JOURNAL OF CATALYSIS **106**, 386–393 (1987)

Metal Loading Effects on CO Hydrogenation of Co/Y Zeolite Prepared by Ion-Exchange and Carbonyl Complex Impregnation

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Received December 2, 1986; revised March 2, 1987

The ion-exchange (IE) and the carbonyl complex impregnation (CI) methods were employed to prepare cobalt clusters encaged in the pores of Y zeolite, and their catalytic behaviors for CO hydrogenation were compared. The reaction was performed with a differential reactor operating at atmospheric pressure, temperature of 230–270°C, and H_2/CO ratio of 2. Some measurements of hydrogen consumption, electron paramagnetic and ferromagnetic resonance, and temperature-programmed desorption were employed to characterize the catalysts. The catalytic behaviors of CO hydrogenation over the IE and CI catalysts were significantly different from each other. The activity of the IE catalysts increased significantly with increasing cobalt loading and reduction temperature, while the activity of the CI catalysts was almost constant irrespective of cobalt loading and reduction temperature. The IE catalysts showed a Schulz–Flory-type hydrocarbon product distribution, but the preference for C_3 and C_4 hydrocarbons was observed in the CI catalysts. The olefin fraction for the IE catalysts decreased with increasing cobalt loading, while the CI catalysts showed constant value with cobalt loading. The fraction of isobutene in C_4 hydrocarbons was significantly higher in the IE catalysts than in the CI ones. The difference in activity and olefin selectivity between the two preparation methods was explained by the acidity modification in the ion-exchanged catalysts.

INTRODUCTION

Recently the preparation of the highly dispersed and reduced zero-valent metal encaged in zeolite support has received considerable attention to control the hydrocarbon product distribution for CO hydrogenation (1–10). Among these, cobalt clusters have been reported to show pronounced selectivity for certain hydrocarbons under specific conditions (*5*, *6*).

In traditional preparations of metal clusters–zeolite catalysts, the guest metal is usually introduced as the cation or a cationic complex precursor by means of the ion exchange. The metal ion is then reduced to the zero-valent metal by hydrogen or the vapors of volatile metals. Another approach is the introduction of metal carbonyl into the zeolite followed by the decomposition of the complex to zero-valent metal clusters.

In this paper cobalt clusters in Y zeolite were made through the ion exchange (IE) and carbonyl complex impregnation (CI) methods, and their activity and selectivity behavior for CO hydrogenation were investigated.

The characterization methods applied together with the reaction study include hydrogen consumption, electron paramagnetic and ferromagnetic resonance (EPR and FMR), and temperature-programed desorption (TPD).

EXPERIMENTAL

Catalysts

Ion exchange (IE) and carbonyl complex impregnation (CI) were employed to prepare cobalt clusters in Y zeolite which was supplied by Strem Chemicals and had a unit cell composition of $Na_{54.9}((AlO_2)_{54.9}(SiO_2)_{137.1})$.

For the preparation of the IE catalysts, $Co(NO_3)_2\ 6H_2O$ was dissolved in a weakly

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0021-9517/87 $3.00

acidic hydrochloride solution (pH = 4.5–4.8) of 0.04 *N*. Na–Y zeolite (5 g) was then mixed with the solution by stirring continuously at 85°C for 48 h. After ion exchange the catalysts were filtered and washed sufficiently with deionized water to remove the remaining metal salt solution and dried in air at 90°C for 12 h. Different cobalt loadings could be obtained by repeating the ion exchange.

The CI catalysts were prepared by physically dispersing cobalt carbonyl ($Co_2(CO)_8$) dissolved in *n*-pentane on Na–Y zeolite. Na–Y zeolite was dehydrated *in vacuo* at 450°C. The impregnation took place in an evacuated, sealed cell over a period of 12 h at −10°C. The mixture was then warmed slowly to room temperature *in vacuo* over a period of 2 h and was maintained under a dynamic vacuum (10^{-3} Torr) for another 24 h. All subsequent manipulations were performed in a glove box with argon atmosphere.

After preparation the IE and CI catalysts were reduced with hydrogen by heating to 500°C at 2°C/min and maintaining the temperature for 18 h. Different catalysts used in the present study can be identified in terms of cobalt loading by the symbols in Table 1, which will be used in the rest of the text.

