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Sb-Containing Metal Oxide Catalysts for the Selective Catalytic Reduction of NO\textsubscript{x} with NH\textsubscript{3}

Qian Xu\textsuperscript{1}, Dandan Liu\textsuperscript{1}, Chuchu Wang\textsuperscript{1}, Wangcheng Zhan\textsuperscript{1}, Yanglong Guo\textsuperscript{1, ∗}, Yun Guo\textsuperscript{1}, Li Wang\textsuperscript{1, ∗}, Qingping Ke\textsuperscript{2} and Minh Ngoc Ha\textsuperscript{3}

\textsuperscript{1} Key Laboratory for Advanced Materials and Research Institute of Industrial Catalysis, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China; Y11140023@mail.ecust.edu.cn (Q.X.); Y30181049@mail.ecust.edu.cn (D.L.); wangyongchuchu@163.com (C.W.); zhanwc@ecust.edu.cn (W.Z.); ylguo@ecust.edu.cn (Y.G.); yunguo@ecust.edu.cn (Y.G.)

\textsuperscript{2} College of Chemistry and Chemical Engineering, Anhui University of Technology, Maanshan 243002, China; Qingke@ahut.edu.cn

\textsuperscript{3} VNU Key Laboratory of Advanced Material for Green Growth, VNU University of Science, Vietnam National University, Hanoi 100000, Vietnam; haminhngoc@hus.edu.vn

* Correspondence: wangli@ecust.edu.cn

Received: 30 August 2020; Accepted: 30 September 2020; Published: 8 October 2020

Abstract: Sb-containing catalysts (SbZrO\textsubscript{x} (SbZr), SbCeO\textsubscript{x} (SbCe), SbCeZrO\textsubscript{x} (SbCeZr)) were prepared by citric acid method and investigated for the selective catalytic reduction (SCR) of NO\textsubscript{x} with NH\textsubscript{3} (NH\textsubscript{3}-SCR). SbCeZr outperformed SbZr and SbCe and exhibited the highest activity with 80% NO conversion in the temperature window of 202–422 °C. Meanwhile, it also had good thermal stability and resistance against H\textsubscript{2}O and SO\textsubscript{2}. Various characterization methods, such as XRD, XPS, H\textsubscript{2}-TPR, NH\textsubscript{3}-TPD, and in situ diffuse reflectance infrared Fourier transform (DRIFT), were applied to understand their different behavior in NO\textsubscript{x} removal. The presence of Sb in the metal oxides led to the difference in acid distribution and redox property, which closely related with the NH\textsubscript{3} adsorption and NO oxidation. Bronsted acid and Lewis acid were evenly distributed on SbCe, while Bronsted acid dominated on SbCeZr. Compared with Bronsted acid, Lewis acid was slightly active in NH\textsubscript{3}-SCR. The competition between NH\textsubscript{3} adsorption and NO oxidation was dependent on SbO\textsubscript{x} and metal oxides, which were found on SbCe while not on SbCeZr.

Keywords: SbCeZr; NH\textsubscript{3}-SCR; active sites; mechanism

1. Introduction

Nitrogen oxide (NO\textsubscript{x}), one of the main environmental contaminants emitted from stationary sources and mobile sources, causes photochemical smog, acid rain, and the depletion of the ozone layer [1,2]. Several technologies have been proposed for NO\textsubscript{x} removal, such as direct decomposition of NO\textsubscript{x}, NO\textsubscript{x} storage reduction (NSR), and the selective catalytic reduction (SCR) process with ammonia (NH\textsubscript{3}-SCR) or hydrocarbons (HC-SCR). The NH\textsubscript{3}-SCR process has been proven to be the efficient method to satisfy the restrict regulations of NO\textsubscript{x} emissions [3]. In general, the NH\textsubscript{3}-SCR reaction is a competitive process between NH\textsubscript{3} oxidation and NO\textsubscript{x} reduction, which are closely affected by reaction temperature. The enhanced oxidation activity at low temperature promotes NO\textsubscript{x} selective reduction, while it also takes a risk for the depletion of NH\textsubscript{3} at high temperature leading to the decrease in NO reduction. Meanwhile, the reaction thermal shock and exhaust components (H\textsubscript{2}O and SO\textsubscript{2}) put forward strict requirements on the design of NH\textsubscript{3}-SCR catalysts.

CeO\textsubscript{2} possesses unique oxygen storage-release capability by the formation of Ce\textsuperscript{3+}/Ce\textsuperscript{4+} redox couples [4], but the maximum NO conversion on CeO\textsubscript{2} was about 30% in the whole temperature range.
range. Compared with mono-metal oxides, dual metal oxides have been more active in NO abatement. The presence of Ti, W, Mo, Mn, and Nb can efficiently broaden the temperature window, especially the introduction of W. Nearly 100% NO\textsubscript{x} conversion could be achieved on CeWO\textsubscript{x} in a wide temperature range (250–425 °C) under a rather high gas hourly space velocity (GHSV) (500,000 h\textsuperscript{-1}). The effects of SO\textsubscript{2} on the SCR over CeO\textsubscript{2} was strongly dependent on the SO\textsubscript{2} content and reaction conditions. An appropriate level for sulfated pretreatment can promote SCR, and the presence of excess SO\textsubscript{2} shows obvious negative effects. Li studied that SO\textsubscript{2} was preferentially bonded with CeO\textsubscript{2} as sulfate species leading to a significant decrease in reducibility and the loss of surface active oxygen groups [5]. Suitable sulfation promoted NH\textsubscript{3} adsorption and favored the formation of oxygen vacancies which facilitated NH\textsubscript{3}-SCR [6]. Hong’s research indicated that the optimal condition for sulfation treatment was 800 ppm SO\textsubscript{2} 1 h at 500 °C [7]. Meanwhile, the thermal stability of the sulfated Ce-based catalyst needs to be further improved [8].

