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Doping effect of cations (Zr^{4+} , Al^{3+} , and Si^{4+}) on $\text{MnO}_x/\text{CeO}_2$ nano-rod catalyst for NH_3 -SCR reaction at low temperature

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ABSTRACT

Thermally stable Zr^{4+} , Al^{3+} , and Si^{4+} cations were incorporated into the lattice of CeO_2 nano-rods (i.e., CeO_2 -NR) in order to improve the specific surface area. The undoped and Zr^{4+} , Al^{3+} , and Si^{4+} doped nano-rods were used as supports to prepare $\text{MnO}_x/\text{CeO}_2$ -NR, $\text{MnO}_x/\text{ZrO}_2$ -NR, $\text{MnO}_x/\text{Al}_2\text{O}_3$ -NR, and $\text{MnO}_x/\text{SiO}_2$ -NR catalysts, respectively. The prepared supports and catalysts were comprehensively characterized by transmission electron microscopy (TEM), high-resolution TEM, X-ray diffraction, Raman and N_2 -physisorption analyses, hydrogen temperature-programmed reduction, ammonia temperature-programmed desorption, in situ diffuse reflectance infrared Fourier-transform spectroscopic analysis of the NH_3 adsorption, and X-ray photoelectron spectroscopy. Moreover, the catalytic performance and $\text{H}_2\text{O}/\text{SO}_2$ tolerance of these samples were evaluated through NH_3 -selective catalytic reduction (NH_3 -SCR) in the absence or presence of H_2O and SO_2 . The obtained results show that the $\text{MnO}_x/\text{SiO}_2$ -NR catalyst exhibits the highest NO_x conversion and the lowest N_2O concentration, which result from the largest number of oxygen vacancies and acid sites, the highest Mn^{4+} content, and the lowest redox ability. The $\text{MnO}_x/\text{SiO}_2$ -NR catalyst also presents excellent resistance to H_2O and SO_2 . All of these phenomena suggest that Si^{4+} is the optimal dopant for the $\text{MnO}_x/\text{CeO}_2$ -NR catalyst.

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1. Introduction

Recently, low-temperature denitration techniques [1–3] have attracted increasing attention for the following reasons. First, the denitration unit can be fixed after the precipitator and desulfurizer without reheating the flue gas, which is beneficial for energy-saving and inhibition of catalyst poisoning caused by dust and SO_2 . Second, denitration reform of coal-fired power

plants can be conveniently achieved without the need to adjust the precipitator and desulfurizer. Finally, low-temperature denitration can be used for some non-electrical industry denitration processes with low-temperature flue gas (below 300 °C) from waste incinerators, glass furnaces, coking furnaces, etc. Low-temperature denitration catalysts are the most important factor in this technique; thus, the investigation of low-temperature denitration catalysts has become highly topi-

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Commercial $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts exhibit excellent catalytic performance for NH_3 -selective catalytic reduction (i.e., $\text{NH}_3\text{-SCR}$) of nitrogen oxides (i.e., NO_x) from the flue gas of stationary sources at 300–400 °C, whereas their performance in low-temperature denitration is not satisfactory [4,5]. Moreover, V_2O_5 exhibits biological toxicity, which can result in secondary pollution [6,7]. Therefore, investigations of low-temperature denitration catalysts have mainly focused on environment-friendly non-vanadium-based transition metal oxides. Specifically, manganese oxides (i.e., MnO_x) have been widely studied for low-temperature $\text{NH}_3\text{-SCR}$ due to their good denitration activity at low temperature [8–14]. In order to further improve the denitration activity and N_2 selectivity, MnO_x species have been loaded onto various supports, such as CeO_2 , TiO_2 , carbon nano-tubes (CNTs), SiO_2 , and $\gamma\text{-Al}_2\text{O}_3$ [15–19]. $\text{MnO}_x/\text{CeO}_2$ catalysts have attracted much more attention for low-temperature denitration due to their good redox ability and the high oxygen storage/release capacity of CeO_2 [20–25]. However, it is well known that the specific surface area and thermal stability of pure CeO_2 are not satisfactory. Fortunately, the incorporation of other cations (such as Zr^{4+} , Sn^{4+} , Ti^{4+} , Si^{4+} , Al^{3+} , and Mg^{2+}) into the lattice of CeO_2 can effectively be used to overcome these drawbacks [26–28].

With the development of techniques for the preparation of nanomaterials, CeO_2 with different morphologies (such as nano-cubes, nano-polyhedrons, nano-rods, and nano-spheres) has been successfully synthesized [21,29–31]. Some research results indicate that CeO_2 nano-rods are more suitable for use as a support than CeO_2 with other morphologies due to the predominantly exposed {110} facet of the CeO_2 nano-rods, which facilitates the formation of oxygen vacancies and interactions with the surface dispersed components [29,30,32]. Therefore, in the present work, we incorporate the thermally stable Zr^{4+} , Al^{3+} , and Si^{4+} cations into the lattice of CeO_2 nano-rods to improve their specific surface area and thermal stability. MnO_x species are then loaded onto these doped supports with the purpose of exploring the doping effect of cations (Zr^{4+} , Al^{3+} , and Si^{4+}) on the $\text{MnO}_x/\text{CeO}_2$ nano-rod catalyst for low-temperature $\text{NH}_3\text{-SCR}$, and finally, the optimal dopant is selected.

