硅烷化对NH₃选择性催化还原NOₓ催化剂
CuCe/BEA水热稳定性的促进作用

徐书浩¹ 林青瑾² 刘双³ 刘静莹¹ 徐海迪⁴,⁵ 王健礼⁴,⁵ 陈耀强¹,³,⁵
(¹ 四川大学化学学院, 四川省环境保护环境催化材料工程技术中心, 成都 610064)
(² 四川大学高分子研究所, 高分子材料工程国家重点实验室, 成都 610064)
(³ 四川大学新能源与低碳技术研究院, 成都 610064)
(⁴ 中国汽车技术研究中心移动源污染排放控制技术国家工程实验室, 天津 300300)
(⁵ 四川大学国家烟气脱硫工程技术研究中心, 成都 610064)

摘要: 采用硅烷化改性NH₃选择性催化还原NOₓ催化剂CuCe/BEA, 以提高催化剂的水热稳定性。X射线衍射, 扫描电子显微镜和¹⁷Al核磁共振谱等研究证实, 硅烷化改性明显抑制BEA分子筛骨架中Si-O-Al键的水解, 保持其结构完整, 从而有效提高水热处理后CuCe/BEA的催化活性。氨气-程序升温还原和原位漫反射傅里叶变换红外光谱研究结果表明, 硅烷化改性的催化剂由于保持更完整的骨架结构能够形成更多的酸性位点。此外, 氨气-程序升温还原和X射线光电子能谱测试表明, 硅烷化改性有利于提高活性铜物种的分散性。因此, 相比于CuCe/BEA催化剂, 硅烷化改性的CuCeSi/BEA催化剂具有更多的酸性位点和高度分散的Cu物种, 共同促进了催化剂的水热稳定性。

关键词: 硅烷化; 分子筛; 水热稳定性; 结构活性关系; 多相催化

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Promotional Effects of Silanization on the Hydrothermal Stability of 
CuCe/BEA Catalyst for Selective Catalytic Reduction of NOₓ with NH₃,

XU Shu-Hao¹ LIN Qing-Jing² LIU Shuang¹ LIU Jing-Ying¹ 
XU Hai-Di*³,⁴,⁵ WANG Jian-Li*³,⁴,⁵ CHEN Yao-Qiang¹,³,⁵
(¹ Sichuan Provincial Environmental Protection Environmental Catalytic Materials Engineering Technology Center, College of Chemistry, Sichuan University, Chengdu 610064, China) 
(² State Key Laboratory of Polymer Materials Engineering, Institute of Polymer Science, Sichuan University, Chengdu 610064, China) 
(³ Institute of New Energy and Low-Carbon Technology, Sichuan University, Chengdu 610064, China) 
(⁴ National Engineering Laboratory for Mobile Source Emission Control Technology, China Automotive Technology & Research Center, Tianjin 300300, China) 
(⁵ Sichuan University FGD (Flue Gas Desulfurization) State Engineering Research Center, Chengdu 610064, China)

Abstract: The hydrothermal stability of CuCe/BEA catalyst is improved by its silanization for selective catalytic reduction of NOₓ with NH₃ (NH₃-SCR). The results indicate that the silanization modification effectively enhances the catalytic activity of CuCe/BEA after the hydrothermal treatment due to significantly inhibit the hydrolysis of Si-O-Al bonds from the BEA skeleton to maintain structural integrity, revealed by X-ray diffraction (XRD), scanning electron microscope (SEM) and ¹⁷Al nuclear magnetic resonance (¹⁷Al NMR). More complete skeleton structure of

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*通信联系人。E-mail: xuhaidi@scu.edu.cn, wanghaiyi@scu.edu.cn
CuCeSi/BEA catalyst results in the formation of more acid sites after the hydrothermal treatment, confirmed by NH$_3$-temperature programmed desorption (NH$_3$-TPD) and in situ diffuse reflectance infrared transform spectroscopy (in situ DRIFTS). Moreover, H$_2$-temperature programmed reduction (H$_2$-TPR) and X-ray photoelectron spectrum (XPS) show that silanization is beneficial to facilitate the dispersion of active copper ions after the hydrothermal treatment. Therefore, more acid sites and highly dispersed Cu species together contribute to higher hydrothermal stability of silanized CuCeSi/BEA than CuCe/BEA catalyst.

