

RESEARCH ARTICLE

Reaction Engineering, Kinetics and Catalysis

Porous washcoat structure in CeO₂ modified Cu-SSZ-13 monolith catalyst for NH₃-SCR with improved catalytic performance

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Abstract

A series of CeO₂ modified Cu-SSZ-13 monolith catalysts were prepared by embedding CeO₂ into the washcoat of Cu-SSZ-13 monolith catalyst through solvent combustion method. These CexCu-SSZ-13 catalysts were studied in the selective catalytic reduction (SCR) of NO with NH₃, among which the Ce2Cu-SSZ-13 catalyst exhibited the best low-temperature activity, hydrothermal stability, and sulfur resistance. The physicochemical properties of the catalysts were characterized using multiple methods. Results showed that the acidity, redox capacity, and ammonia adsorption capacity significantly enhanced after CeO₂ modification, thus leading to the high performance of Ce2Cu-SSZ-13 catalyst. Furthermore, the introduction of CeO₂ induced the fast SCR reaction by promoting the oxidation of NO to NO₂. Analog calculation suggested that the porous structure generated via solvent combustion in the washcoat effectively increased the diffusion rate of reaction. *In situ* diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFT) analysis showed that Brønsted acid sites were the main active center and the reaction followed Eley-Rideal mechanism.

KEYWORDS

low-temperature activity, mass transport, NH₃-SCR, solvent combustion method, SSZ-13 zeolite

1 | INTRODUCTION

Nowadays, the difficulty in reducing NO_x from diesel engines in terms of lean burn (high air/fuel ratios) is aggravated by the unreacted oxygen. Among the various technologies, selective catalytic reduction (SCR) with urea or NH₃ is the most effective for de-NO_x in mobile and stationary sources. However, the traditional vanadium-based catalysts have poor low-temperature activity and high-temperature stability, which leads to a narrow activity window and limits their applications.¹ Recently, ion-exchange zeolite catalysts, such as Cu/Fe-CHA, Fe/beta,

Cu/Fe-SSZ-13, and Cu-ZSM-5, have been regarded as mainstream catalysts because of their wide activity window and flexible active sites.^{2–5} Among these catalysts, Cu-SSZ-13 has been widely commercialized due to its good low-temperature activity and stability.

The small-pore Cu-SSZ-13 catalyst has excellent NH₃-SCR activity and broad activity window that comply with Euro VI and equivalent emission standards. Abundant isolated Cu²⁺ species of the Cu-SSZ-13 catalyst are anchored to the six-membered rings, stabilizing the structure, and active sites of zeolite under hydrothermal aging. However, under harsh hydrothermal aging conditions, Cu ions lose

their anchored active sites to form CuO or CuAl_2O_4 along with aluminum detached from zeolite, resulting in the collapse of the catalyst structure.⁵ In addition, Cu-SSZ-13 is more sensitive to SO_2 in exhaust gas, mainly due to the easy formation of ammonia bisulfate at a temperature below 300°C . Moreover, the adsorption of SO_x on the active sites can form copper sulfate species.² Therefore, the hydrothermal and sulfur resistance of Cu-SSZ-13 need to be further enhanced. Improved preparation methods or element doping have been investigated to overcome the abovementioned difficulties.⁶ For example, Zhao et al.⁷ found that the introduction of Y makes Cu^{2+} ions occupy six-membered rings better and stabilizes the structure of zeolite. As a result, the Y-Cu-SSZ-13 catalyst has enhanced hydrothermal stability. Fe modification also improved the low-temperature activity and hydrothermal stability of Cu-SSZ-13 catalyst with stronger redox capacity and more active sites.⁸ Xu et al.⁹ showed that introducing Zn to the Cu-SSZ-13 catalyst via one-pot synthesis could facilitate the dispersion of isolated Cu^{2+} and its anchor in the structure of SSZ-13, thereby improving the hydrothermal stability of the catalyst.

Recently, CeO_2 has attracted considerable attention because of its excellent oxygen storage and redox capacity in the NH_3 -SCR catalyst. Ce-based catalysts, such as $\text{CrO}_x\text{-CeO}_2$, Mn-Ce, Ce-V-W-Ti, and Sm/Co/Fe/Cr-CeTi have been widely reported.^{10–12} The presence of $\text{Ce}^{3+}/\text{Ce}^{4+}$ in the oxide catalyst promotes the formation of oxygen vacancy, which contributes to the oxidation of NO to NO_2 , thus triggering the “fast SCR” reaction.¹³ The electron transfer between Ce and other metals improves the redox capacity of catalysts. For Cu zeolite catalysts, Ce modification can inhibit the aggregation of active copper species and the deposition of sulfate on the active site, thereby reinforcing the zeolite structure.¹⁴ These properties make Ce a potential catalyst additive/promoter, and many researchers have focused on this topic. For instance, Li et al.¹⁴ deposited a thin CeO_2 layer on the surface of a Cu-SAPO-18 zeolite catalyst, which inhibits the aggregation of isolated Cu^{2+} ions to form CuO_x species and alleviates the deposition of sulfate on the active sites. Similarly, Wang et al.¹⁵ revealed that a Ce-modified Cu-SSZ-13 catalyst significantly restricts the transformation of active Cu^{2+} sites to CuO_x during hydrothermal aging, and the robust interaction between Ce^{3+} and zeolite significantly inhibits dealumination. In summary, Ce in Cu zeolite catalysts can protect isolated Cu^{2+} ions and strengthen the structure of zeolite.

It should be noted that the above studies mainly focus on improving the physicochemical properties and catalytic performance of zeolite powder catalysts by Ce modification. Considering that monolith type catalysts are closer to practical industry applications but very few studies have been reported, therefore, a comprehensive study of Ce modification on the washcoat of monolith type catalysts is necessary and helpful for industrial catalyst development.

Monolith catalysts have been widely used in industrial applications because of the low back pressure, favorable mass/heat transfer property, and high surface-to-volume ratio. NH_3 -SCR reaction is a highly exothermic reaction, and excessive heat must be removed rapidly from the catalyst bed to avoid the oxidation reaction of reactants related to catalytic deactivation. In addition, the mass transport, adsorption, and activation of reactive gases on the catalyst washcoat

are of great importance in gas–solid catalytic reactions. Therefore, in practical application, modification of the washcoat of the monolith catalyst may be a potential solution to improve the catalytic performance. In view of these points, we modified the washcoat of a Cu-SSZ-13 monolith catalyst with Ce through solvent combustion and studied its mass transfer and catalytic influence on NH_3 -SCR reaction. The physicochemical properties of the Ce-modified Cu-SSZ-13 catalyst were characterized by scanning electron microscopy (SEM), powder X-ray diffraction (XRD), UV–visible diffuse reflection spectra (UV–vis), Brunauer–Emmett–Teller (BET) specific surface area analysis, NH_3 temperature-programmed desorption (NH_3 -TPD), temperature programmed reduction of hydrogen (H_2 -TPR), X-ray photoelectron spectroscopy (XPS), and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFT) techniques. This work can provide an important reference for the development of industrial monolith catalysts for NH_3 -SCR.

2 | EXPERIMENTAL

2.1 | Catalyst preparation: Cu-SSZ-13 monolith catalyst

The monolithic coating technique was similar to that in literature.¹⁶ In a typical process, a slurry containing 32 wt% Cu-SSZ-13 powder catalyst (Huizhou Ruihe Co., Ltd, China), 8 wt% γ -alumina (as binder, Aladdin) and 60 wt% deionized water was prepared, and its pH was adjusted to ~ 4 with acetic acid under vigorous stirring. The viscosity was about 2500 cp, which is measured by a Viscometer. The dimensions of the blank cordierite monolith (NGK, Suzhou, China) were 143.8 mm in diameter and 101.6 mm in length with a cell density of 400 cpsi (cells per square inch) and a wall thickness of about 0.18 mm. The washcoat loading was about 180 g (mass of the Cu-SSZ-13 catalyst)/L (geometric volume of the monolith cylinder). The slurry was evenly coated to the cells of the cordierite monolith with a washcoating machine (Wuxi Linlei Co., Ltd, China) by repeating several coating and drying (120°C for 10 min, moisture loss was about 80%) cycles. Finally, the dried monolith catalyst was calcined at 550°C for 2 h in a muffle furnace. The obtained Cu-SSZ-13 coated monolith catalyst was named Cu-Z. In addition, the SSZ-13 zeolite was provided from Huizhou Ruihe. Co., Ltd, China.

2.2 | Catalyst preparation: Ce2Cu-Z-SCS monolith catalyst

To obtain a loose washcoat and facilitate the modification of Ce, the dried monolith catalyst was excised into several small monolithic cylinders with a diameter of 24 mm and length of 38 mm using a bench drill before calcination. A certain amount of cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99%, Aladdin), combustion agent urea ($\text{CH}_4\text{N}_2\text{O}$, 99%, Aladdin), and deionized water were vigorously stirred to obtain a homogenous solution. Thereafter, the small monolith catalyst cylinder

was immersed in the solution for 5 min and the excess solution on the wall of the channels was slowly blown out with compressed air. Then the monolith catalyst cylinder was kept at 100°C for 30 min. Several immersion-drying cycles were carried out to achieve the required Ce loading. The coated monolith was then burned at 400°C for 30 min followed by calcination at 550°C for 2 h. The loading weights of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were 0.5, 1.0, 2.0, and 4.0 g and the mass ratio of cerium nitrate:urea was fixed to 1:2. The modified monolith catalysts were named $\text{Ce}_x\text{Cu-Z-SCS}$ ($x = 0.5, 1, 2, \text{ and } 4$, SCS stands for solvent combustion synthesis), where x represented the weight of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

For comparison, a Ce modified Cu-Z monolith catalyst with $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ loading amount of 2.0 g (named $\text{Ce}_2\text{Cu-Z-IM}$) was prepared via direct impregnation method following similar recipe to the above without urea. Furthermore, the preparation method of pure CeO_2 sample was the same as $\text{Ce}_2\text{Cu-Z-SCS}$, except that Cu-Z monolith was replaced by blank monolith.

2.3 | Catalyst characterization

The physicochemical properties of the synthesized catalysts were characterized using scanning electron microscopy (SEM), powder X-ray diffraction (XRD), UV-visible diffuse reflection spectra (UV-vis), BET specific surface area analysis, NH_3 temperature-programmed desorption (NH_3 -TPD), temperature-programmed reduction of hydrogen (H_2 -TPR), XPS, and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFT). The characterization methods were described in detail in the Supporting Information.

