

SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
5 (1999)

**EFFECT OF ZEOLITE MATRICES
ON THE REDOX AND CATALYTIC PROPERTIES
OF THE Cu IONS IN MFI ZEOLITES**

Roman BULÁNEK^{a1}, Blanka WICHTERLOVÁ^b and Josef TICHÝ^a

^aDepartment of Physical Chemistry, University of Pardubice,
CZ-532 10 Pardubice

^bJ. Heyrovský Institute of Physical Chemistry,
CZ-182 23 Prague

Received September 14, 1999

The aim of the paper is to bring insight into the relationship between the structure, redox properties and catalytic activity in propane oxidation of the Cu ions in high-silica zeolites. Previous studies revealed several defined Cu ion sites characteristic of high-silica zeolites, differing in coordination-siting, positive charges, and population depending on Cu concentration, and content of Al in the framework. It has been a highly important to relate this knowledge on the structure of Cu ion sites to the redox properties and oxidation catalytic activity of the Cu-high-silica zeolites. The reducibility and catalytic activity in propane oxidation was investigated for the Cu ions planted in zeolites of structural types ZSM-5 (MFI) with different Cu/Al/Si compositions, where Na(I) or H(I) ions were present as co-cations, and Cu ions were exchanged at various conditions (concentration and

¹ To whom correspondence should be addressed.

pH). Reducibility of the Cu(II) ions was investigated by temperature-programmed reduction (TPR) with hydrogen, and by vacuum and CO treatment of the zeolites; the relative concentration of the Cu(I) ions was monitored by IR spectra of formed Cu(I)-(CO)_n complexes. Conversion of propane to CO and CO₂ was studied in dependence on temperature in an integral through-flow reactor and evaluated in turn-over-frequency (TOF) values, representing the activity per one Cu ion.

Introduction

Nitrogen oxides formed during combustion and chemical processes represent harmful pollutants in the atmosphere. Catalytic conversion of NO to molecular nitrogen seems at present to be the most suitable way for their removal from the exhaust gases [1,2]. Copper ions planted in so called „high-silica“ zeolites (Si/Al ~ 8) have been recognized as promising catalysts for processes of environment protection as they exhibit high catalytic activity in reactions for abatement of NO_x in highly oxidizing atmosphere, i. e. decomposition of NO and selective catalytic reduction (SCR) of NO with ammonia or hydrocarbons [3–7]. This challenge raised enormous interest in elucidation of the structure, nature and redox properties of the Cu ions planted in zeolites.

Cu ions are embedded into zeolite aluminosilicate matrices with negative framework charge as ion exchanged cations bonded to framework oxygen atoms. However, beside single Cu ions in cationic sites different dispersed CuO species were detected in Cu-zeolites [8–17].

The majority of copper ions in an ion exchanged zeolite is found as single isolated ions localized at defined cationic sites. Geometry of these sites in aluminium-rich zeolites (Si/Al = 1–3) of A, X, Y structures was established by means of XRD. The cationic sites in mordenite were established only for non-transition metal ions. But in high-silica zeolites of ZSM-5 (MFI), ferrierite (FER), mordenite (MOR), and even in erionite (ERI) cationic sites of transition metal ions are not known, as the XRD analysis is not possible, due to the low concentration of cations in these zeolites.

The first pieces of information about coordination of copper in MFI and MOR matrix were obtained from ESR spectra of Cu(II) ions [19–21] and UV-VIS spectra [18]. Wichterlová *et al.* [22–28] investigated siting-coordination of Cu ions in zeolites of MFI, MOR, ERI and FAU structures by using multi-spectroscopical approach. By employing Cu(I) emission spectra, IR spectra of adsorbed NO on Cu(II) and ESR of Cu(II) four Cu ion coordinations in these materials were found (see Table I). Population of these sites by Cu ions depends on the geometry of zeolite framework and its composition (Cu/Al/Si ratios) [25]. Based on a comparison of population of individual sites by Cu ions and catalytic activity of Cu-ZSM-5, the Cu ions in adjacent to one AlO₂⁻ (Cu-IV) were recognized as active si-

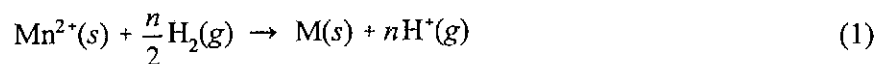
Table I Cu ion siting-coordination: Characteristic Cu(I) VIS emission spectra, IR spectra of Cu(II)–NO and ESR of Cu(II) ions [25]

Cu site denoted	Cu(I) emission, nm	Cu(II)–NO, cm ⁻¹	ESR		Al local arrangement	Cu(II) coordination
			g ₁	A ₁ (G)		
Cu–I	450	1921	2.31	150 – 160	2 AlO ₂ ⁻	square pyramidal
Cu–II	480	1912	2.33	150 – 160	2 AlO ₂ ⁻	square pyramidal
Cu–III	510	1906	not found		?	?
Cu–IV	540	1896	2.28	180	1 AlO ₂ ⁻	square planar

tes in NO decomposition. Study of SCR of NO by hydrocarbons proved that the activities of individual Cu ions in this reaction are also different.

As the single Cu ions localized in high-silica zeolites exhibit unique activity in reactions of NO decomposition and SCR of NO by paraffins (propane) to nitrogen in highly oxidizing atmosphere, which was not found either for supported Cu oxides or other Cu oxidic compounds, it was expected that it should be associated also with unusual Cu(II) – Cu(I) – Cu(0) redox properties. Therefore, it was important to investigate the effect of composition and topology of the framework on the mutual interaction of the Cu ions and zeolite matrices and their redox properties as reflected in the Cu(II) – Cu(I) – Cu(0) reducibility and catalytic activity in oxidation of propane.

Redox properties of Cu-zeolites were studied by means of temperature-programmed reduction by hydrogen. The reduction of Cu ions balanced by negative charge of a zeolite matrix can be described by the equation



The protons formed during the reduction react with the zeolite lattice to produce skeletal hydroxyl groups [29,30]. A lot of possible reaction schemes were suggested [31–38], where formation of the (Cu(II)–H₂) intermediate or migration of either hydrogen species (H₂(I) or H(0)) may be the rate-controlling process.

The main problem in a H₂–TPR profiles of Cu-zeolites is, whether the appearance of two dominant peaks represents a single-stage reduction (Cu(II) to Cu(0)) of two different types of Cu(II) ions or they result from a two-stage reduction (Cu(II) to Cu(I) to Cu(0)) of single Cu ions. Clearly, when more than two peaks are seen, there must be at least two distinct types of Cu(II) ions in the precursor, but the possibility of a two-stage reduction of at least one of the Cu(II) types cannot be

ruled out. Studies of Ni(II) and Cu(II) ions in H-MOR [39], Cu-Y and CuZn-Y zeolites [40] and Cu-MFI [33–35] described reduction of these ions in two-step mechanisms.