Sb compounds are generally classified into the valences of +3 and +5, in which the oxidation state of +5 is more stable. The Sb-containing oxides are Sb\textsubscript{2}O\textsubscript{3}, Sb\textsubscript{2}O\textsubscript{5}, and mixed oxide Sb\textsubscript{2}O\textsubscript{4} that is composed of Sb\textsuperscript{3+} and Sb\textsuperscript{5+} [9]. Sb has been widely used as a promoter for NH\textsubscript{3}-SCR catalysts [6,7]. The surface acid and the redox capability are generally considered to be two necessary factors for NH\textsubscript{3}-SCR catalysts [10–12]. The addition of Sb can improve the dispersion of active species [13] and increase acid sites and the redox property [14], which are due to the strong interaction between SbO\textsubscript{x} and other metal oxides [15,16]. Besides the promotion in activity, the resistance of K\textsubscript{2}O poisoning [17] and SO\textsubscript{2} are also found [18] in Sb-containing catalysts. The role of Sb as a promoter reflects in minimizing the binding affinity between the catalytic surface and the ammonium (bi)sulfates species, which is beneficial for the low-temperature SO\textsubscript{2} resistance [19].

The substitution of Ce\textsuperscript{4+} by Zr\textsuperscript{4+} helps create structural defect, accelerating oxygen diffusion and the formation of surface oxygen species [20], which can consequently promote the redox property [21,22]. CeZrO\textsubscript{x} mixed oxide with remarkable thermal stability shows an enormous advantage in NH\textsubscript{3}-SCR [23,24]. In this study, Sb-containing metal oxides (SbZr, SbCe, SbCeZr) were prepared by citric acid method and investigated for NO\textsubscript{x} removal by NH\textsubscript{3}-SCR. The SbCeZr exhibited higher catalytic activity than SbCe and SbZr catalysts, especially in the presence of H\textsubscript{2}O and SO\textsubscript{2}. The correlation between physicochemical properties and SCR performance was explored by various characterization techniques, and the mechanism was also studied using in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFT).

2. Results and Discussion

2.1. Catalyst Activity

2.1.1. NH\textsubscript{3}-SCR Performance

NO\textsubscript{x} conversions over the catalysts as a function of temperature are illustrated in Figure 1a. Pristine SbO\textsubscript{x} and SbZr showed negligible catalytic activity with NO\textsubscript{x} conversion below 10% in the whole temperature range. Even for CeO\textsubscript{2}, the maximum NO\textsubscript{x} conversion was only 29% at 360 °C. The addition of Sb promoted the NO\textsubscript{x} conversion over Ce-containing catalysts, and SbCeZr exhibited better NH\textsubscript{3}-SCR performance than SbCe. The temperature for 50% conversion (T\textsubscript{50}) was 175 °C over SbCeZr, which was lower than that of SbCe (223 °C). The operation temperature window (NO\textsubscript{x} conversion over 80%) was 202–422 °C over SbCeZr, while it was 261–407 °C over SbCe.
The apparent activation energy of the NH$_3$-SCR reaction is an important factor to evaluate the role and efficiency of the catalyst in the reaction [25]. By calculating the reaction rate constant of the NH$_3$-SCR reaction over SbCeZr and SbCe, the apparent activation energy of the catalysts were obtained. The reaction activation energy over the SbCeZr catalyst (33.3 kJ/mol) was lower than that of the SbCe catalyst (42.1 kJ/mol), which further confirmed the excellent NH$_3$-SCR reaction performance of SbCeZr.

In order to investigate the thermal stability of SbCeZr and SbCe, the catalysts were aged at 700 °C for 4 h in the air before testing. As shown in Figure 1b, aging had a side effect on catalytic activity, which led to the loss in activity and shrink from the operation temperature window. The presence of Zr improved the thermal resistance of thermal shock. $T_{50}$ of aged SbCeZr turned out to be 247 °C and the operation temperature window narrowed to 300–413 °C, resulting from the sintering. The maximum NO$_x$ conversion over aged SbCe was only 73% at 373 °C, i.e., aging led to the significant deactivation.

2.1.2. Effects of H$_2$O and SO$_2$

SO$_2$ and H$_2$O are unavoidable in the feed gas, so the effect on the catalytic activities over SbCeZr and SbCe were investigated. As shown in Figure 2a, the NH$_3$-SCR performance of SbCeZr was slightly affected by SO$_2$ or H$_2$O at temperatures below 220 °C. However, the presence of H$_2$O significantly reduced the catalytic activity at temperatures above 420 °C, which could be attributed to the competitive adsorption between H$_2$O and NH$_3$ [26,27]. In the presence of O$_2$ and SO$_2$, the deposited sulfates on the catalysts led to the decrease of the specific surface area (SSA) [28] and blocked the active sites at low temperature [29]. With increased temperature, the decomposition of sulfates led to the restoration of active sites [30]. The presence of H$_2$O facilitated SO$_2$ oxidation at low temperature and inhibited sulfate decomposition at high temperature. Therefore, the presence of H$_2$O and SO$_2$ had a more detrimental effect than H$_2$O or SO$_2$.

