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Rearrangement of Cationic Sites in CuH–ZSM-5 and Reactivity Loss upon High-Temperature Calcination and Steam Aging

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The state and reactivity of isolated copper ions in Cu–ZSM-5 treated at elevated temperatures were monitored *in situ* by ESR under flowthrough conditions. Steam aging (620–630°C, 17 h) or dry calcination (850–900°C, 30 min) induces a change in Cu^{2+} coordination without noticeable agglomeration or encapsulation of the isolated ions. All Cu^{2+} ions remain accessible to gas-phase molecules: O_2 causes dipole–dipole signal broadening; H_2O sorption leads to the increase of the local crystal field symmetry; and the admission of CCl_4 results in a noticeable change in Cu^{2+} local coordination. At the same time, the reactivity of these altered Cu^{2+} sites and their ability to adsorb different molecules is substantially affected. No stabilization of nitrosyl complexes on specimens calcined at 900°C was observed, distinct from the case of Cu–ZSM-5_{500}. The bond strength between an altered Cu^{2+} site and the strong ligand–NO_2 is decreased. The sorption of C_3H_6 on Cu–ZSM-5_{900} at 20°C is not accompanied by noticeable reduction of Cu^{2+} sites. Even at 500°C in a [C_3H_6 + He] flow a noticeable part of copper ions (20–30%) preserves the Cu^{2+} state. A partial stabilizing effect of the Cu^{2+} cations on framework Al^{3+} in ZSM-5 is demonstrated: the steam aging of pure H–ZSM-5 at 650°C results in an almost total destruction of the sites where Cu^{2+} ions may be exchanged. The introduction of the Cu^{2+} before steaming preserves these sites from total destruction and only a transformation in local topography takes place. The surface moieties, containing both Cu^{2+} and Al^{3+} ions, are a part of the zeolitic framework but must also be "flexible" enough to change symmetry upon additional ligand bonding. The high-temperature calcination or steaming at intermediate temperatures appears to affect this ability. The practical implications are discussed.

INTRODUCTION

Cu–ZSM-5 has become the model catalyst in the study of the low-temperature decomposition of NO to elements and in the selective catalytic reduction (SCR) of NO_x in excess oxygen by organic compounds (1–3). In the last few years Cu–ZSM-5 specimens have been examined by a multitude of physical methods (4–15). The examined specimens varied widely in Cu loading, SiO_2/Al_2O_3 ratio, and preparation procedures. Surface characterization methods often yield contradictory results about the changes in the coordinative and valence states of the copper after treatment by different gas mixtures. The mechanism of CuH–ZSM-5 deactivation upon the high-temperature treatment of the catalysts is also not fully understood.

Previously, we have shown that ESR spectroscopy may be effectively used for monitoring the state of copper ions in Cu–ZSM-5. For ion-exchanged samples with low copper content (no overexchange) the ESR signal is associated with virtually all Cu^{2+} introduced into zeolite (15, 16). It was shown that *isolated* cupric cations in a H–ZSM-5 matrix preserve their oxidation state up to 500°C in the absence of reactive hydrocarbons (or hydrogen) and in the presence of other polar and nonpolar molecules (15–17). Also, the catalytic activity of CuH–ZSM-5 in total oxidation reactions was correlated with the concentration of coordinatively unsaturated square-planar Cu^{2+} cations in CuH–ZSM-5 (18–20). Previously (16, 17) we dealt with the interaction of different molecules with CuH–ZSM-5 precalcined at 500–550°C and active in both total oxidation (18, 19) and SCR (20). The aim of this work is to monitor the physical changes in the CuH–ZSM-5 structure accompanying the high-temperature deactivation of this catalyst as mirrored by the ESR spectrum of the Cu^{2+} ions. The work includes the interaction of different molecules with the same CuH–ZSM-5 catalyst treated under different conditions (steam aging at 620–630°C; dry calcination up to 900°C).

EXPERIMENTAL SECTION

The same sample of Refs. (16, 17) was used, and the apparatus and methods were the same. The ESR spectra, at 20–500°C, were taken in the X-band on the Bruker ESP300 spectrometer, equipped with a high-temperature cavity ER 4111 HT-VT. The Bruker ESP300E software and the special Bruker program WIN-EPR (version

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901201) were used for the treatment (baseline correction, double integration, and subtraction) of the recorded spectra. The ESR signals of Cu^{2+} were registered in the field region 2300–3800 G in two modes: (1) 5 scans with a sweep time of 21 s and (2) 10 scans with a sweep time 42 s. Resonances for microwave power 0.64–6.41 mW were recorded to verify the lack of sample saturation. In some cases, for more accurate measurement of the ESR parameters, the $g_{\|}$-part of the spectra was registered separately (field region 2600–3300 G; modulation amplitude 4.0 G; microwave power 6.41 mW; 10 scans with sweep time 42 s).

