Facile synthesis of KFI-type zeolite for NH_3-SCR reaction

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Abstract: The small-pore KFI-type zeolite was prepared by the hydrothermal conversion of zeolite Y without using organic structure-directing agent (OSDA). The effects of Na^+, K^+ and hydroxide ion on the formation of KFI were investigated by introducing both hydroxide and nitrate salts into synthesis media. The zeolite KFI synthesized at the optimized condition was copper ion-exchanged, and then applied for selective catalytic reduction of NOx with NH_3 (NH_3-SCR) reaction. After severe hydrothermal aging at 800 °C for 16 h, Cu-KFI substantially maintained structural integrity, which is remarkably stable compared with Cu-Chabazite synthesized from organic-free media. The NH3-SCR activity of Cu-KFI catalyst was comparable to that of Cu-SSZ-13 even after hydrothermal aging.

Keywords: Zeolite, Cu-KFI, NH_3-SCR.

1. Introduction

KFI-type zeolite is a small-pore zeolite (pore size = 0.39 nm) which contains lta and pau cage. It has been reported that the KFI-based materials show high activity for the separation of CO_2/N_2 or CO_2/CH_4 mixture gases. Selective catalytic reduction of NO_x with NH_3 (NH_3-SCR) is a well-established technology for reducing NOx from diesel engine exhaust. Recently, small pore zeolite-based catalysts such as Cu-SSZ-13, Cu-SSZ-39, Cu-LTA have brought great attention for NH_3-SCR reaction due to great activity and hydrothermal stability.[1-3] However, the use of organic agents is essential for the synthesis of these catalysts, which is economically and environmentally less favorable. Previously, Cu-Chabazite synthesized from organic-free media was studied for NH_3-SCR but it did not resist the hydrothermal aging at 700 °C. In this study, pure and highly crystalline KFI zeolite was synthesized and applied for NH_3-SCR reaction.

2. Experimental

In a typical synthesis (i.e. standard condition), 1.72 g of $NaNO_3$, 5.11 g of KNO_3, and 4.15 g of 1 M NaOH solution were added to 11.1 g of deionized water in 40 ml Teflon cup. After mixing to dissolve all salts for 1 h, 0.50 g of calcined zeolite Y with the Si/Al_2 of 12 (CBV712) was added and stirred for about 1 min. The resulting mixture was transferred to a stainless steel autoclave and kept at 140 ºC for 3 days in a static oven. The batch composition of the standard condition was as follows: 1 SiO_2 : 0.083 Al_2O_3 : 3.3 Na^+ : 7 K^+ : 0.56 OH^- : 117 H_2O. Cu-KFI was prepared after ion-exchange in NH_4NO_3 followed by $Cu(NO_3)_2$ solution. Then, Cu-KFI was calcined at 550 ºC for 2 h in static air condition. The hydrothermal aging of Cu-KFI catalysts was carried out at 800 ºC for 16 h with 10% H_2O and 15% O_2. For the light-off test of NH3-SCR reaction, feed gas containing 500 ppm NO, 500 ppm NH_3, 8% O2, 5% H_2O and balanced with N_2 was introduced to 0.05 g of catalyst (GHSV=120,000 h^{-1}).

3. Results and discussion

KFI-type zeolite was synthesized using zeolite Y as a starting material and Na^+ and K^+ ions as structure-directing agents. It was found that K^+ ion plays major role for the formation of KFI structure, while both Na^+ and K^+ ions increase the crystallization rate of KFI. We also found that the formation of KFI structure is generally favored at low alkalinity condition. Depending on the synthesis condition such as the amount of Na^+, K^+ and OH^-, KFI zeolites with various Si/Al_2 ratio and crystallinity were obtained. The Cu-KFI catalyst was prepared after ion-exchange in NH_4NO_3 followed by $Cu(NO_3)_2$ solution. Figure 10(a) shows NO_x conversion of calcined Cu-KFI catalysts with different Si/Al_2 ratio and Cu loading. The conversion of all catalysts was almost 100% above at 250 °C. While below at 200 °C, the Cu-KFI with higher copper loading showed better NH_3-SCR activity. After hydrothermal aging at 800 °C for 16 h, the Cu-KFI catalysts still showed substantial activity for NH_3-SCR reaction, while some decrease in activity was observed due to severe aging condition (Figure 1(b)). The degree of the activity change was related to the Si/Al_2 ratio and crystallinity. The Cu-KFI(3) catalyst, which has higher Si/Al_2 ratio and crystallinity than Cu-KFI(2) catalyst, exhibited much higher NH_3-SCR activity after hydrothermal aging despite the same Cu loading. The results demonstrate that Cu-KFI can be used as alternative to Cu-SSZ-13.

Table 1. The Si/Al_2 ratio, Cu loading and crystallite size of Cu-KFI catalysts.

Catalyst	Si/Al_2 ratio	Cu loading (wt%)	Crystallite size (nm)
Cu-KFI(1)	7.5	6.4	57
Cu-KFI(2)	7.5	4.6	57
Cu-KFI(3)	8.3	4.6	94

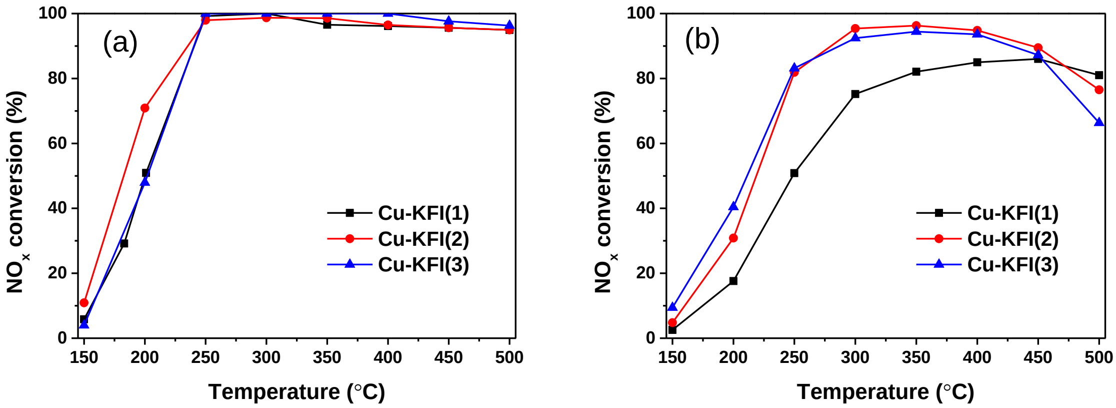

Figure 1. NH_3-SCR activity of Cu-KFI catalysts after calcination at 500 °C (a) and hydrothermal aging at 800 °C.

4. Conclusions

The KFI-type zeolite was synthesized by new method in the inorganic media using zeolite Y as starting material. The KFI zeolite was formed in the presence K^+ ion. The Cu-KFI catalyst showed remarkable NH_3-SCR activity even after severe hydrothermal aging. The activity of calcined Cu-KFI was determined by only copper loading, while the Si/Al_2 ratio and crystallinity greatly affected the hydrothermal stability of Cu-KFI catalyst.

References

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