Influence of organic sulfur gas-phase sulfation on the NH$_3$-SCR activity of CeO$_2$ catalyst: the competitive adsorption and conversion of CS$_2$ and COS at a low hydrolysis temperature

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Abstract:

In this study, a simplified approach is proposed to realize the gas-phase sulfation of CS$_2$ or/and COS at the hydrolysis temperature for further facilitating the NH$_3$-SCR activity of CeO$_2$ in diverse conditions. A low-temperature oxidation conversion process for the adsorbed CS$_2$ or COS on cubic fluorite CeO$_2$ surface is developed. It is found that the gas-phase sulfation of organic CS$_2$ or/and COS at 50 °C enhances the mobility of lattice oxygen of cubic fluorite CeO$_2$ and the concentration of oxygen defects for the sulfated CeO$_2$ catalyst, but the kinds of organic COS/CS$_2$ can regulate the formed types and quality of sulfur-containing species on the catalyst surfaces during the gas-phase sulfation. and the formed sulfates under the gas-phase sulfation of CS$_2$ are more active than those of COS, and CeO$_2$-CS$_2$-50°C-3h presents the best mobility of lattice oxygen, the largest concentration of adsorbed oxygen and the best NH$_3$-SCR activity. Furthermore, the competitive adsorption and conversion of CS$_2$ and COS is disadvantageous for...
the formation of oxygen vacancies on the catalyst surfaces compared to single CS₂ or COS. However, the long-time durability testing coupling re-cycle experiments can optimize the oxygen vacancy defects and increase the concentration of chemisorbed oxygen of the sulfated CeO₂-CS₂+COS-50°C-24h catalyst via optimizing the oxidization of sulfur element to sulfur oxides or/and sulfates, thereby improves its NH₃-SCR activity. And the sulfated CeO₂ catalyst by the gas-phase sulfation of organic COS+CS₂ presents a good stability for NH₃-SCR reaction. This study specifies a novel approach to simplify the gas-phase sulfation process of CeO₂ catalyst, which is valuable in promotion of the NH₃-SCR activity of CeO₂ and reduction of cost in experimental procedures.

**Keywords:** NH₃-SCR, CeO₂, Organic COS/CS₂, Low-temperature gas-phase sulfation, Competitive adsorption and conversion

### 1. Introduction

As the major compounds of organic sulfur, carbonyl sulfide (COS) and carbon disulfide (CS₂) widely present in petrochemical energy sources, including coal, natural gas and water gas [1,2], which have cytotoxic effects on the human central nervous system (CNS) and also can corrode the production equipment, resulting in the poisoning/deactivation of catalysts and the depressed utilization rate of the industrial by-product resources [3-5]. Similar to carbon dioxide (CO₂), COS and CS₂ with the linear molecular configurations are stable at room temperature and difficult to be removed via the traditional adsorption method applied for SO₂ and H₂S [6-8]. Therefore, the catalytic hydrolysis has been promoted to reduce COS/CS₂ due to the low energy consumption, simple operation and few side reactions. The main hydrolysis reactions are listed as follows [2,5]:

\[ \text{CS}_2 + H_2O \rightarrow \text{COS} + H_2S \quad (1) \]
\[ \text{COS} + H_2O \rightarrow CO_2 + H_2S \quad (2) \]
It is clear that the basic sites of catalysts are the active centers for the hydrolysis reaction, which are divided into the weak (-OH groups)/medium basic sites (metal-oxygen pairs, Al-O, Zn-O, Ti-O, Ce-O, etc.) and the strong basic sites (O\(^{2-}\) ions), respectively. It was reported in previous studies that CS\(_2\) and COS were firstly adsorbed on the catalyst surfaces through ion coupling, and interacted with the surface -OH groups and metal-oxygen pairs to produce the intermediate product thiocarbonate (HSCO\(_2^-\)), which subsequently reacted with the basic sites to form H\(_2\)S and CO\(_2\).

Finally, H\(_2\)S was oxidized to elemental sulfur or/and sulfate species by-products by the strong basic sites (O\(^{2-}\), etc.) and partial weak/medium basic sites on the catalyst surfaces [9-12]. Therefore, the catalytic hydrolysis of COS/CS\(_2\) could induce the formation of sulfate species on the catalyst surfaces, thus deactivating and poisoning the hydrolysis activity of the Al\(_2\)O\(_3\)/TiO\(_2\) alkali catalysts, especially under the condition of oxygen in flue gas. However, the doping of cerium oxide effectively inhibited the sulfation of surface alkaline active sites due to its stronger combination ability with sulfate species, and improved the anti-O\(_2\) poisoning of the hydrolysis alkali catalysts [13-17].

Due to the unique 4f electronic structure, cerium dioxide (CeO\(_2\)) presents an excellent oxygen storage capacity (OSC) and a redox ability via the redox cycle of Ce\(^{4+}/Ce^{3+}\), and has attracted a widespread attention in developing a replaced non-vanadium-based catalyst for selective catalytic reduction of NO\(_x\) with NH\(_3\) (NH\(_3\)-SCR) [18-21]. Unfortunately, single CeO\(_2\) exhibits a bad NH\(_3\)-SCR activity owing to the poor surface acidity and the side reactions at high-temperatures, which needs to be optimized. Interestingly, the sulfation has been used to improve the NH\(_3\)-SCR activity of CeO\(_2\) by enhancing its surface acidity. Previous studies had confirmed that the gas-phase sulfation
of SO2 at 300 °C and below could cause sulfate species formed on cubic fluorite CeO2 surfaces, and enhanced its Brønsted acid sites on the basis of retaining Lewis acid sites, thus accelerated the adsorption and activation of NH3 on the cerium-base catalyst surfaces [22-26]. For example, Xie et al. [27] had investigated the influence of SO2 sulfation time on regulating the formed sulfate species on the CeO2 catalyst surface and its NH3-SCR activity, and found that under the sulfation of SO2 at 150 °C, the enhancement of sulfation time increased the formed amount of sulfate on the catalyst surfaces, thus gradually improved the NH3-SCR activity of CeO2 due to the increased Brønsted acid sites, exhibiting a higher adsorption rate of NH3 species than Lewis acid sites. This phenomenon had also been confirmed by the research on the sulfated Ce/TiO2 catalyst [22]. Furthermore, the sulfation temperature could adjust the formed types of sulfate species. Zhang et al. [28] found that the enhancement of sulfation temperature converted the surface sulfates to bulk-like sulfates and even bulk sulfates in the CeO2 catalyst, which promoted the NH3-SCR reaction of CeO2 below 300 °C. Comparatively, the higher temperature bulk-like and/or bulk sulfate species hindered the synergistic catalytic effect between surface sulfates and bulk CeO2, which depressed the promotional effect of sulfation. It should be mentioned that the organic COS/CS2 had also been used to optimize the NH3-SCR activity of CeO2 in our previous research. We found that compared to the traditional inorganic SO2, the reductive COS/CS2 presented better promotional effect on the catalytic performance of NOx reduction over CeO2, and the gas-phase sulfation of CS2 at 300 °C induced more Ce4+ to reduce to Ce3+ and generated more surface defects owing to its stronger reducibility than SO2, thus leading to more oxygen defects and chemisorbed oxygen formed on the CeO2 surfaces [29]. Therefore, the organic sulfur, including COS and CS2, presented stronger optimized effect on the NH3-SCR activity of cerium-based catalyst. However, the gas-phase sulfation of
COS/CS₂ at low temperatures on the NH₃-SCR activity of CeO₂ has been little reported, so it is critical to examine the characteristics of its influence on catalysis at different hydrolysis temperatures.

Actually, the temperature of flue gas emitted from industrial steel, glass or/and boiler typically ranges from 70-150 °C, and the developed alkali catalysts have also been expected to reduce organic sulfur via the low-temperature hydrolysis method, which is beneficial to lower cost by avoiding the reheating of flue gas and reducing the formation of S or/and SO₄²⁻ on the catalyst surfaces to prevent poisoning [16,30,31]. Meanwhile, the gas-phase sulfation temperature also affects the NH₃-SCR activity of cerium-based catalysts, and higher sulfation temperature might induce the formation of thermostable bulk sulfates, which deactivated the activity of cerium-based catalysts through destroying the redox conversion between Ce⁴⁺ and Ce³⁺ [32,33]. However, the gas-phase sulfation at a low temperature could inhibit the formation of bulk sulfate species on the surfaces of CeO₂ catalyst, facilitating the propagation of the redox reaction. Furthermore, the adsorbed surface sulfate species optimized its acid sites and active species, thereby increased the NH₃-SCR activity of CeO₂ [27,34]. Therefore, as the additive to improve the anti-O₂ poisoning of alkali catalysts for the hydrolysis of organic sulfur, CeO₂ presents a stronger combination ability with sulfate species compared to the surface alkaline active sites, thus the sulfated CeO₂ catalysts by organic COS/CS₂ at low-temperatures can exhibit a good NH₃-SCR activity due to the formation of active surface sulfate species. Nevertheless, organic COS or CS₂ might show different adsorption and conversion characteristics on the CeO₂ surfaces under the hydrolysis temperature, affecting the NH₃-SCR activity of the sulfated CeO₂ catalyst attributed to the diversely formed surface sulfate species and active sites.
In this study, organic CS$_2$ or/and COS were used to improve the NH$_3$-SCR activity of CeO$_2$ by the gas-phase sulfation at their low temperature hydrolysis temperatures. It is found that the types of organic sulfur influence the promotional effect of their gas-phase sulfation on the NH$_3$-SCR activity of CeO$_2$, and the gas-phase sulfation of reductive CS$_2$ at 50 °C shows the best promotional effect. Meanwhile, because the co-existence of CS$_2$ and COS reduces the catalyst activity due to their competitive adsorption and conversion, the synergistic effect of organic sulfur types on the physicochemical properties of the gas-phase sulfated CeO$_2$ catalyst at 50 °C was specifically examined. The characterization results are further validated by comparing with theoretical calculations based on density functional theory (DFT) using the Dmol$^3$ module in the Material Studio calculation software. This simple gas-phase sulfation strategy can be generally extended to other supported metal oxide catalysts to improve their catalytic performance of NO$_x$ reduction.