TABLE 1

Symbols of the Catalysts Used in the Present Study

Catalyst	Cobalt loading (wt%)	Preparation method
IE-6	6	Ion exchange
IE-8	8	Ion exchange
IE-9	9	Ion exchange
CI-2	2	Carbonyl complex impregnation
CI-6	6	Carbonyl complex impregnation
CI-8	8	Carbonyl complex impregnation
CI-10	10	Carbonyl complex impregnation

Characterization

The degree of reduction of cobalt ion to cobalt metal for the IE catalysts was obtained from hydrogen consumption which was measured in a closed system with a gas circulating unit. The apparatus is similar to that described by Jacobs *et al.* (*11*).

Consider the procedure

$$Co^{2+} + H_2 \rightarrow Co^0 + 2H^+.$$

The degree of cobalt ion reduction can be calculated from the ratio of the amount of hydrogen consumed and the total amount of cobalt ion in zeolite.

The electron paramagnetic resonance (EPR) spectra of cobalt ion and the ferromagnetic resonance (FMR) spectra of cobalt metal were recorded at *X*-band frequencies on a Varian E-4 spectrometer at the detection temperature −150 through 300°C. DPPH was used as a standard to determine the *g* factors. The quartz sample tube was designed for the *in situ* operation.

For the temperature-programed desorption (TPD) of carbon monoxide 0.5 g catalysts was reduced with hydrogen at 500°C for 18 h, and the stream was switched to helium. On remaining at 500°C for 30 min, the catalysts were cooled to room temperature under the helium stream. After saturating cobalt metal with CO, TPD studies were carried out in flowing helium at 60 cc/min by increasing the temperature linearly at 5°C/min. The stream was analyzed by TCD (Hewlett–Packard 5710A) located immediately downstream from the catalyst. CO_2 formed by the disproportionation of CO was removed before entering the detector using Ascarite (Arthur H. Thomas Co.) which adsorbs CO_2 rapidly. The normal light greenish-brown color turned to white due to the absorption of CO_2 and the formation of sodium carbonate.

Reaction

Kinetic measurements were performed on a quartz tubular microreactor operated at atmospheric pressure. The H_2/CO ratio was 2 and the reaction temperature varied from 230 to 270°C. A steady state was reached after 1 h from the introduction of the reactant, and the rates were taken after 2 h for all catalysts.

Products were separated in a 4-ft × $\frac{1}{8}$-in. column packed with Chromosorb 102 and analyzed with a Hewlett–Packard 5710A gas chromatograph with TCD and FID detectors connected in series. The column temperature was held at 50°C for 2 min and then heated to 150°C at 16°C/min.

RESULTS AND DISCUSSION

Characterization

The degree of reduction of the IE catalysts calculated from the hydrogen consumption is very low (<10%) as listed in Table 2. Divalent cobalt ion is known to be hardly reduced to cobalt metal with hydrogen. Cobalt ion in zeolite had also been reported to be difficult to reduce (*12–14*).

The EPR and FMR spectra of the IE and CI catalysts are shown in Fig. 1. EPR spectra of divalent cobalt ion in the unreduced IE-9 catalyst appears at the *g* value 1.99. In the CI catalysts broad and nearly symmetric peaks are shown at the *g* value 2.17 which was identified to be a FMR peak of cobalt metal in Y zeolite (*12*). In addition, no detectable peaks of divalent cobalt ion are observed in the CI catalysts indicating that cobalt exists as zero-valent cobalt metal. In the IE catalysts, however, sharp peaks of divalent cobalt ion (g = 1.99, ΔH = 10 gauss) appear together with the broad FMR peak of the cobalt metal. This implies that only part of the cobalt ion is reduced to cobalt metal (or that the cobalt ion and metal coexist). Since the *g* value and the peak-to-peak linewidth of FMR spectra in the IE and CI catalysts varied only slightly with the detection temperature (20–300°C) irrespective of cobalt loading, the cobalt metal size is believed to be small enough not to show magnetoanisotropy (*12*).