**Keywords:** silanization; zeolite; hydrothermal stability; structure–activity relationships; heterogeneous catalysis

## 0 Introduction

With the popularization of diesel vehicles in people’s life, the issues of nitrogen oxides (NO$_x$) emission is increasingly serious. NO$_x$ has been an important source of air pollution which could cause significantly harm to both the environment (e.g. acid rain, ozone depletion, photochemical smog, and greenhouse effect) and human health$^{[1-3]}$, the selective catalytic reduction of NO$_x$ with NH$_3$ (NH$_3$-SCR) is an efficient NO$_x$ elimination technology among all NO$_x$ emission control technologies for the diesel exhausts$^{[4,6]}$.

Zeolites (e.g. SAPO-34, BEA, and ZSM-5) as supports with a large specific surface area, channel complex and orderly advantages, can promote the dispersion of active metal species, and abundant surface acid sites from the skeleton of zeolites are beneficial to the adsorption of NH$_3$$^1$.$^9$. Among the reported materials, Cu/BEA catalysts have shown relatively excellent catalytic performance and lower cost, which have attracted wide attention$^{[10-12]}$. However, poor hydrothermal stability of Cu/BEA limited its commercial application due to dealumination of the zeolite and subsequent formation of the inactive species after the hydrothermal treatment$^{[13]}$. To meet the increasingly stringent regulations on emitted NO$_x$, it is essential to improve the hydrothermal stability of Cu/BEA. Zhao et al.$^{[14]}$ found that Ce and Nb additives could not only improve the NO$_x$ conversion of Cu/BEA, but also improve its hydrothermal stability. The hydrothermal stability of Cu-exchanged BEA was obviously improved by the introduction of Fe as the co-active component$^{[15]}$. Our previous work has reported that the hydrothermal stability of Cu/BEA was effectively enhanced by the alkaline metal Ba due to the formation of more isolated Cu$^{2+}$ species from the enhanced interactions between Cu and other surrounding atoms by the addition of Ba$^{[16]}$. The above works mainly focused on stabilizing the active Cu species, but there is little literature to further stabilize the skeleton structure of BEA to our best knowledge. Considering that the hydrothermal stability of the BEA catalyst has an important relationship with the hydrolysis of Si-O-Al bonds in the skeleton of BEA$^{[17]}$. Therefore, the additional silanizing reagent (e.g. ethyl orthosilicate, TEOS) deposited on the surface of BEA would be hydrolyzed firstly to protect against the attack of H$_2$O to Si-O-Al bonds and finally stabilize the structural skeleton of BEA$^{[18]}$.

Herein, the introduction of extraneous Si into CuCe/BEA attempts to improve the hydrothermal stability. $^{27}$Al nuclear magnetic resonance ($^{27}$Al NMR), X-ray diffraction (XRD), NH$_3$-temperature programmed desorption (NH$_3$-TPD), in situ diffuse reflectance infrared transform spectroscopy (in situ DRIFTS), H$_2$-temperature programmed reduction (H$_2$-TPR), and X-ray photoelectron spectrum (XPS) are employed to characterize and compare the effects of Si on the structure and active species of CuCe/BEA catalyst before and after the hydrothermal treatment, with a focus on investigating the enhanced influences of Si on the hydrothermal stability of CuCe/BEA catalyst.