2. Experimental

2.1. Synthesis of CeO$_2$

Based on our previous researches [29,35], a one-pot hydrothermal method was used to obtain CeO$_2$ with cerium nitrate (Ce(NO$_3$)$_3$·6H$_2$O, AR), ammonium bicarbonate (NH$_4$HCO$_3$, AR) and hydrogen peroxide (30% H$_2$O$_2$, AR) as the precursor, precipitant and oxidant, respectively. Firstly, 0.005 mol Ce(NO$_3$)$_3$·6H$_2$O was dissolved in 50 mL distilled water under vigorous stirring for 2 hours until a clear solution is formed. Then, 0.02 mol NH$_4$HCO$_3$ was added into the above solution under the continuous stirring, and a white precipitation is immediately generated. Subsequently, the above white suspension promptly becomes orange accompanied with the release of bubbles when 9 mL H$_2$O$_2$(10 mol/L) was dropped into it. After being vigorous stirred for 3 h, the obtained solution was carefully transferred into a 100 mL Teflon-lined autoclave and then heated at 200 °C for 24 h.
After the hydrothermal treatment, the autoclave was cooled down quickly to room temperature, and then the obtained precipitant was filtered and thoroughly washed several times by distilled water and absolute ethanol. After being dried at 80 °C for 12 h, the sample was calcined at 400 °C for 5 h in a temperature-programmed muffle furnace.

2.2. Synthesis of sulfated CeO$_2$

The gas-phase sulfation of CeO$_2$ was carried out in a tube furnace under a simulated sulfur-containing atmosphere at 300 °C or the hydrolysis temperature of organic sulfur [36,37]. The types and concentrations of organic sulfur were specified as follow: CS$_2$/COS/CS$_2$+COS (the CS$_2$/COS molar ratio of 3:7), the concentration of S element is 200 ppm, and the total flow rate was 500 mL/min with N$_2$ (99.999 vol.%) as balance. In the experiments, the pretreated samples were recorded as CeO$_2$-CS$_2$-t-h, CeO$_2$-COS-t-h and CeO$_2$-CS$_2$+COS-t-h, where t and h represent the temperature and duration of sulfation, respectively. For example, CeO$_2$-CS$_2$-50°C-3h presented the catalyst treated by the gas-phase sulfation of CS$_2$ at 50 °C for 3 h. Furthermore, the sulfated CeO$_2$-CS$_2$+COS-50°C-24h catalysts after the long-time stability test coupling re-cycle experiments and the secondary re-calcination at 400 °C for 5 h are denoted as CeO$_2$-CS$_2$+COS-50°C-24h-CT and CeO$_2$-CS$_2$+COS-50°C-24h-SC, respectively. All samples were screened by 40-60 meshes for the activity evaluation.

2.3. Catalytic activity test

The NH$_3$-SCR catalytic performance at a temperature range of 150~400 °C was tested in a fixed bed micro-reactor by using 0.45 g catalyst (40~60 mesh). The corresponding gas hourly space velocity (GHSV) is 200,000 mL/(g·h) under the total flow rate of 1500 mL/min for the simulated flue gas, comprising 600 ppm NH$_3$, 600 ppm NO, 5 vol.% O$_2$ and balance gas 99.999 vol.% N$_2$. 
After the reaction system reaches a stable state, the activity test data was recorded to avoid the effect of gas adsorption on the catalyst. The concentrations of O₂ and NOₓ at inlet and outlet were continuously monitored by T-350 flue gas analyzer (Testo, Germany), and the NOₓ conversion rate (η) was calculated according to the following formula: 

\[ η = \left(1 - \frac{[NO_x]_{\text{out}}}{[NO_x]_{\text{in}}}\right) \times 100\% \]

where \([NO_x]_{\text{in}}\) and \([NO_x]_{\text{out}}\) represented the inlet and outlet concentrations of gaseous NOₓ (NO and NO₂), respectively.

2.4. Catalyst characterizations

N₂ adsorption-desorption, Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), High-resolution transmission electron microscopy (HR-TEM) and Energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), Raman spectra, Fourier transform infrared spectra (FTIR), X-ray photoelectron spectroscopy (XPS), H₂ temperature programmed reduction (H₂-TPR) and infrared spectroscopy with pyridine desorption (Py-IR) experiments were carried out to investigate the physical-chemical properties of the samples [29,35], and the detailed testing process were given in supporting information (SI).

Furthermore, Thermogravimetric Analysis (TGA) and Derivative Thermogravimetry (DTG) were performed in a \(α\)-Al₂O₃ crucible using PerkinElmer STA6000. Thermogravimetric curves were recorded at a heating rate of 10 °C/min from 30 to 900 °C in nitrogen atmosphere. Thermogravimetric-Mass spectrometry analysis (TG-MS) was used to qualitatively analyze the volatile components released during the heating up of the sulfated CeO₂ catalyst. The TG-MS measurement of the samples was performed in a \(α\)-Al₂O₃ crucible using a TG-MS system (PerkinElmer STA6000 thermal analyzer and STA409 PC-QMS403C mass spectrometry). TG-MS curves were recorded from 50 to 900 °C at a heating rate of 10 °C/min in an argon atmosphere (40
mL/min). In the characterization, the TG-MS diagram was analyzed for evaluating the amount of evolved gas products during the thermal decomposition of a single compound.

2.5. Computational method

The crystal plane (111) of the synthesized CeO\textsubscript{2} catalyst by the one-pot hydrothermal method was regarded as the surface model to obtain the adsorption energies of COS or CS\textsubscript{2} over the sample in this study [35]. All simulation calculations were performed using the Dmol\textsuperscript{3} module in the Material Studio calculation software [38], and the GGA/PBE functional in density functional theory was employed in approximating the electron-related exchange energy [3,39]. The Hubbard parameter U = 5 eV was used to correct the Coulomb interaction of Ce to more accurately describe the valence electron structure of Ce 4f orbital. The density functional semi-core pseudopotential method was adopted for the core electrons of Ce, while the all-electron method was utilized for the core electrons of H, C, O, and S atoms. The double-value plus d-function (DND) basis set 4.4 version and a 5.8 Å orbital cutoff value were applied in the simulation. The energy, gradient, and displacement convergence tolerances were \(1.0 \times 10^{-5}\) Ha, \(2.0 \times 10^{-3}\) Ha/Å, and \(5.0 \times 10^{-3}\) Å, respectively.

In the condition that at least two of these criteria are fulfilled, self-consistent field convergence can be assumed [40]. Theoretically, the unit cell of CeO\textsubscript{2} belongs to the orthorhombic system, with a symmetrical space group of FM-3M. A 3×3×3 Monkhorst-Pack K-point grid was utilized to optimize the bulk structure of CeO\textsubscript{2}. The optimized configuration for the structure is shown in Fig. S1(A). The calculated lattice parameter for the structure is \(a=b=c=5.488\) Å, and compared with the lattice parameter 5.400 Å obtained from the experimental test, the error is less than 2 %, which is within the acceptable range. Thus, it can be considered that the parameters set in this study are reliable. In the model, a periodic CeO\textsubscript{2} (111) surface model with nine atomic layers arranged in a
(4×4) supercell was constructed and a 15 Å vacuum layer was used to prevent the influence of the underlying atoms on the surface calculation. The Monkhorst-Pack grid with a k point of 2×2×1 was sampled in the first Brillouin zone. The optimized CeO$_2$ (111) model is shown in Fig. S1(B).

