Effects of post-treatment method and Na co-cation on the hydrothermal stability of Cu–SSZ-13 catalyst for the selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3}

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\textbf{A B S T R A C T}

Post-treatment with dilute HNO\textsubscript{3} solution after one-pot synthesis was an effective method to prepare excellent Cu–SSZ-13 catalysts for the selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3} (NH\textsubscript{3}–SCR). Using solutions with varying levels of acidity, catalysts with different Cu and Na contents were obtained, and the Cu\textsubscript{3.9}Na\textsubscript{0.8}–SSZ-13 catalyst showed the optimal NH\textsubscript{3}–SCR activity and hydrothermal stability. As co-cations, Na\textsuperscript{+} ions affected the hydrothermal stability of the one-pot-synthesized Cu–SSZ-13 catalysts greatly. Poorer hydrothermal stability was observed for catalysts with higher Na\textsuperscript{+} contents. The results of \textsuperscript{27}Al and \textsuperscript{29}Si NMR spectra proved that Na\textsuperscript{+} ions did not influence the Si/(NaAl) distributions in the catalysts significantly. However, \textsuperscript{H}\textsubscript{2}–TPR profiles indicated that excess Na\textsuperscript{+} ions in the catalysts decreased the stability of Cu species seriously. Thus, poor stability of Cu species caused by excess Na\textsuperscript{+} ions was the direct reason for the poor hydrothermal stability of the catalysts. Because of the negative effect on hydrothermal stability, excess Na\textsuperscript{+} ions should be avoided in Cu–SSZ-13 catalysts prepared by the one-pot synthesis method.

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1. Introduction

The combustion of fossil fuels in mobile power sources gives rise to nitrogen oxides (NO\textsubscript{x}), which are serious air pollutants. The three-way catalyst (TWC) is effective at removing hydrocarbons (HC), carbon monoxide (CO) and NO\textsubscript{x} simultaneously in gasoline engine exhaust [1,2]. Because the TWC is not effective for the removal of NO\textsubscript{x} from diesel engine exhaust under oxygen-rich conditions, various catalyst systems for lean NO\textsubscript{x} purification have been developed, such as lean NO\textsubscript{x} trap (LNT) technology and selective catalytic reduction (SCR) of NO\textsubscript{x} with reducing agents (e.g., NH\textsubscript{3}, urea, hydrocarbons) [3,4]. NH\textsubscript{3}–SCR is a well-established approach to remove NO\textsubscript{x} from diesel engine emission, using V\textsubscript{2}O\textsubscript{5}–WO\textsubscript{3}/TiO\textsubscript{2} or V\textsubscript{2}O\textsubscript{5}–MoO\textsubscript{3}/TiO\textsubscript{2} as typical catalysts. However, the narrow operation temperature window, high activity for oxidation of SO\textsubscript{2} to SO\textsubscript{3}, formation of N\textsubscript{2}O at high temperatures and the toxicity of active vanadium species limit the practical application of V-based catalysts for diesel vehicles [5–7]. Recently, metal-exchanged zeolite catalysts were reported as potential V-free catalysts for the NH\textsubscript{3}–SCR process of diesel vehicles. From the perspective of zeolites, some large and medium pore zeolites have received much attention in the past two decades, such as Y (FAU framework), Beta (BEA framework), and ZSM-5 (MFI framework). Cu and Fe have been the most widely used transition metal ions in NH\textsubscript{3}–SCR zeolite catalysts, owing to their good redox capacity [8,9]. Most of these catalysts show good NH\textsubscript{3}–SCR performance under high gas hourly space velocity (GHSV), which is crucial for their practical application in diesel vehicles with limited installation space on board [10–12]. Nowadays, diesel particulate filters (DPF) are widely used in diesel particulate emission control, and are often used in upstream of the SCR catalyst. The regeneration of DPF always exposes the SCR catalysts to high temperatures (>650 °C) with high moisture [13]. Thus, high hydrothermal stability is necessary for NH\textsubscript{3}–SCR catalysts. However, the ion-exchanged zeolite catalysts described above could not maintain good performance after hydrothermal aging treatment [14,15]. This weakness prevents those catalysts from being commercialized in real world applications.
Recently, the Cu–SSZ-13 catalyst with the chabazite (CHA) structure attracted much attention for NOx removal from diesel engine exhaust due to its excellent performance, hydrothermal stability and high resistance to small hydrocarbon molecules in the NH3–SCR reaction [16–20]. However, the template N,N,N-trimethyl-1-adamantanaminum hydroxide (TMAAdaOH) was needed in the synthesis of SSZ-13 zeolite, resulting in high cost for conventional Cu–SSZ-13 catalysts [21]. The one-pot synthesis method using copper–tetraethylenepentamine (Cu–TEPA) as a novel directing template decreased the synthesis cost greatly, which is beneficial for the wide use of Cu–SSZ-13 catalyst in industry [22]. Because the Cu loading in the initial Cu–SSZ-13 product resulting from one-pot synthesis was relatively high, a large amount of CuO formed in the untreated catalyst after direct calcination. Thus, a post-treatment procedure was necessary to adjust the Cu loading before calcination. It has been reported in our previous work that ion-exchange by NH4NO3 solution was effective in optimizing the Cu loading. The optimal Cu1.8–SSZ-13 catalyst showed very good NH3–SCR performance in the whole operation temperature range [23]. However, large amount of NH4NO3 was used with this method, and the wastewater from the process is aggravating the eutrophication of the aquatic environment. In this study, a new post-treatment method with dilute HNO3 solution was developed. Compared with the use of NH4NO3, this new method reduced the nitrogen-containing pollutants in wastewater greatly. The experimental results also proved that this new post-treatment method is also an effective way to prepare catalysts with better NH3–SCR performance.