2.4 | Catalytic performance test

The catalytic performance of the synthesized catalysts for NH_3 -SCR was evaluated in a bench-scale fixed-bed reactor with a 30 mm inner diameter quartz tube, as shown in Figure S1. The monolith catalyst cylinder was first placed in the middle of the quartz tube and the gap between the catalyst cylinder and the inner wall of the quartz tube was filled with quartz cotton. A gas mixer was installed upstream of the catalyst, and a thermocouple is placed on the inlet side of the catalyst cylinder to control reaction temperature. Water was extracted by quantitative pump and then vaporized by evaporator before flowing through the gas mixer. An FTIR analyzer (MKS MultiGas 6030) was connected to the downstream of the reactor to analyze the effluent gases, for example, NO, NO_2 , N_2O , H_2O , and NH_3 . Meanwhile, a gas distributor was installed at the front of gas mixer to adjust gas concentration. The feed gas composition was as follows: 500 ppm NO, 500 ppm NH_3 , 5 vol% O_2 , 5 vol% H_2O , 50 ppm SO_2 (when used), and N_2 as equilibrium gas. The total gas flow rate was 10.5 L/min, corresponding to a space velocity (GHSV) of 40,000 h^{-1} . The reaction at each selected temperature was stabilized for 30 min before

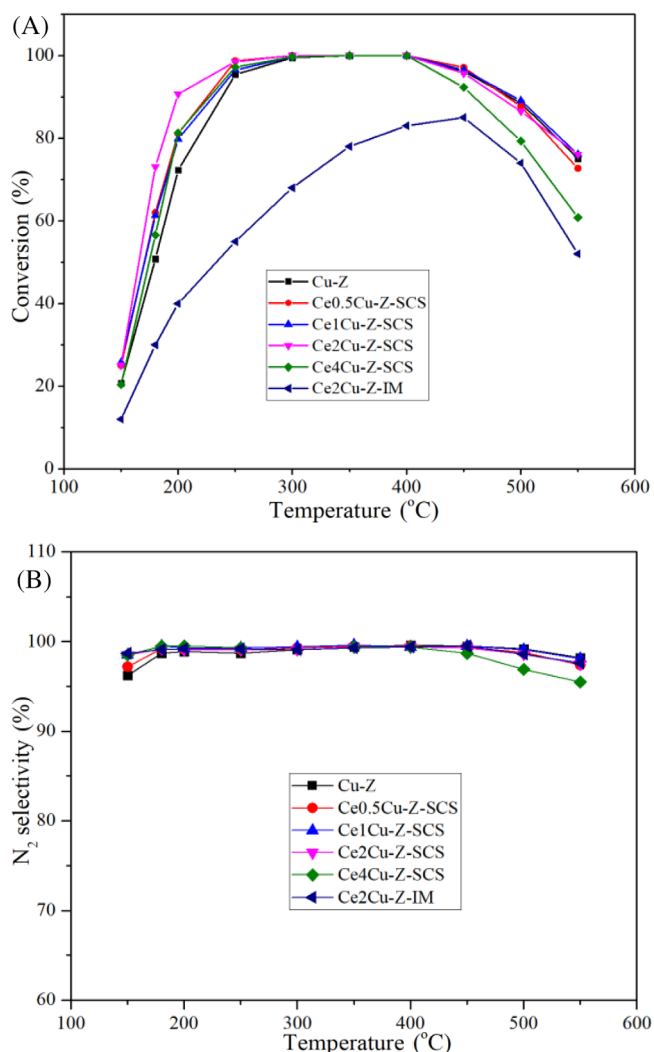


FIGURE 1 NO conversion (A) and N_2 selectivity (B) of different catalyst. The reaction conditions: 400 ppm NH_3 , 400 ppm NO, 5% O_2 , 5% H_2O , Ar balance, and GHSV = 40,000 h^{-1}

sampling. NO conversion and N_2 selectivity were calculated as follows:

$$\text{NO Conversion}(\%) = \left(1 - \frac{[\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \right) \times 100 \quad (1)$$

$$\begin{aligned} \text{N}_2 \text{ Selectivity}(\%) &= \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}} - [\text{NO}_2]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}} \times 100 \quad (2) \end{aligned}$$

The oxidation reactions of NH_3 and NO were also tested separately in the same device. The feed gas was as follows: 500 ppm NH_3 (when used), 500 ppm NO (when used), 5 vol% O_2 , and N_2 as balance. The total flow rate was 10.5 L/min with a GHSV of 40,000 h^{-1} . The NO conversion was calculated by Equation (1), and the NH_3 conversion was calculated as following:

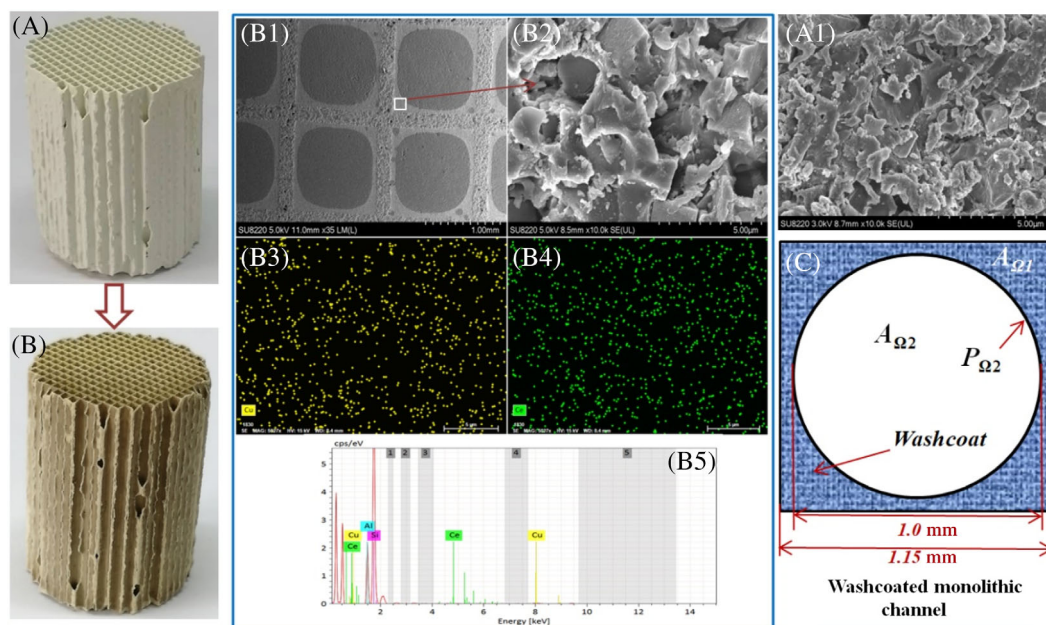


FIGURE 2 Photograph of Cu-Z coated monolith (A), Ce2Cu-Z-SCS coated monolith (B), SEM of frontal channel view of Ce2Cu-Z-SCS catalyst (B1), partial magnification of frontal channel view of Ce2Cu-Z-SCS catalyst (B2), and Ce2Cu-Z-IM catalyst (A1), EDX-Mapping images of Ce2Cu-Z-SCS catalyst (B3–B5), distribution of catalyst washcoat in one channel (C)

$$\text{NH}_3 \text{ Conversion (\%)} = ([\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}) \times 100 / [\text{NH}_3]_{\text{in}} \quad (3)$$

prepared by solvent combustion possessed the best catalytic activity and broadest temperature window among all the catalysts prepared.

3 | RESULTS AND DISCUSSION

3.1 | NH₃-SCR performance

Figure 1A exhibits the results of the typical NH₃-SCR reaction on catalysts without and with different amounts of CeO₂. The NO conversion over the Cu-Z catalyst was approximately 73% at 200°C and above 80% at 210–540°C (activity temperature window). Apparently, the low-temperature activities of CexCu-Z-SCS catalysts prepared using solvent combustion with urea were significantly enhanced compared with that of Cu-Z. Among these CexCu-Z-SCS catalysts, the Ce2Cu-Z-SCS sample possessed the highest low-temperature activity, and a wide activity window of approximately 185–540°C. The catalytic activity of Ce4Cu-Z-SCS was lower than that of Ce2Cu-Z-SCS, suggesting too high loading of Ce may block the active sites of Cu-Z catalyst. Meanwhile, the high-temperature activity also decreased on Ce4Cu-Z-SCS, and the activity window was only 198–495°C. Ce2Cu-Z-IM catalyst prepared without urea show drastically decreased activity, probably because the compact washcoat formed by CeO₂ on the surface of Cu-Z (which can be observed in following SEM image in Figure 2A1) covered the active sites of the catalyst. Therefore, it is deduced that solvent combustion with urea could construct a more porous CeO₂ coating, which promotes the feed gas passing through the CeO₂ coating and reacting on the active sites. In addition, the N₂ selectivity of all catalysts exceeded 90% at the temperature range of 150–550°C, as shown in Figure 1B. To sum up, Ce2Cu-Z-SCS

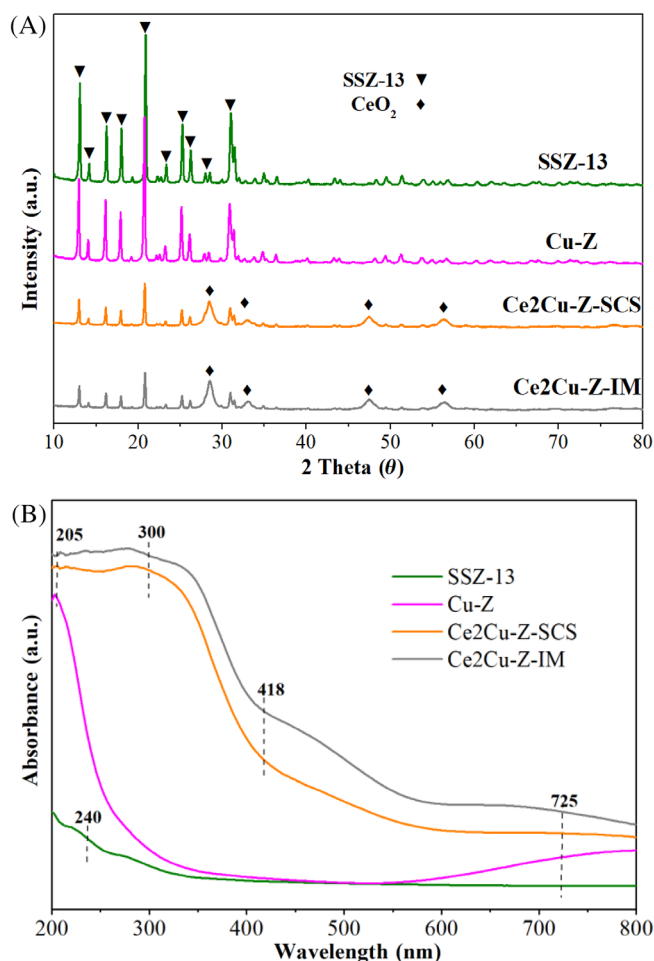
3.2 | Morphological and structural analysis

