



# Influence of partial dealumination of BEA zeolites on physicochemical and catalytic properties of AgAlSiBEA in H<sub>2</sub>-promoted SCR of NO with ethanol

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## ABSTRACT

The two-step postsynthesis method allows obtaining AlSiBEA zeolites with different degree of dealumination (Si/Al = 100 and 200). Physicochemical properties (crystallinity, hydroxyl group coverage, acidic sites and nature of silver species) of AlSiBEA and AgAlSiBEA were investigated by XRD, DR UV–vis, XPS, TEM and FT-IR with CO and pyridine as probe molecules. Catalytic properties of the zeolites were studied in the process of selective reduction of NO with ethanol in the presence of hydrogen in the reaction mixture. It was shown that level of H<sub>2</sub>-promoting effect on the SCR-process depends on the dealumination degree of Ag-containing BEA zeolites and greater effect is observed for the catalysts with higher concentration of Lewis acidic sites.

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## 1. Introduction

Nitrogen oxides (NO<sub>x</sub>) abatement in exhaust gases of lean-burn and diesel engines remains a target for environmental catalysis research. Metal-containing zeolites are known to be promising catalysts for selective catalytic reduction (SCR) of NO<sub>x</sub> with hydrocarbons and oxygenates [1]. Activity of zeolite catalysts depends on the nature of added metal (Cu, Fe, Co, Ag) as well as on the framework type (MFI, BEA, MOR, FAU) [2–4]. Interest in silver-containing catalysts was stimulated after the finding that addition of hydrogen into the reaction mixture enhances the selective reduction of NO<sub>x</sub> [5]. The origin of this effect is still under debate, i.e., the role of H<sub>2</sub> in the reaction mechanism and structural changes

of silver active sites [6–15]. It is most likely that in order to increase the rate of NO<sub>x</sub> conversion hydrogen must accelerate a rate-determining step of the reaction [6,7]. The enhanced activity after H<sub>2</sub> addition was assigned to the formation of the nitrite species that are more reactive than adsorbed nitrate species in C<sub>3</sub>H<sub>6</sub>-SCR reaction on Ag/Al<sub>2</sub>O<sub>3</sub> [7,8]. Other way of hydrogen effect was suggested to be the formation of active oxygen species on Ag clusters on Ag/Al<sub>2</sub>O<sub>3</sub> and Ag-MFI catalysts [9,10], which promote partial oxidation of hydrocarbons to surface acetate [11] or enolic species [12]. Formation of the key intermediate of isocyanate from cyanide was also considered as the rate-determining step and was suggested to be promoted by hydrogen [6,13–15].

However, silver ions and clusters were considered only as active sites of the hydrogen-promoted SCR of NO<sub>x</sub> with hydrocarbons or oxygenates and influence of the acidic sites has not been taken into consideration. It was only proposed [16] that variation in catalytic activity of Ag-containing zeolites in C<sub>3</sub>H<sub>8</sub>-SCR of NO in the presence of H<sub>2</sub> arises from the support effect on the ratio of Ag species, which was shifted to cationic side with the increase of amount and strength of acidic sites in zeolites. The effect of acidic properties of Ag/Al<sub>2</sub>O<sub>3</sub> catalysts on their activity in the SCR of NO<sub>x</sub> with hydrocarbons or oxygenates was highlighted in several recent studies [17–19].

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In a previous work [20], we have shown that promoting H<sub>2</sub>-effect in the SCR of NO with ethanol is observed in the presence of AgBEA (with Si/Al ratio equal to 12.5), whereas it is almost absent on Ag-containing catalysts based on dealuminated BEA (Si/Al = 1000). It was concluded that a necessary condition for H<sub>2</sub>-effect is the presence of silver clusters in close proximity to strong Lewis acidic sites (LAS) in the zeolite catalysts. Therefore, it is expedient to study the influence of intermediate degree of dealumination ( $12.5 < \text{Si/Al} < 1000$ ) on the appearance of H<sub>2</sub>-effect.

