CHEMISTRY LETTERS, pp. 1213-1216, 1986.

# Characterization of Fe Supported Y Type Zeolite by Using ESR and FT-IR

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Spectroscopic investigation using ESR and FT-IR was made on Fe supported Y type zeolite prepared by treating $NH_4Y$ zeolite with a ferric nitrate solution. Superparamagnetism of ESR signal indicated the existence of super fine particles of ferric oxide, while FT-IR measurements suggested small cluster ions containing $Fe^{3+}$ bonded to zeolite lattice. The formation of such small particles was considered to proceed cooperatively with dealumination.

There are two typical methods to prepare Fe supported zeolites; one is an ion exchange method, and the other is a method using metal carbonyls. Boudart et al.[1)] reported that in the ion exchange of Y zeolite with $Fe^{2+}$ ions, exchanged Fe ions exist mostly in the sodalite cage and form Fe-O-Fe bridges when oxidized. The metal carbonyl method using $Fe(CO)_5$ was first investigated by Jacobs et al.[2)] The supported Fe in this case was reported to exist in the super cage of Y type zeolite as highly dispersed clusters of Fe oxide or metal. Most of Fe supported zeolites have so far been prepared under mild conditions where the zeolite lattice can remain almost intact, and investigations have been rarely made on preparation under less mild conditions where modifications of zeolite lattice such as partial dealumination take place. We have found that the Fe supported zeolite prepared under such conditions(FeHY-1, see Table 1) has a unique acid property in the flow of $H_2S/H_2$.[3,4)] This suggests that the sample prepared in this way contains Fe species different from those in the well-known Fe supported zeolites. This letter aims at revealing the Fe species supported under such conditions by sample characterization using ESR and FT-IR.

Iron supported Y type zeolites were prepared as follows. For FeHY-1 and FeHY-2, ammonium ion exchanged Y type zeolite, $NH_4Y$ (UCC;LZY-82), was mixed with solutions containing $Fe(NO_3)_3$ or $FeSO_4$ at room temperature, and stirred under the conditions shown in Table 1. Then the suspension was filtered, washed with distilled water, dried in air at 363 K, and finally calcined in air at 773 K for 3 h. For FeHY-3 and $Fe/SiO_2$, $NH_4Y$ or silica gel(Fuji Davison) was suspended in water, and the droplets of $Fe(NO_3)_3$ solution and $NH_4OH$ solution were added to the suspension while keeping the suspension at pH = 7, in order to have Fe ions precipitated as $Fe(OH)_3$. The subsequent procedures were the same as the above.

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[††] As a participant of Research Association for Residual Oil Processing (RAROP).

The samples were subjected to ESR measurements(X band) in the temperature range 113 K - 283 K on a JEOL spectrometer(JES-FE3XG). FT-IR measurements were carried out using zeolites with various degrees of dealumination on a JEOL spectrometer(JIR40X). Dealuminated Y zeolites, DAHY series, were prepared by treating $NH_4Y$ with HCl at various conditions. FeHY-1 series were obtained by the same procedures as FeHY-1 but using various treatment conditions. FeHY-2 series were obtained by treating DAHY series under the same conditions as adopted to prepare FeHY-2. The amount of supported Fe as well as the $SiO_2/Al_2O_3$ molar ratio after the preparation were measured by Fluorescence spectrometer(Rigaku Denki;3080E). The obtained compositional data are listed in Table 1. The sample prepared from $Fe(NO_3)_3$ solution, has the lowest $SiO_2/Al_2O_3$ ratio, indicating that dealumination took place to a considerable extent during the preparation process.

Table 1. Preparation methods and compositions of catalysts

| Catalyst | Treatment condition | | | | Composition | |
|---|---|---|---|---|---|---|
| | Fe salt solution | Temp /K | Time/h | pH[a)] | $Fe_2O_3$/wt% | $SiO_2/Al_2O_3$[b)] |
| LZY-82 | - | - | - | - | tr | 5.4 |
| FeHY-1 | 0.25M $Fe(NO_3)_3$ | 323 | 2 | 1.0-1.4 | 9.0 | 10.6 |
| FeHY-2 | 1.00M $FeSO_4$ | 363 | 2 | 3.0-5.0 | 11.8 | 6.3 |
| FeHY-3 | $Fe(NO_3)_3$ + $NH_4OH$ | R.T. | 1 | 7.0 | 10.0 | 5.9 |
| $Fe/SiO_2$ | $Fe(NO_3)_3$ + $NH_4OH$ | R.T. | 1 | 7.0 | 9.2 | - |

a) pH of suspension.
b) Molar ratio.

