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Unusually High and Stable Catalytic Activity of Cu/H–ZSM-5 in Methane Oxidation: Correlation with Coordination State of Cu(II) Cations

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Catalytic oxidation of CH_4 with O_2 using Cu(II)-containing H–ZSM-5 was studied. An ESR study was carried out on copper ion distribution and coordination in zeolite. It was shown that H–ZSM-5 zeolite containing isolated Cu(II) cations in coordinatively unsaturated environments demonstrated high and steady-state activity in the redox-type catalytic reaction of methane oxidation. © 1989 Academic Press, Inc.

INTRODUCTION

Polyvalent ion introduction into high-silica zeolites is one method of modification of catalytic properties, hence the interest in this problem. The high and stable activity of ZSM-5-type zeolites in acid–base reactions is well known and the changes in reactivity and selectivity upon their modification by different ions have been investigated widely (*1*, *2*). However, little is known about the possibility of new non-acidic-type (redox, for instance) active site creation as a result of polyvalent ion location in coordinatively unsaturated environments, typical of isolated Cr(V), Cu(II), and V(IV) cations inside H–ZSM-5 channels (*3*, *4*). Only a few examples of such unusual catalytic properties are known. Cu/H–ZSM-5 zeolite was found to be a promising catalyst for the NO decomposition (*5*) and CuH[Fe]–ZSM-5 was found to catalyze CH_3OH oxidation by N_2O (*6*).

This work describes the study of catalytic oxidation of CH_4 with O_2 using copper (II)-containing H–ZSM-5 zeolite. Distribution, coordination, and reactivity of Cu(II) ions in zeolite were studied by ESR spectroscopy.

EXPERIMENTAL

1. Materials

The NH_4 form of homemade ZSM-type zeolite (Si/Al = 21, Na_2O content <0.1 wt%) was used to prepare the copper-containing samples. X-ray data confirmed the high crystallinity of this zeolite having the ZSM-5 framework structure. NH_4–ZSM-5 without a binder was pressed and crushed into 0.5 to 1.5-mm pieces. After drying at 400 K the NH_4–ZSM-5 samples were impregnated with aqueous $Cu(NO_3)_2$ solutions of appropriate concentrations by incipient wetness impregnation (0.7–0.8 cm^3/g of zeolite); samples containing more than 0.5 wt% Cu were prepared by a threefold impregnation to provide a more homogeneous distribution of copper. The samples obtained (0.25–2.8 wt % Cu) were dried in air (at 293 K for 4 h and then at 400 K for 4 h) and calcined at 773 K for 1 h. To study the effect of high-temperature treatment some samples were calcined at temperatures up to 1073 K.

The samples CuO/SiO_2 (0.5 wt% Cu) and Cu–H–mordenite (1.2 wt% Cu) were also prepared for a comparison with the Cu/H–ZSM-5 system. The CuO/SiO_2 catalyst was prepared by impregnation of SiO_2 (~330

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m^2/g) with an aqueous solution of copper ammine and dried at 400 K. CuHM was prepared by a conventional cation-exchange procedure using NH_4–mordenite (Si/Al = 5). The sample was then dried at 400 K and calcined in an air stream at 773 K for 1 h. The copper content of the samples was determined by chemical analysis.

2. Methane Oxidation Activity Measurements

Dried catalyst (0.8 to 2.5 g) was placed in a fixed-bed, continuous, down-flow coaxial reactor (1.8 cm^2) and activated at 773 K with dry air flowing at a rate of 150 ml/min for 1 h. Then the gas mixture of reactants (78 vol% of helium + 22 vol% of oxygen + 265 ppm of methane) was fed to the reactor under 1 atm pressure to start the reaction. (A standard reactant mixture had been prepared under 100 atm from high-purity reagent-grade gases and was used in all catalytic runs.)

Samples of the reactor effluents were taken periodically using a sampling valve and were injected into a chromatograph equipped with a flame ionization detector (the limit of CH_4 detection was 0.05 ppm). Carbon dioxide and water were obtained as products during methane oxidation in all catalytic runs. No other products were detected (limit of detection was 0.3 ppm). Space velocity was obtained from the reactant feed rates and catalyst charges. Space velocity data under typical reactor conditions of 99% CH_4 conversion, 773 K, were used to compare catalyst activities. For some samples the catalytic activity was measured at temperatures from 723 to 773 K to estimate the apparent activation energy of reaction.