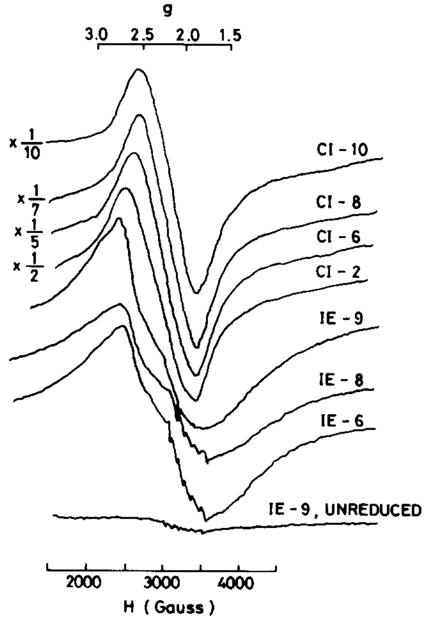

FIG. 1. Electron paramagnetic and ferromagnetic resonance spectra of the IE and CI catalysts (detection temperature = 100°C).

TABLE 2

Degree of Reduction of the IE Catalysts Calculated from Hydrogen Consumption

Catalyst	Degree of reduction (%)
IE-6	8.2
IE-8	7.2
IE-9	8.7

The sizes of the cobalt crystallites were observed with transmission electron microscopy (JEOL 200 CX) using 160-keV electrons. The resolution of the TEM was about 15 Å. No cobalt crystallites of detectable size were found for all catalysts reduced at 500°C for 18 h. Cobalt metal seems to be located within zeolite pores and to be of a size less than that of faujasite supercage (≅1.3 nm).

The shapes of the TPD spectra of CO are significantly different from each other for the IE and CI catalysts as shown in Fig. 2. The IE catalysts show sharp maxima around 120°C, while the CI catalysts show rather broad bands of TPD spectra. This indicates that the nature of active sites of cobalt metal are different from each other in the IE and CI catalysts.

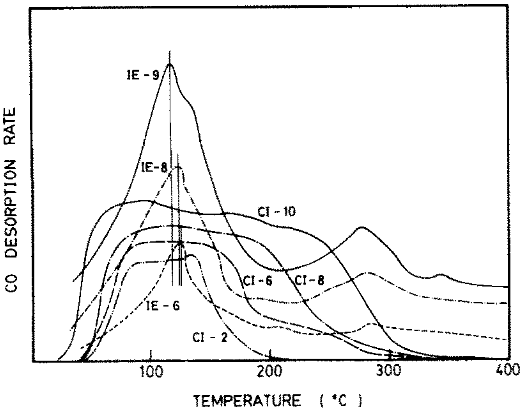

FIG. 2. Temperature-programed desorption spectra of carbon monoxide for cobalt clusters.

Activity

In Fig. 3 are plotted the activities of cobalt clusters for CO hydrogenation vs cobalt loading at 270°C. The activities were represented on the basis of reduced zero-valent cobalt metal. The activity varies significantly with cobalt loading for the IE catalysts, but remains almost constant for the CI catalysts. The activity change in the IE catalysts may be due to the cobalt metal size, i.e., structure-sensitive nature of increasing activity with increasing cobalt metal size (*15*), but the size effect does not seem to be an appropriate explanation because the cobalt metal size does not vary significantly with cobalt loading as evidenced by the FMR spectra.

The activity of the ion-exchanged ruthenium catalysts for CO hydrogenation has been reported to increase with the increase in the acidity of Y zeolites (*3*), and this was ascribed to the electron-deficient character of the metals from the electronic interaction with acidic support (*16–20*). In the IE catalysts Na^+ cations are replaced by Co^{2+} cations. After reduction with hydrogen, two Brønsted acid sites will be produced for each cobalt metal atom. Partial migration of free electrons from metal atoms to the proton of the strongly acidic OH groups results in electron deficiency in metal. Since the degree of cobalt ion reduction for the IE catalysts varies only slightly with cobalt loading (Table 2), more Brønsted acid sites would be formed for the IE catalyst with higher loading (IE-9 catalyst in this case) by the reduction with hydrogen and the metal in it would be the most electron deficient. As the metal becomes more electron deficient, carbon monoxide adsorbs less strongly due to the decrease in the extent of backdonation and hydrogen will compete more strongly with carbon monoxide for adsorption sites, resulting in the increased surface concentration of hydrogen. Therefore the activity of the IE-9 catalysts becomes the highest in the IE catalysts as suggested by Vannice (*21*).

