Sulfur and Water Resistance and Activity of Ru-Ce-Zr-Ox Catalysts for Nitric Oxide Catalytic Oxidation

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Abstract. Most mobile pollution sources have narrow space. Due to its small occupation area, fast selective catalytic reduction (SCR) is more suitable for controlling oxynitride (NOx) in exhausted gas in mobile pollution sources such as vessels. The fast SCR reaction can be divided into two stages: nitric oxide (NO) catalytic oxidation stage and NOx removal stage. This paper focused on the study of NO oxidation catalysts consists of ruthenium-cerium-zirconium (Ru-Ce-Zr) metal-oxides. It was found that the doping of ruthenium (Ru) which is the precious metal, greatly improved the catalytic activity. The NO oxidation rate of catalyst doped with 0.5% Ru at 300 °C was about 15% higher than that without Ru. However, with the increasing content of ruthenium, the sulfur and water resistance of catalysts decreased and the activity of the catalysts was only partially restored after regeneration. The results showed that Ru increased the activity of the catalysts while Ce and Zr improved the resistance of SO2 and H2O. Our work provided a solution to the space problem of mobile pollution sources such as vessels.

1. Introduction
Among the methods of transportation of goods in the world, marine transport accounts for a large proportion. Oxynitride (NOx) and other pollutants in exhausted gas of vessels cause increasingly serious pollution which have destructive effects on the atmosphere and marine environment. Both the Chinese and the international Marine diesel engine emission rules are becoming much more strict than ever, making the controlling of exhausted gas from vessels a great issue which needs further investigations.

Traditional selective catalytic reduction (SCR) process takes up a large space while it is hard to lay out SCR device in limited space in vessels. In order to solve this problem, “fast SCR” attracts more and more attention. Nitric oxide (NO) catalytic oxidation is the intermediate step of fast SCR reaction: a portion of NO is oxidized to NO2, which can accelerate the reaction rate and reduce the volume of catalysts. Tronconi Eet al. [1] used V2O5/WO3/TiO2 catalyst to verify that the denitrification efficiency of fast SCR was better than that of standard SCR reaction at the same space velocity, proving that fast SCR could improve the space velocity of reaction. Ciardelli C et al. [2] also verified that fast SCR reaction has higher activity than standard SCR at the same space velocity by injecting mixed gases of NO, NO2 and NH3 directly. Therefore, it is critical to investigate the technology of NO catalytic oxidation since this method can solve the problem of insufficient SCR installation space in vessels. Since the d orbital of precious metal elements is not filled up, its performance of surface adsorption is stronger and suitable intermediate active compounds can be formed with reactants [3]. Therefore, catalysts with precious metal elements have higher catalytic activity, including the catalytic oxidation of NO [4,5]. Xavier Auvray et al. [6] studied the oxidation activity and stability of catalysts which used alumina as carrier and pd-pt as active component. It was found that the catalyst prepared with...
sequential impregnation had the best performance after pre-treatment, and the NO conversion rate reached 50% at about 180 °C in the heating stage and 50% at about 200 °C in the cooling stage. Among precious metals, the oxidation capacity of ruthenium has also been investigated. Li et al. [7] studied the catalytic oxidation of NO by Ru-catalysts with different supports. The precursor of the active component was RuCl₃ and the results showed that the optimal load of Ru was 2%. X-ray Diffraction results showed no diffraction peak of supports excepted RuO₂. Highly dispersed and amorphous RuO₂ was considered to be the most active component. Adjimi et al. [8] found that the catalytic doped with Ru had the best activity of NO oxidation.

In addition, cerium and zirconium were often used in the study of oxidation catalysts because of their superior storage of oxygen and stability. Shang et al. [9] found that the CoCeZrOₓ catalysts had a strong ability to oxidize NO. Caglar et al. [10] studied catalysts with cerium and zirconium as carriers and found that in the absence of oxygen, part of NO could be oxidized to NO₂, indicating that the catalysts had a good oxygen storage performance.

