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 (refs[1–6]). 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 decomposition[7–22]. By a

Exhibit 2015.001

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 Gaffney[25]. 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 Na_2O : 2.0 K_2O : Al_2O_3 : 5.4 SiO_2 : 224 H_2O. 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-

Exhibit 2015.002

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. Cu^{2+}-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 CuKα 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
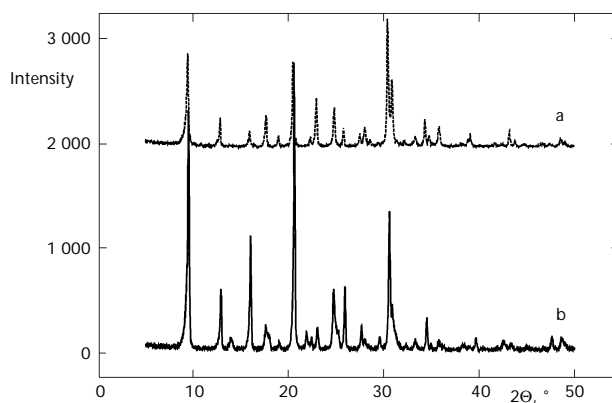

Fig. 1
XRD patterns for chabazite (a), ZnAlPO-34 (b)

Exhibit 2015.003

100 ml/min, a catalyst weight of 300 mg and in the temperature range 620–750 K. The cata-
lysts 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 mea-
surements 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 NO_2 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 NO_2 was detected in the products (detection limit 5 ppm).
Only traces of N_2O were observed by mass spectrometry (Hewlett–Packard, 5971A).

RESULTS AND DISCUSSION

Cu-ZnAlPO-34 molecular sieves activated at 680 K exhibited catalytic activ-
ity 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

Exhibit 2015.004

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-aluminophosphate 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 temperature[18–20].

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.
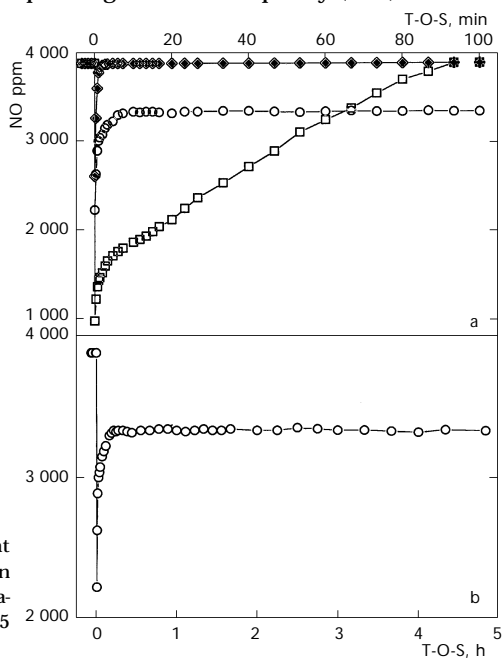

FIG. 2
Dependence of NO concentration at the reactor outlet on the reaction time-on-stream (T-O-S) (◆ Cu-chabazite Cu/Al 0.32, Cu-ZnAlPO-34, Cu/Zn 4.5 ❍ 650 K, ❑ 700 K)

Exhibit 2015.005

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