The ion-exchanged sample of CuH–ZSM-5 (1.27 wt% Cu or 67% of the protons exchanged *nominally* for Cu^{2+} into H–ZSM-5 with $SiO_2/Al_2O_3 = 50$) was used. The zeolite was pressed without binder and crushed into 0.1- to 0.2-mm pieces. Then it was placed in an quartz ampoule for ESR measurements and precalcined in dry air at 500–900°C. Steam aging was done in a flow of wet air (20% of H_2O) at 620–630°C for 17 h.

A coaxial quartz cell was used for *in situ* treatment of the sample in gas flow at 20–550°C (13). The cell, with 15–25 mg of the sample, was placed in the ESR cavity and connected with stainless-steel capillaries of the flow system by Teflon ferrules. The gas flow was regulated by a four-channel readout mass flow controller (MKS Instruments Model 247C). This system permitted the change of the gas mixture composition and the regulation of the gas flow from 1.5 to 18 cm/min.

Pure helium (5.0 grade) and gas mixtures [20.2% vol O_2 + He], [0.41% vol NO + He], [0.39% vol C_3H_6 + He], and [5.0% vol H_2 + He] were used for *in situ* sample treatment. To study the interaction of CuH–ZSM-5 with H_2O or CCl_4, the specimens were saturated in a flow of these compounds diluted in pure He at 15°C.

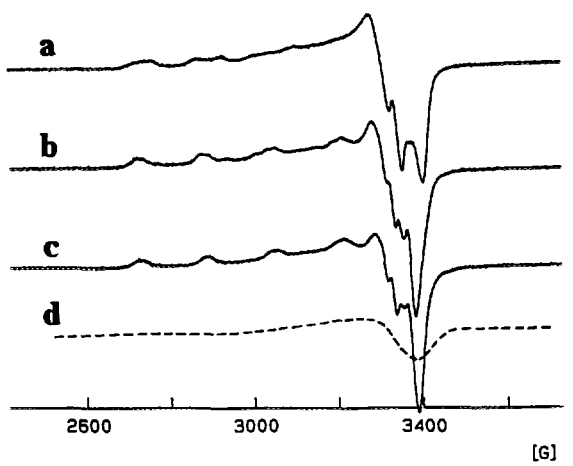


FIG. 1. ESR spectra of CuH–ZSM-5, taken at 20°C *in vacuo*: (a) calcined at 500°C for 5 h; (b) steam aged at 620°C for 17 h; (c) calcined in air at 900°C for 30 min; (d) after air admission to sample (c).

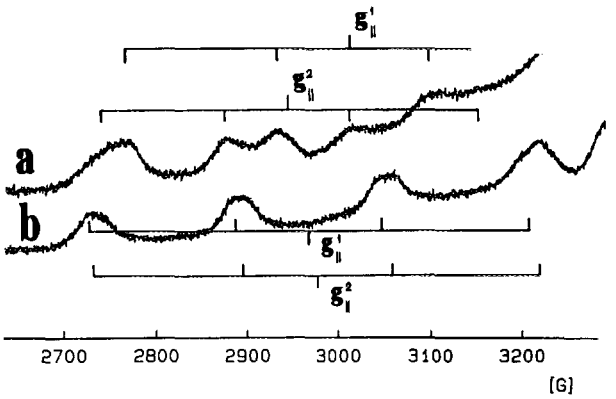


FIG. 2. HFS of ESR spectra ($g_{\|}$) presented in Fig. 1: (a) CuH–ZSM-$5_{500°}$; (b) CuH–ZSM-$5_{900°}$.

In some cases the ESR spectra were taken at 20°C for the samples evacuated after thermal treatment in air. The samples (25–30 mg) were placed in identical quartz ampoules (∅ = 4.0 mm), calcined in a furnace at a given temperature, taken out and immediately connected with the vacuum system, evacuated for 2–3 min (0.03 Torr), and sealed off. Then the spectra were registered and normalized to equal sample weight.