In the CI catalysts, however, the electronic modification by changing the acidity of zeolite support with cobalt loading is not expected. Accordingly the activity of the CI catalysts does not vary significantly with cobalt loading.

The activities of the IE-9, CI-8, and CI-10 catalysts are plotted against reduction temperature in Fig. 4. The activity of the IE-9 catalysts increases significantly with reduction temperature, while that of the CI-8 and CI-10 catalysts remains constant. For the

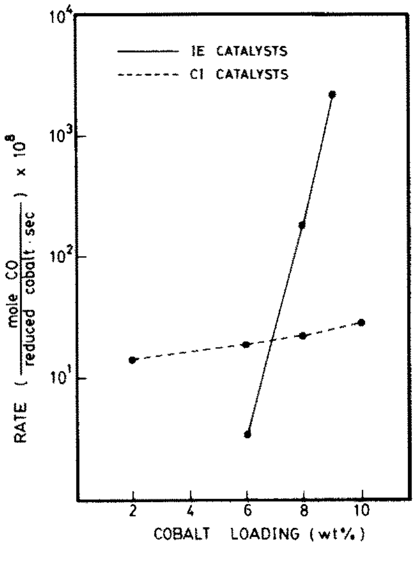

FIG. 3. Changes in activity at 270°C with cobalt loading.

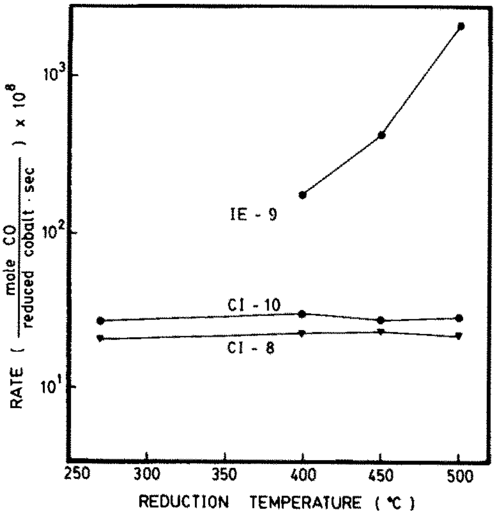

FIG. 4. Changes in activity at 270°C with reduction temperature for the IE-9, CI-8, and CI-10 catalysts.

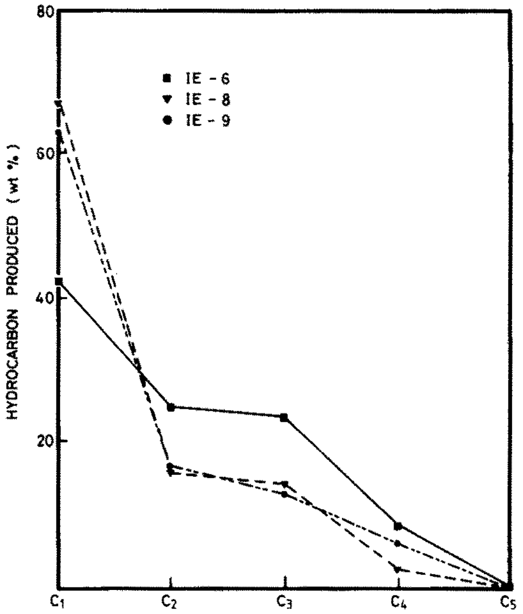

FIG. 5. Product distribution of the IE catalysts at 270°C.

IE catalysts, the degree of reduction will increase with reduction temperature (in the case of IE-9 catalyst, the degree of reduction was 6.0% at 400°C, 7.1% at 450°C, and 8.7% at 500°C, respectively) and the Brønsted acid sites will increase. Accordingly the activity is expected to increase with reduction temperature. However, the change in acidity is not expected in the CI catalysts.

