

Synthesis and characterization of Cu-MFI catalyst for the direct medium temperature range NO decomposition

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In this study the physico-chemical and catalytic properties of copper bearing MFI zeolites (Cu-MFI) with different Si/Al and Si/Cu ratios were investigated. Two different methods for incorporation of metal ions into the zeolite framework were used: the ion exchange from the solution of copper acetate and the direct hydrothermal synthesis. Direct synthesis of a zeolite in the presence of copper-phosphate complexes was expected to generate more active copper species necessary for the desired reaction than the conventional ion exchange method. Direct decomposition of NO was used as a model reaction, because this reaction still offers a very attractive approach to NO_x removal. The catalytic properties of zeolite samples were studied using techniques, such as XRD, SEM, EPR and nitrogen adsorption/desorption measurements at 77 K. Results of the kinetic investigation revealed that both methods are applicable for the preparation of the catalysts with active sites capable of catalyzing the NO decomposition. It was found out that Cu-MFI zeolites obtained through direct synthesis are promising catalysts for NO decomposition, especially at lower reaction temperatures. The efficiency of the catalysts prepared by both methods is compared and discussed.

Keywords: *Cu-MFI zeolite; catalytic properties; direct hydrothermal synthesis; NO decomposition; medium reaction temperature range; redox properties*

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1. Introduction

The copper containing MFI zeolites (Cu-MFI) have been proven to be very active in catalytic reduction of NO_x by ammonia or hydrocarbons as well as in the direct decomposition of NO to nitrogen and oxygen [1–16]. Unfortunately, in the presence of water vapor or sulphur dioxide in the feed, Cu-MFI catalysts suffer from deactivation under high temperature conditions [17]. In the literature several different methods of preparation of Cu-MFI catalysts are described. The methods range from classical ion exchange to solid state exchange, wet impregnation, etc. All these different preparation techniques can lead to different constitutions of the catalyst with respect to dispersion of the active sites, morphology and structure

of the catalyst. Ion-exchange technique using an appropriate copper salt solution has been widely used. There was much effort to elucidate the structure of the copper species in the Cu-MFI catalysts, which included the use of a multitude of spectroscopic techniques. However, the nature of the active sites in the NO decomposition is still under debate [18, 19]. It has been suggested that the activity of Cu zeolites is connected with the presence of Cu⁺ ions [1–3, 8]. As pointed out in the literature, the reducibility of Cu²⁺ strongly depends on the negative framework charge given by the Si/Al ratio [20, 21]. Generally, the interpretation of a catalytic performance depends on a study of intrinsic chemical and physical properties of the catalyst and the recognition of correlation between some of these properties and catalytic performance. The performance of the catalyst in the desired reaction can be affected by the method of preparation,

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resulting in changes in the electronic and structural properties of the active phase. Apart from the method of preparation, the electron states of copper in MFI zeolites (oxidation level and coordination) depend on the basic conditions of the synthesis (pH, concentration of copper precursor, temperature) as well as on conditions of the thermal post-treatment (temperature, time).

In this work two different methods of zeolite preparation were used: conventional ion exchange method and original method of direct incorporation of metal ions present as copper-phosphate complexes during the hydrothermal synthesis. The EPR spectra of copper containing zeolites were studied as a function of preparation method and copper loading. Detailed characterization of the catalysts was performed using several instrumental techniques. The catalytic activity of Cu-MFI zeolites was tested in a fixed-bed reactor. The aim of this study was to provide additional information on the relationship between physicochemical and catalytic properties of Cu-MFI used in NO decomposition.

2. Experimental

2.1. Catalyst preparation and characterization

Two procedures of Cu-MFI catalyst preparation were used. The characteristics of the zeolite samples and the code used for indicating them throughout the text are summarized in Table 1. The first approach was based on ion exchange of Cu^{2+} and Na^+ ions in the parent zeolite (Na-MFI) using copper acetate solution (0.01 M). The initial pH of solution was 6.5 and 6.2 for zeolite sample with Si/Al of 28 and 40, respectively. Starting materials for catalysts preparation were commercial zeolites (Degussa, now Evonik) with different Si/Al ratios (KM-902, Si/Al = 28 and KM-903, Si/Al = 40). 10 g of parent zeolite was treated with 1000 mL of aqueous solution of copper acetate at room temperature. The obtained zeolite samples (Cu-MFI^a and Cu-MFI^b) were filtered and dried in air at 373 K for 2 hours. A complete description of copper exchanged MFI preparation can

