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Ammonia selective catalytic reduction of NO over Ce-Fe/Cu-SSZ-13 catalysts

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Abstract

A series of CHA-type trimetallic composite zeolites of CeₓFeᵧ/Cu-SSZ-13 catalysts were prepared by the one-pot synthesized Cu-SSZ-13 and subsequent ion-exchange with Fe³⁺ and Ce³⁺. The catalysts were characterized including TEM, XRD, XPS, SEM and BET. Their catalytic performances for selective catalytic reduction of NO with NH₃ were investigated. The results of XRD revealed that the crystal structure of zeolite Ce-Fe/Cu-SSZ-13 is the same as Cu-SSZ-13. It was known that larger specific surface areas and smaller pore size were in favor of catalytic reaction from the results of BET and catalytic performance tests. Among the prepared Ceₓ-Feᵧ/Cu-SSZ-13 catalysts, Ce₀.017-Fe₀.017/Cu-SSZ-13 displayed the best SCR performance. The NO conversion was more than 90% between 200 and 500 °C. N₂ selectivity was above 98% within the wider temperature range.
range of 150-550°C. In addition, the catalyst demonstrated sulfur-water tolerance and effective resistance against high space velocity. The phenomena suggest that synergistic effects of Cu, Fe and Ce species improve the SCR performances and make Ce-Fe/Cu-SSZ-13 catalyst as a promising candidate for NH$_3$-SCR technology.

**Key words:** selective catalytic reduction; NO$_x$-removal; SSZ-13; zeolite modification

**Introduction**

Nitrogen oxides emitted by diesel engines are a major kind of air pollutants that are responsible for acid rain, photochemical smog and ozone depletion. With legislation of NO$_x$ emissions becoming more and more stringent, it is urgent to find an effective way to remove such pollutants from the exhaust. Nowadays, one of the most promising technologies to eliminate the NO$_x$ pollution is selective catalytic reduction (SCR) of NO$_x$ with ammonia.$^1$ Recently, Cu/zeolite catalysts with chabazite (CHA) crystal structure, such as Cu-SSZ-13, has received much attention.$^{2,3}$ Cu-SSZ-13 prepared by an ion-exchange method is much more active, selective and hydrothermally stable than Cu-beta and Cu-ZSM-5.$^{4,5}$ However, the template N,N,N-trimethyl-1-adamantammonium hydroxide (TMAdaOH) used in the synthesis of SSZ-13 by Zones$^{6,7}$ is rather expensive. Therefore, it is desirable to find a substitute for the template TMAdaOH. Nuria et al$^8$ suggested that the low-cost methodologies to synthesize Cu-containing CHA catalysts using tetraethylammonium (TEA) as organic structure directing agent (OSDA) could be competitive and attractive for NH$_3$-SCR of NO$_x$. In addition, an economical way for SSZ-13 preparation with the essentially cheap choline chloride as template has been attempted by Chen et al$^9$ and the as-synthesized SSZ-13 zeolite, ion-exchanged by copper nitrate solution, exhibited excellent SCR performance. Furthermore, Ren et al$^{10}$ first used low-cost copper-amine complex as
the template for one-pot synthesis of Cu-SSZ-13 zeolite. Later, Xie et al\textsuperscript{11} had further improved the synthesis method of Cu-SSZ-13 catalyst and indicated that the one-pot synthesized Cu-SSZ-13 catalyst was a promising candidate for the NO\textsubscript{x} elimination from diesel engine exhaust.

At present, more and more researchers are interested in heterobimetallic zeolites because of the complementary advantages and synergistic effects. In order to further improve the activity of the one-pot synthesized Cu-SSZ-13 catalyst, Zhang et al\textsuperscript{12} prepared Fe\textsubscript{x}/Cu-SSZ-13 catalysts by incorporating Fe\textsuperscript{3+} into Cu-SSZ-13 and the catalysts exhibited high NH\textsubscript{3}-SCR activity, excellent N\textsubscript{2} selectivity, robust hydrothermal stability and good tolerance to high space velocity. Ceria has been widely used as an additive of various catalysts because of its excellent oxygen storage capacity and high redox ability via Ce\textsuperscript{4+} to Ce\textsuperscript{3+} transition\textsuperscript{13-15}. Herein, we attempt to modify the Cu/SSZ-13 catalyst with both iron and cerium to develop a more efficient NH\textsubscript{3}-SCR catalyst for the potential application in diesel engine exhaust treatment. In this study, the effects of Fe/Ce ratio, gas hourly space velocity (GHSV) and the concentration of O\textsubscript{2} on the activities for NO reduction are systematically investigated. In addition, the tolerance of the catalyst to H\textsubscript{2}O, SO\textsubscript{2} and CO\textsubscript{2} was studied as well. The catalysts were further characterized through X-ray powder diffraction (XRD), transmission electron microscope (TEM), N\textsubscript{2} adsorption-desorption (BET), scanning electron microscope (SEM) and X-ray photoelectron spectra (XPS).

