The balance of acidity and redox capability over modified CeO$_2$ catalyst for the selective catalytic reduction of NO with NH$_3$

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ABSTRACT

The effect of acidity and redox capability over sulfuric acid-modified CeO$_2$ catalysts were studied for the selective catalytic reduction of NO$_x$ with NH$_3$ (NH$_3$-SCR). The deposition of sulfate significantly enhanced the catalytic performance over CeO$_2$. NO$_x$ conversion over 4H$_2$SO$_4$/CeO$_2$ at 230–440 °C was higher than 90%. The strong redox capability of CeO$_2$ could result in unselective NH$_3$ oxidation and decrease high temperatures catalytic activity and N$_2$ selectivity. The deposition of sulfate increased the acidity and weakened the redox capability, and then increased the high temperature NO$_x$ conversion and N$_2$ selectivity. An appropriate level of acidity also promoted the activity at 190–250 °C over ceria-based catalysts, and with further increase in the acidity, the SCR activity decreased slightly. Weak redox capability lowered the low-temperature catalytic activity. Excellent SCR activity requires a balance of acidity and redox capability on the catalysts.

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Introduction

Nitrogen oxides are important atmospheric pollutants, contributing to serious environmental problems (Bosch and Janssen, 1988; Qi et al., 2004). The selective catalytic reduction of NO$_x$ with NH$_3$ (NH$_3$-SCR) over V$_2$O$_5$-WO$_3$(MoO$_3$)/TiO$_2$ has been widely applied to remove NO$_x$ (Bosch and Janssen, 1988; Busca et al., 2005). However, the vanadia-based catalysts still presented several disadvantages, such as the toxicity and volatilization of V$_2$O$_5$ species, the narrow operating temperature window, high conversion of SO$_2$ to SO$_3$ and low N$_2$ selectivity at high temperatures (Balle et al., 2009; Busca et al., 1998; Dunn et al., 1998; Zhu et al., 2018). Consequently, the development of new non-vanadia based catalysts with excellent catalytic performance is of great urgency.

Cerium oxide (CeO$_2$) has attracted a lot of interests due to the excellent redox properties and strong oxygen storage capability (Bonin et al., 2015; Duan et al., 2018; Wang et al., 2015; Weng et al., 2016; Zhao et al., 2017). Some CeO$_2$-based catalysts, such as CeO$_2$-TiO$_2$ (Shan et al., 2012), CeWO$_4$ (Chen et al., 2011; Shan et al., 2015), Co-CeTi (Liu et al., 2017b) and Zr-CeVO$_4$ (Zhao et al., 2016), have shown good NH$_3$-SCR performance. The acidity of CeO$_2$ catalysts was found to be significantly enhanced by the introduction of tungstate (Chen et al., 2016), niobate (Qu et al., 2013), and sulfate (Zhang et al., 2016a), and which then increased the catalytic activity. The enhanced catalytic performance over...
H₂PO₄-modified CeO₂ was due to the reduction in redox ability and the increase in acidic strength (Yi et al., 2016). The interaction between phosphotungstic acid and CeO₂ contributed to excellent redox properties and favored the surface acidity of phosphotungstic acid-modified CeO₂ catalysts (Song et al., 2017). CeO₂ pretreated with different acids (HCl, HNO₃, HAc, H₂SO₄ and H₂PO₄) was studied, and the sample pretreated by H₂SO₄ was found to exhibit the best catalytic performance (Yao et al., 2017). The 2.5 wt.% SO₄²⁻/CeO₂ catalysts showed the highest catalytic activity and strong resistance to SO₂ and H₂O (Zhang et al., 2017). The CeO₂ catalyst was firstly synthesized via a hydrothermal route and then modified by H₂SO₄ using an impregnation method. The xH₂SO₄/CeO₂ catalyst showed excellent NH₃-SCR activity and strong resistance to H₂O and SO₂, due to the balance of acidity and redox capability.

In this study, acid modification of CeO₂ was conducted to study the coupling of acidity and redox capability of ceria-based catalysts. The CeO₂ catalyst was firstly synthesized via a hydrothermal process and then modified by H₂SO₄ using an impregnation method. The xH₂SO₄/CeO₂ catalyst showed excellent NH₃-SCR activity and strong resistance to H₂O and SO₂, due to the balance of acidity and redox capability.

