Promotional effect of H$_2$O introduction on the NH$_3$-SCR activity of the gas-phase sulfated CeO$_2$ catalyst by organic CS$_2$+COS: Influence of H$_2$O concentration

Jiaxing Liu$^1$, Yafei Zhu$^1$, Zhenchang Sun$^1$, Yanping Du$^2$, Zhibo Xiong$^{1*}$, Fei Zhou$^3$, Jing Jin$^1$, Qiguo Yang$^1$, Wei Lu$^1$

1. School of Energy and Power Engineering, University of Shanghai for Science & Technology, Shanghai, 200093, China
2. School of Engineering, Lancaster University, Lancaster, LA1 4YW, UK
3. Jiangsu Guoxin Jingjiang Power Co. Ltd., Jingjiang 214500, Jiangsu, China

Abstract: Herein, as an indispensable key reactant for the hydrolysis of organic sulfur, H$_2$O was firstly introduced to optimize the NH$_3$-SCR activity of CeO$_2$ by providing the adsorption and reaction spots of catalysis for organic CS$_2$+COS during the low-temperature gas-phase sulfation. The results demonstrate that the introduction of 0.33 vol.% H$_2$O is beneficial to enhance the interaction between organic CS$_2$+COS and cube fluorite CeO$_2$, which not only increases the concentrations of Ce$^{3+}$ ions, chemisorbed oxygen (O$_{\beta}$) and oxygen vacancies on CeO$_2$-CS$_2$+COS surface, but also effectively enhances the redox cycle of Ce$^{4+}$/Ce$^{3+}$ ion pairs and the medium-strong acid sites of catalyst. These all help enhance the promotional effect of organic sulfur low-temperature gas-phase sulfation on the NH$_3$-SCR activity of CeO$_2$ and further improve NO$_x$ reduction over the CeO$_2$-CS$_2$+COS catalyst. However, the introduction of 5.0 vol.% H$_2$O shows a certain inhibitory effect due to the competitive adsorption of excess water and COS+CS$_2$ on the cube fluorite CeO$_2$ surface, which weakens their interaction during the low-temperature gas-phase sulfation, thereby decreases the promotional effect of low concentration water introduction on the NH$_3$-SCR activity of the CeO$_2$-CS$_2$+COS catalyst. Therefore, the results of this research provide a scientific reference for developing the NH$_3$-SCR CeO$_2$-based catalyst in practical applications.

Keywords: NH$_3$-SCR, CeO$_2$, Organic sulfur, Low-temperature gas-phase sulfation, H$_2$O concentration
**1. Introduction**

The rapid development of global economy inevitably leads to an intense demand of energy or/and fuel, thus the traditional fossil fuels (coal, oil, and natural gas, etc.) have been extensively utilized in power generation, transportation and industry [1-3]. However, large fine particulate matter (PM 2.5) and greenhouse gases (CO$_2$, CH$_4$, etc.) are discharged during the utilization of fossil fuels and 3 million tons of CO$_2$ can be emitted for a 500MW coal-fired power plants per year, and the concentration of CO$_2$ in the atmosphere is expected to exceed 500 ppm by 2050 [4,5]. In addition, the toxic and harmful gases such as nitrogen oxides (NO$_x$, mainly NO and NO$_2$) and sulfur-containing compounds (SO$_2$, COS, CS$_2$, etc.) are also produced during the combustion of fossil fuels, which brings many environmental problems [6,7]. For example, the emission of nitrogen oxides and sulfur compounds are prone to oxidation reactions, causing acid rain, photochemical smog, ozone holes and other environmental disasters [8-10]. Therefore, it is necessary to develop an effective method to reduce nitrogen oxide and sulfur compounds.

Compared to inorganic SO$_2$, organic carbonyl sulfide (COS) and carbon disulfide (CS$_2$) are linear triatomic molecules similar to carbon dioxide (CO$_2$), which are less reactive and difficult to be removed [11,12]. At present, catalytic hydrolysis [13,14], hydrogenation [15,16], adsorption and absorption [17-19] have been developed to reduce the emission of organic sulfur. Among them, catalytic hydrolysis has the advantages of low energy consumption, less side reactions and high efficiency, especially when dealing with high levels of organic sulfur. Wang et al. found that the synthesized (Co+Ni)/Al catalyst derived from various hydrotalcite-like compounds presented a good catalytic hydrolysis activity of COS, and the introduction of Ce additive effectively improved its catalytic performance due to the alterations of the structural properties, oxidation properties and surface defect sites [20,21]. At present, the development of the low temperature hydrolysis catalyst to reduce organic sulfur has attracted widespread attention, especially the metal oxide catalysts with a rich pore structure, a good thermal stability, abundant basic sites and a strong anti-poisoning ability. For instance, the introduction of 3DOM structure via the colloidal crystal template method is beneficial to the extraction of the hydrolysis product H$_2$S from the aluminum-based and titanium-based hydrolysis catalysts, inhibiting the
deposition of sulfate species on catalysts surface [22].

Generally, the hydrolysis of organic sulfur is an alkali-catalyzed reaction process: \( \text{H}_2\text{O} \) first adsorbs and dissociates on metal oxides surface to form \(-\text{OH}\) groups, and then \( \text{CS}_2 \) or \( \text{COS} \) intermediates via the interaction of \(-\text{OH}\) group and M-O pair (M: Ti, Al, Fe, Ce, etc.). Subsequently, the formed \( \text{COS} \) can further be converted into \( \text{HSCO}_2^- \) through the above hydrolysis reaction pathway, and the intermediate of \( \text{HSCO}_2^- \) finally decomposes into \( \text{CO}_2 \) and \( \text{H}_2\text{S} \) under the action of \(-\text{OH}\) group and M-O pair to complete the catalytic hydrolysis of organic sulfur [23-27]. Therefore, the surface basic sites of catalyst play a dominant role on the hydrolysis activity of organic sulfur. It should be noted that the active \(-\text{OH}\) groups on the catalyst surface can serve as an alkaline site for the adsorption and activation of organic sulfur, thus promotes the hydrolysis reaction. A large number of literatures had also investigated the effect of \( \text{H}_2\text{O} \) on the hydrolysis efficiency of organic sulfur. Gao et al. [28] pointed out that the absorbed \( \text{H}_2\text{O} \) could dissociate into generate active \(-\text{OH}\) groups for the hydrolysis reaction of \( \text{COS} \) on catalyst surfaces, thus ensured the stable and efficient hydrolysis of organic sulfur. Wang et al. [29] found that the presence of \( \text{H}_2\text{O} \) on the alumina catalyst surface slowed down the deactivation process of organic sulfur hydrolysis by promoting the deposition and adsorption of sulfur and sulfate species at different sites. It is worth noting that the presence of \( \text{H}_2\text{O} \) also has a negative effect on the hydrolysis removal of \( \text{COS/CS}_2 \). Gu et al. [25] reported that the excessive \( \text{H}_2\text{O} \) on catalyst surface led to a competitive adsorption with \( \text{COS} \), which inhibited the hydrolysis reaction and reduced the \( \text{COS} \) removal efficiency. This phenomenon had also been found in the hydrolysis process of \( \text{CS}_2 \) [30]. Furthermore, the presence of \( \text{H}_2\text{O} \) could promote the formation of sulfur-containing species (sulfates), which had been considered to be the main reason for the deactivation of organic sulfur hydrolysis for catalysis [26]. Because the accumulation of sulfur-containing species on the catalyst surface led to the blockage of pore structure, and also reduced the basic sites of catalyst due to the formation of surface sulfates, resulting in the deactivation of organic sulfur hydrolysis [23,31]. Therefore, \( \text{H}_2\text{O} \) plays an essential role in the formation of sulfur-containing species during the hydrolysis process of organic sulfur.