2. Experimental

2.1. Catalyst preparation

These doped ceria-based nano-rod supports were synthesized by a hydrothermal method. The detailed experimental steps are as follows. First, the required amounts of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ or $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$ (i.e., TEOS) were dissolved in deionized water and homogenized by magnetic stirring for 30 min. The above solution was added dropwise to 6 mol L^{-1} NaOH solution with magnetic stirring for another 30 min. The obtained suspension was placed in a Teflon-lined stainless steel autoclave and kept at 100 °C for 24 h. The cooled precipitate was centrifuged and washed several times with deionized water until no pH change

could be observed. The filter cake was then dried at 70 °C for 12 h in a vacuum oven. Finally, these samples were calcined at 400 °C for 3 h in a muffle furnace. The Zr^{4+} , Al^{3+} , and Si^{4+} doped supports are respectively denoted as CZ-NR, CA-NR, and CS-NR, where the molar ratio of Ce/Zr (Al, Si) was 9/1. Furthermore, the $\text{CeO}_2\text{-NR}$ support was also prepared by the same procedure for comparison.

MnO_x was loaded onto the surface of the above supports by a wet impregnation method. In brief, the desired amount of $\text{Mn}(\text{NO}_3)_2$ was dissolved in deionized water with magnetic stirring. The required amount of $\text{CeO}_2\text{-NR}$ or CZ-NR or CA-NR or CS-NR support was added to the $\text{Mn}(\text{NO}_3)_2$ solution and magnetically stirred for 1 h. Subsequently, the suspension was heated at 100 °C in an oil bath to vaporize the water, and oven dried at 100 °C for 12 h. Finally, all the samples were calcined at 400 °C for 3 h in the muffle furnace. The prepared samples are denoted as $\text{MnO}_x/\text{CeO}_2\text{-NR}$, $\text{MnO}_x/\text{CZ-NR}$, $\text{MnO}_x/\text{CA-NR}$, and $\text{MnO}_x/\text{CS-NR}$, respectively; the MnO_x loading was fixed at 1.0 mmol $\text{Mn}^{n+}/100 \text{ m}^2$ support.

2.2. Catalyst characterization

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) characterizations were carried out on a JEM-2100 instrument operating at 200 kV. Each sample was dispersed in ethanol and kept in an ultrasonic bath for 30 min, then deposited on a carbon-covered copper grid for each test.

X-ray diffraction (XRD) patterns were recorded on a Philips X'pert Pro diffractometer with a Ni-filtered $\text{Cu-K}\alpha$ target ($\lambda = 0.15418 \text{ nm}$) and the X-ray tube was operated at 40 kV and 40 mA.

Raman spectra were collected on a Renishaw Invia Laser Raman spectrometer with an Ar^+ laser beam. The excitation wavelength and laser power were 532 nm and 5 mW, respectively.

Brunauer-Emmett-Teller (BET) specific surface area was obtained from the N_2 -physisorption data acquired at $-196 \text{ }^\circ\text{C}$ on a Belsorp-max analyzer. Before the analysis, the sample was degassed under vacuum at 300 °C for 4 h.

H_2 temperature-programmed reduction ($\text{H}_2\text{-TPR}$) was performed on a chemisorption analyzer (TP-5076) with a 7% H_2 -93% Ar mixture as the reductant. Before the reduction, 50 mg of catalyst was pretreated with N_2 at 300 °C for 1 h. After cooling to ambient temperature, the TPR process was started at a rate of $10 \text{ }^\circ\text{C min}^{-1}$.

NH_3 temperature-programmed desorption ($\text{NH}_3\text{-TPD}$) was also performed on the chemisorption analyzer (TP-5076). The catalyst (200 mg) was pretreated with N_2 at 300 °C for 1 h. Thereafter, the catalyst was saturated with a 1% NH_3 -99% N_2 mixture at 100 °C, and then flushed with N_2 for 1 h to remove the gas-phase NH_3 . Finally, the TPD process was carried out at a rate of $10 \text{ }^\circ\text{C min}^{-1}$.

In situ diffuse reflectance infrared Fourier transform spectra (in situ DRIFTS) for NH_3 adsorption were recorded on a Nicolet 5700 FT-IR spectrometer equipped with an MCT detector. Prior to the test, the sample was pretreated with N_2 at 350 °C for 1 h.

The sample background was collected in the cooling process. At room temperature, the sample was exposed to a 1% NH₃-99% N₂ mixture until it became saturated. Finally, the spectrum was recorded at each target temperature by subtracting the corresponding sample background.

X-ray photoelectron spectra (XPS) were acquired on a PHI 5000 VersaProbe system with a monochromatic Al-K α target (1486.6 eV). Before the test, the sample was outgassed in a UHV chamber ($<5 \times 10^{-7}$ Pa). Moreover, the charging effect was compensated by calibration relative to the binding energy of adventitious C 1s at 284.6 eV.

