



Review

Influence of Cu on the catalytic activity of FeBEA zeolites in SCR of NO with NH₃



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ABSTRACT

Two series of Fe and/or Cu containing BEA zeolites were prepared by different procedures: two-step post-synthesis method (Fe_xSiBEA, Cu_xSiBEA and Fe_xCu_xSiBEA) and conventional wet impregnation (Fe_xHAlBEA, Cu_xHAlBEA and Fe_xCu_xHAlBEA) ($x = 1.0$ Fe or Cu wt%). Modification of BEA zeolite resulted in the incorporation of iron and/or copper into vacant T-atom sites of the zeolite framework as evidenced by XRD and DR UV–vis. Transition metals (Cu or Fe) were incorporated into the framework of BEA zeolite as pseudo-tetrahedral Fe (III) or Cu (II) as proved by XRD, DR UV–vis and TPR investigations. All of obtained zeolite materials were found to be active catalysts of selective catalytic reduction of NO with ammonia. Analysis of NO conversion and catalyst reducibility indicated that the latter played an important role in the DeNO_x process. Co-presence of copper in the zeolite structure decreased the reducibility of iron in Fe_xCu_xSiBEA and Fe_xCu_xHAlBEA, and had significant influence on the low temperature NO conversion.

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1. Introduction

Worldwide environmental regulations regarding NO_x emissions from diesel engines have become significantly more stringent

leading to innovative applications of new technologies to resolve this environmental problem. As a potent technology, the selective catalytic reduction (SCR) of NO has been studied intensively [1–4]. Iron and copper based zeolite catalysts are widely employed in selective catalytic reduction of NO with ammonia due to their high temperature durability compared to vanadium based catalysts [5].

Hence, the focus has shifted to the Fe- and Cu-based zeolite catalysts, both of which have demonstrated very high NO reduction efficiencies at high space velocities. The Cu-based catalysts are

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particularly effective at lower temperatures (<620 K) [6,7]. Moreover, NO removal efficiencies over the Cu-based catalysts are found to be rather insensitive of the amount of NO₂ in the feed at lower temperatures [7]. On the other hand, the Fe-based catalysts are active at higher temperatures (>620 K) and give very high NO reduction efficiencies even at very high temperatures (up to 870–970 K) [8,9]. Given the differences in activities of the Cu- and Fe-based catalysts, it seems plausible that a combination of the Fe-zeolite and Cu-zeolite catalysts might achieve high NO conversions over a broader temperature range than the individual catalysts.

A few literature studies considered such combined Fe- and Cu-zeolite systems [10–13]. Metkar and co-worker [10,11] studied the combined Fe- and Cu-zeolite monolithic catalysts. The Fe/Cu dual layer catalyst exhibited superior performance for the SCR reaction. Krocher and Elsener [12], who studied double bed catalytic reactors for the SCR reaction, have found that a Fe-zeolite section followed by a Cu-zeolite bed gives higher NO conversion efficiencies. Girard et al. [13] carried out similar studies on combinations of Fe- and Cu-zeolite monolith. They found that the series combinations of (33%) Fe-zeolite followed by (67%) Cu-zeolite gives the highest NO reduction efficiency throughout the studied temperature range. Similar studies on the series of the Fe and Cu-zeolite catalysts with different individual catalyst lengths were carried out by Theis and McCabe [14]. The approach of the combining of two or more distinct catalysts to achieve the improved performance has been considered in the other reaction systems [15][e.g. 15]. The other studies [16][e.g. 16] reported the use of the so-called dual layer monolithic catalysts for SCR of NO with hydrocarbons (e.g. propene) as reducing agents.

Even though the previous studies showed improvements in NO conversion over the Cu and Fe co-exchanged catalysts [10–16], the effect of the preparation method and state of transition metal present in the zeolite structure is not well documented. Usually, transition metal ions are introduced in the extra-framework position of the zeolite structure by ion exchange method. The objective of the earlier studies [10–16] was to determine if the dual-layer Fe/Cu zeolite catalysts can exhibit improved performance for lean NO reduction. Examination of various combinations of the sequential brick and dual layer catalysts was deeply investigated [10,11]. The general aim of the earlier studies [10,11,16] was to systematically vary the lengths of the Fe- and Cu-zeolite monoliths in order to identify superior axial configurations, along the lines of the pioneering studies of Ford Motor Company [17].

Unfortunately, there are only few recent reports that have been focused on the single layer Fe/Cu-catalysts in SCR–NO using NH₃ as a reducing agent. It is worth to note that zeolite containing simultaneously two metal cations was attempted for broadening of the NO conversion temperature window [10,11]. Even though, the previous studies showed improvements in NO conversion over the Cu and Fe co-exchanged catalyst, the effect of variation of Cu/Fe ratio and preparation method is still not well documented.