### 1. Materials and methods

#### 1.1. Catalyst synthesis

The CeO₂ sample was synthesized by a hydrothermal method. First we dissolved Ce(NO₃)₃ and NaOH in deionized water, respectively and then mixed them to obtain a purple slurry. Subsequently it was transferred into a Teflon-lined stainless-steel autoclave at 120°C and held there for 12 hr. The deionized water and anhydrous ethanol were used to wash the fresh precipitates for removing any possible ionic remnants. Finally, the sample was dried at 60°C overnight and calcined in static air at 550°C for 4 hr.

Sulfuric acid-modified CeO₂ catalysts were prepared via an impregnation route. H₂SO₄ solutions with different concentrations were added to the CeO₂ carrier. After stirring, the mixtures were desiccated at 110°C overnight and calcined in static air at 500°C for 3 hr. The catalysts were designated as xH₂SO₄/CeO₂, where x = 1, 2 and 4 represent the SO₄²⁻ loadings of 7.5, 15 and 30 wt.% added in the process of preparation, respectively. The surface composition of ceria-based catalysts as determined by XPS is present in Table S1 in Supporting Information. Different amounts of sulfur existed in xH₂SO₄/CeO₂ and sulfur mainly existed on the surface.

#### 1.2. Characterization

A Quantachrome Autosorb iQ2 automatic adsorption instrument was applied to measure Nitrogen adsorption/desorption isotherms at −196°C. The samples were degassed at 300°C for 5 hr prior to N₂ physisorption. Surface area and pore structure were determined by the BET equation in the 0.05–0.30 partial pressure range and the Barrett-Joyner-Halenda (BJH) method from the desorption branches of the isotherms, respectively.

Powder XRD measurements were performed by a PANalytical B.V. X’Pert Pro XRD diffractometer using Cu Kα radiation at 40 mA and 40 kV. The 2θ data from 10 to 80° were recorded at 8°/min with the step size of 0.07°.

H₂-TPR experiments were conducted using a Quantachrome ChemStar analyzer. The samples (100 mg) were pretreated in Ar flow (100 ml/min) at 400°C for 30 min and then cooled down to 30°C followed by Ar purging. The reduction temperature was raised to 900°C at 10°C/min in H₂ (5 vol%)/Ar (100 ml/min).

O₂-TPD experiments were carried out on Micromeritics AutoChem 2920 Chemisorption Analyzer. A 100 mg sample was pretreated in He flow at 300°C for 30 min. The sample was then saturated with 5% O₂/He (50 ml/min) for 1 hr at 30°C and purged with He flow for 40 min. Finally, the sample was heated to 1000°C at the rate of 10°C/min in He flow (50 ml/min). The outlet exhaust was detected by TCD.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a PHI Quantum 2000 Scanning ESCA Microprobe with a monochromatized microfocused Al X-ray source. All the binding energies were calibrated using C1s as the reference energy (C1s = 284.6 eV).

#### 1.3. In situ DRIFTS studies

In situ DRIFTS experiments were conducted on an FTIR spectrometer (Thermo Fisher Nicolet iS50) equipped with a Smart Collector and an MCT/A detector cooled by liquid nitrogen. The sample was pretreated in a flow of 20 vol.% O₂/N₂ at 300°C for 30 min, then cooled down to 225°C, and subsequently purged with N₂ for background collection. The reaction conditions were controlled as follows: 300 ml/min total flow rate, 500 ppm NH₃ or 500 ppm NO + 5 vol.% O₂ and N₂ balance. All spectra were recorded by accumulating 100 scans with a resolution of 4 cm⁻¹.

#### 1.4. Activity tests

The NH₃-SCR activity tests over the ceria-based catalysts (40–60 mesh) were conducted in a fixed-bed quartz flow reactor. The inlet gases included 500 ppm NH₃ or/and 500 ppm NO, 5 vol.% O₂ and N₂ balance and GHSV 50,000 hr⁻¹. The effluent gases, including NH₃, NO, N₂O and NO₂, were analyzed by an FTIR gas analyzer (Thermo Fisher IGS).

### 2. Results

#### 2.1. Catalyst characterization

##### 2.1.1. BET and XRD results

The surface area and pore characterization results for ceria-based samples are shown in Table 1. The loading of sulfate on three xH₂SO₄/CeO₂ samples decreased the specific surface area and pore volume in all cases.

