

Interaction of Furans with Cu(II)Y Zeolite Catalysts

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When furan, 2-methylfuran, and 2,5-dimethylfuran were adsorbed on CuY, a new high-field band appeared in the EPR spectrum while the original signal of Cu(II) decreased. X-Ray photoelectron spectra of Cu(II)Y showed the formation of Cu(I) upon adsorption of furan. The interaction of furans with Cu(II) ion in Cu(Y) is interpreted in terms of formation of a charge transfer complex between the furan ring and the Cu(II) ion. Cu(II) ions in CuY are distributed in two nonequivalent environments and Cu(II) ions responsible for the spectrum with $g_{\parallel} = 2.376$ exhibit preferential reactivity to furan compounds.

INTRODUCTION

The main product of vapor-phase hydrogenation of furfural over copper-containing catalysts is furfuryl alcohol, while over a nickel catalyst it is tetrahydrofurfuryl alcohol. Palladium-loaded HY zeolite catalyst shows high selectivity to furan formation, whereas palladium- and nickel-loaded CuY shows selectivity to furfuryl alcohol (1).

When furfural is adsorbed on CuY, the absorption band of 1570 cm^{-1} , representing conjugated double-bond stretching, is shifted to a lower frequency by 15 cm^{-1} . The amount of furan adsorbed on CuY increased with an increasing degree of Cu(II) ion exchange, while there was no change in the amount of tetrahydrofuran adsorbed on CuY with an increasing degree of Cu(II) ion exchange. With the adsorption of furan on CuY a new high-field band having a g factor of 2.002 and a width of 8 G appeared and increased with an increasing amount of furan adsorbed while the original signal of Cu(II) decreased. High selectivity to furfuryl alcohol and the absence of tetrahydrofurfuryl alcohol formation over copper-containing catalyst is interpreted in terms of the interaction between Cu(II) ion and the furan ring of furfural preventing the furan ring from being hydrogenated (1).

In the present work the interaction of furan compounds with Cu(II) ions of CuY zeolite is studied in some detail by means of the electron paramagnetic resonance technique and X-ray photoelectron spectroscopy.

METHODS

The Linde synthetic zeolite NaY (Lot. No. 968050009) was used as the starting material. Sodium ions in the zeolite were exchanged for copper ions in nitrate solution. The degree of exchange was expressed as the percentage of original Na^+ ions replaced by copper ions and designated by n as in $\text{Cu}(n)\text{Y}$.

The EPR spectra were recorded at X-band frequencies on a Varian E-4 spectrometer at room temperature and occasionally at liquid nitrogen temperature. The DPPH standard was used for the determination of g factors. The EPR sample tube was directly connected to a portable vacuum and gas handling system. The zeolite samples were evacuated at 200°C for 2 hr prior to the adsorption. The adsorbates used were reagent grade of Tokyo Kasei.

The ESCA spectra were obtained using a PHI Model 548 ESCA/Auger electron spectrometer with X-ray excitation from $\text{MgK}\alpha$ (1248.5 eV). Furan-adsorbed $\text{Cu}(60)\text{Y}$ sam-

ples used for the ESCA measurements were prepared by evacuating Cu(60)Y powder at 200°C for 2 hr and adsorbing furan at room temperature, and then forming into a pellet of 1 mm thickness. The carbon 1s line (284.3 eV) was used as the reference standard for the determination of binding energies.

RESULTS

The EPR spectrum of dehydrated Cu(15)Y zeolite shows two groups of four



FIG. 1. EPR spectra of Cu(15)Y and effect on furan adsorption at 25°C. (A) Evacuation at 200°C for 4 hr. (B) Furan on Cu(15)Y. (C) Additional furan added to B.

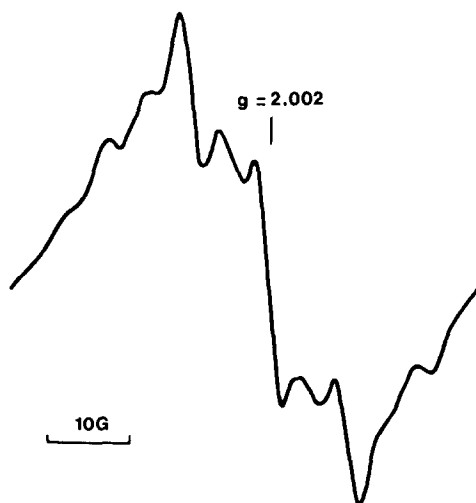


FIG. 2. EPR spectrum of 2-methylfuran adsorbed on Cu(15)Y.

hyperfine lines on the low-field side with $g_{\parallel} = 2.328$ ($A = 162$ G) and $g_{\parallel} = 2.376$ ($A = 126$ G). The value of g_{\perp} was 2.048 ($A = 19$ G). Cu(II) ion in Y zeolite has been studied extensively by EPR and a spectrum of Cu(II) ion in Y zeolite has been reported several times (2–5).

