

CATALYTIC ACTIVITY OF Cu ION-EXCHANGED METALLOALUMINOPHOSPHATES IN NO DECOMPOSITION

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NO decomposition was investigated over Cu ion-exchanged aluminophosphate molecular sieve catalysts. Cu ions in cationic positions balanced by one framework negative charge in the metalloaluminophosphates of AIPO-5 and AIPO-11 structures exhibited catalytic activity in NO decomposition comparable with that of Cu-ZSM-5. No catalytic activity of the Cu ions incorporated during synthesis of molecular sieves into the framework in tetrahedral positions (CuAIPO-11) was observed. The catalytic activity of Cu-MeAIPO-5 and Cu-MeAIPO-11 was observed with various divalent metal ions of the MeAIPO-5 and MeAIPO-11 frameworks (Me = Zn, Mg, Fe, Co) and also with Cu exchanged SAPO-5 molecular sieves. The Cu-MeAIPO-5 and Cu-MeAIPO-11 catalysts differed only in the temperature of the maximum observed catalytic activity.

Key words: Heterogeneous catalysis; NO decomposition; Cu ion-exchanged molecular sieves; AIPO-5; AIPO-11; Zeolites.

Nitrogen oxides produced in various high-temperature combustion processes are at present major air pollutants. Decomposition or selective reduction of NO with hydrocarbons to nitrogen in non-reducing atmosphere has become therefore the main target to be achieved in the field of environmental catalysis. Decomposition of NO to molecular nitrogen and oxygen is the simplest and most attractive approach to NO_x pollution control and also one of the greatest challenges in catalysis.

Despite the substantial effort currently devoted to the development of a suitable catalyst exhibiting high and stable activity in NO decomposition, such behaviour has been observed only for Cu ions implanted at the cationic sites of aluminosilicate zeolite matrices¹⁻⁶. For various metal oxide materials, like Co₃O₄, Mn₂O₃, Sr/La₂O₃ (refs^{7,8}), the decomposition activity was substantially lower; moreover, the activity fell down during a short reaction run.

Cu ions exchanged in the ZSM-5 matrix exhibit unique and time-stable activity among Cu-zeolites, in contrast to the Cu ions exchanged in Y and mordenite structures^{3,5}. Particularly Cu-ZSM-5 zeolites with over-exchanged levels (Cu²⁺/Al > 0.5) reach high NO decomposition activity. But this activity is still not high enough for

industrial application. Moreover, it is necessary to point out that the activity of Cu-zeolites in NO decomposition is sensitive to the presence of water vapour and SO_x . A decrease in catalytic activity, observed in selective catalytic reduction (SCR) of NO by hydrocarbons catalysed by metal-loaded zeolites, was related to the loss of appropriate coordination of the reaction centre to the framework and/or to the framework dealumination⁹⁻¹². Thus, the design of other catalytic systems, stable against the water vapour and SO_x , is highly desirable. So far, all reported attempts to find another inorganic matrix as a support for highly active Cu ions or other mixed-oxide catalysts, exhibiting high and stable decomposition activity, have not been successful.

There is no doubt that the NO decomposition is a redox process¹³. The monomeric Cu site was suggested to be an active site¹⁴⁻¹⁸. In a detail spectral analysis, we have shown¹⁸⁻²⁰ that Cu site active in NO decomposition possesses low positive charge on the divalent Cu cation, is easily reduced, exhibits open, close to planar coordination sphere, and prevails also at high Cu loadings. Although the distribution of aluminium in the framework of high-silica zeolites is not known, a high relative population of this Cu site in ZSM-5 at loadings close to theoretical exchange and at over-exchanged levels led us to suggest that this active Cu ion is adjacent to a single Al framework atom^{15,18}. Their spectral and structural features are also in agreement with the sorption and redox properties of this Cu center²¹. It has a high tendency to preserve a monovalent state even in the presence of oxygen at high temperatures and to prefer formation of dinitrosyl instead of mononitrosyl complexes compared with the other Cu ions. The NO decomposition activity and reducibility of the Cu-ZSM-5 zeolites depending on the Cu/Al/Si ratio implied^{20,21} that the properties of these individual Cu sites are controlled by both the local and global negative framework charge balancing the individual Cu sites.

The understanding of some properties of the Cu active centre for NO decomposition in Cu-ZSM-5 led us to propose a new catalytic system for NO decomposition based on Cu-containing metalloaluminophosphate materials (MeAlPO). It is known²² that different MeAlPO matrices should accommodate other metal cations. The local and global negative framework charge balancing the cationic sites can be supposed rather low due to the low content and expected high dispersion of divalent Me cations in MeAlPO-5 and MeAlPO-11 matrices. Moreover, possible positions of single bare cations in AlPO-5 and AlPO-11 matrices, according to their framework structure²³, should have an open coordination and be accessible to small molecules such as NO. Recently, we published a preliminary study on the catalytic activity of Cu-containing ZnAlPO-11 and MgAlPO-11 (ref.²⁴).