As co-cations in zeolites, Na+ ions often influence the properties of active species and the zeolite support. Torre-Abreu et al. reported that Cu species were more easily reduced in Na+–form Cu–MOR catalysts than H+-form [24]. Sultana et al. reported that a higher amount of Cu+ species was present in the Na+ form of ZSM-5 than in H+-form ZSM-5, which could activate oxygen relatively easily [12]. They also reported a promoting effect of Na+ ions on the retardation of coke formation on Cu–ZSM-5 catalyst [25]. Fung and Hall [26] prepared Fe–ZSM-5 catalyst free of Brønsted acid with the ratio of (Na + Fe)/Al at ca. 1. The catalyst showed much improved hydrothermal stability, and did not show deactivation on aging in wet exhaust gas up to 800 °C [26]. In this study, a relatively large amount of NaOH was used in the synthesis procedure of the initial Cu–SSZ-13 sample, and some Na+ ions always remained in the catalyst even after post-treatment. However, the effects of the residual Na+ ions on the NH3–SCR performance and hydrothermal stability of this type of catalyst are still unclear. Thus, Cu–SSZ-13 catalysts with different Na+ contents were prepared in this study, and the results indicated that the catalysts with higher Na+ content showed poorer hydrothermal stability. Therefore, excess Na+ ions remaining in the catalyst should be avoided in the preparation of Cu–SSZ-13 by the one-pot synthesis method.

2. Experimental

2.1. Catalyst preparation

The initial Cu–SSZ-13 sample was prepared using the method reported previously [23]. In order to obtain suitable Cu loadings in the final catalyst, post-treatment with dilute HNO3 solution was used in this study. A suspension containing the initial sample and dilute HNO3 solution (pH 0, 1, 2, 4) was treated at 80 °C for 12 h. Then, all samples were filtered and washed with distilled water, and dried at 100 °C overnight. Finally, the exchanged samples were calcined at 600 °C with a ramp rate of 1 °C/min to remove residual templates. According to the results of ICP, all catalysts obtained above were denoted as Cu(Na)x–SSZ-13, where “x” and “y” represent the Cu content and Na content in the catalyst by weight, respectively.