3. Results and discussion

3.1. Catalytic performances

Compared to the traditional inorganic SO$_2$, after the gas-phase sulfation at 300 °C for 3 h, the organic CS$_2$ with a stronger reducibility presented a better promotional effect on the NH$_3$-SCR activity of CeO$_2$. This is because more Ce$^{3+}$ and oxygen defects were induced, causing more chemisorbed oxygen formation on the catalyst surfaces. In addition, the gas-phase sulfation of CS$_2$ also facilitated the formation of sulfate species, augmenting the abundance and strength of both Brønsted acid sites and low-temperature Lewis acid sites on the catalyst surfaces [29]. Actually, the low-temperature hydrolysis coupled chemical absorption method had been confirmed to be an effective mean for the removal of organic CS$_2$/COS based on the alkali catalysts, and cerium oxide had also been discovered as an excellent additive to improve their anti-O$_2$ poisoning via depressing the sulfation of components [40,41]. Moreover, previous research indicated that the sulfation temperature could affect the promotional effect of SO$_2$ gas-phase sulfation. Therefore, the influence of sulfation temperature on the NH$_3$-SCR activity of CeO$_2$ were studied for organic CS$_2$, as shown in Fig. S2(A). Interestingly, compared to the sulfation at 300 °C, the low-temperature gas-phase sulfation of reductive CS$_2$ further increases the catalytic performance of NO$_x$ reduction over CeO$_2$, especially at its hydrolysis temperature of 50 °C. The better promotional effect of low-temperature gas-phase sulfation on the NH$_3$-SCR activity of cerium oxide catalyst for organic sulfur COS was validated, as presented in Fig. S2(B). Therefore, it is clear that the gas-phase sulfation of CS$_2$/COS
presents stronger enhancement on the NH$_3$-SCR activity of CeO$_2$ under their hydrolysis temperatures, which implies that there might exist a mutual promotion effect of organic sulfur low-temperature hydrolysis and NO$_x$ reduction over the cerium-based catalyst.

Fig. S2(C) and (D) show the influence of CS$_2$/COS sulfation duration at 50 °C on the activity of CeO$_2$, respectively. It is found that the NO$_x$ reduction over catalysts firstly increases and then decreases, and the suitable sulfate duration is 3 h for CS$_2$ under the gas-phase sulfation conditions. However, CeO$_2$-COS-50°C-24h presents better catalytic performance of NO$_x$ reduction than CeO$_2$-COS-50°C-3h. These demonstrate that the sulfation or transformation of CS$_2$ and COS over CeO$_2$ might be different at the hydrolysis temperature of 50 °C. For featuring the processes, the promotional effect of CS$_2$+COS composite components gas-phase sulfation on the NH$_3$-SCR activity of CeO$_2$ at 50 °C for 3 and 24 h was investigated, as shown in Fig. 1. In consideration of the proportion of each component of blast furnace gas and the experimental simulation conditions, the
concentrations of CS₂ and COS in the simulated flue gas component were set to be 3:7 with the total amount of S element being 200 ppm [39,42,43]. From Fig. 1, it can be found that CeO₂-CS₂-50°C-3h and CeO₂-COS-50°C-3h present better NH₃-SCR activity than CeO₂-CS₂+COS-50°C-3h, which indicates that the co-existence of CS₂ and COS decreases the promotional effect of their gas-phase sulfation on the NOₓ reduction over CeO₂. Interestingly, the enhancement of sulfation duration from 3 to 24 h increases the NH₃-SCR activity of CeO₂-CS₂+COS-50°C-3h. Comparatively, CeO₂-CS₂+COS-50°C-24h presents similar catalytic performance to CeO₂-COS-50°C-3h. This indicates that there might exist a competitive adsorption and conversion of CS₂ and COS over cubic fluorite CeO₂ under the hydrolysis temperature of 50 °C [4,44]. In order to better evaluate the catalytic performance of the CeO₂-CS₂+COS-50°C-24h catalyst treated by organic sulfur at low-temperatures, the NOₓ conversions and N₂ selectivity over the reported Ce-based catalysts modified by the gas-phase sulfation are summarized and shown in Table 1. As seen in the Table 1, the N₂ selectivity of the sulfated catalysts is greater than 95% in the whole active temperature window, which indicates that the gas-phase sulfated catalysts we used in the research have excellent N₂ selectivity. It is also shown in the table that CeO₂-CS₂+COS-50°C-24h exhibits excellent NH₃-SCR activity under the high GHSV of 200,000 mL/(g·h). Therefore, it is evident that the gas-phase sulfation of organic sulfur is an effective measure to optimize the selectivity and the NH₃-SCR activity of cerium-based catalyst simultaneously.

Table 1. The summaries of catalytic activity and N₂ selectivity over the Ce-based catalysts modified by the gas-phase sulfation.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Gas-phase sulfation</th>
<th>NOₓ conversion</th>
<th>Temperature window (°C)</th>
<th>Temperature window (°C) (N₂)</th>
<th>GHSV/MHSV</th>
<th>Reference</th>
</tr>
</thead>
</table>


CeO$_2$-rod-SO$_2$ 350 50-60 350-425 200-500 180,000 mL/(g·h) [24]
S-C6Z4 200 80-90 250-350 100-400 96,000 mL/(g·h) [45]
S-CeO$_2$-72h 150 80-90 350-500 150-550 60,000 mL/(g·h) [46]
S-Ce/Ti 300 80-90 275-325 150-400 120,000 mL/(g·h) [47]
SO$_4^{2-}$/CeO$_2$-VS 100 60-70 275-300 100-300 60,000 mL/(g·h) [48]
S-FCT 250 70-80 270-420 150-420 30,000 mL/(g·h) [49]
CeO$_2$-CS$_2$+COS-50°C-24h 50 96 250-400 / 200,000 mL/(g·h) In this paper

Fig. 2. The effect of H$_2$O and SO$_2$ on the NO$_x$ conversion of CeO$_2$-CS$_2$+COS-50°C-24h catalyst. (Reaction Conditions: reaction temperature 300 °C, [NO] = [NH$_3$] = 600 ppm, [O$_2$] = 5.0 vol.%, [SO$_2$] = 100 ppm (when used), [H$_2$O] = 10.0 vol.% (when used), N$_2$ balance, the total rate=1500 mL/min, GHSV=200,000 mL/(g·h))

Due to the poisoning of H$_2$O or/and SO$_2$ on the NH$_3$-SCR activity of catalyst, the influence of H$_2$O or/and SO$_2$ on the activity of the sulfated CeO$_2$-CS$_2$+COS-50°C-24h catalyst was investigated at 300 ºC herein, as shown in Fig. 2. The NO$_x$ conversion of CeO$_2$-CS$_2$+COS-50°C-24h catalyst at 300 ºC maintains at almost 100% when 100 ppm SO$_2$ is introduced into the simulated flue gas,
indicating that the sulfated CeO$_2$-CS$_2$+COS-50°C-24h catalyst presents excellent anti-SO$_2$ poisoning. Meanwhile, the further introduction of 10.0 vol.% H$_2$O results in a rapid decrease of NO$_x$ conversion to 73% and then remains stable, mainly attributed to the competitive adsorption of H$_2$O and NH$_3$ on the catalyst surfaces [50]. After the removal of H$_2$O, the NO$_x$ conversion quickly recovers to 95% and then gradually decrease. Furthermore, the NO$_x$ conversion doesn’t return to the initial value when SO$_2$ was also cut off. The results show that the deactivation caused by SO$_2$ and H$_2$O on CeO$_2$-CS$_2$+COS-50°C-24h catalyst can be divided into the reversible deactivation and the irreversible deactivation. The reversible deactivation was mainly attributed to the competitive adsorption of SO$_2$ and H$_2$O on the active sites of the catalyst with the reaction gas, while the irreversible deactivation is attributed to the sulfate species formed by SO$_2$ on the catalyst surface covering the active sites and inhibiting the adsorption and conversion of reactants on the catalyst surface [26,51].

### 3.2. Catalyst characterization

#### 3.2.1. Pore structure and surface morphology analysis

Fig. 3. The N$_2$ adsorption-desorption isotherms (A-E) and the pore size distributions (F) of catalysts.
Fig. 3 gives the N$_2$ adsorption-desorption isotherms and pore size distributions of the samples. It can be seen that the gas-phase sulfation of organic sulfur at 50 °C shows no effect on the adsorption-desorption isotherm of CeO$_2$, and all catalysts present type IV of N$_2$ adsorption-desorption isotherms with H3 hysteresis loops [52,53]. In addition, the adsorption capacity of N$_2$ displays significant enhancement at a higher pressure in the range of 0.9–1.0 and the stable adsorption plateau is not observed, demonstrating the mesoporous and macroporous structure due to the accumulation of nanoparticles [9,54]. The pore size distributions in Fig. 3(F) indicate that the gas-phase sulfation of CS$_2$ or COS at 50 °C enlarges the mesopores smaller than 3 nm, but decreases the mesopores larger than 3 nm. And CeO$_2$-CS$_2$-50°C-3h and CeO$_2$-COS-50°C-3h present the concentrated mesopores at 2–4 nm. However, the gas-phase sulfation at 50 °C under the co-existence of COS and CS$_2$ exhibits no effect on the pore size distribution of CeO$_2$, even if the sulfation duration is up to 24 h. This indicates that the co-existence of COS and CS$_2$ might indeed affect their adsorption and conversion on cubic fluorite CeO$_2$ surfaces. The calculated data in Table 2 demonstrates that the gas-phase sulfation of CS$_2$ or COS at 50 °C decreases the BET surface area and the pore volume of CeO$_2$, but the co-existence of COS and CS$_2$ enlarges its BET surface area when the gas-phase sulfation duration is 3 h. Furthermore, CeO$_2$-CS$_2$+COS-50°C-24h still exhibits larger BET surface area and pore volume than CeO$_2$-CS$_2$-50°C-3h and CeO$_2$-COS-50°C-3h. Generally, larger specific surface area is closely related to a higher NH$_3$-SCR activity of catalysts. However, it is noteworthy that CeO$_2$-CS$_2$-50°C-3h with the smallest surface area presents the best catalytic performance of NO$_x$ reduction as shown in Fig. 1. Hence, it can be inferred that the specific surface area may not be the determinant factor on affecting the NH$_3$-SCR activity of the cerium oxide catalyst sulfated by organic COS or/and CS$_2$ at low-temperatures.
To further investigate the influence of organic sulfur gas-phase sulfation on the morphology of CeO$_2$ at their hydrolysis temperature of 50 °C, SEM was utilized and the results are given in Fig. 4 and Fig. S3. Our previous study had pointed out that the as-prepared CeO$_2$ via the one-pot hydrothermal method exhibited disorderly dispersed particles with some agglomeration due to the accumulation of nanoparticles [35]. Meanwhile, the gas-phase sulfation of COS or/and CS$_2$ at 50 °C for 3 h slightly weakened the agglomeration and crystallinity of CeO$_2$, which might be mainly attributed to the formation and deposition of sulphate species or/and sulfur element on the catalyst surfaces. It is seen that the enhancement of sulfation duration to 24 h increases the agglomeration of surface nanoparticles compared to CeO$_2$-CS$_2$+COS-50°C-3h. This might result from larger sulfate species or/and sulfur element deposited on the catalyst surfaces due to the long-term sulfation.