2.3. Measurement of catalytic performance

Measurements of the denitration performance and H₂O+SO₂ tolerance were carried out at steady-state. The reaction gas comprised NO (500 ppm), NH₃ (500 ppm), O₂ (5%), SO₂ (0 or 100 ppm), and H₂O (0 or 5%), with N₂ balance. First, 200 mg of the sample was placed in the reaction tube and pretreated with N₂ at 300 °C for 1 h. The reactions were then allowed to take place at each temperature at a space velocity of 60000 ml g⁻¹ h⁻¹. NO and NO₂ were detected by a flue gas analyzer, while N₂O was measured using a N₂O analyzer. The NO_x conversion was determined as follows:

$$\text{NO}_x \text{ conversion} = \frac{[\text{NO}]_{\text{in}} + [\text{NO}_2]_{\text{in}} - [\text{NO}]_{\text{out}} - [\text{NO}_2]_{\text{out}}}{[\text{NO}]_{\text{in}} + [\text{NO}_2]_{\text{in}}} \times 100\%$$

3. Results and discussion

3.1. Morphology analysis (TEM and HRTEM)

The morphologies and exposed crystal planes of these doped CeO₂-based supports and the corresponding supported MnO_x-based catalysts were determined by TEM and HRTEM characterization, as shown in Fig. 1 (and Fig. S1 in the Supporting Information). The CeO₂-NR support exhibited a regular rod morphology with lengths from 30 to 150 nm and diameters in the range of 5–10 nm (Fig. 1(a)). The lattice fringes with an inter-planar spacing of 0.190 nm were detected in Fig. 1(b), which are attributed to the (220) crystal plane of the {110} facet [29,30,32,33]. Moreover, the rod morphology was also observed for the Zr⁴⁺, Al³⁺, and Si⁴⁺ doped samples (i.e., CZ-NR, CA-NR, and CS-NR supports) in Fig. 1(c, e, g), where the rod length of CZ-NR was obviously shorter than that of the other supports, which suggests that the incorporation of Al³⁺ and Si⁴⁺ can maintain the rod morphology of CeO₂ more efficiently. Furthermore, Fig. 1(d, f, h) shows that the {110} facet was the mainly exposed face for the CZ-NR, CA-NR, and CS-NR supports. These results indicate that the incorporation of Al³⁺ and Si⁴⁺ had no obvious influence on the morphology and exposed crystal plane of CeO₂, while Zr⁴⁺ doping leads to a shorter rod length.

Fig. S1 (in the Supporting Information) demonstrates that all the MnO_x/CeO₂-NR, MnO_x/CZ-NR, MnO_x/CA-NR, and MnO_x/CS-NR catalysts display the original morphologies and exposed crystal planes of the CeO₂-NR, CZ-NR, CA-NR, and CS-NR supports, respectively. In addition, the lattice fringes of

Fig. 1. TEM and HRTEM images of these ceria-based supports: (a, b) CeO₂-NR, (c, d) CZ-NR, (e, f) CA-NR, and (g, h) CS-NR.

MnO_x were absent. These phenomena suggest that the MnO_x species were well dispersed on the surface of the CeO₂-NR, CZ-NR, CA-NR, and CS-NR supports, and did not change the original morphologies and exposed crystal planes of these supports. Furthermore, it is important to gain information about the morphologies of the used catalysts, which is beneficial for understanding the structural stability of these catalysts. Therefore, TEM experiments were carried out on these catalysts after use from room temperature to 250 °C in the NH₃-SCR reaction (Fig. S2; Supporting Information). All of the used catalysts exhibited a rod morphology (the rod length of the used MnO_x/CZ-NR catalyst was obviously shorter than that of the other three samples), which is similar to the TEM images of the corresponding fresh catalysts. The reason may be that these fresh catalysts were obtained by calcination at 400 °C, while the highest temperature used in the reaction was only 250 °C. Thus, the original morphologies could be maintained after use from room temperature to 250 °C in the NH₃-SCR reaction, which suggests that the rod structure of these catalysts exhibits good stability.

3.2. Determination of structure and texture (XRD, Raman, and N₂-physisorption)

The XRD patterns of these supports and the supported MnO_x-based catalysts are displayed in Fig. 2. It can be seen from Fig. 2(a) that the CeO₂-NR support exhibits the typical peaks of

Fig. 2. XRD patterns of (a) supports and (b) catalysts.

the cubic fluorite structure between 20° and 80° (PDF-ICDD 34-0394) [34–36]. For the CZ-NR, CA-NR, and CS-NR supports, only the peaks attributed to cubic fluorite-type CeO_2 were detected, while the diffraction signals of ZrO_2 , Al_2O_3 , and SiO_2 were absent. In addition, the peaks of the CZ-NR, CA-NR, and CS-NR supports shifted slightly to higher angles compared to those of the CeO_2 -NR support, which is because the ionic radii of Zr^{4+} (0.80 Å), Al^{3+} (0.51 Å), and Si^{4+} (0.42 Å) are smaller than that of Ce^{4+} (0.92 Å). The incorporation of Zr^{4+} , Al^{3+} , and Si^{4+} results in shrinkage of the CeO_2 lattice, and further led to a right-shift of the peaks according to the Bragg equation [27,28]. The lattice parameters of these supports were calculated and are listed in Table 1. The lattice parameters of the CZ-NR, CA-NR, and CS-NR supports were smaller than that of the CeO_2 -NR support, which indicates that Zr^{4+} , Al^{3+} , and Si^{4+} (with smaller ionic radii) were indeed incorporated into the lattice of the CeO_2 -NR support. Moreover, the intensity of the XRD peaks of the CZ-NR, CA-NR, and CS-NR supports was weaker than that of the CeO_2 -NR support, whereas the full-width at half maximum height (FWHM) of these doped supports was wider than that of the CeO_2 -NR support, which suggests that the incorporation of Zr^{4+} , Al^{3+} , and Si^{4+} inhibits growth of the CeO_2 grains, and results in a smaller grain size according to the Debye-Scherrer equation [28,36]. All of these results indicate that Zr^{4+} , Al^{3+} , and Si^{4+} were successfully doped into the CeO_2 lattice to generate the Ce-O-M (M = Zr, Al, and Si) solid solution. Fig. 2(b) shows that the $\text{MnO}_x/\text{CeO}_2$ -NR, MnO_x/CZ -NR, MnO_x/CA -NR, and MnO_x/CS -NR catalysts also exhibit the cubic fluorite structure of CeO_2 , while no diffraction signals of MnO_x

