An economical way to synthesize SSZ-13 for an extraordinary performance in Selectively Catalytic Reduction (SCR) of NOx by ammonia

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Introduction

The removal of nitrogen oxides (NOx) coming from auto exhausts has drawn more attention in the past decades because NOx are known to cause lots of environmental problems such as acid rain and photochemical smog in the urban and industrial areas[1]. Series of legislations were established in Europe, United States, and Japan. NOx containing in the exhausts are expected to be reduced to a very limited level. Owing to these increasingly stringent environmental regulations, it becomes urgent to develop the new techniques aiming at the highly efficient auto-emission purification.

SSZ-13 zeolite, a CHA-type aluminosilcate, was verified to be a suitable candidate to develop the promising catalysts for NH_3-SCR of NO reaction[2,3]. However, the conventional method to synthesize the SSZ-13 zeolite involving the use of a very expensive template (N,N,N-trimethyl-1-1-adamantammonium hydroxide)[4]. In this work, an economical way for SSZ-13 preparation was attempted. The as-synthesized SSZ-13 zeolite after ion exchange by copper nitrate solution exhibited a superior SCR performance than the traditional commercial zeolitic catalysts of Cu-Beta and Cu-ZSM-5.

Materials and Methods

SSZ-13 zeolite was presently synthesized by the hydrothermal method with a low cost SDA: choline chloride. H-ZSM-5 ($SiO_2/Al_2O_3 \approx 26$) and H-BEA ($SiO_2/Al_2O_3 \approx 30$) are commercial zeolites (The Novel Zeolites Co.). Cu-zeolites (Cu-ZSM-5, Cu-BEA, Cu-SSZ-13) with ~5wt.% metal loading were prepared via the ion-exchange method. The Cu-zeolites were characterized by XRD, XRF, XPS and H_2-TPR.

Activity measurement was performed in a quartz fixed-bed reactor (0.6 cm i.d.) loading with ~ 0.2 g catalyst under a typical reaction atmosphere of 1000 ppm NO, 1000 ppm NH3 and 6 vol% O_2, balanced by He (corresponding to a gas hourly space velocity of ~50,000 h-1). The effluent gases (NH_3, N_2O, NO and NO_2) were monitored using an infrared gas analyzer (Nicolet Nexus 670) equipped with a 2.4 meter long-path gas cell and TQ analysis software. N_2 concentration was determined using a gas chromatograph (GC, HP5890) equipped with TCD for quantification and combined columns of 5A and TDX-01 for separation.

Results and Discussion

Table 1.BET surface area, pore structures and chemical composition of different zeolites.

Catalysts	Typology	SiO_2/Al_2O_3 Ratio[a]	Cu loading/ wt%[a]	S_{BET}/ m^2g^{-1}	Micropore volume/ cm^3g^{-1}
H/SSZ-13	CHA	12.56		603	0.30
Cu-SSZ-13			4.93	562	0.29
H/ZSM-5	MFI	26.87		325	0.19
Cu-ZSM-5			5.04	286	0.18
H/BEA	BEA	31.53		435	0.21
Cu-BEA			4.95	354	0.19

a. The number are determined by XRF technology.

Table 1 shows the BET surface area, pore structure and chemical composition of the zeolite-based catalysts. It is clear that H-SSZ-13 has the biggest BET surface area (647 m^2/g) and the lowest ratio of SiO_2/Al_2O_3 (12.56) among the investigated samples. Three Cu-zeolites samples have the similar copper loading, which are close to the nominated value (5 wt.%), as evidenced by XRF. The catalytic activities for NH3-SCR of NOx over Cu-zeolites (Cu-ZSM-5, Cu-BEA, Cu-SSZ-13) are illustrated in **Figure 1**. More than 90% NOx conversion was achieved at around 250 °C. Cu-SSZ-13 exhibits a superior activity (NOx conversion > 90% at a relatively wide-temperature range of 150-400 °C) than Cu-ZSM-5 and Cu-BEA at either low temperatures (<200 °C) or high temperatures (>400 °C). Apart from NOx conversion, the conversion of NH_3 as well as the generation of NO_2 and N_2O by-products during NH_3-SCR reaction was also studied. The Cu-SSZ-13 exhibits the best performance among the three samples in all the investigated aspects.

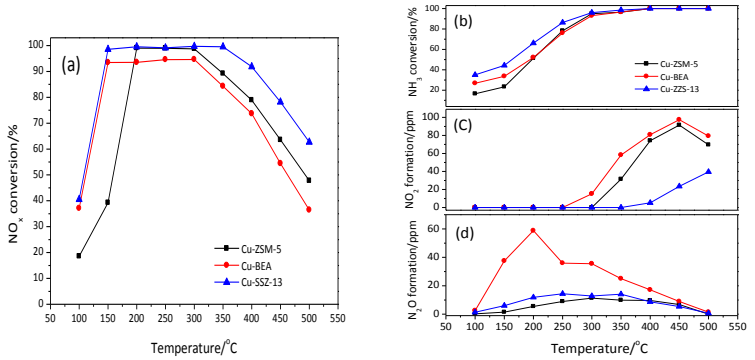

Figure 1. The catalytic activities profiles for NH_3-SCR of NOx over Cu-zeolites(ZSM-5, BEA, SSZ-13).(a)NOx conversion, (b) NH_3 conversion (c) NO_2 formation, (d) N_2O formation. Reaction condition: 0.200g catalyst, 1000ppm NH_3, 1000ppm NO, 6%O_2 and balance He, GHSV=~50,000h^{-1}.

Significance

We synthesized the SSZ-13 zeolite with an economical template.
The Cu-SSZ-13 catalyst exhibits higher activity and better selectivity compared to the commercial ZSM-5 and Beta zeolites.
Our study disclosed the relationship among Cu species, zeolite structure and NH_3-SCR activity.

References

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