Owing to the unique 4f electronic structure, \( \text{CeO}_2 \) presents an excellent oxygen storage capacity (OSC) and redox ability [32], which has been used as the main active components or...
doping additives in the selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3} (NH\textsubscript{3}-SCR). However, pure CeO\textsubscript{2} exhibits bad NH\textsubscript{3}-SCR performance due to the poor surface acidity and NH\textsubscript{3} peroxydation at high temperatures, which limits its application in engineering. Interestingly, the formed surface sulfates during the hydrolysis of organic sulfur might retain Lewis acid sites and enhance Bronsted acid sites of CeO\textsubscript{2}, thus contributes to the adsorption and activation of NH\textsubscript{3} on it surface [33,34]. Actually, the formed sulfate species can serve as the reducible species to promote redox reactions and improve the NH\textsubscript{3}-SCR activity of cerium-based catalysts [35,36]. Therefore, the sulfation treatment, including the gas-phase sulfation of the traditional SO\textsubscript{2} and the liquid-phase sulfation of H\textsubscript{2}SO\textsubscript{4}/(NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}/CS(NH\textsubscript{2})\textsubscript{2}, have been regarded as the effective strategy to improve the de-nitrification activity of cerium-based catalysts mainly via optimizing the surface acidity [37-42]. Our previous study [33] showed that the gas-phased sulfation of organic sulfur (CS\textsubscript{2} or COS) at 300 °C presented a better improvement on the NH\textsubscript{3}-SCR activity of CeO\textsubscript{2} than the traditional SO\textsubscript{2}. Recently, we have found that the gas-phased sulfation of CS\textsubscript{2} or/and COS under the low-temperature hydrolysis conditions can further improve the catalytic performance of NO\textsubscript{x} reduction over the CeO\textsubscript{2} catalyst. The above references indicated that the presence of H\textsubscript{2}O contributed to regulating the formation of sulfur-containing species on the catalyst surface during the low-temperature hydrolysis process, thus might affect the surface acidity of the used cerium-based catalyst, which had been widely proven to improve the NH\textsubscript{3}-SCR activity of CeO\textsubscript{2}. However, the promotional effect of low-temperature hydrolysis of organic CS\textsubscript{2} or/and COS on the NH\textsubscript{3}-SCR activity of CeO\textsubscript{2} catalyst has rarely been studied, especially under the presence of H\textsubscript{2}O.

Furthermore, H\textsubscript{2}O widely co-present with organic sulfur in blast furnace gas, which can affect the hydrolysis of CS\textsubscript{2} or/and COS over catalysts. Meanwhile, cerium oxide had been verified to improve the anti-oxygen poisoning of catalyst for the hydrolysis of organic sulfur by avoiding the sulfation of active species due to its better adsorption of sulfates [21,24]. Therefore, as an indispensable key reactant for the hydrolysis of organic sulfur, H\textsubscript{2}O is proposed for the first time to improve the NH\textsubscript{3}-SCR catalytic activity of CeO\textsubscript{2} during the low-temperature gas-phase sulfation of organic CS\textsubscript{2} and COS, which is more conducive to the synthesis of catalysts with excellent performance in practical engineering. The results demonstrate that the introduction of H\textsubscript{2}O further enhances the promotional effect of CS\textsubscript{2}+COS gas-phase sulfation on the NH\textsubscript{3}-SCR
activity of CeO$_2$ catalyst at the simulated low-temperature for the hydrolysis of organic sulfur.

Furthermore, a series of characterization techniques were employed to investigate the sulfuric acid optimized strategy of the "CS$_2$+COS+H$_2$O" gas-phase sulfation on the physicochemical properties, reduction properties, sulfate species, and NH$_3$-SCR performance of CeO$_2$.

2. Experimental

2.1. Catalyst preparation

Pure CeO$_2$ was synthesized via a one-pot hydrothermal method [33,43], and the used cerium nitrate (Ce(NO$_3$)$_3$·6H$_2$O, AR), ammonium bicarbonate (NH$_4$HCO$_3$, AR) and hydrogen peroxide (H$_2$O$_2$, AR) were purchased from China Pharmaceutical Group Chemical Reagents Co., Ltd. According to the preparation of CeO$_2$ in Scheme 1, 0.005 mol Ce(NO$_3$)$_3$·6H$_2$O was firstly dissolved in deionized water and stirred violently for 2 hours until a clear and transparent solution was obtained. Next, a certain amount of ammonium bicarbonate was added into the mixed solution with a milky white suspension formed. After being stirred for 30 minutes, 9 mL of H$_2$O$_2$ (10 mol/L) was dropped and the milky white solution quickly turned into orange. Finally, the mixed solution was poured into a 100 mL of polytetrafluoroethylene and transferred to stainless steel autoclave. After being hydrothermally heated at 200 °C for 24 hours, the resulting precipitate was washed with deionized water and anhydrous ethanol until the pH reached 7. The obtained precipitate was dried at 80 °C for 12 hours and calcined at 400 °C for 5 hours in a temperature-programmed muffle furnace to obtain pure CeO$_2$ catalyst.

![Scheme 1](image.png)

Scheme 1. Schematic diagram for the preparation of pure CeO$_2$ by the one-pot hydrothermal method.

The gas phase sulfation of CeO$_2$ was carried out in a tube furnace according to the following sulfation conditions (Scheme 2): the total gas flow rate of the simulated COS and CS$_2$ (the molar ratio of 7:3) is 500 mL/min by ensuring the concentration of S element being 200 ppm [33]. A certain concentration of H$_2$O was introduced into the vulcanization test bench via an injection pump and N$_2$ was used as the equilibrium gas. The gas-phase sulfation was carried out.
at 50 °C for 3 hours. For convenience, the pretreated samples were labeled as CeO$_2$-CS$_2$+COS without water, CeO$_2$-CS$_2$+COS-H$_2$O($x$), where $x$ represents the concentration of water ($x = 0.33\%, 1.5\%, 5.0\%)$.

Scheme 2. The low temperature gas-phase sulfation of CeO$_2$ catalyst by organic sulfur.

2.2. Catalytic activity test

The fixed bed reactor was used to test the NH$_3$-SCR catalytic performance of catalysts. The dosage of sample and the total gas flow rate are 0.45 g (40~60 mesh) and 1500 mL/min with the gas hourly space velocity (GHSV) being 200,000 mL/(g·h). The flue gas reaction conditions are as follows: 600 ppm NH$_3$, 600 ppm NO, 5 vol.% O$_2$ and 99.999 vol.% N$_2$ used as the equilibrium gases. The concentration of inlet and outlet flue gas (O$_2$, NO$_x$) was continuously monitored by T-350 flue gas analyzer (Testo, Germany). Then, the NO$_x$ conversion rate ($\eta$) is calculated according to the following formula: $\eta = (1-\frac{[\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}}) \times 100\%$, where $[\text{NO}_x]_{\text{in}}$ and $[\text{NO}_x]_{\text{out}}$ represent the inlet and outlet concentrations of gaseous NO$_x$ (NO and NO$_2$), respectively.

