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 NH$_3$-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 NOx 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 °C for 3 days in a static oven. The batch composition of the standard condition was as follows: 1 SiO$_2$ : 0.083 Al$_2$O$_3$ : 3.3 Na$^+$ : 7 K$^+$ : 0.56 OH$^-$ : 117 H$_2$O. Cu-KFI was prepared after ion-exchange in NH$_4$NO$_3$ followed by Cu(NO$_3$)$_2$ solution. Then, Cu-KFI was calcined at 550 °C for 2 h in static air condition. The hydrothermal aging of Cu-KFI catalysts was carried out at 800 °C for 16 h with 10% H$_2$O and 15% O$_2$. For the light-off test of NH$_3$-SCR reaction, feed gas containing 500 ppm NO, 500 ppm NH$_3$, 8% O$_2$, 5% H$_2$O 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\(_4\)NO\(_3\) 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>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al(_2) ratio</th>
<th>Cu loading (wt%)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-KFI(1)</td>
<td>7.5</td>
<td>6.4</td>
<td>57</td>
</tr>
<tr>
<td>Cu-KFI(2)</td>
<td>7.5</td>
<td>4.6</td>
<td>57</td>
</tr>
<tr>
<td>Cu-KFI(3)</td>
<td>8.3</td>
<td>4.6</td>
<td>94</td>
</tr>
</tbody>
</table>

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