Thus, in contrast to the previous studies [10,11,16][e.g. 10,11,16], in which the dual layer catalysts were thoroughly investigated, our approach is to obtain single zeolite containing simultaneously two metal cations (Cu and Fe) by two-step postsynthesis and conventional wet impregnation procedures. As it was earlier shown [18,19] for iron and copper, it is possible to control the incorporation of Fe or Cu into the framework of BEA zeolite using the two-step postsynthesis method. The catalytic activities of FeCuSiBEA and FeCuHAiBEA in SCR–NO with ammonia were compared with the single metal (Fe or Cu) catalysts. The speciation of transition metals in FeCuSiBEA and FeCuHAiBEA zeolites was determined in order to evidence a “structure-properties” relationship in the selective catalytic reduction of NO with NH₃.

2. Experimental

2.1. Materials

Two series of Cu and/or Fe-containing zeolites were prepared by two-step postsynthesis and conventional wet impregnation procedures. Fe_xSiBEA, Cu_xSiBEA and Fe_xCu_xSiBEA zeolites (where $x = 1.0$ wt% of Fe or Cu, respectively) were prepared by the two-step postsynthesis procedure reported earlier [18,19]. In the first step, 2 g of HAiBEA zeolite, obtained by calcination in air at 823 K for 15 h of tetraethylammonium form of BEA (TEABEA) zeolite (Si/Al = 12.5), provided by RIPP (China) was treated with 13 mol L⁻¹ HNO₃ solution under stirring (4 h, 353 K) to remove aluminium from the zeolite structure. In the second step, 2 g of resulting SiBEA (Si/Al = 1000) obtained after filtration were dispersed in aqueous solutions (pH 2.5) containing 1.8×10^{-3} mol L⁻¹ of Fe(NO₃)₃·9H₂O and/or 1.5×10^{-3} mol L⁻¹ of Cu(NO₃)₂·3H₂O and stirred at room temperature for 24 h. Then, the obtained suspensions were stirred in evaporator under vacuum of a water pump in air at 353 K for 2 h until water was evaporated. The solids with the iron or copper content of 1.0 wt% were labelled as Fe_{1.0}SiBEA, Cu_{1.0}SiBEA and Fe_{1.0}Cu_{1.0}SiBEA, respectively.

Fe_xHAiBEA, Cu_xHAiBEA and Fe_xCu_xHAiBEA zeolites (where $x = 1.0$ wt% of Fe or Cu, respectively) were prepared by conventional wet impregnation method. Firstly, NH₄AlBEA was calcined in air at 773 K for 3 h to obtain the acidic form of BEA zeolite (HAiBEA). Secondly, 2 g of HAiBEA were dispersed in aqueous solutions (pH 3.0) containing 1.8×10^{-3} mol L⁻¹ of Fe(NO₃)₃·9H₂O and/or 1.5×10^{-3} mol L⁻¹ of Cu(NO₃)₂·3H₂O and stirred at room temperature for 24 h. Then, the suspensions were stirred in evaporator under vacuum of a water pump in air at 353 K for 2 h until water was evaporated. The solids with iron or copper content of 1.0 wt% were labelled as Fe_{1.0}HAiBEA, Cu_{1.0}HAiBEA and Fe_{1.0}Cu_{1.0}HAiBEA, respectively.

2.2. Techniques

The structure of the studied samples was determined by powder X-ray diffraction. Diffraction patterns were obtained by a PW 3710 Philips X'pert (Philips X'pert APD) diffractometer using Ni-filtered Cu K α radiation ($\lambda = 1.54056$ Å). The measurements were performed in the range of 2θ from 5 to 50° with a 0.02° step.

Textural properties of the samples were determined by adsorption of nitrogen at 77 K using a Micromeritics ASAP 2010 apparatus. Prior to nitrogen adsorption all the samples were outgassed, first at room temperature and then at 623 K. The specific surface areas were determined from nitrogen adsorption isotherms in the relative pressure (P/P_0) ranging from 0.05 to 0.16 using BET method, while the micropore volume was determined from the P/P_0 below 0.2.

The DR UV–vis spectra were recorded using an Evolution 600 (Thermo) spectrophotometer. The measurements were performed in the range of 200–800 nm with a resolution of 2 nm. DR UV–vis spectroscopy was applied to determine chemical nature of iron and/or copper species in the zeolite structure.

Hydrogen temperature-programmed reduction (TPR) was carried out in a flow of 5% of H₂ in Ar (25 mL min⁻¹). The sample was placed in a quartz microreactor and the quantitative consumption of H₂ from 300 to 1120 K (7.5 K min⁻¹) was monitored by a TCD detector.

2.3. Catalytic tests

Fe_{1.0}SiBEA, Cu_{1.0}SiBEA, Fe_{1.0}Cu_{1.0}SiBEA, Fe_{1.0}HAiBEA, Cu_{1.0}HAiBEA and Fe_{1.0}Cu_{1.0}HAiBEA were studied as catalysts for SCR of NO with ammonia. Catalytic experiments were performed in a fixed-bed flow microreactor system. The reactant

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