Nature and reducibility of Cu ions in high-silica zeolites was also studied by reduction of Cu(II) ions by treatment of Cu-zeolites in vacuum and in atmosphere of CO at various temperatures. IR spectra of CO adsorbed on Cu-zeolites display several bands in the range from 2080 cm^{-1} to 2220 cm^{-1} , whose interpretation is still widely discussed. Absence of knowledge of an initial valence of copper and its state in Cu-CO complexes are the main reasons of controversy interpretation of IR spectra of adsorbed CO. On the basis of the present knowledge we can say that Cu(II) and Cu(0) carbonyls are much less stable than Cu(I) carbonyls at room temperature [41–44]. It follows that weak and unstable bands at higher wavenumbers (above 2160 cm^{-1}) can be ascribed to poor adsorption of CO on Cu(II) ions [41] and bands at wavenumbers below 2100 cm^{-1} to adsorption of CO on Cu(0) [44]. Other bands in a wide range $2160\text{--}2100\text{ cm}^{-1}$ can be ascribed, with high probability, to CO adsorbed on Cu(I) ions.

The aim of this work was to determine and explain redox properties and catalytic activity in oxidation of propane by oxygen of single Cu ions and Cu oxidic species localized in high-silica zeolites of various structures and chemical compositions and to contribute to clarification of unique catalytic redox activity of copper ions in these zeolites in deNO_x reaction. Therefore, we use a combination of temperature programmed reduction by hydrogen (H_2 -TPR) and IR study of CO adsorbed on Cu-zeolites in order to determine and explain redox properties and obtained results related to activity of Cu ions in propane oxidation.

Experimental

Cu-Zeolite Preparation

NH_4^- , H- and Na-forms of zeolites of structural types ZSM-5 (MFI) were kindly provided by the Institute of Oil and Hydrocarbon Gases, Slovnaft, Bratislava. The Cu(II) ion exchange was performed by using $0.0002\text{--}0.10\text{ M}$ CuCl_2 , $\text{Cu}(\text{CH}_3\text{COO})_2$ or $\text{Cu}(\text{NO}_3)_2$ aqueous solutions at a temperature from $25\text{ to }60\text{ }^\circ\text{C}$. By using $\text{Cu}(\text{CH}_3\text{COO})_2$ solution for ion exchange it was possible to achieve a level of Cu/Al ratio higher than 0.5. The pH value of ion exchange solutions was sometimes adjusted with dilute NaOH solution at $\text{pH} = 6$ for preparation of zeolites with a high Cu/Al ratio ($\text{Cu/Al} \geq 0.5$). By with these solutions the probability of rising concentration of $[\text{Cu}(\text{OH})]^+$ and $\text{Cu}(\text{OH})_2$ species in solution was increased, which led to formation of CuO species in zeolites after calcination. The content of Cu, Al and other elements in zeolites was determined by chelatometric titration after the zeolite dissolution. A gravimetric method was used

Table II Preparation and chemical composition of Cu-MFI zeolites

Catalyst	Zeolite			Parameters of ion exchange			
	Si/Al molar	Cu/Al molar	w_{Cu} , wt %	t , h	T , °C	Solution	$V_{\text{sol.}}/w_{\text{zeol.}}$ ml g^{-1}
CuNa-MFI/1	22.6	0.52	2.04	12	25	0.1 M CuCl_2	500
CuNa-MFI/2	22.6	0.50	1.96	12	25	0.00033 M $\text{Cu}(\text{Ac})_2$	2000
CuNa-MFI/3	22.6	0.48	1.84	24	25	0.001 M $\text{Cu}(\text{Ac})_2$	1000
CuNa-MFI/4	22.6	0.48	1.88	12	25	0.001 M $\text{Cu}(\text{Ac})_2$	1000
CuNa-MFI/5*	22.6	0.47	1.78	20	25	0.001 M $\text{Cu}(\text{NO}_3)_2$	500
CuNa-MFI/6	22.6	0.43	1.69	20	25	0.05 M $\text{Cu}(\text{NO}_3)_2$	14
CuNa-MFI/7*	22.6	0.42	1.64	20	25	0.05 M $\text{Cu}(\text{NO}_3)_2$	14
CuNa-MFI/8	22.6	0.28	1.10	12	25	0.01 M CuCl_2	20
CuNa-MFI/9	14.1	0.63	3.93	12×2	25	0.02 M $\text{Cu}(\text{Ac})_2$	2×500
CuNa-MFI/10	14.1	0.59	3.63	12×2	25	0.01 M $\text{Cu}(\text{Ac})_2$	2×500
CuNa-MFI/11*	14.1	0.56	3.45	4	25	0.05 M $\text{Cu}(\text{Ac})_2$	100
CuNa-MFI/12	14.1	0.54	3.35	4	25	0.05 M $\text{Cu}(\text{Ac})_2$	100
CuNa-MFI/13	14.1	0.52	3.05	24	25	0.01 M $\text{Cu}(\text{Ac})_2$	400
CuNa-MFI/14	14.1	0.44	2.75	12	25	0.01 M $\text{Cu}(\text{Ac})_2$	375
CuNa-MFI/15	14.1	0.37	2.24	12×2	25	0.1 M CuCl_2	2×20
CuNa-MFI/16	14.1	0.37	2.23	24	25	0.00053 M $\text{Cu}(\text{Ac})_2$	1 g^{-1}
CuNa-MFI/17	14.1	0.35	2.15	0.5	25	0.1 M CuCl_2	20
CuNa-MFI/18	14.1	0.29	1.85	24	25	0.0003 M $\text{Cu}(\text{Ac})_2$	1000
CuNa-MFI/19	14.1	0.40	2.52	12	25	0.01 M $\text{Cu}(\text{Ac})_2$	200
CuNa-MFI/20	14.1	0.19	1.13	12	25	0.01 M CuCl_2	20
CuNa-MFI/21	14.1	0.02	0.12	24	25	0.001 M CuCl_2	20
CuH-MFI/22	22.6	0.33	1.33	4	60	0.1 M CuCl_2	20
CuH-MFI/23	22.6	0.26	1.05	4	60	0.1 M CuCl_2	20
CuH-MFI/24	22.6	0.03	0.12	4	60	0.001 M CuCl_2	20
CuNH ₄ -MFI/25	12.5	0.12	0.93	12	25	0.01 M CuCl_2	22

* these zeolites were prepared by ion exchange under more basic condition (pH = 6)

for determination of the Si content and the concentration of Ca was determined by atomic absorption spectroscopy. The conditions of the ion exchange and the chemical composition of the resulting Cu exchanged zeolites are given in Table II.