In order to investigate the effect of Na+ ions on NH3–SCR performance over Cu–SSZ-13 catalyst prepared by the one-pot synthesis method, catalysts with the same Cu content and different Na contents were also prepared. The preparation procedure was as described below. The initial Cu–SSZ-13 sample was treated by 1 mol/L NaNO3 solution at pH 1 (adjusted using HNO3 solution) at 80 °C for 12 h. After the same procedure of washing and desiccation described above, half of the obtained sample was calcined directly, and the rest sample was stirred in 1 mol/L NaNO3 solution once more at 80 °C for 12 h before calcination. The calcination procedure and naming method for the two samples were the same as those described above.

In the hydrothermal aging studies, all catalysts were treated in flowing gas composed of air with 10 vol.% H2O at 750 °C for 16 h.

2.2. NH3–SCR activity test

The reaction conditions of SCR activity tests were controlled as follows: 500 ppm NO, 500 ppm NH3, 5 vol.% O2, 5 vol.% H2O (when used), balance N2, and 500 mL/min total flow rate. Catalyst samples (~50 mg) of 40–60 mesh size were used with gas hourly space velocity (GHSV) estimated as 400,000 h⁻¹. The effluent gas was continuously analyzed by an online NEXUS 670-FTIR spectrometer equipped with a heated, low volume (0.2 L) multiple-path gas cell (2 m). The FTIR spectra were collected throughout and the results were recorded when the SCR reaction reached a steady state. The NOx conversion and N2 selectivity were calculated as follows:

\[
\text{NOx conversion} = \left(1 - \frac{[\text{NO}]_{\text{out}} + [\text{NO2}]_{\text{out}}}{[\text{NO}]_{\text{in}} + [\text{NO2}]_{\text{in}}} \right) \times 100\
\]

\[
\text{N2 selectivity} = \frac{[\text{NO}]_{\text{in}} + [\text{NH3}]_{\text{in}} - [\text{NO2}]_{\text{out}} - 2[N2O]_{\text{out}}}{[\text{NO}]_{\text{in}} + [\text{NH3}]_{\text{in}}} \times 100\
\]

2.3. Catalyst characterization

The Cu contents of the catalysts were analyzed using an inductively coupled plasma instrument (OPTIMA 2000DV) with a radial view of the plasma. All samples were dissolved using strong acid solution before testing. The calibration solution was prepared using pure materials. The average of three atomic emission lines was used to determine the Cu contents in the catalysts.

Powder X-ray diffraction (XRD) measurements were carried out on a computerized PANalytical X'Pert Pro diffractometer with Cu Kα (λ = 0.15406 nm) radiation. The data of 2θ from 5 to 40° were collected with the step size of 0.02°.

The H2–TPR experiments were carried out on a Micromeritics AutoChem 2920 chemisorption analyzer. The samples (50 mg) were placed in a quartz reactor and were pretreated at 500 °C for 1 h. Then cooled down to room temperature. Then H2–TPR was performed in 10 vol.% H2/Ar flow of 50 mL/min at a heating rate of 10 °C/min.

Solid state 29Si and 27Al MAS NMR spectra were collected on a Bruker AVANCE III 400 MHz WB Solid–State NMR spectrometer operating at the spectral frequency of 79.52 MHz (Si) or 104.29 MHz (Al). A relaxation delay of 6 s for Si and 1 s for Al was applied to collect single pulse spectra. All measurements were performed at room temperature, and TMS and Al(NO3)3 were used as external references, respectively.
Physicochemical characterization of the catalysts obtained from different post-treatments.

