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Catalytic Conversion of Alkyl Acetate into Alkene and Acetic Acid over Iron(III) Ion-Exchanged H-Mordenite

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The iron(III) ion in H-mordenite was found to act as a very strong oxidizing agent. It accelerates the conversion of alkyl acetate into alkene and acetic acid by withdrawing an electron from the coordinated alkyl acetate. It also oxidizes water into proton and oxygen, and benzene into benzene radical cation.

Silica-rich zeolites containing protons as the exchangeable cations have attracted much attention because of their catalytic activity to convert low-molecular organic compounds into high-molecular ones. The active sites in these catalysts are generally considered to be Brønsted acid ones. The acidity of zeolites increases with increasing silica content, so that silica-rich zeolites such as H-mordenite and ZSM-5 act as very strong acids.

H-mordenite is also known to form radical cations and neutral radicals upon adsorption of organic compounds such as benzene and alkenes.[1—9)] The alkene radical cations were regarded to be reactive intermediates for the catalytic isomerization and condensation of feed alkenes. The active site for the formation of the radical species was believed to be the Lewis acid site generated during calcination of H-mordenite. We have recently studied the mechanism of radical formation upon adsorption of alkenes and found that the active site for the formation is not the Lewis acid site but the iron(III) ion which exists in H-mordenite as an impurity.[11)] We have also found that the radical cations of alkenes do not play an significant role in the catalytic reactions of alkenes.[10)]

The iron(III) ions and radical cations are, however, expected to play important roles if the concentration of the iron(III) ions in H-mordenite is increased. For example, conversion of alkyl acetate into alkene and acetic acid, which is known to proceed through the formation of the acetate radical cation[12—18)] is expected to be accelerated by the iron(III) ions. In the present work electron spin resonance (ESR) and product-analysis study on iron(III) ion-exchanged H-mordenite was carried out to investigate the possibility of catalyzing a chemical reaction through the formation of electron-defficient reactive intermediates.

Experimental

H-mordenite used was JRC-Z HM15 standard catalyst with a $SiO_2/H_2Al_2O_4$ ratio of 15. Previous studies showed that the ability of radical cation formation scarcely depends on the $SiO_2/H_2Al_2O_4$ ratio within a range of 10 to 20. Impurity ions in the mordenite were eliminated by washing the mordenite with concentrated hydrochloric acid. The mordenite was ion-exchanged with the iron(II) ions in the aqueous solution of iron(II) sulfate. After washing with water, the mordenite was dried at 323 K for overnight and then calcined in oxygen flow at 673 K for overnight for oxidizing the iron(II) ions into iron(III) ions. The concentration of the iron ions in the mordenite was determined by the spectrophotometric analysis of the residual iron ions in the solution and the washings.

Organic compounds (benzene, *t*-butyl acetate, 2-propyl acetate, and ethyl acetate) were deaerated and dried under vacuum over dehydrated zeolite 3A.

For measuring an ESR spectrum, about 0.2 g of the mordenite in a quartz tube was evacuated at 373 K, heated overnight in oxygen at 673 K, and then evacuated at the same temperature. The organic compounds were adsorbed on the evacuated mordenite by exposing the vapor of the compound. The ESR spectrum of the mordenite was recorded at 77 K on a Varian E-line spectrometer.

For studying the catalytic activity of the mordenite to the decomposition of alkyl acetates into alkenes and acetic acid, 0.5 g of mordenite in a glass tube was heated under oxygen at 673 K for ten hours and then evacuated. After repeating this procedure four times, 10 cm^3 of alkyl acetate was introduced in the glass tube at 323 K by vacuum distillation. The reaction was carried out at 323 K while vigorously stirring the liquid. A small portion of the liquid was periodically taken out for product analysis with gas chromatography (column: BX-10, 1 m).

Results and Discussion

Effect of Activation. Figure 1 shows the effect of activation on the ESR spectrum of the H-mordenite in which 2.6% of the protons are exchanged with the iron(III) ions (2.6% Fe–HM). The iron(III) ions were scarcely observed for the mordenite which was stored more than two weeks after the calcination. This indicates that the iron(III) ions in the mordenite were already reduced to the iron(II) ions during storage of the sample by reacting water molecules as,

$$4Fe^{3+} + 2H_2O \longrightarrow 4Fe^{2+} + 4H^+ + O_2. \tag{1}$$

Evacuation of the sample at room temperature or 673 K did not give the ESR spectrum of the iron(III) ions. The ESR intensity increased with increasing the number of activation at 673 K in oxygen, which indicates that reaction (1) is reversible and the equilibrium concentration of the iron(III) ions is determined by the temperature and the concentrations of oxygen and water.