2.3. Catalyst characterizations

The surface morphology and structure of catalyst were observed through scanning electron microscopy (SEM) using the ZEISS SIGMA HD instrument. The N$_2$ adsorption-desorption curves were measured at -196 °C using a powder technology ASAP 2460 system instrument. The specific surface area was calculated through the Brunauer-Emmett-Teller (BET) method, while
the Barrett Joyner-Halenda (BJH) method was used to determine the pore volume and pore size
distribution. X-ray diffraction (XRD) patterns were obtained using Cu Kα radiation on a 6100
X-ray diffractometer (Rigaku, Japan) at a scanning rate of 5 °/min from 2θ=10 ° to 80 ° and the
composition of the diffraction peaks was analyzed using MDI Jade 6.0. Raman spectra of
samples were collected on a Raman spectrometer (InVia Reflex, Renishaw), where a laser with a
wavelength of 532 nm was used as the excitation source. Fourier transform infrared (FTIR)
spectra ranging from 400 to 4000 cm⁻¹ were recorded using a Nicolet iS5 FTIR spectrometer,
with a resolution of approximately 4 cm⁻¹.

The X-ray photoelectron spectrometer (XPS, Thermo Fisher Scientific Escalab 250 Xi)
utilizes Al Kα radiation with an excitation energy of 1486.7 eV. The photoelectron spectroscopy
was calibrated with the C1s signal with a binding energy of 284.8 eV and the spectrum was fitted
with the Gaussian-Lorentz function using XPSPEAK software. H₂-temperature programmed
reduction (H₂-TPR) and NH₃-temperature programmed desorption (NH₃-TPD) analyses were
performed using the AutoChem II 2920 instrument from Micromeritics, along with a thermal
conductivity detector (TCD). In the H₂-TPR detection process, 100 mg samples were pretreated
in an Ar atmosphere at 300 °C for 30 minutes, and then cooled to room temperature. The TPR
curves were obtained using a heating rate of 10 °C/min, ranging from 50 to 900 °C in a 10%
H₂/Ar flow. For NH₃-TPD analysis, 100 mg samples were subjected to heating at 500°C for an
hour in the presence of Ar flow and then cooled to 35°C. A continuous flow of 10% NH₃/He (50
mL/min) was directed through the sample tube for a purge time of 2 hours and the desorption of
NH₃ species was carried out in a helium flow to obtained the data at temperatures ranging from
35 to 900 °C. Thermogravimetric analysis (TGA) was conducted using PerkinElmer STA6000 in
an α-Al₂O₃ crucible under a nitrogen atmosphere. Thermogravimetric curves in the temperature
range of 30-900 °C were recorded with a heating rate of 10 °C/min to investigate the thermal
properties and thermal decomposition of the sulfated samples.

3. Results and discussion

3.1. Evaluation of catalytic activity
Fig. 1. (A) The effect of H$_2$O concentration on the NH$_3$-SCR activity of CeO$_2$ during the gas-phase sulfation process. Sulfated conditions: COS:CS$_2$ = 7:3 with the total amount of S element being 200 ppm; the sulfation temperature 50 °C; the sulfation time 3 h; H$_2$O (water vapor) concentrations 0.33 vol.%, 1.5 vol.% and 5.0 vol.%. (B) H$_2$O and SO$_2$ resistance study of CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) catalyst and (C) the long time stability test of CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) catalyst.

The influence of H$_2$O introduction on the NH$_3$-SCR activity of CeO$_2$-CS$_2$+COS catalyst was investigated during the gas-phase sulfation at 50 °C, and the results are given in Fig. 1(A). It can be found that the gas-phase sulfation of COS+CS$_2$ at 50 °C effectively enhances the NH$_3$-SCR activity of CeO$_2$, and the highest NO$_x$ conversion of catalyst is increased from 31% to higher than 90% at the GHSV of 200,000 mL/(g·h). The main reason for the poor catalytic performance of CeO$_2$ might be attributed to the low concentrations of Ce$^{3+}$ ions, active oxygen and acid sites on its surface [44,45]. And the low-temperature gas-phase sulfation of COS and CS$_2$ optimizes these defects and improves the surface concentrations of Ce$^{3+}$ ions, active oxygen and acid sites of CeO$_2$, thereby increases its NH$_3$-SCR activity effectively. This promotional effect of organic sulfur gas-phase sulfation had also been verified by our previous research [33], and COS or CS$_2$ presented a better enhancement on the NH$_3$-SCR activity of CeO$_2$ than the traditional inorganic SO$_2$ when the gas-phase sulfation was carried out at 300 °C. Interestingly, as depicted in Fig. 1(A), the introduction of H$_2$O during the low-temperature gas-phase sulfation of COS and CS$_2$
can further increase the NH$_3$-SCR activity of the CeO$_2$+CS$_2$+COS catalyst, and CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) presents good catalytic performance with a 100% NO$_x$ reduction obtained at the temperature range of 250 ~ 400 °C. However, the enhancement of water concentrations from 0.33 vol.% to 5.0 vol.% decreases this promotional effect. In order to validate the disadvantageous effect of high H$_2$O concentration during the low-temperature gas-phase sulfation, 1.5 vol.% H$_2$O had also been introduced and the NH$_3$-SCR activity of CeO$_2$-CS$_2$+COS-H$_2$O(1.5%) is between the values of CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) and CeO$_2$-CS$_2$+COS-H$_2$O(5.0%). This implies that the introduction of H$_2$O during the low-temperature gas-phase sulfation can optimize the catalytic performance of CeO$_2$+CS$_2$+COS catalyst, but large concentration of water decreases this promotional effect. The previous researches about the sulfated CeO$_2$ and other metals catalyst for NH$_3$-SCR had been summarized in Table S1, and it can be found that compared to other sulfated catalysts in recent years, CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) exhibits excellent low-temperature performance and a wide temperature window even at a high GHSV of 200,000 mL/(g·h). Meanwhile, the influence of CS$_2$/COS molar ratio (7:3, 5:5, 3:7) on the NH$_3$-SCR activity of CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) catalyst was also examined, as shown in Fig. S1. Under the CS$_2$/COS molar ratios of 7:3 and 3:7, the sulfated CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) catalysts present similar denitrification performance, which are better than that of the catalyst treated at the CS$_2$/COS molar ratio of 5:5. Meanwhile, it is generally believed that the organic sulfur in blast furnace gas is mainly composed of COS and the molar ratio of COS/(COS+CS$_2$) is about 70% [24]. Therefore, 7:3 of COS/CS$_2$ molar ratios was chosen for the subsequent research and characterization.