<table>
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<th>Without pretreatment</th>
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<th>pH 2</th>
<th>pH 1</th>
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</table>

3. Results and discussion

3.1. Characteristics of Cu_{x}Na_{y}–SSZ-13 catalysts

All four catalysts exhibited the typical diffraction peaks of the CHA zeolite structure (2θ = 9.5, 14.0, 16.1, 17.8, 20.7 and 25.0°) after post-treatment with dilute HNO_{3} solution adjusted to different pH values (Fig. S1). In order to confirm the effect of acid treatment on the catalyst structure, the relative crystallinity was calculated through comparison of peak intensity changes at 2θ = 9.4, 20.5 and 30.4° before and after acid treatment. No obvious reduction in peak intensity was observed after post-treatment by HNO_{3} solution with pH 4 and pH 2, and the relative crystallinity maintained at ca. 100%. Post-treatment by HNO_{3} solution with pH 1 and pH 0 decreased the peak intensity distinctly, giving relative crystallinity of ca. 82.2% and 26.9%, respectively (Table 1). Thus, post-treatment by dilute HNO_{3} solution with pH higher than 2 did not damage the zeolite structure noticeably. Physicochemical properties of the catalyst without acid treatment were also provided, as shown in Table 1. The SiO_{2}/Al_{2}O_{3} ratio of the catalyst was 8.3, and the metal loading was 10.3 and 4.6 wt.% for Cu and Na, respectively. When dilute HNO_{3} solution with pH 1 or pH 0 was used, the SiO_{2}/Al_{2}O_{3} ratio increased to 10.4 and 23.4, respectively. It was concluded that more aluminum atoms were removed by post-treatment with stronger HNO_{3} acid solution, and more breakdown of the lattice were expected under these conditions. Besides the different SiO_{2}/Al_{2}O_{3} ratios, the Cu and Na content in the obtained catalysts was also decreased with the decrease of pH (Table 1). Thus, the post-treatment by dilute HNO_{3} solution was an effective method to prepare Cu–SSZ-13 catalysts with different SiO_{2}/Al_{2}O_{3} ratios and different metal loadings.

3.2. NH_{3}–SCR performance and hydrothermal stability of Cu_{x}Na_{y}–SSZ-13 catalysts

The NO\textsubscript{x} conversion as a function of reaction temperature between 150 and 550 °C over Cu_{x}Na_{y}–SSZ-13 catalysts at relatively high GHSV (400,000 h\textsuperscript{-1}) is shown in Fig. 1. As the provider of active sites, the Cu loading in the catalysts could affect the NH\textsubscript{3}–SCR performance greatly. Due to its low Cu loading, the Cu\textsubscript{1.7}Na\textsubscript{0.7}–SSZ-13 catalyst did not show very good NH\textsubscript{3}–SCR performance in over the studied temperature range. With the increase of Cu loading from 1.7 wt.% to 4.3 wt.%, the NO\textsubscript{x} conversion was improved significantly, especially in the low temperature range. However, the NO\textsubscript{x} conversion in the high temperature range (>400 °C) decreased distinctly when Cu loading was raised to 5.3 wt.% (only 57% at 550 °C), which should be related to the unselective oxidation of NH\textsubscript{3} in the high temperature range. Although different levels of NO\textsubscript{x} conversion were observed, excellent N\textsubscript{2} selectivity could be obtained for all catalysts, which was nearly 100% over the whole temperature range (Fig. S2). Compared with the others, the Cu\textsubscript{3.9}Na\textsubscript{0.8}–SSZ-13 and Cu\textsubscript{4.3}Na\textsubscript{2.5}–SSZ-13 catalysts showed the best NH\textsubscript{3}–SCR performance, maintaining NO\textsubscript{x} conversion higher than 90% from 200 to 500 °C. Thus, Cu loading at ca. 4.0 wt.% was suitable for Cu–SSZ-13 catalysts prepared by the one-pot synthesis method.

