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State of copper in a working, low-concentration CuH-ZSM-5 catalyst for exhaust gas purification: in-situ ESR monitoring

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Abstract

A flow cell was designed for in-situ ESR monitoring of the state of copper ions in a working Cu-ZSM-5 catalyst at high temperatures. The equilibrium oxidation state of the copper in the catalyst depends both on the temperature and the composition of the gas mixture. At 500°C in [C_3H_6 (or C_2H_5OH) + NO + O_2] with excess oxidant, the condition prevailing during selective catalytic reduction (SCR) of NO_x, virtually all the copper ions preserve the Cu^{2+} state. At 200–350°C in the same gas mixtures a partial reduction of the Cu^{2+} ions is observed. Steam-aging (650–700°C) or dry calcination (850–900°C) of CuH-ZSM-5 lead to the change in Cu^{2+} coordination without noticeable agglomeration or encapsulation of the isolated cations. The drastic loss of catalytic activity due to such treatment is associated with the change in the localized coordination of the isolated cupric sites.

Keywords: Copper; CuH-ZSM-5 catalyst; Exhaust gas purification

1. Introduction

The interaction between cupric ions in CuH-ZSM-5 and different molecules has been recently of considerable interest since it underlies the mechanism of catalytic purification of exhaust gases containing [O_2 + NO + CO + hydrocarbons] [1–5]. Contradictory data has been published about the change in both coordinative and valence states of copper upon the treatment of the samples by different gas mixtures [1,2,6–9].

To clarify this problem we have examined the CuH-ZSM-5 by in-situ ESR under flow conditions at temperatures 20–500°C. The interaction of such molecules as He, O_2, NO, H_2O, CH_4, C_3H_6, and C_2H_5OH with fresh and aged CuH-ZSM-5 is the subject of this work.

2. Experimental

The ESR spectra, at 20–500°C, were taken in the X-band on a Bruker ESP300 spectrometer, equipped with a high temperature cavity ER 4111 HT-VT. The Mn^{2+} ESR signal from a diluted MnO/Al_2O_3 solid solution was used as an internal standard. The Bruker ESP300E software was used for the double integration and subtraction of the recorded spectra. The Cu^{2+} ESR signals were registered in the field region of 2300–3800 G (two scans with sweep time 168 s). Resonances for

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various levels of microwave power were recorded to verify the lack of sample saturation.

The sample of CuH-ZSM-5, containing 1.27 wt.-% Cu, was prepared by a single exchange of H-ZSM-5 ($SiO_2/Al_2O_3 = 50$) with copper acetate solution. The zeolite was pressed without binder and crushed into 0.1–0.2 mm particles. Then it was precalcined in air at 500–520°C for 5 h and placed in a cell for ESR measurements.

A special co-axial quartz cell was used for in situ treatment of the sample in gas flow up to 650°C [10]. For the sample calcination at higher temperatures (650–900°C) the cell was disconnected from the spectrometer, placed into a furnace, calcined at a given temperature, placed again in an ESR cavity and reconnected with the flow system. The gas flow was regulated by a four-channel readout mass flow controller (Model 247C, MKS Instr.). This system permitted to change the composition of the gas mixture and to regulate the flow from 1.5 to 18 cm^3/min. Pure helium (5.0 grade) and the mixtures [20.2% O_2+He], [0.41% NO+He], [0.39% C_3H_6+He] and [5.0% CH_4+He] were used for in situ sample treatment.

3. Results and discussion

3.1. *Quantitation of Cu^{2+} ions in the CuH-ZSM-5 by ESR*

In the studies of CuH-ZSM-5 by ESR the question often arises: is the ESR signal representative of all the Cu^{2+} ions in the sample? We used signals from frozen diluted solutions of $CuSO_4$ for absolute calibration of the ESR spectrum from CuH-ZSM-5 saturated with H_2O. The estimate of the copper concentration derived from ESR data (1.2–1.6 wt.-%) is in good agreement with the result of chemical analysis (1.27 wt.-% Cu) and provides strong evidence that in the sample nominally exchanged below 70% all the cupric ions are isolated and the ESR signal is associated, within the experimental error, with all of them [11].