This contribution presents the results on the activity of the Cu ions introduced from Cu acetate solution into molecular sieves of AlPO-5 and AlPO-11 structures in NO decomposition. The effects of the structural type of matrix as well as of the type of divalent framework cation (Mg, Zn, Co or Fe) on the catalytic activity of these catalysts

were studied. The catalytic activity of Cu-SAPO-5 (with Si in the framework) was also investigated and, for comparison, CuAlPO-11 with Cu ions located in the aluminophosphate framework was also tested. The obtained turnover frequency (TOF) values of NO decomposition per Cu ion of Cu-MeAlPO materials are close to those of the Cu ions at exchangeable sites of aluminosilicate ZSM-5 matrix. The overall activity of these materials is much higher in comparison with those consisting of the metal oxide based materials.

EXPERIMENTAL

Catalyst Preparation

Molecular sieves of MeAlPO-11 and MeAlPO-5 structural types (Me = divalent cation, namely Co, Cu, Fe, Mg, Zn) were synthesized.

MeAlPO-11 molecular sieves have been synthesized in the following way: 12.31 g of pseudo-boehmite (Vista Co.) was added under vigorous stirring to a mixture of 19.77 g of H_3PO_4 (85%) and 50.23 g of distilled water. The gel formed was stirred for at least 2 h at ambient temperature. After that, 9.00 g of dipropylamine (Fluka) in 3.20 g of H_2O was added and the gel was stirred again for 2 h. Then a solution containing 0.54 g of metal acetate in 4.36 g H_2O was added and the resulting gel was stirred for additional 2 h. The synthesis was performed in Teflon-lined stainless-steel autoclave at 470 K for 16 h.

MeAlPO-5 molecular sieves have been synthesized in a way similar to MeAlPO-11 replacing dipropylamine by 76.26 g of 20% water solution of tetraethylammonium hydroxide (Fluka). All other steps including stirring of mixtures remained unchanged. The synthesis was performed in a Teflon-lined stainless-steel autoclave at 430 K for 18 h. The same synthesis procedure was used for preparation of SAPO-5 molecular sieves. Only in the final step, Cab-O-Sil M5 (Cabot Co.) was substituted for metal acetate.

After the synthesis, the autoclave was cooled down by cold water, the product was recovered by filtration, thoroughly washed by deionized water and finally dried at 370 K overnight. Prior to the Cu^{2+} incorporation, the synthesized MeAlPO and SAPO-5 sieves were dried overnight at 450 K or calcined overnight in an oxygen stream at 790 K to remove the template partially or completely.

Ion-Exchange

Cu-MeAlPO-5 and Cu-MeAlPO-11 (with Cu concentration ranging from 1.20 to 4.00 wt.%) and Cu-SAPO-5 were prepared by stirring MeAlPO-5 or MeAlPO-11 in 0.1 or 0.01 M aqueous solution of copper acetate at room temperature for 3 h. The solids were then filtered off, thoroughly washed with distilled water and dried at ambient temperature. Chemical composition of the Cu-containing molecular sieves was determined by atomic absorption spectroscopy after their dissolution; it is given together with details of the procedure in Table I.

Characterization

Powder X-ray diffraction patterns of metalloaluminophosphate molecular sieves were recorded on a Seifert 3000P diffractometer in the Bragg-Brentano geometry arrangement, using $\text{CuK}\alpha$ radiation with a graphite monochromator and scintillation detector. To be sure that the treatment of as-synthesized MeAlPO materials did not change the crystallinity of the molecular sieves, XRD patterns

were recorded after synthesis and drying of the sample at room temperature, after calcination, and after ion-exchange. Cu-MgAlPO-11 catalyst exhibiting a very significant deactivation was checked for its crystallinity after the kinetic run. The XRD patterns are depicted in Figs 1–3.

Diffuse-reflectance (DR) VIS-NIR spectra of hydrated (after the Cu²⁺ ion exchange) Cu²⁺ zeolites were obtained by using Perkin–Elmer Lambda 19 spectrometer equipped with a diffuse reflectance attachment with an integrating sphere coated with BaSO₄ (serving also as a reference sample). The spectra of the catalysts placed in 5-mm thick silica cells were recorded at a speed of 240 nm/s with a scanning step of 1 nm and slit width 5 nm. The absorption intensities were evaluated by the Schuster–Kubelka–Munk theory as $F(R_{\infty}) = (1 - R_{\infty})^2/2R_{\infty}$, where R_{∞} is diffuse reflectance from a semi-infinite layer and $F(R_{\infty})$ is proportional to the absorption coefficient.