The presence of SO$_2$ on SbCe had an influence similar to that on SbCeZr. Unfortunately, the presence of H$_2$O had a detrimental effect on NH$_3$-SCR performance over SbCe. The light-off temperature ($T_{50}$) shifted to 284 °C, and the maximum NO$_x$ conversion was only 66% at 370 °C. When both H$_2$O and SO$_2$ were introduced simultaneously, the synergy effect made the NH$_3$-SCR performance drop even more. $T_{50}$ shifted to high temperature and the maximum NO$_x$ conversion also decreased accordingly. The decrease of NH$_3$-SCR performance was not only related to the formation of ammonium salt on the catalyst surface but also connected with the fact that the active phase was sulfated and then formed stable sulfate species [31].

**Figure 1.** (a) NO$_x$ conversions and (b) thermal stability over the catalysts (reaction conditions: 500 ppm NO, 500 ppm NH$_3$, 5% O$_2$, with Ar balance).
Furthermore, repeated temperature ramps (three times) containing SO\textsubscript{2} over the SbCeZr catalyst and the SbCe catalyst were also conducted. For SbCeZr, the second time was consistent with the third time, and slightly less active than the first time below 250 °C. It suggests that SbCeZr had a better performance of resistance to SO\textsubscript{2} for SbCe, during the three test ramps, the T\textsubscript{80} kept shifting to higher temperatures, which narrowed the operation window.

2.2. Catalyst Characterization

2.2.1. XRD

The XRD patterns of the fresh and aging catalysts are shown in Figure 3. The XRD patterns of CeO\textsubscript{2} and ZrO\textsubscript{2} showed sharp diffraction peaks corresponding to CeO\textsubscript{2} with a cubic fluorite structure (JCPDS 34-0394, 2\textdegree = 28.6°, 47.5°, and 56.4°) and tetrahedral ZrO\textsubscript{2} (JCPDS 50-1089, 2\textdegree = 30.1°, 50.4°, and 60.0°). The typical peaks at 19.8°, 25.7°, and 29.0° over SbO\textsubscript{x} were observed and assigned to Sb\textsubscript{2}O\textsubscript{4} (JCPDS 11-0694). Compared with the XRD pattern of CeO\textsubscript{2}, the diffraction peaks of CeZr shifted to high angles, suggesting that Zr was incorporated into the CeO\textsubscript{2} crystal lattice to form a CeZrO\textsubscript{4} solid solution.

With the introduction of Sb, the diffraction peaks were broadened and weakened, which led to the absence of obvious peaks. No diffraction peaks related to SbO\textsubscript{x} were detected, and a completely amorphous structure was formed on the Sb-containing catalysts. Compared with the fresh samples,
the diffraction peaks of aged catalysts (aging at 700 °C in air for 4 h) intensified, indicating the increase in the grain size.

According to Table 1, the specific surface area (SSA) of SbCeZr (73 m²/g) was slightly higher than that of SbCe (68 m²/g). Combining the value of specific surface area (Table 1) with activity showed that specific surface area was not the decisive factor in catalyst activity. It thus suggested that other factors were affecting activity. The loss of SSA was found after aging, especially on SbCe. The SSA of SbCe-700 °C was only 9 m²/g, which was only 13% of fresh SbCe. However, 57% SSA of SbCeZr was lost after aging. Combining the results of XRD and SSA showed that SbCeZr possessed the higher thermal stability as compared to SbCe.

![Table 1. Brunauer–Emmett–Teller (BET) specific surface area (SSA), bulk phase, and surface atom concentration of the catalysts.](image1)

| Sample  | S_BET (m²/g) | Sb/(Ce+Zr) | Surface Atom Concentration (%) | Sb/(Ce+Zr) | Sb⁵⁺/Sb | Ce³⁺/Ce | O1s/Oα + Oβ |
|---------|--------------|------------|-------------------------------|-------------|---------|---------|-------------|
| SbO₂    | -            | -          | Sb/(Ce+Zr)                   | 50.3        | -       | 38.1    |             |
| SbZr    | 32           | 0.68       | Sb⁵⁺/Sb                      | 1.09        | 55.3    | -       | 33.4        |
| SbCe    | 68           | 1.02       | Ce³⁺/Ce                      | 1.59        | 62.2    | 32.9    | 40.6        |
| SbCeZr  | 73           | 0.57       | O1s/Oα + Oβ                  | 0.66        | 64.3    | 42.1    | 47.8        |

*Specific surface area determined by N₂ adsorption-desorption. Sb/(Ce+Zr) mole ratio detected by ICP-AES. Surface atom concentration detected by XPS analysis.

**2.2.2. XPS**

Figure 4 presented the XPS spectra of Sb 3d, Ce 3d, and O 1s for Sb-containing catalysts, and the surface atom concentration and chemical state are summarized in Table 1. For the SbCeZr catalyst, the bulk phase mole ratio of Sb/(Ce + Zr) was 0.57, slightly lower than the surface atom concentration ratio 0.66. However, as for the SbCe catalyst and SbZr catalyst, the bulk phase mole ratio was much lower than the surface concentration. These results indicated that more Sb existed on the surface of CeO₂ and ZrO₂ over SbCe and SbZr, while more Sb was incorporated into the CeZrO₃.