H$_2$O and SO$_2$ that commonly present in the denitrification process and potentially influence the NH$_3$-SCR activity of catalyst, therefore it is necessary to study the anti-poisoning of H$_2$O or/and SO$_2$ for the CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) catalyst. As shown in Fig. 1(B), when 100 ppm SO$_2$ is introduced into the simulated flue gas, the NO$_x$ reduction of catalyst slowly decreases to 93% and then remains stable, and CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) exhibits excellent resistance to SO$_2$ poisoning. When further introducing 10.0 vol.% H$_2$O, the NO$_x$ conversion rate of CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) rapidly decreases to 53%, which might be due to the competitive adsorption of H$_2$O and the deposition of sulfate species [39,40]. After removing H$_2$O, the activity is promptly recovered to 85%, which indicates that the catalyst deactivation caused by H$_2$O is
reversible. After further stopping the introduction of SO\textsubscript{2}, the activity is not further recovered, indicating an irreversible deactivation of catalyst caused by the deposition of sulfate species. In the meantime, the long-term stability of the NH\textsubscript{3}-SCR activity over the CeO\textsubscript{2}-CS\textsubscript{2}+COS-H\textsubscript{2}O(0.33%) catalyst was also investigated and the results are given in Fig. 1(C). It is found that CeO\textsubscript{2}-CS\textsubscript{2}+COS-H\textsubscript{2}O(0.33%) presents a good stability of the NH\textsubscript{3}-SCR activity, and more than 90% of NO\textsubscript{x} reduction can be maintained after a 60 h test, although its NO\textsubscript{x} reduction decreases from 100% to about 95% at 25–27 h.

Previous studies had shown that an appropriate amount of H\textsubscript{2}O could promote the hydrolysis and conversion of organic sulfur (CS\textsubscript{2} or/and COS) via optimizing the formation of active -OH groups on catalysts surface, but excessive H\textsubscript{2}O inhibited the catalytic hydrolysis due to the competitive adsorption and the introduced concentration of H\textsubscript{2}O could regulate the formation of sulfur-containing species on the catalyst surface during the low-temperature hydrolysis of CS\textsubscript{2} or/and COS [29,46]. Meanwhile, the formed sulfur-containing species, mainly sulfate, were proven to optimize the concentrations of Ce\textsuperscript{3+} ions, active oxygen and acid sites on CeO\textsubscript{2} catalyst surface, which are closely related to its NH\textsubscript{3}-SCR activity. Therefore, CeO\textsubscript{2}-CS\textsubscript{2}+COS-H\textsubscript{2}O(0.33%) and CeO\textsubscript{2}-CS\textsubscript{2}+COS-H\textsubscript{2}O(5.0%) were chosen to be characterized to investigate the influence of H\textsubscript{2}O introduction on the physical-chemical properties of CeO\textsubscript{2}-CS\textsubscript{2}+COS catalyst in the following sections.

3.2. Morphological analysis

Scanning electron microscopy (SEM) was applied to investigate the influence of H\textsubscript{2}O introduction on the morphology of CeO\textsubscript{2} catalyst during the low-temperature gas-phase sulfation of organic CS\textsubscript{2} and COS, and the particle size distributions were also calculated. According to the results in Fig. 2 and 3, CeO\textsubscript{2} presents an irregular morphology composed of dispersed nanoparticles and exhibits a maximum particle size of 2.33 μm. Meanwhile, the low-temperature gas-phase sulfation of CS\textsubscript{2} and COS decreases the crystallinity of nanoparticles on CeO\textsubscript{2} surface and inhibits the occurrence of agglomeration, although CeO\textsubscript{2}-CS\textsubscript{2}+COS also exhibits a disordered granular morphology. Furthermore, the introduction of H\textsubscript{2}O seems to further reduce the agglomeration of surface nanoparticles and causes the particle size to shift towards smaller direction. In particular, the introduction of 5.0 vol.% H\textsubscript{2}O significantly enhances the dispersion of CeO\textsubscript{2} nanoparticles and reduces the average particle size to 0.281 μm. Therefore, the
gas-phase sulfation of organic sulfur at 50 °C decreases the crystallinity of nanoparticles on CeO$_2$ surface due to the formation of surface sulfur-containing species, and the introduction of H$_2$O further improves the dispersion of nanoparticles on catalysts surface. Furthermore, the nanoparticles on CeO$_2$-CS$_2$+COS-H$_2$O(5.0%) surface are more evenly dispersed (Fig. 2(D), Fig. 3(D), Fig. S2(D)), which might be due to the inhibition of excess H$_2$O on the aggregation of sulfate species during the low-temperature gas-phase sulfation of CS$_2$ and COS.

Fig. 2. SEM images of (A) CeO$_2$, (B) CeO$_2$-CS$_2$+COS, (C) CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) and (D) CeO$_2$-CS$_2$+COS-H$_2$O(5.0%) catalysts.

Fig. 3. Particle size distributions of (A) CeO$_2$, (B) CeO$_2$-CS$_2$+COS, (C) CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) and (D) CeO$_2$-CS$_2$+COS-H$_2$O(5.0%) catalysts.

3.3. Texture and structure characterization
Fig. 4. The N\textsubscript{2} adsorption-desorption isotherms (A) and the pore size distributions (B) of the as-prepared catalysts.

Herein, N\textsubscript{2} adsorption-desorption, XRD and Raman were carried out to reveal the influence of H\textsubscript{2}O introduction on the texture and structural properties of the sulfated CeO\textsubscript{2} catalysts by CS\textsubscript{2} and COS at 50 °C. As shown in Fig. 4(A), the adsorption-desorption isotherms of CeO\textsubscript{2} and CeO\textsubscript{2}-CS\textsubscript{2}+COS catalysts belong to type IV with the hysteresis loop of H3 type in the relative pressure range of p/p° = 0.05~1.0 according to the IUPAC classification, indicating the presence of mesoporous structures composed of non-rigid aggregates of nanoparticles [47,48]. In addition, the rapid increase in nitrogen adsorption capacity at the p/p° of 0.8 demonstrates the presence of a macroporous structure [22,49]. Thus, both CeO\textsubscript{2} and CeO\textsubscript{2}-CS\textsubscript{2}+COS catalysts have mesoporous and macroporous hierarchical porous structures, which is confirmed by the BJH desorption pore size distribution calculated from the desorption isotherm of N\textsubscript{2}. From Fig. 4(B), it can be observed that CeO\textsubscript{2} has a narrow and sharp single peak in the range of 2-10 nm belonging to the typical mesoporous structure, and the gas-phase sulfation of CS\textsubscript{2} and COS at 50 °C widens the pore size distribution of CeO\textsubscript{2}. However, the introduction of H\textsubscript{2}O during the gas-phase sulfation makes the low-pressure closure point of nitrogen adsorption and desorption for CeO\textsubscript{2}-CS\textsubscript{2}+COS shift to the right, and both CeO\textsubscript{2}-CS\textsubscript{2}+COS-H\textsubscript{2}O(0.33%) and CeO\textsubscript{2}-CS\textsubscript{2}+COS-H\textsubscript{2}O(5.0%) present more concentrated pore size distribution than CeO\textsubscript{2} and CeO\textsubscript{2}-CS\textsubscript{2}+COS although they also exhibit the mesoporous and macroporous hierarchical porous structures. This indicates that the presence of water might affect the sulfation degree of nanoparticles and the formation of sulfur-containing species on CeO\textsubscript{2}-CS\textsubscript{2}+COS surface during the gas-phase sulfation of CS\textsubscript{2} and COS at 50 °C, which are in accordance with the results of the
morphology. Previous studies had pointed out that an abundance of mesopores could provide more active sites and internal surface area for the NH$_3$-SCR reaction over P-W/CeO$_2$, and the hierarchical porous structure helped to reduce the mass transfer resistance and facilitated the contact between the reactant gas molecules and the active sites on the inner surface of catalyst [50,51]. Therefore, CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) and CeO$_2$-CS$_2$+COS-H$_2$O(5.0%) exhibit slightly worse mesoporous and macroporous hierarchical porous structures than CeO$_2$ and CeO$_2$-CS$_2$+COS. In addition, they have smaller specific surface areas (Table 1). These all demonstrate that the introduction of H$_2$O affect the sulfation degree of nanoparticles and the accumulation of the formed sulfur-containing species during the gas-phase sulfation of CS$_2$ and COS at 50 °C, but the pore structure and specific surface area might not be the determining factor for the NH$_3$-SCR activity of the sulfated CeO$_2$ catalysts by organic sulfur at low-temperatures.

