Seed-assisted solvent-free synthesis of Cu-SSZ-13 with high hydrothermal stability for NH_3 selective catalytic reduction of NOx

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Abstract: H-SSZ-13 seeds were utilized to synthesis relatively high Si/Al (~10) ratio and economical Cu-SSZ-13 zeolite catalysts via a solvent-free method with increasing the degree of crystallinity. This zeolite catalyst showed superior NH_3-SCR performance and outstanding hydrothermal stability due to the more hydrothermally stable Cu^{2+} species located in the D6R cages of the chabazite structure compared to the commercial Cu-SSZ-13 catalysts. The results showed that the Cu-SSZ-13 catalyst prepared by seed-assisted solvent-free method is a promising alternative candidate for actual implementations in diesel engines.

Keywords: NH_3-SCR of NOx, Cu-SSZ-13, Solvent-free synthetic method

1. Introduction

Recently, Cu^{2+} ion-exchanged SSZ-13 (Cu-SSZ-13), a zeolite with the chabazite (CHA) structure, has attracted much attention due to its high deNOx activity and excellent hydrothermal stability in the NH_3-SCR reaction.[1-2] The tradition method of synthesizing SSZ-13 zeolite was first reported by Zones with using an expensive structure-directing agent, N,N,N-trimethyl-1-adamantammonium hydroxide (TMAdaOH)[3]. Then, Cu-SSZ-13 samples are obtained by complex ion exchange procedures. The one-pot synthesis method is a relatively simple way to preparing Cu-SSZ-13, in which copper species can be directly introduced into the CHA cages by using a low cost template copper-tetraethylenepentamine (Cu-TEPA) [4] However, the low Si/Al (~4) of the one-pot synthesized Cu-SSZ-13 limited its hydrothermal stability. Here, a SSZ-13 with higher Si/Al (~10) was prepared by an improved solvent-free method by using economical organic template N,N,N-dimethylethylcyclohexylammonium bromide (DMCHABr) [5]. The NH_3-SCR performance and hydrothermal stability of the solvent-free synthesized Cu-SSZ-13 catalysts were investigated and compared with commercial Cu-SSZ-13 catalysts. The change of framework structure and Cu^{2+} species were also detected after hydrothermal aging (HTA) by XRD, ^{27}Al-NMR, EPR, H_2-TPR and in situ DRIFTS.

2. Experimental

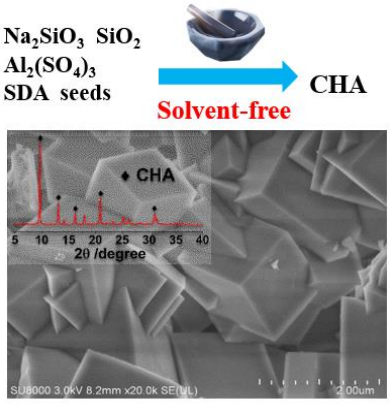

Figure 1. Synthetic method, XRD profiles and SEM image.

H-SSZ-13 zeolites were added as seeds and the initial ratios are Na_2O/SiO_2 (0.22), SiO_2/Al_2O_3 (24), DMCHABr/SiO_2 (0.14) and seeds/catalyst (H-SSZ-13, 5 wt.%). The raw materials were finely ground and transferred to an autoclave with crystallization for 5d at 180 °C. Cu-SSZ-13 catalysts with different Cu loadings were obtained by ion exchange with $Cu(NO_3)_2$ solution (0.1 mol/L). For comparison, the commercial Cu-SSZ-13 catalysts with similar Si/Al (~10) and Cu loadings were also obtained. The obtained catalysts were denoted as Cux-SSZ-13 and commercial-Cux-SSZ-13, where x represents the Cu loadings (wt.%).

The NH_3-SCR reaction conditions were as follows: 500 ppm NO, 500 ppm NH_3, 5 vol.% O_2, balance N_2, and GHSV of 400, 000 h^{-1}. The hydrothermal aging (HTA) conditions: the catalysts were hydrothermally aged by the air with 10 vol.% H_2O at 800 °C for 16h.

3. Results and discussion

As shown in **Figure 1**, the solvent-free synthesized SSZ-13 zeolite showed typical diffraction peaks of CHA structure with pure phase and high degree of crystallization. SEM image showed that the synthesized SSZ-13 exhibited a regular cubic morphology with particle size of 1-2 μm.