H_2 -TPR

Reduction of Cu-zeolites (pre-calcinated in a flow of oxygen at 450 °C) by hydrogen was monitored in the temperature-programmed reduction apparatus (20 – 1000 °C, heating rate 10 °C min⁻¹). A quartz reactor was charged with 140 mg of a dry Cu-zeolite with the grain size of 0.25 – 0.5 mm (content of moisture was determined by DTA-DTG measurement). After leaving the reactor the reduction gas (total flow rate 25 cm³ min⁻¹, 5 vol. % of H₂ in nitrogen) was passed through a freezing trap kept at -78 °C to remove water. Changes of hydrogen concentration in reduction gas were monitored by thermal conductivity detector (TCD).

FTIR Spectroscopy of CO Adsorbed on Cu-Zeolites

The IR spectra were measured in the range from 400 to 4000 cm⁻¹ (with resolution 4 and 0.5 cm⁻¹) by using an FTIR spectrometer Magna System 550 (Nicolet Instrument Corp.) equipped with MCT/B detector, which was kept at the temperature of liquid nitrogen. A thin transparent self-supporting wafer of a zeolite (~ 7 mg cm⁻²) was oxidized in oxygen (13.3 kPa) at 450 °C, followed by a brief evacuation either at 25 °C or at 450 °C. Cu-zeolites were treated in CO (9 kPa) at various temperatures (25 – 450 °C). The spectrum of CO adsorbed at 25 °C was measured for every treatment. The IR spectra were deconvoluted into Gaussian curves. The existence of the deconvoluted bands was confirmed from the experimental spectra in which one band dominated.

The relative concentration of the Cu(I) ions was determined from the area of IR spectra of adsorbed CO normalized on total concentration of copper in the sample. With respect to the fact that the IR spectra showed the presence of bands of monocarbonyl and dicarbonyl species, the areas of the IR spectra were determined as a sum of areas of bands corresponding to monocarbonyl species and half of areas of bands corresponding to dicarbonyl species.

Testing of Catalytic Activity in Propane Oxidation

Catalytic activity of Cu-zeolites in propane oxidation was measured in an integral flow-through reactor with fixed bed in the temperature range from 275 to 510 °C. The total flow rate of inlet gas mixture was 100 cm³ min⁻¹ with composition of 1.6 vol. % of propane, 20.0 vol. % of oxygen and 78.4 vol. % of helium. A 185 mg zeolite sample was mixed with 1.5 cm³ inert SiC to prevent local superheating of the catalyst. Composition of reactants was analysed with a gas chromatograph CHROM 5 equipped with thermal conductivity detector and packed column (length 250 cm, 1/3 Porapak Q and 2/3 Carboxen 80/100), connected „on-line“ to catalytic

apparatus. The reaction was described by propane conversion, yield and selectivity of CO and CO₂. For comparison of catalytic activity of individual samples *TOF* (turn over frequencies) factor was used, i.e. number of propane molecules converted per time per one copper atom in the sample (see Eq.(2))

$$TOF = \frac{N_i}{N_{Cu}} = \frac{n_i^0 X_i N_A}{\frac{W w_{Cu} N_A}{A_{Cu}}} \quad (2)$$

where N_i is number of converted molecules of key reactant per time; N_{Cu} is number of Cu atoms in the sample; X_i is the key reactant conversion; n_i^0 is initial molar flow rate of the key reactant [mol s^{-1}]; N_A is Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$); W is a weight of catalyst [g]; w_{Cu} is the mass fraction of copper in the zeolite and A_{Cu} is atomic weight of copper [g mol^{-1}].

Results

Reduction of Cu-Zeolites Monitored by TPR

The H₂-TPR profiles of Cu-MFI catalysts with the same Si/Al ratio (14.1) and different copper content ($0.19 \leq \text{Cu/Al} \leq 0.59$) are illustrated in Fig. 1. Two re-

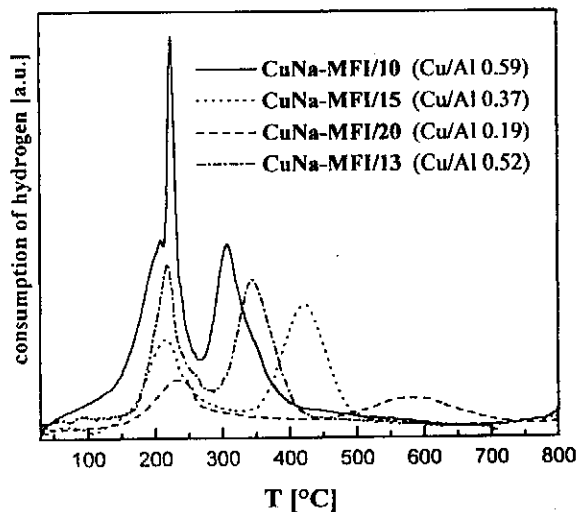


Fig. 1 H₂-TPR profiles of Cu-MFI zeolites with the same Si/Al molar ratio and different copper content

duction peaks were detected for all the catalyst; only the catalyst with the highest concentration of copper exhibited three reduction peaks. It is clearly seen that the temperatures of peak maxima decrease with increasing copper content. This feature indicates that the Cu ions are more easily reduced as the catalyst copper content increases. After plotting the prevailing reduction peak areas in H_2 -TPR patterns of Cu-MFI zeolites against copper concentration in zeolite, we can see that in both cases the data do not show distinct trend to deviate from the common curve in the whole concentration range (Fig. 2). This quantitative correspondence of areas of both peaks in the whole concentration range indicates a two-step reduction process of Cu ions *via* Cu(I) ions as a stable intermediate. It means that the low-temperature peak corresponds to the reduction of Cu(II) to Cu(I) ions and the high-temperature peak corresponds to Cu(I) reduction to Cu(0). The sharp reduction peak appearing in the H_2 -TPR curves of zeolites with very high concentration of copper at temperatures around 250 °C was attributed to one-step reduction of CuO species to Cu(0) (Fig. 3). This was concluded with respect to the resemblance to H_2 -TPR curves of Cu-MFI zeolites prepared by ion exchange in solution of Cu(II) ions with pH = 6 and CuO impregnated SiO₂ or MgO. The shape and position of this peak depends on dispersion, localization in the zeolite and interaction of these species with the zeolite lattice.