Figure 1 shows the EPR spectra of Cu(15)Y and the effect of furan adsorption at room temperature. With the adsorption of furan on Cu(15)Y, a new high-field band with $g = 2.002$ and a width of 8 G appeared and increased with an increasing amount of furan adsorbed, while the original signal of Cu(II) decreased (1). The hyperfine structure was not observed. With the adsorption of 2-methylfuran and 2,5-dimethylfuran, however, the new absorption band with hyperfine structure appeared as shown in Figs. 2 and 3. The spectra of 2-methylfuran can be interpreted in terms of the contribution from three ring protons, one at C_5 , two at C_3 and C_4 , and three from the methyl group. The spectra of 2,5-dimethylfuran can be interpreted in terms of the two ring protons (C_3 and C_4) and six equivalent protons in two methyl groups. The dotted curve in Fig. 3 is the simulated EPR spectrum of 2,5-dimethylfuran using the hyperfine coupling constant of 7.5 G for C_3 and C_4

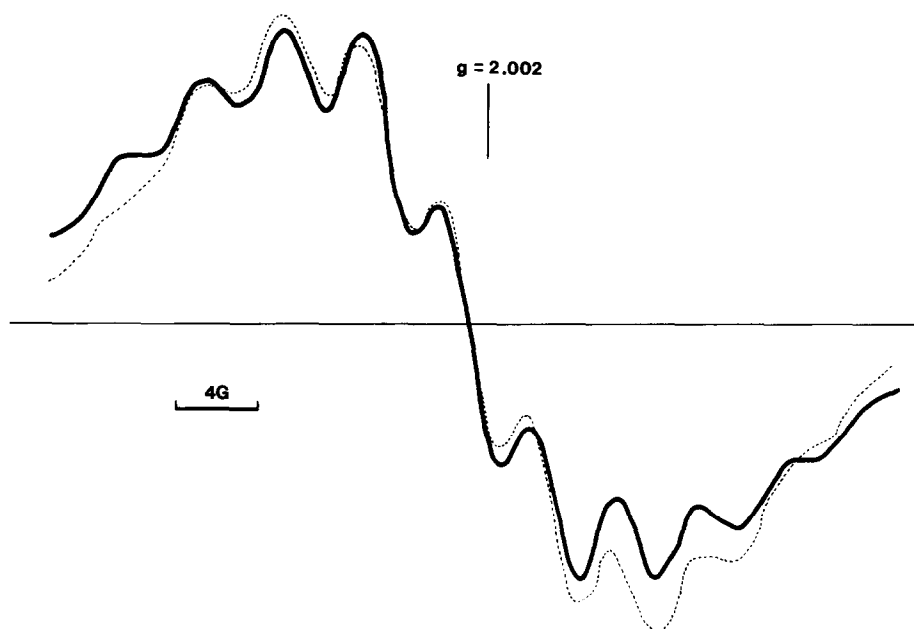


FIG. 3. EPR spectrum of 2,5-dimethylfuran adsorbed on Cu(15)Y at room temperature. Solid line: experimental; dotted line: simulated ($a_{\text{H}_{3,4}} = 7.5$ G, $a_{\text{CH}_3} = 4$ G).

ring protons and 4 G for the six equivalent protons in two methyl groups. No new band was observed when tetrahydrofuran was adsorbed on Cu(15)Y.

Figure 4 shows changes in the new band portion of the EPR spectrum of 2-methylfuran adsorbed on CuY zeolite with the degree of Cu(II) ion exchange. The hyperfine structure of 2-methylfuran disappears gradually with an increasing degree of Cu(II) ion exchange and the new band portion becomes a single broad absorption band in the case of Cu(60)Y. With the addition of 2-methylfuran at room temperature on Cu(60)Y, $g_{\parallel} = 2.328$ of the hyperfine structure of Cu(II) appeared together with the new absorption band with $g_{\perp} = 2.002$ shown in Fig. 5. Figure 6 shows the changes in the parallel parts of the EPR spectrum of Cu(15)Y when the incremental amount of furan was added at room temperature. With the first addition of furan at room temperature the spectrum with $g_{\parallel} = 2.376$ decreased sharply (Fig. 6B). When an additional amount of furan was added, the spectrum with $g_{\parallel} = 2.328$ also showed a de-

crease (Fig. 6C). With further addition of furan the fine structure of Cu(II) ion almost disappeared, as shown in Fig. 6D.

