Catalysis Letters 33 (1995) 57–65

# Preparation of zeolite-entrapped iron clusters by alkali injection followed by reduction with dihydrogen gas

Dong Jun Koh, Jong Shik Chung [1] and Young Gul Kim

*Research Center for Catalytic Technology,*
*Pohang University of Science and Technology (POSTECH),*
*San 31 Hyoja Dong, Pohang 790-784, Korea*

Received 24 June 1994; accepted 31 March 1995

An alkali injection method was used to promote the formation of reduced iron clusters in zeolite Y. By injecting NaOH solution into the pores of iron ion-exchanged zeolite, the iron ions were exchanged back with the injected sodium ions to be precipitated as hydroxide forms. Reduction of these precipitates in hydrogen gas yielded reduced iron clusters inside the zeolite. All preparation procedures should be performed under oxygen-free atmosphere since the re-exchange of the injected sodium ions with $Fe^{3+}$ ions was much more difficult than that with the $Fe^{3+}$ ions. Mössbauer spectra and ferromagnetic resonance spectra of the reduced catalysts revealed that the iron clusters were extremely small and uniform in size.

**Keywords:** iron/zeolite; alkali injection; iron clusters

## 1. Introduction

Generation of metal clusters encaged inside zeolites has attracted a great deal of attention in order to get high dispersion of metal and possible control of selectivity in the Fischer–Tropsch synthesis reaction [1–5]. One of the easiest methods to generate zeolite-encaged metal clusters is the reduction of metal ion-exchanged zeolite with hydrogen gas. However, the method has not been successful for zeolites exchanged with iron or cobalt ion [5–7]. It is known that metal ions having large negative electrochemical potentials cannot be reduced by the conventional reduction with hydrogen gas [8].

An alternative method of preparing reduced iron or cobalt clusters is to employ metal carbonyls [2,3] or organometallic compounds containing zero-valent metal [4]. Ballivet-Tkachenko and Tkachenko [2] introduced iron, cobalt and ruthenium carbonyls into dehydrated NaY and subsequently decomposed the compounds to zero-valent metal clusters under vacuum. However, this method necessitated a

---

[1] To whom correspondence should be addressed.

long adsorption time to obtain homogeneous distribution of metal. In order to improve the reduction of metal ion-exchanged zeolite, metal vapor such as sodium [9–11] or cadmium [1] was used as a reductant instead of hydrogen gas. Another method developed by Scherzer and Fort [12,13] was based on a reaction between metal ion-exchanged zeolite and an anionic metal cyanide complex. An insoluble compound produced inside the zeolite by the reaction could be reduced subsequently with hydrogen gas to generate dispersed metal particles on the zeolite. The preparation yielded iron particles larger than 10 nm [13].

Recently, we have found that injection of a high concentration of NaOH solution into the pores of cobalt-exchanged zeolite could promote the reduction of cobalt ions inside the zeolite [14,15]. It has been suggested that the cobalt ions were detached from the zeolite framework by exchange with the injected sodium ions to be reduced easily with hydrogen gas. Zhang et al. [16] modified this method by impregnating a concentrated aqueous sodium acetate solution into dehydrated cobalt-exchanged zeolite. They reported an enhanced reduction of cobalt ions in the zeolite.

In the present study, the alkali injection method was applied to zeolite exchanged with iron ions, the most difficult species to be reduced. The parameters which affected the formation of iron clusters were studied.

## 2. Experimental

### 2.1. PREPARATION OF CATALYSTS

Iron-exchanged zeolite NaY (designated as FeY) was prepared using NaY (JRC-Z-Y5.6; Tosoh Co., Japan) and dilute ferrous sulfate solution at room temperature in oxygen-free nitrogen atmosphere. The solution pH was adjusted to 4.8 with dilute $H_2SO_4$ solution. Ferrous sulfate solution was slowly added to the slurry until the solution contained three times the stoichiometric amount of iron needed for the complete exchange. The ion exchange was allowed to proceed for 5 h. The slurry was filtered and washed with oxygen-free distilled water (bubbled using nitrogen gas for 8 h) thoroughly, and then dried under vacuum at 333 K overnight. Atomic absorption analysis has shown that the iron loading on the zeolite sample was 3.6 wt% on the dry basis.