Figure 2A exhibits the photo of Cu-Z catalysts, which is obtained by coating Cu-SSZ-13 powder to the monolith cordierite cylinder. The Cu-SSZ-13 washcoat was uniformly distributed on the monolith support. After CeO₂ was loaded using solvent combustion, the overall Cu-Z monolithic catalyst uniformly turned khaki (Figure 2B), suggesting CeO₂ particles were evenly dispersed in the catalyst washcoat. The middle part of Ce2Cu-Z-SCS was excised to observe the washcoat distribution on the frontal channel, as shown in Figure 2B1 and model Figure 2C. The thickness of the catalyst washcoat on the channel was ~0.25 mm at the corners and ~0.12 mm at the sides. In addition, the partial magnification of the frontal Ce2Cu-Z-SCS catalyst washcoat is exhibited in Figure 2B2. A clearly visible porous and loose structure formed inside the washcoat, and this morphology represented the unique feature of solvent combustion method.¹⁷ By comparison, the washcoat structure of Ce2Cu-Z-IM without urea was relatively dense (Figure 2A1), possibly because the loaded CeO₂ particles filled the gaps in the Cu-Z washcoat. Meanwhile, the EDX-Mapping of the area in Figure 2B2 showed that Ce and Cu elements were highly dispersed in the washcoat (Figure 2B3,B). In addition, the Ce:Cu element ratio of 1:5.4 obtained from the energy spectrum was consistent with the ICP test result in Table 1.

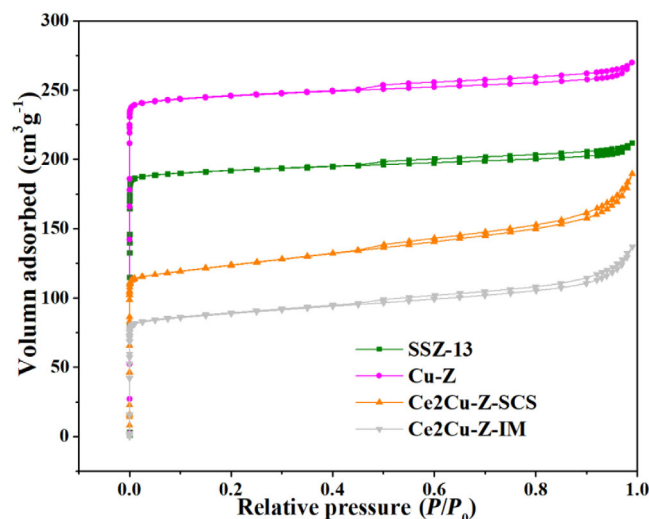
Figure 3A shows the XRD patterns of SSZ-13, Cu-Z, Ce2Cu-Z-SCS, and Ce2Cu-Z-IM catalysts. It should be noted that Cu-Z, Ce2Cu-

TABLE 1 Textural properties of SSZ-13, Cu-Z, Ce₂Cu-Z-SCS, and Ce₂Cu-Z-IM

Catalysts	Concentration (%) ^a			SSA (m ² g ⁻¹) ^b	Pore volume (cm ³ g ⁻¹) ^b
	Si/Al	Cu content	Ce content		
SSZ-13	13.5	0	0	525	0.23
Cu-Z	13.2	3.2	0	476	0.22
Ce ₂ Cu-Z-SCS	13.4	3.1	16.2	468	0.21
Ce ₂ Cu-Z-IM	13.3	3.2	16.4	314	0.17

^aDetermined by ICP-AES.^bObtained by N₂ adsorption isotherms.**FIGURE 3** XRD patterns (A) and UV-Vis Spectroscopy (B) of SSZ-13, Cu-Z, Ce₂Cu-Z-SCS, and Ce₂Cu-Z-IM samples

Z-SCS, and Ce₂Cu-Z-IM powder were obtained by scraping from monolithic catalysts. The diffraction peaks of SSZ-13 and Cu-Z samples showed a typical CHA framework topology,¹⁸ which manifested that the lattice structure of the prepared Cu-Z catalyst could remain intact after Cu ion exchange.¹⁹ Meanwhile, the diffraction peaks of Cu²⁺ species were not observed possibly because they were highly dispersed or below the detection limit.²⁰ After the introduction of Ce species, diffraction peaks attributed to CeO₂ were found. In addition, the intensities of the whole diffraction peaks in Ce₂Cu-Z-SCS and Ce₂Cu-Z-IM weakened compared with that in Cu-Z. This result can

**FIGURE 4** N₂ adsorption-desorption isotherms of SSZ-13, Cu-Z, Ce₂Cu-Z-SCS, and Ce₂Cu-Z-IM

be attributed to the distribution of CeO₂ particles on the Cu-Z surface.⁹ In addition, although the intensity of diffraction peaks of Ce₂Cu-Z-SCS and Ce₂Cu-Z-IM decreased significantly, their CHA framework topology structure diffraction peaks were retained. Thus, the introduction of CeO₂ through solvent combustion and impregnation method could not break the crystal structure of the Cu-Z catalysts.

The coordination and nature of copper were investigated using UV-vis spectra, as shown in Figure 3B. For the SSZ-13 zeolite, a broad absorption peak appeared at ~240 nm, which corresponded to the charge transfer of SSZ-13 zeolite. Cu-Z possessed two main absorption peaks. The intense one at 205 nm represented the charge transfer of zeolite lattice oxygen to the Cu²⁺/Cu⁺ ions, whereas the weak one at ~725 nm was ascribed to the CuO species, which corresponded to the electron d-d transitions of Cu²⁺ in a distorted octahedral coordination surrounded by oxygen.²¹ We can thus infer that the Cu-Z catalyst was dominated by isolated Cu²⁺/Cu⁺. In addition, the charge transfer from the lattice oxygen of zeolite to Cu²⁺/Cu⁺ increased after the introduction of cerium. The absorption peak at ~300 nm was well defined as Ce⁴⁺ in the tetrahedral environment,²² but the peak near 418 nm was not well defined. Ho et al.²³ reported that the absorption of cerium oxide in the UV region generated from the charge transfer between the Ce 4f and O 2p states in Ce⁴⁺ and

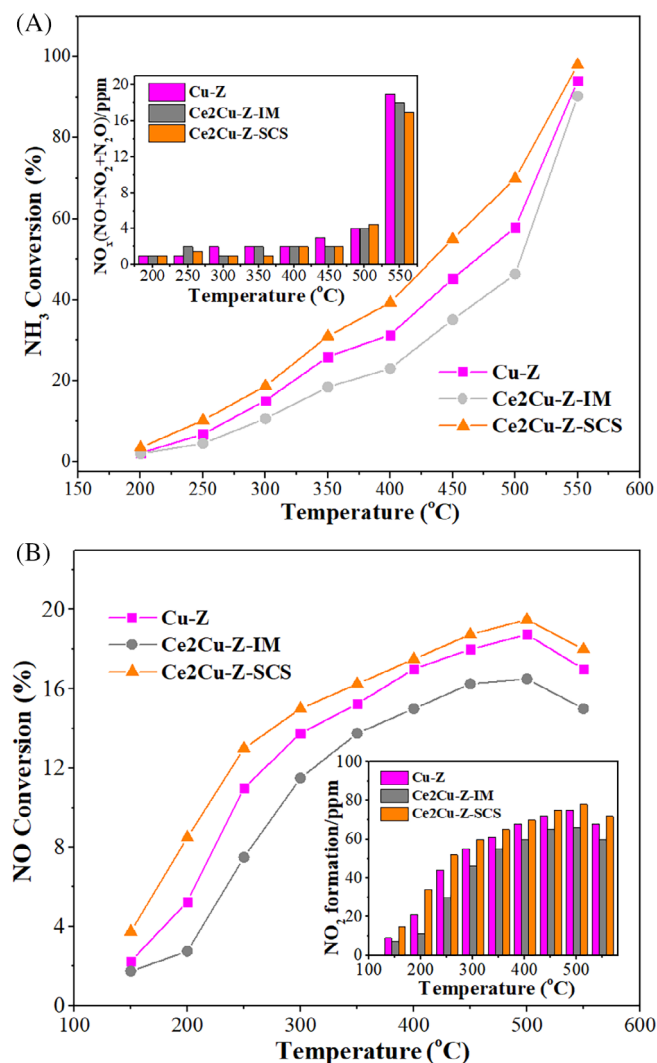


FIGURE 5 NH₃ oxidation (A) and NO oxidation (B) of Cu-Z, Ce2Cu-Z-IM, and Ce2Cu-Z-SCS. Insets show the formed NO_x and NO₂. Reaction condition: [NH₃] = 500 ppm (when used), [NO] = 500 ppm (when used), [O₂] = 5 vol%, N₂ balance, and GHSV = 40,000 h⁻¹

O²⁻ is much stronger than the 4f¹-5d¹ transition from Ce³⁺ in the mixed valence cerium species. This was also verified in Ce2Cu-Z-SCS catalyst from the Ce 3d XPS spectra (Figure S2), which showed both Ce³⁺ and Ce⁴⁺ after the addition of cerium. Thus, we speculated that the peaks of Ce⁴⁺ and Ce³⁺ overlapped at ~418 nm in the UV-vis spectrum. The coexistence of Ce⁴⁺ and Ce³⁺ was beneficial to the oxygen storage capacity and the charge transition in zeolite, thus improving the redox performance of the catalyst, for example, the oxidation of NO to NO₂.²⁴

N₂ adsorption-desorption isotherms are shown in Figure 4. The pristine SSZ-13 support and Cu-SSZ-13 displayed type I isotherms, which were typical characteristics of microporous (<2 nm).^{21,25} Whereas Ce2Cu-Z-SCS and Ce2Cu-Z-IM showed H4-type hysteresis loops in the relative pressure range of 0.4–1.0 P/P₀. This result indicated that Ce species changed both micropore and mesopore