## 1 Experimental

### 1.1 Catalyst preparation

The Cu/BEA catalyst was prepared by an incipient wetness impregnation method. Firstly, 12.32 g commercial H/BEA (n$_H$/n$_Al$=25, Nankai University Catalyst Co., Ltd., China) was dropped into 9.24 mL solution
contained 1.13 g Cu(NO$_3$)$_2$·3H$_2$O (AR, Kelong, Chengdu, China), and then, the mixture was stirred to ensure that the copper ions were dispersed well. Next, the mixture was dried in a water bath to a solid powder and calcined at 550 °C for 3 h in the static air in a tubular furnace. Finally, the calcined Cu/BEA powders were coated on the cordierite monolith (2.5 cm$^3$, 62 cell per cm$^2$, Corning Ltd., USA), and the amount of catalyst deposited on the monolith substrate was about 160 g·L$^{-1}$. The fresh catalyst was denoted as Cu, and the mass fraction of copper was 3% (measured by inductively coupled plasma atomic emission spectrometry, ICP-AES).

CuCe/BEA catalyst was prepared by a two-step method. Firstly, 10.00 g commercial H/BEA was ion-exchanged with 100.00 mL solution contained 4.34 g Ce(NO$_3$)$_3$·6H$_2$O (AR, Kelong, Chengdu, China), which was then filtered, washed with distilled water and dried to obtain Ce/BEA material. Secondly, 9.24 mL solution contained 1.13 g Cu(NO$_3$)$_2$·3H$_2$O was impregnated on 12.32 g Ce/BEA powder by an incipient wetness impregnation method as mentioned above. The fresh catalyst was denoted as CuCe.

CuCeSi/BEA catalyst was obtained by modifying the CuCe/BEA with TEOS (AR, Kelong, Chengdu, China). Firstly, 2.25 mL TEOS was added to 20.00 mL solution of equal proportions of water and ethanol. Then, 10.00 g CuCe/BEA powder was added, stirred magnetically for 12 h, dried in a water bath, and calcined at 550 °C for 3 h in the static air in a tubular furnace. Finally, the coated fresh catalyst was denoted as CuCeSi.

The XRD measurements were achieved by the Rigaku D/MAX ray diffractometer using Cu Kα radiation ($\lambda=0.154$ 18 nm). The X-ray tube was operated at 45 kV and 25 mA. The samples were investigated in the 2θ range of 5°–60° at a scanning speed of 0.02 (°)·min$^{-1}$.

SEM images of the catalyst were observed by field emission scanning electron microscopy (FESEM) on a Hitachi SU8220 instrument operating at 10 kV.

NH$_3$-TPD was also performed on the thermal conductivity detector (Xianquan, TP5076). And approximately 100 mg sample was pretreated under the He gas (30 mL·min$^{-1}$) at 550 °C for 30 min, and then cooled to 120 °C in the above atmosphere. Next, the gas was switched into the NH$_3$ (30 mL·min$^{-1}$) until saturation. After that, the catalyst was flushed by He (30 mL·min$^{-1}$) to remove physical adsorbed NH$_3$. Finally, the NH$_3$-TPD desorption process was started at a linear heating rate of 10 °C·min$^{-1}$ from 120 to 800 °C under the He flow (30 mL·min$^{-1}$).

The Nicolet 6700 spectrometer with a high-temperature environmental cell which contained a KBr window and a DTGS detector was used to measure the in situ DRIFTS of catalysts. Before each test, the sample was pretreated in the pure N$_2$ (300 mL·min$^{-1}$) flow from 50 to 350 °C at a rate of 10 °C min$^{-1}$, and pretreated at 350 °C for 30 min. Then, the background spectra were acquired from 350 to 50 °C per 50 °C. Pure N$_2$ was switched to the adsorption gas (volume fraction of 0.1% NH$_3$, N$_2$ as the balance gas) at 50 °C. Afterwards, the temperature was raised at the rate of 10 °C·min$^{-1}$ from 50 to 350 °C, and the adsorption gas spectra were determined at per 50 °C. Finally, spectra of catalysts were measured by the means of subtracting the background diffuse reflection spectra.

The H$_2$-TPR was carried on the thermal conductivity detector (Xianquan, TP5076). And approximately 100 mg sample was pretreated under volume fraction of 10% O$_2$/N$_2$ (30 mL·min$^{-1}$) at 550 °C for 30 min. Then, the sample was cooled to 50 °C in above atmosphere, and the H$_2$-TPR desorption process was started at a linear heating rate of 10 °C·min$^{-1}$ from 50 to 900 °C under a volume fraction of 10% H$_2$/N$_2$ (30 mL·min$^{-1}$) flow.
The XPS was carried out on a spectrometer (XSAM-800, KRATOS Co.) with Al Kα radiation under ultra-high vacuum (UHV). The C1s peak (284.6 eV) was used for the calibration of binding energy value.