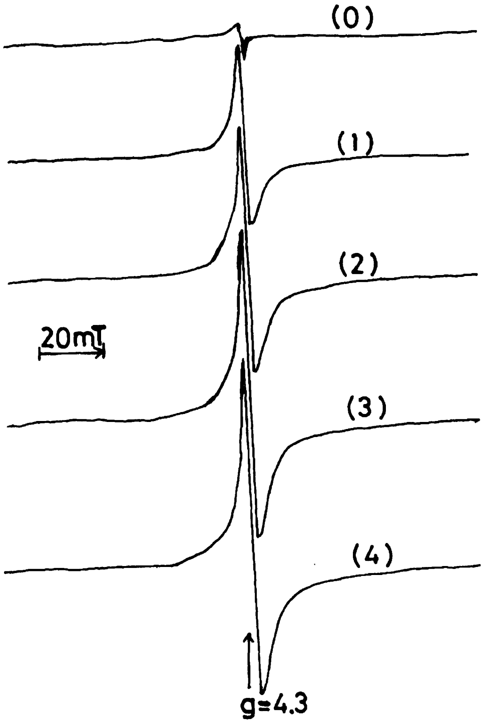


Fig. 1. ESR spectra at 77 K of the iron(III) ions in 2.6% iron(III) ion-exchanged H-mordenite near g=4.3 (0) before, and after (1) once, (2) twice, (3) three times, and (4) four times activation of the mordenite at 673 K in oxygen.

The ESR intensity was constant after four times activation. The ESR intensity after four times activation linearly increased with the concentration of the iron ions in the mordenite. The concentration of the iron(III) ions determined by double integration of the ESR spectrum was approximately the same as that obtained by the spectrophotometric analysis. These results indicate that the iron ions introduced in the mordenite by ion-exchanging is completely oxidized to the iron(III) ions after the four times activation.

As shown in Fig. 2, adsorption of benzene on the activated Fe–HM caused the formation of the radical cation of benzene dimer. The yield of the dimer cation increased with the concentration of the iron(III) ions, which indicates that the radical cation was generated by reaction,

$$\begin{aligned} &\mathrm{Fe^{3+} + C_6H_6 \longrightarrow Fe^{2+} + C_6H_6{}^{\cdot+}},\\ &\mathrm{C_6H_6{}^{\cdot+} + C_6H_6 \longrightarrow (C_6H_6)_2{}^{\cdot+}}. \end{aligned} \qquad (2)$$

In the previous paper we demonstrated that the iron(III) ion in H-mordenite ionizes 2,3-dimethyl-2-butene with the ionization potential of 795 kJ mol^{-1}.[11] The formation of the benzene cation indicates that the ionization ability of the iron(III) ion in the activated H-mordenite should be extended to 891 kJ mol^{-1}.

The radical cation of benzene dimer was not observed when the iron(III) ions were exchanged to the less electronegative copper(II) ions. The ionization ability of the iron(III) ions was lost by exchanging the protons with alkali metal ions, which indicates that the proton acts to strengthen the electronegativity of the iron(III) ions in the mordenite.

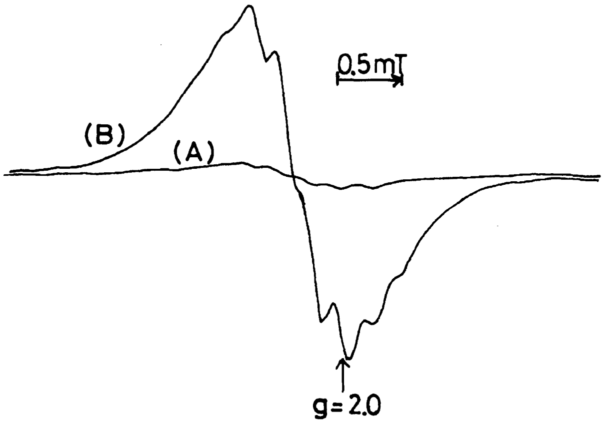


Fig. 2. ESR spectra at 77 K of benzene-adsorbed activated H-mordenite containing (A) 0.2% and (B) 2.6% of the iron(III) ions.