be found elsewhere [22]. In the second approach, the copper containing zeolites were prepared applying direct hydrothermal synthesis, which was performed in two manners. In the first case (Cu,Al-MFI^c), the synthesis was performed from a gel containing a silica and alumina source, tetrapropylammonium bromide and copper phosphate complex, as described previously [23]. In the second case (Cu,Zn-MFI^d), the catalyst was synthesized from gel that contained a silica source, tetrapropylammonium bromide, copper phosphate complex and zinc phosphate complex (without the alumina source). After synthesis, the template was removed by calcination in air at 823 K. The temperature was increased slowly up to desired temperature at a rate of $10 \text{ K}\cdot\text{min}^{-1}$ and then kept for 5 hours.

The zeolite samples prepared by both methods were analysed using different characterization methods. X-ray powder diffraction of powder zeolite samples was performed using Philips PW 1065 with Ni-filtered $\text{CuK}\alpha$ radiation in the 2θ range of 5° to 40° . Before measuring, the samples were degasified at 473 K for 24 hours. SEM images were taken on a Philips XL-30 model equipped with X-ray energy dispersive spectrometer EDS-LINK ISIS. The EPR experiments were performed on a Bruker E-580 FT/CW X-band EPR spectrometer equipped with a standard XSope spectral simulation facilities. The EPR spectra for hydrated samples were recorded at room temperature. DPPH was used as a reference for determining EPR parameters. The specific surface area and pore size distribution were determined by nitrogen sorption using ASAP 2000 ("Micromeritics") automatic apparatus. Software program included Brunauer-Emmett-Teller (BET) and Langmuir surface area analysis, t-plot analysis and pore size distribution according to Baret-Joyner-Halende (BJH) model. The physicochemical properties of prepared zeolite samples are summarized in Table 1.

2.2. Catalyst activity testing

The catalytic measurements were carried out in an integral fixed-bed reactor operating at atmospheric pressure. The reaction was performed in the temperature range of 523 K to 773 K and

Table 1. The physico-chemical properties of the prepared zeolite catalysts.

Zeolite catalyst	Method of preparation	Si/Al ratio	Copper content [wt.%]	Surface area [m ² ·g ⁻¹]	Pore volume [cm ³ ·g ⁻¹]
Cu-MFI ^a	ion exchange	40	1.92	395.2	0.175
Cu-MFI ^b	ion exchange	28	3.65	425.6	0.193
Cu,Al-MFI ^c	direct hydrothermal synthesis	40	0.56	288.7	0.160
Cu,Zn-MFI ^{d*}	direct hydrothermal synthesis	→ ∞	1.39	423.6	0.209

* 1.14 wt.% of Zn (no Al)

at various residence times τ . Residence times were changed varying the total flow rate of the reactant gas (4 % NO/He; Messer Griesheim) over a constant amount of catalyst (0.5 g). The catalyst activity for NO removal was evaluated by conversion of NO into N₂ when the reaction reached a steady-state (30 min from the exposure to stream). Before the activity tests, the zeolite catalysts were pre-treated *in situ* at 773 K for 1 hour under helium flow (50 cm³·min⁻¹) and then cooled to the specified reaction temperature. The reaction products were analyzed by a GC-unit (Varian 3300) using a molecular sieve 5A column, thermal conductivity detector and helium as a carrier gas.

3. Results and discussion

3.1. Physico-chemical properties of Cu-MFI

The morphology of the zeolites was confirmed by SEM. The SEM micrographs for some of the zeolite samples are shown in Fig. 1.