1.3 NH₃-SCR activity measurements

Catalyst activity measurements for NH₃-SCR were tested in a fixed bed quartz flow reactor. The monolith substrate loaded into a horizontal quartz microreactor and the reaction temperature was measured by two K-type thermocouples. The feed gases were regulated by mass-flow controllers and composed of volume fraction of 0.02% NO ($c_{N_O}$), 0.02% NH₃, 5% H₂O and 10% O₂, and N₂ was used as the balance gas with a gas hourly space velocity of 40 000 h⁻¹. Before each test, the catalyst was pretreated at 550 °C in the reaction atmosphere. The concentration of outlet gases ($c_{N_O,out}$) were monitored by an FTIR spectrometer (Antaris IGS, Thermo Fisher Scientific), and the test temperature was varied between 550~150 °C. The NOx conversion was calculated by the followed equation:

$$\text{NOx conversion}=\left(1-\frac{c_{N_O,out}}{c_{N_O,in}}\right)\times 100\%$$

“$c_{N_O,in}$” and “$c_{N_O,out}$” represent the outlet and inlet reactant concentrations of the reactor, respectively.

2 Results and discussion

2.1 Structural and morphological properties

$^{27}$Al NMR spectra are employed to characterize the dealuminization of CuCe and CuCeSi before and after the hydrothermal treatment, as shown in Fig.1. All four samples display three peaks: the peak of chemical shift at 54 is ascribed to the tetracoordinated framework aluminum atoms (AlIV), the peak of chemical shift at 12 is attributed to the pentacoordinated aluminum atom (AlV), and the peak of chemical shift at −13 is assigned to the hesacoordinated aluminum atom (AlVI).

BEA molecular sieve is mainly composed of tetrahedral SiO₄ and AlO₆. AlV is the main Al species in the structure of BEA molecular sieve, showing the largest NMR peak. AlVI may be due to the partial incomplete structure existing in the synthesis of BEA molecular sieve, or the hydrolytic destruction of some BEA zeolite supports occurred during the preparation of the catalyst. AlII is due to the hydrolysis of Si-O-Al bonds in the hydrothermal process, which results in the recoordination of AlII and AlV with H₂O molecules to form Al atoms with hesacoordinated[19-21]. The relative content of AlII over CuCeSi was slightly higher than that in CuCe, as listed in Table 1. AlII species are significantly decreased due to the dealumination for both catalysts after the hydrothermal treatment, although CuCeSi-HT catalyst still possesses higher relative content of AlII after the hydrothermal treatment, indicating that the introduction of Si can inhibit the attack of H₂O molecules on the Si-O-Al bonds, inhibit the occurrence of dealumination and protect the structure of BEA during the process of the hydrothermal treatment.

To investigate the effect of Si on the structure of

![Fig.1 $^{27}$Al NMR spectra of CuCe and CuCeSi catalysts before and after the hydrothermal treatment](image)