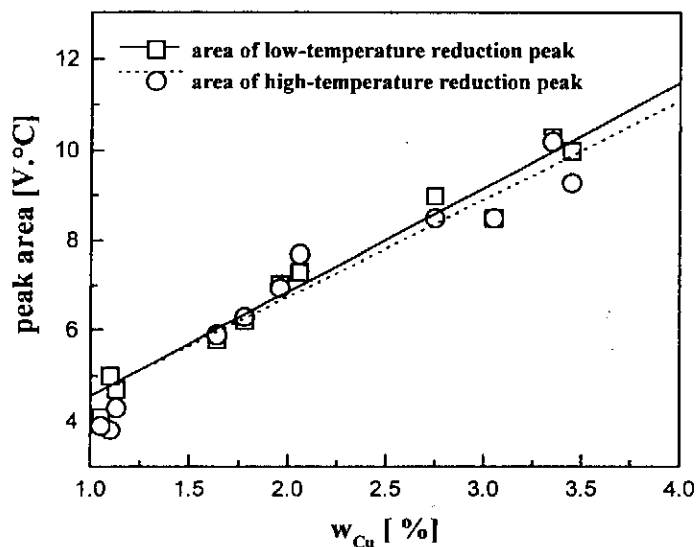


Fig. 2 Dependence of area of reduction peaks on copper content in zeolites

Figure 4 shows the H_2 -TPR profiles of CuNa-MFI catalysts with the same copper content and different Si/Al ratios (14.1 and 22.6). Two reduction peaks were detected for both zeolites: the first one at about 220 °C and the second one in the

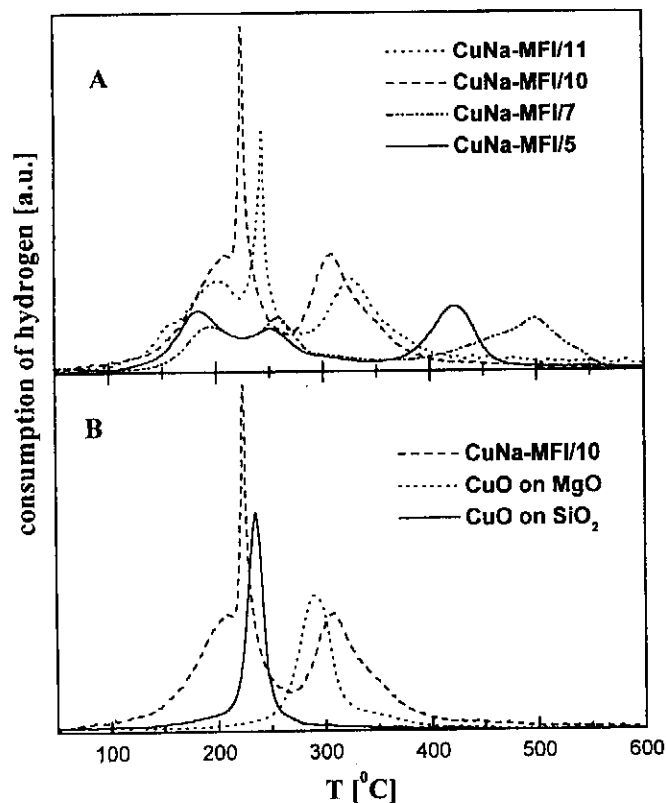


Fig. 3 H₂-TPR profiles of CuNa-MFI zeolites with CuO species: (A) CuNa-MFI zeolites prepared by ion exchange at enhanced pH value; (B) Comparison of H₂-TPR profile of CuNa-MFI/10 with H₂-TPR profiles of CuO on different supports

range of 430 – 580 °C. Shifts of maxima of the reduction peaks in the profiles of CuNa-MFI zeolites with various Si/Al ratios clearly show that reduction of Cu ions takes place more easily in the matrix with lower Al content.

The effect of the co-cation (Na(I), H(I)) on copper reduction is shown in Fig. 5. There is a clear shift to lower temperatures of the CuNa-MFI zeolite H₂-TPR profile with respect to CuH-MFI zeolite, which indicates that copper in sodium form of zeolite is more easily reduced than in proton form. This feature may be due to the inhibition effect for copper reduction caused by acid sites in zeolite [45].

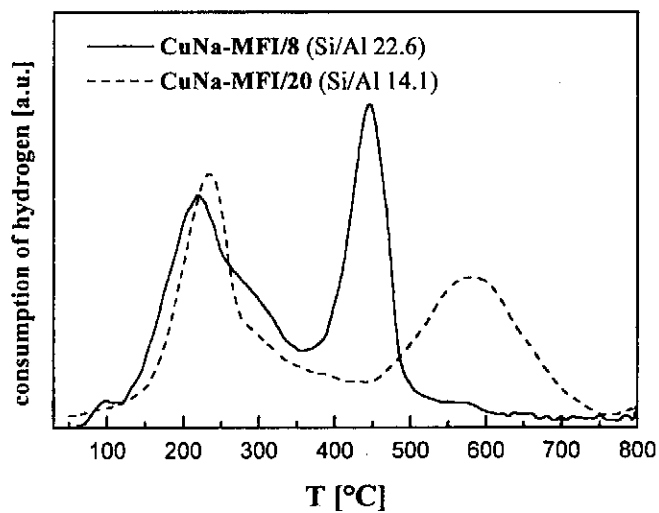


Fig. 4 H_2 -TPR profiles of CuNa-MFI zeolites with the same Cu content (1 wt. %) and different Si/Al molar ratio

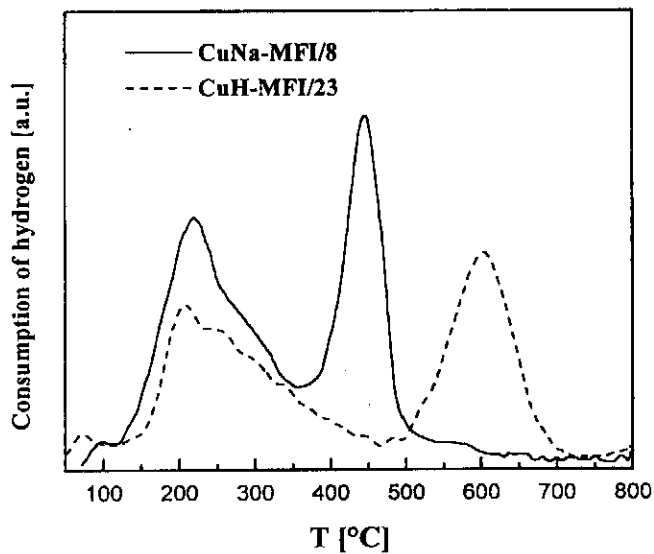


Fig. 5 H_2 -TPR profiles of Cu-MFI zeolites with 1 wt. % of Cu and Si/Al molar ratio 22.6. The effect of type of co-cations on reducibility of Cu ions

Reduction of Cu-Zeolites in Vacuum and CO Monitored by IR Spectra of $\text{Cu}(\text{CO})_n$ complexes

The IR spectroscopy of CO adsorbed on Cu-zeolites was proven as suitable method for detection of reduction of Cu(II) to Cu(I) ions in zeolites after treatment in vacuum and in CO atmosphere. The spectra of $\text{Cu}(\text{I})(\text{CO})_n$ (see Fig. 6) exhibited four absorption bands after evacuation at room temperature (2158, 2147, 2127 and 2110 cm^{-1}), which were interpreted, according to literature [46–56], as absorption bands of C–O vibration. Band at 2158 cm^{-1} (Cu(I)–CO) dominated in the spectra of Cu-MFI zeolites. Highly intensive bands at 2177 and 2151 cm^{-1} (in the atmosphere of CO) were ascribed to symmetrical and antisymmetrical vibration of dicarbonyl species $\text{Cu}(\text{I})-(\text{CO})_2$ (Fig. 7). In contrast to the IR spectra of NO adsorbed on Cu(II), the individual bands of CO adsorbed on Cu(I) were not ascribed to Cu–CO complexes planted at different cationic sites.