**Experimental**

**Preparation of Ce-Fe /Cu-SSZ-13 catalysts**

Cu-SSZ-13 was synthesized by one-pot hydrothermal synthesis method as reported by Zhang\textsuperscript{12}. Ce\textsubscript{x}-Fe\textsubscript{y} /Cu-SSZ-13 catalysts were prepared by subsequent aqueous ion-exchange method. The specific steps are as follows: A certain amount of Cu-SSZ-13 was slowly added into
Fe(NO$_3$)$_3$$\cdot$9H$_2$O solution, with constant stirring at 80° for 8hrs. The formed precipitate was washed by deionized water followed by drying at 110°C and then exchanged with Ce(NO$_3$)$_3$$\cdot$6H$_2$O solution. Finally, the sample was calcined at 550°C for 5hrs. We chose the optimum concentration of Fe(NO$_3$)$_3$$\cdot$9H$_2$O solution at 0.017 mol/L according to the literature reported by Zhang$^{12}$ and obtained a series of Ce$_x$-Fe$_y$/Cu-SSZ-13 catalysts through changing the concentration of Ce(NO$_3$)$_3$$\cdot$6H$_2$O. The x and y represent concentration (unit: mol/L) of the Ce(NO$_3$)$_3$$\cdot$6H$_2$O solution and Fe(NO$_3$)$_3$$\cdot$9H$_2$O solution respectively. The metal weight percentages in the catalysts were measured by ICP analysis. All chemicals used were purchased from Tianjin Huadong Reagent Factory.

**Activity measurements**

The “standard NH$_3$-SCR” experiments were performed in a fixed bed reactor (inner diameter 5mm). The simulated exhaust gases were composed of 500 ppm NO, 500 ppm NH$_3$, 5 vol% O$_2$, 5 vol% H$_2$O (when used), 100 ppm SO$_2$ (when used), 5 vol% CO$_2$ (when used) and balance N$_2$. The total flow rate was 300 mL/min and thus a GHSV from 60000 h$^{-1}$ to 300000 h$^{-1}$ was obtained by changing the volume of the catalyst. The water vapor was injected by a pump (LSP01-1A, Longer Pump Inc.) and an evaporator. A K-type thermocouple was inserted into the center of catalyst bed from the bottom of the reactor and it was connected to a temperature programmed control instrument to monitor the reaction temperature. The concentration of NH$_3$, NO, NO$_2$ and N$_2$O were measured by a Thermo Nicolet IS10 Fourier-transform infrared (FTIR) spectrometer. NO conversion and N$_2$ selectivity of NH$_3$-SCR reaction were defined as:

NO conversion = (1 − [NO]$_{\text{outlet}}$/[NO]$_{\text{inlet}}$) × 100%;

N$_2$ selectivity = (([NH$_3$]$_{\text{inlet}}$−[NO]$_{\text{outlet}}$−[NO$_2$]$_{\text{outlet}}$−2[N$_2$O]$_{\text{outlet}}$−[NH$_3$]$_{\text{outlet}}$)/ ([NH$_3$]$_{\text{inlet}}$−[NH$_3$]$_{\text{outlet}}$))
Characterizations

Powder XRD patterns were obtained by a D8-Focus X-ray diffractometer with Cu Kα radiation (40 kV, 40 mA, λ=0.15418 nm). Diffractometer data were obtained with a step size of 5° for 2θ values from 5° to 40°.

Nitrogen adsorption/desorption isotherms was measured at 77 K with a Micromeritics Tristar-3000 analyzer. Each sample was degassed for 1 h at 90°C and another 3 h at 300°C under N2 atmosphere before the measurement. The specific surface area was calculated using standard BET method at a relative pressure (P/P0) range of 0.05–0.35 and the V-t plot method was utilized to calculate the pore volume.