The solvent-free synthesized $Cu_{2.8}$-SSZ-13 catalysts showed superior NOx conversion activity to the commercial-$Cu_{2.7}$-SSZ-13 catalysts before and after hydrothermal treatment (**Figure 2**). A better hydrothermal stability of the solvent-free synthesized Cu-SSZ-13 catalysts was confirmed according to the results of the catalysts with various Cu loadings (not shown here). In addition, the optimized solvent-free synthesized Cu-SSZ-13 catalysts showed high tolerance to H_2O and SO_2 poisoning (not shown here).

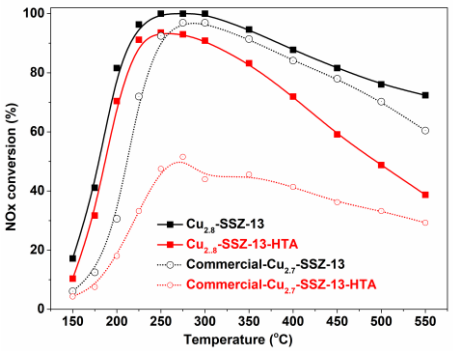

Figure 2. NOx conversion in the NH_3-SCR reaction over the seed-assisted solvent-free synthesized Cu-SSZ-13 catalysts and commercial Cu-SSZ-13 catalysts.

The XRD patterns of the fresh and HTA Cu-SSZ-13 catalysts synthesized by different methods are shown in **Figure 3a**. After hydrothermal aging, both types of Cu-SSZ-13 samples maintained the typical CHA peaks, and only a slight decrease in peak intensity was observed. The H_2-TPR profiles (**Figure 3b**) showed that the Cu^{2+} species of solvent-free synthesized Cu-SSZ-13 were more stable than those of commercial Cu-SSZ-13 catalysts after hydrothermal aging. Many studies have proved that the damage of zeolite framework structure and CuOx clusters from the accumulation of Cu^{2+} species were the primary reasons for the deactivation of Cu-SSZ-13 catalysts during the process of hydrothermal aging. Therefore, based on the XRD and H_2-TPR results, it indicates that the better hydrothermal stability of the solvent-free synthesized Cu-SSZ-13 was mainly attributed to the higher stability of Cu^{2+} species compared to the commercial Cu-SSZ-13.

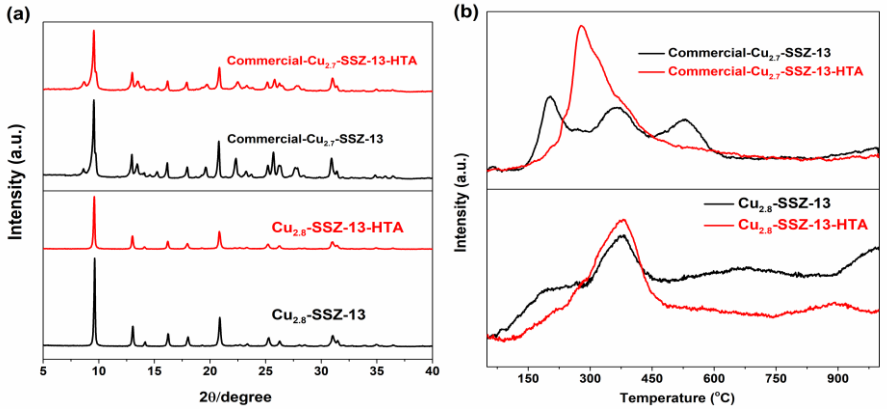

Figure 3 (a) XRD patterns and (b) H_2-TPR profiles of synthesized and commercial Cu-SSZ-13 catalysts

4. Conclusions

The SSZ-13 zeolites with Si/Al (~10) were obtained with an improved solvent-free method by adding seeds. The Cu^{2+} ion-exchanged SSZ-13 catalysts showed outstanding NOx activity and high hydrothermal stability. Compared to the commercial Cu-SSZ-13 catalysts, the Cu^{2+} species of the solvent-free synthesized Cu-SSZ-13 were more stable after hydrothermal aging, resulting in a better hydrothermal stability. Therefore, the improved solvent-free method is suggested to be an outstanding candidate for synthesizing Cu-SSZ-13 catalysts with high activity and hydrothermal stability.

References

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