

EFFECT OF FRAMEWORK CHARGE DENSITY ON CATALYTIC ACTIVITY OF COPPER LOADED MOLECULAR SIEVES OF CHABAZITE STRUCTURE IN NITROGEN(II) OXIDE DECOMPOSITION

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NO decomposition over Cu-loaded molecular sieves of chabazite structure with different framework negative charge density was investigated. Cu-ZnAlPO-34 with framework charge density (Al + P)/Zn = 15 exhibited high and stable catalytic activity in NO decomposition while Cu-chabazite with Si/Al = 2.7 was inactive. This evidences that the number of aluminum atoms balancing Cu ions in cationic sites controls the catalytic activity of Cu ion. Ions balanced by single framework aluminum atoms exhibit high activity in NO decomposition while ions balanced by two framework aluminum atoms are inactive. Topology of cationic sites is not the limiting parameter for NO decomposition over Cu ions located in molecular sieves.

Key words: NO decomposition; Cu ion; Chabazite; ZnAlPO-34; Molecular sieve; Zeolites; Heterogeneous catalysis.

Nitrogen oxides (NO_x) produced in high-temperature combustion processes are major air pollutants at present. Decomposition of NO into molecular nitrogen and oxygen seems to be a very attractive approach to control the NO_x pollution. Despite the substantial effort being currently devoted to development of a suitable catalyst exhibiting high and stable activity in NO decomposition, this challenge has not yet been solved. High catalytic activity has been found only for Cu ions implanted at the cationic sites of zeolite matrices, namely with Cu-ZSM-5 (refs¹⁻⁶). Nevertheless, for industrial application of this process, the conversion is still low; moreover, Cu-ZSM-5 activity is sensitive to the presence of water vapor and SO_x. Despite this fact, Cu-loaded zeolites attract high attention as the most important model system for the investigation of NO decomposition.

Isolated Cu⁺ ions, adjacent Cu and O centers and two neighboring Cu ions (Cu pairs), were suggested to be active in NO decomposition⁷⁻²². By a

detailed spectral analysis, we have shown^{19–21} that the Cu site active in NO decomposition possesses a low positive charge on the divalent Cu cation, is easily reduced, exhibits open, close to planar coordination sphere and is adjacent to a single Al framework atom. Recently, we have suggested one type of six-member ring, located in the straight channel of ZSM-5, to accommodate Cu ions responsible for NO decomposition over Cu-loaded ZSM-5 (ref.²²). Nevertheless, the framework topology and Al distribution in ZSM-5 do not allow to distinguish between the effect of local framework topology of the cationic site and its local framework charge density (the number of framework aluminum atoms forming the cationic site) on the catalytic activity of the Cu ion. Also, investigation of new systems active in NO decomposition, based on Cu-containing MeAlPO-5 and -11 materials^{23,24}, did not lead to elucidation of this problem. Detailed investigation of these catalysts is complicated by a lack of detailed knowledge on cationic sites in these molecular sieves and their low thermal stability. Nevertheless, high catalytic activity of Cu-MeAlPO matrices indicated that high and stable catalytic activity in NO decomposition is not restricted only to aluminosilicate matrices and one type of framework topology.

This contribution presents identification of parameters of cationic sites, necessary for catalytic activity of Cu ions in NO decomposition. Catalytic activity of Cu-loaded molecular sieves of chabazite structure with different framework charge density is reported. Only Cu ions located in matrix with a low density of the framework negative charge (Zn(Al)PO-34) exhibited an activity in NO decomposition while Cu-chabazites (Si/Al = 2.7) were inactive. Thus, the vicinity of only one framework negative charge is substantial for the activity of Cu ion. On the other hand, local topology of the Cu cationic site is not a limiting factor for the Cu ion activity, as follows from different framework topologies of chabazite and ZSM-5.

EXPERIMENTAL

Molecular Sieve Preparation

Synthesis of chabazite was performed using the procedure of Gaffney²⁵. Zeolite Y (Si/Al = 2.7) in the ammonium form was used as a source material after calcination at 550 °C and was mixed with a solution of potassium hydroxide. The batch composition was 0.17 Na₂O : 2.0 K₂O : Al₂O₃ : 5.4 SiO₂ : 224 H₂O. The synthesis took place in a polypropylene bottle with a screw-top lid at temperature of 368 K for 96 h without agitation.

Synthesis of ZnAlPO-34 was performed in the following way. First of phosphoric acid (20.17 g) and pseudoboehmite (11.87 g) (Catapal B, Vista) were added to water (50.5 g) and stirred for 2 h. Then triethylamine (32.4 g) used as organic template was added and stirred for another 2 h. Finally, zinc acetate (1.26 g) in water (7.0 g) was added and the final mix-

ture was thoroughly stirred for another 2 h. The synthesis was carried out in Teflon-lined stainless steel autoclaves at 155 °C for 22 h under agitation.