Figure 7 shows the wide-scan X-ray photoelectron spectra of Cu(60)Y and Cu(60)Y with adsorbed furan. X-Ray photoelectron spectra of furan-adsorbed samples show a large carbon peak. (A small peak of carbon is present in the Cu(60)Y sample, probably due to contamination.)

Figure 8 shows the X-ray photoelectron spectra of Cu(60)Y and Cu(60)Y with adsorbed furan in the $2p$ energy region. Cu(60)Y with adsorbed furan shows a shift in the $2p^{1/2}, 2p^{3/2}$ main peaks by 1.0 eV and the intensity of the satellite peaks are greatly reduced.

Included in Fig. 8 are the $2p$ X-ray photoelectron spectra of CuCl₂ and CuCl for comparison of the Cu²⁺ and Cu⁺ spectra.

DISCUSSION

The EPR spectrum of dehydrated Cu(15)Y shows in parallel part two groups of four hyperfine lines with $g_{\parallel} = 2.328$ and $g_{\parallel} = 2.376$. The appearance of two groups

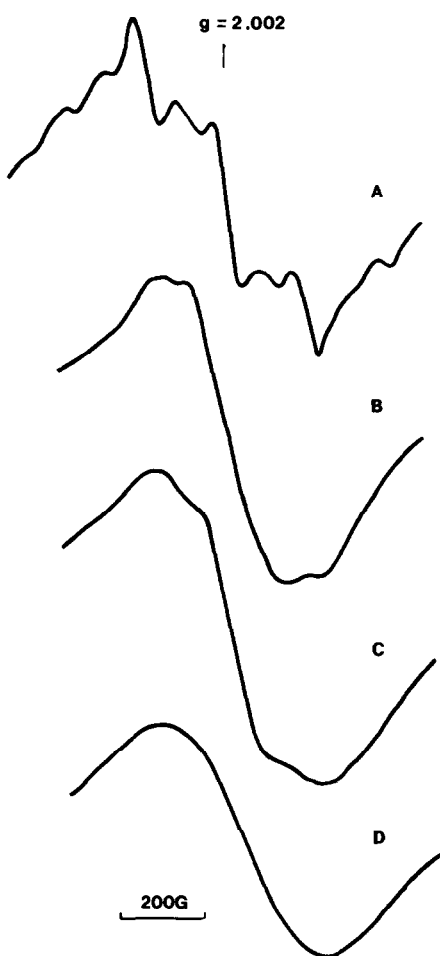


FIG. 4. EPR spectra of 2-methylfuran adsorbed on CuY. (A) Cu(15)Y, (B) Cu(30)Y, (C) Cu(42)Y, (D) Cu(60)Y.

of g_{\parallel} indicates that Cu(II) ions are distributed in at least two magnetically non-equivalent environments. Difference in the behavior of the Cu(II) ion with $g_{\parallel} = 2.328$ and 2.376 is demonstrated in the adsorption of furan on CuY. When the small amount of furan was added at room temperature to Cu(15)Y the spectrum with $g_{\parallel} = 2.376$ decreased sharply while there was almost no change in the spectrum with $g_{\parallel} = 2.328$, as shown in Fig. 7B. With the addition of 2-methylfuran at room temperature on Cu(60)Y, $g_{\parallel} = 2.328$ of the hyperfine structure of Cu(II) appeared together with its new band with $g = 2.002$ (Fig. 5). The ap-

pearance of the spectrum with $g_{\parallel} = 2.328$ of the Cu(II) fine structure can be due to the reduction in the number of Cu(II) ions resulting from the interaction of 2-methylfuran with the Cu(II) ions responsible for the spectrum with $g_{\parallel} = 2.376$. These facts suggest that the Cu(II) ion with $g_{\parallel} = 2.376$ exhibits a preferential reactivity toward furans. Leith and Leach (6) postulated that Cu(II) ions exhibiting a preferential reactivity toward a variety of simple molecules are