Table 1 The physical structural parameters of the as-prepared catalysts

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface area $^a$</th>
<th>Pore volume $^b$</th>
<th>Pore diameter $^c$</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$_2$+COS</td>
<td>127.86</td>
<td>0.280</td>
<td>8.34</td>
</tr>
<tr>
<td>CeO$_2$-CS$_2$+COS-H$_2$O(0.33%)</td>
<td>113.31</td>
<td>0.155</td>
<td>6.43</td>
</tr>
<tr>
<td>CeO$_2$-CS$_2$+COS-H$_2$O(5.0%)</td>
<td>107.25</td>
<td>0.156</td>
<td>6.71</td>
</tr>
</tbody>
</table>

$^a$ BET surface area

$^b$ BJH desorption pore volume

$^c$ BJH desorption pore diameter

According to the X-ray diffraction (XRD) patterns in Fig. 5 and Fig. S3, pure CeO$_2$ presents the typical lattice diffraction peaks attributed to cubic fluorite CeO$_2$ (PDF#34-0394) [40,52], and the low-temperature gas-phase sulfation of CS$_2$ and COS effectively reduces the intensity of the diffraction peaks ascribed to cubic fluorite CeO$_2$. Furthermore, a broad peak at the low scanning angle range of 15 ~ 26 ° appears over the CeO$_2$-CS$_2$+COS catalyst, which is attributed to the sulfur elements or/and the sulfur compounds dominated by hydrated metal sulfates (PDF#37-0762; PDF#24-1250; PDF#24-1216). Interestingly, the introduction of 0.33 vol.% H$_2$O might slightly suppress the sulfation of cubic fluorite CeO$_2$ by CS$_2$ and COS at 50 °C, but
CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) still presents a similar broad peak of sulfur elements or/and compounds to CeO$_2$-CS$_2$+COS. However, the enhancement of H$_2$O concentration from 0.33 vol.% to 5.0 vol.% increases the intensity of this peak, indicating that higher crystallinity sulfur elements or/and compounds are formed in CeO$_2$-CS$_2$+COS-H$_2$O(5.0%). Mu et al. [53] pointed out that the hydrolysis of COS led to a new XRD pattern peak emerging at 2θ = 24.2 ° in 10Cu-Co$_3$O$_4$ catalyst, which was attributed to elemental sulfur. This phenomenon was also found in the CeO$_2$-R catalyst after the catalytic selective oxidation of H$_2$S [54]. In addition, the hydrated metal sulfates could gradually become amorphous during the slow heating process, which further thermally decomposed into the anhydrous sulfate species such as Ce$_2$(SO$_4$)$_3$ and Ce(SO$_4$)$_2$ [55]. Therefore, the low-temperature gas-phase sulfation of organic CS$_2$+COS contributes to the formation of sulfur element or/and compounds in the CeO$_2$ catalyst under the condition of low concentration water, but the enhancement of H$_2$O concentration from 0.33 vol.% to 5.0 vol.% further improves the crystallinity of the formed sulfur-containing species.

Fig. 5. The XRD patterns (Left) and the locally enlarged XRD (14~27 °) (Right) of as-prepared sulfated catalysts.

Fig. 6 gives the Raman spectra of CeO$_2$, CeO$_2$-CS$_2$+COS, CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) and CeO$_2$-CS$_2$+COS-H$_2$O(5.0%) catalysts, and it can be found that three peaks are detected at 464 cm$^{-1}$, 600 cm$^{-1}$ and 1180 cm$^{-1}$ for pure CeO$_2$ catalyst, respectively. The first prominent peak is related to the symmetric stretching vibration of Ce-O-Ce, which is assigned to the F$_{2g}$ characteristic vibration of cubic fluorite CeO$_2$, while the last two vibration peaks are attributed to
the surface oxygen defects \[56,57\]. It is evident that the low-temperature gas-phase sulfation of \(CS_2+COS\) makes the \(F_{2g}\) characteristic peak of CeO\(_2\) shift to a lower wave number via altering its Ce-O-Ce structure \[58-60\], and the introduction of H\(_2\)O further improves the FWHM (full width at half-maximum) and peak intensity of \(F_{2g}\) vibration peak significantly. This indicates that the introduction of H\(_2\)O strengthens the influence of CS\(_2\)+COS low-temperature gas-phase sulfation on refining the grain size of nanoparticles on CeO\(_2\) surface, which is in accordance with the results of SEM and XRD. Jang et al. \[61\] found that the introduction of SiO\(_2\) refined the particle size of CeO\(_2\) with a wider FWHM of the \(F_{2g}\) vibration peak detected for the core/shell CeO\(_2\)-SiO\(_2\).

Furthermore, the relative concentration of oxygen vacancies on the catalyst surfaces could be obtained by calculating the integral area ratio of the peaks at 600 cm\(^{-1}\)+1180 cm\(^{-1}\) and the peak of \(F_{2g}\) characteristic vibration \[62\]. As shown in Fig. S4, the introduction of H\(_2\)O improves the promotional effect of organic CS\(_2\)+COS low-temperature gas-phase sulfation on the relative concentration of oxygen vacancies on CeO\(_2\) surface, but high concentration H\(_2\)O decreases this promotional effect. And the calculated relative concentrations of oxygen vacancies are as follow:

CeO\(_2\)-CS\(_2\)+COS-H\(_2\)O(0.33%) > CeO\(_2\)-CS\(_2\)+COS-H\(_2\)O(5.0%) > CeO\(_2\)-CS\(_2\)+COS > CeO\(_2\), which is consistent with the NH\(_3\)-SCR activity of catalysts. Therefore, the introduction of H\(_2\)O further helps to the generation of oxygen vacancies during the gas-phase sulfation process of organic CS\(_2\)+COS at 50 °C, thus accelerating the conversion frequency between the chemisorbed oxygen and lattice oxygen via the Ce\(^{3+}\)/Ce\(^{4+}\) ion pair, which might be beneficial to promote the oxidation of NO to NO\(_2\) and improves the NO\(_x\) conversion through the 'fast SCR' reaction \[63-65\].
The FTIR spectra of CeO$_2$-CS$_2$+COS, CeO$_2$-CS$_2$+COS-H$_2$O(0.33%), and CeO$_2$-CS$_2$+COS-H$_2$O(5.0%) catalysts are given in Fig. 7. The vibration peaks located at 1627 cm$^{-1}$ and 3417 cm$^{-1}$ are attributed to the bending vibration and stretching vibration of -OH group, respectively [66]. When the content H$_2$O increases to 5.0% during the low-temperature gas-phase sulfation process, a new weak vibration peak attributed to H$_2$O appears at 847 cm$^{-1}$ in CeO$_2$-CS$_2$+COS-H$_2$O(5.0%) [67]. Meanwhile, the formation of sulfate species during the low-temperature gas-phase sulfation results in the detection of multiple vibrational bands at 900–1300 cm$^{-1}$. Among them, the vibration peaks at 979 cm$^{-1}$ and 1043 cm$^{-1}$ are attributed to the characteristics of inorganic chelated bidentate sulfates, caused by the S-O and S=O bond vibrations of surface sulfate species, while the bands at 1116 and 1190 cm$^{-1}$ are caused by the formed bulk sulfates on catalysts surface [65,68]. However, the enhancement of H$_2$O content from 0.33 vol.% to 5.0 vol.% weakens the intensity of the vibrational band caused by sulfate species, which is reasonable due to the enhanced interaction between the groups of -OH and SO$_4^{2-}$ [69].
3.4. Surface active components analysis

