NOTES Bull. Chem. Soc. Jpn., 65, 2884—2886 (1992) [Vol. 65, No. 10

Shape-Selectivity Effect of Highly Reduced Cobalt-Exchanged Zeolite in the Fischer–Tropsch Reaction

Young Seub LEE,† Dong Jun KOH, Jong Shik CHUNG,*
and Young Gul KIM
Department of Chemical Engineering, Pohang Institute of Science and Technology
and Research Institute of Science and Technology (POSTECH/RIST),
P.O. Box 125, Pohang 790-600, Korea

(Received February 10, 1992)

Synopsis. Cobalt-exchanged zeolites, when reduced by sodium injection followed by treatment in dihydrogen at 450 °C, showed an enhanced production of long chain and linear form of hydrocarbons with a bimodally distributed non Schultz–Flory distribution. Long chain linear hydrocarbons of C_{12}—C_{20} were believed to be produced on cobalt clusters located inside zeolite cage.

There have been research interests for the preparation of small metal clusters encaged inside zeolite to obtain a shape selectivity effect in the Fischer–Tropsch reaction.[1—4] However, for iron or cobalt which is known to be active catalyst for the synthesis reaction, it has been found that metal ion in zeolite is not reduced to metal in a high degree by the conventional heating in hydrogen gas.[5,6] Reduction with metal vapors such as cadmium or sodium[1,7,8] and deposition of a volatile organometallic compound having zerovalent cobalt into zeolite in an air-free environment[2—4] have been employed to obtain zeolite-encaged metal clusters. The Fischer-Tropsch reaction tests on these catalysts showed a high selectivity to a certain olefin[1] or a sharp tail-off of produced hydrocarbons above C_4.[3]

Recently Suzuki et al.[9,10] used a very simple method to promote the oxidation of metal ions such as Zn, Ni, and Co which were ion-exchanged into zeolites. After the ion exchange, they soaked the samples in an alkali solution of pH 10. The conventional air calcination transformed the metal ions into metal oxides which exhibited a high catalytic activity for CO oxidation. During the study of iron-loaded mordenites,[11] we also found that injection of an alkali solution of high concentration (3—5 equiv) into the pores of the ion-exchanged zeolites could promote the reduction of ion-exchanged iron cations; about 27% of iron in zeolite was found to be reduced after heating in hydrogen gas at 450 °C.

In the present study, the alkali injection method was applied to the cobalt-exchanged zeolites, and it has been found that catalysts having highly reduced cobalt clusters inside zeolite pores can easily be prepared by this method. Unlike the cut-off in hydrocarbon chain observed by others, the catalyst showed an enhancement in the chain length; that is, mainly linear forms (normal paraffin and 1-alkene) of hydrocarbons up to C_{20} were formed with a bimodal distribution in the selectivity pattern.

Experimental

The catalysts were prepared as follows. The cobalt ions were loaded onto a Y zeolite (NaY; Si/Al=5.4, Tosoh Co., Japan) by a conventional ion-exchange method by using an aqueous solution of $Co(NO_3)_3$ (hereafter abbreviated as CoY). The cobalt loading was found to be 7.0 wt% on the dry basis of zeolite. The injection of the alkali solution into the pores of the zeolite was performed as follows: The cobalt-exchanged zeolite (CoY) was first dehydrated by heating it in helium at 300 °C for 3 h. After cooling down to room temperature, the sample was impregnated with 5 equiv aqueous solution of NaOH to the incipient wetness. The alkaline-injected slurry was immediately filtered and washed with 1 equiv NaOH solution and then dried at 120 °C (abbreviated as CoY–Na). The washing step was intended to remove any cobalt deposit left on the exterior surface of the zeolite crystallites. An impregnated catalyst with a cobalt loading of 7.2% (Co/Y) was also prepared from NaY (the same described above) by the incipient wetness method. All the catalysts were reduced with dihydrogen at 450 °C for 8 h before the reaction or other experiments. The reduced Co/Y catalyst was washed with 1 equiv NaOH solution to neutralize acidic sites on the zeolite (Co/Y–Na). The CO hydrogenation reaction was carried out in an once-through fixed-bed reactor made of a quartz tube (10 mm in diameter) by a flow method. Impurities such as iron carbonyl, oxygen and water in the CO gas was purified as previously described.[11] The extent of reduction was measured by oxygen titration at 450 °C under the assumption that the oxidation of reduced cobalt proceeds to Co_3O_4.