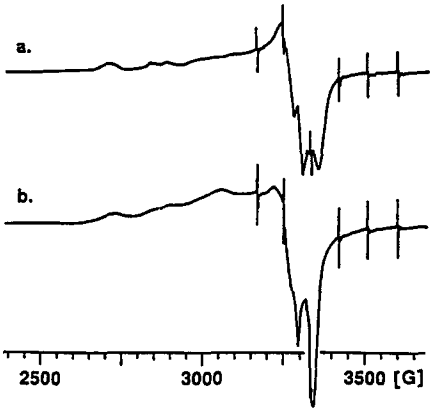

Fig. 1. ESR spectra, at 20°C, of CuH-ZSM-5 precalcined at 500°C: (a) in He flow; (b) after sorption of NO_2.

3.2. *High-temperature treatment of CuH-ZSM-5 in O_2 and He flow*

The experiment with changing gas composition was used to obtain the maximum accuracy of measurement. The sample was precalcined in situ at 500°C and cooled down in [O_2+He] flow. After that the gas flow was switched to pure He at 20°C and the ESR signal was registered (Fig. 1a). Then the sample was heated to 500°C, held for 1 h, cooled to 20°C, and the resulting ESR spectrum was taken. The two ESR signals are identical in shape, and it is possible to compare spectra by subtraction which is more rigorous than comparison of the double integral values. The difference in intensities for two spectra is about 3%. Hence, in thoroughly purified He spontaneous reduction of the cupric ions is negligible up to 500°C [10,11].

3.3. *Interaction of CuH-ZSM-5 with NO and [NO + O_2]*

Noticeable broadening of the parent ESR spectrum (Fig. 1a) occurs in [NO+He] flow at 20°C due to interaction between Cu^{2+} ions and paramagnetic NO molecules in the zeolitic channels. Some decrease in signal intensity also occurs. The effect is not fully reversible at 20°C in He flow: to restore completely the parent spectrum treatment at ca. 150°C is necessary. Therefore, ESR spectroscopy permits monitoring of formation of the

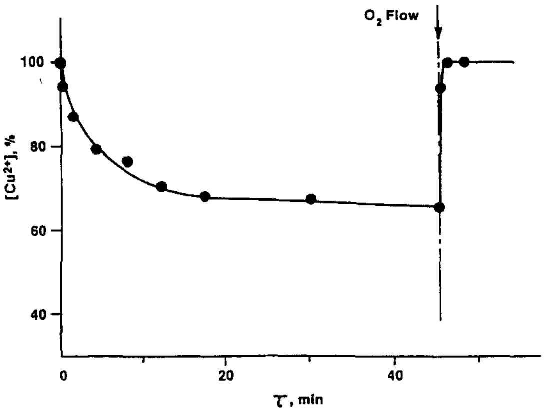

Fig. 2. Change in the intensity of Cu^{2+} ESR signal during the treatment of CuH-ZSM-5 at 500^{2+} by [CH_4 + He] flow. The arrow points to the switch to [O_2 + He].

rather weak nitrosyl (or dinitrosyl) complexes. The interaction with NO alters mainly the most coordinatively unsaturated square-planar cupric ions.

Strong adsorption complexes of Cu^{2+} with NO_2 are formed upon treatment of CuH-ZSM-5 by an [NO + O_2] mixture. ESR spectrum shown on Fig. 1b demonstrates the strong influence of NO_2 sorption, at 20°C, on the coordination of the Cu^{2+} cations. Surprisingly, the complete increase of symmetry to octahedral does not occur. The spectrum (Fig. 1b), with $A_{\parallel} = 165$ G and $g_{\parallel} = 2.29$, is typical of a crystal field of rather low symmetry (distorted five-coordinated environment). This state is stable: the purging of the sample with pure He flow at 200°C does not change this signal, and even the calcination of the sample at 300°C does not eliminate all ligands. The presence of these complexes may alter the reactivity of the copper sites at $T < 300$°C.

