

## EFFECT OF CARBON DEPOSITS ON THE PROPERTIES OF Co/Y-ZEOLITE CATALYSTS FOR CO HYDROGENATION

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**Abstract**—Co/Y-zeolite catalysts were prepared by three different preparation methods of excess-water (EW), ion-exchange(IE) and carbonyl complex-impregnation(CI), and they were deposited by carbon through the disproportionation of carbon monoxide at different temperatures. CO hydrogenation was performed on the fresh and carbon deposited Co/Y-zeolite catalysts respectively, and the results were compared with each other. CO hydrogenation was carried out in a differential reactor operating at atmospheric pressure, temperature of 270-400°C and H<sub>2</sub>/CO ratio of 2. Temperature programmed surface reaction (TPSR) of carbon deposits was performed in a thermogravimetric flow system to obtain a better understanding of the carbon deposits. The large cobalt metals existing mainly at the exterior surface of zeolite crystals in the EW catalyst had a great affinity to carbon deposits, but the small cobalt metals in the IE and CI ones were highly resistant to carbon deposits. The hydrocarbon product distributions were hardly affected by carbon deposits, while the production of olefinic hydrocarbons was enhanced significantly.

### INTRODUCTION

Long history of CO hydrogenation has mainly aimed at improving the product selectivity, and metal-containing zeolite catalyst system has recently appeared as a promising candidate for the control of product selectivity in CO hydrogenation because zeolite can be used to prepare catalysts containing highly dispersed metals, to show molecular-sieving selectivity and to induce polyfunctional activity. Cobalt clusters, which were restricted into the pores of zeolites, have been reported to show anomalously high selectivity for certain hydrocarbons under specific conditions. Nazar et al. [1] have reported that main products are C<sub>4</sub> olefins on finely dispersed cobalt metal in NaY zeolite. Cobalt metal in A zeolite yielded propylene as the sole product [2]. Tkatchenko et al. [3,4] have shown that small cobalt metallic aggregates in NaY zeolite are the prerequisite to induce a hydrocarbon chain length limitation.

In our laboratory Co/Y-zeolite catalysts were employed for CO hydrogenation as the candidates for the improvement of product selectivity [5,6]. The finely dispersed cobalt metals in NaY zeolite turned out to be

able to produce C<sub>3</sub> and C<sub>4</sub> hydrocarbons in large quantities. Although the finely dispersed cobalt metals are excellent for the synthesis of certain hydrocarbons, their durability during the reaction is also important. Agrawal et al. [7] observed that cobalt catalyst deactivates more rapidly by carbon deposits as compared with nickel and ruthenium catalysts. In addition carbon deposition rate was known to be more rapid on smaller metal particles [8,9]. Therefore the outstanding advantage of finely dispersed cobalt metals for the improvement of product selectivity may have the possibility to be cancelled out by the affinity of the catalysts to carbon deposits. In the present study, Co/Y-zeolite catalysts were prepared by three different preparation methods of excess-water(EW), ion-exchange(IE) and carbonyl-complex impregnation(CI), and their behaviors for carbon deposition as well as the effects of carbon deposits on CO hydrogenation over the catalysts were investigated.

### EXPERIMENTAL

#### Catalyst and Materials

Three different preparation techniques of the excess-water(EW), ion exchange (IE) and carbonyl complex-impregnation (CI) were used to prepare Co/Y-zeo-

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lite catalysts. The NaY zeolite support was supplied from Strem Chemicals and had unit cell composition of  $\text{Na}_{54}\text{g}[(\text{AlO}_2)_{54}(\text{SiO}_2)_{137}]$ . The EW catalyst was prepared by mixing NaY zeolite powders continuously at 85°C for 24 h with an aqueous  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution to have 10 wt% cobalt loading, followed by the evaporation of water at 85°C for 24 h. For the preparation of the IE catalyst  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in a weakly acidic hydrochloride solution ( $\text{pH} = 4.5\text{--}4.8$ ) to have a concentration of 0.04 N and was mixed with 5 g NaY zeolite by stirring at 85°C for 48 h. By repeating the ion-exchange four times the IE catalyst having 9 wt% cobalt loading could be obtained. The CI catalyst having 10 wt% cobalt loading was prepared by physically dispersing cobalt carbonyl  $[\text{Co}_2(\text{CO})_8]$  dissolved in n-pentane on NaY zeolite, followed by the decomposition of cobalt carbonyl to cobalt metal. The impregnation took place in an evacuated, sealed cell over a period of 12 h at  $-10^\circ\text{C}$ . The mixture was then warmed slowly to room temperature in vacuo over a period of 2 h, and was maintained under a dynamic vacuum of  $10^{-3}$  torr. All subsequent manipulations were performed in a glove box with argon-atmosphere. All the catalysts were reduced with hydrogen by heating to 500°C at 2°C/min linearly and holding at the temperature for 18 h.