In this section, XPS (X-ray Photoelectron Spectroscopy) technique was employed to investigate the influence of H$_2$O introduction on the dispersion of elements on catalysts surface. As shown in Fig. 8(A), the Ce 3d XPS spectra could be deconvoluted into eight peaks via the Lorentz/Gaussian method. Among them, u' and v' are attributed to Ce$^{3+}$ species (3d$^{10}$ 4f$^1$), and the other peaks are ascribed to the Ce$^{4+}$ electronic state (3d$^{10}$ 4f$^0$) [49]. In addition, the low-temperature gas-phase sulfation of organic CS$_2$+COS increases the molar ratio of Ce$^{3+}$/(Ce$^{3+}$+Ce$^{4+}$) on CeO$_2$ surface and makes the Ce 3d spectra of catalyst shift to a higher binding energy direction by approximately 0.6 eV, indicating the electron-induced effect between Ce, O and S species, which alters the electron cloud density around Ce [70,71]. Interestingly, the introduction of H$_2$O improves this electron-induced effect and further increases the molar ratio of Ce$^{3+}$/(Ce$^{3+}$+Ce$^{4+}$) on CeO$_2$-CS$_2$+COS surface. However, as shown in Table 2, the enhancement of H$_2$O concentration from 0.33 vol.% to 5.0 vol.% reduces this promotional effect and makes the surface Ce$^{3+}$/(Ce$^{3+}$+Ce$^{4+}$) molar ratio of CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) decrease from 36.42 % to 33.15%. Generally, the generation of oxygen vacancies is associated with the electron transfer of Ce$^{4+}$/Ce$^{3+}$ ion pair, and the presence of Ce$^{3+}$ can aggravate the charge imbalance and promote the redox cycle of Ce$^{4+}$/Ce$^{3+}$, thus heightens the activation of oxygen on the catalysts surfaces and results in the generation of more oxygen vacancies [72,73]. Therefore, the further enhancement of H$_2$O introduction on the surface Ce$^{3+}$/(Ce$^{3+}$+Ce$^{4+}$) molar ratio of

![Fig. 7. FTIR spectra of the sulfated CeO$_2$ catalysts by COS+CS$_2$ at 50 °C.](image-url)
CeO$_2$-CS$_2$+COS might be an important reason for increasing the NH$_3$-SCR activity of catalyst. However, the introduction of higher concentration H$_2$O (5.0 vol.%) results in a stronger competitive adsorption between H$_2$O and organic CS$_2$+COS, which might affect the conversion of the adsorbed CS$_2$+COS on cubic fluorite CeO$_2$ surface, thus decreases the Ce$^{3+}$/(Ce$^{3+}$+Ce$^{4+}$) molar ratio of CeO$_2$-CS$_2$+COS-H$_2$O(0.33%).

As shown in Fig. 8(B), the O 1s spectrum of pure CeO$_2$ can be fitted into three peaks, which belongs to the lattice oxygen existing in cubic fluorite CeO$_2$ (O$_\alpha$, 529.1 eV), the chemisorbed oxygen (O$_\beta$, 530.0 eV) and the lattice oxygen bonded with Ce$_2$O$_3$ (O$_\gamma$, 531.8 eV), respectively [74]. Meanwhile, the low-temperature gas-phase sulfation of CS$_2$+COS leads the O 1s XPS binding energy of CeO$_2$ shifting to a higher value, while only O$_\alpha$ and O$_\beta$ are detected for the sulfated CeO$_2$ catalysts due to the formation of Ce-O-S bonds [75]. Interestingly, the introduction of H$_2$O further increases the binding energy of O 1s of CeO$_2$-CS$_2$+COS catalyst. Furthermore, as shown in Table 2, the presence of H$_2$O during the low-temperature gas-phase sulfation of CS$_2$+COS improves the concentration of chemical adsorption oxygen (O$_\beta$) on catalyst surface, but excessive water leads to a decrease of this value. The regular pattern of H$_2$O introduction on the surface O$_\beta$ concentration is in accordance with that of Ce$^{3+}$/(Ce$^{3+}$+Ce$^{4+}$) molar ratio. A large number of studies had demonstrated that the surface chemisorbed oxygen had a higher mobility than the lattice oxygen, which was easy to be activated and played an important role in the oxidation reaction. Consequently, higher surface molar ratio of O$_\beta$/(O$_\alpha$+O$_\beta$+O$_\gamma$) are generally regarded to be beneficial to improve the oxidization of NO to NO$_2$ and the 'fast SCR' process (NO + NO$_2$ + 2NH$_3$ = 2N$_2$ + 3H$_2$O) [76,77].

From Fig. 8(C), it can be found that the S 2p spectra of the sulfated CeO$_2$ catalysts can be fitted into three peaks located at 163.8 eV, 168.3 eV and 169.3 eV (±0.3 eV), and the last two peaks belong to S$^{6+}$ species. Meanwhile, the peak located about 163.8 eV is attributed to sulfur, which is different from the formation of sulfate species (SO$_4^{2-}$, etc.) in CeO$_2$ catalyst during the gas-phase sulfation of inorganic SO$_2$ [54,78]. However, the introduction of H$_2$O decreases the intensity of S 2p spectra of CeO$_2$-CS$_2$+COS, thereby reduces the concentrations of the formed S$^{6+}$ and S species on catalyst surface. As shown in Table 2, the introduction of H$_2$O during the low-temperature gas-phase sulfation of CS$_2$+COS helps to increase the surface molar ratio S$^{6+}$/(S$^{6+}$+S), and the enhancement of H$_2$O concentration from 0.33 vol.% to 5.0 vol.% not only
increases the formed surface total concentration of $S^{6+}$ and $S$, but also further improves the molar ratio $S^{6+}/(S^{6+} + S)$ on CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) surface. Therefore, it can be included that lower concentration of sulfur-containing species might be helpful to the NH$_3$-SCR activity of the sulfated CeO$_2$ catalyst.

![Figure 8](A) Ce 3d, (B) O 1s, and (C) S 2p XPS spectra of the as-prepared catalyst.