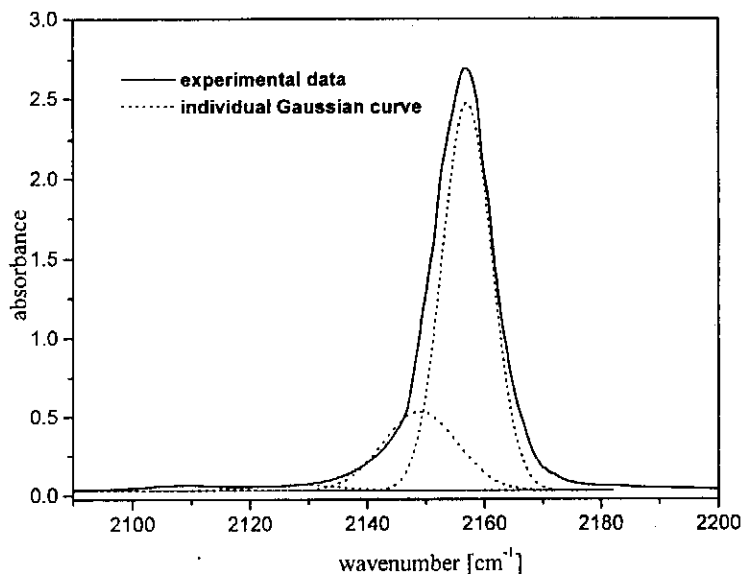


Fig. 6 The IR spectrum of CO adsorbed on Cu–MFI/20 after evacuation at room temperature

Dependence of relative concentration of Cu(I) ions in zeolites on temperature of CO treatment was obtained from intensities of bands of IR spectra of CO adsorbed on Cu-zeolites (Fig. 8). The relative concentration of Cu(I) ions increased with increasing treatment temperature. This growth was higher in the whole temperature range for samples with higher Cu/Al and Si/Al ratios. It is evident that a part of the Cu ions undergo reduction to Cu(I) ions already during evacuation and following adsorption of CO at room temperature. This part of the Cu ions represents

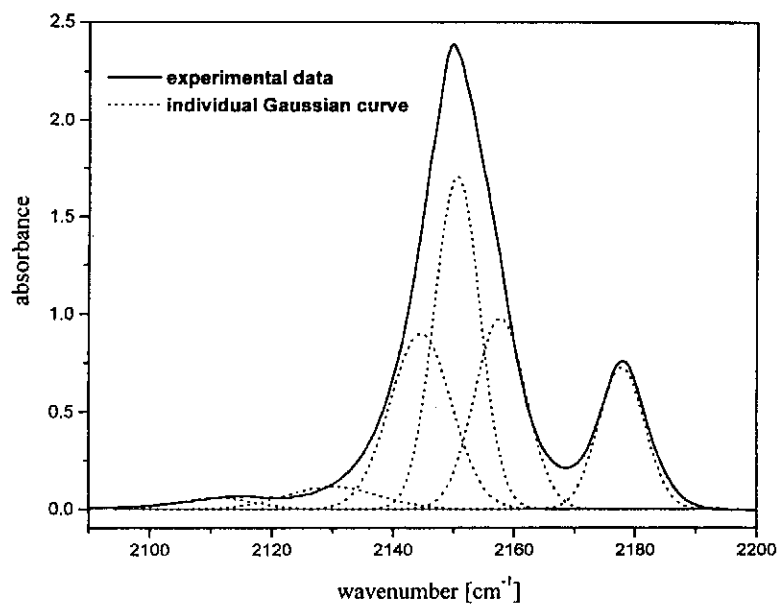


Fig. 7 The IR spectrum of CO adsorbed on Cu-MFI-20 in the CO atmosphere (9 kPa)

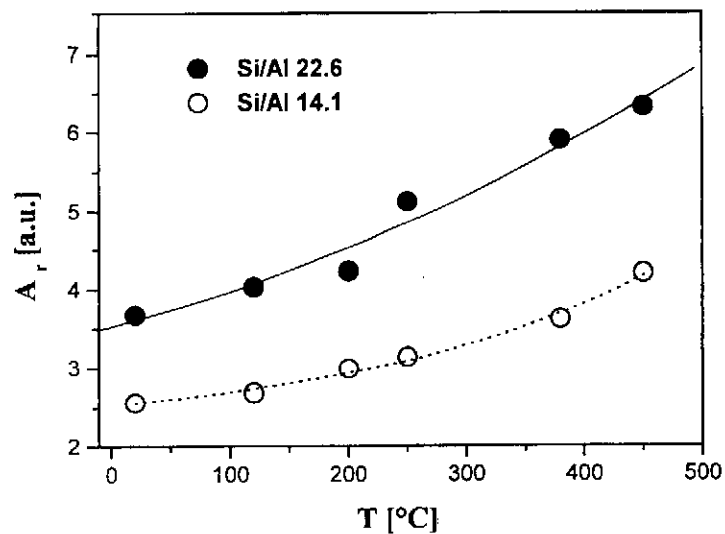


Fig. 8 Dependence of relative concentration of Cu(I) in zeolite (A_r) on treatment temperature and concentration of Al in zeolite matrix. Measured on zeolites CuNa-MFI/8 and CuNa-MFI/20 with copper content 1 wt. %

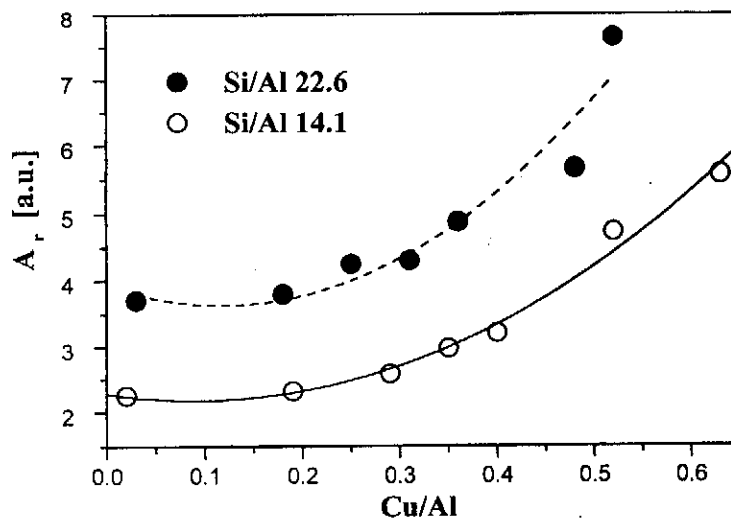


Fig. 9 Dependence of relative amount of Cu(I) ions in zeolite (A_r) as a function of Cu/Al ratio after adsorption 9 kPa of CO on fresh oxidized sample

most easily reducible copper ions. The relative amount of these Cu ions increased in MFI zeolite with increasing content of copper and decreasing concentration of aluminium in the framework (Fig. 9).