3. ESR Measurement

ESR spectra in the *X* band (λ = 3.2 cm) were taken, at 77 and 293 K, with DPPH (g = 2.0036) as a standard. The samples (~100 mg), placed in quartz ampoules, were calcined in air at 773 K for 1 h and then evacuated at 293 K for 5 min. In some cases the samples taken from the reactor after catalytic runs were placed into ampoules and evacuated at 293 K. Evacuation of the samples was necessary to prevent broadening of Cu(II) ESR lines, caused by dipole–dipole interactions of cations with O_2 molecules.

RESULTS

ESR spectra of the samples dried at 400 K (Fig. 1a) showed considerable dispersion of the copper. A noticeable part of the copper was located in the form of weakly associated, hydrated, octahedral Cu(II) complexes. Calcination of the samples in air at

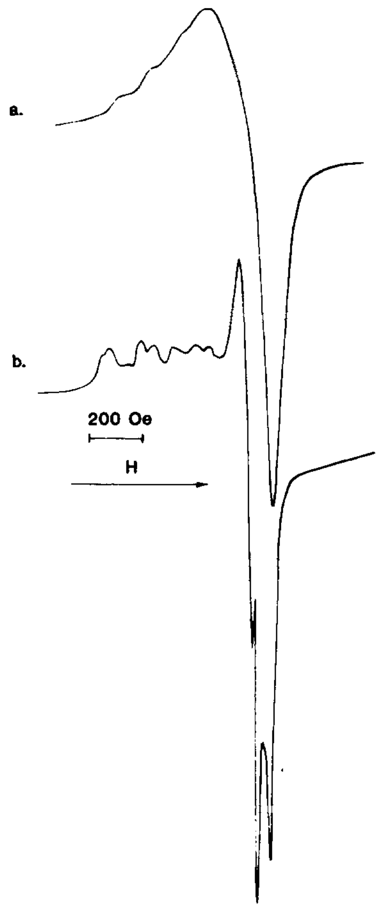

FIG. 1. ESR spectra at 293 K of evacuated 1% Cu/H–ZSM-5 samples. (a) Dried at 400 K; (b) calcined at 773 K for 1.

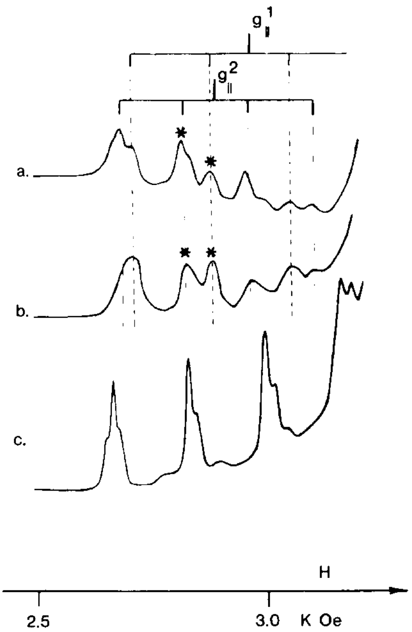

FIG. 2. Part of the ESR spectra (parallel components) at 293 K of copper-containing zeolites. (a) 0.25 wt% Cu, calcined at 773 K; (b) 1.0 wt% Cu, calcined at 773 K; (c) 1.0 wt% Cu, calcined at 1073 K.