were observed. These results suggest that the MnO_x species were well dispersed on the surface of the CeO_2 -NR, CZ-NR, CA-NR, and CS-NR supports, or/and exist in the clustered state, and are not within the detection-limit of the XRD technique.

Raman spectroscopy was employed to further investigate the structures of these supports and supported MnO_x -based catalysts, as presented in Fig. 3. As shown in Fig. 3(a), the CeO_2 -NR support exhibits a strong Raman scattering peak at 464 cm^{-1} and a broad weak band around 610 cm^{-1} . The first strong peak is attributed to the F_{2g} vibration mode of cubic fluorite-type CeO_2 , while the latter is related to defect-induced modes (denoted as D, e.g., oxygen vacancies) on the surface of CeO_2 [32,37,38]. With regard to the CZ-NR, CA-NR, and CS-NR supports, only the F_{2g} and D bands could be observed, while the signals of ZrO_2 , Al_2O_3 , and SiO_2 were not detected. Moreover, compared to the profile of the CeO_2 -NR support, the F_{2g} peak of these doped supports shifted slightly to the low-wavenumber direction and weakened to some extent. These findings suggest that Zr^{4+} , Al^{3+} , and Si^{4+} are incorporated into the lattice of CeO_2 , which is consistent with the XRD results. Interestingly, it is widely recognized that the intensity ratio of the D and F_{2g} (i.e., $I_D/I_{F_{2g}}$) bands may indicate the relative concentration of oxygen vacancies on the surface of ceria-based materials [22,32,37]. The $I_D/I_{F_{2g}}$ ratio of these supports is also presented in Fig. 3(a), where the values for the CZ-NR, CA-NR, and CS-NR supports are slightly larger than that of the CeO_2 -NR support, which indicates that the incorporation of Zr^{4+} , Al^{3+} , and Si^{4+} can increase the concentration of oxygen vacancies on the surface of CeO_2 . From Fig. 3(b), it was found that the $\text{MnO}_x/\text{CeO}_2$ -NR, MnO_x/CZ -NR, MnO_x/CA -NR, and MnO_x/CS -NR catalysts also presented a strong peak (F_{2g}) and a broad weak band (D) without the signals of MnO_x , which suggests that the MnO_x species were well dispersed on the surface of the CeO_2 -NR, CZ-NR, CA-NR, and CS-NR supports (supported by the XRD results). Furthermore, the $I_D/I_{F_{2g}}$ values of these MnO_x -based catalysts (inset in Fig. 3(b)) are remarkably larger than those of the corresponding supports, which indicates that the loaded MnO_x species can interact with these supports to generate more oxygen vacancies. Notably, the MnO_x/CS -NR catalyst had the most

Table 1

Lattice parameters and N_2 -physisorption results of the ceria-based supports.

Sample	Lattice parameter (Å)	BET specific surface area ($\text{m}^2\text{ g}^{-1}$)	Total pore volume ($\text{cm}^3\text{ g}^{-1}$)	Average pore diameter (nm)
CeO_2 -NR	5.419	68	0.1370	7.2
CZ-NR	5.396	111	0.1965	6.7
CA-NR	5.402	109	0.3742	16.6
CS-NR	5.407	105	0.2532	15.5

Fig. 3. Raman spectra of (a) supports and (b) catalysts.

oxygen vacancies among these MnO_x -based catalysts.

Textural data for these supports were obtained from N_2 -physorption experiments, as listed in Table 1. The BET specific surface area and total pore volume of the CZ-NR, CA-NR, and CS-NR supports were obviously larger than those of the CeO_2 -NR support, which is related to the fact that the incorporation of Zr^{4+} , Al^{3+} , and Si^{4+} inhibits growth of the CeO_2 grains, and thus results in a smaller grain size (supported by the XRD results). Moreover, the increase in the BET specific surface area and total pore volume is beneficial for dispersion of the MnO_x species on the surface of these doped supports.

3.3. Analysis of redox properties (H_2 -TPR)

H_2 -TPR was used to explore the redox properties of these MnO_x -based catalysts, and the results are displayed in Fig. 4. The data show that the $\text{MnO}_x/\text{CeO}_2$ -NR, MnO_x/CZ -NR, MnO_x/CA -NR, and MnO_x/CS -NR catalysts all exhibit three reduction peaks in the temperature range of 200–500 °C, attributed to gradual reduction of the MnO_x species (i.e., $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4 \rightarrow \text{MnO}$, denoted as α , β , and γ , respectively) [2,39–41]. The quantitative H_2 -TPR data are summarized in Table 2. The peak temperature of the MnO_x/CZ -NR, MnO_x/CA -NR, and MnO_x/CS -NR catalysts was higher than that of the $\text{MnO}_x/\text{CeO}_2$ -NR catalyst, which indicates that the incorporation of Zr^{4+} , Al^{3+} , and Si^{4+} leads to greater difficulty in reducing the MnO_x species. The lessened reduction ability is beneficial for inhibiting the non-selective catalytic oxidation of NH_3 during the NH_3 -SCR reaction, which results in decreased generation of N_2O as a by-product. Furthermore, Table 2 shows that the practical H_2 consumption of these MnO_x -based cata-