Table 1 Integrated area (A) of AlII atoms in CuCe and CuCeSi catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_{Al^{IV}}$</th>
<th>$A_{Al^{V}}$</th>
<th>$A_{Al^{VI}}$</th>
<th>$A_{Al^{IV}} + A_{Al^{V}} + A_{Al^{VI}}$ / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCe</td>
<td>922.7</td>
<td>94.2</td>
<td>32.0</td>
<td>88.0</td>
</tr>
<tr>
<td>CuCeSi</td>
<td>945.6</td>
<td>5.1</td>
<td>70.5</td>
<td>92.6</td>
</tr>
<tr>
<td>CuCe-HT</td>
<td>530.1</td>
<td>103.2</td>
<td>78.1</td>
<td>74.5</td>
</tr>
<tr>
<td>CuCeSi-HT</td>
<td>648.9</td>
<td>35.3</td>
<td>52.3</td>
<td>88.1</td>
</tr>
</tbody>
</table>
BEA, XRD patterns of CuCe, CuCeSi, and their hydrothermal samples are shown in Fig. 2. Only diffraction peaks ascribed to the typical structure of BEA were detected over all samples and no obvious other diffraction peaks ascribed to Cu$_x$O$_y$ and SiO$_2$ species$^{22-24}$ (Fig.2a). No peaks assigned to metallic or metal oxides species can be observed in Fig.2a, which could be that they are highly dispersed, or the concentration is too low to meet the detection limitation of XRD, or they do present as isolated metal species in the BEA molecular skeleton$^{25}$. The main diffraction peak at $2\theta=22.5^\circ$ was not shifted and no significant difference between the crystallinity of CuCe and CuCe Si indicates little effect of Si on the structures of BEA. Compared with the fresh catalysts, the intensity of the characteristic diffraction peaks of BEA decreased to a certain extent for the HT catalysts, indicating that the structure of catalysts is destroyed during the process of the hydrothermal treatment, which is consistent with the $^{27}$Al NMR results.

In order to further evaluate the sample crystallinity changes before and after the hydrothermal treatment more accurately, it is assumed that the crystallinity of fresh Cu catalyst was 100%, and the relative content changes were calculated through the main diffraction peak of $2\theta=22.5^\circ$, the results are shown in Fig. 2b. Although the crystallinity of both catalysts was affected by the hydrothermal treatment, the crystallinity of CuCe was declined by 15.4%, while that of CuCeSi was only 7.1%. The above phenomena suggest that the modification of Si can prevent the destruction of the skeleton structure of BEA zeolite during the process of the hydrothermal treatment, protect the integrity of the skeleton structure.

The SEM images displayed in Fig. 3 show the effect of Si on the morphology of CuCe before and after the hydrothermal treatment. CuCe and CuCeSi have...
the characteristic regular morphology of BEA zeolite, but due to the low amount of Si, there was no obvious difference between them. After hydrothermally treated at 700 °C for 10 h, the surface morphology of the catalysts are severely damaged, but CuCeSi-HT could retain more regular morphology than CuCe-HT. Combined with $^{27}$Al NMR and XRD, the results show that Si modification can effectively inhibit the hydrolysis of Si-O-Al bonds, protect the skeleton and morphological of BEA and improve the hydrothermal stability of CuCe.

2.2 NH$_3$ adsorption

The hydrolysis of BEA skeleton will lead to the loss of surface acidity of zeolite during the process of the hydrothermal treatment, and it is well known that the surface acidity of the catalyst plays a crucial role in NH$_3$-SCR reaction. So NH$_3$-TPD was employed to investigate the influence of Si on the surface acidity of CuCe before and after the hydrothermal treatment (Fig.4). Three desorption peaks were detected in the NH$_3$-TPD curves of all samples in Fig.4. The low-temperature desorption peak (α) at 150~250 °C can be classified as NH$_3$ adsorbed on the weak silanol (Si-OH) group, which is the Lewis acid sites generated by the structural defect. The medium-temperature desorption peak (β) at 250~400 °C can be attributed to the NH$_3$ species adsorbed on the strongly acidic hydroxyl group, that is, the Brønsted acid sites. The high-temperature desorption peak (γ) above 400 °C can be attributed to the strong Lewis acid sites generated by the introduced copper ions. The surface acidity of CuCe is slightly depressed after introducing Si, which may be caused by the hydrolysis of TEOS at the acid sites of BEA, part of the acid sites of BEA was covered by SiO$_2$ after calcined, preventing it from adsorbing NH$_3$. Moreover, the amount of acid sites of the fresh catalysts was decreased significantly after the hydrothermal treatment, which may be caused by H$_2$O molecules attack the Si-O-Al bonds during the hydrothermal treatment process leading to structural collapse of BEA zeolite, resulting in less acidic sites. Interestingly, Si modification can inhibit the loss of surface acidity of CuCe during the hydrothermal treatment, and the amount of acidic sites of CuCeSi-HT was even higher than CuCe-HT. NH$_3$-TPD results show that the modification of Si can stabilize the surface acidity of the catalyst and inhibit the loss of surface acidity of catalyst during the hydrothermal treatment.