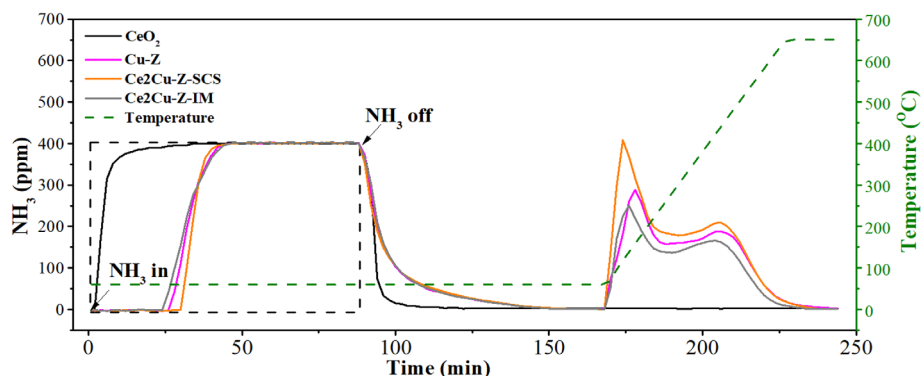
structure of the catalyst after introducing to the catalyst washcoat.²⁶ In addition, the pore volume and specific surface area of catalysts are also summarized in Table 1. The pore volume and specific surface area over Cu-Z slightly decreased after Cu ion exchange, then, nearly unchanged after the introduction of Ce species using solvent combustion method. However, compared with Cu-Z, the pore volume of Ce2Cu-Z-IM prepared via impregnation method decreased from 0.22 to 0.17 cm³/g⁻¹, and the specific surface area decreased from 476 to 314 m²/g⁻¹, suggesting Ce species could cover the surface and partially blocked the pores channels of Cu-Z catalyst.²¹

3.3 | Oxidation of NH₃ and NO

Ammonia oxidation, the primary competitive reaction in NH₃-SCR, is detrimental because it lowers the NO_x conversion and generates by-products such as N₂O and NO₂.²⁷ In the present study, NH₃ oxidation behavior was investigated to determine the strength of copper active sites. As shown in Figure 5A, it mainly underwent two processes: the NH₃ oxidation at low temperatures was slow and occurred at the copper sites in the six-membered ring of zeolite, whereas that at high temperatures occurred at the copper sites in the eight-membered ring (large cages) with high activation energy and catalytic activity according to previous analysis.²⁸ The NH₃ conversion of Cu-Z was lower than 15% at temperatures below 300°C but increased significantly with further increases in temperatures. Simultaneously, negligible by-product NO_x (less than 5 ppm) was observed below 500°C and only 17 ppm even at 550°C. This finding was in line with the high N₂-selectivity of Cu-Z for NH₃-SCR (Figure 1B). The NH₃ conversion of Ce2Cu-Z-IM was obviously lower than that of Cu-Z possibly because of cerium species impregnated in the Cu-Z washcoat. The formation of CeO₂ filled the washcoat space and blocked the copper sites in zeolite, which decreased the number of exposed active sites. However, the introduction of CeO₂ through solvent combustion significantly improved the NH₃ conversion of Ce2Cu-Z-SCS. After urea was burned at a high temperature, the washcoat formed a loose and porous structure that increased the number of exposed copper active sites and thus promoted the NH₃ oxidation reaction. Meanwhile, the copper active sites exposed in the washcoat were a key factor to boost the standard NH₃-SCR reaction (Figure 1A). Moreover, the introduction of CeO₂ did not increase the selectivity of NH₃ oxidation to NO_x (inset in Figure 5A), agreeing with its high N₂ selectivity in standard NH₃-SCR reaction (Figure 1B).

In metal ion-exchanged zeolite catalysts, NO oxidation is an important SCR reaction rate step to improve catalytic performance, and the formation of NO₂ is the key intermediate gas for the “fast SCR” reaction.^{29,30} Therefore, NO oxidation reaction was studied on the copper ion-exchanged zeolite catalysts. Figure 5B displays the curve of the steady-state NO oxidation to NO₂ over the different catalysts. The feed gas was 500 ppm NO and 5% O₂, and the total flow of gas was 500 ml min⁻¹. In Figure 5B, NO oxidation rate at low temperatures was mainly kinetically controlled. The oxidation of NO to NO₂ is a reversible reaction and its conversion is limited by

FIGURE 6 NH_3 -TPD of the CeO_2 , Cu-Z, Ce2Cu-Z-SCS, and Ce2Cu-Z-IM catalysts



thermodynamics equilibrium at high temperatures.³¹ Cu-Z showed a NO conversion of less than 5% below 200 $^{\circ}\text{C}$, which gradually increased with the increasing temperature. The reversible reaction ($2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$) dominated at temperatures above 500 $^{\circ}\text{C}$, which reduced NO oxidation equilibrium conversion. The trend of NO oxidation reaction on Ce2Cu-Z-IM was similar to that on Cu-Z, but showed a lower value, agreeing with its inferior SCR performance (Figure 1A). This result can be ascribed to the CeO_2 formed using impregnation method which filled the washcoat pores and severely blocked the copper active sites. In contrast, the NO oxidation conversion rate of Ce2Cu-Z-SCS increased rapidly from 150 to 300 $^{\circ}\text{C}$, suggesting Ce2Cu-Z-SCS was superior to the two other catalysts for NO oxidation. Namely, “fast SCR” occurs more easily on Ce2Cu-Z-SCS. Verma et al.³² reported that the NO oxidation on the Cu_xO_y species (Cu-O_y-Cu), which were the active sites for NO oxidation in the eight-membered ring, was more facile than that on the isolated Cu^{2+} ion near the six-membered ring. In Ce2Cu-Z-SCS, the CeO_2 formed through solvent combustion possibly modified the washcoat of the monolithic catalyst and increased the number of exposed Cu active sites, especially the Cu_xO_y system in the eight-membered rings, thereby improving the NO oxidation activity. Meanwhile, the introduced CeO_2 possessed excellent oxygen storage capacity and promoted the O_2 activation in the catalyst washcoat, which also contributed to the NO oxidation and even the SCR reaction.³⁰ In addition, Figure 5B inset exhibits the amount of formed NO_2 , which was proportional to the NO conversion rate. Compared with the other catalysts, Ce2Cu-Z-SCS generated more NO_2 , which could trigger the “fast SCR” reaction and improve the low temperature catalytic activity.

3.4 | Surface acidity

NH_3 -TPD tests were performed to investigate the Lewis and Brønsted acids of the different catalysts. Figure 6 presents the adsorption and desorption of ammonia over the different catalysts as a function of time and temperature. In the transient adsorption process, the shorter ammonia breakthrough time suggests a lower amount of ammonia stored under the same NH_3 concentration and temperature.^{16,33} In the present study, the NH_3 signal of Cu-Z was

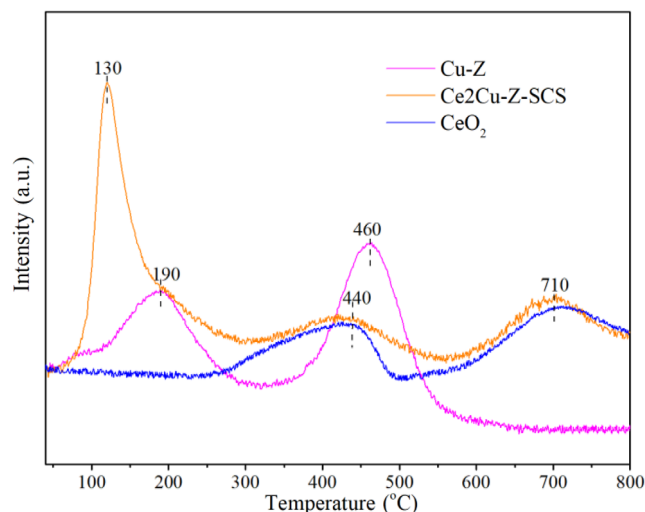


FIGURE 7 H_2 -TPR of the CeO_2 , Cu-Z, and Ce2Cu-Z-SCS samples

detected at 32 min (breakthrough time), whereas the breakthrough time of Ce2Cu-Z-IM was 31 min. The marginally shorter breakthrough time of Ce2Cu-Z-IM than the other catalysts was mainly due to the doped CeO_2 occupying the NH_3 adsorption sites, which decreased the NH_3 adsorption capacity. As expected, the NH_3 breakthrough time (35 min) of Ce2Cu-Z-SCS was much longer than those of the two other catalysts. The formed porous structure of Ce2Cu-Z-SCS which is observed by SEM (Figure 2B2) effectively improved the NH_3 adsorption capacity.³³ In addition, the NH_3 diffusion and adsorption rate of Ce2Cu-Z-SCS was significantly faster compared to the two other catalysts, which can be deduced from the steeper curve from the onset of NH_3 breakthrough to saturation. Thus, the formed porous washcoat was conducive to the NH_3 diffusion rate and improved the NH_3 -SCR efficiency, which would be analyzed in detail later.