As can be seen, the ZSM-5 crystals of the Cu-MFI^a and Cu,Al-MFI^c exhibit a typical elongated prismatic shape. The distinguished morphology of the Cu,Al-MFI^c catalyst seen in Fig. 1b is responsible for the exceptionally low surface area and pore volume of this catalyst (Table 1). It has also the lowest activity in NO decomposition at 573 K (as will be discussed later), in spite of the fact that the amount of dispersed copper and degree of its dispersion are between those of CuMFI^a and Cu,Zn-MFI^d (Table 2). The size and morphology of Cu,Zn-MFI^d crystals are shown in Fig. 1d. Addition of the zinc phosphate complex to the synthesis

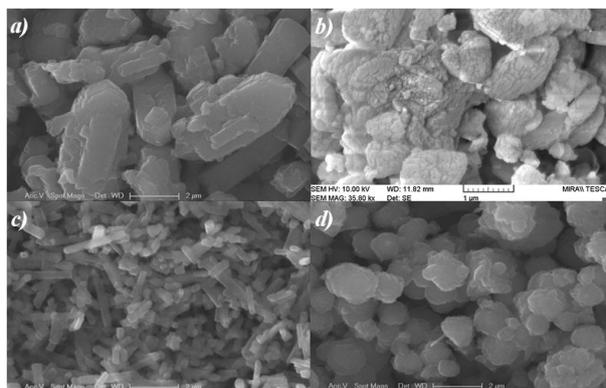


Fig. 1. SEM images of zeolite samples: (a) Cu-MFI^a, (b) Cu-MFI^b (c) Cu,Al-MFI^c, (d) Cu,Zn-MFI^d.

mixture appears to have an impact on the physical properties of MFI. This is in line with the fact that SO₄²⁻, PO₄³⁻ etc. anions affect the kinetics of zeolite crystallization [24].

The structure and crystallinity of the Cu-MFI samples was verified by X-ray diffraction (Fig. 2). All the spectra display the bands characteristic of Cu-MFI zeolites. Other phases such as CuO for higher Cu loading are not visible. It can be seen that Cu,Zn-MFI^d has the framework topology of MFI. The physical properties of the catalysts, such as specific surface area and total pore volume are given in Table 1. It can be seen that Cu,Zn-MFI^d zeolite has favorable values of both specific surface area and pore volume.

Fig. 3 shows the EPR spectra of Cu-containing zeolite. Since the Cu⁺ ions and Cu²⁺ ions in CuO clusters or [Cu-O-Cu]²⁺ are silent for EPR, these spectra can, with high probability, be assigned to isolated Cu²⁺ ions [25–27]. The evaluated parameters obtained from the prominent peaks positions in

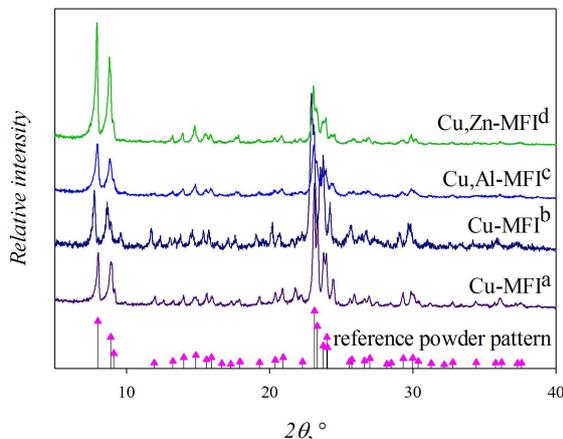


Fig. 2. X-ray diffraction patterns of the zeolite samples Cu,Zn-MFI^d, Cu,Al-MFI^c, Cu-MFI^b and Cu-MFI^a. Vertical arrows represent the peak positions of the reported powder patterns for the corresponding material (JCPDS-ICDD Card No. 37-0361).

the EPR spectra for corresponding copper species are given in Table 2.

The g and A parameters of these species are close to those ascribed in the literature to octahedral coordination [10, 18, 28–30]. The largest intensity of the EPR spectra is observed for the high Cu-loaded catalyst prepared by the ion exchange method (1.92 wt.% Cu in Cu-MFI^a). Although the EPR spectra of Cu-MFI^a and Cu,Zn-MFI^d (no Al) samples are qualitatively similar there are some differences in the intensity of the EPR signal assigned to the Cu²⁺ species. In the case of Cu,Zn-MFI^d, it is evident some kind of the superimposition of two very close axial signals, suggesting the presence of two types of isolated copper species in slightly different microenvironments. This might be connected with the presence of zinc in the zeolite structure. A Cu,Al-MFI^c catalyst shows axially symmetric signals that have relatively broad line width and unresolved hyperfine features in comparison with other two catalyst samples. The EPR spectra for sample Cu,Al-MFI^c indicates presence of several types of copper sites in the zeolite framework and some of them are probably copper clusters. From comparison of EPR spectra for these three samples it can be observed that different types of the copper species co-exist on the accessible catalytic surface.