The morphology of the catalysts was observed by the field emission scanning electron microscope (FESEM, Nanosem 430). X-ray photoelectron spectroscopy (XPS) analysis was conducted with a PHI-1600 instrument using Mg Kα radiation (1253.6 eV) as X-ray source. TEM observations were carried out using a Tecnai G2 F-20 transmission electron microscope with a field-emission gun operating at 200 kV.

Results and discussion

The influence of ion exchange level on NH3-SCR activity

The catalytic activity of Ceₓ-Feᵧ/Cu-SSZ-13 (x=0–0.15, y=0.017) were studied from 150 to 550 under 150000 h⁻¹. Fig. 1(a) shows NO conversion vs temperature. The NO conversion over Ceₓ-Feᵧ/Cu-SSZ-13 (x=0.06–0.15, y=0.017) increased rapidly below 200 and reached above 90% in the temperature range of 200 to 500. Especially within the temperature range of 150 to 225, NO conversion increased significantly with x increasing from 0 to 0.017. For example, the
NO conversion over Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13 and Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13 at 175°C are 76.8% and 86.2%, respectively. However, there was only a little increase of NO conversion with x increasing from 0 to 0.017 within the temperature range of 250 to 550°C. In addition, NO conversion decreased with x increasing from 0.017 to 0.15 between 150°C and 550°C due to the blocking of the “channel” of zeolites$^{12}$. Clearly, Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13 showed the best catalytic activity in a wider operation temperature window from 150 to 550°C. As presented in Fig. 1(b), there was almost no NO$_2$ in the outlet gases and the concentration of N$_2$O was less than 6 ppm. Obviously, the concentration of N$_2$O reached the maximum value at 250°C, which was correspond to the lowest N$_2$ selectivity. Fig. 1(b) also showed that N$_2$ selectivity over Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13 catalyst was above 98% in the temperature between 150°C and 550°C, which made Ce-Fe/Cu-SSZ-13 catalyst as a promising candidate for NH$_3$-SCR technology.

Effects of GHSV on NH$_3$-SCR Activity

The NH$_3$-SCR catalyst in diesel vehicles usually undergoes different GHSV in the practical application. Fig. 2 showed NO conversion over Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13 under different GHSV. It was clear that with the increase of GHSV from 60 000 h$^{-1}$ to 300 000 h$^{-1}$, NO conversion decreased significantly at low temperature below 200°C, yet there was only a little effect on the higher temperature (225-350°C) SCR activity. Especially within the temperature range of 400°C to 550°C, there almost no effect on NO conversion. Remarkably, the catalyst showed high NO conversion exceeding 90% during the temperature range of 225 to 500°C under a rather high GHSV of 300 000 h$^{-1}$, indicating that this catalyst is effectively resistant against high space velocity.

The effect of O$_2$ concentration on the SCR activity

The influence of O$_2$ concentration on NO conversion over Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13 catalyst
was investigated at 300 °C under 150 000 h\(^{-1}\) and the result was exhibited in Fig. 3. The NO conversion increased from 75.6% to 99.4% with the concentration of O\(_2\) increasing from 0 to 3 vol%. The increased catalytic activity might be related to the role that O\(_2\) played in the reaction. Two possible explanations may be that the main role of O\(_2\) is H-abstraction from adsorbed NH\(_3\), resulting in NH\(_2\) species, and secondly, O\(_2\) can be needed to react with NO to form an active intermediate species\(^{16-18}\). However, as the concentration of O\(_2\) continued to increase, NO conversion remained unchanged indicating that O\(_2\) is saturated.

The Influences of SO\(_2\), CO\(_2\) and H\(_2\)O on NH\(_3\)-SCR activity

Fig. 4(a) shows the effects of H\(_2\)O and SO\(_2\) on the catalytic activity of Ce\(_{0.017}\)-Fe\(_{0.017}\)/Cu-SSZ-13 catalyst at 300 °C under 150 000 h\(^{-1}\). When 5 vol% H\(_2\)O was added, the activity of the catalyst remained at the previous high level at 300 °C. This suggested that the catalyst was highly water-resistant under these SCR conditions. When 100 ppm SO\(_2\) was added into the feed gases, there was a slight decrease of the NO conversion. The decrease was attributed to the competitive adsorption between SO\(_2\) and NO\(^{19}\), so the conversion was restored to its original level after removing SO\(_2\). However, when 100 ppm SO\(_2\) and 5 % H\(_2\)O were injected into the reaction system simultaneously, NO conversion decreased considerably compared with only 100 ppm SO\(_2\) or 5 vol% H\(_2\)O, which might be related to the formation of sulfates that could poison the active sites or block the zeolite pores and the competitive adsorption between SO\(_2\) and NO on the active sites\(^{20}\).