Table 2. The physical structural parameters of the as-synthesized catalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface area a $(m^2/g)$</th>
<th>Pore volume b $(cm^3/g)$</th>
<th>Pore diameter c $(nm)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>119.62</td>
<td>0.199</td>
<td>6.44</td>
</tr>
<tr>
<td>CeO$_2$-CS$_2$-50°C-3h</td>
<td>108.27</td>
<td>0.168</td>
<td>6.14</td>
</tr>
<tr>
<td>CeO$_2$-COS-50°C-3h</td>
<td>108.28</td>
<td>0.150</td>
<td>6.44</td>
</tr>
<tr>
<td>CeO$_2$-CS$_2$+COS-50°C-3h</td>
<td>127.86</td>
<td>0.280</td>
<td>8.34</td>
</tr>
<tr>
<td>CeO$_2$-CS$_2$+COS-50°C-24h</td>
<td>111.54</td>
<td>0.239</td>
<td>8.18</td>
</tr>
</tbody>
</table>

a BET surface area
b BJH desorption pore volume
c BJH desorption pore diameter
Fig. 4. The SEM images of (A) CeO$_2$-CS$_2$-50°C-3h, (B) CeO$_2$-COS-50°C-3h, (C) CeO$_2$-CS$_2$+COS-50°C-3h and (D) CeO$_2$-CS$_2$+COS-50°C-24h catalysts.

Fig. 5. The TEM/HR-TEM images and the elemental mapping images of the as-prepared CeO$_2$-CS$_2$+COS-50°C-24h catalyst. The TEM/HR-TEM analysis was used to further elucidate more detailed morphological information of CeO$_2$-CS$_2$+COS-50°C-24h catalyst, and the results are shown in Fig. 5. According to the Fig. 5(A), it can be observed that this sulfated catalyst exhibits nanoparticle morphology and
agglomeration, which is consistent with the findings of SEM. Furthermore, the HR-TEM image in
Fig. 5(B) indicates that the interplanar spacings on the surface are about 0.316 nm and 0.275 nm,
corresponding to the lattice fringes of the (111) and (100) facets of cubic fluorite CeO₂, respectively.
However, our previous research found that the as-synthesized CeO₂ catalyst by the one-pot
hydrothermal method exposed the (111) crystal plane [35]. This indicates that the gas-phase
sulfation of CS₂ and COS at 50 °C for 24 h might result in a transformation of partial (111) facet to
(100) facet of cubic fluorite CeO₂ on the catalyst surfaces. It should be mentioned that CeO₂-
CS₂+COS-50°C-24h presents a uniform distribution of Ce, O, and S elements across the catalyst
surfaces in a consistent distribution trend according to the elemental mapping images in Fig. 5(C-
E). This demonstrates that the gas-phase sulfation of organic CS₂+COS contributes to resulting in
the formation of high dispersive sulfates and sulfur on the surface of CeO₂ catalyst, which might be
beneficial to the redox capacity and surface acidity of catalyst.

3.2.2. XRD

The X-ray diffraction (XRD) patterns of samples were measured and it was found that the low-
temperature gas-phase sulfation of organic COS or/and CS₂ could effectively reduce the intensity
of cubic fluorite CeO₂ crystal in cerium oxide catalyst. Thus, in order to clearly reveal the effect of
organic sulfur types, the XRD patterns of the sulfated catalysts and the standard cards of the
corresponding sulfur-containing species are presented in Fig. 6 with the XRD of CeO₂ and its
standard card (#34-0394) shown in Fig. S4 for comparisons. CeO₂ presents high crystalline cubic
fluorite structures. After the gas-phase sulfation of organic COS or/and CS₂ at 50 °C, there still exists
the main cubic fluorite CeO₂ for the sulfated catalysts. However, a new broad diffraction peak
appears at 10–30 °, which might be attributed to sulfates or/and sulfur elemental deposition.
According to the enlarged XRD patterns at 10–35 ° in Fig. 6(B), the wider peak of the sulfated catalysts at a lower scanning angle (15–26 °) corresponds to sulfates (Ce₂(SO₄)₃·2H₂O #37-0762, Ce(SO₄)₂·4H₂O #24-1250 and Ce₂(SO₄)₃·(OH)₂·4H₂O, #24-1216) and sulfur compounds [55,56]. Sun et al. [57] found that the low-temperature oxidation of H₂S could bring a broad diffraction peak of sulfur elements at approximately 25 ° formed in the nitrogen-rich mesoporous carbon catalyst. Meanwhile, in our previous study, the gas-phase sulfation of CS₂ at 300 °C could not promote a new diffraction peak formed at 10–30 ° [29]. This indicates that the gas-phase sulfation of organic COS/CS₂ under their hydrolysis temperature of 50 °C contributes to promoting the formation of sulfate and sulfur compounds than those at 300 °C. It should be mentioned that CeO₂-CS₂+COS-50°C-3h presents the similar bread diffraction peak to CeO₂-CS₂-50°C-3h at 15–26 °, while the other two catalysts exhibit a stronger and more concentrated peak at this angle. This indicates that competitive adsorption and conversion of CS₂ and COS over CeO₂ again. When the gas-phase sulfation duration is 3 h for the coexistence of CS₂+COS, CS₂ might play a leading role in the formation of sulfur-containing species on the catalyst surfaces compared to COS. However, the enhancement of sulfation duration from 3 h to 24 h might increase the adsorption and conversion of COS on the catalyst surfaces, and CeO₂-CS₂+COS-50°C-24h presents the similar bread diffraction peak to CeO₂-COS-50°C-3h at 15–26 °. It should be mentioned that according to the results in Fig.1, CeO₂-COS-50°C-3h and CeO₂-CS₂+COS-50°C-24h also exhibit similar catalytic performance of NOₓ reduction. This demonstrates that the formed types and quality of sulfur-containing species might play an important role on the NH₃-SCR activity of the sulfated CeO₂ catalysts, which can be regulated by the kinds of organic COS/CS₂ during the gas-phase sulfation at 50 °C.
3.2.3. Raman

Raman spectroscopy was employed to further examine the structural properties of the CeO₂ catalysts treated by organic COS or/and CS₂ at the hydrolysis temperature of 50 °C. According to the results in Fig. 7(A), three Raman spectra peaks can be observed for all catalysts. Among them, the band at 464 cm⁻¹ corresponds to the F₂g symmetric vibration of cubic fluorite CeO₂, resulting from the symmetric breathing mode of O atoms around the Ce⁴⁺ cation of cubic fluorite CeO₂ [25,58]. Furthermore, as shown in Fig. 7(B), the gas-phase sulfation of organic COS or/and CS₂ makes this peak shift from 464 cm⁻¹ to 461 cm⁻¹, which can be attributed to the enhancement of oxygen vacancies and Ce³⁺ cations due to the reduction of cubic fluorite CeO₂. This is due to the increase of the unit parameters of CeO₂ and reduction of its bond force constant, thus resulting in the improvement of NH₃-SCR activity [59,60].
Fig. 7. The Raman spectra of CeO$_2$, CeO$_2$-CS$_2$-50°C-3h, CeO$_2$-COS-50°C-3h, CeO$_2$-CS$_2$+COS-50°C-3h and CeO$_2$-CS$_2$+COS-50°C-24h catalysts: (A) overall view (B–D) locally enlarged view.