Product Distribution

The hydrocarbon product distribution with the IE and CI catalysts is shown in Figs. 5–7. The products are represented as the number of carbon atoms per molecule and their respective concentrations are plotted as weight percent.

The IE catalysts show a Schulz–Flory-type product distribution (Fig. 5), while a marked amount of higher hydrocarbons, mainly C_3 and C_4, is formed for the CI catalysts (Fig. 6). The pattern of the non-Schulz–Flory-type product distribution of the CI-8 catalyst remains unchanged with reaction temperature (Fig. 7), and also remained unchanged for the other CI catalysts.

Nazar *et al.* (*5*) made cobalt clusters in Na–Y zeolite via bis(toluene)cobalt precursor and found a pronounced selectivity of C_4 olefins at 230–260°C. An anomalous product distribution was also observed for catalyst samples formed by the reduction of Co/Na–A and Co/Na–Y with cadmium va-

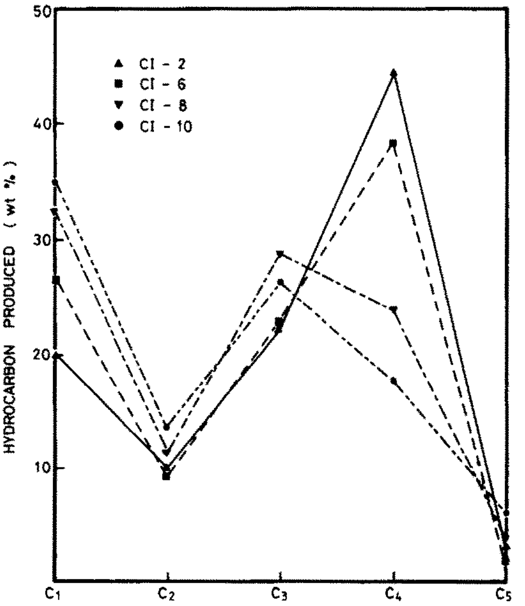

FIG. 6. Product distribution of the CI catalysts at 270°C.

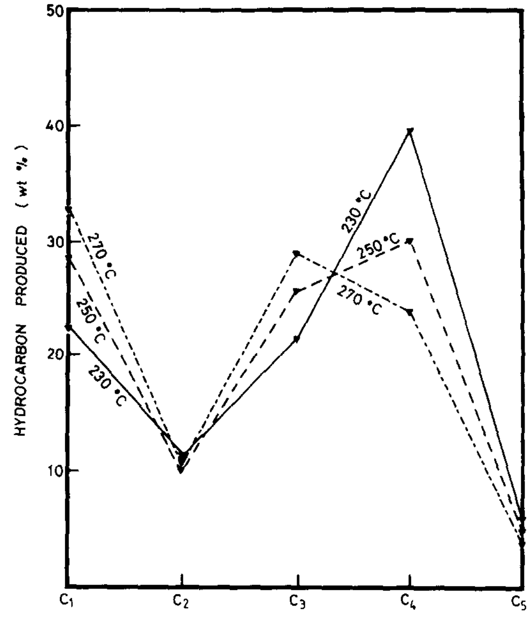

FIG. 7. Changes in the product distribution of the CI-8 catalysts with reaction temperature.

por (6). Although the difference in operating conditions (temperature and pressure) makes it difficult to compare their result with our system, it is nevertheless interesting that the cobalt clusters in Na–A zeolite are very selective toward propene, and the cobalt clusters in Na–Y zeolite are fairly selective toward butane. These selectivities toward certain hydrocarbons were ascribed to the small size and/or narrow size distribution of cobalt metal (5).

Although the preference for C_3 and C_4 hydrocarbons in our CI catalysts may be understood in this manner, the product distribution of the IE catalysts cannot be explained only by the small size and/or narrow size distribution of cobalt clusters. Considering only the effect of the size and/or size distribution of cobalt metal, the pattern of the hydrocarbon product distribution in the IE catalysts should be analogous to that in the CI catalysts as the sizes of cobalt crystallites are small in both the IE and CI catalysts. Therefore the difference in the product distribution between the IE and CI catalysts should be explained in a different way.