For this purpose Ag-containing partially dealuminated BEA zeolites (with Si/Al ratio of 100 and 200) were prepared using the two-step postsynthesis method [21–24]. The present work aimed to investigate the influence of partial dealumination of AgBEA zeolites on their physicochemical properties (crystallinity, acidity, nature of silver species) and catalytic performance in the H<sub>2</sub>-promoted SCR of NO with ethanol.

## 2. Experimental

### 2.1. Catalysts preparation

Silver containing BEA zeolite was prepared by the two-step postsynthesis method: in the first step, TEABEA zeolite provided by RIPP (China) was treated in 6 or 8 mol L<sup>-1</sup> HNO<sub>3</sub> aqueous solution (353 K) to obtain partially dealuminated supports AlSiBEA (Si/Al = 100) or AlSiBEA (Si/Al = 200) with the vacant T-atom sites (T = Al). Then the suspension was recovered by centrifugation, washed with distilled water and dried at 353 K. The resulting partially dealuminated zeolites were labeled as AlSiBEA(100) and AlSiBEA(200), where Si/Al ratio was marked in parenthesis.

To prepare Ag-containing zeolites, 2 g of AlSiBEA (Si/Al = 100) and AlSiBEA (Si/Al = 200) was firstly stirred under aerobic conditions for 2 h at 298 K in 200 mL of AgNO<sub>3</sub> (Fluka silver nitrate with high Ph Eur purity with Ag >99.8%) aqueous solution (pH = 2.3) with different concentrations of 0.9, 2.7 and 5.4 · 10<sup>-3</sup> mol L<sup>-1</sup> to obtain the zeolites with various Ag content. Then the suspension was stirred in evaporator under vacuum of a water pump for 2 h in air at 353 K until the water was evaporated. The resulting solid containing 0.5, 1.5 and 3.0 Ag wt % were labeled as Ag<sub>0.5</sub>AlSiBEA(100), Ag<sub>1.5</sub>AlSiBEA(100) and Ag<sub>3.0</sub>AlSiBEA(100) or Ag<sub>0.5</sub>AlSiBEA(200), Ag<sub>1.5</sub>AlSiBEA(200) and Ag<sub>3.0</sub>AlSiBEA(200), respectively, with Si/Al ratio marked in parenthesis.

Preparation and physicochemical properties of AgAlBEA and AgSiBEA were described earlier [25,26]. To prepare AgAlBEA zeolite, firstly, the TEABEA zeolite was calcined at 823 K for 15 h to obtain AlBEA (Si/Al = 12.5) and secondly, the latter was impregnated with AgNO<sub>3</sub> aqueous solution. AgSiBEA zeolite was prepared by the two-step postsynthesis method: treatment of TEABEA zeolite in 13 mol L<sup>-1</sup> HNO<sub>3</sub> aqueous solution (4 h, 353 K) in the first step to obtain a dealuminated (Si/Al = 1000) and organic-free SiBEA support and stirring of SiBEA under aerobic conditions for 2 h at 298 K in 200 ml of aqueous AgNO<sub>3</sub> solution followed by stirring in evaporator under vacuum of the water pump for 2 h in air at 353 K until evaporation of the water.

### 2.2. Catalysts characterization

X-Ray Fluorescence chemical analysis was performed at room temperature on a SPECTRO X-LabPro apparatus.

Powder X-ray diffraction (XRD) was recorded at room temperature and ambient atmosphere on a Bruker D8 Advance diffractometer using the CuK $\alpha$  radiation ( $\lambda = 154.05$  pm).

Analysis of the acidic properties of samples was performed by adsorption of pyridine and CO followed by Fourier transform infrared spectroscopy (FT-IR). Before analysis, the samples were

pressed at  $\approx 1$  ton · cm<sup>-2</sup> into thin wafers of ca. 10 mg cm<sup>-2</sup> and placed inside the IR cell.

