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High activity of mononuclear copper present in the framework of CuSiBEA zeolites in the selective catalytic reduction of NO with NH_3

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ABSTRACT

Cu_xSiBEA zeolites (with x = 1–7.5 Cu wt %) prepared by a two-step postsynthesis method which consists in the first step of dealumination of parent BEA zeolite to obtain aluminum-free SiBEA support and then in the second step, of contacting the obtained material with an aqueous solution of copper nitrate, were used in this work as catalysts of SCR of NO with ammonia. XRD, TPR and FTIR investigations showed that up to 2 wt % of Cu was successfully incorporated into zeolite beta structure as framework mononuclear Cu(II). The FTIR of pyridine sorption revealed that the incorporation of copper into zeolite framework led to the creation of new Lewis acidic sites which were responsible for high activity of Cu_xSiBEA zeolite catalysts in SCR of NO with ammonia. The catalytic activity of Cu_xSiBEA in SCR of NO with ammonia used as a reducing agent strongly depends on the nature and environmental of copper in BEA structure. The $Cu_{1.0}SiBEA$ catalyst with predominantly framework Cu(II) was the most active and selective among the tested samples in wide temperature range. In contrast, the application of Cu_xSiBEA zeolite catalysts with higher Cu content (>than 2 wt % of Cu) containing a mixture of framework and extra-framework Cu(II) resulted in low NO conversion in SCR at high temperature range, as well as, the high concentration of undesired N_2O in outgas stream. It indicates that octahedral Cu(II) and/or copper oxides present in extra-framework position of SiBEA zeolite promote at high temperature ammonia oxidation.

1. Introduction

Selective catalytic reduction of NO_x with ammonia is a widely applied method of nitric oxides removal from exhaust of power plants [1,2]. It is also of interest for the treatment of NO_x emissions from heavy duty diesel engines [3,4]. In case of stationary sources, the standard SCR catalyst is $V_2O_5/TiO_2/MnO_3$. However due to its narrow temperature window it cannot be applied for mobile sources. Moreover, conventional three way catalysts are not able to remove NO_x from diesel engine because of oxygen over abundance. Thus, other types of catalysts are intensively studied, in order to find the most efficient one. Among the many tested candidates [5–7], the most promising are zeolite-based materials promoted with transition metal ions such as Cu and/or Fe [8–11].

Many researches indicated isolated metal ions in exchanged positions as active species responsible for high NO conversion and excellent N_2 selectivity. Xue et al. [12] concluded that Cu^{2+} ions displaced into cavity of SAPO-34 are responsible for high activity at low temperature. However, Pereda-Ayo et al. [13] observed that isolated Cu(II) ions located in pores of BETA and ZSM-5 zeolite maintained NO_x conversion at high temperature range. Additionally, there are still a lot of questions to answer about reaction mechanisms and the formation of by-products from competitive reactions of ammonia oxidation.

Others very important factors for potential catalysts application on industry scale are their stability and durability. It is well known that zeolite materials may be damaged by hydrothermal treatment resulting in dealumination [14], crystalline structure disordering [15] or metal ions migration [16,17]. In order to avoid such effects and retain catalytic properties for a long time, improvements in catalyst synthesis or post-synthesis modification are proposed. One of the such proposal way was the application of materials with CHA zeolite structure which seemed to be more resistant to steam than large pores zeolites [18,19]. On the other hand, Dzwigaj et al. [20,21]

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have proposed two-step postsynthesis method as an attractive alternative to obtain almost completely dealuminated beta zeolite with excellent dispersion of metal ions in the form of isolated mononuclear framework species. They used two-step postsynthesis method which consists of the creation of vacant T-atom sites by nitric acid treatment of parent beta zeolite and the subsequent incorporation of metal ions into framework of SiBEA zeolite by reaction with silanol groups associated with vacant T-atom sites.

In this work the two-step postsynthesis method was applied to obtain zeolite beta catalysts with isolated mononuclear Cu(II) incorporated into zeolite framework highly active in selective catalytic reduction of NO with NH_3.

2. Experimental

2.1. Catalyst preparation

A TEABEA zeolite with atomic Si/Al ratio of 17 was treated i) in air at 823 K for 15 h to remove organic template and obtain an organic-free HAlBEA zeolite (Si/Al = 19) or ii) with nitric acid solution ($c = 13$ mol dm^{-3}, 353 K) over 4 h in order to remove aluminum species and obtain SiBEA zeolite. As obtained SiBEA with atomic Si/Al ratio of 1300 was washed several times with distilled water and dried at 368 K overnight. SiBEA zeolite was contacted with an aqueous copper nitrate solution which concentration varied from 1.96×10^{-3} to 1.47×10^{-2} mol dm^{-3} and stirred for 24 h at 298 K. Then, the suspension was stirred in the evaporator under vacuum of a water pump for 2 h at 333 K, until water was evaporated. Cu-containing SiBEA samples after calcination at 773 K (2 K h^{-1}) for 3 h were labeled as C-Cu_xSiBEA (with x = 1–7.5 wt %), where C state for calcined.

2.2. Catalysts characterization

XRD profiles were recorded at room temperature on a PANalytical Empyrean diffractometer using the CuKα radiation ($\lambda = 154.05$ pm).