Results and Discussion

The results of the steady-state activity tests for the Fischer–Tropsch reaction (CO/H_2 mole ratio, 1.0) and the degree of reduction are shown in Table 1. As expected, the ion-exchanged CoY was hardly reduced and its catalytic activity was very low. However, the NaOH-treated catalyst, CoY–Na, showed a remarkable enhancement in the degree of reduction, whose value was as high as that of the impregnated catalyst, Co/Y. The average particle size of reduced cobalt for the impregnated catalyst, Co/Y, was found to be about 12 nm when estimated by the X-ray line broadening, whereas the alkali-injected CoY–Na did not show any cobalt peak because of severe line broadening, suggesting that the particle size is less 3 nm. We presumed that the injection of the alkali solution of such a high concentration into the zeolite pores caused the cobalt ions to be exchanged back with the injected sodium ions. The cobalt ions detached from the zeolite framework may be precipitated as a hydroxide form[9,10] as shown in Eq. 1.

$$\mathrm{Co^{2+}\cdots Y + 2NaOH \rightarrow Co(OH)_2 + 2Na^{+}\cdots Y} \qquad (1)$$

The detached cobalt ions which are located inside zeolite pores can be reduced easily now with hydrogen gas at 450 °C.

---

† Present address: 1st Lab., Samsung General Chemicals Research Center, P.O. Box Suwon 111, Korea.

Table 1. Degree of Reduction of Cobalt and Activity Measurements for Fischer–Tropsh Reaction on Various Cobalt-Loaded Y Zeolites

Catalyst	Percent reduced cobalt	Conversion	TOF[a)]	Hydrocarbon selectivity (%)			Average carbon number
				Linear form		Branched form	
		%	$\times 10^4\,s^{-1}$	1-Olefin	*n*-Paraffin		
CoY	Trace	0.05	—	26.5	63.7	9.8	1.8
Co/Y	78.0	3.4	42.0	36.2	30.5	33.3	3.5
Co/Y-Na	80.2	1.1	1.5	71.5	25.0	3.5	4.8
CoY-Na	72.0	1.0	1.3	62.0	31.2	6.8	8.2

Reaction conditions: 240°C, 1 atm and CO/H_2 mole ratio of 1.0, W/F (gcat min ml^{-1})=0.0033 for Co/Y and 0.033 for others.

a) Turnover frequency: molecules of CO converted (exclusive of CO_2) per atom of reduced cobalt exposed on the surface per second. Dispersion of cobalt cluster in the CoY-Na was assumed to be 100%.

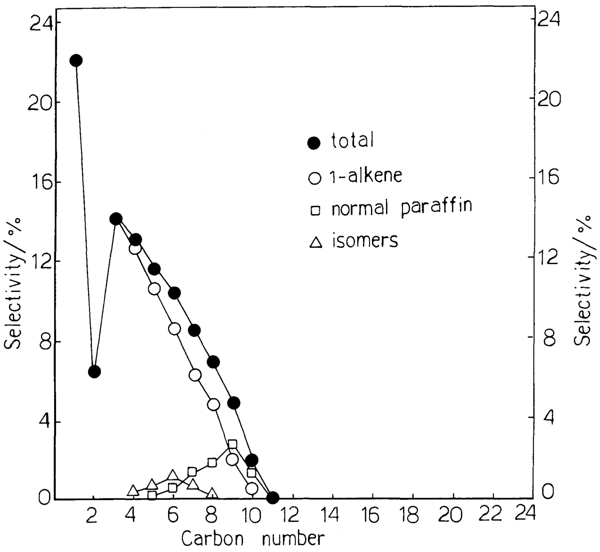

Fig. 1. Selectivity patterns of Co/Y-Na during the synthesis reaction at 240 °C.

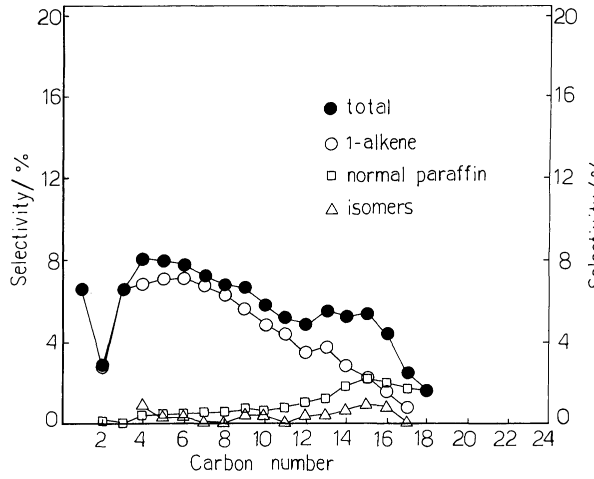

Fig. 2. Selectivity patterns of CoY-Na during the synthesis reaction at 240 °C.