Catalytic Activity of Cu-Zeolites in Propane Oxidation

To analyse the effect of MFI Si/Al ratio and copper content on propane oxidation, set of CuNa-MFI catalysts with different Cu concentrations and Si/Al ratios were studied. If Cu-zeolites contained only individual Cu ions coordinated to zeolite lattice, it was possible to evaluate the effect of Cu/Al/Si composition of zeolite on its activity. From the data obtained on Cu-MFI zeolites (Fig. 10) it is clear that total conversion and TOF factor at 300 °C increases with higher concentration of Cu and lower content of Al in the zeolite framework. An increase in catalytic activity is accompanied by an increase in CO₂ selectivity.

The presence of CuO species in Cu-MFI zeolites led to enhanced values of propane conversion (therefore TOF) and CO₂ selectivity in comparison with the activity of individual Cu ions (Fig. 11). With regard to the small content of CuO species in zeolites (in this case about 0.18 wt.%) it is obvious that catalytic activity of these species was high. Since structure of these species could not be defined, an additional spectrum of various types of CuO species was present, it was difficult to determine their activities expressed by *TOF*.

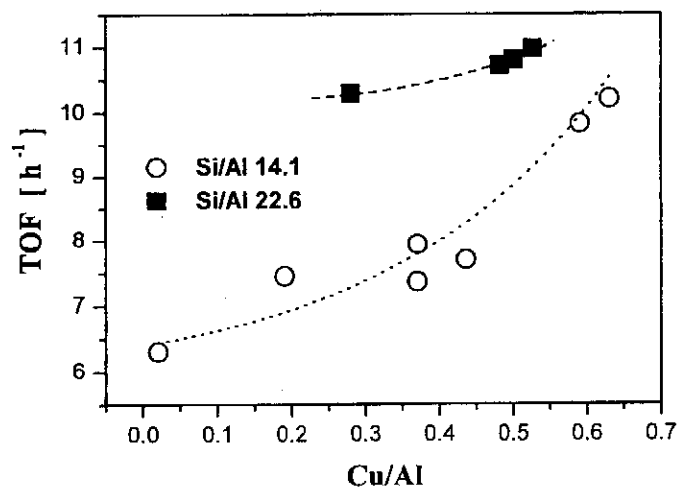


Fig. 10 The effect of content of copper on catalytic activity of Cu-MFI catalysts in propane oxidation at 300 °C

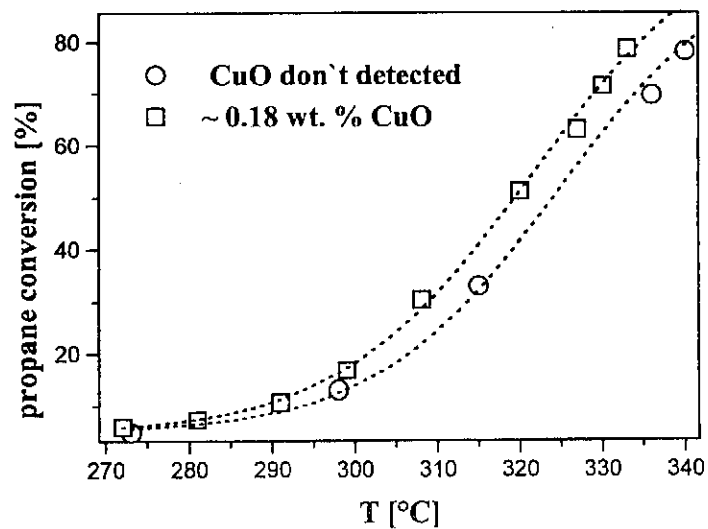


Fig. 11 The effect of presence of CuO species on propane oxidation as a function of temperature

Propane oxidation was also greatly influenced by the type of co-cation present together with Cu ions in the zeolites. CuH-MFI exhibited much lower catalytic activity and reaction was conducted more selectively to CO than CuNa-MFI (Fig. 12). Temperature dependence of CO selectivity on CuH-MFI was constant contrary to CuNa-MFI zeolites, where it decreased with increasing temperature.

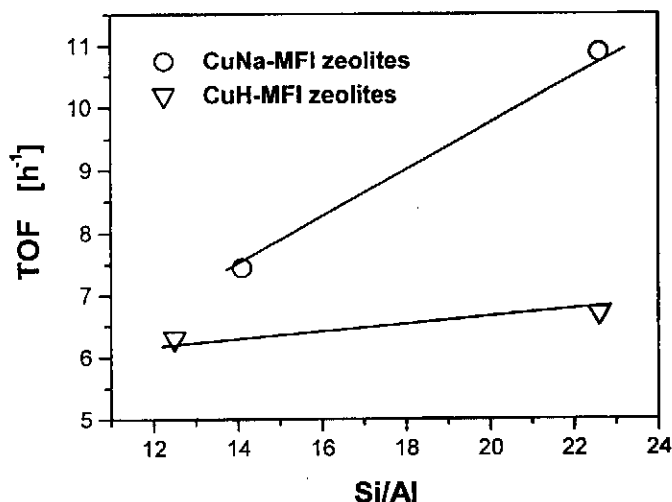


Fig. 12 The effect of type of co-cation present together with Cu ions in zeolite on *TOF* for propane oxidation at 300 °C. For comparison zeolites with 1 wt. % were used

Discussion

From the results obtained it follows that the redox properties represented by reducibility and catalytic activity of individual Cu ions coordinated to framework of high-silica zeolites (i) are completely different from those of bulk CuO and CuO dispersed on amorphous inorganic supports, (ii) depend dramatically on the structural type of the zeolite, degree of ion exchange, presence of co-cations and concentration of aluminium in the lattice.