3.4. High-temperature treatment of CuH-ZSM-5 with CH_4

Treatment of the CuH-ZSM-5 in [2% CH_4 + He] flow at 500°C is accompanied by a gradual change in the shape of the ESR signal and a fall in the integral intensity, as shown in Fig. 2. A constant signal intensity attained after 20 min corresponds to the reduction of ca. 40% of the Cu^{2+} by CH_4 at 500°C. No sharp ESR line at $g = 2.002$, which is typical of a carbonaceous residue, was observed. Backswitching the gas flow to [3% 0_2 + He] at 500°c is accompanied by a very fast restoration of the parent Cu^{2+} ESR signal, both in intensity and shape. The same process of the fast restoration of the Cu^{2+} spectrum takes place upon the use of [0.4% NO + He] at 500°C. The restoration of the initial state begins in a [5% 0_2 + He] flow at temperatures as low as 200°C, and the full restoration of the original Cu^{2+} concentration and coordination is reached at 300°C. This behavior is also typical in the reoxidation by NO flow. Thus, the CuH-ZSM-5 demonstrates unexpected behavior in high-temperature treatment by pure methane. Typically, the high-temperature interaction of CuH-ZSM-5 with H_2 or hydrocarbons other than CH_4 results in a quantitative reduction of all Cu^{2+} cations and particles of metallic Cu form on the outer surface of the zeolitic crystals. For such samples the reoxidation in oxygen at 500°C is accompanied by a gradual, rather slow, migration of the Cu^{2+} ions back into the zeolitic voids. The rate of a solid state reaction becomes negligible at 200–300°C. For the sample prereduced by methane, the process of restoration of the initial state of Cu^{2+} in cationic positions of ZSM-5 is completed at 300°C. This may be rationalized if, in CH_4 flow at 500°C, the reduction of Cu^{2+} to Cu^{+} only takes place and these ions preserve their initial positions inside the zeolite.

The results also show a marked difference in the reactivity between the two main types of Cu^{2+} cations in CuH-ZSM-5. The change in ESR signal upon the treatment of the sample in CH_4, O_2 and NO is related mainly to the disappearance and restoration of the isolated ions coordinated in the most unsaturated square planar environment. These results agree with the data obtained in previous work [12,13], where a noticeable difference in reactivity of two main types of the Cu^{2+} ions in CuH-ZSM-5 has been observed. At 500°C in methane flow, reduction of the most reactive square-planar coordinated Cu^{2+} ions to Cu^{+} takes place. The reoxidation of cuprous to cupric ions at 500°C by NO or O_2 is very fast, and most of the copper in CuH-ZSM-5 retains the cupric state in mixtures of CH_4 with excess oxidant.

3.5. *Interaction of CuH-ZSM-5 with C_3H_6 or ethanol at 20–200°C*

In propene flow at 20°C, the filling of the CuH-ZSM-5 channels by oligomers formed in the process is accompanied by the reduction of ca. 2/3 of Cu^{2+} ions, and at 200–300°C the complete reduction of cupric ions takes place.

As mentioned above, the sorption of NO_2 on CuH-ZSM-5, at 20°C, results in the formation of a strong adsorption complex of rather low symmetry. Presence of strong ligands influence the subsequent interaction between these modified Cu^{2+}sites and C_3H_6 molecules. ESR data shows that the sorption of propene on CuH-*ZSM*−$5/_{NO_2}$ is not accompanied by any substantial drop in the signal intensity, as distinct from the case of pure CuH-ZSM-5. At the same time, a noticeable change in the coordination of the cupric ion is observed due to formation of a mixed adsorption complex. The preadsorption of NO_2 inhibits the reduction of the cupric ions with propene at ambient temperature.

Ethanol sorption at 20–100°C results only in a change of the Cu^{2+} coordination due to the octahedral complex formation. However, at $T > 200°C$ the reduction of Cu^{2+} takes place in $[C_2H_5OH + He]$ flow.

