



Communication

Improvement of low-temperature catalytic activity over hierarchical Fe-Beta catalysts for selective catalytic reduction of NO_x with NH₃Na Zhu^{a,b,1}, Zhihua Lian^{a,1}, Yan Zhang^{a,c}, Wenpo Shan^{a,c,*}, Hong He^{a,b,c,d}^a Center for Excellence in Regional Atmospheric Environment and Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China^b University of Chinese Academy of Sciences, Beijing 100049, China^c Ningbo Urban Environment Observation and Research Station-NUEORS, Institute of Urban Environment, Chinese Academy of Sciences, Ningbo 315800, China^d State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

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ABSTRACT

Hierarchical Fe-Beta obtained by hydrothermal synthesis exhibited higher low-temperature NH₃-SCR activity than conventional Fe-Beta. In order to identify the main factors leading to the difference in catalytic activity, we investigated the pore structure, acidity and Fe sites of the hierarchical Fe-Beta and conventional Fe-Beta. The enhanced activity of hierarchical Fe-Beta was mainly due to the increase of the quantity of active Fe species. NH₃-TPD and DRIFTS results of NH₃ adsorption clearly verified that hierarchical Fe-Beta had more Lewis acid sites, which is beneficial to the adsorption and activation of NH₃. The H₂-TPR, UV-vis DRS, and EPR results confirmed that the hierarchical Fe-Beta had more isolated active Fe species, which may be associated with that the hierarchical structure introduced more structural defects as ion-exchange sites. Based on the analysis of kinetics experiments and the above-mentioned characterizations, it can be concluded that the improvement of NH₃-SCR activity was not due to an intrinsic effect of the specific structural characteristics, but was related to more Fe active sites and better dispersion of Fe species in the hierarchical Fe-Beta.

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Iron-based zeolites (mostly Fe-ZSM-5 and Fe-Beta) have been extensively investigated because of their high activity and thermal stability for the selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) [1–6]. Compared with ZSM-5, Beta zeolite is an attractive host for iron and Fe-Beta zeolite has higher activity than Fe-ZSM-5 in some catalytic reactions [7,8]. Many studies focused on Fe-Beta catalysts for N₂O decomposition [8–11] and NH₃-SCR, especially on the active sites and hydrothermal stability [1,12,13]. Previous studies suggested that the low-temperature NH₃-SCR activity of Fe-Beta could be enhanced by bimetallic doping (such as Cu [14], Mn [15], Ce [16,17]) and high-temperature H₂-pretreatment [2,6].

Hierarchical zeolites contain both micro and meso-/macrospores, which can eliminate diffusion limitations and promote the

accessibility of reactants to the active sites [18–21]. The predominant approach for the synthesis of hierarchical structure zeolites is demetallation (desilicization and dealumination) and recrystallization with the surfactants [19,22]. Previous studies suggested that NH₃-SCR activity was enhanced by introducing hierarchical structure to Fe-ZSM-5 [23,24]. However, there are few open literatures about hierarchical Fe-Beta for NH₃-SCR.

In this work, hierarchical Fe-Beta zeolites catalysts were prepared by hydrothermal synthesis and evaluated for NH₃-SCR. The preparation procedure and activity tests are shown in the Support information. It was found that the low-temperature activity of hierarchical Fe-Beta was higher than that of Fe-Beta. The structure and activity relationship was discussed in detail.

