Catalysis Letters 10 (1991) 289–296

Alkane oxidation on isolated Cu^{2+} ions in zeolitic matrix: a relation between catalytic activity and Cu^{2+}-site local topography

A.V. Kucherov, T.N. Kucherova and A.A. Slinkin

N.D. Zelinsky Institute of Organic Chemistry, USSR Academy of Sciences, Moscow B-334, Leninsky Prosp. 47, USSR

Received 22 April 1991; accepted 6 July 1991

Catalytic ethane oxidation, with O_2, using H-ZSM-5 and H-mordenite containing different discrete types of isolated Cu(II) cations was studied. An ESR spectroscopic study was carried out on copper ion coordination in zeolites. It was shown that the intrinsic activity of Cu(II) ion depends strongly on the Cu^{2+}-site local topography. Covalent-bonded Cu(II) cations in the most coordinatively unsaturated square-planar coordination in H-ZSM-5 demonstrated the highest activity in C_2H_6 complete oxidation.

Keywords: ESR; selective oxidation; copper-catalysis; zeolite; ethane

1. Introduction

Copper(II)-containing supported catalysts are well known to be active in redox processes (alkane oxidation, for instance). At the same time, the surface of complex heterogeneous catalysts usually contain many types of isolated and clustered ions differing in coordinative and valent states, and the elucidation of a relation structure/properties is too difficult for such systems. Polyvalent ion introduction into high-silica zeolites is a way of preparation of more simple diluted systems with regular location of isolated cations (Cu^{2+}, for example) in a few discrete types of local environment [1–5]. Such systems are interesting from the catalytic point of view: CuH-ZSM-5 zeolites were found to be promising catalysts for the NO decomposition [6,7], methylaromatic ammoxidation [8] or CH_4 traces complete oxidation [9].

Thermal treatment of Cu(II)-containing high-silica zeolites as well as the introduction of different anionic ligands (F^-; PO_4^{3-} permits the local topography of isolated Cu^{2+}-sites [2] to be changed. So, the comparative catalytic testing of such systems containing only isolated cations diluted in zeolitic matrix enables us to elucidate the influence of local crystal field symmetry on catalytic properties of isolated Cu^{2+} ions.

This work describes the detailed study of catalytic C_2H_6 oxidation, with O_2, on isolated Cu(II) cations located in different coordinative states inside H-ZSM-5 or HM channels. Distribution and coordination of Cu^{2+} ions in zeolites were studied by ESR spectroscopy.

2. Experimental

1. MATERIALS

X-ray data confirmed the high crystallinity of the parent NH_4-ZSM-5 (Si/Al $= 21$; Na_2O content $< 0.1\%$ wt.) having the ZSM-5 framework structure. NH_4-zeolite without binder was pressed and crushed into 0.5 to 1.5 mm pieces. After drying at 400 K the samples were impregnated with aqueous $Cu(NO_3)_2$ or $Cu_3(PO_4)_2$ solutions of appropriate concentrations (incipient wetness impregnation; 0.7–0.8 cm^3 per 1 g of zeolite). Cu/H-ZSM-5 and Cu-P/H-ZSM-5 obtained (1.5% wt. Cu) were dried at 400 K and calcined in an air stream at 773 K for 5 h or at 1023 K for 2 h; Cu/HM (1.2% wt. Cu) was prepared by a conventional cation-exchange procedure using NH_4-M (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 was determined by chemical analysis.

2. ETHANE OXIDATION ACTIVITY MEASUREMENTS

Dried catalyst (80–90 mg; 0.25–0.5 mm pieces) was placed in a fixed-bed quartz microreactor (0.15 cm^3) and activated at 773 K with dry air flowing at the rate of 50 ml/min for 5 h. Then the temperature of catalytic run was fixed (543–673 K) and the gas mixture of reactants [80.8 vol.% of He + 18.3 vol.% of $O_2 + 0.87$ vol.% of C_2H_6] was fed to the reactor under 1.0 atm. pressure. Catalyst activities were measured at low alkane conversion, in contrast with results obtained in [9] where space velocity data under 99% CH_4 conversion at 773 K were used to compare catalyst activities.