As a probe molecule, NH$_3$ can further explore the changes of acidity and acid sites of catalysts before and after the hydrothermal treatment. The in situ DRIFTS results of NH$_3$ adsorption on the catalysts after the hydrothermal treatment are shown in Fig.5. Brønsted and Lewis acid sites can be both detected on the two HT catalysts via NH$_3$ adsorption. The Brønsted acid sites (3 361, 3 282 and 3 178 cm$^{-1}$) are mainly provided by zeolite supports, while the Lewis acid sites (1 627, 1 251 and 1 159 cm$^{-1}$) are mainly derived from Si-OH in the structure and the introduced active copper species. It can be observed that the Brønsted acid sites are the dominant acid sites for both catalysts. In order to more intuitively compare the adsorption of NH$_3$ between two catalysts and their acidity at the same

![Fig 4](image-url)
temperature, the comparison results of NH$_3$ adsorption spectra at 350 °C are listed in Fig.5c. It can be clearly seen that, CuCeSi-HT has more Brønsted acid sites than CuCe-HT at 350 °C, which is from the Si-O-Al bonds on the zeolite skeleton structure, and this result is consistent with the NH$_3$-TPD, indicating that Si modification can protect the surface acid sites. Combined with XRD and $^{27}$Al NMR results, CuCeSi-HT catalyst with a more complete skeleton structure due to the introduction of Si provides more Brønsted acid sites for adsorption and activation of NH$_3$ than CuCe catalyst, which may improve NH$_3$-SCR activity.

### 2.3 Redox properties

Isolated Cu$^{2+}$ species are the main active species of CuCe for NH$_3$-SCR reaction. As shown in Fig.6, H$_2$-TPR profiles of all samples can be divided into four reduction peaks$^{[12-24]}$: the first peak (α) centered at 262 °C and the third peak (δ) located at 447 °C can be assigned to the two-step reduction of isolated Cu$^{2+}$ to Cu$^0$; the second peak (β) at 357 °C is related the reduction of CuO to Cu$^0$, and the last peak (γ) at 554 °C is related to Cu$^+$ self-reduction (SCu$^+$) to Cu$^0$. H$_2$ consumptions were quantitatively calculated according to the CuO reference sample, and the results are summed up in Table 2. The decrease of isolated Cu$^{2+}$ species was clearly observed in CuCe modified by Si, possibly due to the blocking and covering of the structures and active components by SiO$_2$. H$_2$ consumptions of all peaks were decreased after the hydrothermal treatment, but it can be seen from the quantitative results that the amount of isolated Cu$^{2+}$ species in CuCeSi-HT was unexpectedly higher than that in CuCe-HT, and its amount of CuO was lower than that of CuCe-HT.

XPS has been widely used in the semiquantitative evaluation of catalyst surface species. In order to further characterized the chemical state of Cu species, the Cu2p XPS spectra of the catalysts before and after the hydrothermal treatment are shown in Fig.7. All samples show characteristic peaks of Cu$^{2+}$ species, including the main peaks of the Cu2p spin orbit split$^{[25]}$ (Cu2p$_{3/2}$ and Cu2p$_{1/2}$ at 933–937 eV and 953–956 eV, respectively) and one satellite peak near 944.6 eV.