It should be mentioned that the relative intensity of the Raman peak at 461 or 464 cm$^{-1}$ for all catalysts decreases as follows: CeO$_2$-CS$_2$-50°C-3h > CeO$_2$-CS$_2$+COS-50°C-24h > CeO$_2$-COS-50°C-3h > CeO$_2$-CS$_2$+COS-50°C-3h, demonstrating that the reduction of Ce$^{4+}$ to Ce$^{3+}$ in cubic fluorite CeO$_2$ is closely related to the reducibility of CS$_2$ and COS even if the gas-phase sulfation was carried out at 50 °C. And reductive CS$_2$ presents a stronger reduction of Ce$^{4+}$ to Ce$^{3+}$ than COS, thus the replacement of partial CS$_2$ by COS decreases its ability of reduction. Interestingly, the coexistence of COS and CS$_2$ presents the worst reducibility of cubic fluorite CeO$_2$, but the enhancement of sulfation time up to 24 h could improve this reducibility. These indicate that there exists a competitive adsorption and conversion of CS$_2$ and COS over CeO$_2$ under the hydrolysis
temperature of 50 °C for the coexistence of COS+CS₂. As illustrated in Fig. 7 (C) and (D), the bands at 600 cm⁻¹ and 1180 cm⁻¹ can be attributed to the characteristic peaks of surface oxygen defects, which are related to the intrinsic Vo (oxygen vacancy) formation during Ce⁴⁺→Ce³⁺ reaction [50,61]. The adsorbed organic COS or/and CS₂ could react with the oxygen-containing functional groups (-OH, O²⁻, O₂⁺, etc.) on CeO₂ surface to form sulfate species and elemental sulfur during the gas-phase sulfation process [15,56]. As a result, partial Ce-O bond of cubic fluorite CeO₂ might be destroyed, leading to the improvement of Ce³⁺ ions and oxygen vacancies. The latter is considered to accelerate the conversion frequency between chemisorbed oxygen and lattice oxygen during the converting of Ce⁴⁺/Ce³⁺, which is beneficial to the oxidization of NO to NO₂, thus increasing the NH₃-SCR activity via the 'fast SCR' reaction [62-64]. Therefore, the concentrations of oxygen vacancies or defects for all catalysts were obtained by calculating the relative peak intensity ratio of (I₆₀₀+I₁₁₈₀)/I₄₆₁. As depicted in Fig. S5, the gas-phase sulfation of CS₂ or/and COS at 50 °C enhances the generation of relative oxygen vacancies on CeO₂ surface. Specifically, CeO₂-CS₂-50°C-3h exhibits nearly twice the amount of relative oxygen vacancies of the CeO₂ catalyst, but the co-existence of CS₂ and COS depresses their promotional effect on the formation of oxygen vacancies even if the sulfation time is up to 24 h. This demonstrates that the improvement of Ce⁴⁺ to Ce³⁺ does not bring the corresponding oxygen vacancies on the catalyst surfaces, and the competitive adsorption and conversion of CS₂ and COS is disadvantageous for the formation of oxygen vacancies compared to single CS₂ or COS.

3.2.4. XPS analysis

X-ray Photoelectron Spectroscopy (XPS) tests were conducted to investigate the effect of organic CS₂ or/and COS sulfation on the dispersion of elements and their relative concentrations on
CeO$_2$ surface. As shown in Fig. 8(A), there exist both Ce$^{3+}$ (u' and v') and Ce$^{4+}$ (u, u'', u''', v, v'', and v''') on the catalyst surfaces by fitting the XPS spectra of Ce 3d into eight characteristic peaks [65-67], but the gas-phase sulfation of organic COS or/and CS$_2$ at 50 ºC can make the binding energy of Ce 3d XPS spectra shift to higher value, indicating the interaction between CS$_2$/COS and CeO$_2$, which reduces the electron cloud density around cerium ion and alters the chemical environment of Ce and O species [9,68]. Generally, the electron transfer process from Ce$^{4+}$ to Ce$^{3+}$ is useful to promote the creation of oxygen vacancies, and the presence of Ce$^{3+}$ could boost the charge imbalance and facilitate the redox cycle between Ce$^{4+}$ and Ce$^{3+}$, thus improves the catalyst activity towards oxygen molecule activation and reaction [69-71]. Therefore, the molar ratios of Ce$^{3+}$/(Ce$^{3+}$+Ce$^{4+}$) were calculated and the results are given in Table 3. It can be found that the gas-phase sulfation of organic COS or/and CS$_2$ at 50 ºC increases the surface Ce$^{3+}$/(Ce$^{3+}$+Ce$^{4+}$) molar ratio of CeO$_2$, especially the gas-phase sulfation of CS$_2$ for 3 h. Interestingly, the co-existence of COS and CS$_2$ decreases the sulfation of Ce$^{4+}$ on CeO$_2$ surface compared to CS$_2$ and COS, and CeO$_2$-CS$_2$+COS-50ºC-3h presents a higher surface concentration of Ce species and a lower Ce$^{3+}$/(Ce$^{3+}$+Ce$^{4+}$) molar ratio than CeO$_2$-CS$_2$-50ºC-3h and CeO$_2$-COS-50ºC-3h. In addition, the enhancement of sulfation time up to 24 h can further decrease the concentration of Ce species on CeO$_2$-CS$_2$+COS-50ºC-3h surface and enlarge its surface Ce$^{3+}$/(Ce$^{3+}$+Ce$^{4+}$) molar ratio, which is similar to the value of CeO$_2$-COS-50ºC-3h. This regularity is consistent to the XRD results as shown in Fig. 6 and the phenomenon of long sulfation for the co-existence of COS and CS$_2$ might be approximate to the sample sulfated using COS at 50 ºC for 3 h.
**Fig. 8.** The XPS spectra of CeO$_2$, CeO$_2$-CS$_2$-50°C-3h, CeO$_2$-COS-50°C-3h, CeO$_2$-CS$_2$+COS-50°C-3h and CeO$_2$-CS$_2$+COS-50°C-24h catalysts: (A) Ce 3d, (B) O 1s, (C) S 2p.

**Table 3.** Surface compositions and atomic ratios of the as-prepared catalysts calculated from XPS.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Atomic concentrations (%)</th>
<th>Atomic ratios (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ce</td>
<td>O</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>36.16</td>
<td>63.84</td>
</tr>
<tr>
<td>CeO$_2$-CS$_2$-50°C-3h</td>
<td>31.75</td>
<td>64.05</td>
</tr>
<tr>
<td>CeO$_2$-COS-50°C-3h</td>
<td>31.03</td>
<td>63.88</td>
</tr>
<tr>
<td>CeO$_2$-CS$_2$+COS-50°C-3h</td>
<td>32.15</td>
<td>63.24</td>
</tr>
<tr>
<td>CeO$_2$-CS$_2$+COS-50°C-24h</td>
<td>30.74</td>
<td>64.18</td>
</tr>
<tr>
<td>CeO$_2$-CS$_2$+COS-50°C-24h-CT</td>
<td>31.55</td>
<td>63.59</td>
</tr>
</tbody>
</table>
Numerous studies had pointed out that the surface chemisorbed oxygen presented higher mobility than lattice oxygen, and its enlargement could facilitate the oxidation of NO to NO₂, thus increased the activity of catalyst by promoting the fast NH₃-SCR reaction [50,62]. According to the results in Fig. 8(B) and Table 3, there exist three oxygen on the catalysts surfaces, attributing to the lattice oxygen (Oₐ), the surface chemisorbed oxygen (O₈, such as O²⁻ and O₂²⁻) and the lattice oxygen (Oₙ) bonded to Ce₂O₃ in cubic fluorite CeO₂ located at about 529 eV, 530 eV and 531.8 eV, respectively [72-74]. The gas-phase sulfation of organic COS or/and CS₂ at 50 °C also enlarges the binding energies of O 1s and increases the molar ratio of O₈/(Oₐ+O₈+Oₙ) on CeO₂ surface and the values of O₈/(Oₐ+O₈+Oₙ) molar ratio decreases as follows: CeO₂-CS₂-50°C-3h > CeO₂-CS₂+COS-50°C-24h > CeO₂-CS₂+COS-50°C-3h > CeO₂, which is similar to the regulation of surface Ce³⁺/(Ce³++Ce⁴⁺) molar ratios. Therefore, there exists a consistency in the catalytic performance of catalysts and the surface concentrations of chemisorbed oxygen and Ce³⁺ [75].

As shown in Fig. 8(C), the gas-phase sulfation of COS or/and CS₂ at 50 °C promotes the formation of S⁶⁺ on CeO₂ surface according to the fitting peaks of S 2p at approximately 168~170 eV, indicating the existence of sulfate species, which is consistent with the earlier research findings [26,29]. However, different from the gas-phase sulfation effect of SO₂, another new peak emerges at 163.8±0.5 eV under the action of organic CS₂ or/and COS at 50 °C for 3 h, which is attributed to sulfur element [5,10,55]. In terms of the results of XRD, it is inferred that there exist both sulfur and sulfate species on the catalysts surfaces. Meanwhile, the types of organic sulfur can affect the formed amount of sulfur species (S) and the ratio of S⁶⁺/S, and the content of S on the surface of CeO₂-COS-50°C-3h (5.09%) is higher than that of CeO₂-CS₂-50°C-3h (4.20%) while CeO₂-CS₂+COS-
50°C-3h has 4.61% of S on its surface. But the enhancement of sulfation time up to 24 h improves the formed S amount to 5.08%. This suggests the existence of partial CS$_2$ can decrease the formed amount of sulfur species on CeO$_2$-COS-50°C-3h surface, even if the sulfation time is up to 24 h. It should also be mentioned that the surface concentrations of Ce, O and S are very close for CeO$_2$-COS-50°C-3h and CeO$_2$-CS$_2$+COS-50°C-24h catalysts, and their calculated surface molar ratios of Ce$^{3+}$/Ce($^{3+}$+Ce$^{4+}$), O$_{\beta}$/O($\alpha$+O$_{\beta}$+O$_{\gamma}$) and S$^{6+}$/S are also very close, which are consistent with the NH$_3$-SCR activity of CeO$_2$-COS-50°C-3h and CeO$_2$-CS$_2$+COS-50°C-24h catalysts. This demonstrates that there exists a similar degree of sulfation for cubic fluorite CeO$_2$ for both the sulfated CeO$_2$-COS-50°C-3h and CeO$_2$-CS$_2$+COS-50°C-24h catalysts, and the enhancement of sulfation duration from 3 h to 24 h under the co-existence of COS+CS$_2$ improves the adsorption and conversion of COS on the catalyst surfaces. Therefore, the sulfated CeO$_2$-COS-50°C-3h and CeO$_2$-CS$_2$+COS-50°C-24h catalysts present a similar NH$_3$-SCR activity.