Before CO adsorption experiment, the wafers were activated by calcination at 723 K for 2 h in flowing 2.5% O<sub>2</sub>/Ar and then outgassed at 573 K (10<sup>-3</sup> Pa) for 1 h. Following thermal treatment, the samples were cooled down to 100 K. CO was introduced in increasing amounts up to an equilibrium pressure of 133 Pa. Infrared spectra were recorded using a Bruker Vertex 70 spectrometer (resolution – 2 cm<sup>-1</sup>, 128 scans). The spectra were obtained after subtraction of the spectrum recorded after calcination and prior to CO adsorption.

Before pyridine adsorption/desorption experiments, the wafers were activated by calcination in static conditions at 773 K for 1 h in O<sub>2</sub> (2 · 10<sup>4</sup> Pa) (or in H<sub>2</sub> flow) and then outgassed under secondary vacuum at 673 K (10<sup>-3</sup> Pa) for 1 h. The wafers were contacted at 423 K with gaseous pyridine. The spectra were recorded after pyridine desorption at 423, 573 and 673 K using Spectrum One FT-IR spectrometer (resolution – 1 cm<sup>-1</sup>, 12 scans). The reported spectra were obtained after subtraction of the spectrum recorded after calcination and prior to pyridine adsorption.

Diffuse reflectance (DR) UV–vis spectra were recorded at ambient atmosphere on a Cary 5000 Varian spectrometer equipped with a double integrator with polytetrafluoroethylene as reference.

### 2.3. Catalytic tests

Catalytic activity tests were carried out in a fixed-bed flow quartz reactor at atmospheric pressure. Samples with grains of 0.5–1.0 mm (0.5 cm<sup>3</sup>,  $\approx 0.3$  g) were loaded into the reactor. Gas feed for the reaction was 500 ppm NO, 1000 ppm C<sub>2</sub>H<sub>5</sub>OH, 10% O<sub>2</sub>, 0.5% H<sub>2</sub> in He with the gas hour space velocity of 24,000 h<sup>-1</sup>. The gas feed was adjusted by mass-flow controllers (Chromatek-Crystal FGP). Before reaction, the catalyst was heated to 773 K at a heating rate of 20 degrees · min<sup>-1</sup> in a flow of O<sub>2</sub>/He (or H<sub>2</sub>/He when hydrogen was added to the reaction mixture) and held for 1 h, then cooled to 453 K with a further step-heating in reaction gas feed to a temperature of conversion measurement. The steady-state activity was measured after 30 min reaction at a certain temperature. The temperature was controlled through an Autonics TZN45 temperature controller using a chromel-alumel thermocouple. The concentration of NO was continuously monitored using a chemiluminescence gas analyzer (344HL04, Ukraine). The products were analyzed by gas chromatograph (TCD) (Kristallyuks 4000M, Metachrom, Russia) with a CaA column (for NO, N<sub>2</sub>, CO) and a Polisorb-1 column (for N<sub>2</sub>O, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, ethanol). Catalytic activity was characterized by NO conversion to N<sub>2</sub> and temperatures of its achievement.

## 3. Results and discussion

### 3.1. Characterization of AlSiBEA and AgAlSiBEA

#### 3.1.1. Crystallinity of the samples

X-ray diffractograms of AlSiBEA(100) and AlSiBEA(200), i.e., after partial removal of aluminum atoms, are similar with TEABEA zeolite calcined at 823 K for 15 h (AlBEA(12.5)) [25,26], suggesting that the dealumination does not significantly affect the structure and crystallinity of BEA zeolite are preserved (Fig. 1).

A narrow diffraction peak near 22.5° is generally taken as evidence of lattice contraction/expansion of the BEA structure [27,28]. The d<sub>302</sub> spacing, calculated from the corresponding  $2\theta$  value, decreases from 3.950 Å (AlBEA with  $2\theta$  of 22.48°) [26] to 3.947 Å (AlSiBEA(100) with  $2\theta$  of 22.50°) and to 3.940 Å (AlSiBEA(200) with  $2\theta$  of 22.54°) suggesting a matrix contraction, consistent with the removal of aluminum from the zeolite framework.

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