![Fig.5 In situ DRIFTS results of NH$_3$ adsorption over CuCe-HT (a) and CuCeSi-HT (b); Comparison of NH$_3$ adsorption of catalysts under the hydrothermal treatment at 350 °C (c)](image)

![Fig.6 H$_2$-TPR spectra of fresh (a) and hydrothermal treated (b) CuCe and CuCeSi catalysts](image)
which is assigned to CuO\(^{36}\). Cu\(2p_{3/2}\) peaks are deconvoluted to the band at 933.8 and 936.7 eV, which are assigned to CuO and isolated Cu\(^{2+}\) species in ion-exchanged positions, respectively\(^{37}\). In order to better analyze the differences in the distribution of surface elements before and after the hydrothermal treatment of catalysts, the quantitative calculation results are shown in Table 3. There are significant differences in the distribution of copper species among different catalysts. For fresh catalysts, the content of isolated Cu\(^{2+}\) species on the surface of CuCeSi is lower than that of CuCe due to Si coverage, which is consistent with the TPR results (Table 3). After the hydrothermal treatment, the content of isolated Cu\(^{2+}\) is increased for both catalysts, possibly because the copper species in the bulk phase migrated to the surface and mainly existed in isolated Cu\(^{2+}\) and CuO forms. Isolated Cu\(^{2+}\) of 0.82% was detected on CuCeSi-HT, higher than that of 0.64% in CuCe-HT, which is consistent with H\(_2\)-TPR. In addition, the ratio of Cu\(^{3+}\)/CuO increased from 0.28 to 0.42, indicating that the addition of Si can inhibit the aggregation of isolated Cu\(^{2+}\). Combined with the results of H\(_2\)-TPR and XPS, it can be concluded that the addition of Si can inhibit the aggregation of isolated Cu\(^{2+}\) to form CuO during the process of the hydrothermal treatment, so more isolated Cu\(^{2+}\) species could improve the low-temperature SCR activity, while less CuO species can weaken the oxidation of high-temperature NH\(_3\). Therefore, the addition of Si may be beneficial to maintain the NH\(_3\)-SCR activity of CuCeSi-HT in the entire reac-

**Table 2** Quantitative analysis of the H\(_2\)-TPR profiles of the fresh and hydrothermal treated CuCe and CuCeSi catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>α (Cu(^{2+}) to Cu(^{3+})) / (μmol·g(^{-1}))</th>
<th>β (CuO to Cu(^{3+})) / (μmol·g(^{-1}))</th>
<th>δ (Cu(^{3+}) to Cu(^{2+})) / (μmol·g(^{-1}))</th>
<th>γ (SCu(^{3+}) to Cu(^{2+})) / (μmol·g(^{-1}))</th>
<th>Total H(_2) consumption / (μmol·g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCe</td>
<td>77.0</td>
<td>62.7</td>
<td>173.2</td>
<td>70.3</td>
<td>383.2</td>
</tr>
<tr>
<td>CuCeSi</td>
<td>61.5</td>
<td>66.5</td>
<td>56.3</td>
<td>153.2</td>
<td>337.5</td>
</tr>
<tr>
<td>CuCe-HT</td>
<td>41.3</td>
<td>64.2</td>
<td>109.5</td>
<td>9.6</td>
<td>224.6</td>
</tr>
<tr>
<td>CuCeSi-HT</td>
<td>50.4</td>
<td>54.2</td>
<td>36.4</td>
<td>67.4</td>
<td>208.5</td>
</tr>
</tbody>
</table>

**Table 3** Surface chemical composition and contents over catalysts before and after the hydrothermal treatment

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass fraction of surface Cu / %</th>
<th>Mass ratio of isolated Cu(^{2+}) to CuO</th>
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<tbody>
<tr>
<td></td>
<td>Isolated Cu(^{2+})</td>
<td>CuO</td>
</tr>
<tr>
<td>CuCe</td>
<td>0.29</td>
<td>2.03</td>
</tr>
<tr>
<td>CuCeSi</td>
<td>0.26</td>
<td>1.86</td>
</tr>
<tr>
<td>CuCe-HT</td>
<td>0.64</td>
<td>2.32</td>
</tr>
<tr>
<td>CuCeSi-HT</td>
<td>0.82</td>
<td>1.97</td>
</tr>
</tbody>
</table>
The presence of Si stabilizes the skeleton temperature range after hydrothermal treatment.