3.2.5. TG-DTG and TG-MS

In order to distinguish the influence of organic sulfur types on the formed sulfur species on CeO$_2$ surfaces, TG were conducted and the results are given in Fig. 9. As illustrated, there exist three major weight loss peaks at the temperature range of 30–900 °C for all the sulfated CeO$_2$ catalysts. Among them, the weight loss peaks observed below 200 °C and above 600 °C are attributed to the desorption of physically adsorbed water/hydroxyl groups and the decomposition of metal sulfate species, respectively [76,77]. In addition, the weight loss peak at 200–500 °C is primarily attributed to the oxidation of sulfur to SO$_2$, which had been validated by TG-MS. As shown in Fig. 10, the TG-MS results of CeO$_2$-CS$_2$+COS-50°C-24h at 50–900 °C demonstrate that the gas produced in the first weight loss interval (below 200 °C) is H$_2$O (m/z=18), attributed to the desorption of physically
adsorbed water and hydroxyl groups, and only SO$_2$ gas (m/z=64) was detected at the second weight loss range of 200–500 °C [78,79]. This suggests that the deposited sulfur can react with the oxygen-containing functional groups on CeO$_2$ surface to generate SO$_2$. During the third weight loss range (above 600 °C), SO$_2$ (m/z=64) and O$_2$ (m/z=32) are simultaneously produced due to the decomposition of metal sulfate species as follows [80,81]:

$$\text{Ce}(SO_4)_2 \rightarrow \text{CeO}_2 + 2\text{SO}_2 \uparrow + \text{O}_2 \uparrow$$  \hspace{1cm} (4)

$$\text{Ce}_2(SO_4)_3 \rightarrow 2\text{CeO}_2 + 3\text{SO}_2 \uparrow + \text{O}_2 \uparrow$$  \hspace{1cm} (5)

![Fig. 9. The TG-DTG curves of CeO$_2$-CS$_2$-50°C-3h, CeO$_2$-COS-50°C-3h, CeO$_2$-CS$_2$+COS-50°C-3h and CeO$_2$-CS$_2$+COS-50°C-24h catalysts.](image)
Fig. 10. The TG-MS curves of the as-prepared CeO2-CS2+COS-50°C-24h catalyst.

The proportions of sulfur and sulfate species formed in catalysts are calculated and shown in Table 4. Notably, the enhancement of sulfation time up to 24 h can increase the deposited amount of S, which is approximate to the sulfur content of sulfate. Furthermore, the gas-phase sulfation of COS presents a stronger promotional effect on the deposition of sulfur than that of CS2. CeO2-CS2-50°C-3h shows the best low-temperature NH3-SCR activity with the least amounts of both sulfur and sulfate, which indicates that metal sulfate species might not be the dominant role on the catalytic performance of NOx reduction over the sulfated CeO2 catalysts.

Table 4. The calculated proportion of sulfate species and sulfur element from the TG-DTG curves.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sulfur element (%)</th>
<th>Sulfate species (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO2-CSz-50°C-3h</td>
<td>0.25</td>
<td>4.29</td>
</tr>
<tr>
<td>CeO2-COS-50°C-3h</td>
<td>0.64</td>
<td>6.47</td>
</tr>
<tr>
<td>CeO2-CSz+COS-50°C-3h</td>
<td>0.54</td>
<td>5.44</td>
</tr>
<tr>
<td>CeO2-CSz+COS-50°C-24h</td>
<td>2.55</td>
<td>6.13</td>
</tr>
</tbody>
</table>

3.2.6. The properties of redox ability
The reduction or/and sulfur deposition during the gas-phase sulfation of organic CS₂ or/and COS at 50 °C might affect the redox properties of CeO₂, which are regarded as crucial factors on its NH₃-SCR activity. Thus, the H₂-TPR of all samples were carried out and the results are given in Fig. 11. CeO₂ displays two broad reduction peaks at 400–550 °C (region I) and 700–900 °C (region III), which are attributed to the reduction of Ce⁴⁺ to Ce³⁺ on the surface and subsurface and the reduction of bulk Ce⁴⁺ to Ce³⁺, respectively. However, one new reduction peak emerges at 500–700 °C (region II) after the gas-phase sulfation of organic CS₂ or/and COS at 50 °C, owing to the reduction of metal sulfate species [82,83]. Yang et al. [84] had pointed out that one reduction peak located at 595 °C arose from the formed SO₄²⁻ species during the gas-phase sulfation of SO₂. Furthermore, the gas-phase sulfation of organic CS₂ at 50 °C makes the first reduction peak of CeO₂ shift to lower temperature, indicating an improvement in redox performance [22,81], while the existence of COS does not affect the peak position of this reduction peak. However, according to the results in Fig. 11(C) and Table 5, CeO₂-COS-50°C-3h presents higher temperature for the peak position and larger integral area than CeO₂-CS₂-50°C-3h at region II. Interestingly, the partial substitution of COS with CS₂ can slightly decrease these peak position temperature and integral area of CeO₂-COS-50°C-3h. But the enhancement of sulfation time up to 24h increases the integral area of CeO₂-CS₂+COS-50°C-3h at region II, and CeO₂-CS₂+COS-50°C-24h presents the highest reduction temperature of SO₄²⁻ species. In addition, the integrated areas of the reduction peak in the III region of the sulfated catalysts are larger than that of CeO₂. These all indicate that the gas-phase sulfation of organic CS₂ or/and COS at 50 °C contributes to enhancing the mobility of lattice oxygen of cubic fluorite CeO₂ [85], and CeO₂-CS₂-50°C-3h presents the best mobility of lattice oxygen and the largest
concentration of adsorbed oxygen, which is in accordance with the results of Raman and XPS spectra.

Table 5. The calculated peak areas for the H2-TPR spectra of catalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>H2-TPR peak area (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
</tr>
<tr>
<td>CeO2</td>
<td>922</td>
</tr>
<tr>
<td>CeO2-CS2-50°C-3h</td>
<td>729</td>
</tr>
<tr>
<td>CeO2-COS-50°C-3h</td>
<td>479</td>
</tr>
<tr>
<td>CeO2-CS2+COS-50°C-3h</td>
<td>462</td>
</tr>
<tr>
<td>CeO2-CS2+COS-50°C-24h</td>
<td>369</td>
</tr>
</tbody>
</table>

Fig. 11. The H2-TPR profiles of CeO2, CeO2-CS2-50°C-3h, CeO2-COS-50°C-3h, CeO2-CS2+COS-50°C-3h and
3.2.7. The properties of surface acidity

The surface acidity is widely recognized as a pivotal factor on influencing the catalytic reactions. In order to investigate the acid characteristics and quantity of the as-prepared catalysts, Fourier transform infrared (Py-IR) measurements of pyridine desorption were conducted at 150 °C and 300 °C, which are associated with weak acid sites and medium-strong acid sites, respectively [86]. As illustrated in Figure 12, the band at 1540 cm\(^{-1}\) corresponds to pyridine adsorption on the Brønsted acid site [87], while bands at 1442 cm\(^{-1}\), 1575 cm\(^{-1}\), and 1600 cm\(^{-1}\) signify pyridine adsorption on the Lewis acid site [88]. Furthermore, the band at 1489 cm\(^{-1}\) indicates the interaction of pyridine molecules with both Brønsted and Lewis acid sites [89]. As shown in Table 6, the quantity of Lewis acid sites and Brønsted acid sites was determined according to the Py-IR curves at 150 °C and 300 °C. Interestingly, CeO\(_2\)-CS\(_2\)-50°C-3h exhibits stronger surface acid sites, including both weak acid and medium-strong acid sites, than CeO\(_2\)-COS-50°C-3h, although less sulfate (SO\(_4^{2-}\)) and total sulfur content (S) formed on its surface according to the results of TG-DTG and XPS. This demonstrates that the kind of organic sulfur during the gas-phase sulfation at 50 °C can regulate the formed types and quality of sulfur-containing species in the as-prepared CeO\(_2\) catalyst, which play different role on the formation of acid sites for catalyst, and the gas-phase sulfation of CS\(_2\) at 50 °C brings much less sulfur-containing species compared to COS, but better promotional effect on the formation of acid sites. Xie also pointed out that larger sulfates might be disadvantageous to the formation of acid sites for catalyst [90]. Furthermore, the partial substitution of COS by CS\(_2\) during the gas-phase sulfation improves both weak acid and medium-strong acid sites of CeO\(_2\)-COS-50°C-3h, and this promotional effect is further enhanced by extending the
sulfonation time to 24 h. And CeO$_2$-CS$_2$+COS-50°C-24h presents stronger weak acid and medium-
strong acid sites than CeO$_2$-CS$_2$-50°C-3h, although its low-temperature NO$_x$ conversions are still
lower than the latter. It is worth noting that the B/L values in CeO$_2$-COS-50°C-3h and CeO$_2$-
CS$_2$+COS-50°C-24h catalysts are larger, which is usually thought to be related to more sulfate
species formed on the catalyst surfaces. Therefore, it can be inferred that the deposition of larger
sulfur-containing species, including sulfates and elemental sulfur, on the surface of CeO$_2$-
CS$_2$+COS-50°C-24h catalyst might block the active sites, leading to less NH$_3$-SCR activity
compared to CeO$_2$-CS$_2$-50°C-3h [22,91].