RESULTS AND DISCUSSION

1. *Change in the Number and in the Local Structure of Cationic Sites in CuH–ZSM-5 after High-Temperature Treatment*

Figures 1 and 2 allow the comparison of the Cu^{2+} ESR spectra of CuH–ZSM-5 treated under different conditions. It is clearly seen that either steam aging or high-temperature dry calcination influence strongly the fine structure of the Cu^{2+}-ESR signal. This is usually associated with changes in the local environment of the isolated Cu^{2+} sites. Table 1 summarizes the ESR parameters of Cu^{2+} ions relating to Figs. 1 and 2.

TABLE 1

The ESR Parameters of Cu^{2+} Ions in CuH–ZSM-5 Treated under Different Conditions

Sample treatment	$g_{\|}$	$g_{\perp}$	$A_{\|}$, (G)	$A_{\perp}$, (G)
Dry calcination,	2.325	2.06	154	19
500°C; 5 h	2.27	2.045	174	~28
Dry calcination,	2.32	~2.06	156	~23,
900°C; 30 min	2.315		159	Unresolved
Steam aging,	2.32	~2.06	155	~23,
620°C; 17 h	2.31		157	Unresolved

The results agree with those obtained earlier [21, 22] and show that the two main coordinations typical of CuH–ZSM-$5_{500°}$ (square planar and square pyramidal) disappear and two new types of Cu^{2+} ions environment are formed. Formally, the coordinations of these ions may be treated as either two moderately distorted square pyramids or very strongly distorted six-coordinated environments. The transformations resulting from either steam aging at 620°C or dry calcination at 850–900°C are practically the same (Fig. 1; Table 1). The most exact comparison of $g_{\|}$-parts (Figs. 1b and 1c), obtained by subtraction permits the conclusion that the spectrum of the steam-aged sample may be described as a superposition of ≥90% of signal 1c and ≤10% of signal 1a. Treatment of the parent CuH–ZSM-$5_{500°}$ at 550°C for 4 h is not accompanied by any change of the ESR spectrum shown on Fig. 1a. Some transformation of spectrum 1a begins at $T_{calc.}$ ~650°C, and the spectrum obtained may be treated as a superposition of 90% of signal 1a and 10% of signal 1c. The stepwise calcination of the sample at 750 and 800°C for 1 h and 900°C for 0.5 h induces a progressively larger transformation of spectrum 1a ⇒ 1c without a decrease in the integral signal intensity. The gradual decrease of the signal intensity becomes measurable upon the more prolonged (≥1 h) calcination of the sample at 900°C.

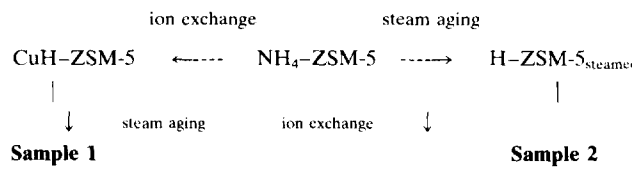
While high-silica zeolites with the pentasil structure (ZSM-5, ZSM-11) are relatively resistant to calcination and steam aging, treatment at $T < 850$°C destroys a part of Al-containing framework sites by dealumination. This happens, though, without loss of crystallinity and the long-term order of the lattice, as measured by XRD, is preserved. For example, XRD analysis of a series of differently treated ZSM-5 samples, including steaming at ~800°C for 6 h or at ~720°C for 65 h, revealed that the crystalline structure remained intact (23). We have also carried out comparative XRD measurements of the two Cu–ZSM-5 samples calcined at 500 and 800°C for 2 h. The diffraction patterns were obtained at room temperature on a DRON-3 diffractometer with Cu$K\alpha$ radiation. The two samples show an identical ZSM-5 structure. Taking into account the accuracy of the method, we conclude that the integral crystallinity loss does not exceed 3%.

In the previous work (21, 22) no quantitative ESR data were obtained. In the present work the Bruker ESP300E software affords the double integration of the ESR spectra with a rather high accuracy (±5%) (15). The quantitative comparison of the spectra in Fig. 1 demonstrates that transformation of the local environment of isolated Cu^{2+} sites is not accompanied by measurable reduction of normalized double integral (DI/N) values, which is the measure of signal intensity. It was shown earlier (15, 16) that the ESR signal shown in Fig. 1a is associated with all the copper introduced into our CuH–ZSM-5 sample by ion exchange. Therefore, *all the cupric ions*, within the experimental error, *remain well isolated after the high-temperature treatment, and the transformation of the local spatial configuration of isolated sites is not accompanied by measurable aggregation of the Cu^{2+} ions.*

An attempt was made to transform the CuH–ZSM-$5_{900°}$ by rehydration under hydrothermal conditions typical of the ZSM-5 zeolite synthesis. The sample was placed into a thick quartz capillary and H_2O was added. After evacuation of air, the capillary, with the sample and liquid water, was sealed off, placed into furnace, heated slowly from 20 to 175°C, and held at this temperature overnight (15 h). After removal from the capillary the sample was dried, calcined at 500°C for 30 min, and evacuated. The two Cu^{2+}-ESR signals from the sample before and after treatment were identical, and only a faint broad line with no hfs was obtained by signal subtraction. Thus, no measurable reverse transformation of the altered Cu^{2+} sites can be induced by rehydration.