Fig. 1 presents the XRD results of ceria-based catalysts. The main peaks were assigned to CeO₂ with the cubic fluorite structure (43–1002) for all samples. The intensity of diffraction peaks for xH₂SO₄/CeO₂ catalysts was weaker than that of CeO₂, illustrating a loss of crystallinity. Due to the coverage and blockage of pores by sulfates, the specific surface area and crystallinity both decreased in the following sequence:

\[
\text{CeO}_2 < \text{xH}_2\text{SO}_4/\text{CeO}_2 < \text{H}_2\text{SO}_4/\text{CeO}_2
\]
CeO$_2$ > 1H$_2$SO$_4$/CeO$_2$ > 2H$_2$SO$_4$/CeO$_2$. In addition, low intensity diffraction peaks ascribed to Ce$_2$(SO$_4$)$_3$ (27–0573), Ce(SO$_4$)$_2$ (70–2097) and CeOSO$_4$ (39–0515) were observed for the 4H$_2$SO$_4$/CeO$_2$ catalyst, indicating the existence of sulfates. The formation of new crystalline phases led to the slightly greater surface area and stronger crystallinity of 4H$_2$SO$_4$/CeO$_2$ than 2H$_2$SO$_4$/CeO$_2$. No peaks due to sulfate species were observed over 1H$_2$SO$_4$/CeO$_2$ and 2H$_2$SO$_4$/CeO$_2$, which could be due to the small quantity of sulfate species in these samples.

2.1.2. H$_2$-TPR and O$_2$-TPD results
H$_2$-TPR experiments was conducted to study the redox properties of ceria-based catalysts and the results are exhibited in Fig. 2a. According to the literature (Lian et al., 2015; Peng et al., 2012), the reduction peaks between 300 and 550°C and between 700 and 900°C for the CeO$_2$ catalyst can be attributed to the reduction of surface Ce$^{4+}$ to Ce$^{3+}$ and bulk Ce$^{4+}$ to Ce$^{3+}$, respectively. A distinctive H$_2$ reduction peak at 550–650°C was detected over xH$_2$SO$_4$/CeO$_2$, which was mainly assigned to the reduction of sulfate (Lian et al., 2017; Yang et al., 2013), due to the fact that the H$_2$ consumption of Ce$^{4+}$ was small. It indicates that the catalyst was covered with a substantial amount of sulfate species. With increased sulfate loading on the catalysts, the reduction temperature became higher and the amount of H$_2$ consumption was larger. Although the amount of reducible species was larger, the reduction temperature for xH$_2$SO$_4$/CeO$_2$ was much higher than for CeO$_2$. The active temperature window in the NH$_3$-SCR reaction was below 500°C. In this temperature range CeO$_2$ presented stronger redox capability than xH$_2$SO$_4$/CeO$_2$.

O$_2$-TPD results are shown in Fig. 2b. An O$_2$ desorption peak ($\beta$) centered at 425°C appears on CeO$_2$. As for acid-modified samples, a distinct desorption peak ($\gamma$) is observed in the temperature range of 600–800°C. The $\beta$ and $\gamma$ desorption peak are attributed to the oxygen-vacancy adsorbed oxygen and O$^2$ stripped from lattice oxygen sites, respectively (Ma et al., 2015; Sui et al., 2017). The desorption of surface active oxygen at low temperature indicated that CeO$_2$ provides a better oxidation environment for NH$_3$-SCR of NO than acid-modified samples.

2.1.3. XPS results
The ceria-based catalysts were studied by XPS to understand the chemical states of oxygen present on the surface. Fig. 3 shows the XPS of O 1 s signals. The primary peaks at 528–532 eV were attributed to the lattice oxygen species (denoted as O$_{\text{latt}}$) and the additional shoulder peaks at 532–535 eV were assigned to the surface oxygen species (denoted as O$_{\text{surf}}$) (Andreoli et al., 2015; Liu et al., 2017a). The relative surface concentration ratios of O$_{\text{surf}}$/O$_{\text{latt}}$ for the ceria-based catalysts...
were also listed in Fig. 3. The O\(_2\) ratios increased in the following order: CeO\(_2\) < 1H\(_2\)SO\(_4\)/CeO\(_2\) < 2H\(_2\)SO\(_4\)/CeO\(_2\) < 4H\(_2\)SO\(_4\)/CeO\(_2\). This indicated that there is more abundant surface oxygen on xH\(_2\)SO\(_4\)/CeO\(_2\). However, the oxygen species from surface SO\(_4^{2-}\) presented low oxidation activity, from the H\(_2\)-TPR results.