The NH_3 desorption curve exhibited three peaks. The peak at $\sim 170^{\circ}\text{C}$ was attributed to the ammonia desorption at the physically adsorbed NH_3 and/or weak acid sites,⁷ the peak at $\sim 250^{\circ}\text{C}$ was ascribed to the consumption of ammonia adsorbed at the Lewis acid sites,³⁴ and the peak at 450°C was attributed to the consumption of ammonia adsorbed at the Brønsted acid sites.^{5,14,26,35} Almost no NH_3

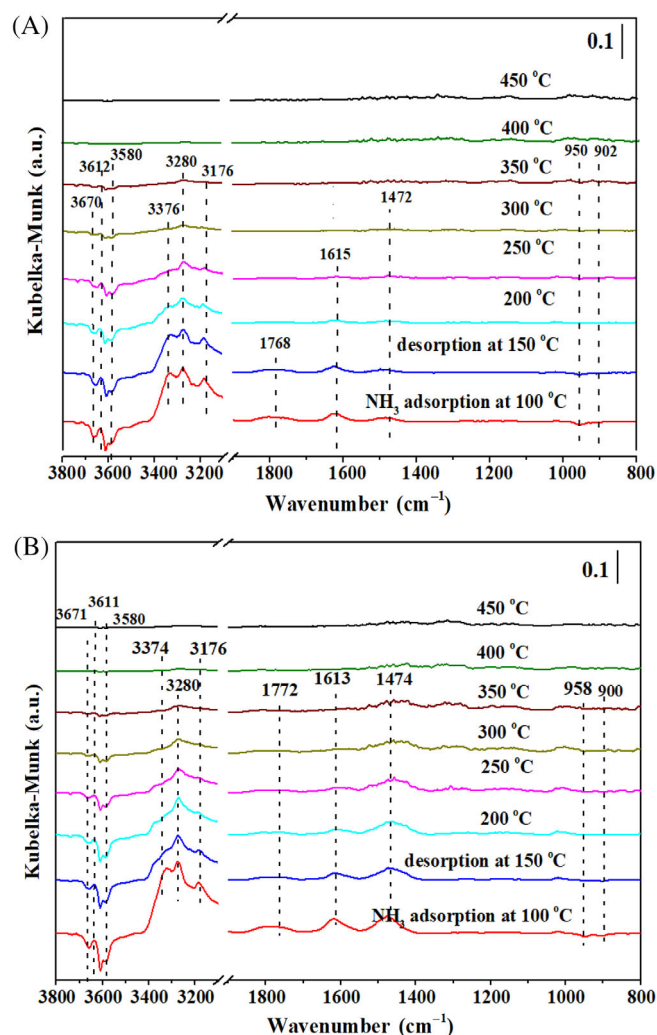


FIGURE 8 *In situ* DRIFT spectra of NH_3 adsorption over Cu-Z (A) and Ce₂Cu-Z-SCS (B)

was adsorbed on monolith supported pure CeO_2 , as shown in Figure 6, suggesting that the acidity of Cu-Z, Ce₂Cu-Z-IM, and Ce₂Cu-Z-SCS catalysts mainly comes from Cu-Z. The NH_3 desorption peak area decreased in the order of Ce₂Cu-Z-SCS > Cu-Z > Ce₂Cu-Z-IM. Ce₂Cu-Z-IM prepared by impregnation method showed a decrease in acidity due to CeO_2 occupying the acid sites. In contrast, the Ce₂Cu-Z-SCS washcoat with a loose and porous structure exposed more acidic sites. In addition, the NH_3 desorption peaks at the Brønsted acid sites were stronger than those at the Lewis acid sites. The Brønsted acid sites could contribute to NH_3 adsorption and possibly directly participate in the reaction, thus promoting the SCR reaction more effectively.

3.5 | H_2 -TPR analysts

H_2 -TPR was performed to study the effect of cerium modification on the oxidation valence state of the catalyst, as shown in Figure 7. The

copper species reduction in zeolite mainly undergoes two processes: (1) Cu^{2+} is reduced to Cu^+ at low temperatures and (2) Cu^+ is reduced to Cu at high temperatures.^{15,21} The reduction peak of Cu-Z at $\sim 190^\circ\text{C}$ was ascribed to the reduction of Cu^{2+} to Cu^+ on the $\text{Cu}(\text{OH})^+-\text{Z}$ nearby the eight-membered rings and $\text{Cu}^{2+}-2\text{Z}$ at the six-membered rings, whereas the peak at $\sim 460^\circ\text{C}$ was attributed to the reduction of Cu^+-Cu .^{36,37} In addition, the H_2 -TPR of pure CeO_2 as a reference exhibited two main reduction peaks, the peak at $\sim 440^\circ\text{C}$ was the reduction peak of surface captured oxygen, and the peak at $\sim 710^\circ\text{C}$ was the reduction peak of lattice oxygen.^{11,14} After the introduction of CeO_2 , the reduction peaks of Ce₂Cu-Z-SCS shifted to a lower temperature compared with that of Cu-Z. For instance, the peak at 460°C ascribed to the reduction of $\text{Cu}^{2+}-\text{Cu}^+$ shifted to 440°C , whereas the peak at 190°C attributed to the reduction of Cu^+-CuO shifted to approximately 130°C . The fact revealed that the introduction of CeO_2 significantly enhanced the reducibility of Cu species, and thus contributed to its excellent low temperature catalytic activity.^{21,37} In addition, the strength of the peak at 130°C on Ce₂Cu-Z-SCS increased significantly compared with the peak at 190°C on Cu-Z. Meanwhile, the strength of the peak at 440°C on Ce₂Cu-Z-SCS which corresponds to the reduction in surface captured oxygen decreased greatly compared with that on pure CeO_2 . This result may be ascribed to the synergistic effect between Cu and Ce, which promoted the reduction capacity of the catalyst.

4 | IN SITU DRIFT ANALYSIS

4.1 | Adsorption of NH_3

In situ DRIFT experiments of NH_3 adsorption were performed to further determine the surface acidity of the catalysts. The catalysts were exposed to NH_3 at 100°C for 30 min and purged with Ar, followed by desorption at 100 – 450°C , as shown in Figure 8. For Cu-Z, the negative bands at 3670, 3612, and 3580 cm^{-1} were ascribed to the bridging hydroxyl groups ($\text{Si}-\text{OH}-\text{Al}$).³⁸ The bands at 3000 – 3400 , 1768, and 1472 cm^{-1} were attributed to the symmetric and asymmetric bending vibrations of N–H bonds generated by NH_4^+ adsorption on Brønsted acid sites, whereas the band at 1615 cm^{-1} was assigned to the symmetric and asymmetric bending vibration of N–H generated by NH_3 on Lewis acid sites.^{39–41} In addition, the negative peaks at 902 and 960 cm^{-1} were attributed to the T–O–T stretching vibration generated by NH_3 adsorbed on the Cu sites.^{21,42} The intensity of the peak decreased with increasing temperature and almost vanished when the temperature exceeded 400°C . The NH_3 adsorption of Ce₂Cu-Z-SCS was similar to that of Cu-Z. The nearly identical stretching vibration peaks (958 and 900 cm^{-1}) of T–O–T indicated that the Cu^{2+} ions residing closely to the framework were unchanged. However, the peaks at 3000 – 3400 , 1613, and 1474 cm^{-1} of Ce₂Cu-Z-SCS were stronger than those of Cu-Z during the NH_3 adsorption at 100°C . These results revealed that the introduction of CeO_2 increased the number of Brønsted and Lewis acid sites, and the former was the main type, agreeing with the NH_3 -

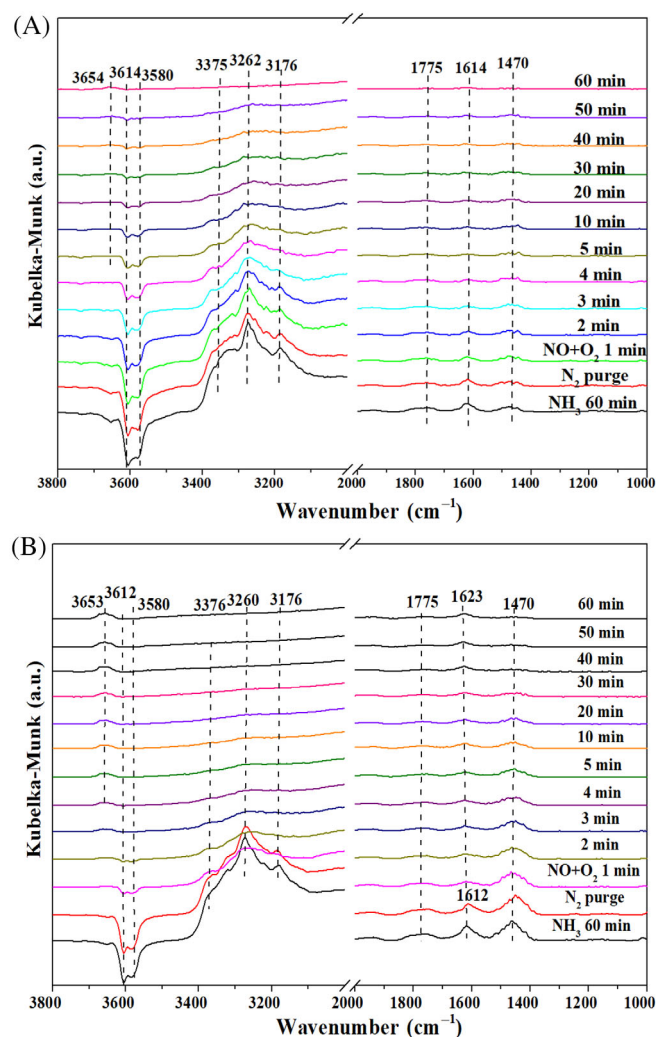


FIGURE 9 *In situ* DRIFT spectra of the reaction of NO + O₂ and adsorbed NH₃ on Cu-Z (A) and Ce2Cu-Z-SCS (B). Condition: Ar balance, 500 ppm NH₃, 5% O₂, 500 ppm NO, and 200 ml min⁻¹ total flow, at 200°C

TPD results. The improvement in catalyst surface acidity enhanced the catalytic performance. Furthermore, the peak at 1474 cm⁻¹ of Cu-Z was negligible when the temperature exceeded 250°C, but it was still obvious at 350°C for Ce2Cu-Z-SCS, suggesting that the introduction of CeO₂ improved the content and strength of Lewis acid sites. Namely, CeO₂ promoted the adsorption and activation of NH₃ thus led the excellent activity of Ce2Cu-Z-SCS throughout the temperature range.

4.2 | Reaction between NO and adsorbed NH₃

The catalysts were exposed to 500 ppm NH₃ at 200°C with a total gas flow of 200 ml/min to investigate further the NH₃ adsorption property. *In situ* DRIFT signals were collected at different times, as shown in Figure S3. Obviously, the peak positions of both catalysts were similar, but the peak intensity of Ce2Cu-Z-SCS was significantly

enhanced compared with that of Cu-Z, especially at 1612 and 1470 cm⁻¹, which belonged to the NH₃ adsorption peaks on Lewis and Brønsted acid sites, respectively. Thus, the introduction of CeO₂ improved the NH₃ adsorption capacity and acidity. In addition, the peak growth rate of Ce2Cu-Z-SCS was faster compared to Cu-Z. This behavior indicated that the introduction of CeO₂ could enhance ammonia adsorption efficiency.