Catalytic Activity

Catalytic activity of Cu-exchanged metalloaluminophosphates was tested in a down-flow glass microreactor with inner diameter 5 mm, NO inlet of 4 000 ppm in helium, total feed of 100 ml/min, a catalyst weight of 300 mg and in the temperature range 470–1 000 K. The catalysts were activated in a helium stream (99.996%) with a temperature increase of 5 K/min up to 720 K, held for 1 h, and cooled down to the reaction temperature. The activity was measured at temperatures differing by 50 K.

TABLE I

Chemical composition of Cu aluminophosphates and conditions of Cu ion incorporation

Molecular sieve	Cu, wt.%	Cu/Me	Me/Al	Cu in solution mol/l	Solution/Matrix ml/g	Time of exchange, h	Template removed at K
Cu-ZnAlPO-11	2.1	0.75	0.08	0.05	40	3	450
Cu-ZnAlPO-11	2.0	0.70	0.08	0.05	40	3	790
Cu-MgAlPO-11	1.7	0.65	0.07	0.01	100	3	450
Cu-MgAlPO-11	1.9	0.70	0.07	0.01	100	3	790
Cu-ZnAlPO-5	2.8	1.25	0.05	0.10	50	3	450
Cu-ZnAlPO-5	3.5	1.40	0.06	0.01	100	12	450
Cu-ZnAlPO-5	3.0	1.20	0.06	0.10	50	3	790
Cu-MgAlPO-5	2.3	1.10	0.07	0.01	100	1.5	450
Cu-MgAlPO-5	2.5	1.05	0.08	0.01	100	1.5	450
Cu-MgAlPO-5	2.1	1.00	0.07	0.01	100	1.5	790
Cu-MgAlPO-5	0.8	1.20	0.03	0.01	100	1.5	790
Cu-CoAlPO-5	2.2	1.15	0.05	0.01	50	3	450
Cu-CoAlPO-5	2.3	1.20	0.05	0.01	50	3	790
Cu-FeAlPO-5	2.1	1.40	0.04	0.01	100	3	450
Cu-FeAlPO-5	1.9	1.25	0.04	0.01	100	3	790
Cu-SAPO-5	1.6	0.85	0.05	0.01	100	3	450
CuAlPO-11	1.4	–	0.04	Cu incorporation during synthesis			450
CuAlPO-11	1.5	–	0.04	Cu incorporation during synthesis			790

To achieve the temperature of the next measurement, the catalyst was heated up in a NO/helium stream with an increase of 5 K/min. The NO conversion reached in 30–60 min after stabilization of the working temperature was taken as a characteristic value. NO and NO₂ were analyzed with an accuracy of 0.5% at the inlet and outlet of the reactor with a chemiluminescence analyser Vamet 138 (Czech Republic). No NO₂ was detected in the products (detection limit 5 ppm). Only traces of N₂O were observed by mass spectrometry (Hewlett–Packard, 5971A).

RESULTS

DR VIS-NIR spectra of fully hydrated Cu-MeAlPOs exhibited a broad band between 7 000 and 19 000 cm⁻¹. This band is characteristic of the Cu²⁺ ion with octahedral or bipyramidal coordination²⁵. No differences were found in the shape and position of this Cu²⁺ band for the Cu²⁺ ions exchanged in different MeAlPO structural types or with different metal ions substituted at MeAlPO (Me = Zn, Mg, Fe, Co). Typical normalized spectrum of hydrated Cu-MgAlPO-5 is compared with the spectra of hydrated Cu-ZSM-5 samples with different Cu/Si/Al ratios in Fig. 4. The absorption band of Cu-MgAlPO-5 exhibited a significant shift (1 000 cm⁻¹) of the high-frequency edge to higher wavenumbers in comparison with the spectra of Cu-ZSM-5. Moreover, the intensity of this band was 1.5–2.5 times higher with Cu-MeAlPO catalysts compared with Cu-ZSM-5 zeolites of similar Cu loadings. It is necessary to mention that the absorption intensity of the Cu²⁺ band in hydrated Cu-ZSM-5 varies in the same range depending on

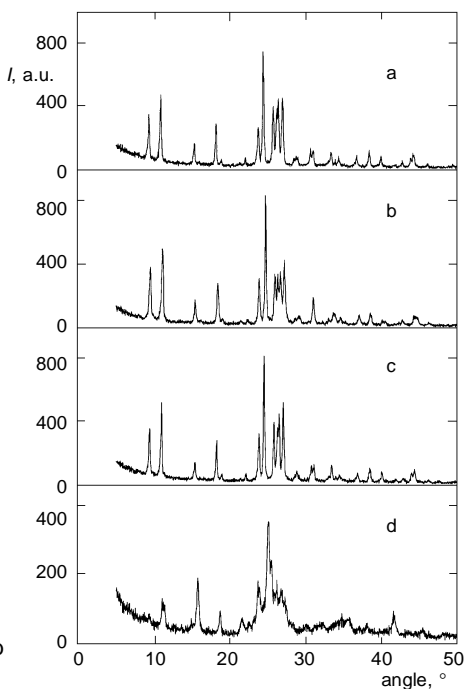


FIG. 1

XRD pattern for MgAlPO-11 (a as-synthesized, b calcined, c Cu ion-exchanged, d after reaction)

Cu/Si/Al ratio and conditions of the ion exchange²⁶. The calcination of synthesized MeAlPOs in oxygen stream at 790 K before Cu ion incorporation did not affect the position and shape of the Cu²⁺ absorption band (see Fig. 5).