![Figure 4. XPS spectra for (a) Sb3d, (b) Ce3d, and (c) O1s over the catalysts.](image2)

Figure 4a showed the Sb 3dᵢ/₂ spectra of Sb-containing catalysts and SbOₓ. Because of the O 1s and Sb 3dₗ/₂ photoemission line overlapping around 530.0 eV, the Sb3dᵢ/₂ spectra at higher binding energy were used. This peak could be separated into two contributions—the Gaussian line centered at 540.4 eV corresponds to antimony with an oxidation state of Sb⁵⁺, while the peak at 539.6 eV corresponds to Sb³⁺ [9,16,32]. As shown in Table 1, the proportion of Sb⁵⁺ increase followed the order of SbOₓ < SbZr < SbCe < SbCeZr. The ratio of Sb⁵⁺ over SbOₓ was 50.3%, meaning an equal proportion of Sb⁵⁺ and
Sb\textsuperscript{3+}, i.e., Sb\textsubscript{2}O\textsubscript{4} was the main species in SbO\textsubscript{x}, which was in line with the XRD results. It was obvious that the concentration of Sb\textsuperscript{5+} over the SbCeZr was significantly improved to 64.3%.

Figure 4b presents the Ce 3d spectra of the catalysts. The Ce 3d peaks could be deconvoluted into four pairs of spin-orbit doublets. Four main peaks in 3d\textsubscript{3/2} at 881.9, 884.9, 887.8, and 898.0 eV were labeled as V, V', V'', and V''', respectively. The four main peaks in 3d\textsubscript{5/2} at 900.8, 903.0, 907.4, and 916.2 eV were labeled as U, U', U'', and U''', respectively. The peaks labeled as V' and U' corresponded to Ce\textsuperscript{3+} and the other peaks labeled as V, V'', U, U'', and U''' corresponded to Ce\textsuperscript{4+} [12,33]. From the Ce 3d XPS spectra, it could be concluded that the Ce\textsuperscript{3+} and Ce\textsuperscript{4+} species coexisted in all the samples, and the ratios of Ce\textsuperscript{3+/Ce\textsuperscript{4+} + Ce\textsuperscript{3+}} of all the catalysts are listed in Table 1. The Ce\textsuperscript{3+/Ce\textsuperscript{4+} + Ce\textsuperscript{3+}} ratio over SbCeZr (42.1%) was higher than that over SbCe (32.9%). The presence of Sb\textsuperscript{5+} led to the increase of the Ce\textsuperscript{3+} concentration due to the redox reaction Sb\textsuperscript{5+} + Ce\textsuperscript{3+} ↔ Sb\textsuperscript{5+} + Ce\textsuperscript{4+}. The transformation of Ce\textsuperscript{4+} to Ce\textsuperscript{3+} created the charge imbalance and oxygen vacancy, facilitating the adsorption of oxygen species or activation of reactants in NH\textsubscript{3}-SCR [34].

The O 1s spectra of all the catalysts are displayed in Figure 4c. The spectra were deconvoluted into two peaks. The peak at 530.2 eV was attributed to lattice oxygen (O\textsubscript{β}), and the other one at around 531.2 eV was denoted to surface chemisorbed oxygen (O\textsubscript{α}). O\textsubscript{α} species usually correlated with oxygen defects or surface oxygen, such as O\textsubscript{2−} or O\textsuperscript{2−} [35–37]. The relative ratios of O\textsubscript{α}/(O\textsubscript{α} + O\textsubscript{β}) by peak deconvolution over the samples were 47.8%, 40.6%, and 33.4% over SbCeZr, SbCe, and SbZr, respectively, suggesting more surface chemisorbed oxygen formed over SbCeZr.

2.2.3. H\textsubscript{2}-TPR

The redox property of catalysts plays an important role in the NH\textsubscript{3}-SCR reaction [37,38]. Figure 5 shows the H\textsubscript{2}-TPR profiles of the catalysts. CeO\textsubscript{2} showed two reduction peaks centered at 474 and 781 °C, which were attributed to the reduction of surface oxygen and bulk oxygen of CeO\textsubscript{2}, respectively [22,39]. SbO\textsubscript{x} also showed two reduction peaks centered at 616 and 701 °C, which could be ascribed to the reduction of Sb\textsuperscript{5+} to Sb\textsuperscript{3+} and Sb\textsuperscript{3+} to Sb\textsuperscript{0}, respectively [9]. The reduction profiles of SbZr were similar to those of SbO\textsubscript{x} with the reduction temperature shifting to lower temperature.

![Figure 5. H\textsubscript{2}-TPR profiles of the catalysts.](image-url)
SbOₓ and CeO₂, which also led to the higher reduction temperature. By contrast, with the help of ZrO₂, the strong interaction between SbOₓ and CeO₂ was weakened, resulting in the lower onset reduction temperature of active oxygen.

2.2.4. NO-TPD

NO-TPD experiments were performed to investigate the adsorption and oxidation properties of NOₓ on different catalysts. NO-TPD profiles and the calculated NOₓ adsorption capacity are presented in Figure 6 and Table 2, respectively. The NO desorption peak below 100 °C was attributed to physical adsorbed NO, and the one at about 260 °C was attributed to chemical adsorbed NO [34]. Since the strength of NO bonding to the ceria surface depends on the reduction degree of support (unsaturated sites) [41], it could be concluded that the Ce³⁺ content on the SbCeZr surface was much higher than that of SbCe, which was consistent with the XPS result.

Table 2. H₂ consumption, NH₃ desorption amount, and strong acid and NOₓ adsorption capability of the catalysts.

| Sample   | H₂ Consumption * (mmol/g) | NH₃-TPD Result b | NOₓ Adsorption Capability c (mmol/g) |
|----------|---------------------------|------------------|-------------------------------------|
|          | Acid Amount (mL/g) | B/(A + B + C + D) | (C + D)/(A + B + C + D) | NOₓ | NO₂ |
| SbZr     | 5.17                    | 0.78             | 0.38                               | 0.27 | 138.7 | 15.8 |
| SbCe     | 4.30                    | 0.95             | 0.34                               | 0.30 | 63.5  | 8.6  |
| SbCeZr   | 3.81                    | 1.46             | 0.40                               | 0.29 | 147.7 | 46.7 |

* The amount of H₂ consumption quantified by CuO as a calibration reference. b Acid amount and acid ratio calculated by NH₃ desorption peak area in NH₃-TPD. c NOₓ adsorption capability calculated from NO-TPD.