Catalytic Conversion of Alkyl Acetate. Figure 3 shows the spectral change of 2.6% Fe–HM at 293 K after the adsorption of 2-propyl acetate. The spectrum is composed of mainly 13 lines due to 12 equivalent methyl protons of the 2,3-dimethyl-2-butene radical cation.[10] A small amount of the dimer radical cation of 2,3-dimethyl-2-butene with 25 hyperfine lines due to 24 equivalent methyl protons is also observed

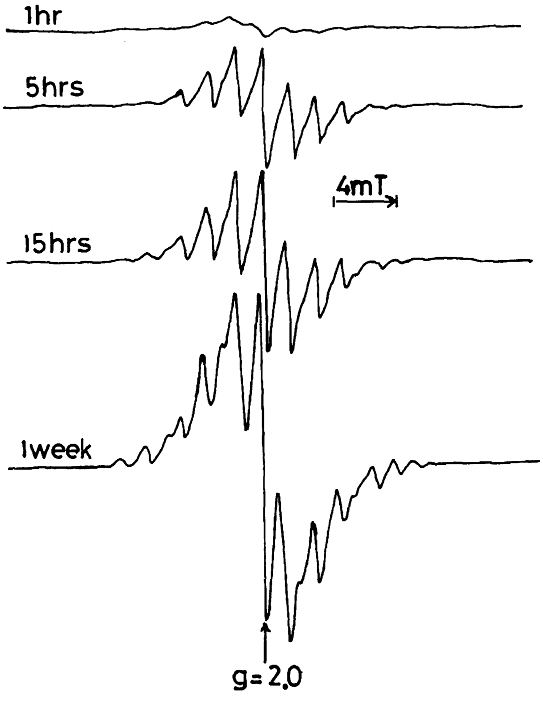


Fig. 3. ESR spectra at 77 K of 2-propyl acetate-adsorbed activated H-mordenite containing 2.6% of the iron(III) ions at 1 h, 5 h, 15 h, and one week after the adsorption.

on the spectrum at one week after the adsorption. Observation of no dimer cation within 15 h after the adsorption indicates that the concentration of the 2,3-dimethyl-2-butene is not high enough to generate more stable dimer cation. The concentration increases with the reaction time, so that a part of the monomer cation is converted to the dimer cation at one week after the adsorption.

Figure 4 shows the ESR spectra of 2.6% Fe–HM immediately after the adsorption of *t*-butyl acetate. The spectra consist of 25 lines due mainly to the dimer radical cations of 2,3-dimethyl-2-butene. The 13 lines due to the monomer cation is overlapped on the spectra. Formation of the dimer cation indicates that the amount of generated 2,3-dimethyl-2-butene is enough for the formation of the dimer cation. The intensity of the ESR spectrum did not depend on the reaction time at 293 K after the adsorption, which indicates that the formation of 2,3-dimethyl-2-butene from *t*-butyl acetate is much faster than that from 2-propyl acetate. The yield of the radical species increased with the number of activation and therefore with the concentration of the iron(III) ions.

Formation of the same radical cations from different alkyl acetates indicates that 2,3-dimethyl-2-butene is generated by condensation and isomerization of alkene molecules which are produced by the dissociation of alkyl acetate, as

$$CH_3COOC_nH_{2n+1} \longrightarrow CH_3COOH + C_nH_{2n}. \quad (3)$$

Adsorption of ethyl acetate to Fe–HM did not give any ESR spectrum near $g=2.0$, which implies that the rate of the dissociation increases with the molecular weight of the alkyl group.

The gas chromatographic study of the product molecules generated by the adsorption of *t*-butyl acetate on the Fe–HM showed that the product are composed of acetic acid and alkene mixtures. The gas chromatographic pattern of the alkene mixtures was the same as that obtained after the adsorption of isobutene on H-mordenite, which implies that isobutene generated by reaction (3) was converted to another alkenes by condensation and isomerization in the mordenite with the aid of the protons acting as very strong Brønsted acid.

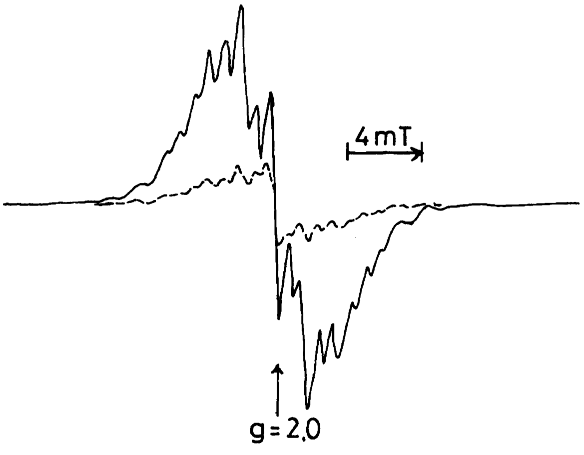
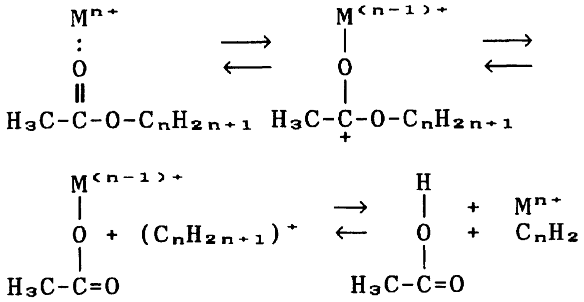


Fig. 4. ESR spectra at 77 K of 2.6% iron(III) ion-exchanged H-mordenite immediately after the adsorption of *t*-butyl acetate. The number of activation before the adsorption is once for the broken line and four times for the solid line.