MeAlPO-5, MeAlPO-11, and SAPO-5 matrices containing Cu, not calcined at high temperature before Cu incorporation, exhibited a high catalytic activity in NO decomposition in the temperature range from 520 to 920 K. Typical temperature dependencies of the NO conversion over Cu-MeAlPO-5 and Cu-MeAlPO-11 are shown in Fig. 6. The

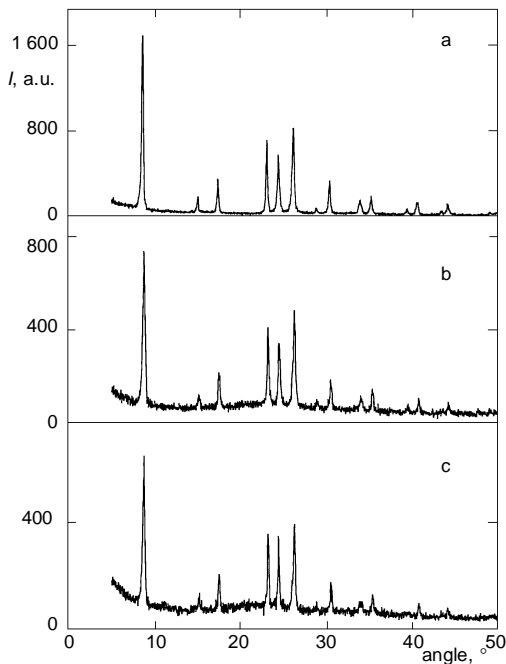


FIG. 2
XRD pattern for ZnAlPO-5 (a as-synthesized, b calcined, c Cu ion-exchanged)

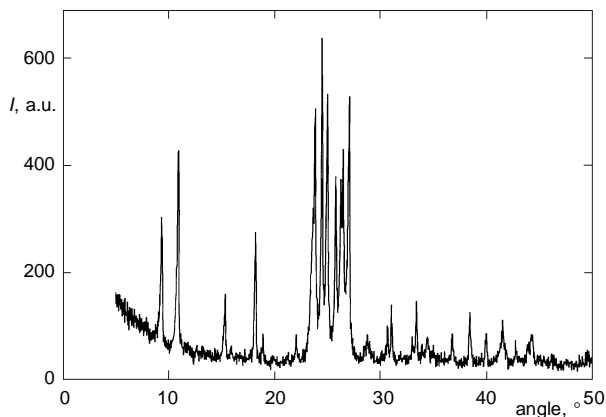


FIG. 3
XRD pattern of as-synthesized CuAlPO-11

maximum values of NO conversion and corresponding temperatures for Cu-MeAlPO-5, MeAlPO-11, and Cu-SAPO-5 prepared under different conditions and compared with CuAlPO-11 are summarized in Table II. It is seen that the structural type of the molecular sieve matrix affected only the temperature of maximum catalytic activity which is significantly higher for Cu-MeAlPO-11 than for Cu-MeAlPO-5 and Cu-SAPO-5 (900–930 K compared with 530–780 K, respectively). The highest value of NO conversion over Cu-ZSM-5 catalyst, found under the same reaction conditions^{15,18}, is given in Table II for comparison. XRD patterns of Cu exchanged MeAlPO samples did not indicate structural changes induced by Cu exchange, as evidenced in Figs 1a–1c and 2a–2c.

If MeAlPO catalysts were calcined in an oxygen stream at 790 K before exchange of Cu ions, only negligible catalytic activity of these Cu-MeAlPO catalysts was obtained, as follows from Table II. The loss of catalytic activity was not accompanied by a collapse of framework reflected by XRD. The negligible effect of the calcination before the ion-exchange on the XRD patterns is documented in Figs 1 and 2. The catalytic activity of CuAlPO-11 with Cu ions incorporated during synthesis and located in framework positions was negligible. Also in this case XRD pattern evidenced good crystallinity, as shown in Fig. 3.