Figure 6. NO-TPD profiles of the catalysts.

NO₂ came from the oxidation of adsorbed NO by active oxygen on the catalyst surface. The desorption temperature and peak area correlated with the adsorption strength and oxidation ability of NO. The ability of the catalyst for oxidizing NO to NO₂ plays an important role in improving the catalytic activities since it can promote the occurrence of the “fast SCR” reaction [42,43]. Considering the temperature range of the NH₃-SCR reaction, the desorbed peaks in the temperature range of 150–400 °C were mainly discussed.

The main NOₓ desorption peak of SbCe was at 245 °C, slightly lower than those of SbCeZr (258 °C) and SbZr (273 °C). The calculated NOₓ amount was in the order of the following sequence: SbCeZr > SbZr > SbCe. There were no obvious differences in the NOₓ desorption amount between SbCeZr and SbZr, but the amount of NOₓ desorption on SbCeZr was almost 2 times higher than that of SbCe. It is worth mentioning that 31.7% NO converted to NO₂ on SbCeZr, while only 13.5% NO did so on SbCe. With the help of NO₂, the “fast SCR” occurred and facilitated NOₓ removal.
2.2.5. NH₃-TPD

Surface acidity of the catalysts plays a key role in the adsorption and activation of NH₃ [44,45]. NH₃-TPD experiments were conducted to characterize the acid amount and strength according to peak area and desorption temperature, and the profiles are shown in Figure 7. Four broad peaks could be observed in the NH₃-TPD profiles in the temperature range of 100–450 °C. NH₃ desorption peaks at low temperature (<200 °C) were associated with NH₃ desorption from weak acid sites derived from coordinatively unsaturated Ceⁿ⁺ or Zrⁿ⁺ sites [46,47], and the peaks in the temperature range of 200–300 °C were assigned to the dissociation of NH₄⁺ on Brønsted acid sites associated with surface hydroxyl groups. The peaks at temperatures higher than 300 °C were denoted as NH₃ desorption from strong Lewis acid [48–50]. The original weak Lewis acidity of CeO₂ and ZrO₂ was also increased by SbOₓ loading, which could be attributed to the electron withdrawing of SbOₓ species in proximity of Ceⁿ⁺/Zrⁿ⁺ Lewis acid sites. The NH₃ species desorbed from acid sites (>200 °C) played a decisive role in the NH₃-SCR reaction [51,52].

The nature of the active sites could be assessed based on the quantity of sites and their intrinsic activity [49]. Quantitative analysis was employed to compare the amount of acid sites, and the ratios of different species based on the deconvoluted results are also shown in Table 2. The amount of acid sites had the following sequence: SbCeZr > SbCe > SbZr. The large total acid amount was found over SbCeZr (1.46 mL/g), which was nearly 2 times as much as that on SbZr (0.78 mL/g). It suggested that the interaction among the catalyst components facilitated the increase in acid amount.

![Figure 7. NH₃-TPD profiles of the catalysts.](image)

2.3. In Situ DRIFT

2.3.1. Adsorption of NH₃

The adsorption and activation of NH₃ play an important role in the NH₃-SCR reaction [53]. The adsorption of NH₃ was investigated by in situ DRIFT shown in Figure 8. The bands at 3166, 3241, and 3357 cm⁻¹ were assigned to N-H stretching vibration modes of the coordinated NH₃ [54,55]. The bands at 1198 and 1599 cm⁻¹ were attributed to coordinated NH₃ linked to Lewis acid sites (NH₃-L) [34,56], and the bands at 1440 and 1689 cm⁻¹ were assigned to asymmetric and symmetric bending vibrations of NH₄⁺ bound to Brønsted acid sites (NH₄⁺-B) [15,40,50]. The band at 1258 cm⁻¹ was assigned to the deformation vibration of NH₃ bonded to Lewis acid [57].
which further confirmed the occurrence of the reaction.

The further investigation on the consumption rate of NH$_3$ was found over SbCeZr, presenting the strong NH$_3$ (3624 cm$^{-1}$) adsorption and activation of NH$_3$ for SCR reaction [58]. The adsorption and activation of NH$_3$ deformation vibration of NH$_3$-$B$ species (1429, 1679 cm$^{-1}$) the SbCeZr and (1450, 1689 cm$^{-1}$) the SbCe catalysts after NH$_3$ adsorption on SbCeZr. After exposure in NH$_3$ for 60 min, the di

Figure 8. The in situ diffuse reflectance infrared Fourier transform (DRIFT) of NH$_3$ adsorption over (a) the SbCeZr and (b) the SbCe catalysts at 200 °C.

NH$_4^+$-B species (1440 cm$^{-1}$) appeared after exposing in NH$_3$ for 8 min over SbCeZr as shown in Figure 8a, and the adsorbed band turned intensive with the consumption of surface hydroxyl groups (3624 cm$^{-1}$). However, the appearance of NH$_3$-L species (1198 cm$^{-1}$) lagged behind. Unlike SbCeZr, NH$_4^+$-B species (1429, 1679 cm$^{-1}$) and NH$_3$-L species (1167, 1256 cm$^{-1}$) were observed synchronously over SbCe (Figure 8b). Compared with SbCe, an obvious blue shift of NH$_3$ adsorption on acid sites was found over SbCeZr, presenting the strong NH$_3$ adsorption on SbCeZr. After exposure in NH$_3$ for 60 min, the difference in the distribution of NH$_4^+$-B and NH$_3$-L species was found. It should be recalled that a great discrepancy was noticed for the bands of NH$_4^+$-B and NH$_3$-L species in two samples. By calculating the band intensity of NH$_3$ adsorption, a high proportion of NH$_4^+$-B species was found on SbCeZr, while the proportions of NH$_4^+$-B and NH$_3$-L species on SbCe were similar. The presence of abundant Brønsted and Lewis acid sites on the SbCeZr catalyst should be responsible for the improvement in SCR activities over a wide temperature range [58].