Sodium-treated FeY samples were prepared by several methods. Before the sodium treatment, the ion-exchanged FeY was reduced in flowing hydrogen at 573 K for 1 h, then cooled down to room temperature. This procedure was aimed at reducing any $Fe^{3+}$ ions to $Fe^{2+}$ ions (designated as Fe(II)Y). Likewise, Fe(III)Y was obtained after oxidation in flowing oxygen for 1 h. They were then soaked in 1 N NaOH solution (not $O_2$-free) under air atmosphere for 10 min. This was followed by filtering and drying under vacuum at 333 K overnight. The final samples were designated as Fe(II)Y–1Na(Air) and the Fe(III)Y–1Na(Air), repectively.

Another preparation was done under nitrogen atmosphere to avoid the oxidation of Fe(II)Y. Fe(II)Y, after preparation, was immediately introduced in oxygen-free (bubbled using nitrogen for 8 h) NaOH solution, and the slurry was stirred for 10 min under nitrogen atmosphere in a glove box. After the samples were filtered and dried under vacuum at room temperature, they were designated as Fe(II)Y–0.5Na($N_2$) and Fe(II)Y–1Na($N_2$), in which 0.5 N NaOH and 1 N NaOH solution were used, respectively.

All the dried samples were heated to 723 K at a heating rate of 5 K/min in a hydrogen flow, then reduced for 10 h. X-ray diffraction patterns of the reduced samples confirmed that the original structure of Y zeolite was maintained. No peaks of iron species were detected for all the samples.

### 2.2. MÖSSBAUER SPECTROSCOPY

Mössbauer spectra of iron-loaded zeolite samples were collected using a constant acceleration Mössbauer controller (Austin Science Associates, model S-600) Mössbauer spectrometer, connected to a multichannel analyzer (Seiko EG&G, model MCA 7800). The spectrometer was operated in a constant acceleration mode, with 10 mCi single line γ-ray source of $^{57}$Co diffused into a Rh matrix. The hyperfine spectrum of iron foil was used to provide a linearity check and to define a zero for the isomer shift. The data was fitted with some constraints to give the minimum value of the sum of squares of the deviations between the experimental and calculated value with Lorentzian line shape. About 300 mg of sample was pressed into a self-supporting wafer and charged in an in situ cell for reduction treatment in flowing hydrogen. All the spectra were taken at room temperature.

### 2.3. FERROMAGNETIC RESONANCE SPECTROSCOPY (FMR)

FMR spectra were recorded with a Brucker ER-200D SRC spectrometer. The spectrometer was operated in the X-band microwave frequency of 9.45 GHz using 100 kHz field modulation frequency and 2.0 mW microwave power. Diphenylpicrylhydrazine (DPPH) was used to calibrate the standard *g*-value.

## 3. Results

Fig. 1 shows the Mössbauer spectrum of the ion-exchanged FeY sample reduced with hydrogen at 723 K. The spectrum shows two doublets that can be assigned to $Fe^{2+}$. In zeolite Y, the outer doublet has been assigned to ferrous cations in $S_I$ site and the inner one to ferrous cations in $S_{I'}$, $S_{II'}$, and/or $S_{II}$ site [17–19]. The outer doublet is bigger than the inner one, suggesting that most of the ferrous cations exist in the relatively inaccessible $S_I$ sites of hexagonal prisms. It is also clear that no ferrous cation in the zeolite is reduced to the metallic state by the conventional reduction with hydrogen gas.