Individual Cu-MeAlPO catalysts exhibited different time stability of NO conversion. Catalytic activity of some catalysts was stable in the range of tens of hours (Fig. 7a), but the activity of some samples significantly decreased in a short time (less than 1 h),

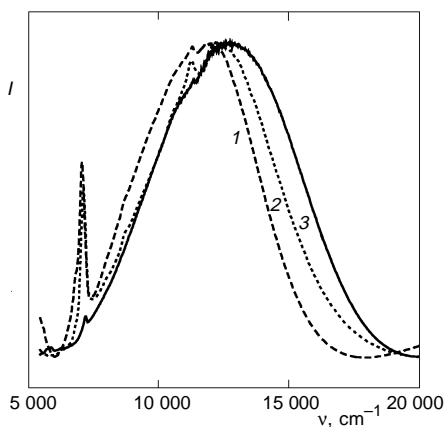


FIG. 4

Normalized DR VIS-NIR spectra (I) of hydrated Cu^{2+} ions in molecular sieves (1 Cu-ZSM-5 (Si/Al 14.3, Cu/Al 0.18), dominant presence of Cu-hexaquo complex; 2 Cu-ZSM-5 (Si/Al 22.5, Cu/Al 0.48), significant presence of monovalent $[\text{Cu}^{2+}(\text{H}_2\text{O})_5\text{X}]^+$ complex; 3 Cu-MgAlPO-5 (Cu/Mg 0.50))

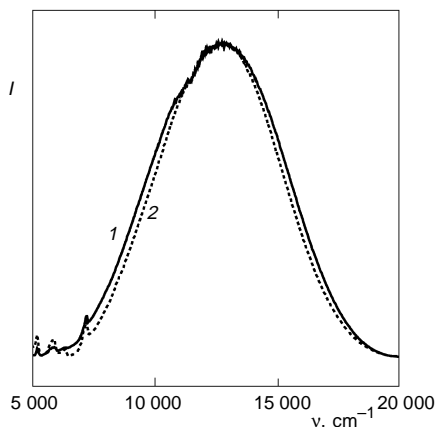


FIG. 5

Effect of calcination before Cu ion exchange on the normalized DR VIS-NIR spectra (I) of hydrated Cu-ZnAlPO-5 (1 Cu ion-exchange to non-calcined ZnAlPO-5, 2 Cu ion-exchange to calcined ZnAlPO-5)

as it is documented in Fig. 7b. The samples losing catalytic activity with time are marked in Table II by asterisk. We did not find any correlation between the decrease in the catalytic activity and the type of matrix and/or nature of metal cation. However, the higher was the reaction temperature, the significantly faster was the decrease in activity, as it is shown in Fig. 7b. The dependence of the NO conversion on time-on-stream given in Fig. 7 evidences that the initial behaviour of the NO conversion over Cu-MeAlPOs is similar to the well-known transient behaviour of NO decomposition observed on reduced Cu-ZSM-5 (ref.²⁷).

TABLE II
Catalytic activity of Cu-containing metalloaluminophosphates

Catalyst	Cu, wt. %	Conversion, %	TOF, s ⁻¹	Temperature of maximum conversion, K	Template removed at K
Cu-ZnAlPO-11	2.1	25	1.3	900	450
Cu-ZnAlPO-11	2.0	0	0		790
Cu-MgAlPO-11	1.7	17*	1.1	930	450
Cu-MgAlPO-11	1.9	0	0		790
Cu-ZnAlPO-5	2.8	20	0.8	730	450
Cu-ZnAlPO-5	3.5	18*	0.6	680	450
Cu-ZnAlPO-5	3.0	0	0		790
Cu-MgAlPO-5	2.3	9*	0.4	730	450
Cu-MgAlPO-5	2.5	16	0.7	780	450
Cu-MgAlPO-5	2.1	0	0		790
Cu-MgAlPO-5	0.8	0	0		790
Cu-CoAlPO-5	2.2	8	0.4	530	450
Cu-CoAlPO-5	2.3	0	0		790
Cu-FeAlPO-5	2.1	7*	0.4	770	450
Cu-FeAlPO-5	1.9	0	0		790
Cu-SAPO-5	1.6	21	1.4	780	450
CuAlPO-11	1.4	0	0		450
CuAlPO-11	1.5	0	0		790
Cu-ZSM-5	2.0	36	1.9	720	–

* Decrease of catalytic activity with time.

