Iron-substituted *BEA zeolite for reduction of NO with NH_3

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Introduction

Selective catalytic reduction (SCR) by ammonia is one of the promising techniques to reduce the emission of NOx from diesel engines[1]. Iron- or copper-exchanged zeolites are widely used as the catalysts for SCR. Iron zeolites show better performance at high temperatures, and the catalytic activity is greatly affected by NO/NO_2 in the gaseous stream. On the other hand, copper zeolites can remove NOx efficiently at temperatures below 200°C, even in the absence of NO_2. However, the main disadvantage of copper zeolites such as Cu/SSZ-13 is their high cost[2].

We developed a novel iron-substituted zeolite with a *BEA structure (Fe-BEA), which can overcome the disadvantages of conventional iron-exchanged zeolites for SCR. Material characterization was carried out by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analyses. Fe-BEA exhibited excellent catalytic activity at temperatures below 300°C after 20 h of hydrothermal aging at 700°C.

Materials and Methods

Fe-BEA was synthesized by the following method. Sodium silicate (SiO_2 30%, Na_2O 9.1%, Al_2O_3 0.01%), 98% sulfuric acid, water, and iron nitrate nonahydrate were used to prepare the precursor gel. 35%TEAOH, 48% NaOH, water, and commercial beta seeds were added to the gel with stirring. The composition of the reaction mixture was $67SiO_2$:Fe_2O_3:$0.031Al_2O_3$:$13.3Na_2O$:10TEAOH:$667H_2O$. The mixture was transferred to 80-ml stainless-steel autoclaves and heated at 170°C with rotation. After the reaction, the solid content was filtered, washed, and dried at 110°C overnight.

SCR of NO with ammonia was carried out at 150°C–500°C in a fixed bed flow reactor, using 1.5 ml of pelletized, crashed, and sieved catalyst under a gas hourly space velocity (GHSV) of 60,000 h^{-1}. The following gasous composition was used: 200 ppm NO, 200 ppm NH_3, 10% O_2, 3%H_2O, balance N_2. Prior to the reaction, the samples were calcined under flowing air for 2 h at 600°C in order to remove the organic structure-directing agent. Hydrothermal aging was carried out in air flow with 10 vol% H_2O at 700°C for 20 h, with a GHSV of 6,000 h^{-1}.

Results and Discussion

The results of powder XRD analysis indicate that the as-synthesized Fe-BEA has the *BEA phase with no impurities. From elemental analysis, the Si/Al_2 and Si/Fe_2 molar ratios are found to be 720 and 23, respectively. The iron content of Fe-BEA reaches 7.3 wt%, which to the best of our knowledge, is the highest amount of isomorphously substituted iron in the *BEA structure reported thus far. The sample is white to off-white in color, suggesting that the iron atoms are completely incorporated in the *BEA framework.

Figure 1 shows the SEM image of Fe-BEA. Although no fluorine is used in the current synthesis, the Fe-BEA crystals have a well-defined truncated square bipyramidal shape, which is typically observed in the case of beta zeolites synthesized using fluorine[3].

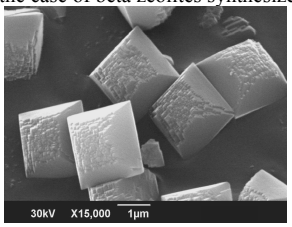

Figure 1. SEM image of Fe-BEA.

Figure 2 shows the SCR result for Fe-BEA in comparison with the conventional Fe ion exchanged beta zeolite prepared from commercial beta. Fe-BEA exhibits excellent catalytic activity, especially at temperatures below 300°C. Even after hydrothermal aging, the NOx conversion at 200°C observed with Fe-BEA is twice that observed with the aged conventional Fe/beta. The extremely rich iron content and high crystallinity of Fe-BEA are considered to be the main factors for the high conversion.

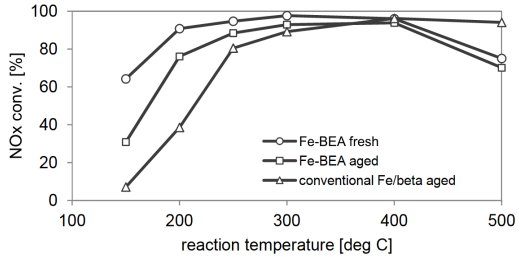

Figure 2. SCR results for fresh Fe-BEA, Fe-BEA calcined at 600°C, and Fe-BEA hydrothermally aged at 700°C for 20 h. Results for conventional Fe/beta are shown for comparison.

Significance

Novel iron-substituted *BEA zeolite was developed and demonstrated to be a highly active catalyst for the NH_3-SCR reaction. The extremely rich iron content and high crystallinity of this zeolite appear to be the key properties responsible for its high catalytic activity.

References

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