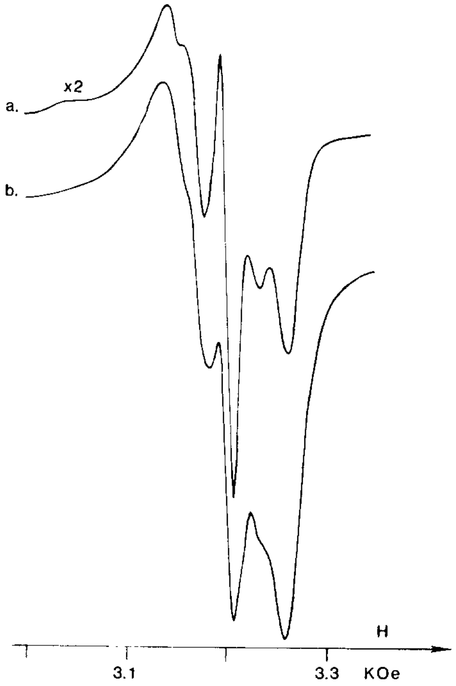

FIG. 3. Part of the ESR spectra (perpendicular components) at 77 K of copper-containing zeolites calcined at 773 K for 1 h. (a) 0.25 wt% Cu; (b) 1.0 wt% Cu.

773 K resulted in the formation of isolated, coordinatively unsaturated Cu(II) ions, as shown by the hyperfine structure in the ESR spectra (Fig. 1b). Parameters of ESR spectra (Figs. 2 and 3) showed that the samples calcined at 773–823 K contained two main types of isolated Cu(II) cations located in square planar environments ($g_{\parallel}^1 = 2.27$; $A_{\parallel}^1 = 172$ Oe; $g_{\perp}^1 = 2.045$; $A_{\perp}^1 \simeq 30$ Oe) and one in a square pyramidal environment ($g_{\parallel}^2 = 2.33$; $A_{\parallel}^2 = 142$ Oe; $g_{\perp}^2 = 2.07$; $A_{\perp}^2 \simeq 18$ Oe). The absorption lines marked with asterisks (Fig. 2) offer the best possibility for comparing the relative concentrations of two types of isolated ions. Figure 4 presents the correlation between the concentration of the above two types of isolated Cu(II) ions and the total copper content in zeolite. Double integration of lines in Fig. 2 is a problem, and the ratios in Fig. 4 are estimated from a comparison of line amplitudes (Fig. 2, asterisks) taking into account that the widths of these lines in different ESR spectra are practically the same.

Calcination of Cu/H-ZSM-5 at 1073 K resulted in the formation of the ESR spectrum shown in Fig. 2c. Inlet of O_2 led to considerable and reversible broadening of the Cu(II) ESR spectra.

The ESR spectrum of the sample of 1.2%

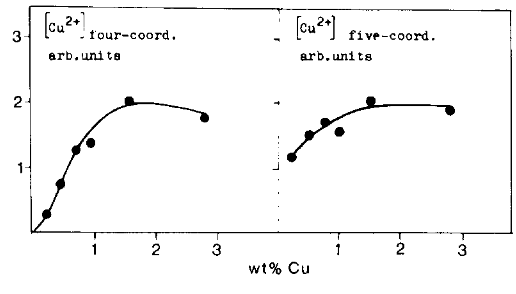

FIG. 4. Correlation between the concentrations of four- and five-coordinated Cu^{2+} ions and the total copper content in zeolite.

CuHM calcined at 773 K showed the presence of weakly interacting Cu(II) cations coordinated in a square pyramidal environment.

Both concentration and coordination of Cu(II) in CuHM and Cu/H–ZSM-5 samples did not change as a result of catalytic runs at 773 K for 6–10 h.

The ESR spectrum of fresh 0.5% CuO/SiO_2 catalyst showed the presence of weakly interacting surface copper–ammonia complexes. Calcination of the catalyst at 773 K in reactant mixture flow for 4 h led to the clustering of Cu(II) ions but the sample retained its pale blue color. After subsequent treatment of the used sample with ammonia solution and drying, a full restoration of the ESR spectrum arising from surface copper–ammonia complexes was observed. Therefore, no aggregation of Cu(II) in a bulk CuO phase occurred in CuO/SiO_2 during the catalytic runs.

The study of catalytic CH_4 oxidation showed that activity of pure H–ZSM-5 was negligible at 773 K. Catalytic activity of Cu/H–ZSM-5 increased within the first 5–10 min on stream and then reached a steady state. No drop in the effectiveness of the catalysts was found at 773 K after 10 h of continuous use. The thermal treatment of the samples in air at 823 K for 15 h did not result in any decrease in catalytic activity. Figure 5 gives the catalytic activity of Cu/H–ZSM-5, in CH_4 oxidation at 773 K, as a function of total copper content in the zeolite. Figure 6 presents a plot of activity vs number of square planar Cu(II) cations only. Calcination of Cu/H–ZSM-5 at 1073 K for 2 h resulted in a 1000-fold drop in catalytic activity of the samples.