ESR spectra of FeHY-1,FeHY-2, and FeHY-3 at room temperature are shown in Fig.1. Two kinds of signals, i.e., a sharp one at g = 4.3 and a broad one at g = 2.3 were observed in every sample. According to literature,$^{5,6)}$ the signal at g = 4.3 is ascribed to isolated $Fe^{3+}$ ions which are present at ion exchange sites or incorporated in the zeolite lattice. The signal at g = 2.3 has been assigned to ferric oxide by Derouane et al.$^{5)}$ The spectra confirm that a part of supported Fe ions exist as ferric oxide in FeHY-1 and FeHY-2. Most interesting information concerning the state of the ferric oxide was collected by changing the temperature of measurement. It is known that $\alpha$-$Fe_2O_3$ becomes superparamagnetic when the particle size is sufficiently small.$^{7)}$ The Morin temperature of $\alpha$-$Fe_2O_3$, the temperature below which paramagnetism is lost, is known to be lowered as the particle size decreases.$^{8)}$ The signal intensities at g = 2.3 for the

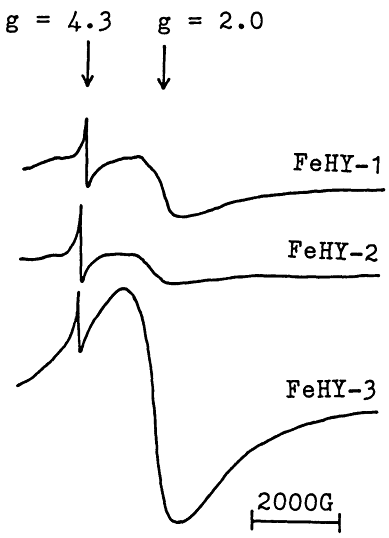

Fig.1. ESR spectra of Fe supported zeolites.
(measured after evacuation in 1 h at 393 K)

four samples are depicted as a function of reciprocal temperature in Fig.2. The intensities for FeHY-2, FeHY-3, and Fe/$SiO_2$ have maxima or inflection at about 200 K. Thus the Morin temperature of $\alpha$-$Fe_2O_3$ in these samples is estimated to be about 200 K, which corresponds to $\alpha$-$Fe_2O_3$ particles with a size of 400 - 1000 A according to Takada.8) On the other hand, FeHY-1 shows paramagnetism at the whole temperature range examined. The Morin temperature in this case is considered to be lower than the lowest measurement temperature, 113 K. This indicates a particle size less than 250 A. Thus the ferric oxide supported in FeHY-1 should be much finer than in the other samples. We estimate that the fine ferric oxide particles are formed through hydrolysis of $Fe^{3+}$ ions in the zeolite cavity; the polymerization or coagulation of ferric hydroxide is limited by the steric hindrance due to the cavity.

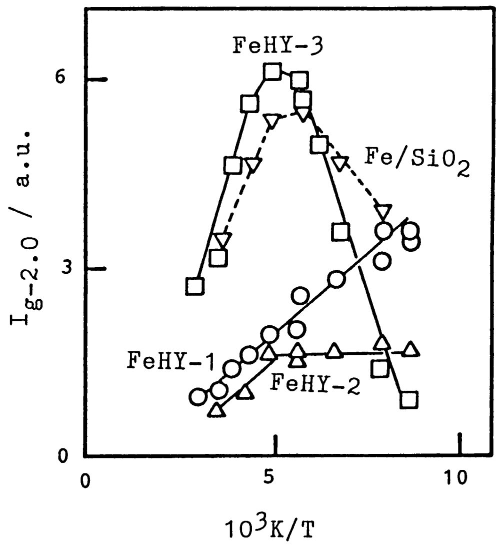

Fig.2. Dependence of the signal intensity on the ESR measurement temperature.