The effects of H\(_2\)O and CO\(_2\) on the catalytic activity of Ce\(_{0.017}\)-Fe\(_{0.017}\)/Cu-SSZ-13 catalyst were illustrated in Fig. 4(b). It was clear that pure CO\(_2\) and the co-presence of CO\(_2\) and H\(_2\)O in feed gases almost had no effect on NO conversion.

Fig. 5 shows the effect of Ce doping on SO\(_2\) resistance. It is clear that Ce-doped catalyst
(Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13) showed a remarkable enhancement in sulfur-water tolerance compared with Ce$_0$-Fe$_{0.017}$/Cu-SSZ-13. The improvement of sulfur tolerance might be attributed to that the doping of Ce could efficiently retard the formation of surface sulfation species$^{21}$.

Fig. 6 shows the effect of temperature on SO$_2$ resistance of Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13. A continuous decline in NO conversion from 99.4% to 66.6% occurred after 100 ppm SO$_2$ and 5 vol% H$_2$O were added for 12 h at 300°C. When the temperature was maintained at 350 °C, NO conversion decreased from 95% to 86.8% after 100 ppm SO$_2$ and 5 vol% H$_2$O were added for 1 h, then the NO conversion became stable for another 11 h. The deactivation role of SO$_2$ over the catalyst might be related to the formation of ammonium sulfate. (NH$_4$)$_2$SO$_4$ decomposition involves the initial decomposition to NH$_3$ and NH$_4$HSO$_4$ at around 300°C and the subsequent decomposition of surface NH$_4$HSO$_4$ species to NH$_3$ and SO$_2$ at 350°C.$^{20,22}$ After removal of SO$_2$ and H$_2$O, NO conversion restored to some extent at both 300°C and 350°C. Obviously, there was almost no effect of SO$_2$ and H$_2$O on the NO conversion when the temperature is higher than 400°C. The results above suggested that the impact of SO$_2$ on NO conversion could be eliminated by increasing temperature.

The results of TEM

Fig. 7 shows the TEM micrographs of Ce$_{0.006}$-Fe$_{0.017}$/Cu-SSZ-13, Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13 and Ce$_{0.15}$-Fe$_{0.017}$/Cu-SSZ-13. The small dark spots were attributed to oxide metal nanoparticles (CeO$_2$, α-Fe$_2$O$_3$ and CuO) and the faint background represented the SSZ-13 support. It could be clearly seen that, oxide metal nanoparticles were well dispersed on the surface of the catalysts.

XRD patterns results

The XRD patterns of Ce$_x$-Fe$_y$/Cu-SSZ-13 catalysts and JCPDS reference of SSZ-13 were shown in Fig. 8. All catalysts exhibited the characteristic peaks corresponding to SSZ-13 zeolite
structure (2θ = 9.5°, 14.0°, 16.1°, 17.8°, 20.7°, 25.0°, 26.1° and 30.9°) with a perfect degree of crystallization, indicating that the original zeolite structure remained intact. The diffraction peaks of CeO₂, α-Fe₂O₃ and CuO were not observed among all catalysts, indicating that the copper, iron and cerium species as oxide metal nanoparticles were well dispersed on the surface of SSZ-13 support, which was confirmed by the results of TEM images.

The results of BET

Fig. 9 showed the results of N₂ adsorption-desorption isotherms and pore-size distribution of Ceₓ-Feᵧ/Cu-SSZ-13 catalysts. According to the IUPAC classification, all adsorption-desorption isotherm curves of the samples in Fig. 9(a) can be considered as a combination of type I and type IV, indicating the presence of microporous and slit shaped pores. Fig. 9(b) showed that Ce₀-Fe₀.017/Cu-SSZ-13, Ce₀.006-Fe₀.017/Cu-SSZ-13, Ce₀.017-Fe₀.017/Cu-SSZ-13 and Ce₀.15-Fe₀.017/Cu-SSZ-13 catalysts had only a narrow visible peak at around 3.94nm, 3.99nm, 3.92nm, and 4.38nm respectively, indicating that excessive loading of Ce resulted in larger pore size. The pore structure parameters of all samples were listed in Table 1. It is clear that the surface area and pore volume of Ceₓ-Feᵧ/Cu-SSZ-13 catalysts decreased with the increasing of cerium content indicating that excessive Ce loading results in agglomeration that blocked the “channel” of catalysts. Remarkably, Ce₀.006-Fe₀.017/Cu-SSZ-13 and Ce₀.017-Fe₀.017/Cu-SSZ-13 catalysts with larger surface area and smaller pore size exhibited higher catalytic activity compared with Ce₀.15-Fe₀.017/Cu-SSZ-13 catalyst combined with Fig. 1 and Table 1. The results were in accordance with the previous report that larger specific surface areas and smaller pore size were in favor of catalytic reaction²³.