Hydrogen and helium (Matheson, 99.999% purity) were further purified by passing through an Oxytrap (Alltech) followed by a molecular sieve trap. Carbon monoxide (Takachiho, 99.95% purity) was passed through a molecular sieve trap to remove water and metal carbonyls.

### Characterization

The measurements of the amount of carbon deposited and the temperature programmed surface reaction (TPSR) of carbon deposits were performed in a thermogravimetric flow system. Ten to fifteen milligram samples were placed in a platinum container and were reduced with hydrogen at 500°C for 18 h. The stream of hydrogen was then switched to that of helium and the sample was remained for another 30 min at 500°C, followed by the cooling to the temperature of carbon deposition. Carbon was deposited through the disproportionation of carbon monoxide ( $2\text{CO} \rightarrow \text{C} + \text{CO}_2$ ) flowing at 20 cc/min over the suspended sample at each deposition temperature (250, 300, 350 and 400°C) for 4 h. After the sample being cooled to room temperature under helium stream, TPSR experiments were carried out with flowing hydrogen at 20 cc/min by heating the sample linearly at 20°C/min.

### CO Hydrogenation

CO hydrogenation reaction was performed in a differential reactor operating at atmospheric pressure.

The  $\text{H}_2/\text{CO}$  ratio was 2 and the reaction temperature was varied from 270°C to 400°C. Products were separated in a 4 ft  $\times$  1/8 in column packed with Chromosorb 102 and were analyzed in a gas chromatograph (Hewlett Packard 5710A) with TCD and FID detectors connected in series. The column temperature was held for 2 min at 50°C and then programmed to 150°C at 16°C/min.

## RESULTS AND DISCUSSION

### Thermogravimetric Analysis

The changes in the size and location of cobalt metal particles with three different preparation methods were investigated previously [5]. Cobalt metals in the EW catalyst were very bulky in size and existed mainly at the exterior surface of zeolite crystals, while no cobalt metals of detectable size could be observed in the IE and CI catalysts.

Figure 1 shows a series of TPSR curves of the EW catalyst for the reaction between the carbon deposits and hydrogen. Results obtained from Figure 1 confirm that two forms of carbon, a relatively active and a relatively inactive form based on their reactivity toward hydrogen, are deposited on the surface of cobalt metals in the EW catalyst during the disproportionation of carbon monoxide. Two peaks at  $200^\circ\text{C} \pm 10^\circ\text{C}$  and  $400 \pm 10^\circ\text{C}$  are close to those at 199 and 403°C for atomic carbon and polymeric carbon respectively, which were designated on Ni/ $\text{Al}_2\text{O}_3$  catalyst by McCarty and Wise [10]. With increasing deposition temperature, the fraction of atomic carbon decreases significantly and the formation of less active polymeric carbon increases. Adsorbed CO on cobalt surface was known to undergo dissociation above 150°C forming surface atomic carbon species [11]. The decreasing

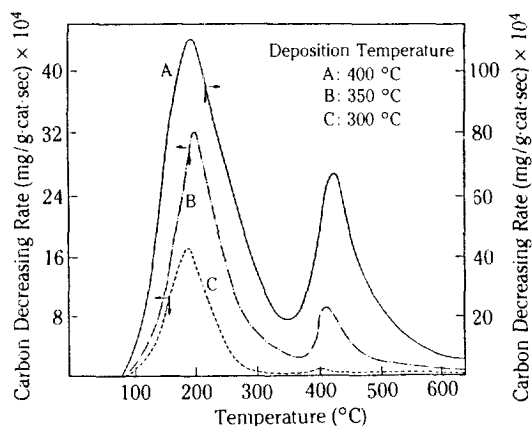


Fig. 1. TPSR curves of the carbon deposits with hydrogen on the EW catalyst.

fraction of atomic carbon with increasing deposition temperature is suggestive of the configurational transformation of atomic carbon into polymeric, crystalline graphitic carbon and bulk metal carbide [11-14].