The results of reaction tests in the coversion range of 0.5—2% showed several interesting features. First of all, the NaOH treatment of reduced Co/Y decreased the turnover frequency (TOF) in a great amount, probably due to doping of sodium on the cobalt surface. However, TOF of the NaOH-treated catalyst, Co/Y-Na, was about the same as that of CoY-Na. This result supports that cobalt particles in CoY-Na are in cluster size, since we have assumed that, during the calculation of TOF, the cobalt dispersion of CoY-Na be 100%. Secondly, the NaOH-treated catalysts, CoY-Na and Co/Y-Na, showed a suppression in the formation of branched hydrocarbons, indicating that branched hydrocarbons are formed by secondary reactions (e.g., isomerization) of linear hydrocarbons on acidic sites of zeolite. Thirdly, it should be noted that, concerning the carbon chain length of products, the impregnated Co/Y-Na produced hydrocarbons up to C_{12}, while the CoY-Na catalyst was found to produce hydrocarbons of C1 to C20, as shown in Figs. 1 and 2. Besides that the CoY-Na exhibits an extention effect in the hydrocarbon chain, the product distribution is more or less bimodal and a major portion of hydrocarbons above C_{10} is normal paraffins. It is believed that such a strong chain extension effect and the bimodal type distribution with CoY-Na are caused by cobalt clusters located inside the zeolite cage. Examination of the CoY-Na catalyst by a high resolution TEM revealed the existence of both large cobalt particles around 5—20 nm and small cobalt clusters around 1—1.5 nm. Therefore, hydrocarbons below C_{12} in Fig. 2 are produced by outer cobalt particles and those above C_{12} are produced by inner cobalt clusters. These results are rather surprising since it has been well known that large cobalt particles are responsible for long chain hydrocarbons[12] and that small metal clusters produce mainly small olefins.[13,14]

Reaction intermediates (primary linear form of 1-alkenes) formed on cobalt clusters located deep inside zeolite pores may have more chance to polymerize into higher 1-alkenes, but they are susceptible to undergo secondary reactions such as isomerization and hydrogenation on acidic sites of the support to produce normal paraffins and branched hydrocarbons during a hold-up inside the zeolite pores. Our observation does not agree with the results observed with other zeolite-entrapped cobalt clusters in which a sharp tail-off above C_4[1,3] or C_9[2,4] is ascribed to the shape selectivity effect of zeolite cage. Probably, their results were disguised by the presense of acidic sites on zeolites since no effort to neutralize acid sites has been done. Indeed, there is a report for the formation of appreciable amounts of branched hydrocarbon isomers.[3)]

The CoY–Na catalyst did not show any appreciable deactivation during 3 d of the reaction at 260 °C. A gradual decrease in activity was observed only at reaction temperatures higher than 300 °C. It is also noticeable that the critical temperature at which the gradual activity decrease is observed is much higher with CoY–Na than with other conventional zeolite-entrapped cobalt cluster catalysts, reported previously;[1)] the latters showed the gradual activity decrease even around 180 °C. More detailed studies to characterize morphology and physical properties of the CoY–Na catalyst are currently under way in our laboratory.

We thank the Korean Science Foundation for the support of this work.

References

1) D. Fraenkel and B. C. Gates, *J. Am. Chem. Soc.*, **102**, 2478 (1980).
2) D. Ballivet-Tkatchenko and I. Tkatchenko, *J. Mol. Catal.*, **13**, 1 (1981).
3) L. F. Nazar, G. A. Ozin, F. Hugues, G. Godber, and D. Rancourt, *J. Mol. Catal.*, **21**, 313 (1983).
4) K. C. McMahon, S. L. Suib, B. G. Johnson, and C. H. Bartholomew, *J. Catal.*, **106**, 47 (1987).
5) Y. Y. Huang and J. R. Anderson, *J. Catal.*, **40**, 143 (1975).
6) J. C. Kim and S. I. Woo, *Appl. Catal.*, **39**, 107 (1988).
7) W. Gunsser, J. Adolph, and F. Schnidt, *J. Magn. Magn. Mater.*, **15**, 1115 (1980).
8) J. B. Lee, *J. Catal.*, **68**, 27 (1981).
9) M. Suzuki, K. Tsutsumi, H. TaKahashi, and Y. Saito, *Zeolites*, **8**, 381 (1988).
10) M. Suzuki, K. Tsutsumi, H. TaKahashi, and Y. Saito, *Zeolites*, **8**, 387 (1988).
11) H. G. Yun, S. I. Woo, and J. S. Chung, *Appl. Catal.*, **68**, 97 (1991).
12) L. Fu and C. H. Bartholomew, *J. Catal.*, **92**, 376 (1985).
13) F. Hugues, J. A. Delmon, P. Bussiere, A. K. Smith, J. M. Basset, and D. Oliver, *J. Phys. Chem.*, **86**, 5136 (1982).
14) H. J. Jung, M. A. Vannice, L. N. Mulay, R. M. Stanfield, and W. N. Delgass, *J. Catal.*, **76**, 208 (1982).