One probable candidate is the catalytic cracking of the primarily formed long-chain hydrocarbons to shorter chain ones through the dual functional action between cobalt metal and Brønsted acid sites. To verify this small amounts (3.6 μmol) of *n*-octane and *n*-octene in the hydrogen stream were injected into H–Y zeolite and IE catalysts, respectively, much of which was transformed into C_2 (traces), C_3, C_4, C_5, and C_6 on H–Y zeolite, while the conversion to shorter chain hydrocarbons was negligible on the IE catalysts. The same results were also obtained for the injection of *n*-pentane, *n*-hexene, and *n*-hexane. The possibility of cracking in the IE catalysts is then ruled out.

Another candidate may be the difference in the nature of active sites of cobalt metal between the IE and CI catalysts as predicted from the different shapes of TPD spectra (Fig. 2).

In Fig. 8 the olefin fractions of the IE-8 and CI-8 catalysts are plotted against conversion. The olefin fractions are high at a low conversion level, and decrease with conversion, indicating that ethene and pro-

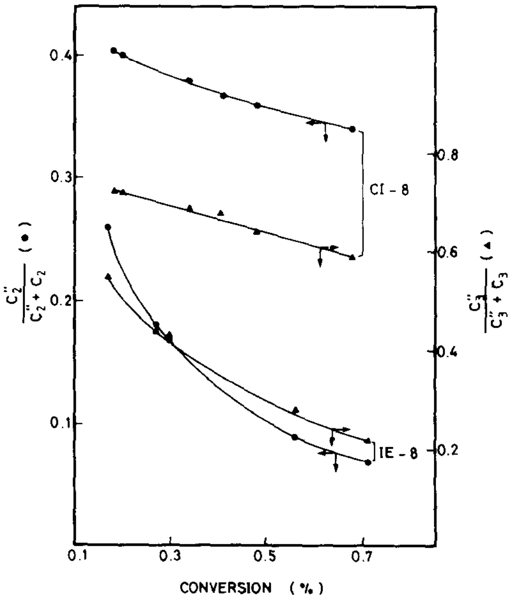

FIG. 8. Changes in the olefin fraction of the IE-8 and CI-8 catalysts with conversion at 270°C.

pene are the primary products which can either be hydrogenated to the paraffins or propagate to the higher hydrocarbons. Since the hydrocarbon product distribution depended only slightly on the conversion, the decreased amount of olefins with conversion is believed to be hydrogenated to corresponding paraffins rather than be incorporated to propagation step. As shown in Fig. 8 the decreasing rate of the olefin fraction with conversion for the IE-8 catalyst is much greater than that for the CI-8 catalyst, and this shows that the primarily formed olefins on the IE-8 catalyst hydrogenate more easily to the paraffins.

Figure 9 shows the fractional increase or decrease in the rate of formation of C_1–C_5 hydrocarbons by adding ethene to the feed gas ($CO : H_2 : C_2H_4 = 1 : 2 : 0.01$ in molar ratio). The fractional increase in the rate of formation of C_2–C_5 hydrocarbons, especially for C_4 and C_5 hydrocarbons, is significant for the CI-8 catalyst and negligible for the IE-8 catalyst. It is noted that with the IE-8 catalyst C_5 hydrocarbon was not formed as before by adding ethene to the feed. On the other hand, the addition of ethene slightly decreases the rate of formation of methane on the CI-8 catalyst. Therefore the olefins on the CI-8 catalyst are believed to propagate more readily to higher hydrocarbons.

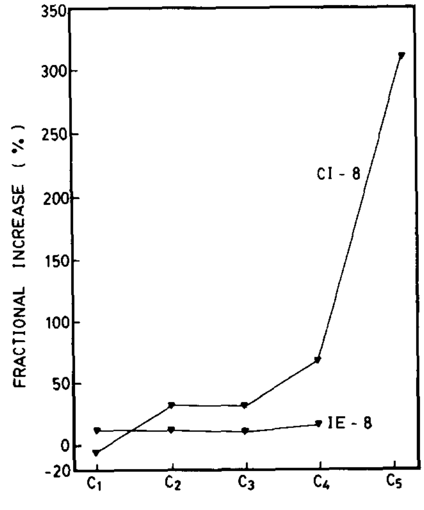

FIG. 9. Effect of the addition of ethene to the feed gas on the product distribution of the IE-8 and CI-8 catalysts at 270°C ($CO : H_2 : C_2H_4 = 1 : 2 : 0.01$ in molar ratio).