The results of SEM
The SEM micrographs of Ce\textsubscript{0.017}-Fe\textsubscript{0.017}/Cu-SSZ-13 are shown in Fig. 10. It is clear that the sample was made of hexagonal crystal. The average particle size of the catalyst is about 2.5µm. In addition, It can be seen from the image that the catalyst shows perfect degree of crystallization which is in accordance with the results of XRD.

**The metal dispersion**

The metal dispersion of Ce\textsubscript{0.017}-Fe\textsubscript{0.017}/Cu-SSZ-13 determined by XPS and ICP was shown in Table 2. It is clear that Fe and Ce species are mostly dispersed on the surface of the catalyst Ce\textsubscript{0.017}-Fe\textsubscript{0.017}/Cu-SSZ-13 through post-synthesis cation exchanges. The good metal dispersion was favorable to the synergetic effects.

**Conclusions**

A series of CHA-type trimetallic composite zeolites of Ce\textsubscript{x}-Fe\textsubscript{y}/Cu-SSZ-13 catalysts were prepared by the one-pot synthesized Cu-SSZ-13 and subsequent ion-exchange with Fe\textsuperscript{3+} and Ce\textsuperscript{3+}. The results of XRD revealed that the zeolite structure remained intact after both Fe and Ce incorporation into Cu-SSZ-13. The SEM micrographs showed that the sample was made of hexagonal crystal. Ce\textsubscript{0.017}-Fe\textsubscript{0.017}/Cu-SSZ-13 have a large BET specific surface area (503 m\textsuperscript{2}/g) and a narrow pore size distribution (3.92 nm). Excessive Ce loading would result in agglomeration that blocked the “channel” of catalysts. Larger specific surface areas and smaller pore size were in favor of catalytic reaction, which can be concluded combined catalytic performance tests with the results of BET. Among the prepared Ce\textsubscript{x}-Fe\textsubscript{y}/Cu-SSZ-13 catalysts, Ce\textsubscript{0.017}-Fe\textsubscript{0.017}/Cu-SSZ-13 catalyst showed the best catalytic performance. The good metal dispersion of Ce\textsubscript{0.017}-Fe\textsubscript{0.017}/Cu-SSZ-13 was favorable to the synergetic effects. It presented super NH\textsubscript{3}-SCR activity, excellent N\textsubscript{2} selectivity in a relatively wide temperature range, strong resistance to high space velocity as well as good tolerance.
to CO$_2$ and H$_2$O. In addition, Ce$_{0.017}$Fe$_{0.017}$/Cu-SSZ-13 (Ce-doped catalyst) showed a remarkable enhancement in sulfur-water tolerance compared with Ce$_0$-Fe$_{0.017}$/Cu-SSZ-13. The impact of SO$_2$ on NO conversion could be eliminated by increasing temperature. Further studies on the mechanism of the reaction are in progress.

References


**Figure captions**
Fig. 1 NO conversion over Ce$_x$-Fe$_y$/Cu-SSZ-13 catalysts under GHSV of 150000 h$^{-1}$ (a), N$_2$ selectivity of Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13 catalyst (b).

Fig. 2 NH$_3$-SCR activity over Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13 under different GHSV

Fig. 3 NH$_3$-SCR activity over Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13 catalyst at 300°C under GHSV of 150 000 h$^{-1}$ at different O$_2$ concentration

Fig. 4 NO conversion over Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13 catalyst at 300°C under GHSV of 150 000 h$^{-1}$ in the co-presence of H$_2$O + SO$_2$ (a); H$_2$O + CO$_2$ (b).