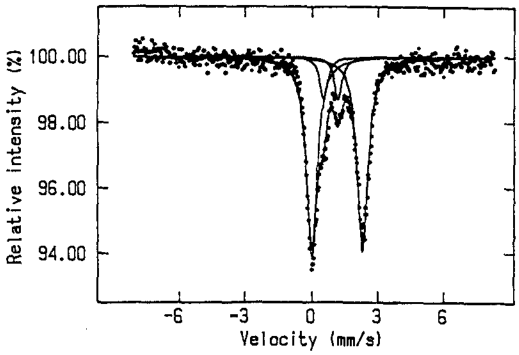
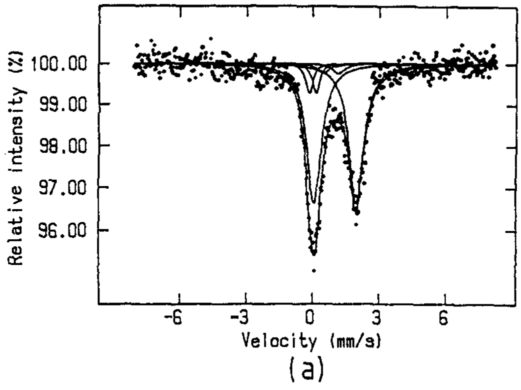
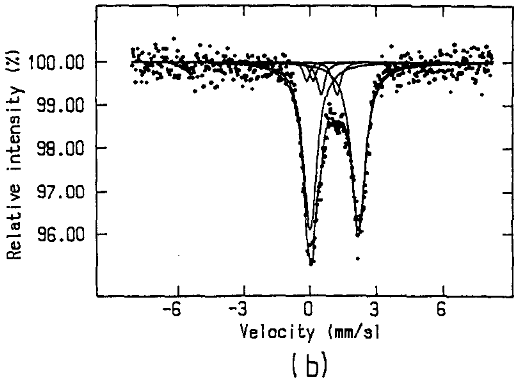


Fig. 1. Mössbauer spectrum of the reduced FeY sample.

Mössbauer spectra of the reduced Fe(II)Y–1Na(Air) and Fe(III)Y–1Na(Air) samples are shown in fig. 2. In addition to the two doublets of $Fe^{2+}$ ions, Fe(II)Y–1Na(Air) exhibited another doublet with a low isomer shift. This new doublet has an isomer shift of 0.02 mm/s and a quadrupole splitting of 0.31 mm/s. The isomer



(a)



(b)

Fig. 2. Mössbauer spectra of the reduced samples. (a) Fe(II)Y–1Na(Air), (b) Fe(III)Y–1Na(Air).

shift is in good agreement with the values reported for small iron clusters [4,9]. The absence of magnetic hyperfine splitting suggests that the iron is in the form of a superparamagnetic particle [4,9,20,21]. The fraction of the superparamagnetic iron is 9.5%. The spectrum of Fe(III)Y–1Na(Air) is similar to that of Fe(II)Y–1Na(Air), except that the fraction of superparamagnetic iron is only 4.8%. Therefore, it is believed that the oxidation of $Fe^{2+}$ ions to $Fe^{3+}$ ions hinders the re-exchange of sodium ions with iron ions in the FeY zeolite.

Mössbauer spectra of the Fe(II)Y-Na($N_2$) samples are shown in fig. 3. The spectra show two doublets of $Fe^{2+}$ ions, one other doublet of superparamagnetic iron, and another doublet which is assigned to $Fe^{3+}$ ions. The amount of the superparamagnetic iron was increased with an increase in the concentration of the injected NaOH solution. For comparison, the Mössbauer parameters for the all reduced samples are summarized in table 1.

To confirm the idea that the injected sodium ions are exchanged back with the iron ions in the zeolite framework, the FMR spectra of the dried Fe(II)Y–Na($N_2$) samples were obtained. A strong signal developed around $g = 2.3$ as shown in fig. 4

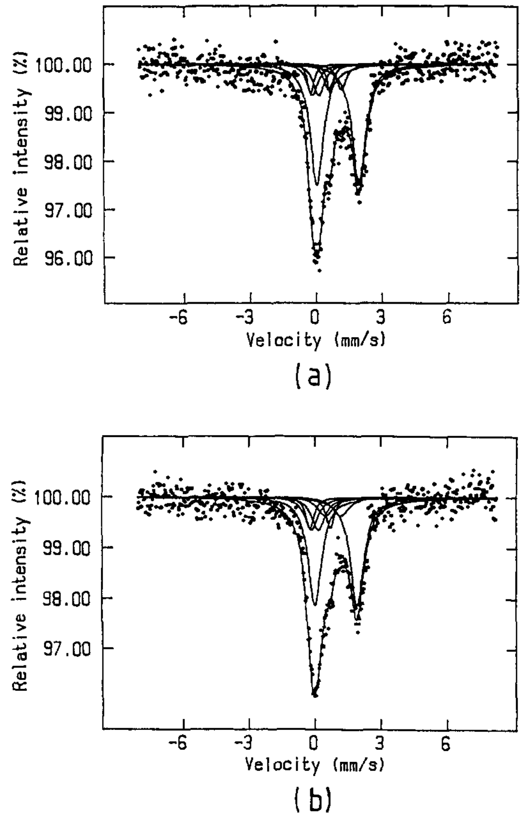


Fig. 3. Mössbauer spectra of the reduced samples. (a) Fe(II)Y–0.5Na($N_2$), (b) Fe(II)Y–1Na($N_2$).