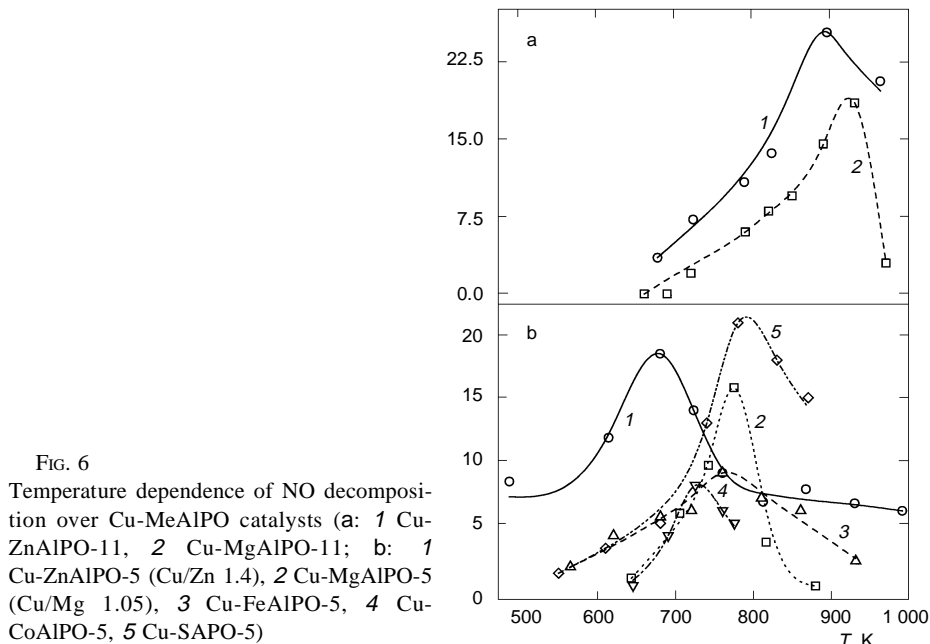


FIG. 6

Temperature dependence of NO decomposition over Cu-MeAlPO catalysts (a: 1 Cu-ZnAlPO-11, 2 Cu-MgAlPO-11; b: 1 Cu-ZnAlPO-5 (Cu/Zn 1.4), 2 Cu-MgAlPO-5 (Cu/Mg 1.05), 3 Cu-FeAlPO-5, 4 Cu-CoAlPO-5, 5 Cu-SAPO-5)

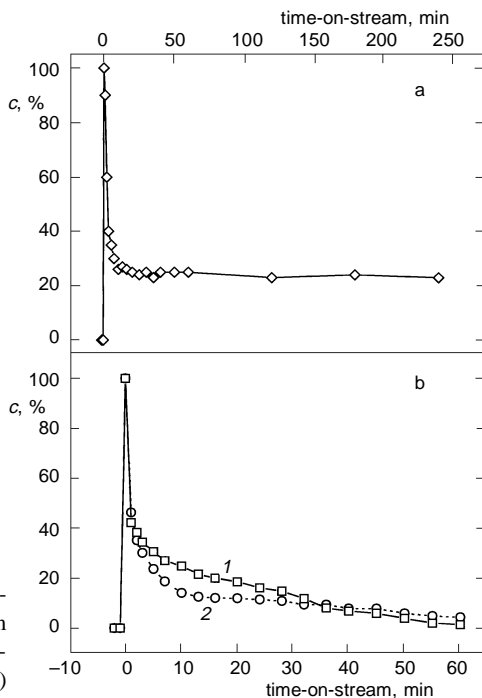


FIG. 7

Dependence of NO concentration on the reactor outlet on the reaction time-on-stream (a: Cu-ZnAlPO-11, 880 K; b: 1 Cu-MgAlPO-11, 860 K, 2 Cu-MgAlPO-11, 700 K)

DISCUSSION

Catalytic activity of Cu-metalloaluminophosphate catalysts active in NO decomposition (expressed as conversion of NO per 0.1 g of catalyst) is comparable with that of Cu-ZSM-5 zeolites (*i.e.* 2–9% and 2–12%; *cf.* refs^{9–12,15,24}), the catalytic activity of exchanged Cu ions, expressed as turnover frequency (TOF) is also comparable with that observed for the Cu ion located in ZSM-5 (*i.e.* $0.3\text{--}1.2 \cdot 10^{-3} \text{ s}^{-1}$ and $0.3\text{--}1.95 \cdot 10^{-3} \text{ s}^{-1}$, respectively). On the other hand, Cu-MeAlPO catalysts exhibited wider temperature range of high catalytic activity (470–950 K) compared with Cu-ZSM-5 (570–770 K).

The values of NO conversion and TOF summarized in Table II evidence that there is no substantial difference in the catalytic activity of exchanged Cu ions given by different structural types of metalloaluminophosphate matrices (MeAlPO-5 and MeAlPO-11), by metal substituted in the framework in MeAlPO (Zn, Mg, Fe, Co), and by the metalloaluminophosphate or silicoaluminophosphate matrix (SAPO-5). This indicates that the catalytic activity of the Cu ion in NO decomposition is not substantially affected by the nature of the bridging framework oxygen (P–O–Me in metalloaluminophosphates or Si–O–Al in silicoaluminophosphates). On the other hand, the catalytic activity of CuAlPO-11 with Cu ions incorporated into the aluminophosphate framework was negligible. The XRD pattern of this sample indicated good crystallinity and its AlPO-11 structure (see Fig. 3). We can assume that the Cu ions incorporated in the framework positions are not active in NO decomposition.