2. *Stabilizing Effect of Cu^{2+} Cations on the Ion-Exchanged Sites in ZSM-5 Structure*

In previous work from this laboratory (6) it was noted by following ^{27}Al NMR spectra that the exchange of the proton by the cupric ion in H–ZSM-5 has an observable stabilizing effect on the magnitude of the ^{27}Al NMR signal after steam treatment at elevated temperatures. Here we examined whether this stabilizing interaction between isolated copper cations and aluminum ions in the ZSM-5 framework is observable by the ESR of the cupric ion. We compared two steam-aged CuH–ZSM-5 samples differing by the sequence of the preparation steps: the first one was exchanged with copper and then steam aged, and in the second, the pure H–ZSM-5 was steamed and then exchanged with copper, as shown in the scheme below:



ESR spectra of these two samples, taken at the same magnification with samples of equal weight, are shown in Fig. 3. The DI/N values for two spectra differ by a factor of 15. Hence, the aging of pure H–ZSM-5 in a stream containing 20% H_2O at 620°C results in almost total destruction of framework Al-sites where the isolated Cu^{2+} cations may be exchanged. *The introduction of the Cu^{2+} before steaming preserves these sites from total destruction, and only a transformation in local topography takes place.* Hence, these results confirm the stabilizing effect of Cu^{2+} cations on framework tetrahedral Al^{3+} in ZSM-5 as observed by ^{27}Al MAS NMR (6).

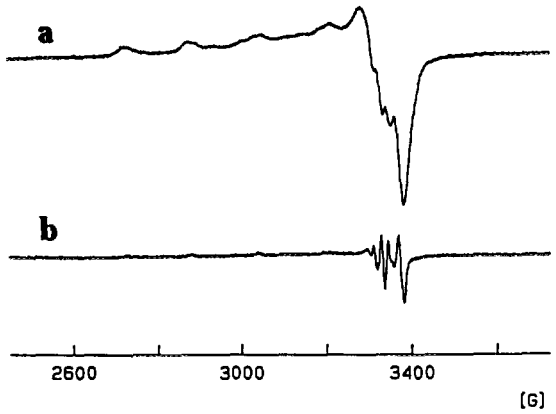


FIG. 3. Cu^{2+}-ESR spectra, taken at 20°C *in vacuo*: (a) steam aged CuH–ZSM-5; (b) Cu^{2+} exchanged after steam aging the H–ZSM-5.

3. *Interaction of CuH–ZSM-5$_{900°}$ with O_2, H_2O and CCl_4*

Figure 1d demonstrates the effect of the admission of air, at 20°C, on evacuated CuH–ZSM-$5_{900°}$. The change of a well-resolved spectrum (Fig. 1c) to the broad signal without resolved components (Fig. 1d) is completely reversible: oxygen removal by the flow of He or by evacuation leads to the restoration of the spectrum Fig. 1c. Therefore, all altered Cu^{2+} sites in CuH–ZSM-$5_{900°}$ remain accessible for interaction with paramagnetic O_2 molecules from the gas phase; i.e., *no encapsulation of isolated Cu^{2+} ions results from the high-temperature treatment.*

Transformation of the ESR signal (Fig. 1c) caused by H_2O sorption, at 20°C, also confirms the accessibility of all the altered Cu^{2+} sites. Changes in the ESR signal parameters (Table 2) show the commonly observed increase of the local crystal field symmetry by the linking of H_2O ligands to Cu^{2+} ions. As was mentioned above, CuH–ZSM-$5_{900°}$ contains two types of Cu^{2+} ions differing in the distortion of the local environment. Interaction with O_2 and H_2O alters both types of cations. However, the sorption of CCl_4, at 20°C, demonstrates the difference in properties of the two types of Cu^{2+} ions.