2.3.2. Adsorption of NH$_3$ Followed by Introduction of NO + O$_2$

The spectra of introducing NO + O$_2$ into the catalysts after NH$_3$ adsorption as a function of time were recorded and are shown in Figure 9. The decrease of NH$_4^+$-B and NH$_3$-L species on SbCeZr with the introduction of NO + O$_2$ presented the reaction between NO$_x$ and adsorbed NH$_3$ species (Figure 9a). The intensities of the bands ascribable to NH$_3$-L and NH$_4^+$-B species were reduced after NH$_3$ adsorption, showing that these surface species were able to react with the mixture of NO and O$_2$ at 200 °C. A deeper insight into the reduction of band intensity with the reaction time over the catalysts was essential. The further investigation on the consumption rate of NH$_3$-L and NH$_4^+$-B species showed the slightly faster disappearance of NH$_3$-L species than NH$_4^+$-B species in the reaction. Extending the exposure time led to the appearance of nitrate species, such as bridged nitrate (1605 and 1247 cm$^{-1}$) [59], bidentate nitrate (1579, 1559, and 1516 cm$^{-1}$) [55], and monodentate nitrate (1541 cm$^{-1}$) [60]. The recovery of the negative broad band of surface hydroxyl groups (3441 cm$^{-1}$) was attributed to the formation of water, which further confirmed the occurrence of the reaction.
Figure 9. The in situ DRIFT of NO + O₂ reacting with preadsorbed NH₃ species over (a) the SbCeZr and (b) the SbCe catalysts at 200 °C.

As shown in Figure 9b, the phenomenon that occurred on SbCe was similar to that on SbCeZr, i.e., the appearance of nitrate species at the expense of the disappearance of adsorbed NH₃. The disappearance of NH₃-L species confirmed that NH₃-L species could be involved in the reaction, and NH₃-L species were slightly active compared with NH₄⁺-B species. The adsorbed NH₃ on the catalyst surface reacted with NO/NO₂ in the gas phase, following the Eley-Rideal (E-R) mechanism.

2.3.3. Co-Adsorption of NO + O₂

The adsorption of NO + O₂ was investigated by in situ DRIFT. As shown in Figure 10a, bridged nitrate (1245, 1606 cm⁻¹), bidentate nitrate (1579, 1559, 1519 cm⁻¹), and monodentate nitrate (1539 cm⁻¹) were formed on SbCeZr after exposure to NO + O₂ for 30 min. The NH₃ adsorption rate was much faster than the NO₃⁻ generation rate. With the exposure time prolonged, the bands of nitrate intensified accordingly. Bridged nitrate seemed dominant in all the kinds of nitrates. In the case of SbCe (Figure 10b), rather weak bands of nitrates were observed after the exposure to the same feed gas for the same time, and the adsorption intensity of bridged nitrate was rather weaker than that of the monodentate and bidentate nitrates. It could be seen that Sb interacted with different metals (Ce or CeZr), resulting in the difference in the NO₃⁻ species distribution on the catalyst surface.

Figure 10. The in situ DRIFT of NO + O₂ co-adsorption over (a) the SbCeZr and (b) the SbCe catalysts at 200 °C.
2.3.4. Adsorption of NO + O₂ Followed by Introduction of NH₃

Compared with the results of NO + O₂ reacting with preadsorbed NH₃ (Figure 9), the effects of adding NH₃ to preadsorbed NO + O₂ (Figure 11) on activity were not so obvious. It is worth mentioning that a new band linked to NH₄⁺-B species (1440 cm⁻¹) gradually formed over SbCeZr as the exposure time increased. However, the bands linked to NH₃-L (1599 and 1198 cm⁻¹) were not detected. Therefore, the formed nitrate species had detrimental effects on NH₃ adsorption on Lewis sites, but negligible effects on NH₃ adsorption on Brønsted acid sites.

![Figure 11. The in situ DRIFT of NH₃ reacting with preadsorbed NO + O₂ over (a) the SbCeZr and (b) the SbCe catalysts at 200 °C.](image)

On the contrary, there were no bands related to NH₃ adsorption over SbCe even after prolonging the exposure time up to 30 min. The phenomena illustrated that the formed nitrate species significantly inhibited NH₃ adsorption. Combined with the results of Figure 11, this indicated that NH₃ adsorption and NO₃ oxidation could be competitive on SbCe, but not on SbCeZr.

2.4. Discussion

NO₃ conversions over CeO₂ and SbOₓ were very low, but it increased significantly when they were combined together. Compared with CeO₂, the reason for the improvement of catalytic activity over SbCeOₓ was due to alleviating nitrate adsorption and leaving more active sites for NH₃ adsorption and activation [40]. Considering the competitive adsorption between NH₃ and nitrate species, we prepared SbCeZr and investigated it for NH₃-SCR performance. SbCeZr outperformed SbCe not only in activity and stability but also in SO₂ and water tolerance. SbCeZr exhibited high activity with NOₓ conversion over 80% in the temperature range of 202–422 °C. The introduction of H₂O and SO₂ had little influence on the activity of SbCeZr, but an adverse effect on the catalytic activity of SbCe was found.