Fig. 12. The desorption spectra of pyridine for the as-prepared CeO$_2$-CS$_2$-50°C-3h, CeO$_2$-COS-50°C-3h, CeO$_2$-CS$_2$+COS-50°C-3h and CeO$_2$-CS$_2$+COS-50°C-24h catalysts at (A) 150 °C and (B) 300 °C.

Table 6. The concentration and distribution of Lewis (L) and Bronsted (B) acid sites on the as-prepared CeO$_2$-CS$_2$-
50°C-3h, CeO$_2$-COS-50°C-3h, CeO$_2$-CS$_2$+COS-50°C-3h and CeO$_2$-CS$_2$+COS-50°C-24h catalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Weak acid (μmol/g)</th>
<th>Medium-strong acid (μmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
<td>L</td>
</tr>
<tr>
<td>CeO$_2$-CS$_2$-50°C-3h</td>
<td>25.66</td>
<td>99.68</td>
</tr>
<tr>
<td>CeO$_2$-COS-50°C-3h</td>
<td>16.34</td>
<td>25.62</td>
</tr>
<tr>
<td>CeO$_2$-CS$_2$+COS-</td>
<td>29.89</td>
<td>60.92</td>
</tr>
</tbody>
</table>
50°C-3h
CeO₂-CS₂+COS-
50°C-24h

56.26   94.68   0.594   150.94   39.30   47.68   0.824   86.98

3.3 Discussion and long-time durability testing coupling re-cycle experiments

The results of TG, H₂-TPR and XPS show the influence of organic sulfur types on the formed amount of sulfate species (SO₄²⁻) during the gas-phase sulfation of organic COS or/and CS₂ at 50°C, which has been regarded as an important factor on the promotional effect of acid sites and NH₃-SCR activity of CeO₂ catalyst. Therefore, in order to investigate the relationship between the formed amount of sulfate species and the NH₃-SCR activity, the amount of sulfate species obtained through different characterization techniques were normalized based on CeO₂-CS₂-50°C-3h. From Fig. 13, it can be found that the law of the calculated normalized sulfate content of TG, H₂-TPR and XPS are consistent, and the gas-phase sulfation of COS presents stronger promotional effect on the formation of sulfate than that of CS₂, although CeO₂-CS₂-50°C-3h exhibits larger acid sites and the best NH₃-SCR activity. This indicates that the formed amount of sulfate might not be the determining factor on the NH₃-SCR activity of the sulfated CeO₂ catalysts by organic COS or/and CS₂ at 50°C. Furthermore, the formed sulfate under the gas-phase sulfation of CS₂ might be more active based on the acid sites and the NH₃-SCR activity than those of COS, and the adsorption and transformation of COS and CS₂ are different on cubic fluorite CeO₂ surface at 50°C. It should be mentioned that the formed amount of sulfate for COS+CS₂ falls between those of CS₂ or COS when the sulfation time is 3 h, and the enhancement of sulfation time up to 24 h increases the formed amount of sulfate slightly, but the value remains approximately the same as that of CeO₂-COS-50°C-3h. This suggests that the adsorption of sulfate reaches a saturation point on cubic fluorite CeO₂ surface during the sulfation process of organic COS or/and CS₂ [27].
Based on the above characterization analysis, under the hydrolysis temperature of 50 °C, the adsorption and conversion of CS₂ or/and COS over cubic fluorite CeO₂ are inferred as follows:

\[ \text{CS}_2 + [O] \rightarrow \text{COS} + S \]  \hspace{1cm} (6)

\[ \text{COS} + [O] \rightarrow \text{CO}_2 \uparrow + S + \text{SO}_4^{2-} \]  \hspace{1cm} (7)

\[ S + [O] \rightarrow \text{SO}_2 \uparrow + \text{SO}_4^{2-} \]  \hspace{1cm} (8)

Fig. 13. Normalized sulfate content of different characterization techniques.
Firstly, CS$_2$ could be adsorbed over CeO$_2$ and reacts with its surface inherent oxygen-containing functional groups to generate S and COS. And then, the formed COS is adsorbed again and oxidized to gas-phase CO$_2$, S and SO$_4^{2-}$, which are deposited or adsorbed on CeO$_2$ surfaces. In the meantime, the deposited partial S can be further oxidized to SO$_2$ or/and SO$_4^{2-}$ by the oxygen-containing functional groups on the catalyst surfaces. Therefore, compared to COS, the reductive CS$_2$ presents a stronger promotional effect on the formation of adsorbed oxygen and the mobility of lattice oxygen on cubic fluorite CeO$_2$ surface, thus more deposited S can be oxidized to gas-phase SO$_2$ for the gas-phase sulfation of CS$_2$ at 50 °C than that of COS. As a result, CeO$_2$-CS$_2$-50°C-3h exhibits less both sulfur and sulfate than CeO$_2$-COS-50°C-3h. This also can explain the reduced formation of sulfur and sulfate on CeO$_2$-CS$_2$+COS-50°C-3h surface comparing to CeO$_2$-COS-50°C-3h. Furthermore, for the co-existence of COS+CS$_2$, the formed amount of sulfate does not increase with the enhancement of sulfation time up to 24 h linearly, which might be attributed to the
consumption of the oxygen-containing functional groups on CeO$_2$ surfaces. Thus, more sulfur deposits on the CeO$_2$-CS$_2$+COS-50°C-24h surface when the sulfation time increases from 3 h to 24 h. However, the depositing sulfur is easy to be oxidized to sulfur oxide or/and sulfates according to the weight loss at 200–500 °C of TG-DTG (Fig. 9) and TG-MS (Fig. 10) for the sulfated CeO$_2$-CS$_2$+COS-50°C-24h catalyst, which might affect its NH$_3$-SCR activity. Therefore, in order to investigate the thermal stability of the sulfated CeO$_2$ catalyst by organic sulfur, the sulfated CeO$_2$-CS$_2$+COS-50°C-24h catalyst had been re-calcined in air atmosphere at 400 °C for 5 h, and the corresponding NH$_3$-SCR activity of CeO$_2$-CS$_2$+COS-50°C-24h-SC was given in Fig. S6 for comparisons. As shown in Fig. S6, the re-calcination in air atmosphere at 400 °C only results in a slight decrease in the NH$_3$-SCR activity of 200–300 °C for the sulfated CeO$_2$-CS$_2$+COS-50°C-24h catalyst, and CeO$_2$-CS$_2$+COS-50°C-24h-SC also exhibits excellent catalytic performance of NO$_x$ reduction, demonstrating that the sulfated CeO$_2$ catalyst by organic sulfur at a hydrolysis temperature presents a good stability for NH$_3$-SCR reaction. Furthermore, a long-time durability testing at 300 °C coupling re-cycle experiments were also carried out for the sulfated CeO$_2$-CS$_2$+COS-50°C-24h catalyst to study the stability of NH$_3$-SCR reaction. In addition, FTIR, Raman and XPS were used to investigate the change of sulphate structure on the surface of CeO$_2$-CS$_2$+COS-50°C-24h catalyst after the long-time durability testing at 300 °C coupling re-cycle experiments, and the results are shown in Fig. 14, Fig 15 and Fig. S7, respectively.

As shown in Fig. 14, the sulfated CeO$_2$-CS$_2$+COS-50°C-24h catalyst presents a good stability for NH$_3$-SCR reaction, and its NO$_x$ conversion at 300 °C under the GHSV of 200,000 mL/(g·h) keeps at 100% for up to 60 hours of testing. Interestingly, the results of the first re-cycle testing demonstrate that the long-time testing at 300 °C for 28 h improves the low-temperature NH$_3$-SCR
activity of the sulfated CeO$_2$-CS$_2$+COS-50$^\circ$C-24h catalyst, and the NO$_x$ conversions at 175 $^\circ$C, 200 $^\circ$C and 225 $^\circ$C during the first re-cycle testing increase by 4%, 8% and 4%, respectively.