As shown in Fig. 1, it was clear that the Beta was active for the SCR reaction in a narrow temperature range of 375–500 °C. Acidity may account for its catalytic performance [25,26]. Hierarchical Beta zeolite showed obviously improved NO conversions in the whole temperature range. This result indicated that hierarchical Beta zeolite may have more acid sites than Beta, which will be verified in the subsequent NH₃-TPD and NH₃ adsorption sections. After the doping of Fe, the Fe-Beta and hierarchical Fe-Beta indicated highly

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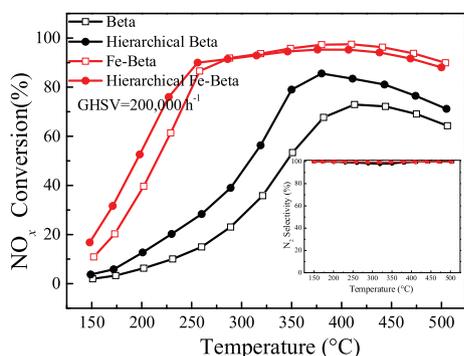


Fig. 1. NO_x conversion and N_2 selectivity (inserted) results of Fe-Beta and Beta catalysts. Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 500$ ppm, $[\text{O}_2] = 5$ vol%, N_2 balance and $\text{GHSV} = 200,000 \text{ h}^{-1}$.

improved SCR activity as compared with Beta and hierarchical Beta in the whole temperature of 150–500 °C. Hierarchical Fe-Beta showed enhanced low-temperature SCR activity compared with Fe-Beta obtained using the same ion-exchanged procedure. All of these catalysts presented excellent N_2 selectivity. The relationship of structure and activity was discussed in detail as follows.

The XRD patterns (Fig. S1 in Supporting information) show that all samples are phase-pure zeolites with the BEA framework structure. The peak intensity of Fe-Beta and hierarchical Fe-Beta declined, which may be due to the collapse or blocking of the partial micropore of zeolite. FeO_x species were not detected, which may be due to the Fe species existing as amorphous or high dispersion on the zeolite support [27,28].

The textural properties in Table S1 and Fig. S2 (Supporting information) show that the total volume, external surface area and BET surface area of hierarchical Beta are larger than those of Beta, indicating that mesopores and/or macropores are introduced into Beta to form hierarchical structure [19,20]. After doping with Fe, the BET surface area of both Fe-Beta and hierarchical Fe-Beta decreased, indicating that the partial micropore may be blocked, in agreement with the XRD results. ICP analysis revealed that the Fe content of Fe-Beta and hierarchical Fe-Beta was 2.82% and 3.71%, respectively, suggesting that hierarchical Fe-Beta could achieve a large amount of iron at the exchange sites under the identical ion-exchange procedure.

Comparing TEM images of hierarchical Fe-Beta (Figs. S3c and d in Supporting information) with those of Fe-Beta (Figs. S3a and b in Supporting information), the smaller crystal size and some hollow Beta structure were obtained during the hydrothermal synthesis, indicating the formation of micro-macroporous structure. This result is in accordance with the BET results. In Fig. S3c, the hollow zeolite was made of a polycrystalline micro-mesoporous shell and macropore core. Previous studies suggested that hollow Beta single crystals were much more difficult to prepare [18]. The absence of Al zoning prohibited the use of the dissolution-recrystallization strategy employing in the synthesis of hollow Beta zeolite single crystals [29].

UV-vis DR spectroscopy is an effective and common method for determining the nature and distribution of Fe species in Fe-zeolites. Fig. S4a (Supporting information) shows the UV-vis DR spectra of the Fe-Beta samples. The spectra were deconvoluted into sub-bands, which can be attributed to specific Fe species in the Fe-zeolites. The bands at 211 and 277 nm were respectively assigned to isolated Fe^{3+} ions in tetrahedral and octahedral coordination environments [30]. The bands at 300–400 nm indicated the presence of small oligomers $\text{Fe}_x^{3+}\text{O}_y$ in the zeolite channels [8,28], and the adsorption bands above 400 nm were attributed to the presence of bulky Fe_2O_3 nanoparticles on the external surface of the zeolite [31,32]. Fig. S4b (Supporting information) shows the UV-vis DR spectra of hierarchical Fe-Beta samples, the peak attributions are similar to Fe-Beta samples. The

amount of Fe species was estimated semi-quantitatively based on the relative intensities of these sub-bands derived from UV-vis DR spectra and the total Fe loading in the zeolite. The data in Table S2 in Supporting information shows that isolated Fe^{3+} ions are the predominant species in Fe-Beta and hierarchical Fe-Beta catalysts. Previous studies suggested isolated Fe^{3+} species are active sites for NH_3 -SCR on Fe-Beta catalysts [4,5,25,33,34]. When the Fe loadings were considered, the hierarchical Fe-Beta had the larger content of isolated Fe^{3+} species than Fe-Beta, resulted in the enhanced NH_3 -SCR performance.