Samples of the reactor effluents were injected periodically into a chromatograph. Carbon dioxide and water were obtained as major products in all catalytic runs. Traces of ethene were also detected in some runs. The space velocity ranged from $1.2 \cdot 10^4$ to $6 \cdot 10^4$ h^{-1}. After the catalytic testing the catalyst charge in the reactor was calcined in an air stream at 1023 K for 2 h and the catalytic testing at 573–773 K was repeated.

3. ESR MEASUREMENTS

X-band ESR spectra were taken at 77 K, and 293 K with DPPH ($g = 2.0036$) as a standard. The samples (50–80 mg), placed in quartz ampoules, were

Table 1

Zeolite	Calcination temperature (K)	ESR parameters				Cu(II) local environment
		$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ 10^{-4} cm^{-1}	$A_{\perp}$ 10^{-4} cm^{-1}	
Cu/HM	773 and 1023	2.32	2.055	144	19	square pyramidal
Cu/H-ZSM-5	773	2.27	2.045	175	29	square planar
		2.31	2.06	153		square pyramidal
	1023	2.30	2.05	156	23.5	distorted square pyramidal
		2.31	2.05	156	23	
Cu-P/H-ZSM-5	773	2.29		172		distorted square pyramidal
		2.33		160		square pyramidal
	1023	2.35		153		distorted octahedral
		2.40		120		octahedral
		2.41		125		

calcined in air at 773 K and then evacuated at 293 K for 5 min. In some cases the samples taken from the reactor after catalytic runs were purged by He, placed into ampoules and evacuated at 293 K. Evacuation of the samples was necessary to prevent dipole-dipole broadening of Cu(II) ESR lines, caused by interaction of cations with O_2 molecules. Interaction of the samples with pyridine (Py) was studied in air at 293 K. Precalcined zeolites were impregnated by Py for 10 min and then evacuated for 1 h.

3. Results and discussion

ESR data show that high temperature treatment of zeolites in air results in the stabilization of isolated Cu(II) ions in different local environments. Parameters of ESR spectra as well as Cu^{2+} coordinations are listed in table 1. Assignment of specific ESR spectra to different modes of Cu(II) coordination has been given in refs. [2,10–13]. ESR data confirm a 100% dispersion of Cu(II) in all samples studied.

The different geometry of zeolitic channels stabilizes Cu(II) in different local environments (HM; H-ZSM-5). However samples differing drastically in a local topography of isolated Cu^{2+}-sites may also be prepared on the basis of the same ZSM-5 zeolitic matrix (table 1). Two procedures after scope for the change of Cu^{2+} coordination mode in H-ZSM-5 from a square-planar environment to an octahedral one: (1) calcination at different temperatures; (2) introduction of anionic species. Fig. 1 demonstrates such influence of calcination temperature and PO_4^{3-} introduction on the hyperfine structure of Cu(II) ESR spectra.

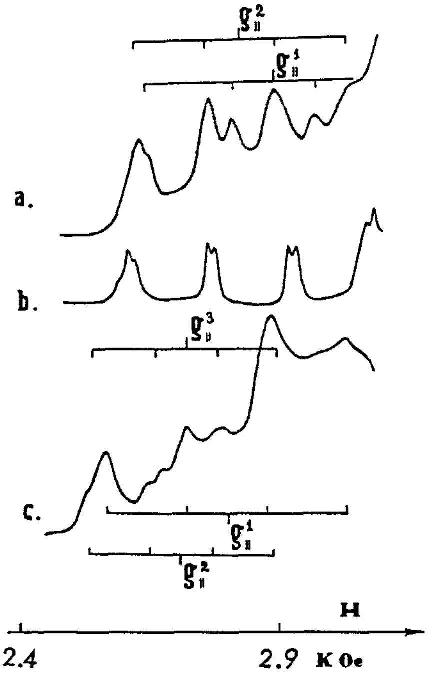

Fig. 1. Part of the ESR spectra (parallel components) at 77 K of copper-containing H-ZSM-5: (a)–Cu/H-ZSM-5 calcined at 773 K; (b)–Cu/H-ZSM-5 calcined at 1023 K; (c)–Cu-P/H-ZSM-5 calcined at 1023 K. (ESR-spectra remain unchanged after catalytic runs.)