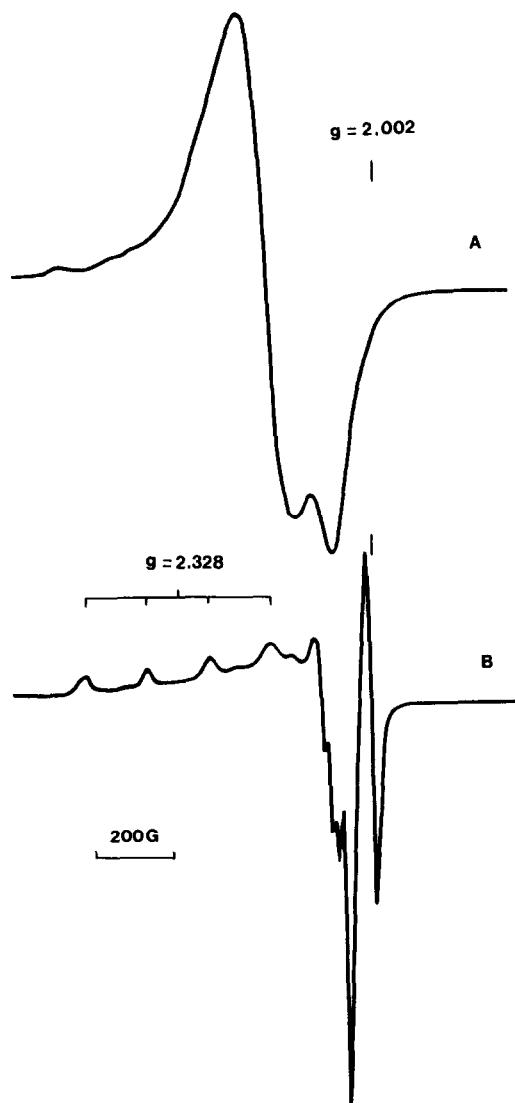


FIG. 5. EPR spectra of Cu(60)Y and effect on 2-methylfuran adsorption at 25°C. (A) Evacuation at 200°C for 4 hr. (B) 2-Methylfuran on Cu(60)Y.

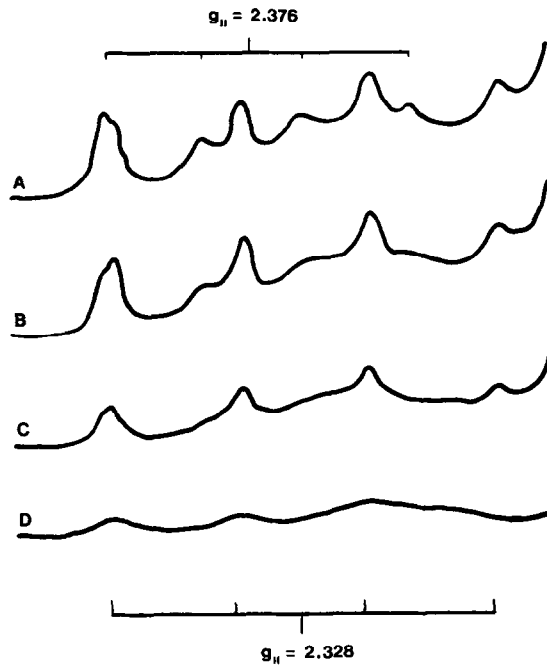


FIG. 6. Changes in the EPR spectrum (g_{\parallel} portion) of Cu(15)Y with an incremental amount of furan added at room temperature. (A) Cu(15)Y. (B, C, D) Cu(15)Y with adsorbed furan. Amount of furan adsorbed increases in the order B, C, D.

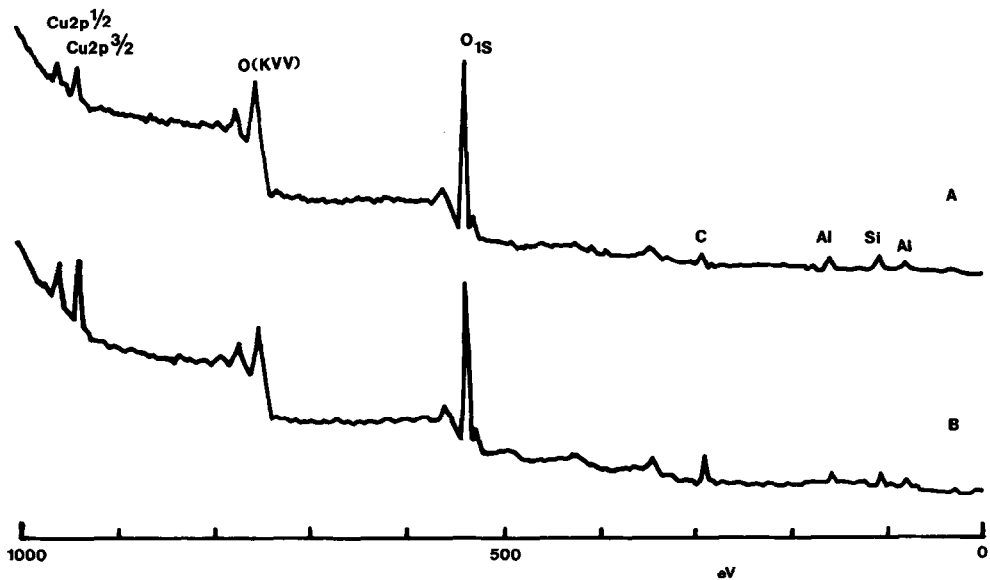


FIG. 7. Changes in the X-ray photoelectron spectrum of Cu(15)Y. (A) Cu(60)Y. (B) Cu(60)Y with adsorbed furan.