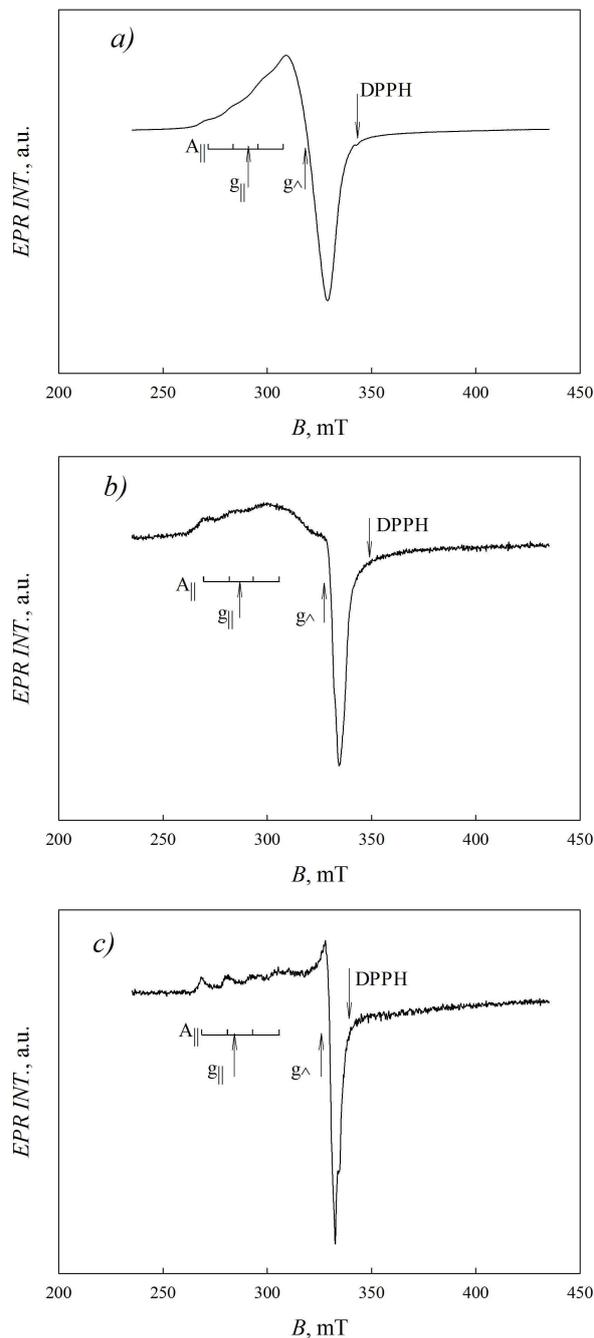


Fig. 3. EPR spectra of hydrated Cu-MFI at room temperature: (a) Cu-MFI^a, (b) Cu,Al-MFI^c, (c) Cu,Zn-MFI^d.

3.2. Preliminary catalyst screening

During the preliminary investigations, catalytic activity as well as the operational and thermal stability of Cu-MFI^a catalyst was investigated in

Table 2. Evaluated parameters obtained from the prominent peaks position in EPR spectra for corresponding Cu^+ centers.

Zeolite catalyst	$A_{ }$ [mT]	$g_{ }$	g_{\perp}	Intensity of EPR signal [a. u.]
Cu-MFI ^a	12.0	2.371	2.129	17.25
Cu,Al-MFI ^c	12.4	2.372	2.072	2.53
Cu,Zn-MFI ^d	12.4	2.392	2.081	1.83

the reactions at 723 K at different flow rates of the reactant gas. During this investigation it was found that the stationary activity of the catalyst was achieved within 60 minutes from the start of the experiment with a fresh catalyst and that it did not change for 3 hours. After this, the reaction was repeated with the same catalyst for several times at the same working conditions in order to test the operational stability of the catalyst upon reuse. The activity of the catalyst after reuse was identical to its stationary activity achieved during the first run. The obtained results indicate excellent operational stability of the catalyst under the specified reaction conditions which was confirmed by comparison of the experiments performed under different flow rates of the reactant gas on the fresh and reused catalysts as presented in Fig. 4.