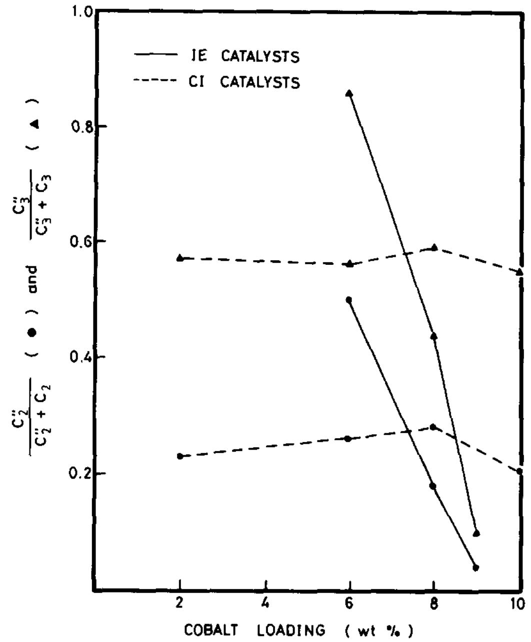

FIG. 10. Changes in the olefin fraction with cobalt loading at 270°C (space velocity = 1200 h^{-1}).

Considering the results of Figs. 8 and 9, it is reasonable that the olefins on cobalt crystallites in the IE catalysts take a smaller part in the propagation step than those in the CI catalysts resulting in the different hydrocarbon product distribution between the IE and CI catalysts. As suggested by Fraenkel and Gates (*6*) the environment and structure of the catalytically active species evidently seem to be important for the nature of cobalt metal as well as the size effect of cobalt metal.

The olefin fraction decreases significantly with the increase of cobalt loading in the IE catalysts, while it remains almost constant in the CI catalysts (Fig. 10). The decrease in the IE catalysts is due to the enhanced concentration of surface hydrogen which hydrogenates the primarily formed olefins to paraffins. Similar results were observed on ion-exchanged ruthenium in Y zeolite (*3*). The constancy of the olefin fraction

TABLE 3

Ratio of Isobutene/*n*-butene for Cobalt Clusters at 270°C

Catalyst	$\text{iso-C}_4''/n\text{-C}_4''$
IE-6	3.3
IE-8	6.8
IE-9	7.1
CI-2	0.1
CI-6	0.2
CI-8	0.1
CI-10	0.1

with cobalt loading for the CI catalysts manifests itself when the neutrality of the support is taken into consideration.

The formation of isobutene in C_4 hydrocarbons is significant for the IE catalysts, but is small for the CI ones (Table 3). Formation of isobutene in the IE catalysts results from the dual functional action between cobalt metal and Brønsted acid sites.

CONCLUSIONS

Cobalt clusters encaged in Y zeolite showed different catalytic behaviors for CO hydrogenation with different preparation methods, i.e., ion-exchange (IE) and carbonyl complex impregnation (CI).

The activity of the IE catalysts increased significantly with increasing cobalt loading and reduction temperature, while the activity of the CI catalysts was nearly constant irrespective of cobalt loading and reduction temperature. This was explained by the changes in acidity of the catalysts with cobalt loading and reduction temperature.

The increasing acidity with cobalt loading in the IE catalysts seemed to decrease the olefin fraction, but the neutrality of the CI catalysts was believed to make the olefin fraction constant with cobalt loading.

Schulz–Flory-type hydrocarbon product distributions were observed in the IE catalysts, while the preference for C_3 and C_4 hydrocarbons appeared in the CI catalysts. This difference in the hydrocarbon product distribution between the IE and CI catalysts seemed to be due to their difference from each other in chain propagating ability.

The dual functional activity between cobalt metal and Brønsted acid site was believed to result in the marked formation of isobutene in the IE catalysts.

ACKNOWLEDGMENTS

This work was partially supported by the grants from the Korea Science and Engineering Foundation, which was sponsored by the Korean Ministry of Science and Technology.

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