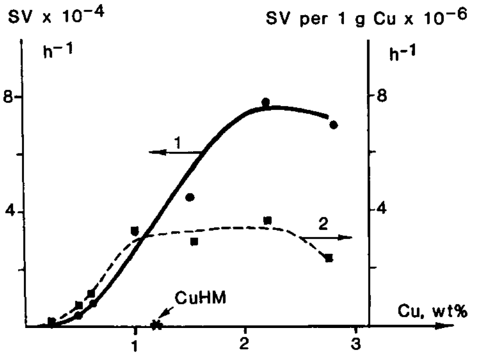

FIG. 5. Space velocity data (99% CH_4 conversion, 773 K) for different Cu/H–ZSM-5 samples. (1) Total; (2) per gram of copper.

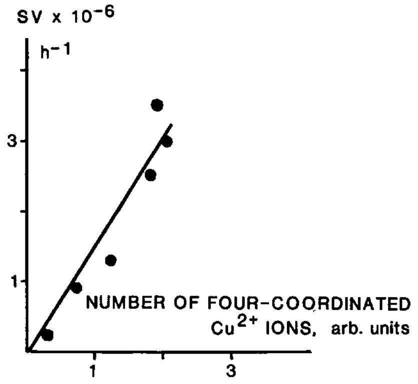

FIG. 6. Correlation between the activity of Cu/H–ZSM-5 samples (99% CH_4 conversion, 773 K) and the number of four-coordinated Cu(II) ions.

The rate of reaction was measured at 723–773 K for the samples 0.75% Cu/H–ZSM-5 and 1.5% Cu/H–ZSM-5 to calculate the apparent enerrgy of activation. Partial pressure dependencies of the rate were taken to be first order in CH_4 and zero order in O_2, and the apparent activation energy was obtained for two samples as ~28 kcal/mol.

Cu(II) cations in H–ZSM-5 were easily reduced by H_2 at 573–673 K and microcrystals of Cu^0 formed on the outer surface of the zeolite. The catalytic activity of a reduced sample of 1.0% Cu/H–ZSM-5 was also studied. Figure 7 presents the change of catalytic activity of the prereduced Cu/H–ZSM-5 upon the reoxidation of the sample by reactant mixture at 773 K.

Steady-state 99% conversion of CH_4 was achieved on CuHM and CuO/SiO_2 catalysts; however, the space velocity was quite low at 773 K (400 h^{-1} for CuHM and ~100 h^{-1} for CuO/SiO_2). The activity of 1.2% CuHM is marked on Fig. 5 by the

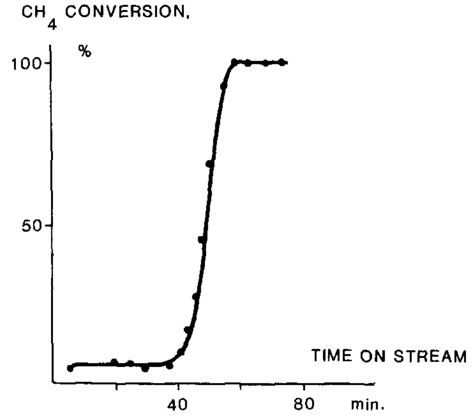

FIG. 7. The change in catalytic activity of a prereduced sample 1.5 wt% Cu/H–ZSM-5 in CH_4 oxidation at 773 K ($U = 3.6 \times 10^4$ h^{-1}).

asterisk for comparison with the Cu/H–ZSM-5 system.