**Table 2** Surface composition and atomic ratio 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$_2$+COS</td>
<td>32.15</td>
<td>63.24</td>
</tr>
<tr>
<td>CeO$_2$-CS$_2$+COS-H$_2$O(0.33%)</td>
<td>32.73</td>
<td>63.94</td>
</tr>
<tr>
<td>CeO$_2$-CS$_2$+COS-H$_2$O(5.0%)</td>
<td>33.25</td>
<td>62.73</td>
</tr>
</tbody>
</table>

* The sum of $S$ and $S^{6+}$. 
3.5. Thermogravimetric analysis

Thermogravimetric analysis was done to further investigate the influence of H$_2$O introduction on the formed sulfur-containing species over CeO$_2$-CS$_2$+COS-H$_2$O catalyst. The results are shown in Fig. 9. It can be clearly seen that there exists an apparent weight-loss for the TG-DTG curves as the temperature increases, which can be divided into three parts. The weight loss peak observed in the range of 30-200 °C is attributed to the desorption of physically absorbed water and dehydroxylation [52,72], and the desorbed values in this stage are 2.14%, 2.44% and 2.37% for CeO$_2$-CS$_2$+COS, CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) and CeO$_2$-CS$_2$+COS-H$_2$O(5.0%), respectively. Consequently, the introduction of H$_2$O slightly increases the content of physically adsorbed water and hydroxyl groups in the sulfated CeO$_2$ catalysts by organic CS$_2$+COS at 50 °C, which might be beneficial to the NH$_3$-SCR activity of catalyst. Guo et al. [79] claimed that SO$_4^{2-}$, O$_2^{2-}$ and hydroxyl-like (-OH) species could function as Brønsted acid sites to enhance the adsorption of NH$_3$ and consequently improved the NO$_x$ removal efficiency of catalyst. Peng et al. [80] also mentioned that sulfate species promoted the ionization of water adsorbed on the catalyst surfaces, resulting in the formation of more hydroxyl group and more Brønsted acid sites. In addition, the XRD and XPS analyses validate the formation of sulfur element in the sulfated CeO$_2$-CS$_2$+COS, CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) and CeO$_2$-CS$_2$+COS-H$_2$O(5.0%) catalysts. Thus, the slight weight losses observed between 200-600 °C might be ascribed to the emission of SO$_2$ due to the oxidation reaction of sulfur and oxygen-containing functional groups in this temperature range. Finally, the third stage of weight losses began at 650 °C is attributed to the thermal decomposition of sulfate species [37,38], and approximately 5.44 %, 4.07 % and 3.07 % were calculated for CeO$_2$-CS$_2$+COS, CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) and CeO$_2$-CS$_2$+COS-H$_2$O(5.0%) catalysts, respectively. Therefore, the introduction of H$_2$O decreases the formed amount of sulfate species in the sulfated CeO$_2$ catalysts, although they had been reported to adsorb NH$_3$ as a stable acidic site and presented a strong thermal stability. And it can be inferred that there exists a competitive adsorption of H$_2$O and CS$_2$+COS on cubic fluorite CeO$_2$ surface, which reduces the formation of sulfate species, but the hydroxyl groups dissociated by H$_2$O enhances the interaction between organic CS$_2$+COS and cubic fluorite CeO$_2$, which affects the physical and chemical properties of catalyst. Furthermore, the appropriate amount of -OH group as the additives for Brønsted acid sites enhances the
adsorption capacity of NH$_3$ [46]. However, excess water significantly inhibits the chemical adsorption of CS$_2$ and COS on catalyst surfaces due to a stronger competitive adsorption among them and depresses the hydrolysis of organic sulfur, thus further reduces the production of sulfate species in CeO$_2$ catalyst. This demonstrates that the positive impact of hydroxyl groups might be outweighed by the negative effect of the competitive adsorption of H$_2$O and COS/CS$_2$ under the condition of excess water [26,81], although the enhancement of H$_2$O concentration from 0.33 vol.% to 5.0 vol.% further improves the molar ratio of S$^{6+}/$(S$^{6+}$+S) on CeO$_2$ surface calculated from the results of XPS spectra.

Fig. 9. The TG-DTG curves of CeO$_2$-CS$_2$+COS, CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) and CeO$_2$-CS$_2$+COS-H$_2$O(5.0%).

3.6. The properties of redox ability
Fig. 10. The H$_2$-TPR patterns of CeO$_2$, CeO$_2$-CS$_2$+COS, CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) and CeO$_2$-CS$_2$+COS-H$_2$O(5.0%) catalysts.

H$_2$-TPR was carried out to investigate the influence of H$_2$O introduction on the reducibility of CeO$_2$-CS$_2$+COS catalyst and the results are shown in Fig. 10. It is reported that two reduction peaks of pure CeO$_2$ at about 495 °C and 830 °C belongs to the reduction of surface Ce$^{4+}$ to Ce$^{3+}$ and bulk Ce$^{4+}$ to Ce$^{3+}$ [61], respectively. Meanwhile, the low-temperature gas-phase sulfation of CS$_2$+COS makes the reduction peak of CeO$_2$ at 495 °C shifting to left and disappearing due to the formation of surface sulfate and the interaction of Ce and S species in the catalyst [70,82]. Furthermore, this treatment also leads the reduction peak of bulk CeO$_2$ at 830 °C shifting to a lower temperature owing to the enhanced mobility of the lattice oxygen for cubic fluorite CeO$_2$ by the gas-phase sulfation of reductive organic CS$_2$+COS [83], thus improves the reducibility of bulk CeO$_2$. It should be mentioned that a new high peak attributed to the reduction of surface sulfate species appears at 605 °C, 585 °C and 571 °C for the sulfated CeO$_2$-CS$_2$+COS, CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) and CeO$_2$-CS$_2$+COS-H$_2$O(5.0%) catalysts, respectively [34].

According to previous studies, the formation of sulfate species increased the surface active oxygen concentration, thus enhanced the adsorption of NH$_3$ and promoted the low-temperature oxidation of NO [40,65]. This indicates that the gas-phase sulfation of organic CS$_2$+COS increases the reducibility of CeO$_2$ catalyst effectively. Furthermore, the introduction of H$_2$O
makes the reduction peak ascribed to sulfate species of CeO$_2$-CS$_2$+COS moving to the low
temperature direction, which implies that the gas-phase sulfation of organic CS$_2$+COS at the
presence of water helps to further improve the reducibility of sulfate species although their
formed amounts also decrease. Therefore, the introduction of H$_2$O further contributes to improve
the reducibility of CeO$_2$-CS$_2$+COS, which is beneficial to the NH$_3$-SCR activity of the catalyst.

3.7. The properties of surface acidity

Similar to the redox ability, the surface acidity is regarded as another critical factor of
influencing the NH$_3$-SCR activity of catalyst. Therefore, the NH$_3$-TPD test was carried out to
investigate the effect of H$_2$O introduction on the surface acidity of CeO$_2$-CS$_2$+COS during the
low-temperature gas-phase of organic CS$_2$+COS. According to the NH$_3$-TPD spectrum in Fig. 11,
a wide desorption peak of NH$_3$ species was observed at 50-450 °C, which was attributed to weak
acid sites and medium-strong acid sites via fitting it into five desorption peaks (labeled as I, II,
III, IV and V) [84]. Previous studies indicate that there exists a positive correlation between the
surface acid sites and the desorption temperature of NH$_3$ species for the NH$_3$-SCR catalysts
[85,86]. Therefore, the relative ratio of the integrated area for these five NH$_3$ desorption peaks
were calculated, as summarized in Table 3. Pure CeO$_2$ has a considerable proportion of weak
acid sites (74.83 %), but the low-temperature gas-phase sulfation of CS$_2$+COS significantly
increases the proportion of medium-strong acid sites, which is further enhanced by introducing
H$_2$O during the sulfation process, although the introduction of H$_2$O decreases the formed amount
of surface or/and bulk sulfation species according to the results of XPS spectra and TG-DTG
curves. Jin et al. [87] pointed out that the inclusion of HSiW resulted in an increase of the surface
acid sites of CeO$_2$, especially the number of medium-strong acid sites, thus improved the
NH$_3$-SCR activity of catalyst. This phenomenon was also reported in the Cu-SSZ-13 catalyst
[88]. Therefore, the intensity of medium-strong acid sites plays a significant impact on the
NH$_3$-SCR activity, and the formation of sulfate species helps to enhance the intensity of
medium-strong acid sites for CeO$_2$ catalyst, which has also been proven by the gas-phase
sulfation of CS$_2$+COS at 50 °C. Furthermore, the introduction of 0.33 vol.% H$_2$O makes the
CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) catalyst presenting the best medium-strong acid intensity, although
it decreases the formed amount of surface or/and bulk sulfation species. The increase of H$_2$O
content from 0.33 vol.% to 5.0 vol.% increases the amount of sulfate species detected on
CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) surface according to XPS results, but slightly reduces its medium-strong acid sites. This may be one of the reasons for the decrease of the catalytic performance of CeO$_2$-CS$_2$+COS-H$_2$O(0.33%), and thus both the surface sulfate species and the bulk sulfate species can affect the NH$_3$-SCR acidity of CeO$_2$ catalyst.