Table 1
Mössbauer spectroscopy parameters of reduced samples

| Sample | IS (mm/s) | QS (mm/s) | Relative area (%) | Species[a] |
|---|---|---|---|---|
| FeY | 1.15 | 2.31 | 85.7 | $Fe^{2+}$ |
| | 0.86 | 0.66 | 14.3 | $Fe^{2+}$ |
| Fe(II)Y–1Na(Air) | 1.04 | 1.91 | 85.0 | $Fe^{2+}$ |
| | 0.84 | 0.65 | 5.5 | $Fe^{2+}$ |
| | 0.02 | 0.31 | 9.5 | SP $Fe^0$ |
| Fe(III)–1Na(Air) | 1.13 | 2.10 | 85.5 | $Fe^{2+}$ |
| | 0.88 | 0.69 | 9.7 | $Fe^{2+}$ |
| | 0.01 | 0.29 | 4.8 | SP $Fe^0$ |
| Fe(II)Y–0.5Na($N_2$) | 1.02 | 1.92 | 66.6 | $Fe^{2+}$ |
| | 0.89 | 0.60 | 10.2 | $Fe^{2+}$ |
| | 0.24 | 0.90 | 8.1 | $Fe^{3+}$ |
| | 0.02 | 0.30 | 15.1 | SP $Fe^0$ |
| Fe(II)Y–1Na($N_2$) | 1.00 | 1.92 | 59.0 | $Fe^{2+}$ |
| | 0.86 | 0.68 | 12.3 | $Fe^{2+}$ |
| | 0.26 | 0.93 | 10.6 | $Fe^{3+}$ |
| | 0.02 | 0.32 | 18.1 | SP $Fe^0$ |

[a] SP denotes superparamagnetic $Fe^0$.

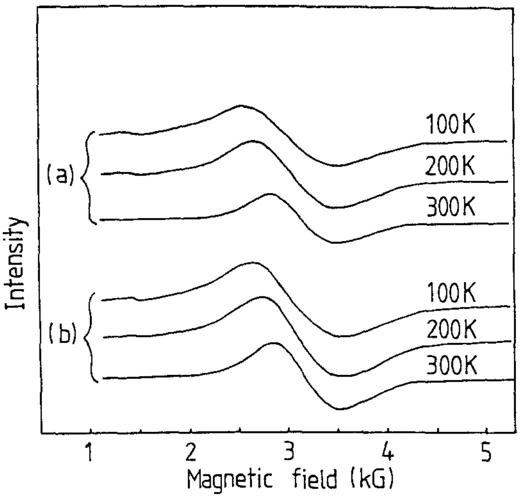


Fig. 4. FMR spectra of the dried samples. (a) Fe(II)Y–0.5Na($N_2$, (b) Fe(II)Y–1Na($N_2$).

was little affected as a function of the recording temperature. The signal could be observed at such an extremely low temperature as 100 K. The signal at $g = 2.3$ has been assigned to the hydroxidic or oxidic $Fe^{3+}$ species precipitated on the zeolite [22–24]. Therefore, it is obvious that the ion-exchanged iron ions in zeolite are re-exchanged with the injected sodium ions, and that the iron ions are precipitated as hydroxide forms.

Fig. 5 shows FMR spectra of Fe(II)Y–Na($N_2$) samples after the hydrogen reduction. A strong FMR signal at $g = 2.08$–$2.14$ was observed at such a low temperature as 100 K. Since the resonance signals are uniform and their intensities are almost independent of temperature, which are typical features of very small superparamagnetic particles, iron particles seem to be located within the pores of zeolite as finely dispersed clusters.