In order to probe the hydrothermal stability, the above-mentioned four catalysts were further treated in air with 10 vol.% H\textsubscript{2}O at 750 °C for 16 h. The NH\textsubscript{3}–SCR activity of the aged catalysts is also shown in Fig. 1. The aged Cu\textsubscript{3.3}Na\textsubscript{1.7}–SSZ-13 and Cu\textsubscript{4.3}Na\textsubscript{2.5}–SSZ-13 catalysts almost lost their NH\textsubscript{3}–SCR activity completely, while Cu\textsubscript{5.3}Na\textsubscript{0.7}–SSZ-13 and Cu\textsubscript{3.9}Na\textsubscript{0.8}–SSZ-13 catalysts exhibited better hydrothermal stability. Importantly, the aged Cu\textsubscript{3.3}Na\textsubscript{0.8}–SSZ-13 catalyst showed the best hydrothermal stability, with NO\textsubscript{x} conversion higher than 80% from 200 to 450 °C. Therefore, the post-treatment by dilute HNO_{3} solution with pH 1 was the optimal procedure to prepare the catalyst with both excellent NH\textsubscript{3}–SCR performance and high hydrothermal stability. The NH\textsubscript{3}–SCR performance of fresh Cu\textsubscript{3.9}Na\textsubscript{0.8}–SSZ-13 catalyst was also tested under the simulated condition with water, as shown in Table 2. The presence of 5 vol.% H\textsubscript{2}O decreased the NO\textsubscript{x} conversion at low temperatures (<200 °C) mainly due to the competitive adsorption by H\textsubscript{2}O adsorption, and increased the NO\textsubscript{x} conversion at high temperatures (>400 °C) probably due to the inhibition effect of H\textsubscript{2}O on the unselective catalytic oxidation of NH\textsubscript{3} [23]. Nevertheless, the NO\textsubscript{x} conversion maintained nearly 100% from 225 to 550 °C, indicating the catalyst also do well under the condition with water.

In order to evaluate the degradation of the zeolite structure caused by the hydrothermal aging, XRD measurements were performed for the aged catalysts, as shown in Fig. 2. The aged Cu\textsubscript{4.3}Na\textsubscript{2.5}–SSZ-13 and Cu\textsubscript{5.3}Na\textsubscript{3.7}–SSZ-13 catalysts showed complete collapse of the zeolite structure, with a broad feature representing an amorphous phase, which was consistent with their
total loss of NH3–SCR performance as described above. Some CuO was detected in the aged Cu5.3Na3.7–SSZ-13 catalyst. Because NH3 could be over-oxidized to NOx in the presence of CuO, negative NOx conversion at high temperatures (>450 °C) was achieved for the aged Cu5.3Na3.7–SSZ-13 catalyst (Fig. 1). Little change was observed for the hydrothermally aged Cu3.9Na0.8–SSZ-13 catalyst, indicating its very good hydrothermal stability. Although the typical peaks of the CHA structure were also maintained for the aged Cu1.7Na0.7–SSZ-13 catalyst, the intensity of the zeolite peaks decreased significantly and an amorphous phase was apparent. It was hypothesized that the excessive dealumination of this catalyst was an important factor in its decreased hydrothermal stability.