Inlet of oxygen leads to reversible drastic dipole-dipole broadening of all Cu(II) ESR spectra i.e. isolated copper(II) ions are fully accessible for O_2 molecules. Moreover, all Cu^{2+} cations in our samples are capable of interaction with Py molecules: Py sorption results in an immediate transformation of different Cu^{2+}-ESR signals listed in table 1 into the same new spectrum with ESR-parameters of $g_{\parallel} = 2.30$–2.31; $g_{\perp} = 2.06$ and $A_{\parallel} = (156$–$163) \cdot 10^{-4}$ cm^{-1}. Intensity of such ESR signals from different samples treated with Py is practically the same. So, Py as a strong ligand is able to form specific complexes with all types of Cu^{2+} ions inside H-ZSM-5 channels [4,5], and anionic phosphorato-species do not hinder this interaction. It may be concluded that any noticeable aggregation or incapsulation of copper(II) does not occur as a result of either calcination or PO_4^{3-} introduction. Therefore, the set of samples prepared allows us systematically to probe the intrinsic catalytic properties of isolated Cu^{2+} ions differing in local environment only.

The Cu(II) ESR spectra of the post-reactor samples are identical to those of the samples before catalytic runs (fig. 1). Therefore, the coordination geometry of the copper species in all samples remains unchanged during the catalytic reaction.

The study of catalytic C_2H_6 oxidation by O_2 shows that activity of pure H-ZSM-5 is negligible up to 823 K. So, the parent zeolitic matrix may be treated

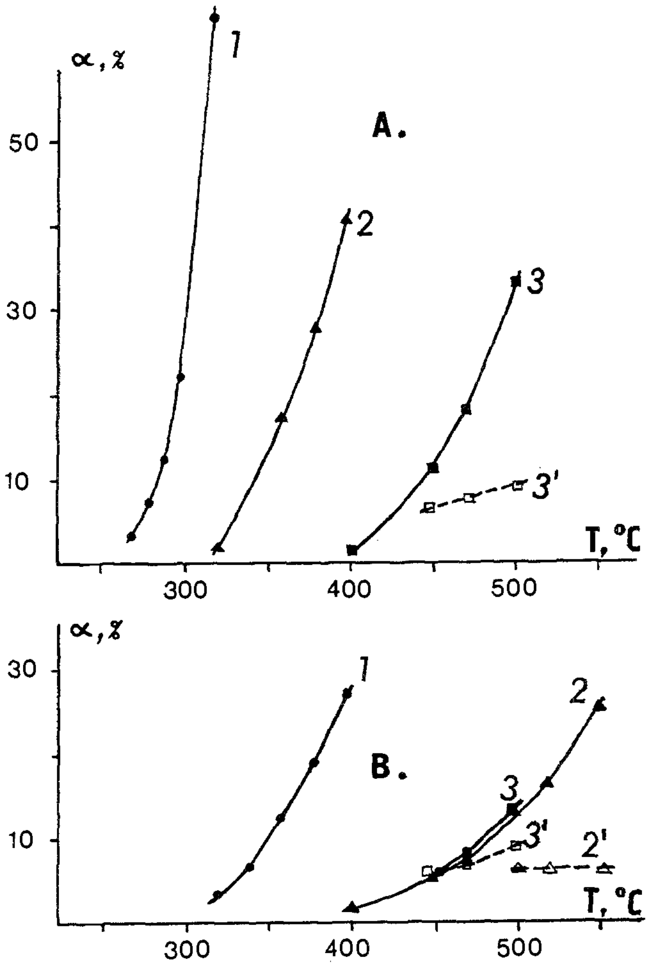

Fig. 2. Correlation between the C_2H_6 conversion to CO_2+H_2O ($V=2\cdot10^4$ h^{-1}) and the temperature of reaction for the samples calcined at 773 K (a) and 1023 K (b): (1)-Cu/H-ZSM-5; (2)-Cu-P/H-ZSM-5; (3)-Cu/HM. (dotted lines-C_2H_6 to C_2H_4 conversion).

as a fully inert catalyst support, and Cu(II) stabilization alone results in the formation of active sites. This conclusion agrees fully with the data of our previous work where CH_4 oxidation on Cu/H-ZSM-5 has been studied [9].