The presence of Zr influenced the distribution of Sb on the surface or bulk. According to ICP-AES and XPS results (Table 1), the surface amount of Sb on SbCe was much higher than that on SbCeZr, displaying the enrichment of Sb on the SbCe surface. However, H₂-TPR indicated the strong interaction between SbOₓ and CeO₂. Unlike SbCe, the presence of Zr made the distribution of Sb, Ce, and Zr uniform and weakened the interaction between SbOₓ and CeO₂. The weakened interaction also brought about abundant Sb⁵⁺ species on the catalyst surface (Table 1) and the lower onset reduction temperature of active oxygen (Figure 5). Furthermore, the generation of NOₓ during NO-TPD (Figure 6) also illustrated the enhancement in reducibility, which facilitated the “fast SCR” reaction during NH₃-SCR [32].

The adsorption of NH₃ on the catalyst surface was considered as the initial step of the NH₃-SCR reaction [15], so NH₃ adsorption played an important role during NOₓ removal. Compared with SbCe, NH₃ adsorption was enhanced on SbCeZr, which was attributed to the increase of Brønsted and Lewis
acid amounts (Figure 7). The acid distribution on the catalysts was different. The amount of Brønsted acid was higher than the amount of Lewis acid on SbCeZr, whereas the amount of Brønsted acid was similar to that of Lewis acid on SbCe. Meanwhile, in situ DRIFT experiments of NH₃ adsorption also confirmed the strong adsorption of NH₃ and the faster adsorption rate on SbCeZr (Figure 8). The reaction rate of NOₓ with NH₃ adsorbed on Lewis acid was slightly faster than that with NH₄⁺ adsorbed on Brønsted acid (Figure 9) (E-R mechanism).

It is worth mentioning that the formed nitrates had negligible effects on the adsorption of NH₃ over SbCeZr; however, detrimental impacts were found over SbCe. It meant that NO oxidation and NH₃ adsorption were both around Ce⁺⁺⁺ sites, so there was competition between them. Amorphous ZrO₂ possessed abundant hydroxyl [61], which showed obvious acidity properties. Then, the strong withdrawing effects of SbOₓ further increased the acid amount and strength of ZrO₂, which was confirmed by the high NH₃ desorption amount (Figure 7). Therefore, the separation of active sites alleviated the competition effects between NO oxidation and NH₃ adsorption, thus promoting NOₓ removal.

Given the above discussion, it was shown that the strong acid and weak reducibility of SbZr made it less active in NH₃-SCR. However, a strengthened interaction was found between SbOₓ and CeO₂, favoring NOₓ removal. Unfortunately, the competition between NO oxidation and NH₃ adsorption on the same active sites still needed to be alleviated to improve its thermostability and activity in the presence of H₂O and SO₂. In the presence of ZrO₂, NH₃ adsorption and NO oxidation on different active sites widened the operation window.

3. Materials and Methods

3.1. Catalyst Preparation

The SbCe, SbCeZr, and SbZr catalysts, where the molar ratio of Sb/Ce and Zr/Ce was 1.0, were prepared by the citric acid method. First, Sb(CH₃COO)₃ was dissolved in a solution of citric acid, then Zr(NO₃)₄ and Ce(NO₃)₄ were added. The molar ratio of citric acid to total metal components (the sum of Ce, Zr, and Sb) was 1.5. Then, the resultant mixture was stirred at 80 °C in a water bath until forming a gel. The gel was dried at 110 °C for 12 h to form a porous, foamlike solid. Finally, the precursor was calcined at 500 °C for 3 h in a muffle furnace (SX2, Shanghai Pudong Rong-Feng Scientific Instrument Co. Ltd., Shanghai, China). After calcining, the sample was crushed and sieved to 40–60 mesh prior to evaluation. CeO₂, SbOₓ, and ZrO₂ were also prepared by the same method.

3.2. Catalytic Activity Testing

The catalytic activities of the catalysts for the selective catalytic reduction of NOₓ with NH₃ in excess oxygen were conducted at atmospheric pressure in a fixed-bed continuous flow quartz reactor. In the evaluation, a 200 mg portion of catalyst (40–60 mesh) was applied, and the feed gas contained 500 ppm NO, 500 ppm NH₃, 5% O₂, 5% H₂O (when used), 100 ppm SO₂ (when used), and Ar balance. The total flow was 300 mL/min and the gas hourly space velocity (GHSV) was about 150,000 h⁻¹. A Thermo Fisher NO-NOₓ-chemiluminescence analyzer (Waltham, MA, USA) was used to detect the concentration of NO and NO₂ before and after the reaction. The catalyst bed was heated at 2 °C/min, held for 45 min every 50 °C, and then the concentration of NOₓ was measured. NOₓ conversion was calculated using the following equation:

\[
\text{NO}_x\text{ conversion} = \frac{[\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}} \times 100\% \tag{1}
\]

where \([\text{NO}_x]_{\text{in}}\) and \([\text{NO}_x]_{\text{out}}\) represented the inlet and outlet concentrations of NOₓ, respectively.
3.3. Catalyst Characterization

The N$_2$ adsorption–desorption isotherms were measured on a Quantachrome NOVA1200 analyzer (Norcross, GA, USA) at $-196 \, ^\circ$C to obtain the surface area of the catalysts. Before measurement, the catalyst was degassed at 180 $^\circ$C until it reached a stable vacuum of approximately 5 mTorr. After calculating the desorption data using the Brunauer–Emmett–Teller (BET) method, the specific surface area was obtained. The X-ray diffraction (XRD) patterns were carried out on a Bruker/D8 diffractometer (Karlsruhe, Germany) with Cu K$_\alpha$ radiation ($\lambda = 0.154 \, $nm). The X-ray photoelectron spectroscopy (XPS) spectra were obtained using a Thermo Scientific ESCALAB 250 spectrometer analyzer (Waltham, MA, USA), using a monochromatized Al-K$_\alpha$ source (1486.6 eV), and the binding energy of adventitious carbon (284.6 eV) was taken as a reference.