Fig. 4. H_2 -TPR profiles of the catalysts.

lysts is clearly larger than the corresponding theoretical H_2 consumption (presented in brackets), which indicates that the reduction peaks of α , β , and γ not only correspond to the reduction of MnO_x species, but also have contributions from the reduction of these ceria-based supports. Interestingly, the actual H_2 consumption of the MnO_x/CZ -NR, MnO_x/CA -NR, and MnO_x/CS -NR catalysts was significantly larger than that of the $\text{MnO}_x/\text{CeO}_2$ -NR catalyst, which suggests that the incorporation of Zr^{4+} , Al^{3+} , and Si^{4+} increases the amount of reducible species. It is generally recognized that the NH_3 -SCR reaction involves a redox cycle and an acid cycle [42]. Thus, the increase in the reducible species over the MnO_x/CZ -NR, MnO_x/CA -NR, and MnO_x/CS -NR catalysts may contribute to the redox cycle in the NH_3 -SCR reaction.

Table 2

Peak temperature and H_2 consumption of the catalysts obtained from H_2 -TPR.

Catalyst	Peak temperature (°C)			H_2 consumption ($\mu\text{mol g}^{-1}$)			
	T_α	T_β	T_γ	S_α	S_β	S_γ	$S_\alpha+S_\beta+S_\gamma$
$\text{MnO}_x/\text{CeO}_2$ -NR	248	325	384	938	523	316	1777 (642)
MnO_x/CZ -NR	288	374	423	1506	482	298	2286 (1012)
MnO_x/CA -NR	257	342	395	1143	691	331	2165 (996)
MnO_x/CS -NR	263	345	405	1173	709	268	2150 (962)

Fig. 5. NH_3 -TPD profiles of the catalysts.

3.4. Study of surface acidity (NH_3 -TPD and in situ DRIFTS of NH_3 adsorption)

The NH_3 -TPD profiles of these MnO_x -based catalysts are presented in Fig. 5. This Fig. shows that the $\text{MnO}_x/\text{CeO}_2$ -NR and MnO_x/CZ -NR catalysts exhibit four desorption peaks between 100 and 600 °C (labeled as I, II, III, and IV, respectively), which are attributed to the desorption of physisorbed NH_3 species, as well as the desorption of chemisorbed NH_3 species, from the weak acid sites, medium-strong acid sites, and strong acid sites, respectively [18,43–46]. For the MnO_x/CA -NR and MnO_x/CS -NR catalysts, apart from the four aforementioned desorption peaks, an extra shoulder peak was observed at high temperature (denoted as V), which may be related to the desorption of chemisorbed NH_3 species from the hydroxyl groups bonding to Al^{3+} and Si^{4+} ions. Some interesting deductions can be made from the quantitative NH_3 -TPD analysis (Table 3). The total number of acidic sites of the MnO_x/CZ -NR, MnO_x/CA -NR, and MnO_x/CS -NR catalysts is obviously higher than that of the

Table 3

Quantitative analysis of NH_3 -TPD over the catalysts.

Catalyst	Acid amount (a.u.)					Total acid amount (a.u.) $S_I + S_{II} + S_{III} + S_{IV} + S_V$
	S_I	S_{II}	S_{III}	S_{IV}	S_V	
$\text{MnO}_x/\text{CeO}_2$ -NR	829	387	936	641	—	2793
MnO_x/CZ -NR	819	562	1142	1418	—	3941
MnO_x/CA -NR	578	621	1243	1603	267	4312
MnO_x/CS -NR	658	595	1514	1481	224	4472

$\text{MnO}_x/\text{CeO}_2$ -NR catalyst, which indicates that the incorporation of Zr^{4+} , Al^{3+} , and Si^{4+} can efficiently improve the surface acidity of the $\text{MnO}_x/\text{CeO}_2$ -NR catalyst. Notably, the MnO_x/CS -NR catalyst has the largest number of acidic sites among these MnO_x -based catalysts, which is conducive to the adsorption and activation of NH_3 molecules, and further enhances the denitration performance for NH_3 -SCR reaction.

Therefore, the MnO_x/CS -NR catalyst was selected as the representative sample to further distinguish the Brønsted (B) acid sites and Lewis (L) acid sites on the catalyst surface through in situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) analysis of the NH_3 adsorption, as shown in Fig. 6. For comparison, the in situ DRIFTS data for NH_3 adsorption over the $\text{MnO}_x/\text{CeO}_2$ -NR catalyst are also presented in this Fig. Fig. 6(a) shows that when the $\text{MnO}_x/\text{CeO}_2$ -NR catalyst was saturated with a 1% NH_3 -99% N_2 mixture at room temperature, signals of NH_3 coordinated to the L acid sites appeared at 1056, 1117, 1291, 1549, and 1589 cm^{-1} , while the vibration band of NH_4^+ bonded to the B acid sites appeared at 1425 cm^{-1} [36,47–51]. Interestingly, the intensity of the vibration bands related to the B acid sites and L acid sites weakened with an increase in temperature, and some signals of the L acid sites disappeared at 300 and 350 °C, which suggests that the adsorbed NH_3 species on the surface of the $\text{MnO}_x/\text{CeO}_2$ -NR catalyst can be desorbed and transformed with an increase in temperature. For the MnO_x/CS -NR catalyst (Fig. 6(b)), upon saturation with a 1% NH_3 -99% N_2 mixture at room temperature, the vibration bands of the B acid sites and L acid