In both syntheses, the products were recovered by filtration, washed repeatedly with deionized water and dried at ambient temperature. The crystallinity and phase purity were determined using X-ray powder diffraction. The diffraction pattern of chabazite is depicted in Fig. 1a, for ZnAlPO-34 in Fig. 1b.

Isostructural chabazite and ZnAlPO-34 (structural code CHAB) were equilibrated four times with 0.5 M NaCl (20 ml of solution per 1 g of a zeolite) for 12 h. After ion exchange, Na-CHAB sieves were washed with distilled water and dried at room temperature. Cu²⁺-CHAB sieves with Cu concentration varying from 0.4 to 12.5 wt.% were prepared by ion exchange of Na-CHAB sieves with aqueous solution of Cu acetate. pH of Cu acetate-CHAB solutions varied during the ion exchange procedure from 5.1 to 5.6. Samples were carefully washed with distilled water, dried at ambient temperature and grained. Detailed conditions of the sample preparation and chemical composition of Cu-CHAB samples are given in Table I.

Characterization

Powder X-ray diffraction patterns of synthesized molecular sieves were recorded on a Siemens D5005 diffractometer in the Bragg-Brentano geometry arrangement, using CuK α radiation with a graphite monochromator and scintillation counter. To verify that the treatment of as-synthesized MeAlPO material 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.

Catalytic Activity

Catalytic activity of Cu-exchanged molecular sieves was tested in a down-flow glass microreactor with inner diameter 5 mm, introducing 4 000 ppm of NO in He, total feed of

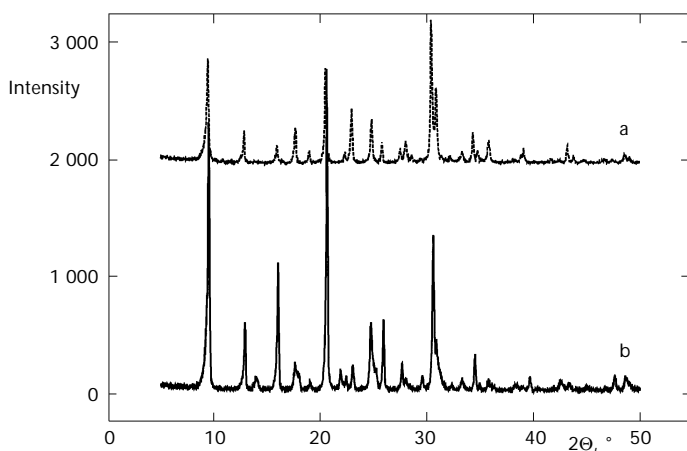


FIG. 1
XRD patterns for chabazite (a), ZnAlPO-34 (b)

100 ml/min, a catalyst weight of 300 mg and in the temperature range 620–750 K. The catalysts were activated in a He stream (99.996%) with a temperature increase of 5 K/min up to 680 or 720 K, held for 1 h, and cooled down to the reaction temperature. To achieve the temperature of the next measurement, the catalyst was heated in a NO/He stream with a temperature increase of 5 K/min. The temperature step between two temperatures of measurements was 30 K. 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 AND DISCUSSION

Cu-ZnAlPO-34 molecular sieves activated at 680 K exhibited catalytic activity in NO decomposition in the temperature range 620–700 K while Cu-ZnAlPOs-34 activated at 720 K exhibited significantly lower activity (maximum 50% of the activity of samples activated at 680 K, not shown in figures) and Cu-chabazites were inactive. Figure 2a depicts the dependence of NO concentration at the reactor outlet on the reaction time-on-stream. At first a sharp decrease in NO concentration was observed, followed at lower reaction temperature by leveling off to a constant conversion, reached within 30 min. This dependence of the NO conversion on time-on-stream evidences that the initial behavior of the NO conversion over Cu-MeAlPO-34 is similar to the well-known transient behavior of NO

TABLE I
Chemical composition and conditions of preparation of Cu-CHAB molecular sieves