3.6. *High temperature interaction of CuH-ZSM-5 with [hydrocarbon + oxidant] gas mixtures*

The dynamic state of CuH-ZSM-5 during the SCR catalytic process at 300–500°C in gas mixtures with changing ratios of components is of the most direct relevance to the understanding of the behavior of a catalytic site. To this end we followed the oxidation of propene and ethanol by O_2 and NO at 500 and 300°C.

The equilibrium valence state of copper in CuH-ZSM-5 dependsboth on the temperature and the stoichiometry hydrocarbon/oxidant in the flow.

Our data demonstrates unambiguously that at steady-state, under typical conditions of selective catalytic reduction (SCR) at 500°C with a large excess of oxygen, virtually all of the copper is present in the Cu^{2+} state (Fig. 3). The dynamic equilibrium $Cu^{2+} \rightleftarrows Cu^{+}$ is shifted completely to the left. The reoxidation of any reduced sites by O_2, or even more so by NO_2, is very fast. However, in the same gas mixtures at 250–300°C gradual reduction of a part of Cu^{2+} occurs. Thus, only at lower temperatures or/and close to stoichiometry this equilibrium begins to shift to the right(Fig. 3).

3.7. *Steam-aging and deactivation of CuH-ZSM-5*

ESR data shows that steam-aging (650–700°C, 14 h) or dry calcination (850–900°C, 30 min) of CuH-ZSM-5 induce a change in Cu^{2+} coordination without noticeable agglomeration or encapsulation of the isolated ions. Two ESR spectra of the same CuH-ZSM-5 sample calcined at 500° and 900°C (Fig. 4) illustrate this conclusion.

A drastic change in the fine structure of the Cu^{2+} ESR signal is observed (Fig. 4a, Fig. 4b) demonstrating the transformation of the local topography of the Cu^{2+} sites as a result of high-temperature treatment. At the same time, the change in the normalized double integral (DI/N) value does not exceed 5%. All Cu^{2+} ions remain accessible for the molecules from the gas phase: O_2 causes reversible dipole–dipole signal broadening; sorption of H_2O results in the modification of the ESR signal structure showing the increase of the local crystal field symmetry. Hence, there is no observable aggregation or encapsulation of isolated Cu^{2+} ions accompanying the transformation of the local site structure.

At the same time, the reactivity of these altered Cu^{2+} sites and their ability to adsorb different molecules is substantially diminished.

Measurable broadening of the ESR spectrum (Fig. 4b) occurs in [NO + He] flow as a result of dipole–dipole interaction with paramagnetic NO molecules. However, for the catalyst calcined at

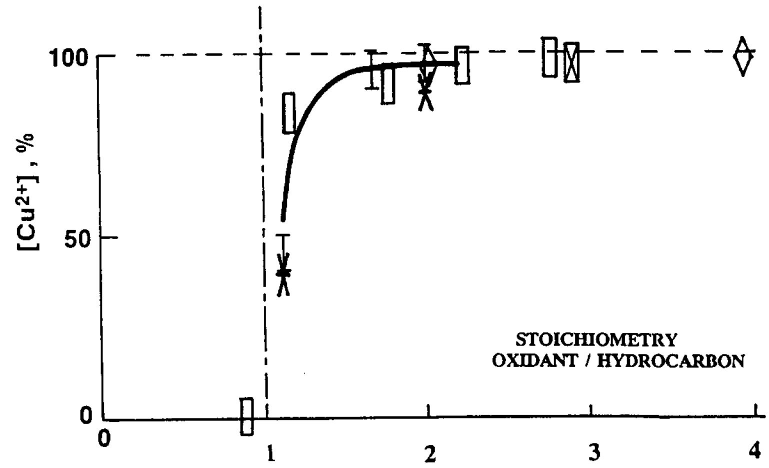

Fig. 3. The dependence between the part of copper in CuH-ZSM-5 retaining the Cu^{2+} state and the composition of the gas flow:□–[$C_3H_6+O_2$]; I–[C_3H_6+NO]; ⊠–[$C_3H_6+O_2+NO$]; ■–[$C_2H_5OH+O_2$], 500°C; *–[$C_3H_6+O_2$], 300°C.