Acidic properties of zeolite samples were determined by adsorption of pyridine (Py) followed by infrared spectroscopy. First, the samples were prepared in form of self-supported wafers of ca. 10 mg cm^{-2} and transferred into the IR cell. The activation procedure before pyridine sorption was as follows: (i) the wafers were calcined in a static atmosphere of O_2 (~3.0×10^4 Pa) at 723 K for 3 h and then outgassed under secondary vacuum at 573 K (10^{-3} Pa) for 1 h, (ii) the wafers were contacted at room temperature with gaseous Py (133 Pa) via a separate cell containing liquid pyridine. The spectra were recorded with a Bruker Vector 22 spectrometer (resolution 2 cm^{-1}, 128 scans) after desorption at 423 and 573 K for 1 h. The final spectra were obtained after subtraction of the spectrum recorded before pyridine adsorption from the one obtained after pyridine adsorption. The concentration of Brønsted and Lewis acidic sites was estimated using parameters calculated by Emeis [22].

The TPR-H_2 measurements were carried out on an AutoChem 2910 apparatus (Micromeretics) equipped with a thermal conductivity detector (TCD) in the temperature range of 298–1250 K with a linear heating rate of 7 K min^{-1}, hydrogen stream flow (5% H_2/Ar) of 40 cm^3 min^{-1} and samples weight of 0.1 g.

2.3. Catalytic measurements

The activity of CuSiBEA catalysts in selective catalytic reduction (SCR) of NO with ammonia was measured in a conventional fixed-bed reactor. Temperature was measured inside the reactor with a thermocouple and controlled with an electronic controller (LUMEL RE19). The composition of reaction mixture was: 1000 ppm NO, 1000 ppm NH_3, 3.5 vol.% O_2 and He as balance. The gas mixture was fed using calibrated electronic mass flow controllers (BETA-ERG). The total gas flow was 0.1 dm^3 min^{-1} and catalyst mass was 0.2 g. Additional set of tests for several catalyst with addition of 500 ppm SO_2 to substrate stream was carried out in order to study influence of SO_2 presence on catalyst performance. The concentration of NO and N_2O were analyzed by FTIR detectors (ABB 2000 AO series). The NO_2 forming over SCR process was catalytically converted into NO with ABB Advance SCC-K converter before the exhaust gas was analyzed on the FTIR detectors. Thus, total amount of NO_x was registered as to NO concentration.

Before the catalytic tests the samples were pretreated in oxygen/helium mixture (0.1 dm^3 min^{-1}) in the temperature range 298–798 K with a linear heating rate of 2 K min^{-1} and then for 1 h at 798 K. The standard test conditions were 1 h at 423–773 K with increasing the reaction temperature every 50 K interval. The NO conversions were calculated from the measured concentration of nitric oxide. N_2 selectivity was calculated based on following formula:

$$N_2\ selectivity\ (\%) = \frac{([NO]_{in} - [NO]_{out}) - [N_2O]_{out}}{[NO]_{in} - [NO]_{out}} \times 100 \qquad (1)$$

Applied earlier by Moreno-Tost et al. [23] and Bin et al. [24].

The SCR reaction rates per gram of Cu were calculated from NO conversion with the equation [12]:

$$R_r\left[mol_{NO} \cdot g_{Cu}^{-1} \cdot s^{-1}\right] = \frac{X_{NO} \times V\ \left[dm^3 \cdot s^{-1}\right]}{m\ [g]\ \times\ 22.4\ \left[dm^3 \cdot mol^{-1}\right]} \qquad (2)$$

where R_r is reaction rate, X_{NO} NO conversion, V flow rate and m mass of Cu.

3. Results and discussions

3.1. XRD and FTIR studies

Changes in the structure of zeolite BEA may be monitored by XRD measurements within a given series of zeolite samples taking into account the position of the diffraction reflex (302) at $2\theta = 22.5°–22.6°$ which shifts are the evidences of contraction and/or expansion of zeolites structure.

For HAlBEA zeolite the d_{302} spacing decreased from 3.943 Å (with 2θ of 22.53°) to 3.911 Å (SiBEA) (with 2θ of 22.72°) suggesting the zeolite structure contraction consistent with the dealumination of zeolite BEA. The impregnation of SiBEA with Cu precursor led to the increase of the d_{302} spacing, from 3.911 Å (SiBEA) (with 2θ of 22.72°) to 3.926 Å ($Cu_{1.0}$SiBEA) (with 2θ of 22.63°) and to 3.933 Å ($Cu_{2.0}$SiBEA) (with 2θ of 22.59°) (Fig. 1). The shifts of the main diffraction reflex positions may be interpreted as the expansion of the BEA structure and the incorporation of Cu ions into the framework of SiBEA zeolite, in agreement with the earlier study on MoSiBEA and CoSiBEA zeolites [25,26].

Moreover, none of the studied diffractograms contained reflexes related to other phases, indicating no amorphization of zeolite structure and no formation of copper oxides crystallites.

Infrared spectroscopy is a powerful tool to examine the structure and the environment of active species in microporous materials, especially in case of surface hydroxyl groups. Fig. 2 shows the FTIR spectra of SiBEA, $Cu_{2.0}$SiBEA and $Cu_{4.0}$SiBEA zeolites. For SiBEA three characteristic bands at 3736, 3705 and 3520 cm^{-1} may be attributed to isolated internal, terminal internal and hydrogen-bonded silanol groups, respectively, situated at vacant T-atom sites forming hydroxyl nests [14,27]. The impregnation of SiBEA