In the IE and CI catalysts where cobalt metal particles were proved to be finely dispersed inside the zeolite pores [5], however, the amounts of carbon deposits were negligible, indicating that the small cobalt metal particles in the pores of zeolite are very resistant to carbon deposits. This result is highly incompatible with the previous reports that the surface having lower coordination number sites is more favorable for the formation of carbon [15] and the carbon deposition rate is more rapid on smaller metal particles [8,9]. Although the reason for the anomalously high resistance of small cobalt metals in the IE and CI catalysts to carbon deposition has yet to be answered in detail, the specific environments of the zeolite pores which envelope the small cobalt particles seem to have played an important role in protecting the cobalt metals from carbon deposition.

### CO Hydrogenation

Figure 2 shows the changes in the normalized rate of CO hydrogenation with increasing deposition temperature from 250 to 400°C. The rate in the EW catalyst decreases only slightly after deposition at 250°C for 4 h, while above 50-fold decrease in rate is observed at the deposition temperature of 400°C. Aforementioned results for TPSR experiments showed that the atomic carbon in the EW catalyst transforms morphologically into polymeric and graphitic carbon with increasing temperature of carbon deposition. The highly inactive polymeric and/or graphitic carbon seem to be prevalent on cobalt surface at the deposition tempera-

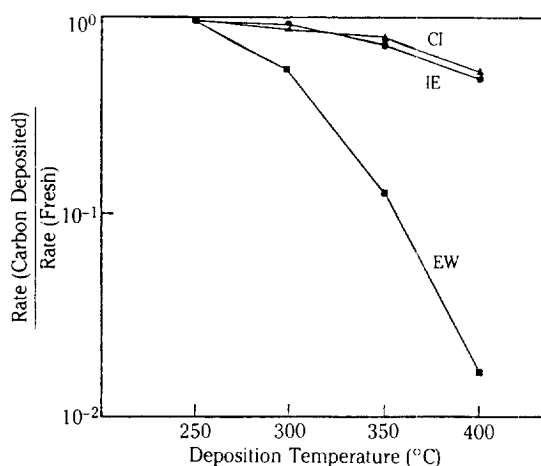


Fig. 2. Changes in the normalized rate of CO hydrogenation with deposition temperature (The rates were measured at 270°C).

ture of 400°C. Accordingly the significant drop in rate with increasing deposition temperature seems to result from the blockage of active sites by the less active polymeric and/or graphitic carbon. The rates in the IE and CI catalysts, however, decrease only slightly as compared to that in the EW catalyst, which manifests itself when remembering the negligible formation of surface carbon on the small cobalt metallic aggregates restricted into the pores of the zeolite. On cobalt [7,16] and ruthenium [17] catalysts which had been deposited by inactive carbon, the activation energy was reported to decrease significantly. In Figure 3 are shown the Arrhenius plots of the Co/Y-zeolite catalysts which were previously deposited by carbon monoxide at 400°C for 4 h. The EW catalyst has activation energy (or slope) of 17 Kcal/mole, while the activation energies of the IE and CI catalysts are almost the same as those obtained for the fresh catalysts. The activation energies of the fresh IE, CI and EW catalysts were 28.5, 29.3 and 31.5 Kcal/mole, respectively. From the Arrhenius plots for the fresh Co/Y-zeolite catalysts (Figure 4), a certain shift in activation energy (or slope) is known to occur in the EW catalysts around 350°C, and the activation energy which was calculated from

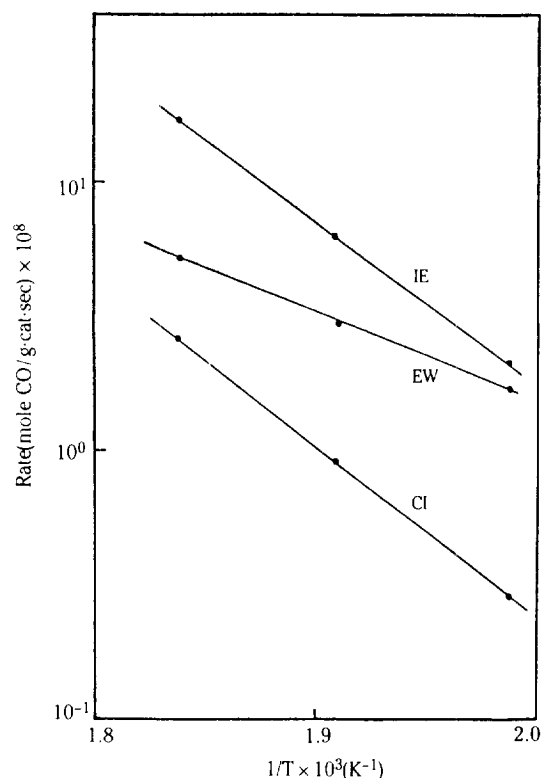


Fig. 3. Arrhenius plots of the carbon deposited Co/Y-zeolite catalysts at 400°C.