Figure 4 shows the changes in the Cu^{2+}-ESR signal accompanying the admission of CCl_4 molecules. It is clearly seen that one set of lines in the parent spectrum (Fig. 4a) remains intact after CCl_4 sorption, whereas the parameters of the second one are changed very noticeably (Fig. 4b). Such an effect due to filling of the CuH–ZSM-5 channels by inert molecules was observed earlier for Xe and *n*-hexane sorption (24). A small but measurable change in the symmetry of the Cu^{2+} environment for only one of the two types of sites was observed. The "symmetrization" of the local crystal field caused by CCl_4 sorption at 20°C is much more pronounced when compared with the effect of Xe or hexane (24). The effect is not fully reversible at 20°C in He flow. However, purging by He at 100°C for 30 min restores the parent ESR signal (Fig. 4a). Therefore, the physical sorption of saturated CCl_4 molecules, i.e., the filling of the zeolitic channels, causes some displacement of the Cu^{2+} ion in one of the two discrete sites, i.e. the two altered positions of Cu^{2+} location in CuH–ZSM-$5_{900°}$ differ in their "rigidity." The observations related to the sorption of CCl_4 cannot be rationalized by the geometric inaccessibility of a fraction of the copper ions since all the ions are accessible for interaction with the larger propene molecules.

Table 2 summarizes the effect of the sorption of different molecules on the ESR parameters of the Cu^{2+} signal from CuH–ZSM-$5_{900°}$. The determination of the coordination states of Cu^{2+} from the ESR parameters was made earlier (18). From ESR of Cu-complexes of known geometry it was established that the lowering of the local crystal field symmetry of the Cu^{2+} ion from octahedral to square planar is accompanied by a decrease in $g_\parallel$ from 1.38 to 1.27 and corresponding increase in $A_\parallel$ from 120 to ~180 G (25–28). The difference in the ESR parameters given in Tables 1 and 2 and shown in Figs. 2 and 4 is well-resolved and affords a satisfactory assignment.

TABLE 2

Values of ESR Parameters of the Cu^{2+}-ESR Signal from CuH–ZSM-$5_{900°}$ after Sorption of Different Molecules

Adsorbate	$g_\parallel$	$g_\perp$	$A_\parallel$ (G)	$A_\perp$ (G)
—	2.32	~2.06	156	~23,
	2.315		159	Unresolved
CCl_4	2.32		156	
	2.345		141	
H_2O	2.36		115	
NO_2	2.31		159	
C_3H_6	2.39	2.08	105	
	2.37		115	

4. *Interaction of CuH–ZSM-5$_{900°}$ with NO and [NO + O_2]*

Sorption of NO. Noticeable broadening of the parent spectrum from CuH–ZSM-$5_{900°}$ (Fig. 1c) is noted in [NO + He] flow at 20°C due to the interaction between Cu^{2+} ions and paramagnetic NO molecules filling the zeolitic channels. However, the effect is completely reversible at 20°C, as distinct from the case of NO sorption on CuH–ZSM-$5_{500°}$ (16). The treatment of the sample with a stream of pure He for 10 min leads to the restoration of the parent ESR signal shown in Fig. 1c, and subtraction of the two signals gives back the baseline. Therefore, no stabilization of nitrosyl (or dinitrosyl) complexes upon the adsorption of NO on altered Cu^{2+} sites of CuH–

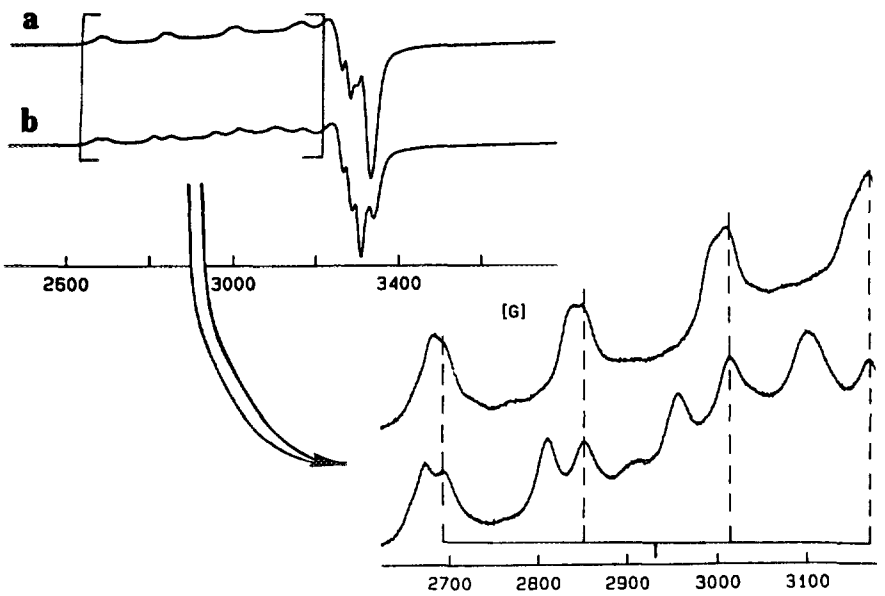


FIG. 4. Effect of CCl_4 sorption, at 20°C, on ESR signal from CuH–ZSM-$5_{900°}$: (a) in He flow; (b) after 30 min in [He + CCl_4] flow.