H2-TPR profiles of the four Cu5.3Na3.7–SSZ-13 catalysts are shown in Fig. 3. Reduction of isolated Cu2+ in zeolites has been proposed to follow a two-step mechanism, namely the reduction from Cu2+ to Cu+ (at lower temperatures) and the reduction from Cu+ to Cu0 (at higher temperatures). However, the reduction of the dispersed bulk CuO to Cu0 occurred in a single step in the low temperature range (200–300 °C) [23,29,30]. According to the profile of the fresh Cu5.3Na3.7–SSZ-13, Cu3.9Na0.8–SSZ-13 and Cu4.3Na2.5–SSZ-13 catalysts, the integrated area for H2 consumption below 500 °C contributed ca. 49, 49 and 50% of the total H2 consumption area, respectively. Thus, it is reasonable to conclude that only isolated Cu2+ was present in the above three catalysts. The peaks at 170, 222 and 345 °C could be assigned to the reduction of Cu2+ located in different cationic sites to Cu+ [23]. The H2 consumption below 400 °C for the Cu5.3Na3.7–SSZ-13 catalyst contributed ca. 61% of the total, indicating that the reduction from Cu2+ to Cu0 also occurred in the low temperature range. Thus, the peak at ca. 207 °C was assigned to the reduction peak of highly dispersed CuO in the catalyst, although it was not observed in XRD profile. Compared with isolated Cu2+, Cu0 was found to be less efficient for SCR reactions in the low temperature range (<200 °C) [31]. Thus, the Cu5.3Na3.7–SSZ-13 catalyst did not show the best dNOx efficiency although it had the highest Cu loading. It was reported that the high stability of active species is an important factor for Cu/zeolite catalysts with high hydrothermal stability, and the reduction from Cu+ to Cu0 was expected when the chabazite structure began to degrade [32,33]. Thus, isolated Cu2+ ions with higher reduction temperature from Cu+ to Cu0 are expected to be more stable in the chabazite structure. The Cu1.7Na0.7–SSZ-13 and Cu1.9Na0.8–SSZ-13 catalysts showed extremely high reduction temperature for Cu+ to Cu0 reduction (at ca. 900 °C), which indicated the excellent stability of Cu2+ species in these materials. However, no Cu species with such high stability was observed in Cu5.3Na3.7–SSZ-13 and Cu3.9Na0.8–SSZ-13 catalysts. Considering these two catalysts possessed an almost intact zeolite structure (Table 1), the poor stability of Cu species should be the reason for their poor hydrothermal stability. Therefore, isolated Cu2+ species with extremely high thermal stability are necessary to obtain a Cu–SSZ-13 catalyst with both good NH3–SCR performance and high hydrothermal stability. Based on the composition of Cu4.3Na2.5–SSZ-13 and Cu3.9Na0.8–SSZ-13 catalysts, it was hypothesized that the Na+ ions in the catalysts affected their hydrothermal stability seriously, as will be discussed below in detail.

Ion exchange by NH4NO3 solution was also proved to be an effective post-treatment method to prepare Cu–SSZ-13 catalyst, and the optimal Cu3.8Na1.2–SSZ-13 catalyst showed very good NH3–SCR activity [23]. In order to compare the two catalysts obtained by different methods, the turn-over frequency (TOF) of NOx over Cu species at 150 °C was calculated, where the NOx conversion was less than 40% [34]. Assuming that all Cu species were active in the studied catalysts, the TOF was defined as the number of NOx molecules converted per Cu per second. Although the two catalysts contained nearly equal amounts of Cu, their NH3–SCR performance was quite different. Not only did the fresh Cu3.9Na0.8–SSZ-13 catalyst show higher TOF (1.69 × 10−3 s−1) than the fresh Cu3.8Na1.2–SSZ-13 catalyst (0.84 × 10−3 s−1), the aged Cu3.9Na0.8–SSZ-13 catalyst also showed higher TOF (1.26 × 10−3 s−1) than the aged Cu3.8Na1.2–SSZ-13 catalyst (0.64 × 10−3 s−1). Therefore, post-treatment by dilute HNO3 solution was better than the procedure using NH4NO3 solution to prepare a catalyst with excellent NH3–SCR activity and hydrothermal stability.