Previous studies revealed the structure of Cu ions in high-silica zeolite matrices of MFI, FER and MOR. Also population of the individual types of Cu ions in MFI zeolites depending on the concentration of Cu ions (Cu/Al ratio) and content of aluminium in the zeolite matrix (Si/Al ratio) was established [24,25]. Cu ions occur in two dominant sitings-coordinations with characteristic positive changes on the Cu(II) ions as detected by electron density transfer from NO molecule to Cu(II) ions, Cu ions of the types Cu-II and Cu-IV (see Table I) [25]. It indicates that the

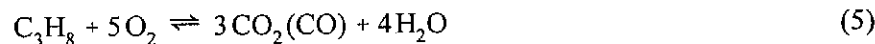
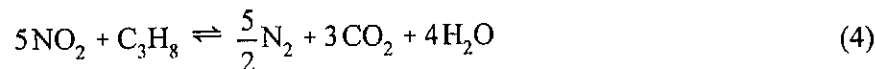
density of the local negative charge of the framework, which compensates positive charge of adjacent cation is, besides Cu ion coordination, important for the redox properties of Cu ions in high-silica zeolites. This density is determined by distribution of framework Al in the zeolite matrix. Considering statistical distribution of Al in the lattice, we assume that concentration of isolated AlO_2^- sites, which are able to compensate only one positive charge (i.e. monovalent complex of divalent cation), increases with decreasing Al content. Population of Cu-IV ions increases with increasing Cu concentration in MFI zeolites, with decreasing content of Al in zeolite framework and by ion exchange carried out with $\text{Cu}(\text{CH}_3\text{COO})_2$ solution or in alkaline solutions ($\text{pH} = 6$), when „monovalent“ ions $(\text{Cu}(\text{II})-\text{L}^-)$ are present in the solution. This is in agreement with the finding that the Cu-IV ions are compensated by low negative framework charge.

This model of Cu ion structure in high-silica zeolites, described for Cu ions in MFI zeolite matrices, is discussed in this study in connection with reducibility and catalytic activity of the Cu ions. Considering the dependence of reducibility and catalytic activity in propane oxidation of the Cu ions in MFI zeolites on one side and the dependence of population of Cu-II and Cu-IV sites on the concentration of Cu and the Al content in the zeolite lattice on the other side, it follows that the Cu-IV ions show much easier reducibility and higher catalytic activity in propane oxidation in comparison with the Cu-II type ions. This is also in agreement with the suggested open coordination and low positive charge on the Cu(II) ion of the Cu-IV type.

The fact that a part of the Cu ions, especially at high Cu concentration and low content of framework Al in MFI zeolite, is in a monovalent state after treatment in highly oxidizing atmosphere (O_2 at 670 K) with following evacuation and CO adsorption at room temperature, indicates a high preference of this part of the Cu ions for a monovalent state. In view of the above-mentioned dependence of the Cu ions reducibility on Cu/Al/Si compositions, we can conclude that these ions are the Cu-IV ions or their part depending on the zeolite treatment. Easy reducibility of the Cu-IV ions or stability of a monovalent state is in agreement with a conclusion that these ions are active sites for NO decomposition to molecular nitrogen and oxygen [22-28], which proceeds only on the Cu(I) ions able to exist in oxidizing atmosphere.

Analogously, with SCR of NO by propane it was found a higher activity of the Cu ions in ZSM-5 zeolite with $\text{Cu}/\text{Al} = 0.5$, i.e. according to our suggestions in the zeolite with a high concentration of the Cu-IV ions. The SCR of NO is a complex process covering several steps (see Eqs (3) – (5)).





While the oxidation of NO to NO₂ is a very easy process (limited by thermodynamic equilibrium) at temperatures above 200 °C, in the next step NO₂ and O₂ compete for propane oxidation. If the Cu-zeolite contains only single Cu-IV and Cu-II type of ions, the rate of NO₂ reduction by propane prevails and from the dependence of the reaction rate on the Cu concentration it follows, that the activity of the Cu-IV ions is higher than that of the Cu-II ions. But if the rate of oxidation of propane by oxygen is much faster than by NO₂, then the rate of SCR of NO decreases, too. This is an example of Cu-zeolites which, besides single ions coordinated in defined sites, contain dispersed CuO species. Their reducibility was high in comparison with isolated Cu ions, the reduction proceeded in one step from Cu(II) to Cu(0) and exhibited high catalytic activity in propane oxidation as well. This high redox activity is connected with the existence of the supposed C–O–Cu–O–Cu– bondings in CuO species and on the other hand in a weak bonding of Cu ions to skeletal oxygens. In SCR of NO the CuO species have been indicated as not active owing to their too high activity in propane oxidation by oxygen to CO₂. In regard of impossibility of CuO species to stabilize monovalent state of the Cu ions, they are not able to catalyse NO decomposition to molecular nitrogen and oxygen either.

It is clear that fine tuning of redox properties of the Cu ions by their coordination to zeolite lattice of different local geometry and negative charge enables to reach high activity in SCR of NO₂ (Cu-II/Cu-IV) with a minimum of propane oxidation by oxygen and high activity in NO decomposition to molecular nitrogen and oxygen. This is the reason, why the zeolites with transition metal ions are still the only catalysts able to exhibit high activity in SCR of NO by hydrocarbons in a high excess of oxygen existing in exhaust gases of combustion processes.

Conclusion

The present study of reducibility and catalytic activity in propane oxidation of the Cu ions localized in high-silica zeolite matrices proved that

- redox properties of the Cu ions can be changed by their coordination to zeolite lattice oxygen atoms in a wide range; the redox properties of these Cu ion sites are very different from the redox properties of CuO species deposited on zeolites and amorphous supports (for example SiO₂, Al₂O₃),
- redox properties of the Cu ions in a ligand field of skeletal oxygen atoms depend, besides geometry of the ligand field, mainly on total (delocalized) negative charge of the zeolite matrix given by a content of Al in the zeolite framework, and on the local negative charge of the lattice oxygen atoms coordinated to the cation, which is controlled by distribution of aluminium in the lattice,
- Cu(II) ions balanced by one negative charge, AlO₂⁻, are incorporated into zeolites as (Cu(II)-L⁻)⁺ complexes, they can contain extralattice oxygen and/or exhibit "reduced" positive charge,
- Cu ions coordinated in zeolites exhibit, depending on their coordination and negative charge of the framework, a high degree of stabilization of monovalent state of the Cu ions.

These extraordinary, and easy to control by surrounding matrix, redox properties of the Cu ions coordinated in high-silica zeolites predestine these materials to be promising highly active and selective catalysts for reactions of NO decomposition to molecular nitrogen and oxygen and complex reaction of SCR of NO by paraffins in highly oxidizing atmosphere.

Acknowledgements

The authors thank Dr. F. Dušek for the helpful advice on the TPR measurements and Dr. T. Grygar and Dr. M. Pouzar for chemical analysis of zeolites. A financial support of the Grant Agency of the Czech Republic (project no. 203/96/1089) is highly acknowledged.

References

1. Shelef M.: Catal. Rev.-Sci. Eng. **11**, 1 (1975).
2. Bosch H., Janssen F.J.: Catal. Today **2**, 1 (1987).
3. Iwamoto M., Furukawa H., Mine Y., Uemura F., Mikuriya S., Kagawa S.: J. Chem. Soc. Chem. Commun. **1986**, 1272 (1986).
4. Iwamoto M., Furukawa H., Kagawa S.: Stud. Surf. Sci. Catal. **28**, 943 (1986).
5. Iwamoto M., Hamada H.: Catal. Today **10**, 57 (1991).
6. Iwamoto M., Yahiro H., Shundo S., Yu-u Y, Mizuno N.: Shokubai (Catalyst) **32**, 430 (1990).