The VIS-NIR spectra of hydrated samples of Cu-MeAlPOs and Cu-SAPO-5 exhibiting a broad band with maximum at $12\,500 \text{ cm}^{-1}$ were similar to those of Cu-ZSM-5 or to the spectrum of Cu^{2+} ion in aqueous solution indicating hexa-coordinated Cu^{2+} ions^{25,28}. It was shown in our previous work²⁸ that the position of the high-frequency edge of the Cu^{2+} absorption band could be used as an evidence for the deformation of octahedral environment of the Cu^{2+} ion resulting in its tetragonal bipyramidal coordination corresponding to the replacement of one water molecule by another ligand (OH^- , COO^-). Moreover, the edge shift may serve as a semi-quantitative measure of the number of these ions with bipyramidal coordination. As shown in Fig. 4, the shift of the Cu^{2+} absorption band of Cu-MgAlPO-5 is significantly larger than that observed for Cu-ZSM-5 with substantial presence of the $[\text{Cu}^{2+}(\text{H}_2\text{O})_5(\text{COO})^-]^+$ ion. This indicates that a predominant part of the Cu^{2+} ions was incorporated in the MeAlPO molecular sieves as $[\text{Cu}^{2+}(\text{H}_2\text{O})_5\text{X}^-]^+$ complexes present in the exchange solution. Also an increase in the Cu^{2+} absorption coefficient in metalloaluminophosphate matrices, compared with ZSM-5, indicated a lowering of the coordination symmetry of the Cu^{2+} ion. This is in a good agreement with a lower density of the negative charge in the MeAlPO and SAPO-5 matrices. In this case, divalent Cu^{2+} ions could be stabilized in the metalloaluminophosphate molecular sieves only with difficulties. In contrast, the stabilization of apparently monovalent $[\text{Cu}^{2+}(\text{H}_2\text{O})_5\text{X}^-]^+$ complexes in MeAlPO channels is feasible. We can conclude that Cu was exchanged in the MeAlPO and SAPO ma-

trices as Cu^{2+} ions in monovalent $[\text{Cu}^{2+}(\text{H}_2\text{O})_5\text{X}^-]^+$ complexes balanced by single negative framework charges. Such Cu ions exchanged to the cationic sites are responsible for the catalytic activity of Cu-loaded metalloaluminophosphate molecular sieves in NO decomposition. Moreover, the similarity of the transition behaviour of NO conversion over Cu-MeAlPO-5 and Cu-MeAlPO-11 and reduced Cu-ZSM-5 (*cf.* Fig. 7 and refs.^{27,29}) indicates that also in Cu-MeAlPO catalysts, a monovalent copper is the active site.

The significant difference in the temperature of maximum of the catalytic activity observed for Cu-MeAlPO-5 and Cu-MeAlPO-11 cannot be easily explained by different properties of the Cu ions in these matrices. Both these matrices possessing a one-dimensional channel system (shown schematically in Fig. 8) exhibit similar local arrangements of possible cationic sites because channel walls are composed in both cases of similar deformed six-rings, as depicted in detail in Fig. 9. Thus, local geometry of Cu ions in both matrices can be assumed to be very similar. Moreover, the local and global charge densities can be assumed to be similar due to the similar chemical composition and framework structure. It follows that the redox properties of the Cu ions in

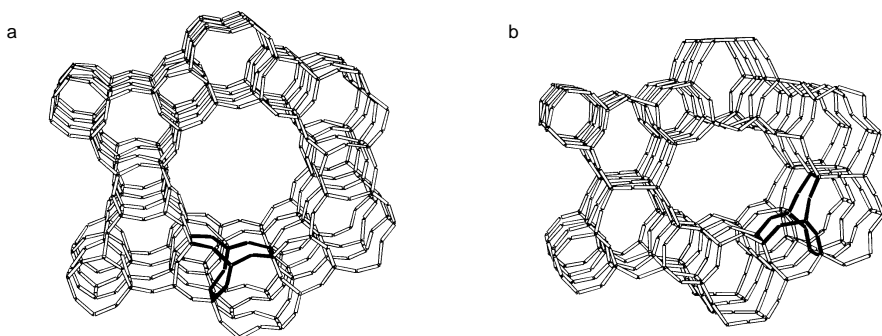


FIG. 8

Framework structures of AlPO-5 (a) and AlPO-11 (b)