ZSM-$5_{900°}$ takes place. In our previous work it was shown that the interaction with NO alters mainly the most coordinatively unsaturated square-planar cupric ions in CuH–ZSM-$5_{500°}$ (16) but this reactive type of Cu^{2+} ion disappears completely as a result of high-temperature treatment of the catalyst.

NO_2 sorption. At $T < 400$°C reversible formation of NO_2 takes place in the gas mixtures [NO + O_2], and the equilibrium of this gas-phase reaction is shifted completely to NO_2 at 20°C. ESR spectra shown in Fig. 5 demonstrate the influence of NO_2 adsorption on the coordination of the Cu^{2+} cations. Treatment of CuH–ZSM-$5_{900°}$ in a [0.33% vol NO +4.0% vol O_2 + He] flow at 20°C results in a fast and irreversible transformation of the parent ESR signal (Fig. 5a) to a new spectrum shown in Fig. 5b. The parameters of this spectrum (Table 2) are typical of cupric ions located in a crystal field of rather low symmetry (distorted five-coordinated environment). This state is stable at 20°C: treatment of the sample in He stream for 1 h does not change this signal. The calcination of the sample in He flow at 100°C for 30 min does not eliminate ligands, but a full restoration of the initial spectrum occurs by purging the sample in a flow of He at 200°C for 30 min. NO_2 sorption on CuH–ZSM-$5_{500°}$ is much stronger: no transformation of the formed nitroxo-complex occurs at 200°C, and only purging by He at $T > 350$°C eliminates all the chemisorbed NO_2 (16). The bond strength between altered Cu^{2+} site and such a strong ligand as NO_2 is also substantially lowered by the high-temperature treatment. While NO_2 is formally paramagnetic its paramagnetism is rather weak. The magnetic susceptibility of NO_2 is small, 3.26 $\tilde{\omega} \times 10^6$ cgs, as compared to 106.2 and 48.66 for O_2 and NO, respectively (29). At ambient temperatures NO_2 readily pairs into diamagnetic dimers, N_2O_4. Hence, the lack of a marked Cu^{2+}-ESR signal decrease or broadening upon Cu–ZSM-5 interaction with NO_2 is not surprising.

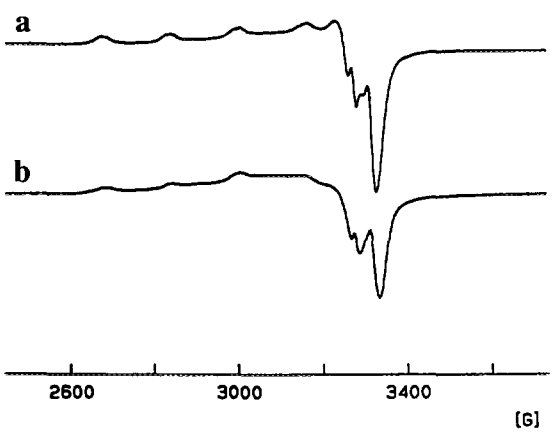


FIG. 5. ESR spectra, at 20°C, of CuH–ZSM-$5_{900°}$: (a) in He flow; (b) after sorption of NO_2.

5. *Treatment of CuH–ZSM-5_{900} by [C_3H_6 + He]*

C_3H_6 sorption at 20°C. Figure 6 shows the ESR signal of CuH–ZSM-$5_{900°}$ in a 15 cm^3/min flow of [0.39% C_3H_6 + He] taken at 20°. A gradual irreversible change in the fine structure of the ESR signal is not accompanied by a noticeable decrease in the signal intensity (DI/*N* value), as distinct from the case of propene sorption on

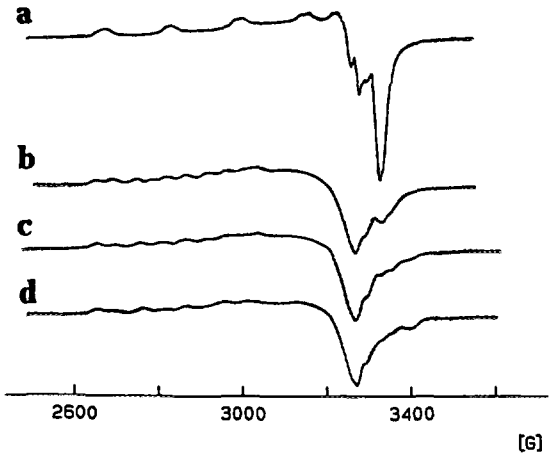


FIG. 6. ESR spectra, at 20°C, of CuH–ZSM-$5_{900°}$: (a) in He flow; (b) in [C_3H_6 + He] flow, 6 min; (c) in [C_3H_6 + He] flow, 60 min; (d) in He flow, 50 min.