7. Held W., Konig A., Richter T., Puppe L.: SAE Paper, 900496 (1990).
8. Lei G.-D., Adelman B.J., Sárkány J., Sachtler W.M.H.: Appl. Catal. B **5**, 245 (1995).
9. Sárkány J., d'Itri J.L., Sachtler W.M.H., Catal. Lett. **16**, 241 (1992).
10. Beutel T., Sárkány J., Lei G.-D., Yan J.Y., Sachtler W.M.H.: J. Phys. Chem. **100**, 845 (1996).
11. Ebitani K., Morokuma M., Morikava A.: Stud. Surf. Sci. Catal. **84**, 1501 (1994).
12. Ebitani K., Morokuma M., Kim J.-H., Morikava A.: J. Catal. **141**, 725 (1993).
13. Anpo M., Matsuoka M., Shioya Y., Yamashita H., Giamello E., Morterra C., Che M., Patterson H.H., Webber S., Ouelette S., Fox M.A.: J. Phys. Chem. **98**, 5744 (1994).
14. Centi G., Perathoner S., Shioya Y., Anpo M.: Res. Chem. Interm. **17**, 125 (1992).
15. Hamada H., Matsubayashi N., Shimada H., Kintaichi Y., Ito T., Nishijima A.: Catal. Lett. **5**, 189 (1990).
16. Shpiro E.S., Grünert W., Joyner R.W., Baeva G.N.: Catal. Lett. **24**, 159 (1994).
17. Shpiro E.S., Joyner R.W., Grünert W., Hayes N.W., Siddiqui M.R.H., Baeva G.N.: Stud. Surf. Sci. Catal. **84**, 1483 (1994).
18. Schoonheydt R.A.: Catal. Rev.-Sci. Eng. **35**, 129 (1993).
19. Kucherov A.V., Slinkin A.A., Kondratev D.A., Bondarenko T.N., Rubinstein A.M., Minachev Kh.M.: Zeolites **5**, 320 (1985).
20. Jacobs P.A., de Wilde W., Schoonheydt R.A., Uytterhoeven J.B.: J. Chem. Soc. Farad. Trans. I **72**, 1221 (1976).
21. Larsen S.C., Aylor A., Bell A.T., Reimer J.A.: J. Phys. Chem. **98**, 11533 (1994).
22. Wichterlová B., Dědeček J., Vondrová A.: J. Phys. Chem. **99**, 1065 (1995).
23. Dědeček J., Wichterlová B.: J. Phys. Chem. **98**, 5721 (1994).
24. Wichterlová B., Dědeček J., Tvarůžková Z.: Stud. Surf. Sci. Catal. **84**, 1555 (1994).
25. Dědeček J., Sobalík Z., Tvarůžková Z., Kaucký D., Wichterlová B.: J. Phys. Chem. **99**, 16327 (1995).
26. Wichterlová B., Dědeček J., Sobalík Z.: Stud. Surf. Sci. Catal. **94**, 641 (1995).
27. Wichterlová B., Sobalík Z., Vondrová A.: Catal. Today, **29**, 149 (1996).
28. Wichterlová B., Dědeček J., Sobalík Z., Vondrová A., Klier K.: J. Catal. **169**, 194 (1997).
29. Beyer H., Jacobs P.A., Uytterhoeven J.B.: J. Chem. Soc. Faraday I **72**, 674 (1976).
30. Bhatia S., Beltramini J., Do D.D.: Catal. Today **7**, 308 (1990).
31. Gentry J.S., Hurst N.W., Jones A.: Ibid. **75**, 1688 (1979).
32. Jacobs P.A., Tielen M., Linart J.P., Uytterhoeven J.B., Beyer H.: J. Chem. Soc.

- Faraday I **72**, 2793 (1976).
33. Beutel T., Sárkány J., Lei G.-D., Yan J.Y., Sachtler W.M.H.: J. Phys. Chem. **100**, 845 (1996).
 34. Sárkány J., d'Itri J.L., Sachtler W.M.H.: Catal. Lett. **16**, 241 (1992).
 35. Sárkány J., Sachtler W.M.H.: Zeolites **14**, 7 (1994).
 36. Leith I.R., Leach H.F.: Proc. R. Soc. A. **330**, 247 (1972).
 37. Kemball C., Leach H.F., Leith I.R.: J. Chem. Res. **274**, 4 (1977).
 38. Bond G.C., Namijo S.N., Wakeman J.S.: J. Mol. Catal. **64**, 305 (1991).
 39. Exner H., Fetting F.: Chem. Eng. Technol. **14**, 428 (1991).
 40. Campos-Martín J.M., Guerrero-Ruiz A., Fierro J.L.: Catal. Lett. **41**, 55 (1996).
 41. Davydov A.: *IR Spectroscopy Applied to Surface Chemistry of Oxides*, Nauka, Novosibirsk 1984.
 42. Aubke F., Wang C.: Coord. Chem. Rev. **137**, 483 (1994).
 43. Huang K.H.: J. Mol. Catal. **64**, 85 (1991).
 44. Hollins P.: Surf. Sci. Rep. **16**, 51 (1992).
 45. Jones A., McNicol B.: *Temperature Programmed Reduction for Solid Materials Characterization*, p. 24, M. Decker, New York 1986.
 46. Miessner H., Landmesser H., Jaeger N., Richter K.: J. Chem. Soc. Faraday Trans. **93**, 3417 (1997).
 47. Coudurier G., Decamp T., Praulaud H.: J. Chem. Soc., Faraday Trans. **78**, 2661 (1982).
 48. Spoto G., Zecchina A., Bordiga S., Ricchiardi G., Matra G.: Appl. Catal. B **3**, 151 (1994).
 49. Hadjiivanov K., Kantcheva M., Klissurski D.: J. Chem. Soc., Faraday Trans. **92**, 4595 (1996).
 50. Hwang I.C., Kim D.H., Woo S.I.: Catal. Lett. **42**, 177 (1996).
 51. Campos-Martín J.M., Guerrero-Ruiz A., Fierro J.L.G.: Catal. Lett. **41**, 55 (1996).
 52. Zecchina A., Bordiga S., Lamberti C., Spoto G., Carnalli L., Areán C.O.: J. Phys. Chem. **98**, 9577 (1994).
 53. Iwamoto M., Hoshino Y.: Inorg. Chem. **35**, 6918 (1996).
 54. Kuroda Y., Yoshikawa Y., Kumashiro M., Nagao M.: J. Phys. Chem. B **101**, 6497 (1997).
 55. Lamberti C., Bordiga S., Salvalaggio M., Spoto G., Zecchina A., Geobaldo F., Vlaic G., Bellatreccia M.: J. Phys. Chem. B **101**, 344 (1997).
 56. Howard J., Nicol J.M.: Zeolites **8**, 142 (1988).