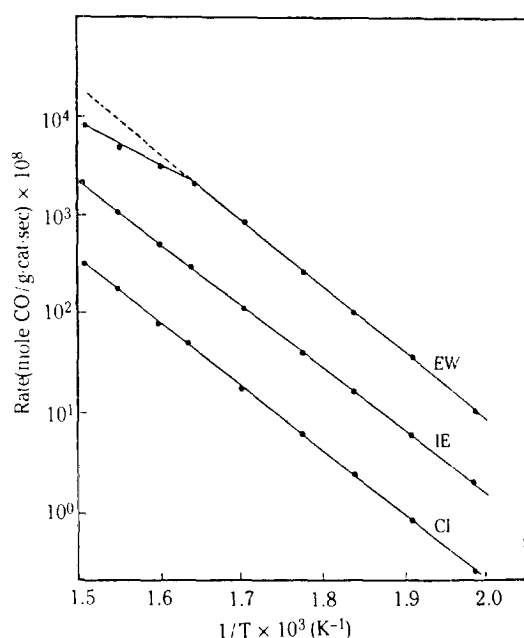


Fig. 4. Arrhenius plots of the fresh Co/Y-zeolite catalysts.

the slope at higher than 350°C has the same value as that obtained on the catalyst which had been deposited by carbon monoxide at 400°C for 4 h. In the IE and CI catalyst, however, no decline in activation energy upto 400°C is observed. Above result for the activation energy provides a further evidence for the high resistance of the IE and CI catalyst to the deactivation by carbon deposits.

The effect of carbon deposits on the hydrocarbon product distribution on the EW catalyst is shown in Table 1. The distribution was obtained at about 0.5% conversion. The products are represented as the number of carbon atoms per molecule and their re-

Table 1. Effect of carbon deposits on the hydrocarbon product distribution in the EW catalyst (reaction temperature = 270°C)

Deposition Temperature (°C)	Product distribution (wt %)				
	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>
*	54.9	11.2	18.1	10.4	5.4
250	56.2	10.9	17.8	11.1	4.0
300	54.2	8.9	19.4	12.1	5.4
350	55.6	10.4	17.1	11.6	5.3
400	52.7	12.1	17.6	10.1	7.5

\* The catalyst which was not previously deposited by carbon.

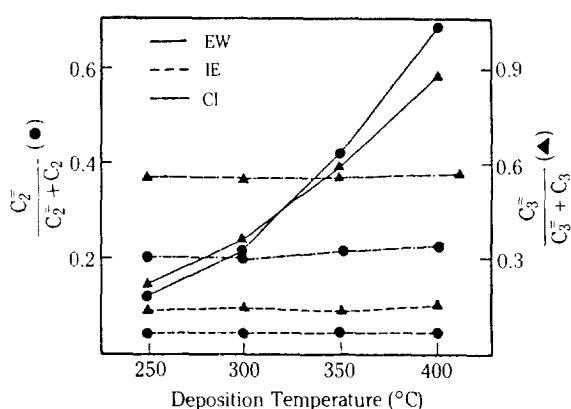


Fig. 5. Changes in the olefin fraction with deposition temperature (reaction temperature = 270°C).

spective concentrations are listed as weight percent. The effect of carbon deposits is known to be almost negligible irrespective of the temperature of carbon deposition. As expected, the product distributions of the IE and CI catalysts were not influenced by carbon deposits.

The influence of carbon deposits on the olefin fraction is even more dramatic. The olefin fractions in the EW catalyst increased significantly as the catalyst was deposited by carbon monoxide at increasing temperature, and eventually olefinic hydrocarbons became to appear as the main products on the catalyst deposited at 400°C for 4 h (Figure 5). As suggested by Agrawal et al. [16] the shift in selectivity of paraffins to olefins is believed to be due to the reduction in the ability of the hydrogenation of primarily formed olefins to the corresponding paraffins on the deactivated catalyst.

## CONCLUSIONS

Co/Y-zeolite catalysts were prepared by the three different preparation methods, i.e., excess-water(EW), ion-exchange(IE) and carbonyl complex-impregnation (CI), and their behaviors for the deactivation by carbon deposits were investigated.

The large cobalt metals existing mainly at the exterior surface of zeolite crystals in the EW catalyst had a great affinity to carbon deposits, while the finely dispersed metals in the IE and CI ones were highly resistant to carbon deposits. Carbon deposits on the surface of the EW catalyst hardly affected the hydrocarbon product distribution, while significant enhancement in the production of olefinic hydrocarbons was observed.

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