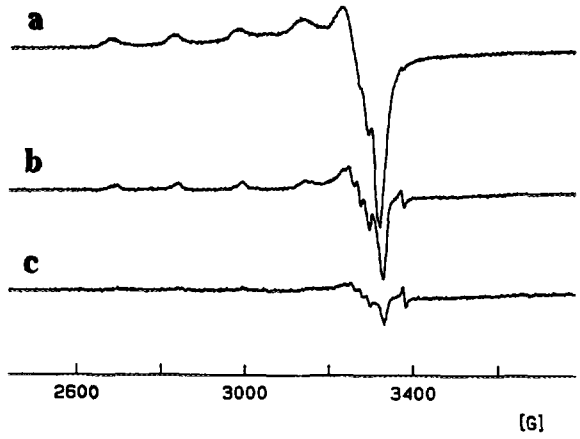


FIG. 8. ESR spectra, at 300°C, of CuH–ZSM-$5_{900°}$: (a) in He flow; (b) in [C_3H_6 + He] flow, 5 min; (c) in [C_3H_6 + He] flow, 13 min.

CuH–ZSM-$5_{500°}$, where the signal intensity decreases by about two-thirds due to the reduction of the ESR-active Cu^{2+} ions (20). The time dependence of the decrease of the normalized signal intensity (DI/N) for the two samples is plotted in Fig. 7. It is obvious that *the reducibility of Cu^{2+} sites in ZSM-5 is substantially attenuated as a result of the high-temperature calcination of CuH–ZSM-5.* Only bonding of additional ligands, without change in valence state of altered Cu^{2+} sites, takes place upon propene sorption at room temperature. Even subsequent heating of the sample at 100°C for 20 min does not lead to a noticeable fall in the signal intensity. The lack of the usual line-broadening effect of O_2 on the Cu^{2+}-ESR signal (Fig. 6d) shows that the chemisorbed alkene effectively shields the Cu^{2+} ions. The lowered reducibility becomes even more visible when observing the sample interaction with C_3H_6 at higher temperatures.

Reduction of CuH–ZSM-5 by C_3H_6 at 300 and 500°C. It was shown earlier (20) that the quantitative reduction of Cu^{2+}, by propene, in CuH–ZSM-$5_{500°}$ takes place at 200°C. For CuH–ZSM-$5_{900°}$ the complete reduction of all Cu^{2+} ions is not reached even at 500°C. Figure 8 shows the gradual disappearance, at 300°C, of the ESR signal of CuH–ZSM-$5_{900°}$ in a [C_3H_6 + He] stream. The switch to pure He flow results, however, in a substantial restoration of the signal. To rationalize this unexpected result we may assume that a given fraction of the Cu^{2+} ions is not reduced but forms charge-transfer complexes with some carbonaceous species at 300°C. Destruction and removal of these complexes in He flow produces the observed restoration of the Cu^{2+}-ESR signal. If so, an experiment at yet higher temperature could be more informative.

Figure 9 shows the gradual change of the same ESR signal in [C_3H_6 + He] stream at 500°C. The signal quickly loses ~75% of its original intensity (Figs. 9a–9b) and then

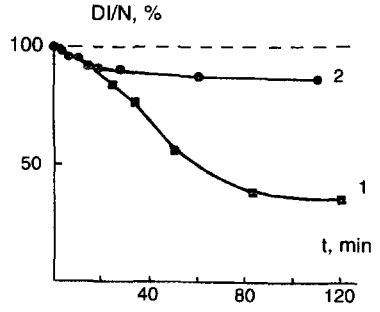


FIG. 7. Change of the Cu^{2+}-ESR signal upon interaction of CuH–ZSM-5 with propene at 20°C with time: (1) CuH–ZSM-$5_{500°}$; (2) CuH–ZSM-$5_{900°}$.