Figure 5 shows the catalytic conversion of *t*-butyl acetate at 323 K over the activated mordenite. The conversion ratio is expressed by the amount of generated acetic acid relative to the feed acetate. The activated sodium ion-exchanged mordenite did not show the catalytic activity. The activated H-mordenite containing no iron(III) ion showed the catalytic activity, which indicates that the proton catalyzes the dissociation of *t*-butyl acetate. The initial activity was increased about 2.5 times by the exchange of 2.6% protons with the iron(III) ions, and 4 times by 10.5% exchange. These results indicate that the iron(III) ion accelerates the conversion much more than the proton. Although the initial rate of the conversion depended on the content of the iron(III) ions, the plateau value of the conversion was independent of the amount of the iron(III) ions. The reaction was under equilibrium state after 8 h.

Taking the ESR results into account, the role of the proton or the iron(III) ion in the dissociation of alkyl acetate into alkene and acetic acid is considered as follows;



$$\begin{array}{c}M^{n+}\\ : \\ O \\ \| \\ H_3C-C-O-C_nH_{2n+1}\end{array} \rightleftarrows \begin{array}{c}M^{(n-1)+}\\ | \\ O \\ | \\ H_3C-\underset{+}{C}-O-C_nH_{2n+1}\end{array} \rightleftarrows$$

$$\begin{array}{c}M^{(n-1)+}\\ | \\ O \\ | \\ H_3C-C=O\end{array} + (C_nH_{2n+1})^{+} \rightleftarrows \begin{array}{c}H\\ | \\ O \\ | \\ H_3C-C=O\end{array} \begin{array}{c}+\\ +\end{array} \begin{array}{c}M^{n+}\\ C_nH_{2n}.\end{array} \quad (4)$$

Here M^{n+} denotes the iron(III) ion or the proton. The coordinated ion withdraw an electron from alkyl acetate to convert the acetate into the carbonium ion. The carbonium ion then dissociates into protonated alkene and acetic acid. The rate of the scission therefore increases with increasing stability of protonated alkene. The proton affinities of alkenes increases in the order of ethylene (P.A.=681 kJ mol^{-1}), propylene (P.A.=752 kJ mol^{-1}) and isobutene (P.A.=820 kJ mol^{-1}),[19] so that the conversion of *t*-butyl acetate is the fastest among the alkyl acetates examined. The rate of dissociation also increases with increasing the rate of formation of the carbonium ion. The rate of formation increases with increasing ability of the coordinated cation to withdraw an electron from alkyl acetate, so that the iron(III) ion acts as a more active catalyst than the proton.

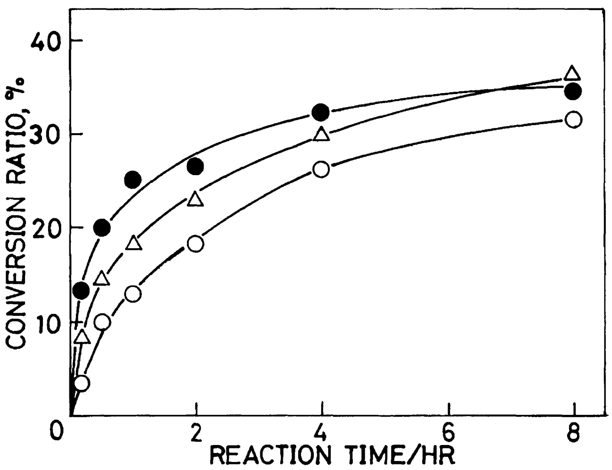


Fig. 5. Catalytic conversion of 10 cm^3 *t*-butyl acetate into alkene and acetic acid over 0.5 g of activated H-mordenite containing (○) 0%, (△) 2.6%, and (●) 10.5% of the iron(III) ions.

Another explanation for the acceleration of the conversion is that the electron-withdrawing ability of the coordinated proton is enhanced by the iron(III) ion which is not directly coordinated to alkyl acetate. It is difficult to rule out this mechanism, since the iron(III) ion acts as a strong electron acceptor and the catalyst only when the residual exchangeable cation is the proton. However we prefer the former mechanism since the iron(III) ion in H-mordenite has a very strong ability of ionizing neutral molecules.

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