DISCUSSION

ESR spectra show that a noticeable part of the copper introduced in NH_4–ZSM-5 by impregnation is dispersed in the zeolite after drying as hydrated octahedral Cu(II) complexes (Fig. 1a). The calcination of the samples at 773 K results in a transition to lower symmetry of Cu(II) ions. Assignment of specific ESR spectra to different types of Cu(II) coordination has been given in Refs. (*7–10*). Two main types of isolated Cu(II)-ion coordination are clearly distinguished in the samples calcined at 773–823 K. From the analysis of spectra (Figs. 1–3) it may be concluded that Cu(II) isolated ions are located both in square pyramidal and in square planar coordinations. These ESR data fully agree with our results obtained earlier from study of solid-state interaction of copper compounds with H–ZSM-5 (*3*). The spectra obtained coincide also with the signals from Cu/H–ZSM-5 samples prepared by ion exchange (*11*). As noted in (*3*), Cu(II) ions which migrate from the outer surface of H–ZSM-5 are coordinated in the same cationic positions as Cu(II)-exchanged cations. The results obtained in (*12, 13*) also agree with our data.

It is interesting to note that not only the number of isolated Cu(II) ions increases but also the ratio between two main types of Cu(II) isolated cations changes with the increase in total copper content in the zeolite (Figs. 2 and 3). Comparison of intensities of the absorption lines marked with the asterisks (Fig. 2a) enables an estimate to be made of the ratio (five-coordinated Cu^{2+}/four-coordinated Cu^{2+}) as (2–3)/1 for the sample 0.25% Cu/H–ZSM-5. This ratio is equal to (0.7–1)/1 for the sample 1.0% Cu/H–ZSM-5 (Fig. 2b); i.e., the preferable formation of five-coordinated Cu^{2+} cations takes place at low copper content. In other words, the concentration of square planar Cu(II) ions increases more slowly than that of the square pyramidal species with an increase in total copper concentration in the zeolite, as shown in Fig. 4.

The intensity of ESR spectra from isolated Cu(II) ions reaches a limit at 1.5–2.0 wt% Cu, and a further rise in the total copper content is not accompanied by a change in the number of isolated Cu(II) cations in the zeolite. This fact agrees with our earlier results (*3*). We concluded that the quantity of copper which may be introduced in H–ZSM-5 as isolated Cu^{2+} cations is limited only by the number of accessible cationic vacancies and the excess of CuO is preserved on the outer surface of the zeolitic crystals. The maximum quantity of isolated Cu(II) cations was estimated as representing 30–40% of the Al^{3+} content in the zeolitic lattice. For the H–ZSM-5 sample used (Si/Al = 21) this maximum concentration of copper in cationic sites corresponds to 1.4–1.9 wt% Cu.

Let us now compare the above-mentioned data with the catalytic properties of Cu/H–ZSM-5 samples. It is clearly seen from Fig. 5 that stabilization of Cu(II) ions in parent inactive H–ZSM-5 results in the formation of active sites. The activity per gram of Cu (Fig. 5, curve 2) increases up to 1 wt% Cu which demonstrates an inhomogeneity of catalytic sites. By comparison of catalytic data (Fig. 5) with the results obtained from the study of Cu^{2+} location and coordination (Figs 1–4) it may be assumed that the high catalytic activity is determined only by the formation of the most coordinatively unsaturated square planar Cu(II) ions. The number of such ions is negligible in 0.25% Cu/H–ZSM-5 and the majority of copper is coordinated in this inactive sample as isolated square pyramidal Cu(II) ions (Fig. 4). The rise in the total copper content to 1.0 wt% results in a considerable increase in the number of square planar Cu^{2+} cations (Figs. 2 and 4) which correlates well with the increase in activity (Fig. 5). When the number of isolated Cu(II) cations in zeolite reaches a maximum (at 1.5–2.0 wt% Cu) the activity of the catalyst also reaches a limit (Fig. 5, curve 2), and a further increase in the total copper content in zeolite does not lead to an increase in activity. Thus, the excess CuO on the outer surface of the zeolite does not contribute noticeably to Cu/H–ZSM-5 catalytic activity in CH_4 oxidation. A good correlation between the amount of square planar Cu(II) and the activity of Cu/H–ZSM-5 (Fig. 6) demonstrates the decisive role of the most coordinatively unsaturated square planar ions.