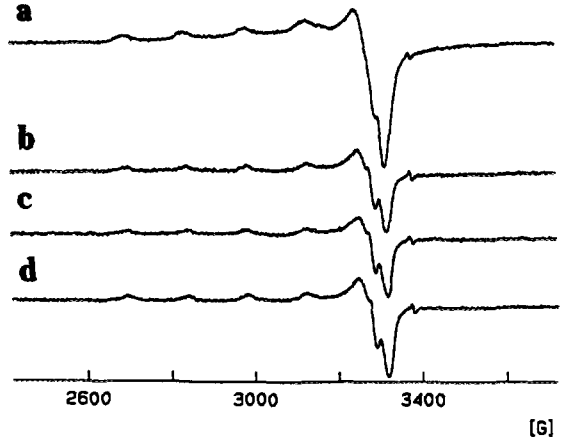


FIG. 9. ESR spectra, at 500°C, of CuH–ZSM-$5_{900°}$: (a) in He flow; (b) in [C_3H_6 + He] flow, 3 min; (c) in [C_3H_6 + He] flow, 21 min; (d) after switch to He flow.

remains unchanged as shown in the sequence of spectra 9b–9d. Taking into account the accuracy of the method, we conclude that *20–30% of the Cu^{2+} sites in CuH–ZSM-5 altered by calcination at 900°C loses its ability to change the oxidation state upon redox treatment.* The results obtained agree well with the recent work (30) where the behavior of reduction–reoxidation in the CuH–ZSM-5 system was studied by quantitative measurement of O_2 absorption, at 20–550°C, on prereduced samples. It was shown there that for CuH–ZSM-$5_{500°}$ the stoichiometry of processes corresponds to 100% transformation $Cu^{2+} \rightleftarrows Cu°$, but for the calcined sample CuH–ZSM-$5_{850°}$ the extent of reduction was only ~75%. It is worth noting that the samples used in this work were also used in catalytic experiments to evaluate activity in total oxidation of ethane (31). The catalytic activity of pure H–ZSM-5 is negligible up to 500°C while the active Cu-containing samples catalyze the complete ethane oxidation selectively, and no products other than CO_2 and H_2O are detected in the 280–400°C range. When following the conversion of ethane on Cu–ZSM-5 as a function of temperature it is observed that the activity is drastically affected by treatment, in particular by calcination at 750–800°C. Plotting the activity data in Arrhenius coordinates and extrapolating the results to lower temperatures and conversions permit the comparison of activities, represented as turnover numbers, of all the samples at 330°C at low conversion. The change in the specific activity of a Cu^{2+} sample caused by a stepwise calcination in the 500–900°C range, tracks satisfactorily the relative concentration of the square-planar Cu^{2+} ions as determined by ESR. This confirms once more that the square-planar Cu^{2+} ions play a crucial role in the catalytic activity of ZSM-5-based copper catalysts.

CONCLUDING REMARKS

All the results obtained for Cu^{2+} sites altered by the high-temperature treatment or steam aging of CuH–ZSM-5 must be taken as evidence of a treatment-induced bonding change between the isolated Cu^{2+} ions and framework oxygens. These oxygens are linked in turn to the Al^{3+} ions. Such hypothetical elements of the structure are a part of the zeolitic framework but flexible enough to change symmetry upon additional ligand bonding. The high-temperature treatment irreversibly alters these structural elements. Quantum-chemical calculations for three-dimensional models of such sites, if rigorous enough, may confirm or deny our assumptions.

It is quite plausible that the loss of catalytic activity of CuH–ZSM-5 after high-temperature treatment in the presence of steam, or even in its absence at higher temperatures, may be associated with the observed changes in the local topography of the isolated Cu^{2+} sites, observed in this work. The evidence above attests clearly that steaming at 620°C or short calcination at 900°C does inhibit the chemisorption on the active sites and the reducibility of these sites. This is just a consequence of a relatively subtle structural rearrangement that happens before the dealumination, such as observed by MAS NMR, takes place and much before the active metal is disengaged from the zeolite structure by agglomeration or the zeolite structure itself suffers massive heat damage, i.e., loss of crystallinity as observed by X-ray diffraction.

The SCR catalytic activity-structural rearrangement nexus in Cu–ZSM-5 catalysts remains to be studied further, although it was observed before that relatively mild catalytic conditions applied for relatively short times are detrimental to the SCR activity (6). In particular one kind of catalytic site, most probably those in the square-planar coordination, is susceptible to this deactivation. The indications are that ZSM-based catalysts are less sturdy in withstanding deactivating environments than could previously be ascertained by other methods and that the practical range of conditions for potential useful application may be severely limited.

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