### Table 2

<table>
<thead>
<tr>
<th>NOx Conversion (%)</th>
<th>150</th>
<th>175</th>
<th>200</th>
<th>225</th>
<th>250</th>
<th>300</th>
<th>350</th>
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<td></td>
<td>12.1</td>
<td>29.8</td>
<td>58.4</td>
<td>99.8</td>
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</tbody>
</table>

### 3.3 Influence of Na+ on NH3–SCR performance of Cu3.9Na0.8–SSZ-13 catalysts

Three catalysts with the same Cu content and different Na+ contents were prepared in this study, which were denoted as Cu3.9Na0.8–SSZ-13, Cu3.9Na1.7–SSZ-13 and Cu3.9Na2.2–SSZ-13 on the basis of elemental analysis results. The NH3–SCR performance of the fresh and aged catalysts is shown in Fig. 4. With the increase of Na+ content in the catalysts, only a small decrease of NOx conversion was observed for the fresh catalysts. However, after hydrothermal treatment in air with 10 vol% H2 at 750 °C for 16 h, the NOx conversion decreased greatly along with the increase of Na+ content. When the Na+ content increased from 0.8 to 1.7 wt.%, the NOx conversion decreased greatly. If more Na+ ions were loaded (ca. 2.2 wt.%), the catalyst became almost completely inactive for NH3–SCR reaction. The above results indicated that the presence of excess Na+ ions in the catalyst could severely decrease the hydrothermal stability of the Cu–SSZ-13 catalyst prepared by the one-pot synthesis method.

The XRD profiles of the aged Cu3.9Na0.8–SSZ-13 catalysts are shown in Fig. 5. Compared with the aged Cu3.9Na0.8–SSZ-13 catalyst, the peak intensity of the chabazite structure decreased greatly accompanied by the appearance of amorphous phase for the aged...
Fig. 4. NH3–SCR performance of fresh (solid symbol) and aged Cu3.9Nax–SSZ-13 catalysts (hollow symbol).

Fig. 5. XRD profiles of Cu3.9Na–SSZ-13 catalysts after hydrothermal aging at 750 °C for 16 h.

Cu3.9Na1.7–SSZ-13 catalyst. Even more seriously, the CHA structure disappeared completely for the aged Cu3.9Na2.2–SSZ-13 catalyst with the highest Na+ content. It is well known that a catalyst having more breakdown of the zeolite lattice structure or more unstable active species are more easily inactivated by hydrothermal treatment. Therefore, the effects of Na+ ions on the zeolite framework and the Cu species will be discussed below.

Solid state NMR experiments were carried out to characterize the framework of the Cu3.9Na8–SSZ-13 catalysts. 27Al solid state NMR results can provide information about the structural environment of Al atoms in zeolites. The Al atom in the framework has 4-fold coordination (AlIV), which presents a typical chemical shift of 50–60 ppm. However, if the Al atom is removed from the zeolite framework, the Al atom can be located outside the lattice, showing a 6-fold-type coordination (AlVI) with a 0–10 ppm chemical shift in 27Al NMR spectra [35,36]. As shown in Fig. 6(A), a small amount of AlVI atoms were detected for the Cu3.9Na0.8–SSZ-13 catalyst, while only AlIV atoms existed in Cu3.9Na1.7–SSZ-13 and Cu3.9Na2.2–SSZ-13 catalysts. According to the results of ICP analysis, the bulk SiO2/Al2O3 ratio was 10.4, 12.8 and 12.4 for Cu3.9Na0.8–SSZ-13, Cu3.9Na1.7–SSZ-13 and Cu3.9Na2.2–SSZ-13 catalysts, respectively. Compared with the bulk SiO2/Al2O3 ratio of the initial Cu–SSZ-13 sample, the SiO2/Al2O3 ratios of all these catalysts were improved to a certain extent. This was direct evidence that dealumination occurred for all the three catalysts, although no evidence of AlVI atoms was observed in the two catalysts with higher Na+ content. Because much more NaNO3 (1 mol/L) was added in the preparation procedure of Cu3.9Na1.7–SSZ-13 and Cu3.9Na2.2–SSZ-13 catalysts, it was thought that the Al3+ (AlVI) caused by dealumination was removed along with NO3− in the washing process. Thus, 27Al solid state NMR results did not clearly indicate whether or not the Na+ ions affected the zeolite framework in the post-treatment process, and more characterization was necessary to answer this question.