Precious metal catalysts have high catalytic activity along with the characteristics of oxidation resistance, corrosion resistance and so on [11-12]. While the precious metal is extremely expensive since it is rare on earth. Its dosage must be reduced if it is to be used in industry. Although the research on the oxidation activity of precious metal catalysts has made good progress, there were few reports about their sulfur and water resistance. SO₂ and H₂O are essential components in exhausted gas of vessels. So how to further improve sulfur and water resistance of catalysts under the condition of guaranteeing its oxidation activity is a big difficulty at present. The fast SCR technology can be widely used in industry only by overcoming this difficulty.

In our study, a series of Ru-Ce-Zr-Oₓ catalysts were prepared by coprecipitation method. The experiment of NO conversion was carried out in a fixed-bed microreactor. The oxidation activity, sulfur and water resistance and deactivation mechanism of catalysts were all discussed in this article.

2. Experimental

2.1. Catalysts Preparation

RuₓCeₓZrₙO₂ (x = 0.00%, 0.25%, 0.50%, 0.75%, 1.00% and y:z = 1:1) was prepared by coprecipitation method. The RuCl₃·xH₂O, Ce(NO₃)₂·6H₂O and Zr(NO₃)₂·5H₂O nitrates were dissolved in 50 ml of deionized water simultaneously. The mixed nitrate solution was placed in a water bath at 70 ℃ and stirred. The sodium hydroxide solution (1 mol/L) was added slowly to it to make the pH of the solution around 9 ~10, then continue stirring for 3 h. After stirring, the obtained product was dried in a oven at 110 ℃ for 12 h after centrifuging for five times. Finally, the solid was calcinated at 350 ℃ for 3 h in the air. These composite oxides were denoted as RₓCZ.

2.2. Catalyst Characterization

Surface-area measurements of different catalysts were determined by N₂ physisorption on Gemini V (Micrometrics Co., American) at 77 K. The sample was pre-treated at 110 ℃ for 1 h to remove impurities adsorbed on the surface and in the pores of catalysts. Temperature-programmed reduction (H₂-TPR) experiments were carried out using feed gas containing H₂ in Ar on a AutoChem II 2920 (Micrometrics Co., American) and starting from room temperature to 800 ℃. The hydrogen concentration was determined by a thermal conductivity detector (TCG). Thermo gravimetric (TG) were tested by a TG/DTA6300 (NSK Ltd., Japan), and the samples were tested from room temperature to 800 ℃ with heating rate of 10 °C·min⁻¹. Fourier Transform infrared spectroscopy (FT-IR) spectra were recorded by a Nicolet 6700 spectrometer (Thermo Co., American) with a wave number ranging from 1000 cm⁻¹ to 2000 cm⁻¹ to explore the possible species of sulfates. Spectra was obtained from 32 scans with a resolution of 4 cm⁻¹.

2.3. Catalyst Measurements
The NO conversion activity of catalysts was carried out from 160 °C to 320 °C in a fixed-bed vertical quartz tubular reactor (i.d.20 mm) under atmospheric pressure. Schematic diagram of the device was shown in figure 1. The catalyst powder was placed on the reaction bed and the thermocouple was inserted above the catalyst layer to control the reaction temperature. The reactant gas composition was as follows: 0.07 vol% NO, 0.02 vol% SO₂, 5 vol% O₂ and N₂ as balance at a whole flow rate of 1000 ml·min⁻¹, corresponded to a gas hourly space velocity (GHSV) which was 30000 h⁻¹. The gas was mixed in the mixing tank before entering the reactor. The NOₓ was monitored online using a nitrogen oxides analyzer (42i-HL, Thermo Electron Co., American). The conversion rate of NO can be calculated by the following formula:

\[
\text{NO conversion} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \quad (1)
\]

Where [NO]_{\text{in}} and [NO]_{\text{out}} represent the concentrations of NO in the inlet and outlet gas stream respectively.