The saturated ammonia adsorbed on the catalyst surface was purged by N₂ gas for 30 min, and the intensities of ammonia adsorption peaks over the two catalysts decreased gradually, as exhibited in Figure 9 and Figure S4. As shown in Figure 9A, the peaks intensities of Cu-Z at 3000–3400, 1470, 1614, 1775, 3614, and 3580 cm⁻¹ gradually weakened along with the introduction of NO + O₂ and nearly vanished after 60 min. A new peak at 3654 cm⁻¹ corresponding to OH stretching vibration was detected, probably due to the reaction among NO, O₂, and adsorbed ammonia.⁴⁰ Interestingly, no nitrate species formed on the catalyst surface as NO + O₂ was continuously fed. In Ce2Cu-Z-SCS catalyst, Brønsted acid was still the dominant site after purging by N₂, and the intensity of each peak was stronger than that of Cu-Z. The intensity of each peak changed with time as NO + O₂ was introduced, as shown in Figure 9B. The Brønsted acid sites (1470 and 1775 cm⁻¹) gradually decreased with the extension of NO + O₂ introduction time, and almost disappeared at 60 min. Simultaneously, the peak at 3000–3400 cm⁻¹ (Brønsted acid sites) dropped sharply and then disappeared after 10 min, which was much faster than the other peaks. Thus, the Brønsted acid sites were the main intermediates for SCR reaction, and the introduction of CeO₂ significantly improved the reaction between NO + O₂ and NH₃ adsorbed at 3000–3400 cm⁻¹. In addition, the peak at 1612 cm⁻¹ (Lewis acid site) decreased slightly with the addition of NO + O₂, and then shifted to 1623 cm⁻¹, which was associated with the generation of NO₂ on the catalyst surface.^{13,40} These results confirmed that the introduction of CeO₂ contributed to the oxidation of NO to NO₂, thus triggering the fast SCR reaction and leading to the superior low temperature catalytic activity.

4.3 | Influence of mass transport

Mass transport is an important factor in catalytic reaction, and the influence of mass transport over catalytic processes was studied in this work. Considering that the cerium premodified catalyst was cut from a Cu-Z monolith catalyst (143.8 × 101.6 mm). Thus, we assumed their washcoat thickness was similar. In cerium modification, urea as a combustion agent occupied the gaps of the particles in the washcoat during preparation, which burned to form a rich porous structure during calcination, and the washcoat thickness of Ce2Cu-Z-SCS slightly increased compared with that of Cu-Z. The modification enhanced porosity in the washcoat could promote the mass transfer efficiency and reduce the diffusion limitation without affecting the intrinsic zeolite structure.⁴³ The transport processes of fluid in the monolith channel present four major paths: (1) the diffusion of external gas on the washcoat surface; (2) washcoat diffusion in the intercrystalline voids; (3) washcoat diffusion within the pores of the zeolite crystallites;

(4) gas convection flow, that is, the flow of gas mixture in the channel. These paths are calculated as follows:

1. Convection time: $t_c = L/\langle u \rangle$;
2. Washcoat diffusion time: $t_{d,w} = R_{\Omega 2}^2/D_e$;
3. External mass transfer time or transverse diffusion time: $t_e = R_{\Omega 1}^2/D_f$;
4. Intracrystalline diffusion time: $t_{d,c} = R_{\Omega 3}^2/D_{e,c}$; and
5. Reaction time: $t_r = (C_i/r_i)(R_{\Omega 1}/R_{\Omega 2})$.

Here, L is the length of the channel; $\langle u \rangle$ is the space velocity of the gas in the channel; $R_{\Omega 2}$ is the effective washcoat thickness (defined as the ratio of the cross-sectional area of the washcoat to the perimeter between the gas and the washcoat interface, $R_{\Omega 2} = A_{\Omega 1}/P_{\Omega 2}$); D_e is the effective diffusion coefficient of reactants in the monolith channel. $R_{\Omega 1}$ is the effective transverse diffusion length in the washcoat (defined as the ratio of the cross-sectional area to $P_{\Omega 2}$, $R_{\Omega 1} = A_{\Omega 2}/P_{\Omega 2}$); D_f is the diffusion coefficient of the gas phase reactant, which was calculated according to the Formula S1; $R_{\Omega 3}$ is the radius of zeolite crystal particle; and $D_{e,c}$ is the effective diffusion coefficient in zeolite crystal. Although the effective diffusion time in zeolite was uncertain, the gas effective diffusion coefficient in zeolite was estimated by Chae et al.⁴⁴ to range from 10^{-8} to 10^{-9} . This result was consistent with the assumption of Huang et al. that the effective average diffusion coefficient in Fe-ZSM-5 is 10^{-8} .⁴⁵ In this article, we assumed that the value of $D_{e,c}$ is 10^{-8} ; C_i is the concentration of the reactant system, and R_i is the reaction rate of the gas.

The Weisz–Prater modulus (ψ), which is used to determine whether the washcoat has a diffusion limitation, is defined as:

$\psi = R_{\Omega 2}^2 R_i / D_e C_i$. When $\psi < 1$, the mass transfer limitation is negligible; $\psi > 1$, then mass transfer limitation exists in the washcoat. The main washcoat parameters are presented in Table 2.

The characteristic diffusion time was investigated to provide insights into the overall rate control process.³¹ Table 3 summarizes the values of these characteristic time and the Weisz–Prater modulus (ψ) of Ce2Cu-Z-SCS for the standard reaction ($4\text{NH}_3 + 4\text{NO} + \text{O}_2 = 4\text{N}_2 + 6\text{H}_2\text{O}$). The characteristic reaction time was always larger than the other characteristic time in the temperature range we studied, suggesting that the process was mainly controlled by intrinsic kinetics.⁴⁶ In addition, at temperatures below 250°C , the Weisz–Prater modulus (ψ) was less than 1, which implied the absence of washcoat transfer limitation at this temperature range and that the process was controlled solely by kinetics. Also, when the temperature exceeded 250°C , the ψ was greater than 1, which indicated a mass transfer limitation in the washcoat. Given the combined effect of diffusion and kinetics, the NO conversion showed an obvious inflection point at approximately 250°C . By comparison, the characteristic diffusion time of Cu-Z was simulated. (Table S1) Obviously, the washcoat diffusion time of Ce2Cu-Z-SCS was lower than that of Cu-Z. This is in accordance with the previous results of NH_3 -TPD in Figure 6, in which the NH_3 adsorption was faster and easier to reach saturation. In conclusion, the modification of CeO_2 using solvent combustion method promoted the gas diffusion in washcoat.

4.4 | Hydrothermal stability and sulfur resistance

Normally, diesel exhaust contains higher concentrations of water vapor, in which the water molecules will attack the aluminum sites in the zeolite under high temperatures, resulting in dealumination, and the destruction of the zeolite.⁵ Herein, hydrothermal aging was performed at 650 and 750°C for 100 h in the presence of 10% H_2O to study the stability of the catalysts. Figure 10A displays the NO conversion of Cu-Z and Ce2Cu-Z-SCS before and after hydrothermal aging. For Cu-Z, the NO conversion at low temperatures ($<300^\circ\text{C}$) decreased obviously after treatment at 650°C , for example, the NO conversion at 200°C decreased from 72% to 55%. Also, the NO

TABLE 2 Washcoat parameters of Cu-Z and Ce2Cu-Z-SCS

Parameter	Cu-Z	Ce2Cu-Z-SCS
L (mm)	38.1	38.1
$R_{\Omega 1}$ (mm)	0.26	0.25
$R_{\Omega 2}$ (mm)	0.158	0.171
a (nm)	3.417	3.420
$D_{e,c}$ (ms^{-1})	10^{-8}	10^{-8}

TABLE 3 The estimated characteristic times and Weisz–Prater modulus (ψ) over Ce2Cu-Z-SCS for the standard selective catalytic reduction (SCR) reaction (150 – 500°C)

Temperature ($^\circ\text{C}$)	$t_c \times 10^3$ (s)	$t_{d,w} \times 10^3$ (s)	$t_e \times 10^3$ (s)	$t_{d,c} \times 10^6$ (s)	$t_r \times 10^3$ (s)	ψ
150	85.65	41.79	1.72	0.22	130.41	0.21
200	54.31	39.31	1.42	0.22	119.70	0.56
250	49.12	37.19	1.20	0.22	67.15	1.50
300	44.83	35.35	1.03	0.22	43.70	1.83
350	41.24	33.74	0.89	0.22	38.72	1.86
400	38.17	32.31	0.78	0.22	30.21	1.94
450	35.53	31.03	0.69	0.22	28.06	2.30
500	33.24	29.88	0.62	0.22	27.29	2.54
550	31.22	28.83	0.56	0.22	26.04	3.05

conversion decreased further to 47% after hydrothermal aging at 750°C, and the deterioration ratio was ~34.7%. In contrast, the NO conversion for Ce₂Cu-Z-SCS after aging at 750°C was 66%, which corresponded to a deterioration ratio of 26.7%. Therefore, modification of cerium effectively enhanced the hydrothermal resistance of Cu-SSZ-13, although the catalytic performance decreased to a certain extent after aging. Usui et al.² stated that Ce promoted the hydrothermal aging resistance of zeolite catalyst by filling the defect site of zeolite that absorbed water molecules thus reducing the possibility of aluminum sites being attacked by water molecules. We further studied the influence of hydrothermal aging on ammonia adsorption for Cu-Z and Ce₂Cu-Z-SCS, as shown in Figure S5. In the ammonia adsorption process, the breakthrough times of both catalysts were significantly shortened. This result indicated that the ammonia adsorption capacity of the catalyst decreased markedly after hydrothermal aging. In ammonia desorption, the ammonia desorption peaks of Lewis acid were very close to those of the fresh catalysts. However, the

NH₃ desorption peaks of Brønsted acid dropped sharply, which may be the main reason for the degradation of catalyst performance.

Diesel engines produce a certain amount of SO₂, which is easily oxidized to SO₃, and then reacts with NH₃ to form sulfate or hydrogen sulfate. These sulfates cannot decompose below 300°C, which deposit on the catalyst surface or block the active sites, resulting in a serious decrease in catalytic activity. Among many commercial SCR catalysts, Cu-zeolite catalysts are highly sensitive to SO₂.⁴⁷ So in this work, the NH₃-SCR activity of Cu-Z and Ce₂Cu-Z-SCS was further investigated at 250°C in the presence of 50 ppm SO₂ and NO conversions is shown in Figure 10B. For Cu-Z, NO conversion decreased rapidly from 95% to 82% in the first 1 h and then decreased slowly to ~70% after 16 h. Moreover, its catalytic activity could not recover after cutting off SO₂ supply, indicating that this process was an irreversible reaction. Similar results were observed in Ce₂Cu-Z-SCS. However, NO conversion decreased more slowly on Ce₂Cu-Z-SCS compared to Cu-Z, and was subsequently maintained at ~85%. In addition, the influence of H₂O on catalyst performance was also investigated at 250°C, as shown in Figure S6. The catalytic performance of Cu-Z and Ce₂Cu-Z-SCS nearly unchanged within 20 h, indicating that water had no adverse effect on the catalyst life at low temperature. The results proved that the modification of Ce also improved the sulfur resistance, making it more advantageous in practical applications.