The redox treatment of Cu/H–ZSM-5 allows us to demonstrate once more the relation between Cu(II) location in zeolite and activity of the catalyst. The sample reduced by H_2 is the pure H form of zeolite containing Cu^0 microcrystals on the outer surface. In agreement with our earlier investigations (*3*), reoxidation of the reduced sample at 773–823 K is accompanied by a gradual migration of Cu(II) ions from the outer surface into zeolitic channels and their stabilization in cationic positions. This process of Cu(II) redistribution correlates very well with the gradual rise in CH_4 oxidation rate, shown in Fig. 7. ESR data confirm that the complete restoration of catalytic activity, achieved after 6 h of use, is accompanied by a full restoration of Cu(II) as isolated ions in both concentration and coordination.

Comparison of the Cu/H–ZSM-5 system with CuHM and CuO/SiO_2 also permits demonstration of the unusually high activity of square planar Cu(II) cations introduced into H–ZSM-5 channels. It must be noted that Cu(II) in our samples CuHM and CuO/SiO_2 does not form any CuO phase. The dispersion of copper on supports may be estimated as 100%, and all Cu(II) ions are accessible for reactant molecules. Thus, the specific activity of Cu(II) ions is compared in each case.

Copper-containing samples are well known as active catalysts for oxidation reactions (*8, 10, 14, 15*). Under our typical reactor conditions (773 K), 99% conversion of CH_4 was achieved on Cu/HM and CuO/SiO_2. However, these samples (which do not contain square planar Cu(II)) show a much lower activity than Cu/H–ZSM-5. In our opinion, the results obtained demonstrate clearly the influence of isolated ion coordination on its catalytic properties.

Let us now briefly discuss the large drop in Cu/H–ZSM-5 activity following the high-temperature treatment. It must be taken into account that the calcination of Cu/H–ZSM-5 at 1073 K for 1–2 h does not reduce noticeably the number of isolated Cu(II) ions accessible to reactants. At the same time, a considerable change in the Cu(II) ligand environment occurs. The ESR spectra of the samples calcined at 1073 K show the preservation of the two discrete types of Cu(II)-ion environment (Figs. 1c and 2c). The coordination of these ions may be treated as a square pyramid distorted to a planar square (*3, 11*). The most unsaturated square planar Cu(II) coordination disappears completely as a result of high-temperature treatment.

The mechanism of catalytic activation of reactants is not clear now. It is difficult to imagine a linkage between Cu(II) ions and saturated nonpolar molecules of methane. The possibility of alkane molecule interaction with coordinatively unsaturated Cu(II) ion in H–ZSM-5 has been studied (*16*). It was found that physical adsorption of *n*-hexane and xenon is accompanied by some changes in the hyperfine structure of the Cu(II) ESR signal. Such influence of nonlocalized physical adsorption of inert gas atoms or alkane molecules was explained by a slight geometrical displacement of Cu(II) cations due to dispersion forces. In our opinion, the activation of the O_2 molecule due to the interaction with a low-coordinated Cu(II) ion is more probable than that of the CH_4 molecule. In any case, the catalytic data show the decisive role of isolated low-coordinated Cu(II) cations in CH_4 oxidation. The zeolite structure may be treated as a macroligand which provides stabilization of Cu(II) in such an unsaturated environment. It must be noted, however, that a considerable part of the cationic vacancies in Cu/H–ZSM-5 is not occupied by Cu(II) cations. Therefore, the strong acid OH groups are also located in channels of Cu/H–ZSM-5 calcined at 773–823 K. Gentry *et al.* (*17*) concluded that both the Brønsted acidity of a catalyst and the copper content in CuK–*X* zeolites are important in determining catalytic activity. On the other hand, it was shown that CH_4 adsorption inside the channels of decationated ZSM-5 results in a noticeable change in both chemical shifts and spin–spin interaction constants in CH_4 NMR spectra (*18*). The possibility cannot be excluded that the combination of low-coordinated Cu(II) cations with a strong Brønsted acid site is necessary to provide the total CH_4 oxidation, and that the activity drop upon the high-temperature calcination is due to the dehydroxylation and replacement of protonic acid sites for Lewis acid sites. We hope that this problem will be clarified further by a study of the catalytic properties of Cu/H–ZSM-5.

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