29Si solid state NMR spectra could give relevant information about the arrangement of Si and Al atoms in the framework. The application of this technology is based on the fact that the 29Si chemical shift is very sensitive to its environment, in other words, the number of aluminum–oxygen tetrahedra connected to each silicon-oxygen tetrahedron (Si(nAl)). The framework SiO2/Al2O3 ratio could be calculated using the areas of different Si(nAl) by the following equation [36,37]:

\[
\text{Si/Al} = \frac{\sum_{n=0}^{4} \text{Isi(Al)}}{\sum_{n=0}^{4} 0.25n\text{Isi(Al)}}
\]

The advantage of this calculation method is that the effect of extra-framework aluminum is eliminated, and the results can represent the stability of a zeolite better than the bulk SiO2/Al2O3 ratio. Fig. 6(B) shows the 29Si solid state NMR spectra and the optimal deconvolution of the relevant peaks corresponding to Cu3.9Na–SSZ-13 catalysts. The five signals at ca. −85, −90, −95, −100 and −105 ppm correspond to distinct Si(4Al), Si(3Al), Si(2Al), Si(1Al) and Si(0Al), respectively.

Table 3: Calculated areas of the different types of Si(nAl) signals from deconvolution of 29Si NMR spectra for Cu3.9Na–SSZ-13 catalysts.

<table>
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<tr>
<th>Catalysts</th>
<th>Si(4Al)</th>
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<th>Si(2Al)</th>
<th>Si(1Al)</th>
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<td>1.14</td>
<td>10.22</td>
<td>16.03</td>
<td>42.87</td>
<td>29.74</td>
</tr>
</tbody>
</table>

Fig. 6. Solid state 27Al and 29Si NMR spectra of Cu3.9Na–SSZ-13 catalysts: (a) Cu3.9Na0.8–SSZ-13; (b) Cu3.9Na1.7–SSZ-13; (c) Cu3.9Na2.2–SSZ-13.
The area of each peak was of Na+ ions on Cu species, and the results are shown in Fig. 7. As a structure of Cu species together, and the H2 reduction peaks at 179, 247, with the poor NH3–SCR performance as described above for the ability of the catalyst was reflected through its effect on Cu species. The aggregation to CuO more likely happened with a higher Na content. The Cu species in the Cu–SSZ-13 catalysts prepared by the one-pot synthesis method. Migration of Cu species to less stable state and species in the Cu–SSZ-13 catalysts prepared by the one-pot synthesis method. Decreased stability of Cu species resulting from excess Na+ ions was the direct reason leading to the poor hydrothermal stability of the Cu–SSZ-13 catalysts prepared by the one-pot synthesis method.

4. Conclusions

The post-treatment by dilute HNO3 solution was an effective method to adjust the Cu and Na contents in the Cu–SSZ-13 catalyst prepared by one-pot synthesis method. The optimal Cu3.9Na0.8–SSZ-13 catalyst obtained from the post-treatment by dilute HNO3 solution with pH 1 showed the best NH3–SCR activity and hydrothermal stability. As co-cation, Na+ ions affected the hydrothermal stability of the one-pot synthesized Cu–SSZ-13 catalysts greatly. The catalysts with higher Na+ content showed poorer hydrothermal stability. The results of 27Al and 29Si NMR spectra indicated that the catalysts with different Na+ contents possessed almost the same zeolite structure. However, the H2–TPR results illustrated that the stability of Cu species decreased seriously along with the increase of Na+ ions in the catalysts. Thus, the Cu species with poor stability aroused by high Na+ content resulted in the poor hydrothermal stability of the catalysts. Therefore, it is better to precisely control the amount of Na+ ions maintained in Cu–SSZ-13 catalysts prepared by one-pot synthesis method to obtain the excellent NH3–SCR performance and hydrothermal stability simultaneously.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2015.05.032.

References