Molecular sieve	Cu/Al or Cu/Zn	Si/Al or (Al+P)/Zn	Na/Al or Na/Zn	Cu concentra- tion in solution (M)	Solution/ zeolite, ml/g	Time of exchange, h
Cu-CHAB	0.08	2.7	0.84	0.005	65	1
Cu-CHAB	0.15	2.7	0.68	0.01	60	3
Cu-CHAB	0.22	2.7	0.51	0.01	110	12
Cu-CHAB	0.32	2.7	0.26	0.01	110 + 110	3 + 15
Cu-ZnAlPO-34	0.13	15	0.82	0.01	50	16
Cu-ZnAlPO-34	0.97	15	<0.05	0.10	90	16
Cu-ZnAlPO-34	4.5	15	<0.05	0.10	100 + 100	12 + 24

decomposition observed on reduced Cu-ZSM-5 or Cu-MeAlPO-5 and -11 molecular sieves^{23,24,26}. Thus, the nature of reaction centers in these matrices is similar. At reaction temperatures lower than 670 K, the catalyst activity was stable for hours, as it is documented in Fig. 2b. At reaction temperatures higher than 680 K, the catalyst activity significantly decreased with time and samples became inactive, as it is shown in Fig. 2a. This deactivation at higher temperatures was also observed for other Cu-alumino-phosphate catalysts (Cu-MeAlPO-5 and -11) and should be associated with lower thermal stability of MeAlPO molecular sieves^{23,24}. This suggestion is supported by observed lower catalytic activity of samples activated at 720 K because the dispersion of Cu ions in molecular sieves is not usually affected by the treatment at this temperature¹⁸⁻²⁰.

In Fig. 3, the temperature dependence of stabilized conversion of NO over Cu-ZnAlPO-34 is depicted. The activity increased with temperature, but this increase was cut after reaching the temperature of catalyst deactivation at 680 K. The maximum values of the stable conversion of NO were taken as characteristic values of NO conversion over these catalysts and are summarized, together with corresponding turn-over frequency (TOF), in Table II.

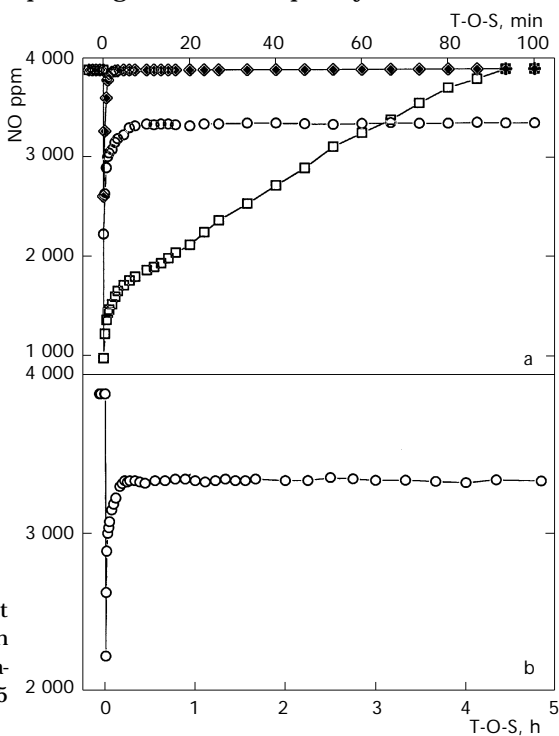


FIG. 2

Dependence of NO concentration at the reactor outlet on the reaction time-on-stream (T-O-S) (◆ Cu-chabazite Cu/Al 0.32, Cu-ZnAlPO-34, Cu/Zn 4.5 ○ 650 K, □ 700 K)

Cationic sites in chabazite are well known²⁵⁻³². Cations in site I (for notation see refs²⁶⁻³²) are located in the chabazite cavity and coordinated to three framework oxygens of the regular six-member ring above the six-member ring plane. Site II of the chabazite cavity is occupied only in partially hydrated chabazites. Site III is inside the hexagonal prism. Ions at this site can hardly play the role of catalytic center as their coordination sphere is fully occupied. Site IV corresponds to the cations located in the eight-member ring connecting chabazite cavities. Cu⁺ ions in dehydrated form occupy only sites I and IV (ref.³³) and only these sites are shown in

TABLE II
Catalytic activity of Cu-CHAB molecular sieves

Catalyst	Cu, wt%	Cu/Al or Cu/Zn	Conversion, %	TOF · 10 ⁻⁴ , s ⁻¹
Cu-ZnAlPO-34	12.5	4.5	14.2	0.9
Cu-ZnAlPO-34	2.4	0.97	6.5	2.0
Cu-ZnAlPO-34	0.4	0.13	2.4	4.5
Cu-CHAB	7.6	0.32	0	0
Cu-CHAB	5.2	0.22	0	0
Cu-CHAB	3.6	0.15	0	0
Cu-CHAB	1.9	0.08	0	0