Furthermore, this promoting effect is further enhanced by the following long-time testing of other 32 h. This demonstrates that the long-time durability testing coupling re-cycle experiments indeed affects the NH$_3$-SCR activity of the sulfated CeO$_2$-CS$_2$+COS-50$^\circ$C-24h catalyst via influencing the conversion of the formed sulfur-containing species on the catalyst surfaces. The FTIR spectra depicted in Fig. 15(A) indicates that there exist the bending and stretching vibrations of -OH group (3415 cm$^{-1}$ and 1628 cm$^{-1}$), the S-O and S=O bonds attributed to surface sulfates (1040 cm$^{-1}$ and 979 cm$^{-1}$, inorganic chelating bidentate sulfates) and bulk sulfates (1120 cm$^{-1}$) for both CeO$_2$-CS$_2$+COS-50$^\circ$C-24h and CeO$_2$-CS$_2$+COS-50$^\circ$C-24h-CT catalysts, respectively [92-94]. However, CeO$_2$-CS$_2$+COS-50$^\circ$C-24h-CT presents slightly weaker intensity of these FTIR peaks than CeO$_2$-CS$_2$+COS-50$^\circ$C-24h. This demonstrates that the long-time durability testing coupling re-cycle experiments decreases the adsorbed capacity of sulfur-containing species on the surface of CeO$_2$-CS$_2$+COS-50$^\circ$C-24h catalyst. Interestingly, according to the results in Fig. 15(B), the long-time durability testing coupling re-cycle experiments induces the appearance of a Raman peak at 998 cm$^{-1}$, which is attributed to the S-O asymmetric vibration of sulfate ions [25]. Meanwhile, this treatment enhances the intensity of vibration band at 600 cm$^{-1}$, indicating the long-time durability testing coupling re-cycle experiments contributes to improving the oxygen vacancy defects of the sulfated CeO$_2$-CS$_2$+COS-50$^\circ$C-24h catalyst effectively (Fig. S5). Furthermore, the results of XPS spectra in Fig. S7, Fig. 15(C), Fig. 15(D) and Table 3 demonstrate that the long-time durability testing coupling re-cycle experiments makes the binding energy attributed to the lattice oxygen (O$_{\alpha}$) shift to right and induces the disappearance of S 2p peak ascribed to sulfur element for the sulfated CeO$_2$-
CS$_2$+COS-50°C-24h catalyst. This indicates that the formed sulfur element of the sulfated CeO$_2$-CS$_2$+COS-50°C-24h catalyst could be slowly oxidized to sulfur oxides or/and sulfates during the long-time durability testing coupling re-cycle experiments. At the same time, both the concentration of Ce element and \( \Omega_\beta/(\Omega_\alpha+\Omega_\beta+\Omega_\gamma) \) molar ratio on the catalyst surface are also improved. To sum up, the long-time durability testing coupling re-cycle experiments can lead to the oxidization of sulfur element to sulfur oxides or/and sulfates, optimizing the oxygen vacancy defects and increasing the concentration of chemisorbed oxygen of the sulfated CeO$_2$-CS$_2$+COS-50°C-24h catalyst. These phenomena indicate that the adsorption and conversion of sulfur-containing species on cubic fluorite CeO$_2$ surfaces might play an important role on the physical-chemical properties and the NH$_3$-SCR activity of the sulfated CeO$_2$ catalyst by organic CS$_2$ or/and COS.

Fig. 15. The FTIR spectra (A), Raman Spectra (B) and XPS spectra of (C) O 1s and (D) S 2p for the CeO$_2$-CS$_2$+COS-50°C-24h and CeO$_2$-CS$_2$+COS-50°C-24h-CT catalysts.
3.4. Competitive adsorption analysis

![Fig. 16. The optimized geometry and calculated adsorption energy of COS and CS$_2$ on CeO$_2$ (111): (A) correspond to the adsorption of COS at O top site; (B) correspond to the adsorption of CS$_2$ at Ce-O bridge site.]

In this study, the adsorption energy of COS and CS$_2$ on the optimized CeO$_2$ (111) crystal plane were calculated to reveal their competitive adsorption on the catalyst surface. As shown in Fig. S8 and Fig. 16, four adsorption configurations of COS/CS$_2$ on CeO$_2$ (111) were involved: O-top site, Ce-top site, O-O bridge site, and Ce-O bridge site. The results indicate that the most stable adsorption configuration of COS involved the bonding of the S atom in COS to the O-top atom of CeO$_2$ (111) crystal plane (Fig. 16(A)), with an absolute adsorption energy value in the order of O-top site (1.453 eV) > Ce-O bridge site (1.316 eV) > Ce-top site (0.517 eV) > O-O bridge site (0.451 eV). Similarly, for CS$_2$, the absolute value of the adsorption energy is in the order of Ce-O bridge site (2.688 eV) > O-O bridge site (2.600 eV) > Ce-top site (2.480 eV) > O-top site (2.158 eV), indicating that the most stable adsorption configuration of CS$_2$ is the bonding of the S atom in CS$_2$ to the Ce-O bridge site of CeO$_2$ (111) crystal plane (Fig. 16(B)). The calculated adsorption energy of CS$_2$ on the CeO$_2$ (111) crystal plane is stronger than that of COS. The adsorption energy of gas molecules on the material surface is determined by their electronic structure and the molecules with unsaturated chemical bonds have a stronger adsorption capacity due to their stronger chemical bonds.
with surface atoms [95-97]. Basically, the hydrolysis process of organic sulfur involves three steps: adsorption, activation and hydrolysis. Hence, higher adsorption energy is beneficial for the adsorption of organic sulfur gas on the catalysts surface, which in turn is favorable for the subsequent reaction process [39,98]. However, it is worth noting that although the adsorption energy of CS$_2$ on CeO$_2$ (111) crystal plane is higher than that of COS, more sulfate species (TG, XPS, H$_2$-TPR) are generated in CeO$_2$ during the sulfation of COS. Sui et al. [99] found that the 1% Cu$^{2+}$/Al$_2$O$_3$ catalyst with the lowest adsorption capacity of CS$_2$, presented the excellent conversion of CS$_2$ and had larger formation of sulfate/sulfite species on its surface, which indicated that there was no correlation between the adsorption capacity and conversion of CS$_2$. Based on the calculated adsorption energy and the formed amount of sulfate species, it is clear that there is no intrinsic relationship between the adsorption capacity of COS/CS$_2$ on CeO$_2$ surface and the formed amount of sulfate species.

4. Conclusions

In this study, the gas-phase sulfation of CS$_2$ or/and COS was carried out at the hydrolysis temperature of organic sulfur for the first time to improve the NH$_3$-SCR activity of CeO$_2$ catalyst. Compared with the previous sulfation treatment of CeO$_2$ with CS$_2$/COS at 300 °C, the gas-phase sulfation at 50 °C exhibits a more prominent promotion effect on the NH$_3$-SCR activity. The results show that CeO$_2$-CS$_2$-50°C-3h exhibits the best NO$_x$ reduction performance, while there exists a competitive adsorption relationship between CS$_2$ and COS when they coexist in sulfurized flue gas, which could negate this promoting effect. The characterization results show that the adsorption and conversion of sulfur-containing species on cubic fluorite CeO$_2$ surfaces play an important role on the physical-chemical properties and the NH$_3$-SCR activity of the sulfated CeO$_2$ catalyst by organic
CS$_2$ or/and COS. The gas-phase sulfation of organic CS$_2$ or/and COS at 50 °C contributes to enhancing the mobility of lattice oxygen of cubic fluorite CeO$_2$ and the concentration of oxygen defects for the sulfated CeO$_2$ catalyst, but the adsorption and transformation of COS and CS$_2$ are different on cubic fluorite CeO$_2$ surface at 50 °C, and the kinds of organic COS/CS$_2$ can regulate the formed types and quality of sulfur-containing species on the catalyst surfaces during the gas-phase sulfation at 50 °C. In addition, the formed sulfates under the gas-phase sulfation of CS$_2$ might be more active than those of COS, although the gas-phase sulfation of COS presents stronger promotional effect on the formation of sulfates than that of CS$_2$. Furthermore, the competitive adsorption and conversion of CS$_2$ and COS is disadvantageous for the formation of oxygen vacancies on the catalyst surfaces compared to single CS$_2$ or COS. However, the long-time durability testing coupling re-cycle experiments leads to the oxidization of sulfur element to sulfur oxides or/and sulfates, optimizing the oxygen vacancy defects and increasing the concentration of chemisorbed oxygen of the sulfated CeO$_2$-CS$_2$+COS-50°C-24h catalyst, thereby improves its NH$_3$-SCR activity. And the sulfated CeO$_2$ catalyst by the gas-phase sulfation of organic COS+CS$_2$ presents a good stability for NH$_3$-SCR reaction. This study specifies a novel approach to simplify the gas-phase sulfation process of CeO$_2$ catalyst, which is valuable in promotion of the NH$_3$-SCR activity of CeO$_2$ and reduction of cost in experimental procedures.

**CRediT authorship contribution statement**

*Zhibo Xiong:* Conceptualization, Funding acquisition, Writing - review & editing. *Zhenchang Sun and Jiaxing Liu:* Writing - original draft, Methodology, Validation. *Yanping Du:* Methodology, Writing - review & editing. *Yafei Zhu:* Software, Methodology. *Fei Zhou:* Investigation, Supervision. *Jing Jin:* Investigation, Supervision, Writing - review & editing. *Qiguo Yang:* Investigation, Supervision, Writing -.
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the National Science Foundation of China (No. 51406118), the Bureau of Shanghai Municipal Science and Technology (No. 23010503500), Program of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning (No. QD2015017).

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