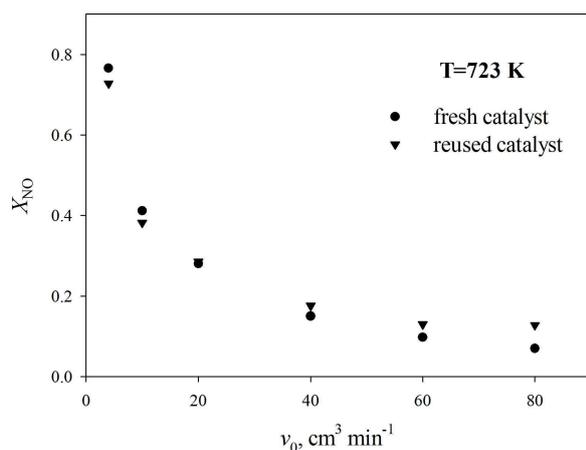


Fig. 4. Dependence of NO conversion for obtained different flow rates of the reactant gas 723 K for fresh and reused Cu-MFI^a catalyst.

Additionally, the thermal stability of the catalyst was investigated through the influence of the

calcination temperature on the activity of Cu-MFI^a catalyst in the direct decomposition of NO. From the results presented in Fig. 5 it can be seen that the catalyst maintains the initial activity after calcination up to 873 K after which the activity slightly decreases for the catalyst calcined at higher calcination temperatures.

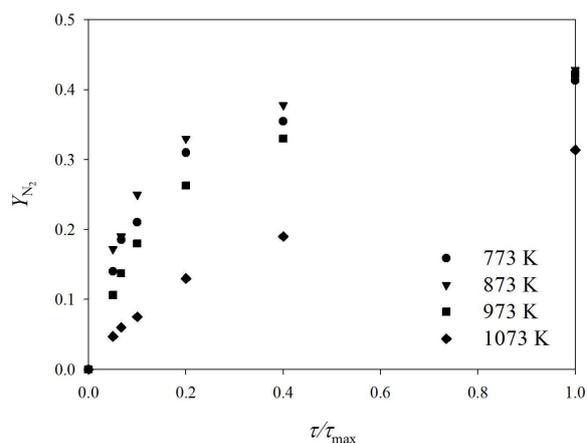


Fig. 5. Influence of the pre-reaction thermal treatment of the catalyst at different calcination temperatures on the molar fraction of nitrogen in the reaction products for Cu-MFI^a catalyst at different normalized residence times.

This is most probably the consequence of structural changes that occur in the catalyst at $T > 873$ K that have an inherent effect on its catalytic properties. In fact, the catalysts calcined at 973 K and 1073 K exhibit a decrease in measured specific surface area from $395.2 \text{ m}^2 \cdot \text{g}^{-1}$ to $387.1 \text{ m}^2 \cdot \text{g}^{-1}$ and $378.7 \text{ m}^2 \cdot \text{g}^{-1}$, respectively, what can be taken as a confirmation of the induced structural changes in the catalyst during its thermal treatment. However, since the direct decomposition of NO is conducted at lower reaction temperatures, it can be expected that a prolonged exposure of the catalyst to temperatures below 873 K will not change its properties or affect its thermal stability during the reaction.

3.3. Catalytic activity of prepared Cu-MFI

Fig. 6 summarizes the results obtained with different catalysts at a relatively low reaction temperature, e.g. 523 K and 623 K, respectively.

The change in molar fraction of the products at the reactor exit was used as a measure of the catalyst activity. As expected, the molar fraction of NO at the reactor exit decreases with increasing residence times in the reactor. The values of residence times (τ) were normalized by dividing by the maximum value (τ_{\max}) to simplify the calculation and presentation of the experimental results.