The temperature-programmed reduction of H$_2$ (H$_2$-TPR) and the temperature-programmed desorption of NH$_3$ (NH$_3$-TPD) were performed on a PX200 apparatus (Tianjin Pengxiang Technology Co. Ltd., Tianjin, China) with a thermal conductivity detector (TCD). For the H$_2$-TPR experiment, a 100 mg portion of catalyst was pretreated in N$_2$ at 300 $^\circ$C for 30 min, then cooled down to 30 $^\circ$C. Finally, the catalyst was heated from 30 $^\circ$C to 800 $^\circ$C at a rate of 10 $^\circ$C/min in 5% H$_2$/Ar (40 mL/min). For the NH$_3$-TPD, a 100 mg portion of catalyst was pretreated at 500 $^\circ$C under a flow of Ar (50 mL/min) for 1 h, and the pretreated catalyst was exposed to a flow of 10% NH$_3$/Ar (40 mL/min) for 1 h at 100 $^\circ$C. Then, the sample was flushed by Ar (50 mL/min) for 1 h and heated from 100 $^\circ$C to 500 $^\circ$C at 10 $^\circ$C/min.

The temperature-programmed desorption of NO (NO-TPD) experiments were conducted on custom-made equipment with a NO$_3$ analyzer. Before testing, a 200 mg portion of catalyst was pretreated at 500 $^\circ$C under a flow of Ar (300 mL/min) for 1 h; after cooling to room temperature, the pretreated catalyst adsorbed NO with a flow of 500 ppm NO/Ar (300 mL/min) for 1 h. The catalyst was flushed by Ar (300 mL/min) for 1 h and then heated from room temperature to 500 $^\circ$C at 10 $^\circ$C/min.

In situ DRIFT spectra were collected using an FTIR spectrometer (Thermo Nicolet 6700, Waltham, MA, USA) with an MCT detector cooled by liquid nitrogen. Before each experiment, the catalyst was pretreated at 300 $^\circ$C in Ar (50 mL/min). After the temperature cooling to 200 $^\circ$C, 1000 ppm NH$_3$/Ar was introduced into the IR cell and the background was subtracted from the sample spectra. After adsorption saturation, 1000 ppm NO + 5% O$_2$/Ar was introduced to replace NH$_3$ at 200 $^\circ$C. The experiment of NO + O$_2$ adsorption and reaction with NH$_3$ was carried out following a similar process. First, the catalyst was pretreated at 300 $^\circ$C for 1 h in Ar (50 mL/min), then 1000 ppm NO + 5% O$_2$/Ar adsorption was carried out at 200 $^\circ$C, and finally 1000 ppm NH$_3$/Ar was introduced to replace NO + O$_2$.

4. Conclusions

Sb-containing metal oxides (SbZr, SbCe, SbCeZr) were prepared by citric acid method and investigated for NH$_3$-SCR. SbCeZr exhibited the higher performance in NH$_3$-SCR than SbCe and SbZr, and NO$_x$ could be removed with 80% conversion in the temperature range of 202–422 $^\circ$C. SbCeZr owned excellent activity even in the presence of water and SO$_2$, and the thermostability was improved compared with SbCe. Hence, SbCeZr seemed to be a good candidate for the practical application in deNO$_x$. The presence of Sb in the metal oxides led to the difference in acid distribution and redox property, which was closely related to the NH$_3$ adsorption and NO oxidation. Bronsted acid and Lewis acid distributed evenly on SbCe, while Bronsted acid dominated on SbCeZr. Although high amounts of acid were on SbZr, poor redox led to its negligent performance in NH$_3$-SCR. The enhancement in redox ability promoted the generation of nitrates on SbCe. However, the competition between NO oxidation and NH$_3$ adsorption on the same active sites limited its application. In the presence of ZrO$_2$, the interaction between Sb and Ce was weakened, which further increased the acid amount and redox property. The form of “dual active sites” favored the NH$_3$ adsorption and nitrate generation.
Author Contributions: Conceptualization, Q.X. and L.W.; methodology, Q.X., D.L. and C.W.; validation, L.W. and Y.G. (Yun Guo); formal analysis, Q.X., L.W., Q.K. and M.N.H.; investigation, D.L., Q.K. and M.N.H.; resources, W.Z., Y.G. (Yun Guo) and Y.G. (Yanglong Guo); data curation, Q.X., Q.K. and L.W.; writing—original draft preparation, Q.X. and L.W.; writing—review and editing, Q.X., L.W. and W.Z.; project administration, Y.G. (Yanglong Guo); funding acquisition, Y.G. (Yun Guo) and Y.G. (Yanglong Guo). All authors have read and agreed to the published version of the manuscript.

Funding: This project was supported financially by the National Key Research and Development Program of China (2016YFC0204300) and the National Natural Science Foundation of China (21976057 and 21922602), as well as the “Shanghai Science and Technology Innovation Plan” Program (19DZ1208000), and Fundamental Research Funds for the Central Universities.

Conflicts of Interest: The authors declare no conflict of interest.

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