![Fig. 11. The fitted NH$_3$-TPD curves of CeO$_2$, CeO$_2$-CS$_2$+COS, CeO$_2$-CS$_2$+COS-H$_2$O(0.33%) and CeO$_2$-CS$_2$+COS-H$_2$O(5.0%) catalysts.](image)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Relative ratio of desorption sub-peaks (%)</th>
<th>Relative ratio of different acids (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak I Peak II Peak III Peak IV Peak V</td>
<td>Weak acid Medium-strong acid</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>44.49 30.34 9.67 6.89 8.61</td>
<td>74.83 25.17</td>
</tr>
<tr>
<td>CeO$_2$-CS$_2$+COS</td>
<td>31.18 32.65 18.18 10.22 7.77</td>
<td>63.83 36.17</td>
</tr>
<tr>
<td>CeO$_2$-CS$_2$+COS-H$_2$O(0.33%)</td>
<td>29.25 33.32 20.27 9.48 7.68</td>
<td>62.57 37.43</td>
</tr>
<tr>
<td>CeO$_2$-CS$_2$+COS-H$_2$O(5.0%)</td>
<td>30.90 31.76 21.43 11.56 4.35</td>
<td>62.66 37.34</td>
</tr>
</tbody>
</table>

As an essential reactant for the hydrolysis of organic CS$_2$ or/and COS, the introduction of appropriate H$_2$O could enhance the adsorption and conversion performance of organic sulfur on the surface of metal oxide catalysts [89,90]. Therefore, water was introduced into the low-temperature gas-phase sulfation of CS$_2$+COS over CeO$_2$ catalyst in order to further improve its NH$_3$-SCR activity for the first time, and the introduction of 0.33 vol.% H$_2$O promotes the adsorption of CS$_2$+COS on cubic fluorite CeO$_2$ surface and the interaction among them, thus
further enhances the optimization effect of reducing organic CS$_2$+COS on the electronic state of CeO$_2$. This increases the content of Ce$^{3+}$ ions, chemisorbed oxygen (O$_β$) and oxygen vacancies on CeO$_2$-CS$_2$+COS surface. Furthermore, the introduction of appropriate amount of H$_2$O effectively enhances the redox cycle of Ce$^{4+}$/Ce$^{3+}$ ion pairs, and further increases the medium-strong acid although it decreases the formed amount of surface or/and bulk sulfation species for the sulfated CeO$_2$ catalyst by organic CS$_2$+COS at 50 °C. These all help to improve the NH$_3$-SCR performance of CeO$_2$ catalyst. However, excess water (5.0 vol.%) enhances the competitive adsorption of H$_2$O and COS/CS$_2$, which is slightly unbeneficial to the promotional effect of water introduction on the NH$_3$-SCR activity of CeO$_2$ catalyst during the gas-phase sulfation of CS$_2$+COS at 50 °C.

4. Conclusions

In summary, as an indispensable key reactant for the hydrolysis reaction of organic sulfur, H$_2$O was introduced during the low-temperature gas-phase sulfation of CS$_2$+COS, which has been verified to be a simple and effective method to improve the NH$_3$-SCR performance of CeO$_2$ catalyst. The formation of hydroxyl groups dissociated from H$_2$O are beneficial to the adsorption of CS$_2$ and COS on CeO$_2$ surface, and enhances the interaction among them, although the introduction of H$_2$O decreases the formed amount of surface or/and bulk sulfation species. Furthermore, the introduction of H$_2$O increases the concentrations of Ce$^{3+}$ ions, chemisorbed oxygen (O$_β$) and oxygen vacancies on CeO$_2$-CS$_2$+COS surface, which also effectively enhances the redox cycle of Ce$^{4+}$/Ce$^{3+}$ ion pairs and increases the medium-strong acid sites. These all contributes to further improving the promotional effect of CS$_2$+COS low-temperature gas-phase sulfation on the NH$_3$-SCR activity of CeO$_2$. However, it is imperative to be noted that the introduction of excessive H$_2$O might result in a reduced diffusion of COS and CS$_2$ on the hydrolysis center of CeO$_2$ and weakens their interaction during the low-temperature gas-phase sulfation, negating the promotional effect of H$_2$O introduction on the NH$_3$-SCR activity of the CeO$_2$-CS$_2$+COS catalyst. The study can provide a scientific reference for the development of the CeO$_2$-based catalysts in the practical application of NH$_3$-SCR technology.

CRediT authorship contribution statement

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

**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).

**References**


[26] X. Sun, H.T. Ruan, X. Song, L.N. Sun, K. Li, P. Ning, C. Wang. Research into the reaction process and the


SO₂ treatment on nano-CeO₂ of different morphologies for selective catalytic reduction of NOₓ with NH₃. 

Morphology-Sensitive Sulfation Effect on Ceria Catalysts for NH₃-SCR. Top. Catal. 63 (2020) 932-943, 

http://dx.doi.org/10.1016/j.apcatb.2013.01.028.

Temperature Effects on the Catalytic Activity of CeO₂ in NH₃-Selective Catalytic Reduction Conditions. J. 

Sulfation Promotes the Performance of the Sulfated CeO₂ Catalyst for Low-Temperature Selective 
Catalytic Reduction of NOₓ by NH₃: Redox Property versus Acidity. ACS. Sustain. Chem. Eng. 9 (2021) 
967-979, https://doi.org/10.1021/acssuschemeng.0c08427.

NOₓ via Selective Adsorption and Activation of Reactants over Ce⁴⁺-SO₄²⁻ Pair Sites. ACS. Catal. 12 (2022) 
11306-11317, https://doi.org/10.1021/acscatal.2c02699.

[40] X.J. Yao, Z. Wang, S.H. Yu, F.M. Yang, L. Dong. Acid pretreatment effect on the physicochemical property 
http://dx.doi.org/10.1016/j.apcata.2017.06.003.


[55] B.M. Casaria, V. Langerb. New Structure Type among Octahydrated Rare-Earth Sulfates,
β-Ce\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}·8H\textsubscript{2}O, and a new Ce\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}·4H\textsubscript{2}O Polymorph. Z. Anorg. Allg. Chem. 633 (2007) 1074-1081, https://doi.org/10.1002/zaac.200700003.


[69] J. Li, H.S. Wu, B. Ma. Preparation of bimodal mesoporous silica containing cerious salt and its application