Fig. 6. NH_3 -adsorption in situ DRIFTS of (a) $\text{MnO}_x/\text{CeO}_2$ -NR and (b) MnO_x/CS -NR.

sites could be detected. Compared with Fig. 6(a), the relative intensity of the band of the B acid sites of the $\text{MnO}_x/\text{CS-NR}$ catalyst was remarkably stronger than that of the $\text{MnO}_x/\text{CeO}_2\text{-NR}$ catalyst, which indicates that the incorporation of Si^{4+} effectively increases the number of B acid sites. It is generally accepted that B acid sites play a more important role in the low-temperature $\text{NH}_3\text{-SCR}$ reaction than L acid sites [19,52]. Furthermore, the intensity change of all the vibration bands of the $\text{MnO}_x/\text{CS-NR}$ catalyst with an increase in temperature was more pronounced than for the $\text{MnO}_x/\text{CeO}_2\text{-NR}$ catalyst (especially from 100 to 150 °C), which suggests that the $\text{MnO}_x/\text{CS-NR}$ catalyst is more effective for activation of the adsorbed NH_3 species. These results suggest that the $\text{MnO}_x/\text{CS-NR}$ catalyst may exhibit better denitration performance than the $\text{MnO}_x/\text{CeO}_2\text{-NR}$ catalyst for the low-temperature $\text{NH}_3\text{-SCR}$ reaction.

3.5. Surface chemical state analysis (XPS)

The surface properties of the denitration catalysts play an important role in the $\text{NH}_3\text{-SCR}$ reaction. Hence, the surface chemical states of these MnO_x -based catalysts were analyzed by XPS, as presented in Fig. 7. The Mn 2p spectra in Fig. 7(a) show six bands for the $\text{MnO}_x/\text{CeO}_2\text{-NR}$, $\text{MnO}_x/\text{CZ-NR}$, $\text{MnO}_x/\text{CA-NR}$, and $\text{MnO}_x/\text{CS-NR}$ catalysts, ascribed to the Mn 2p_{1/2} and Mn 2p_{3/2} signals of Mn^{4+} , Mn^{3+} , and Mn^{2+} , respectively [53,54]. It is commonly recognized that Mn^{4+} is more effective for the elimination of NO_x than the Mn^{3+} and Mn^{2+} ions [55]. Therefore, the

relative content of Mn^{4+} on the surface of these MnO_x -based catalysts was calculated, as presented in Table 4. The Mn^{4+} content of the $\text{MnO}_x/\text{CZ-NR}$, $\text{MnO}_x/\text{CA-NR}$, and $\text{MnO}_x/\text{CS-NR}$ catalysts was higher than that of the $\text{MnO}_x/\text{CeO}_2\text{-NR}$ catalyst. The reasons may be as follows: first, the larger BET specific surface area of the CZ-NR, CA-NR, and CS-NR supports is beneficial for dispersion of the Mn-precursor, which can promote the oxidation of Mn^{2+} to high-valence Mn^{4+} during the calcination process; second, the incorporation of Zr^{4+} , Al^{3+} , and Si^{4+} strengthens the electronic interaction between the doped supports and the surface-dispersed MnO_x species, which can lead to the generation of more Mn^{4+} . Notably, the $\text{MnO}_x/\text{CS-NR}$ catalyst had the highest Mn^{4+} content among these MnO_x -based catalysts, which may contribute to the excellent denitration performance for the low-temperature $\text{NH}_3\text{-SCR}$ reaction.

Fig. 7(b) shows the O 1s spectra of these MnO_x -based catalysts, demonstrating the presence of two types of oxygen species on the surface of the $\text{MnO}_x/\text{CeO}_2\text{-NR}$, $\text{MnO}_x/\text{CZ-NR}$, $\text{MnO}_x/\text{CA-NR}$, and $\text{MnO}_x/\text{CS-NR}$ catalysts, i.e., lattice oxygen species with a signal centered at 529.2 eV (denoted as O_β) and surface adsorbed oxygen species with a signal at 531.7 eV (denoted as O_α) [50,56]. It is generally recognized that the ratio of the areas of the O_α and $\text{O}_\alpha+\text{O}_\beta$ peaks (i.e., $\text{O}_\alpha/(\text{O}_\alpha+\text{O}_\beta)$) is an indicator of the relative content of surface adsorbed oxygen species, and an increase in the O_α content can promote the oxidation of NO to NO_2 , and further enhances the denitration performance for the low-temperature $\text{NH}_3\text{-SCR}$ reaction through a fast selective catalytic reduction (SCR) pathway [50]. There-

Fig. 7. XPS results of the catalysts. (a) Mn 2p; (b) O 1s.

Table 4

Surface composition and atomic ratio of the catalysts analyzed by XPS.