Catalytic activity of copper(II)-containing samples reaches a steady state within the first 10–15 min on stream: no drop in the effectiveness of the catalysts occurs after 6–10 h of continuous use. Fig. 2 gives the catalytic conversion of ethane on the samples listed in table 1 as a function of temperature. The apparent activation energy calculated from these data is listed in table 2. From fig. 3, which presents a plot of C_2H_6 conversion vs. contact time for some samples, it may be concluded that the reaction rate is zero order in ethane. Linear dependence of lgα from the inverse temperature (fig. 4), con-

Table 2
Apparent activation energy of C_2H_6 complete oxidation.

Sample	Temperature of calcination (K)	E (kcal/mol)
Cu/HM	773	30
	1023	21
Cu/H-ZSM-5	773	40
	1023	22
Cu-P/H-ZSM-5	773	33
	1023	21

firms that the kinetics of catalytic oxidation may be described by the zero-order rate equation at all temperatures. It is seen from fig. 2 that activities of our samples differ drastically and no direct comparison of all experimental catalytic data at one fixed temperature is possible. The representation of results given in fig. 4 allows an extrapolation of catalytic data for a formal comparison of catalyst activities at one temperature, as shown by dotted lines.

The contribution of partial oxidation becomes measurable at temperatures above 673 K on the less active catalysts (Cu/HM; Cu-P/H-ZSM-5/1023 K), and the conversion of ethane to ethene is shown on fig. 2 by dotted lines. However, the most active samples catalyse the complete C_2H_6 oxidation selectively, and in all catalytic runs no products other than CO_2 and H_2O were detected up to 673 K.

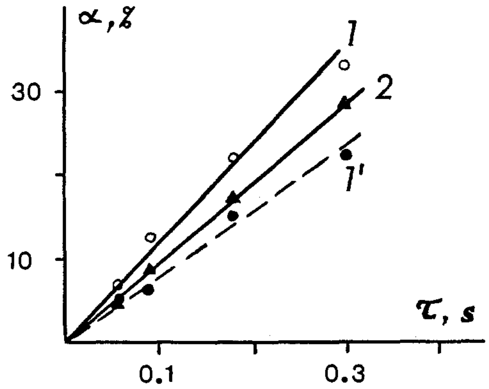

Fig. 3. Correlation between the oxidative activity of Cu(II)-containing samples and the contact time: (1)–Cu/H-ZSM-5/773 K, testing at 573 K; (1')–Cu/H-ZSM-5/1023 K, testing at 653 K; (2)–Cu-P/H-ZSM-5/773 K, testing at 633 K.

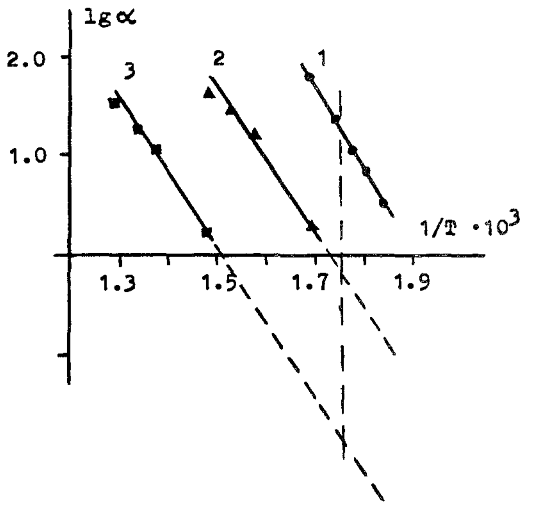

Fig. 4. Correlation between the logarithm of C_2H_6 conversion (α) and the inverse temperature of reaction. (1)–Cu/H-ZSM-5, calcined at 773 K; (2)–Cu-P/H-ZSM-5, calcined at 773 K; (3)–Cu/HM calcined at 773 K.

In catalysis by zeolites the role of diffusion is quite serious. No special testing of this problem was carried out in our work, but it may be noted that both a zero-order kinetics (fig. 3) and great values of activation energy (table 2) are not typical of diffusional processes. So, it is safe to assume that diffusive constraints play a minor role upon our catalytic runs.