The XPS spectra in Ce 3d region and the relative ratio of Ce\(^{3+}\) are shown in Fig. S1. The surface Ce\(^{3+}\) ratio on CeO\(_2\) was higher than acid-modified catalysts, which could favor to the formation of surface active oxygen. Therefore, CeO\(_2\) presents stronger redox capability, which is in accordance with the O\(_2\)-TPD results.

2.2. In situ DRIFTS

Fig. 4a presents the DRIFT spectra of NH\(_3\) adsorption on CeO\(_2\) and acid-modified CeO\(_2\) catalysts at 225°C. The surface of the catalysts were covered by several different ammonia species after NH\(_3\) adsorption. The peaks at 1432 cm\(^{-1}\) were ascribed to the bending vibrations of NH\(_4^+\) on Brønsted acid sites (Liu et al., 2017b; Yu et al., 2017; Zhang and Hou, 2016). The bands assigned to N-H stretching vibration region of coordinated NH\(_3\) on Lewis acid sites were also observed at 3390, 3260 and 3157 cm\(^{-1}\) (Ma et al., 2016; Zhang et al., 2015b). The negative band at 1362 cm\(^{-1}\) on xH\(_2\)SO\(_4\)/CeO\(_2\) derived from the coverage of sulfate species by NH\(_3\), while the coverage or hydration of part of the residual sulfate species by H\(_2\)O resulted in the negative band at 1385 cm\(^{-1}\) (Liu et al., 2011). The amount of acid sites increased in the following sequence: CeO\(_2\) < 1H\(_2\)SO\(_4\)/CeO\(_2\) < 2H\(_2\)SO\(_4\)/CeO\(_2\) < 4H\(_2\)SO\(_4\)/CeO\(_2\), indicating that the acidity on CeO\(_2\) surface was significantly improved by H\(_2\)SO\(_4\) modification, including Lewis acid sites and Brønsted acid sites. The NH\(_2\)-TPD results also indicated more acid sites of 1H\(_2\)SO\(_4\)/CeO\(_2\) than that of CeO\(_2\) (Fig. S2).

DRIFT spectra of NO + O\(_2\) adsorption on ceria-based catalysts at 225°C are shown in Fig. 4b. When CeO\(_2\) was exposed to NO + O\(_2\), several bands attributed to nitrate species were detected, including bridging nitrate (1210 and 1596 cm\(^{-1}\)), bidentate nitrate (1565 and 1249 cm\(^{-1}\)) and monodentate nitrate (1534 cm\(^{-1}\)) (Ma et al., 2016; Zhang et al., 2015a). There were no nitrate species adsorbed on xH\(_2\)SO\(_4\)/CeO\(_2\), in accordance with the NO-TPD results (Fig. S3). The formation of nitrate might be inhibited by the strong acidity of xH\(_2\)SO\(_4\)/CeO\(_2\).

To study the reactivity of adsorbed ammonia species in NH\(_3\)-SCR reaction on 4H\(_2\)SO\(_4\)/CeO\(_2\), in situ DRIFTS of the reaction between NO + O\(_2\) and pre-adsorbed NH\(_3\) at 225°C were recorded as a function of time (Fig. 5a). The surface was covered with several adsorbed ammonia species after exposure to NH\(_3\). When introducing NO + O\(_2\), we can see that the peaks attributed to adsorbed NH\(_3\) species diminished gradually. One band ascribed to H\(_2\)O at 1612 cm\(^{-1}\) (Lian et al., 2017) was detected at the same time. No nitrate species or other nitrogenous intermediates were observed on the surface during the whole reaction process, indicating an Eley–Rideal reaction mechanism between gaseous or weakly adsorbed NO and adsorbed NH\(_3\) species.

The above results exhibited that no adsorbed NO\(_x\) species formed on 4H\(_2\)SO\(_4\)/CeO\(_2\), in good accordance with the results shown in Fig. 5b. No bands assigned to adsorbed NO\(_x\) species were observed after NO + O\(_2\) adsorption at 225°C. When ammonia was introduced, bands attributed to NH\(_3\) adsorption species were detected, including ionic NH\(_4^+\) on Brønsted acid sites (1432 cm\(^{-1}\)) and N-H stretching vibration bands from coordinated NH\(_3\) (3390, 3260 and 3157 cm\(^{-1}\)). The results indicated that the reaction between adsorbed NO\(_x\) species and adsorbed NH\(_3\) species did not occur. Therefore, the NH\(_3\)-SCR reaction over the 4H\(_2\)SO\(_4\)/CeO\(_2\) catalyst mainly followed the Eley–Rideal mechanism, similar to the CeO\(_2\)-HF catalyst in literature (Yang et al., 2016).