Another approach to characterize the Fe species supported in FeHY-1 was carried out by use of FT-IR. The lattice of Y type zeolite consists of Si-O and Al-O bonds. Since the force constant(k) of Si-O bond is larger than that of Al-O bond, IR absorption bands for the stretching vibrational modes of internal $TO_4$ tetrahedron(T = Si or Al) shift to higher wavenumbers as the content of Al in the zeolite lattice decreases.9) At the same time, the unit cell of zeolite lattice shrinks with a decrease in Al content. Thus for a series of zeolite sample(DAHY series),whose Al contents were changed variously through dealumination, the wavenumber of antisymmetric stretching vibration(950-1250 $cm^{-1}$) of $TO_4$($TO_{4asym}$) could be linearly related with the unit cell dimension, as shown in Figure 3. Data for FeHY-1 series, FeHY-2 series and FeHY-3 are also plotted in the same figure. Apparently the plots for FeHY-2 series and FeHY-3 fall on the correlation line drawn for DAHY series. This means that the Fe species supported in these samples have no effect on $TO_{4asym}$ and therefore they must be present as bulky oxide and/or ferric ions at the ion exchange sites of zeolite. In contrast, the plots for FeHY-1 series deviate largely from the above correlation line, falling on an independent correlation line. This deviation clearly indicates that at least a part of supported Fe in this case affects directly $TO_{4asym}$ and/or unit cell dimension. One of the possible explanations for this phenomenon is that $Fe^{3+}$ ions are exchanged at the $Al^{3+}$ sites of zeolite lattice. However, this possibility is not consistent with the result of the Mössbauer spectroscopy carried out separately, which denied the existence of significant amount of $Fe^{3+}$ ions tetrahedrally coordinated with oxide ions.10) Thus we assume that the Fe species in question are small cluster ions comprising Fe and O which are bonded to zeolite lattice at the dealuminated sites. Formation of Fe containing cluster ions from solution proceeds through hydrolysis and oligomerization of $Fe^{3+}$ ions. These steps produce $H^+$ ions and can accelarate dealumination from zeolite lattice. Thus the cluster ion formation and the dealumination may proceed cooperatively at localized places not only on the outer surface of zeolite but also in the super cage. It is inferred that the bonding of the cluster ions to zeolite lattice affects the wavenumber of $TO_{4asym}$ and causes the observed deviation of the correlation line for FeHY-1 series from that for DAHY series.

As mentioned above, ESR measurements showed the existence of very fine ferric oxide particles in FeHY-1, while FT-IR measurements suggested the cluster ions of Fe oxide bonded to zeolite lattice. It is not clear at present how the fine particles shown by ESR are related with the cluster ions suggested by FT-IR. It is felt that the ferric oxide particles supported in FeHY-1, though being very fine, have some dispersion in particle size. Only those small cluster ions which bonded to zeolite lattice are responsible to the shift of $TO_{4asym}$, while all particles are involved in the ESR measurements. Anyway the existence of such small ferric oxide particles is a feature characteristic to FeHY-1, and their formation seems to be deeply associated with dealumination from zeolite lattice. The small ferric oxide particles, especially those bonded to zeolite lattice, may be responsible for the unique acid property of FeHY-1.

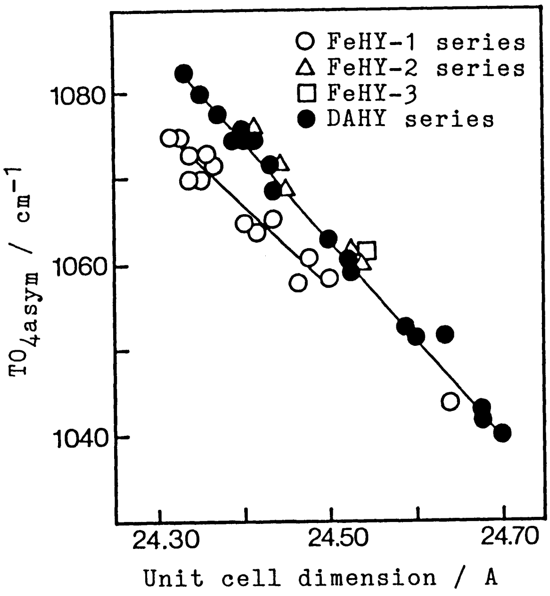

Fig.3. Correlation between $TO_{4asym}$ and U.D.

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( Received April 12, 1986)