Catalyst	Atomic concentration (at.%)						Atomic ratio (%)	
	Mn	O	Ce	Zr	Al	Si	$\text{Mn}^{4+}/(\text{Mn}^{2+}+\text{Mn}^{3+}+\text{Mn}^{4+})$	$\text{O}_\alpha/(\text{O}_\alpha+\text{O}_\beta)$
$\text{MnO}_x/\text{CeO}_2\text{-NR}$	2.54	78.60	18.86	—	—	—	33.17	38.58
$\text{MnO}_x/\text{CZ-NR}$	3.07	72.18	22.56	2.19	—	—	34.65	37.32
$\text{MnO}_x/\text{CA-NR}$	2.70	77.09	18.96	—	1.25	—	35.05	17.53
$\text{MnO}_x/\text{CS-NR}$	2.12	75.06	18.47	—	—	4.35	37.49	21.19

Fig. 8. Catalytic performance of these ceria-based supports and corresponding catalysts. (a) NO_x conversion; (b) N₂O concentration.

fore, the O_α content of the surface of these MnO_x-based catalysts was calculated, and is also listed in Table 4. The O_α content of the MnO_x/CZ-NR, MnO_x/CA-NR, and MnO_x/CS-NR catalysts was smaller than that of the MnO_x/CeO₂-NR catalyst, which suggests that the incorporation of Zr⁴⁺, Al³⁺, and Si⁴⁺ may inhibit the fast SCR pathway, and further negatively affects the low-temperature NH₃-SCR reaction.

3.6. Evaluation of denitration performance and H₂O+SO₂ tolerance (NH₃-SCR reaction)

The denitration performance of these CeO₂-based supports and corresponding MnO_x-based catalysts is displayed in Fig. 8. The NO_x conversion data in Fig. 8(a) show that the CZ-NR, CA-NR, and CS-NR supports exhibit slightly higher catalytic activity than the CeO₂-NR support, and loading with MnO_x could obviously enhance the catalytic activity of the supports. Notably, the MnO_x/CS-NR catalyst gave the best catalytic activity among these catalysts above 100 °C. The reasons may be as follows: first, the MnO_x/CS-NR catalyst possesses the largest amount of oxygen vacancies, which may enhance dissociation of the NO_x molecules; second, it has the largest number of acid sites, which can promote the adsorption and activation of NH₃ molecules; finally, it has the highest Mn⁴⁺ content, which is conducive to the elimination of NO_x. However, the MnO_x/CZ-NR catalyst exhibits the lowest NO_x conversion among these catalysts in the 50–200 °C range, which may be because the incorporation of Zr⁴⁺ into the lattice of CeO₂ shortens the length of the nano-rods and further decreases the extent of exposure of the active {110} facet. Moreover, the NO_x conversion curves of these catalysts exhibit a similar trend as a function of temperature, i.e., an initial increase with an increase in temperature and a subsequent decline with a further increase in the temperature, because the non-selective catalytic oxidation of NH₃ results in a decrease in the amount of reductant, which is maximal at 200 °C.

It is well known that MnO_x-based catalysts generally exhibit poor N₂ selectivity as their very strong redox properties lead to the non-selective catalytic oxidation of NH₃ to N₂O

(by-product). Therefore, the concentration of N₂O generated in the reaction process was monitored, as shown in Fig. 8(b). Almost no N₂O was formed over these CeO₂-based supports over the entire temperature range, whereas the N₂O concentration increased significantly for the reaction over these MnO_x-based catalysts in the 100–250 °C range. In addition, the MnO_x/CS-NR catalyst presented the lowest N₂O concentration among these catalysts over the entire temperature range, which may be related to its lower redox ability and effective activation of NH₃. These two factors partially inhibit the non-selective catalytic oxidation of NH₃ to generate N₂O. Combining the results of Fig. 8(a) and (b), it is found that the MnO_x/CS-NR catalyst exhibits the best denitration performance in the present study.

Fig. 9 shows the H₂O+SO₂ tolerance of the MnO_x/CeO₂-NR, MnO_x/CZ-NR, MnO_x/CA-NR, and MnO_x/CS-NR catalysts at 200 °C. Steady-state NO_x conversion over these MnO_x-based catalysts was easily achieved in the absence of H₂O and SO₂ (within the first 120 min). However, all the catalysts exhibited an obvious decrease in the NO_x conversion (about 20%) once H₂O and SO₂ were introduced (from 120 to 600 min). According to the literature [2,44,57], this change may be derived from competitive adsorption between the reactants and toxic molecules, the deposition of sulfates, and sulfation of the active species.

Fig. 9. Resistance to water and sulfur dioxide over these catalysts at 200 °C.

Finally, the NO_x conversion with these MnO_x -based catalysts could be partially restored after the removal of H_2O and SO_2 , with a decline in the activity of only about 3% relative to the original values (the last 120 min). These experimental results suggest that the decrease in the NO_x conversion over these catalysts caused by H_2O and SO_2 occurs mainly by reversible reactions, with some irreversible deactivation. Furthermore, the similar trend in the NO_x conversion based on measurement of the $\text{H}_2\text{O}+\text{SO}_2$ tolerance indicates that these catalysts might follow the same deactivation mechanism. Overall, the $\text{MnO}_x/\text{CS-NR}$ catalyst generally presented the highest NO_x conversion among these catalysts despite the absence or presence of H_2O and SO_2 , which suggests that $\text{MnO}_x/\text{CS-NR}$ is the most promising catalyst in the present work.