2.3. Catalytic performance

NO\(_x\) conversion over the ceria-based catalysts is exhibited in Fig. 6a. The CeO\(_2\) catalyst exhibited low activity, with a
maximum NO\textsubscript{x} conversion of 60% at 330°C. The modification of CeO\textsubscript{2} by H\textsubscript{2}SO\textsubscript{4} led to a remarkable enhancement of NH\textsubscript{3}-SCR activity at 190–440°C. With further increase in the sulfate loading, NO\textsubscript{x} conversion decreased slightly at low temperature (190–250°C) and increased at high temperature (250–440°C). The N\textsubscript{2} selectivity also increased with the sulfate loading on the catalysts.

Previous studies have shown that at low temperatures the redox properties of a catalyst are the key factors governing the reactivity, while at high temperatures the surface acidity plays a crucial role in the NH\textsubscript{3}-SCR reaction (Li et al., 2008; Lietti, 1996; Liu et al., 2006). From the H\textsubscript{2}-TPR results, the onset temperature of H\textsubscript{2} reduction for CeO\textsubscript{2} was much lower than that of xH\textsubscript{2}SO\textsubscript{4}/CeO\textsubscript{2}. CeO\textsubscript{2} presented much stronger redox capability at low temperature than the sulfate-modified CeO\textsubscript{2} catalysts. Therefore, CeO\textsubscript{2} showed the highest NO oxidation activity. NH\textsubscript{3} oxidation over CeO\textsubscript{2} produced large amounts of NO, NO\textsubscript{2} and N\textsubscript{2}O, leading to the decrease of NO\textsubscript{x} conversion and N\textsubscript{2} selectivity at high temperature. The deposition of sulfate increased the acidity and weakened the redox capability of the catalysts. As a result, the separate NH\textsubscript{3} oxidation and separate NO oxidation activities decreased with the increase of sulfate loading. Therefore, NO\textsubscript{x} conversion and N\textsubscript{2} selectivity increased at high temperature. At the same time, the weaker redox capability at low temperature resulted in lower NO\textsubscript{x} conversion at 140–190°C for xH\textsubscript{2}SO\textsubscript{4}/CeO\textsubscript{2} than that for CeO\textsubscript{2}.

However, redox capability and acidity are both essential for SCR over ceria-based catalysts in the middle temperature range, such as 190–250°C. From the DRIFTs results, the deposition of sulfate strongly enhanced the acidity of CeO\textsubscript{2}. The presence of more acid sites favors the adsorption and activation of ammonia in NH\textsubscript{3}-SCR reaction and then enhances the catalytic performance. Therefore, the low-temperature NO\textsubscript{x} conversion of CeO\textsubscript{2} at 190–250°C was boosted notably after modification by sulfate. However, further increase in acidity led to a decline in the redox capability based on H\textsubscript{2}-TPR results, and the activity also decreased slightly.

Though CeO\textsubscript{2} showed high NO oxidation activity, NH\textsubscript{3} oxidation activity was low. This might be due to the fact that
CeO₂ has weak acidity and cannot adsorb and activate NH₃ effectively.

Strong redox capability could lead to the over-oxidation of NH₃ and decrease the NOₓ conversion and N₂ selectivity at high temperature. Strong acidity could enhance the catalytic activity and reduce the over-oxidation of NH₃. However, an excess of acid sites might cover part of the redox sites and result in a decrease in the low temperatures catalytic activity. Achieving appropriate redox capability and acidity simultaneously will result in an excellent NH₃-SCR catalyst.

4. Conclusions

To study the influence of the acidity and redox capability, CeO₂ catalysts were modified by H₂SO₄ using an impregnation method for the selective catalytic reduction of NOₓ by NH₃. A series of xH₂SO₄/CeO₂ catalysts all showed significantly better NH₃-SCR performance than CeO₂ at 190–440°C. CeO₂, with strong redox capability, showed low NOₓ conversion and N₂ selectivity at high temperature. With the increase of acidity, the high temperature activity and N₂ selectivity increased at 250–440°C. The appropriate level of acidity also enhanced the NH₃-SCR activity at 190–250°C. Too much acid sites could weaken the redox capability and decrease the catalytic activity slightly at low temperature. The proper balance of acidity and redox capability will result in an excellent NH₃-SCR catalyst.

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Appendix A. Supplementary data

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References