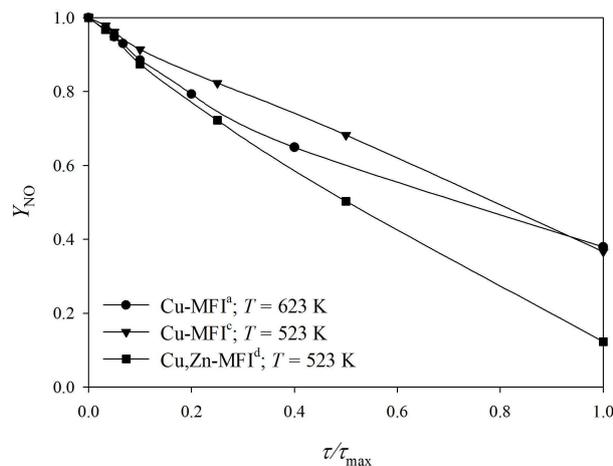


Fig. 6. Molar fraction of NO in the reaction products as a function of normalized residence times at temperatures lower than 623 K.

Our previous study on Cu-exchanged MFI showed only a minor activity in NO decomposition at temperatures lower than 579 K [22]. However, the activities of the catalysts prepared by direct hydrothermal synthesis were comparable to those of Cu-exchanged MFI even at 523 K, in spite of the lower Cu-loading. The possible explanation for such behavior can be linked to the higher dispersion of Cu^{2+} species supported on zeolite catalysts prepared by direct hydrothermal synthesis, and the higher purity of synthesized zeolite in comparison to the commercial ones. The rate at which active copper sites catalyze the NO decomposition should be correlated with the intensity of the electron paramagnetic resonance (EPR) signal, which is attributed to the presence of the Cu^{2+} species that are easily auto-reducible to the active Cu^+ species. However, according to the results shown in Table 2 and in Fig. 6, there is no correlation between the intensity of EPR signal and the activity of Cu-MFI catalysts in NO decomposition. In case

of the low Cu-loaded zeolite catalyst (0.56 wt.% of Cu in Cu,Al-MFI^c) the EPR signal intensity is even higher than in the catalyst with higher Cu-loading (Cu,Zn-MFI^d), although both of them have been prepared by direct hydrothermal synthesis. On the other hand, the signal intensities of the zeolites with similar Cu loadings (Cu-MFI^a and Cu,Zn-MFI^d) are quite different. As shown in Fig. 6, the best results in NO decomposition at lower reaction temperature (<623 K) are observed with Cu,Zn-MFI^d catalyst. As reported by Dossi. et. al. [31] the copper containing silicalite-1, having the MFI topology with similar Cu loading like in our study, but without framework Al^{3+} ions was found to be almost inactive for the NO decomposition. Obviously, the role of zinc is related to stabilization of copper species active in NO decomposition at lower reaction temperatures.

The next series of experiments was performed over Cu,Zn-MFI^d samples at various reaction temperatures ranging from 423 K to 773 K (Fig. 7). It can be seen that the molar fraction of the unreacted NO in the reaction products increases with temperature (or activity of Cu,Zn-MFI^d decreases with the temperature increase). This type of anti-Arrhenius temperature dependence is usually an indication of the reaction mechanism that changes with temperature [32]. On the other hand, it is very likely that at least two types of Cu^{2+} species are present in slightly different environments due to interaction with zinc: easily auto-reducible at 773 K and less auto-reducible.

Comparison of Cu-exchanged zeolite catalysts with different Si/Al ratios and of Cu, Zn-MFI^d catalyst at higher reaction temperature (>723 K) is shown in Fig. 8. The activity of copper exchanged MFI zeolites in NO decomposition increases with the increase in Si/Al ratio or with the decrease in aluminium content in the zeolite. Similar results were reported in the literature [21]. It is important to emphasise that in zeolite with a lower Al content the auto-reducibility of Cu^{2+} species is much higher than in those with a higher Al content. These results are relevant for practical applications of Cu-MFI, because their hydrothermal stability also increases with increasing Si/Al ratio.