4. Conclusions

The thermally stable Zr^{4+} , Al^{3+} , and Si^{4+} cations were incorporated into the lattice of $\text{CeO}_2\text{-NR}$ to prepare $\text{MnO}_x/\text{CeO}_2\text{-NR}$, $\text{MnO}_x/\text{CZ-NR}$, $\text{MnO}_x/\text{CA-NR}$, and $\text{MnO}_x/\text{CS-NR}$ catalysts for low-temperature $\text{NH}_3\text{-SCR}$ with the purpose of exploring the doping effect and screening the optimal dopant. These samples were characterized in detail, and the key conclusions are as follows: (1) the incorporation of Zr^{4+} , Al^{3+} , and Si^{4+} does not change the rod-like structure and exposed active {110} facet of $\text{CeO}_2\text{-NR}$, but Zr^{4+} doping shortens the rod length; (2) the BET specific surface area of $\text{CeO}_2\text{-NR}$ can be effectively enlarged by Zr^{4+} , Al^{3+} , and Si^{4+} doping, which is beneficial for dispersion of the MnO_x species; (3) the $\text{MnO}_x/\text{CS-NR}$ catalyst has the largest number of oxygen vacancies, the largest number of acid sites, and the highest Mn^{4+} content, which result in the best denitration performance; (4) the Si^{4+} -doped catalyst not only exhibits the best denitration performance, but also displays good

$\text{H}_2\text{O}+\text{SO}_2$ tolerance, which indicates that Si^{4+} is the optimal dopant for the $\text{MnO}_x/\text{CeO}_2\text{-NR}$ catalyst in the present work.

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Graphical Abstract

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Doping effect of cations (Zr^{4+} , Al^{3+} , and Si^{4+}) on $\text{MnO}_x/\text{CeO}_2$ nano-rod catalyst for $\text{NH}_3\text{-SCR}$ reaction at low temperature

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Zr^{4+} , Al^{3+} , and Si^{4+} were incorporated into a $\text{MnO}_x/\text{CeO}_2\text{-NR}$ catalyst. The Si^{4+} -doped catalyst exhibits the best denitration performance due to the largest number of oxygen vacancies, the largest number of acid sites, and highest Mn^{4+} content.

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MnO_x/CeO₂纳米棒催化剂在低温NH₃-SCR反应中的阳离子(Zr⁴⁺, Al³⁺, Si⁴⁺)掺杂效应

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摘要: 低温脱硝技术由于具有无需再加热烟气、方便燃煤电厂脱硝改造以及适用于一些烟气温度较低的非电力行业脱硝场合等优点, 吸引了越来越多研究者的关注。低温脱硝催化剂是该技术中最关键的单元, 因此其配方开发及相关工作已成为近年来的研究热点之一。

商业化V₂O₅-WO₃/TiO₂催化剂在300–400 °C的固定源烟气脱硝中表现出优异的性能, 然而其低温脱硝性能却差强人意。并且, V₂O₅具有生物毒性, 会造成二次污染。因此, 低温脱硝催化剂的开发主要集中在环境友好的非钒基催化剂上。其中, MnO_x基催化剂由于具有优异的低温脱硝性能而成为重点研究对象。特别是MnO_x/CeO₂催化剂由于CeO₂良好的氧化

还原性能和较高的储释氧容量,引起了低温脱硝领域越来越多研究者的兴趣.然而,众所周知,CeO₂的比表面积和热稳定性并不令人满意.幸运的是,研究表明,阳离子掺杂可有效地克服CeO₂的上述缺点.

此外,随着纳米材料制备科学与技术的发展,不同形貌的CeO₂已经能可控合成.研究表明,CeO₂纳米棒比其它形貌的CeO₂更适合用作载体,因为CeO₂纳米棒主要暴露的{110}晶面易于形成氧空位以及和表面分散组分产生强相互作用.因此,在本工作中,我们在CeO₂纳米棒的晶格中掺入热稳定的Zr⁴⁺,Al³⁺,Si⁴⁺等阳离子以提高其比表面积和热稳定性,并以该CeO₂纳米棒为载体负载MnO_x,考察了Zr⁴⁺,Al³⁺,Si⁴⁺等阳离子掺杂对MnO_x/CeO₂纳米棒催化剂低温脱硝性能的影响,筛选出最佳的掺杂离子.

对制备的样品进行了透射电子显微镜、高分辨透射电子显微镜、X射线衍射、拉曼光谱、氮气物理吸附、氢气程序升温还原、氨气程序升温脱附、氨气吸附原位漫反射红外光谱和X射线光电子能谱等一系列表征分析,并利用氨气-选择性催化还原(NH₃-SCR)反应评价了其脱硝性能和抗水抗硫性能.结果表明, Si⁴⁺掺杂的MnO_x/CeO₂纳米棒(MnO_x/CS-NR)催化剂具有最多的氧空位、表面酸性位和Mn⁴⁺因而表现出最佳的脱硝活性.由于其氧化还原性能适当减弱,有效地抑制了氨气的非选择性催化氧化,从而表现出最低的N₂O生成量.此外, MnO_x/CS-NR催化剂还显示出最佳的抗水抗硫性能.综上所述, Si⁴⁺是MnO_x/CeO₂纳米棒催化剂的最佳掺杂离子.

关键词: MnO_x/CeO₂纳米棒催化剂; 掺杂效应; 氧空位; 表面酸性; 低温氨气选择性催化还原反应

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