Let us now compare the structural data with the catalytic properties of Cu(II)-containing zeolites. It is clearly seen from ESR data that our samples contain isolated Cu^{2+} ions only, and that all these ions are capable of interacting readily with reactant molecules. This result agrees with other data (refs. [2,5,14]). In other words, the samples do not differ noticeably in the total number of accessible active Cu^{2+}-sites diluted in an inert support, and the specific activity of Cu^{2+} ion is compared in each case. Therefore, the drastic difference in specific catalytic activity of the samples, as shown in figs. 2 and 4, gives unambiguous evidence that the intrinsic activity of Cu^{2+}-site is determined mainly by the degree of Cu(II) coordinative unsaturation (or by a local topography of Cu^{2+}-site). The comparison of extrapolated data, as shown in fig. 4, demonstrates that a 1000-fold change in specific activity of isolated Cu^{2+}-site may occur as a result of local topography transformation. Activity of the sample Cu/H-ZSM-5/773 K (which contains the most coordinatively unsaturated square planar Cu(II) ions) exceeds activities of the samples containing five-coordinated Cu^{2+} ions by a factor of 30-100. Subsequent transformation of copper(II) environment to the most symmetrical octahedral one (Cu-P/H-ZSM-5/1023 K) results in a further activity fall by a factor of ~ 30. Such a drastic suppression of complete oxidation is accompanied by a selectivity change: an activity in high-temperature partial oxidation becomes measurable for the samples with more symmetrical Cu^{2+} environments (fig. 2).

Preliminary experiments with N_2O as C_2H_6 oxidant on the same catalysts demonstrate that the process depends strongly on the type of oxidant. In this case a pure H-ZSM-5 cannot be treated as inert support. A detailed comparative analysis of this problem will be a subject of our further work.

4. Conclusions

The H-ZSM-5 structure as a macroligand is able to provide stabilization of Cu(II) in the most coordinatively unsaturated square planar environment. Such isolated low-coordinated Cu(II) cations play the decisive role in catalytic low temperature complete oxidation of alkanes. Regulation of local topography of Cu^{2+}-site in H-ZSM-5 by either anionic ligand introduction or thermal treatment permits effectively the catalytic properties of active site to be changed.

References

[1] A.V. Kucherov, A.A. Slinkin, D.A. Kondratyev, T.N. Bondarenko, A.M. Rubinstein and Kh.M. Minachev, Zeolites 5 (1985) 320.

[2] A.V. Kucherov and A.A. Slinkin, Zeolites 6 (1986) 175.

[3] Y. Sendoda and Y. Ono, Zeolites 6 (1986) 209.

[4] C.E. Sass and L. Kevan, J. Phys. Chem. 92 (1988) 5192.

[5] M.W. Anderson and L. Kevan, J. Phys. Chem. 91 (1987) 4174.

[6] M. Iwamoto, H. Furukawa, Y. Mine, F. Uemura, S. Mikurija and S. Kagawa, J. Chem. Soc., Chem. Commun. (1986) 1272.

[7] Y. Li and W.K. Hall, J. Phys. Chem. 94 (1990) 6145.

[8] D. Fraenkel, J. Molec. Catal. 51 (1989) L1.

[9] A.V. Kucherov, A.A. Slinkin, S.S. Goryashenko and K.I. Slovetskaja, J. Catal. 118 (1989) 459.

[10] V.F. Anufrienko, H.G. Maksimov, V.G. Shinkarenko, A.A. Davydov, Yu.A. Lokhov, N.N. Bobrov and K.G. Ione, in: *Application of Zeolites in Catalysis*, eds. G.K. Boreskov and Kh.M. Minachev (Académiai Kiado, Budapest, 1979) 109.

[11] J.H. Lunsford, in: *Magnetic Resonance in Colloid and Interface Science*, eds. J.P. Fraissard and H.A. Resing (Reidel, Dordrecht, 1980) 67.

[12] A.A. Shklayev and V.F. Anufrienko, Z. Strukt. Khim. 16 (1975) 1082.

[13] L. Kevan, in: *Reviews of Chemical Intermediates*, Vol. 8 (Elsevier, Amsterdam, 1987) 53.

[14] A.A. Slinkin, A.V. Kucherov, N.D. Chuvylkin, V.A. Korsunov, A.L. Kliachko and S.B. Nikishenko, J. Chem. Soc., Faraday Trans. 1, 85 (1989) 3233.