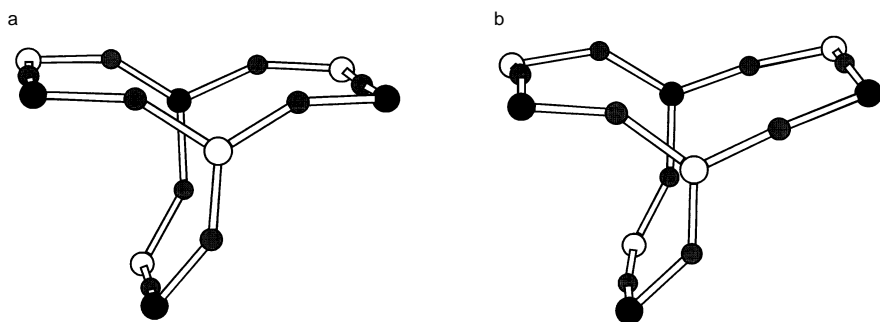


FIG. 9

Detail of channel wall six-rings, forming possible cationic sites in MeAlPO-5 (a) and MeAlPO-11 (b)

both matrices should be similar. This suggestion is in a good agreement with the observed similarity of the temperature dependence of the NO decomposition over Cu-MeAlPO-5 catalysts with different chemical composition (Me = Zn, Mg, Fe, Co) and different metal contents. On the other hand, AlPO-5 and AlPO-11 matrices differ in the channel size (7.3 Å and 3.9×6.3 Å, respectively, *cf.* ref.²³). This leads us to the suggestion that the catalytic activity in NO decomposition in small pore matrices with a one-dimensional channel system (such as AlPO-11) might be controlled by diffusion.

The MeAlPO-5 and MeAlPO-11 frameworks are known to be stable during a template removal carried out at high temperatures (770–870 K) in an oxygen or inert gases^{30–32}. XRD patterns of our calcined (790 K, oxygen stream) MeAlPO-5 and MeAlPO-11 samples (*cf.* Figs 1 and 2) did not indicate any structural changes. Nor VIS-NIR spectra did indicate changes of the aluminophosphate matrices (*cf.* Fig. 5). Thus, there are no structural reasons for complete loss of the catalytic activity of Cu samples prepared by the ion exchange of calcined metalloaluminophosphate catalysts (*cf.* Table II). In fact, there is only one difference between non-active and active samples. The template was completely removed by calcination at a high temperature before the Cu ion exchange. On the other hand, we can assume the presence of a small amount of template in the MeAlPO matrix, balancing negative charge of the framework, after template removal under mild conditions (drying at 450 K). Recently, *ab initio* calculations on CoAlPO-5 and CoAlPO-11 showed, that the breaking of the Co–O bond and removal of the framework oxygen may occur during treatment of the template-free CoAlPO materials³³. Thus, we propose that the Cu ions are coordinated to the framework oxygens in the cationic site and exhibit catalytic activity in the case that the ion-exchange was performed in the presence of template molecules. The residual template molecules are removed during activation of sample before catalytic test. If calcination is followed by the Cu ion-exchange, Cu ions are coordinated to the defects or to the terminal OH groups formed during the calcination/ion exchange/catalyst activation procedure. An opposite model, when the Cu ions are coordinated to the defects in the presence of template and to cationic positions in template-free MeAlPO can be excluded. It is difficult to believe that in template-free MeAlPO there are occupied only cationic positions and not also defect sites (occupied by the template in template-containing MeAlPO). Thus, catalytic activity of template-containing molecular sieves must be followed also by the activity of a template-free catalyst.

The decrease in catalytic activity in NO decomposition, observed with some Cu-MeAlPO catalysts during the reaction, could be caused by the direct deactivation of active sites, *i.e.* Cu ions in cationic positions forming catalytic centers, or by the transformation of the MeAlPO matrix. Significant loss in the crystallinity of the Cu-MeAlPO accompanied by the observed decrease in the catalytic activity (*cf.* Fig. 1) indicated that the deactivation of Cu-MgAlPO-11 is caused by the collapse of the MgAlPO-11 structure. Thus, the increase in stability of the molecular sieve framework and in density of

negative charge in the framework may lead to further improvement of catalytic activity in NO decomposition using Cu-exchanged aluminophosphate molecular sieves.

CONCLUSIONS

Cu ions exchanged to metal-substituted aluminophosphates of MeAlPO-5 and MeAlPO-11 structural types are active in NO decomposition. Their activity is comparable with that observed for Cu-ZSM-5. The activity of Cu ions exchanged in metalloaluminophosphate matrices is independent of the type of ion replacing Al in the framework (Mg, Zn, Co, Fe) and of the way of introducing the framework negative charge to the matrix (MeAlPO, SAPO).

While Cu ions located in the cationic positions in the vicinity of one framework negative charge exhibited high catalytic activity, the activity of the Cu ions in the aluminophosphate framework was negligible.

Temperatures of the maxima of the catalytic activity were significantly higher for Cu-MeAlPO-11 compared with Cu-MeAlPO-5 (870–920 K vs 670–770 K).

Removal of templates after the synthesis of MeAlPO molecular sieves by calcination at 790 K followed by Cu ion exchange leads to inactive Cu-MeAlPO catalysts. This should be explained by cleavage of the Me–O bond causing substantial changes in the local coordination of the Cu ion.

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