## 4. Discussion

The alkali injection method was tried to prepare zeolite-encaged iron clusters. The sodium ions injected into the zeolite pores are believed to be re-exchanged with iron ions to form an oxidic or hydroxidic form of iron precipitates,

$$\text{Fe-Y} + 2\text{NaOH} \rightarrow \text{Fe(OH)}_2 + 2\text{NaY} \qquad (1)$$

Reduction of these iron precipitates with hydrogen gas is much easier than that of the ion-exchanged iron ions, which are chemically attached to the zeolite framework in order to keep charge balance [25].

However, the degrees of reduction (5–18%) obtained with the sodium-treated FeY are much lower than those with the sodium-treated CoY [15] (in the range of 70%). Unlike the CoY, in the case of FeY the elimination of air contact during the

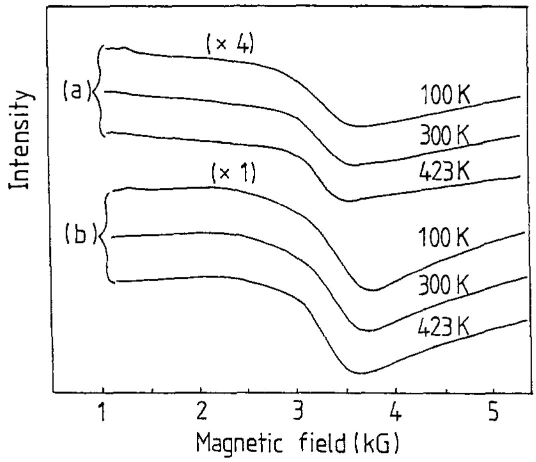


Fig. 5. FMR spectra of the reduced samples. (a) Fe(II)Y–0.5Na($N_2$), (b) Fe(II)Y–1Na($N_2$).

sodium injection is a necessary condition to achieve a high degree of reduction as shown in the results of table 1. Garten et al. [19] have observed that the oxidation of $Fe^{2+}$-Y at room temperature in wet oxygen leads to the formation of ferric ions. Both oxygen and water should exist for the oxidation. Indeed, the Mössbauer spectrum of the Fe(II)Y–1Na(Air) which was subjected to a vacuum drying step has revealed (although not shown here) that all iron species exist as $Fe^{3+}$ species. When the sodium treatment was done under a nitrogen blanket, FMR spectra (fig. 4) show the presence of superparamagnetic oxidic or hydroxidic $Fe^{3+}$ species, not free $Fe^{3+}$ ions. It is well known that $Fe(OH)_2$ is easily oxidized upon exposure to air [26]. Therefore, it is believed that the $Fe(OH)_2$ precipitates detached from the zeolite framework are slowly oxidized to hydroxidic $Fe^{3+}$ species, probably FeO(OH), during the vacuum drying step. From the results, it is established that the re-exchange of the $Fe^{3+}$ ions with the sodium ions is more difficult than that of the $Fe^{2+}$ ions, probably because of its high ionization potential [25].

For the NaOH-injected FeY, the degree of reduction was found to be lower than that for the NaOH-injected CoY [15]. The following explanation may be suggested for the low degree of reduction. According to Delgass et al. [18], the $Fe^{2+}$ ions in the FeY dehydrated at low temperatures are mainly located at the $S_I$ sites of the hexagonal prism. Further dehydration can move the $Fe^{2+}$ ions out of the plane of the hexagonal window and into the $S_{I'}$ sites of the sodalite cage. In spite of the movement, however, most of the $Fe^{2+}$ ions are located in the relatively inaccessible $S_I$ sites [18,19,27]. The large area fraction of the outer doublet in our FeY sample also supports the above observation. Therefore, the re-exchange of the $Fe^{2+}$ ions with the injected sodium ions would be relatively limited. Furthermore, the iron precipitates formed in the hexagonal prism sites may be dispersed atomically and strongly interact with the zeolite framework owing to the small size of the cage. Therefore, it is not easy to reduce these species. The $Fe^{3+}$ ionic species in the Mössbauer and FMR spectra, which are not observed in the reduced FeY, may be assigned to these species.

Mössbauer spectra reveal that the reduced iron behaves as superparamagnetic, indicating that iron clusters have a size less than 1.3 nm [9,21]. The formation of very small iron clusters can also be supported by FMR spectra of the reduced samples. The low blocking temperature below 100 K and relatively constant intensity of FMR spectra as a function of temperature clearly indicate that the reduced iron has uniform particles of a cluster size [3,28]. The catalysts did not show any sintering and growth in particle size when temperature was kept below 300°C. However, after the CO hydrogenation reaction at 350°C for 8 h, the blocking temperature in the FMR spectra was increased above 100 K, indicating an increase in particle size.