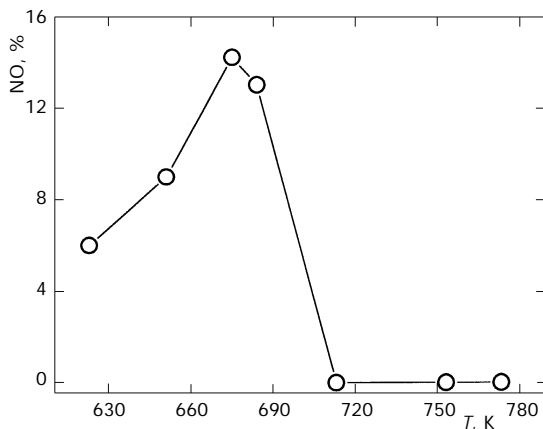


FIG. 3
Temperature dependence of NO decomposition over Cu-ZnAlPO-34 catalyst (Cu/Zn 4.5, 0.30 g of catalyst)

Fig. 4. MeAlPO-34 is isostructural with chabazite structure³⁴ and the local topology of the cationic sites of Cu-ZnAlPO-34 structure is identical. Thus, Cu species active in NO decomposition in Zn-AlPO-34 are coordinated to the regular six-member or eight-member rings. However, these types of rings are not present in the ZSM-5 or MeAlPO-5 and -11 structures, in which ions are assumed to be coordinated to various deformed six-member rings^{22,24,35}. This indicates that the local topology of cationic site is not a crucial parameter controlling the catalytic activity of Cu ions in NO decomposition.

The only possible difference in Cu siting between chabazite and ZnAlPO-34 has to be associated with the change in the framework negative charge density, reflected in the Si/Al ratio of chabazite and the (Al + P)/Zn ratio of ZnAlPO-34. In the case of chabazite with Si/Al \approx 2.7, at least 93% of cationic sites contain two aluminum atoms, as follows from simple statistic calculation. This assumption is supported by full ion exchange of divalent ions in chabazite (Me²⁺/Al ratio 0.5) observed for Co-, Mn- and Ca-chabazites²⁶⁻³². On the other hand, in the case of ZnAlPO-34 with a significantly lower density of framework negative charge ((Al + P)/Zn = 15), the probability of the presence of two framework aluminum atoms at cationic sites formed by six- or eight-member rings is significantly lower. Thus, we can suppose that sites containing only one Al atom are negligible in chabazite and, in contrast, they prevail in ZnAlPO-34. The low density of the framework negative charge can also affect the relative number of cationic sites formed by six- or eight-member rings. In the chabazite framework, all rings contain aluminum atoms forming cationic sites and the ra-

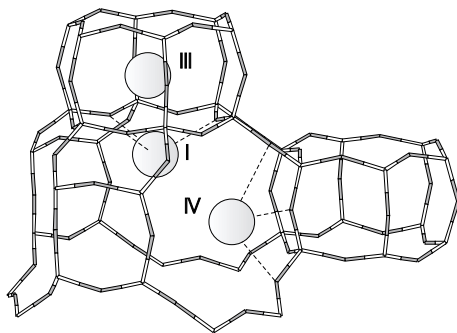


FIG. 4

Cu sites occupied in ion-exchanged dehydrated chabazite and their notation according to refs²⁶⁻³²

tio of sites formed by six- and eight-member rings is given by their frequency in the framework. In ZnAlPO-34 with low density of negative charge, rings without Al atom can be present. In this case, the ratio of sites formed by six- and eight-member rings is given by the Al distribution in the framework.

Because all Cu-chabazites contain Cu ions located both in six- and eight-member rings, as reported in our previous study³³, the inactivity of Cu-chabazites in NO decomposition is caused by the presence of two framework aluminum atoms in every cationic site of the matrix. The difference in the turn-over frequency values in NO decomposition by Cu-ZnAlPO-34 samples with different Cu loading can be explained by the difference in the occupation of sites with different catalytic activity or by formation of Cu_xO_y species in highly loaded Cu-ZnAlPO-34. The presence of these species is reflected in high Cu exchange level ($\text{Cu}/\text{Al} = 1.4$); these species do not exhibit catalytic activity³⁶.

CONCLUSIONS

Cu ions exchanged to ZnAlPO-34 molecular sieves exhibit high and stable catalytic activity in NO decomposition, while Cu ions exchanged to chabazite are inactive.

The density of the framework negative charge has been found to be the crucial parameter controlling the activity in NO decomposition of Cu ions located in molecular sieves. Cu ions balanced by two framework negative charges (two framework aluminum atoms) are inactive; however, Cu ions balanced by a single framework negative charge exhibit catalytic activity.

Catalytic activity of Cu ions is not restricted to only one type of local topology of the cationic site. Both Cu ions located in regular six-member or eight-member rings (CHAB structure) and in elongated or deformed six-member rings (ZSM-5, MeAlPO-5 and -11) exhibit catalytic activity in NO decomposition.

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