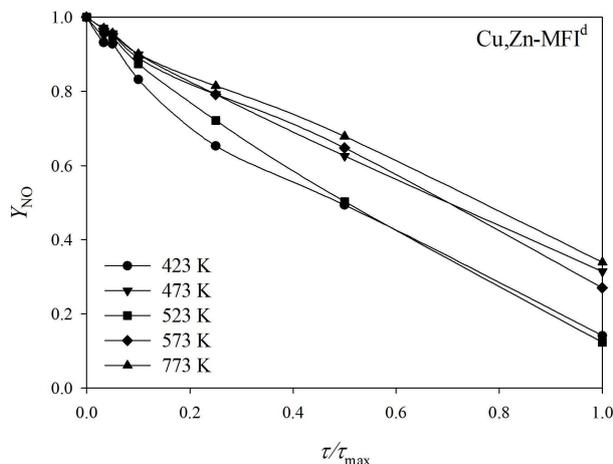


Fig. 7. Molar fraction of NO in the reaction products as a function of normalized residence times at different reaction temperatures (Cu,Zn-MFI^d zeolite).

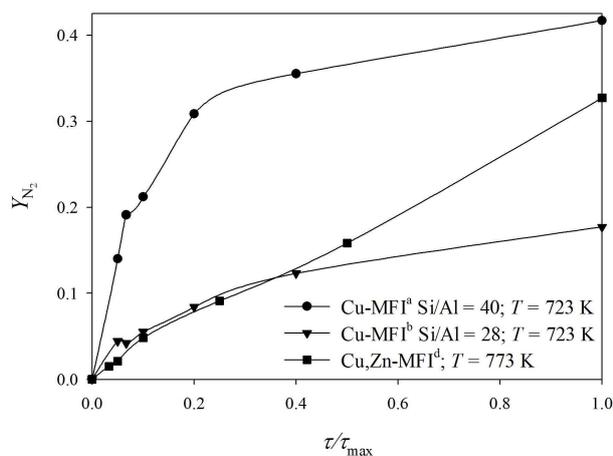


Fig. 8. Comparison of different catalysts in NO decomposition at higher reaction temperature (>723 K).

Based on the presented results it is evident that the isolated copper species are probably the most active sites for the NO decomposition. From Fig. 8 it can be seen that even at 773 K Cu,Zn-MFI^d zeolite shows high activity comparable to that of Cu-exchanged MFI, irrespective of their Si/Al ratio and Cu content. This is probably connected with the redox properties of Cu species obtained by direct hydrothermal synthesis.

4. Conclusions

This study deals with physico-chemical and catalytic properties of Cu-MFI catalysts prepared by two different methods. The results demonstrate that copper bearing MFI zeolites prepared by direct hydrothermal synthesis are promising catalysts for NO decomposition, especially at lower reaction temperature. Apparently, the direct hydrothermal synthesis of Cu-MFI could lead to the development of new active and stable catalysts that may find a practical application. Activity of Cu-MFI catalyst increases with the increase in Si/Al ratio, which leads to the conclusion that the active sites are isolated copper sites. The results reveal that the Cu²⁺/Cu⁺ interconversion is probably reversible. In the future work particular emphasis will be put on the exact nature of the active copper species generated in MFI framework as a function of preparation method.

Acknowledgements

The authors acknowledge financial support of the Croatian Ministry of Science, Education and Sports. Special thanks go to Boris Rakvin for performing EPR measurements.

References

- [1] IWAMOTO M., HAMADA H., *Catal. Today*, 10 (1991), 57.
- [2] LI Y., HALL W.K.J., *J. Phys. Chem.*, 94 (1990), 6145.
- [3] ČEJKA J., CENTI G., PEREZ-PARIENTE J., ROTH W.J., *Catal. Today*, 179 (2012), 2.
- [4] LISI L., PIRONE R., RUSSO G., STANZIONE V., *Chem. Eng. J.*, 154 (2009), 341.
- [5] DEENG K.D., MOHAMED A.R., BHATIA S., *Chem. Eng. J.*, 103 (2004), 147.
- [6] MARTINEZ C., CORMA A., *Coordin. Chem. Rev.*, 255 (2011), 1558.
- [7] PEREDA-AYO B., DE LA TORRE U., ILLÁN-GÓMEZ M.J., BUENO-LÓPEZ A., GONZÁLEZ-VELASCO J.R., *Appl. Catal. B-Environ.*, 147 (2014), 420.
- [8] WICHTERLOVA B., DEDECEK J., SOBALIK Z., VONDOVA A., KLIER K., *J. Catal.*, 169 (1997), 194.
- [9] SHICHI A., KATAGI K., SATSUMA A., HATTORI T., *Appl. Catal. B-Environ.*, 24 (2000), 97.
- [10] CARL P.J., LARSEN S.C., *J. Phys. Chem. B*, 104 (2000), 6568.
- [11] MODEN B., DA COSTA P., FONFE B., LEE D.K., IGLESIA E., *J. Catal.*, 209 (2002), 75.
- [12] KURODA Y., IWAMOTO M., *Top. Catal.*, 28 (1–4) (2004), 111.
- [13] LEE D.K., *Korean J. Chem. Eng.*, 21 (3) (2004), 611.