## 5. Conclusion

The alkali injection method was tried to prepare iron clusters inside zeolite pores.

In the re-exchange process of iron ions with sodium ions, oxygen in the NaOH solution played an important role. The presence of iron precipitates detached from the zeolite framework was confirmed by the FMR spectra of the dried samples. Mössbauer spectra showed that the reduced iron was in the form of superparamagnetic particles. Additionally, a low blocking temperature below 100 K and relatively constant intensity of the spectra as a function of temperature in the FMR measurements suggested that the reduced iron had uniform particles of a cluster size.

## References

[1] D. Fraenkel and B.C. Gates, J. Am. Chem. Soc. 102 (1980) 2478.
[2] D. Ballivet-Tkatchenko and I. Tkatchenko, J. Mol. Catal. 13 (1981) 1.
[3] K.C. McMahon, S.L. Suib, B.G. Johnson and C.H. Bartholomew, J. Catal. 106 (1987) 47.
[4] L.F. Nazar, G.A. Ozin, F. Hugues, J. Godber and D. Rancourt, J. Mol. Catal. 21 (1983) 313.
[5] J.C. Kim and S.I. Woo, Appl. Catal. 39 (1988) 107.
[6] Y.Y. Huang and J.R. Anderson, J. Catal. 40 (1975) 143.
[7] K. Inamura, R. Iwamoto, A. Iino and T. Takyu, J. Catal. 142 (1993) 274.
[8] Z. Zhang, W.M.H. Sachtler and S.L. Suib, Catal. Lett. 2 (1989) 395.
[9] F. Schmidt, W. Gunsser and J. Adolph, ACS Symp. Ser. 40 (1977) 291.
[10] H.M. Ziethen, H. Winkler, A. Schiller, V. Schunemann, A.X. Trautwein, A. Quazi and F. Schmidt, Catal. Today 8 (1991) 427.
[11] J.B. Lee, J. Catal. 68 (1981) 27.
[12] J. Scherzer and D. Fort, J. Catal. 71 (1981) 111.
[13] J. Scherzer, J. Catal. 80 (1983) 465.
[14] D.J. Koh, J.S. Chung and Y.G. Kim, J. Chem. Soc. Chem. Commun. (1991) 849.
[15] J.S. Chung, H.G. Yun, D.J. Koh and Y.G. Kim, J. Mol. Catal. 79 (1993) 199.
[16] Z. Zhang, Y.-G. Yin and W.M.H. Sachtler, Catal. Lett. 18 (1993) 73.
[17] W.R. Balse, W.M.H. Sachtler and J.A. Dumesic, Catal. Lett. 1 (1988) 275.
[18] W.N. Delgass, R.L. Garten and M. Boudart, J. Phys. Chem. 73 (1969) 2970.
[19] R.L. Garten, W.N. Delgass and M. Boudart, J. Catal. 18 (1970) 90.
[20] F. Hugues, J.A. Dalmon, P. Busslere, A.K. Smith, J.M. Basset and D. Oliver, J. Phys. Chem. 86 (1982) 5136.
[21] H.J. Jung, M.A. Vannice, L.N. Mulay, R.M. Stanfield and W.N. Delgass, J. Catal. 76 (1982) 208.
[22] E.G. Derouane, M. Mestdagh and L. Vielvoye, J. Catal. 33 (1974) 169.
[23] B.D. McNicol and G.T. Pott, J. Catal. 25 (1972) 223.
[24] B. Wichterlova, L. Kubelkova, J. Novakova and P. Jiru, Stud. Surf. Sci. Catal. 12 (1982) 143.
[25] P.A. Jacobs, Stud. Surf. Sci. Catal. 12 (1982) 71.
[26] S. Budavari et al., ed., *The Merck Index*, 11th Ed. (Merck, New Jersey, 1989) p. 634.
[27] J.R. Pearce, W.J. Mortier and J.B. Uytterhoeven, J. Chem. Soc. Faraday Trans. I 77 (1981) 937.
[28] L.E. Iton, R.B. Beal and P.J. Hamot, J. Mol. Catal. 27 (1984) 95.