5 | DISCUSSION

The introduction of CeO₂ increased the ratio of isolated Cu²⁺/Cu⁺ (see Figure 3B) in Ce₂Cu-Z-SCS. The coexistence of Ce³⁺ and Ce⁴⁺ (Figure S2) improved the oxygen storage capacity and facilitated the electron transfer of Ce and Cu ($\text{Cu}^+ + \text{Ce}^{4+} \rightleftharpoons \text{Cu}^{2+} + \text{Ce}^{3+}$), which led to the facile NO oxidation to NO₂. The oxidation reaction of NO on Cu-O_y-Cu species near the eight-membered rings was easier than that on isolated Cu²⁺ in the six-membered rings. Thus, it can be deduced that solvent combustion was more likely to be associated with the exposure of Cu-O_y-Cu species on eight-membered rings in the washcoat. Furthermore, the H₂-TPR results revealed that the temperature of Cu²⁺ reduced to Cu⁺ significantly decreased on Ce₂Cu-Z-SCS, namely, the introduction of CeO₂ effectively improved the redox capacity. Meanwhile, the reduction peak intensity increased, which probably arised from a cyclic reaction ($\text{Cu}^+ + \text{Ce}^{4+} \rightleftharpoons \text{Cu}^{2+} + \text{Ce}^{3+}$). Acidity is an important factor to improve SCR catalyst performance. The acidity of the catalysts increased significantly after the introduction of CeO₂ as shown in NH₃-TPD (Figure 6). Almost no NH₃ was adsorbed on pure CeO₂. Therefore, the enhancement of Brønsted acid on Ce₂Cu-Z-SCS does not directly come from the NH₃ adsorption on CeO₂. Namely, NH₃ adsorption occurs mainly on the zeolite and Cu active sites.^{48,49} For Cu-Z, more NH₃ is adsorbed on Brønsted acid sites than that on the Lewis acid sites. After CeO₂ modification (Ce₂Cu-Z-SCS), NH₃ adsorbed on Brønsted acid sites and Lewis acid sites were both improved, and the growth trend of the two acid sites was similar. As a

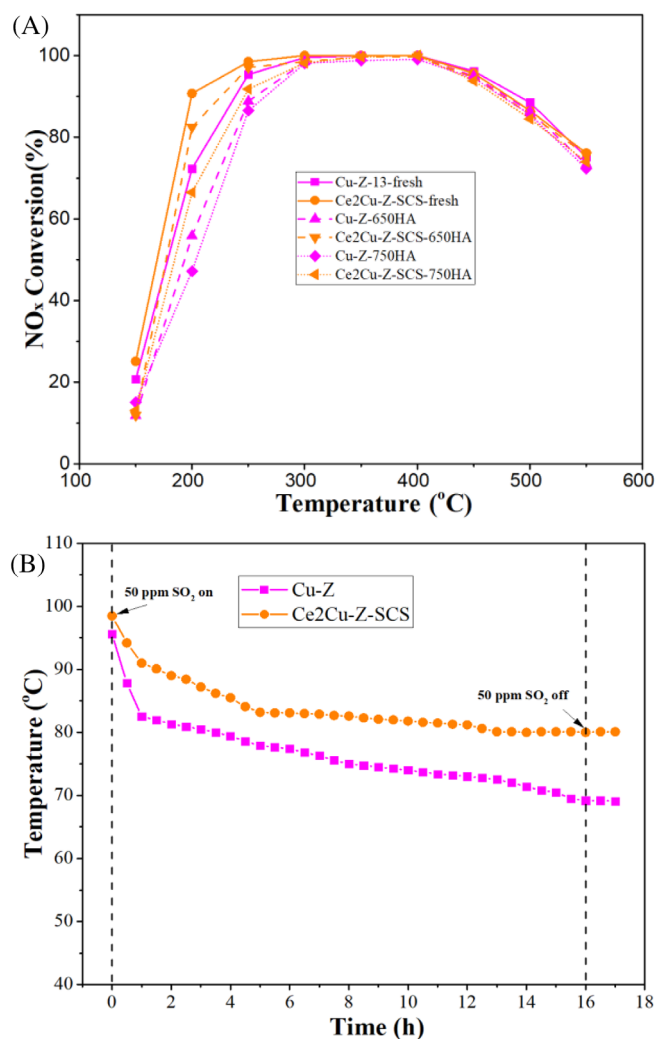


FIGURE 10 NO conversion of Cu-Z and Ce₂Cu-Z-SCS before and after hydrothermal aging (A), SO₂ (B) resistance life test of the Cu-Z and Ce₂Cu-Z-SCS catalysts at 250°C

result, NH_3 adsorbed on Brønsted acid sites was still more than that on Lewis acid sites for $\text{Ce}_2\text{Cu-Z-SCS}$, which is consistent with that on Cu-Z . Since Cu active sites play an important role in NH_3 adsorption, it can be deduced that the washcoat modification of Cu-Z by solvent combustion method results in more exposed Cu active sites, which contribute to the significantly increased acidity. Li et al.⁵⁰ confirmed that Brønsted acid sites could store ammonia in Cu-SSZ-52 catalyst and could be converted into Lewis acid, then participating in SCR reaction. However, the transformation of Brønsted acid sites into Lewis acid sites was not observed on $\text{Ce}_2\text{Cu-Z-SCS}$ in the *in situ* DRIFT of the reaction between NO and adsorbed NH_3 . Namely, the Brønsted acid sites directly participated and dominated in the reaction, suggesting these acid sites were the main active intermediates. The reaction between adsorbed NH_4^+ on the Brønsted acid sites and NO gas followed the Eley–Rideal mechanism. Also, in the *in situ* DRIFT of the reaction between NO and ammonia adsorption, no NO_x species were found on the catalyst surface with the continuous introduction of NO gas. We therefore can conclude that the SCR reaction in this work only followed the E–R mechanism. Macroscopically, solvent combustion formed a loose and porous washcoat structure on the monolith catalyst, which improved the diffusion rate of reactants in the washcoat.¹⁷ In addition, the number of exposed active sites of catalysts synthesized via solvent combustion increased, which effectively enhanced the reaction rate. In all, CeO_2 modification via solvent combustion increases both mass transfer and reaction rates for SCR process.

6 | CONCLUSION

This work demonstrated a solvent combustion-modified $\text{Ce}_2\text{Cu-Z-SCS}$ monolith catalyst for NH_3 -SCR. The optimized catalyst exhibited excellent low-temperature activity and a wide active temperature window (NO conversion >80%) of 187–540°C. The low-temperature catalytic activity of $\text{Ce}_2\text{Cu-Z-SCS}$ was significantly higher than that of Cu-Z . In addition, the hydrothermal stability and sulfur resistance of $\text{Ce}_2\text{Cu-Z-SCS}$ were superior to those of Cu-Z . The NH_3 -TPD revealed that the CeO_2 -modified Cu-SSZ-13 catalyst significantly improved the diffusion rate of NH_3 in the washcoat, which was attributed to the formation of pore structures in the washcoat during solvent combustion. Meanwhile, the adsorption capacity of ammonia was markedly increased. Namely, the acidity of the catalyst was enhanced, which improved the catalytic activity. Furthermore, the introduction of CeO_2 facilitated the oxidation of NO to NO_2 , thus inducing a fast-SCR reaction. The porous structures formed in the washcoat increased the diffusion rate of reactants, which further boosted the reaction rate. *In situ* DRIFT results indicated that Brønsted acid sites were the main active sites, and the reaction followed an E–R mechanism.

AUTHOR CONTRIBUTIONS

Wuyuan Liu: Data curation (lead); formal analysis (lead); investigation (lead); methodology (lead); writing – review and editing (lead). **Zhaoying Wang:** Investigation (supporting); methodology (supporting); resources (supporting). **Ming Sun:** Formal analysis (supporting); investigation (supporting); methodology (supporting); writing – review and editing

(supporting). **Jiajian Gao:** Formal analysis (equal); methodology (equal); writing – review and editing (equal). **Lifeng Wang:** Formal analysis (supporting); methodology (supporting); resources (supporting). **Zihan Gao:** Formal analysis (supporting); investigation (supporting); resources (supporting). **Yingying Xu:** Formal analysis (supporting); investigation (supporting); resources (supporting). **Xiangyun Zhao:** Data curation (supporting); formal analysis (supporting); methodology (supporting); resources (supporting). **Cheng Zhang:** Formal analysis (supporting); methodology (supporting); resources (supporting). **Lin Yu:** Data curation (equal); funding acquisition (lead); investigation (equal); methodology (equal); project administration (lead); writing – review and editing (lead).

CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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REFERENCES

- Song L, Ma K, Tian W, et al. An environmentally friendly FeTiSO_x catalyst with a broad operation-temperature window for the NH_3 -SCR of NO_x . *AIChE J.* 2019;65:10.
- Usui T, Liu Z, Ibe S, et al. Improve the hydrothermal stability of Cu-SSZ-13 zeolite catalyst by loading a small amount of Ce. *ACS Catal.* 2018;8(10):9165–9173.
- Liu J, Liu J, Zhao Z, Tan J, Wei Y, Song W. Fe/Beta@SBA-15 core-shell catalyst: interface stable effect and propene poisoning resistance for NO abatement. *AIChE J.* 2018;64(11):3967–3978.
- Liu J, Cheng H, Zheng H, et al. Insight into the potassium poisoning effect for selective catalytic reduction of NO_x with NH_3 over Fe/Beta. *ACS Catal.* 2021;11(24):14727–14739.
- Luo J, Kamasamudram K, Currier N, Yezerets A. NH_3 -TPD methodology for quantifying hydrothermal aging of Cu/SSZ-13 SCR catalysts. *Chem Eng Sci.* 2018;190:60–67.
- Han L, Cai S, Gao M, et al. Selective catalytic reduction of NO_x with NH_3 by using novel catalysts: state of the art and future prospects. *Chem Rev.* 2019;119(19):10916–10976.
- Zhao Z, Yu R, Shi C, et al. Rare-earth ion exchanged Cu-SSZ-13 zeolite from organotemplate-free synthesis with enhanced hydrothermal stability in NH_3 -SCR of NO_x . *Cat Sci Technol.* 2019;9(1):241–251.
- Zhang R, Li Y, Zhen T. Ammonia selective catalytic reduction of NO over Fe/Cu-SSZ-13 . *RSC Adv.* 2014;4:52130–52139.
- Xu R, Wang Z, Liu N, Dai C, Zhang J, Chen B. Understanding Zn functions on hydrothermal stability in a one-pot-synthesized Cu & Zn-SSZ-13 catalyst for NH_3 selective catalytic reduction. *ACS Catal.* 2020;10(11):6197–6212.
- Zhao K, Han W, Lu G, Lu J, Tang Z, Zhen X. Promotion of redox and stability features of doped Ce-W-Ti for NH_3 -SCR reaction over a wide temperature range. *Appl Surf Sci.* 2016;379:316–322.
- Liu W, Gao Z, Zhao X, Gao J, Yang R, Yu L. Promotion effect of chromium on the activity and SO_2 resistance of CeO_2 - TiO_2 catalysts for the NH_3 -SCR reaction. *Ind Eng Chem Res.* 2021;60(31):11676–11688.
- Liu H, Fan Z, Sun C, et al. Improved activity and significant SO_2 tolerance of samarium modified CeO_2 - TiO_2 catalyst for NO selective catalytic reduction with NH_3 . *Appl Catal Environ.* 2019;244:671–683.
- Liu W, Gao Z, Sun M, et al. One-pot synthesis of $\text{Cr}_x\text{Mn}_y\text{CeTiO}_x$ mixed oxides as NH_3 -SCR catalysts with enhanced low-temperature