- [14] SMEETS P.J., SELS B., VAN TEEFFELN F.R.M., LEEMAN H., HENSEN E.J.M., SCHOONHEYDT R.A., *J. Catal.*, 256 (2008), 183.
- [15] SCHAY Z., JAMES V.S., PAL-BORBELY G., BECK A., RAMASWAMY A.V., GUCZI L., *J. Mol. Catal. A-Chem.*, 162 (2000), 191.
- [16] ROY S., HEGDE M.S., MADRAS G., *Appl. Energ.*, 86 (2009), 2283.
- [17] FIERRO G., FERRARIS G., MORETTI G., *Appl. Catal. B-Environ.*, 91 (2009), 499.
- [18] PARK S.K., KURSHEV V., LUAN Z., LEE C.W., KEVAN L., *Micropor. Mesopor. Mat.*, 38 (2000), 255.
- [19] PULIDO A., NACHTIGALL P., *Chem. Cat. Chem.*, 1 (2009), 449.
- [20] DĚDEČEK J., WICHTERLOVÁ B., *J. Phys. Chem.*, 98 (1994), 5721.
- [21] WICHTERLOVA B., DEDECEK J., VONDROVA A., *J. Phys. Chem.*, 99 (4) (1995), 1065.
- [22] TOMAŠIĆ V., GOMZI Z., ZRNČEVIĆ S., *Appl. Catal. B-Environ.*, 18 (1998), 233.
- [23] KATOVIC A., GIORDANO G., KOWALAK S., *Impact of Zeolites and Another Porous Materials on new Technologies at the Beginning of a New Millenium*, in: AIELLO R., TESTA F., GIORDANO G. (Eds.), *Studies in Surface Science and Catalysis*, Vol. 142, Elsevier, Amsterdam, 2002, p.39.
- [24] TOKTAREV A.V., ECHEVSKII G.V., *Hofmeister Anion Effect on the Formation of Zeolite Beta*, in: GÉDÉON A., MASSIANI P., BABONNEAU F. (Eds.), *Studies in Surface Science and Catalysis*, Vol. 174, Elsevier, Amsterdam, 2008, p.167.
- [25] BEUTEL T., SARKANY J., LEI G.D., YAN J.Y., SACHTLER W.M.H., *J. Phys. Chem.*, 100 (1996), 845.
- [26] YAN J.Y., LEI G.D., SACHTLER W.M.H., KUNG H.H., *J. Catal.*, 161 (1996), 43.
- [27] SORIA J., MARTINEZ-ARIAS A., MARTINEZ-CHAPARRO A., CONESA J.C., SCHAY Z., *J. Catal.*, 190 (2000), 352.
- [28] ANPO M., MATSUOKA M., SHIOYA Y., YAMASHITA H., GIAMELLO E., MORTERRA C., CHE M., PATTERSON H.H., WEBBER S., OUELLETTE S., FOX M.A.J., *J. Phys. Chem.*, 98 (1994), 5744.
- [29] LARSEN S.C., AYLOR A., BELL A.T., REIMER J.A.J., *J. Phys. Chem.*, 98 (1994), 11533.
- [30] SOB CZAK I., ZIOLEK M., RENN M., DECZYK P., NOWAK I., DATURI M., LAVALLEY J.C., *Micropor. Mesopor. Mat.*, 74 (2004), 23.
- [31] DOSSI C., FUSI A., RECCHIA S., PSARO R., MORETTI G., *Micropor. Mesop. Mat.*, 30 (1999), 165.
- [32] LAIDLER K.J., *Chemical Kinetics*, McGraw-Hill, London, 1965.

Received 2015-10-12

Accepted 2015-12-03