenation probe reaction results. The chemisorption of H_2 on the very small size of cobalt clusters in Co-IE-5.4 was suppressed, while the CO chemisorption was not suppressed. The extraordinarily low catalytic TON's and 100% selectivity toward to olefinic hydrocarbons are supporting the suppression of H_2 chemisorption on the small cobalt clusters of Co-IE-5.4.

This work was partially funded by KAIST Basic Research Grant (1985) and KOSEF Basic Fundamental Research Grant (1986—1989).

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