EPR spectroscopy was further employed to identify the nature of different Fe species, the corresponding results are illustrated in Fig. S5 (Supporting information). Signals at $g=2.0$, $g=4.3$ and $g=8.8$ were observed for Fe-Beta and hierarchical Fe-Beta. The signals at $g=4.3$, $g=8.8$ and $g=2$ were generally attributed to isolated Fe species in tetrahedral and distorted tetrahedral coordination [30,35], isolated Fe species with a distorted octahedral environment [8,13] and isolated Fe species in a high symmetry octahedral coordination or oligonuclear Fe_xO_y clusters [8,28], respectively. Overall, the EPR signal intensity of hierarchical Fe-Beta was higher than Fe-Beta, illustrating the amount of isolated Fe species on hierarchical Fe-Beta was higher than that of Fe-Beta, in agreement with UV-vis DRS results.

In order to investigate the redox performance of the samples, the H_2 -TPR experiments were conducted and the results are shown in Fig. 2. There is no clear H_2 consumption signal for the Beta and hierarchical Beta. Two reduction peaks appeared on the Fe-Beta and hierarchical Fe-Beta. The overlapped reduction peaks centered at 354 °C (369 °C) and 441 °C (499 °C) were attributed to the reduction of isolated Fe^{3+} to Fe^{2+} [36] and oligomeric iron oxo species or tiny Fe_2O_3 into Fe_3O_4 , respectively [37–39]. The reduction temperature of Fe species over hierarchical Fe-Beta was lower than Fe-Beta, which may be due to the better dispersion of Fe species. The amount of H_2 consumption of hierarchical Fe-Beta was larger than Fe-Beta, indicating that hierarchical Fe-Beta catalyst had more Fe active sites. The better redox performance resulted in the enhanced NH_3 -SCR activity on the hierarchical Fe-Beta.

In view of the analysis of UV-vis DRS, EPR and H_2 -TPR results above, we have confirmed that more Fe active species existed on the hierarchical Fe-Beta and dispersed better than those on Fe-Beta, which may be due to the specific hierarchical structure.

To identify the strength of the acid sites of hierarchical Fe-Beta, the NH_3 -TPD experiments were carried out and the results are shown in Fig. 3. Beta zeolite showed NH_3 desorption peaks at the range of 100–500 °C, assigning to the desorption of ammonia species from weak Lewis acid sites (167 °C), strong Lewis acid sites (262 °C and 330 °C) and strong Brønsted acid sites (373 °C) [25,37,40]. The intensity of the desorption peak at 262 °C was much stronger than that of peak at 373 °C, suggesting that Beta zeolite had more Lewis acid sites because of its structural defects caused by the unsaturated bonding of silicon [41,42]. When

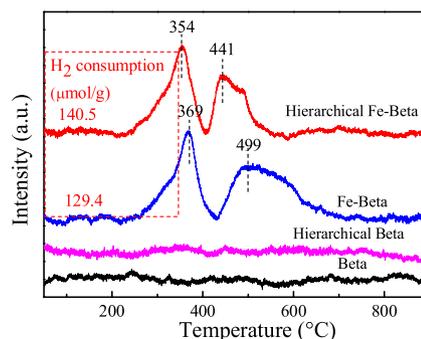


Fig. 2. H_2 -TPR results of the different Beta samples.

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