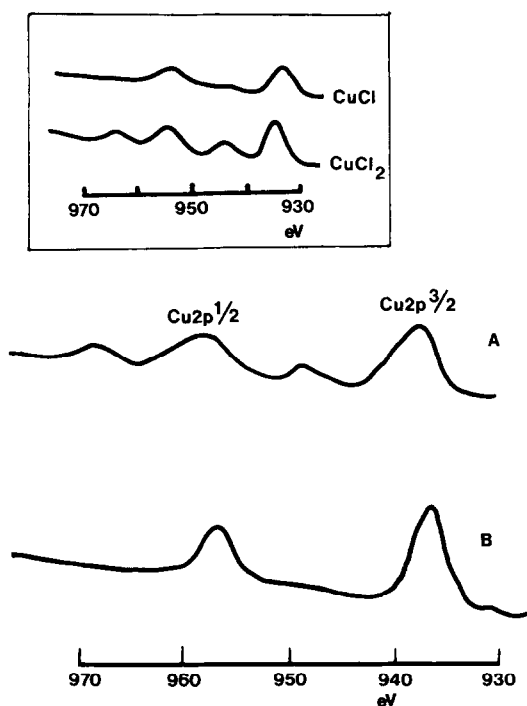


FIG. 8. Changes in the X-ray photoelectron spectrum of Cu(60)Y in the $2p$ energy region. (A) Cu(60)Y. (B) Cu(60)Y with adsorbed furan.

located in site II', whereas the less reactive cations are in the relatively inaccessible site I'. The fact that with increasing amount of furan adsorbed on Cu(15)Y the spectrum with $g_{\parallel} = 2.328$ also decreased suggests that Cu(II) ion located in relatively inaccessible sites can migrate toward the supercage to interact with furan.

With the adsorption of furan on Cu(15)Y a new high-field narrow band with $g = 2.002$ having no hyperfine structure appeared and increased with an increasing amount of furan adsorbed, while the original signal of Cu(II) decreased. The disappearance of the signal of Cu(II) can be interpreted in terms of the transfer of an electron from the furan ring to the Cu(II), giving Cu(I), which is EPR inactive. Rupert (8) has observed a new high-field narrow band with a g factor of 2.0024 upon adsorption of a series of polynuclear aromatic compounds on Cu(II)-exchanged mont-

morillonite and interpreted the results in terms of a formation of radical cations.

Formation of Cu(I) upon adsorption of furan is also demonstrated in the X-ray photoelectron spectra of Cu(60)Y and Cu(60)Y with adsorbed furan in the $2p$ energy region. Cu(60)Y with adsorbed furan showed a shift in the $2p^{1/2}$, $2p^{3/2}$ main peaks by 1.0 eV and a great reduction in the intensity of the satellite peaks. $2p$ X-ray photoelectron spectra of CuCl and CuCl₂ taken to compare the difference in the spectra of Cu(II) and Cu(I) showed the absence of satellite peaks in CuCl spectra. From the studies of the X-ray photoelectron spectra of a large number of cupric and cuprous compounds Frost *et al.* (7) have shown that the cupric compounds have satellite peaks while the cuprous compounds do not.

Absence of the hyperfine structure due to the ring proton in the case of furan-Cu(15)Y may be attributed to exchange narrowing. Rupert has shown that electron exchange between radical cations formed on Cu(II)-exchanged montmorillonite or between radical and neutral diamagnetic species results in the single exchange-narrowed EPR band (8). The appearance of the hyperfine structure in the case of 2-methylfuran-Cu(15)Y and 2,5-dimethylfuran-Cu(15)Y may be attributed to reduced interaction between the furan rings due to the presence of side chains. The hyperfine structure, however, disappeared gradually with increasing degree of Cu(II) ion exchange and the spectra of 2-methylfuran-adsorbed Cu(60)Y showed a single broad absorption band. This can be interpreted in terms of static dipolar broadening due to increased copper ion concentration.

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