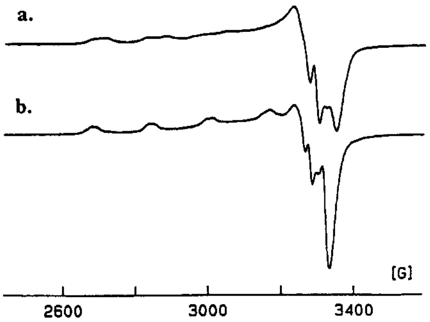

Fig. 4. ESR spectra, at 20°C, of the sample CuH-ZSM-5 calcined at (a) 500°C for 5 h, (b) and at 900°C for 0.5 h.

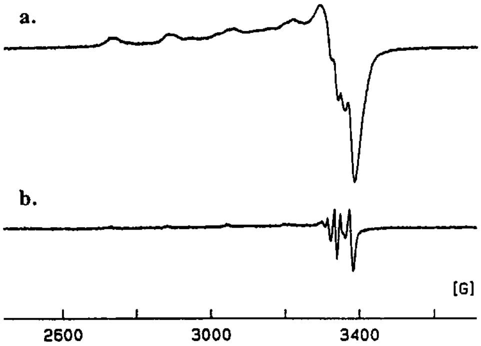

Fig. 5. ESR spectra, at 20°C, of two samples: (a) steamed CuH-ZSM-5; (b) Cu on presteamed H-ZSM-5.

900°C the effect is completely reversible at 20°C, and no stabilization of nitrosyl complexes could be observed, as distinct from the case of CuH-ZSM-5/$_{500^{\circ}}$.

Formation of adsorption complexes of Cu^{2+} with NO_2 is observed for CuH-ZSM-5/$_{900^{\circ}}$ in [$NO+O_2$] flow, and the change in Cu^{2+} symmetry due to the ligands is irreversible at 20°C. However, the purging of the sample with He flow at 150–200°C results in complete restoration of the parent ESR signal (Fig. 4b) demonstrating the quantitative removal of ligands. As mentioned, for the CuH-ZSM-5/$_{500^{\circ}}$ only the treatment at $T>300$°C permits to remove the same ligands. Thus the bond strength between altered Cu^{2+} site and such a strong ligand as NO_2 is decreased.

Sorption of C_3H_6 on CuH-ZSM-5/$_{900^{\circ}}$ at 20°C is not accompanied by noticeable reduction of the altered Cu^{2+} sites. Some reduction of cupric ions takes place at $T>200$°C but even at 500°C in [C_3H_6+He] flow a noticeable part of copper ions (between 1/4 and 1/3) preserves the Cu^{2+} state.

These quite surprising results could be taken as evidence of a link between the Cu^{2+} ions and the framework oxygens, linked in turn, to the Al^{3+} ions. Such hypothetical reconstructed elements of the structure have to be a part of the zeolitic framework but be flexible enough to change symmetry upon additional ligand linking.

To verify the possibility of such a mutual stabilizing interaction between copper and aluminum ions we compared two steam-aged CuH-ZSM-5 samples differing in preparation: the first one was exchanged with copper and then steam-aged; in the second case the pure H-ZSM-5 was steamed and then exchanged with copper. ESR spectra of the two samples of equal weight at the same magnification are shown in Fig. 5. The DI/N values for two spectra differ by a factor of 15. The aging of pure H-ZSM-5 in a stream containing 20% H_2O at 650°C results in almost total destruction of framework Al-sites where the isolated Cu^{2+} cations may be exchanged. Conversely, the introduction of the Cu^{2+} before steaming preserves these sites from total destruction, and only a transformation in local topography takes place. These results agree with the data of recent work [14] where a partial stabilizing effect of Cu^{2+} cations on framework tetrahedral Al^{3+} in ZSM-5 was demonstrated by ^{27}Al MAS NMR. It is plausible that the loss of catalytic activity of CuH-ZSM-5 after high-temperature treatment in the presence of steam may be associated partially or entirely with changes in the local topography of the isolated Cu^{2+} sites without the necessity for the still more drastic dealumination.

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