Fig. 5 NO conversion over Ce$_0$-Fe$_{0.017}$/Cu-SSZ-13 and Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13 at 300°C under GHSV of 150 000 h$^{-1}$ in the co-presence of H$_2$O + SO$_2$

Fig. 6 NO conversion over Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13 at different temperature under GHSV of 150 000 h$^{-1}$ in the co-presence of H$_2$O + SO$_2$

Fig. 7 TEM images of Ce$_{0.006}$-Fe$_{0.017}$/Cu-SSZ-13 (a), Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13 (b) and Ce$_{0.15}$-Fe$_{0.017}$/Cu-SSZ-13 (c)

Fig. 8 XRD patterns of Ce$_x$-Fe$_y$/Cu-SSZ-13 catalysts and JCPDS reference of SSZ-13 zeolite

Fig. 9 N2 adsorption-desorption isotherms (a) and pore-size distribution curves (b) of Ce$_x$-Fe$_y$/Cu-SSZ-13 catalysts

Fig. 10 SEM images of Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13

Table 1 The physicochemical properties of Ce$_x$-Fe$_y$/Cu-SSZ-13 catalysts

Table 2 Metal dispersion (%) of Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13
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Fig. 2 NH$_3$-SCR activity over Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13 under different GHSV.
Fig. 3 NH₃-SCR activity over Ce₀.₀₁₇Fe₀.₀₁₇/Cu-SSZ-13 catalyst at 300 °C under GHSV of 150 000 h⁻¹ at different O₂ concentration.

Fig. 4 NO conversion over Ce₀.₀₁₇Fe₀.₀₁₇/Cu-SSZ-13 catalyst at 300 °C under GHSV of 150 000 h⁻¹ in the co-presence of H₂O + SO₂ (a); H₂O + CO₂ (b).
Fig. 5 NO conversion over Ce$_{0.0017}$-Fe$_{0.017}$/Cu-SSZ-13 and Ce$_{0.0017}$-Fe$_{0.017}$/Cu-SSZ-13 at 300 ℃ under GHSV of 150 000 h$^{-1}$ in the co-presence of H$_2$O + SO$_2$

Fig. 6 NO conversion over Ce$_{0.017}$-Fe$_{0.017}$/Cu-SSZ-13 at different temperature under GHSV of 150 000 h$^{-1}$ in the co-presence of H$_2$O + SO$_2$
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Fig. 9 N2 adsorption-desorption isotherms (a) and pore-size distribution curves (b) of Ce$_x$Fe$_y$/Cu-SSZ-13 catalysts
Table 1 The physicochemical properties of $\text{Ce}_x\text{Fe}_y$/Cu-SSZ-13 catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$ (m$^2$/g)$^a$</th>
<th>Pore volume (cm$^3$/g)$^b$</th>
<th>Average pore diameter (nm)$^c$</th>
<th>Concentration(wt%)$^d$</th>
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<tr>
<td>$\text{Ce}<em>0\text{Fe}</em>{0.017}$/Cu-SSZ-13</td>
<td>522</td>
<td>0.220</td>
<td>3.90</td>
<td>3.44 1.27</td>
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<tr>
<td>$\text{Ce}<em>{0.006}\text{Fe}</em>{0.017}$/Cu-SSZ-13</td>
<td>511</td>
<td>0.214</td>
<td>3.97</td>
<td>0.67 3.10</td>
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<tr>
<td>$\text{Ce}<em>{0.017}\text{Fe}</em>{0.017}$/Cu-SSZ-13</td>
<td>503</td>
<td>0.194</td>
<td>3.91</td>
<td>0.82 3.48</td>
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<tr>
<td>$\text{Ce}<em>{0.15}\text{Fe}</em>{0.017}$/Cu-SSZ-13</td>
<td>458</td>
<td>0.186</td>
<td>4.31</td>
<td>0.87 3.28</td>
</tr>
</tbody>
</table>

$^a$ Calculated by BET method.

$^b$ Calculated by t-plot method.

$^c$ Calculated using the BJH method with desorption branch.

$^d$ Characterized by ICP-OES.

Table 2 Metal dispersion (%) of $\text{Ce}_{0.017}\text{Fe}_{0.017}$/Cu-SSZ-13

<table>
<thead>
<tr>
<th>Sample</th>
<th>metal dispersion (%)$^a$</th>
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</thead>
<tbody>
<tr>
<td>$\text{Ce}<em>{0.017}\text{Fe}</em>{0.017}$/Cu-SSZ-13</td>
<td>84.76 100 25.09</td>
</tr>
</tbody>
</table>

$^a$ metal dispersion(%)=the number of metal atoms on the surface/ total number of metal atoms in the bulk.