2.4 NH$_3$-SCR activity

The curves of NO$_x$ conversion as a function of reaction temperatures in NH$_3$-SCR reaction over Cu, CuCe and CuCeSi catalysts are shown in Fig. 8. It can be seen that both CuCe and CuCeSi catalysts show similar NO$_x$ conversions except higher NH$_3$-SCR activity of CuCeSi catalyst than that of CuCe catalyst above 500 °C in Fig. 8a. Their low-temperature NO$_x$ conversion both higher than that of Cu catalyst, and their values of $T_{x0}$ (the reaction temperature when the NO$_x$ conversion rate reaches 90%) are shifted to 186 °C from 218 °C of Cu catalyst, decreased by about 30 °C. After the hydrothermal treatment at 700 °C for 10 h, the catalytic activities have a significant loss over all catalysts at the temperature below 500 °C (as shown in Fig. 8b). However, the maximum NO$_x$ conversion over CuCeSi-HT was 85% in the temperature range of 175 to 400 °C, which is higher than CuCe-HT and Cu-HT (80% and 78%, respectively). Furthermore, CuCeSi-HT can retain over 80% NO$_x$ conversion between 200-550 °C, while CuCe-HT and Cu-HT have over 80% NO$_x$ conversion only in the high temperature range, indicating that Si modification can improve the hydrothermal stability of the CuCe catalyst to some extent.

Combined with the characterization results to analyze, for fresh catalysts, the amount of isolated Cu$^{2+}$ and the surface acid sites are slightly reduced in CuCeSi compared with CuCe due to the covering effect of SiO$_2$ generated by TEOS in the calcined process on the catalyst surface. But their NH$_3$-SCR activity are almost the same, probably because CuCeSi possesses enough isolated Cu$^{2+}$ and acid sites to maintain the optimal activity. After the hydrothermal treatment, the attack of H$_2$O molecules on the Si-O-Al bonds causes the collapse of zeolite skeleton structure, resulting in the decrease of isolated Cu$^{2+}$ and surface acid sites content, which leads to the decrease of catalysts activity. However, after the addition of Si, TEOS hydrolyze on the acid sites and cover the surface to play a certain protective role, thus preventing H$_2$O molecules from attacking the Si-O-Al bonds in the process of hydrothermal treatment, which is conducive to stabilizing the structure of zeolite skeleton. The more complete skeleton structure helps to stabilize the acid sites on the catalyst surface (particularly Brønsted acid sites), and inhibit the aggregation of isolated Cu$^{2+}$. Therefore, compared with CuCe-HT, CuCeSi-HT has more isolated Cu$^{2+}$ and more surface acid sites, and finally, exhibits better NH$_3$-SCR activity than CuCe-HT.

![Fig. 8 NO$_x$ conversion as a function of the reaction temperature over Cu, CuCe and CuCeSi during NH$_3$-SCR]

3 Conclusions

In summary, the hydrothermal stability of CuCe catalyst is effectively improved through the modification of Si. The presence of Si stabilizes the skeleton structure of the zeolite, which improves the amount of acid sites on the catalyst surface and the dispersion of copper ions, and finally leads to the improvement of the hydrothermal stability of the catalyst. The results of XRD, SEM and $^{27}$Al NMR reveal that the addition of Si
can protect the Si-O-Al bonds, inhibit the attack of H$_2$O molecules in the process of hydrothermal treatment, so as to protect the skeleton structure of zeolite and improve the stability. The NH$_3$-TPD and in situ DRIFTS results show that more complete skeleton structure is beneficial to protect the structural acid sites on the surface of zeolite and reduce the loss of the amount of acid sites during the process of the hydrothermal treatment. The results of XPS and H$_2$-TPR show that although the modification of Si covered some active sites on the catalyst surface, a more complete skeleton structure is beneficial to improve the dispersion of copper ions and inhibit the migration and aggregation of copper ions to form CuO. Therefore, the modification of Si can provide more acid sites and highly dispersed Cu species which finally improve the hydrothermal stability of CuCe catalyst for NH$_3$-SCR. This study proves the feasibility of adding Si to stabilize zeolite skeleton, which is helpful to improve the hydrothermal stability of catalysts and develop catalysts with excellent activity for NH$_3$-SCR.

References:

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