- catalytic activity and sulfur resistance. *Chem Eng Sci.* 2022;251:117450.
14. Li Y, Song W, Liu J, et al. The protection of CeO₂ thin film on Cu-SAPO-18 catalyst for highly stable catalytic NH₃-SCR performance. *Chem Eng J.* 2017;330:926-935.
 15. Wang J, Peng Z, Qiao H, et al. Cerium-stabilized Cu-SSZ-13 catalyst for the catalytic removal of NO_x by NH₃. *Ind Eng Chem Res.* 2016;55(5):1174-1182.
 16. Metkar PS, Salazar N, Muncrief R, Balakotaiah V, Harold MP. Selective catalytic reduction of NO with NH₃ on iron zeolite monolithic catalysts: steady-state and transient kinetics. *Appl Catal Environ.* 2011;104(1-2):110-126.
 17. Andreoli S, Deorsola F, Galletti C, Pirone R. Nanostructured MnO catalysts for low-temperature NO SCR. *Chem Eng J.* 2015;278:174-182.
 18. Zhang D, Yang RT. NH₃-SCR of NO over one-pot Cu-SAPO-34 catalyst: performance enhancement by doping Fe and MnCe and insight into N₂O formation. *Appl Catal Gen.* 2017;543:247-256.
 19. Wang L, Gaudet JR, Li W, Weng D. Migration of Cu species in Cu/SAPO-34 during hydrothermal aging. *J Catal.* 2013;306:68-77.
 20. Cheng C, Mao L, Shi J, et al. NiCo₂O₄ nanosheets as a novel oxygen-evolution-reaction cocatalyst in-situ bonded on g-C₃N₄ photocatalyst for excellent overall water splitting. *J Mater Chem A.* 2021;9:12299-12306.
 21. Han S, Cheng J, Ye Q, Cheng S, Kang T, Dai H. Ce doping to Cu-SAPO-18: enhanced catalytic performance for the NH₃-SCR of NO in simulated diesel exhaust. *Micropor Mesopor Mater.* 2019;276:133-146.
 22. Kadgaonkar MD, Laha SC, Pandey RK, Kumar P, Mirajkar SP, Kumar R. Cerium-containing MCM-41 materials as selective acylation and alkylation catalysts. *Catal Today.* 2004;97(4):225-231.
 23. Chunman H, Jimmy C, Tszyan K, Angelo C, Lai S. Morphology-controllable synthesis of mesoporous CeO₂ nano- and microstructures. *Chem Mater.* 2005;17:4514-4522.
 24. Geng Y, Chen X, Yang S, Liu F, Shan W. Promotional effects of Ti on a CeO₂-MoO₃ catalyst for the selective catalytic reduction of NO_x with NH₃. *ACS Appl Mater Interfaces.* 2017;9(20):16951-16958.
 25. Zhang T, Li J, Liu J, et al. High activity and wide temperature window of Fe-Cu-SSZ-13 in the selective catalytic reduction of NO with ammonia. *AIChE J.* 2015;61(11):3825-3837.
 26. Zhang T, Qiu F, Li J. Design and synthesis of core-shell structured meso-Cu-SSZ-13@mesoporous aluminosilicate catalyst for SCR of NO with NH₃: enhancement of activity, hydrothermal stability and propene poisoning resistance. *Appl Catal Environ.* 2016;195:48-58.
 27. Kwak J, Tonkyn RG, Kim D, Szanyi J, Peden C. Excellent activity and selectivity of Cu-SSZ-13 in the selective catalytic reduction of NO_x with NH₃. *J Catal.* 2010;275(2):187-190.
 28. Xie K, Leistner K, Wijayanti K, Kumar A, Kamasamudram K, Olsson L. Influence of phosphorus on Cu-SSZ-13 for selective catalytic reduction of NO_x by ammonia. *Catal Today.* 2017;297:46-52.
 29. Lai S, Meng D, Zhan W, Guo Y, Zhang Z, Lu G. The promotional role of Ce in Cu-ZSM-5 and in situ surface reaction for selective catalytic reduction of NO_x with NH₃. *RSC Adv.* 2015;5:90235-90244.
 30. Zhang L, Du T, Qu H, Chi B, Zhong Q. Synthesis of Fe-ZSM-5@Ce/mesoporous-silica and its enhanced activity by sequential reaction process for NH₃-SCR. *Chem Eng J.* 2017;313:702-710.
 31. Metkar PS, Balakotaiah V, Harold MP. Experimental and kinetic modeling study of NO oxidation: comparison of Fe and Cu-zeolite catalysts. *Catal Today.* 2012;184(1):115-128.
 32. Verma A, Bates S, Anggara T, et al. NO oxidation: a probe reaction on Cu-SSZ-13. *J Catal.* 2014;312:179-190.
 33. Dhillon PS, Harold MP, Wang D, Kumar A, Joshi SY. Enhanced transport in washcoated monoliths: application to selective lean NO_x reduction and ammonia oxidation. *Chem Eng J.* 2019;377:119734.
 34. Liu J, Liu J, Zhao Z, Wei Y, Song W. Fe-Beta@CeO₂ core-shell catalyst with tunable shell thickness for selective catalytic reduction of NO_x with NH₃. *AIChE J.* 2017;63(10):4430-4441.
 35. Leistner K, Xie K, Kumar A, Kamasamudram K, Olsson L. Ammonia desorption peaks can be assigned to different copper sites in Cu/SSZ-13. *Catal Lett.* 2017;147(8):1882-1890.
 36. Bergman S, Dahlin S, Mesilov V, et al. In-situ studies of oxidation/reduction of copper in Cu-CHA SCR catalysts: comparison of fresh and SO₂-poisoned catalysts. *Appl Catal Environ.* 2020;269:118722.
 37. Xie L, Liu F, Ren L, Shi X, Xiao F-S, He H. Excellent performance of one-pot synthesized Cu-SSZ-13 catalyst for the selective catalytic reduction of NO_x with NH₃. *Environ Sci Technol.* 2013;48(1):566-572.
 38. Wang D, Jangjou Y, Liu Y, et al. A comparison of hydrothermal aging effects on NH₃-SCR of NO over Cu-SSZ-13 and Cu-SAPO-34 catalysts. *Appl Catal Environ.* 2015;165:438-445.
 39. Zhang L, Li L, Cao Y, et al. Getting insight into the influence of SO₂ on TiO₂/CeO₂ for the selective catalytic reduction of NO by NH₃. *Appl Catal Environ.* 2015;165:589-598.
 40. Wang D, Zhang L, Kamasamudram K, Epling WS. In situ-DRIFTS study of selective catalytic reduction of NO_x by NH₃ over Cu-exchanged SAPO-34. *ACS Catal.* 2013;3(5):871-881.
 41. Ma S, Zhao X, Li Y, et al. Effect of W on the acidity and redox performance of the Cu_{0.02}Fe_{0.2}WTiO_x (α = 0.01, 0.02, 0.03) catalysts for NH₃-SCR of NO. *Appl Catal Environ.* 2019;248:226-238.
 42. Luo J, Wang D, Kumar A, et al. Identification of two types of Cu sites in Cu/SSZ-13 and their unique responses to hydrothermal aging and sulfur poisoning. *Catal Today.* 2016;267:3-9.
 43. Dudák M, Novák V, Kočí P, Marek M, Blanco-García P, Thompson D. Impact of zeolite and γ-alumina intra-particle diffusion on the performance of a dual layer catalyst. *Chem Eng J.* 2016;301:178-187.
 44. Chae H, Choo S, Choi H, Nam I-S. Direct use of kinetic parameters for modeling and simulation of a selective catalytic reduction process. *Ind Eng Chem Res.* 2000;39:1159-1170.
 45. Huang H, Long R, Yang R. Kinetics of selective catalytic reduction of NO with NH₃ on Fe-ZSM-5 catalyst. *Appl Catal Gen.* 2002;235:241-251.
 46. Bhatia D, McCabe RW, Harold MP, Balakotaiah V. Experimental and kinetic study of NO oxidation on model Pt catalysts. *J Catal.* 2009;266(1):106-119.
 47. Ramachandran B, Herman R, Choi S, Harvey G, Lyman CE, Sale JW. Testing zeolite SCR catalysts under protocol conditions for NO_x abatement from stationary emission sources. *Catal Today.* 2000;55:281-290.
 48. Lezcano-Gonzalez I, Deka U, Arstad B, et al. Determining the storage, availability and reactivity of NH₃ within Cu-Chabazite-based ammonia selective catalytic reduction systems. *Phys Chem Chem Phys.* 2014;16:1639-1650.
 49. Zhang Y, Shi J, Huang Z, et al. Synchronous construction of CoS₂ in-situ loading and S doping for g-C₃N₄: enhanced photocatalytic H₂-evolution activity and mechanism insight. *Chem Eng J.* 2020;401:126135.
 50. Li R, Zhu Y, Zhang Z, et al. Remarkable performance of selective catalytic reduction of NO_x by ammonia over copper-exchanged SSZ-52 catalysts. *Appl Catal Environ.* 2021;283:119641.

SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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