3. Results and discussion

3.1. Catalytic Activity

![Figure 2. NO oxidation of RₓCZ catalysts in different temperatures. Reaction condition: [NO] = 0.07 vol%, [O₂] = 5 vol%, N₂ balance, GHSV = 30000 h⁻¹](image)
The activity curves of RxCZ catalysts at different temperatures were shown in figure 2. The activity of catalysts increased with the addition of Ru. When the temperature reached 300 °C, the oxidation rate of NO by RxCZ (x ≥ 0.5%) catalysts can reach above 40%, while Ru-free catalysts failed to reach the same value. Based on previous experiments, when the NO conversion rate was between 40% and 55%, it was optimal for fast SCR reaction. The temperature range corresponding to this range of conversion rate was called the effective temperature window. As can be seen from the figure, the effective temperature window of R0.5CZ catalyst was from 300 °C to 350 °C.

| No. | sample        | surface area catalysts/(m²·g⁻¹) | pore volume/(cm³·g⁻¹) | pore diameter (nm) |
|-----|---------------|---------------------------------|-----------------------|-------------------|
| 1   | R0.00CZ       | 132                             | 0.12                  | 3.0               |
| 2   | R0.25CZ       | 139                             | 0.12                  | 2.9               |
| 3   | R0.50CZ       | 155                             | 0.13                  | 3.0               |
| 4   | R0.75CZ       | 150                             | 0.14                  | 3.0               |
| 5   | R1.00CZ       | 151                             | 0.12                  | 2.9               |

The specific surface area, pore volume and pore size of RxCZ catalysts were listed in table 1. With the addition of Ru, the specific surface area of the catalyst increased firstly, then decreased slightly to about 150 m²·g⁻¹ and keep steady. Meanwhile, the pore volume also increased firstly, then decreased. It can be seen from table 1 that the pore diameter of catalyst was small, about 3.0 nm on average.

Figure 3. (a) N₂ adsorption and desorption curves of RxCZ catalysts. (b) Size distribution of RxCZ catalysts. (c) H₂-TPR profiles of R0.0CZ and R0.5CZ. (d) Thermal gravimetric analysis of R0.0CZ, R0.5CZ and R1.0CZ.
The N₂ adsorption and desorption curve of RₓCZ catalysts were shown in figure 3(a). All the five catalysts are V-type adsorption isotherms and H₂-type hysteresis cycles, indicating that the pore structure of RₓCZ catalysts was complicated. As can be seen from the particle size distribution of RₓCZ catalysts shown in figure 3(b), the catalysts had both medium and micro pores [13]. The H₂-TPR of representative catalysts (R₀.₀CZ, R₀.₅CZ) were tested and the results showed that the hydrogen reduction peak of the catalyst with 0.₅% Ru was significantly shifted to the lower temperature than Ru-free one. R₀.₅CZ started consuming hydrogen at 100 °C, indicating that the addition of Ru improved the low temperature redox ability of the catalyst [8], which was consistent with the results obtained in the performance test of the catalysts in figure 2. Because of low calcination temperature, the catalysts were in an amorphous state, the hydrogen absorption peaks of Ru and Ce were mixed and difficult to distinguish. However, obviously, the area of hydrogen consumption peak of R₀.₅CZ was larger than that of R₀.₀CZ, which proved that the redox performance of R₀.₅CZ was indeed better than that of R₀.₀CZ.

It can be seen from the TG test results that the weight loss from room temperature to 100 °C corresponded to the evaporation of water absorbed by the catalysts. The amount of water adsorbed in R₀.₀CZ was the largest, accounting for about 5% of the total mass of the catalyst, while R₁.₀CZ only accounted for about 2%. This indicated that the dispersion of Ru on the surface of the catalysts weakened the hydroscopicity of the catalysts. From 400 °C to 600 °C, the catalyst also had a process of rapid loss of weight. It corresponded to the partially decomposed cerium hydroxide and zirconium hydroxide. With the addition of Ru, the weight loss of the catalysts decreased significantly, indicating that Ru helped to lower the decomposition temperature of cerium hydroxide and zirconium hydroxide. After the calcination of the catalysts, only a small amount of cerium hydroxide and zirconium hydroxide remained undecomposed. So the weight loss of R₀.₅CZ and R₁.₀CZ were less than R₀.₀CZ from 400 °C to 600 °C.

3.2. The sulfur and water resistance of catalysts

Figure 4. (a) Effects of SO₂ on the activity of RₓCZ catalysts. (b) Effects of H₂O on the activity of RₓCZ catalysts. (c) Effects of SO₂ and H₂O on the activity of RₓCZ catalysts. (d) FT-IR spectra of...
fresh catalysts and poisoned catalysts. Reaction condition: [NO] = 0.07 vol%, [O2] = 5 vol%, N2 balance, GHSV = 30000 h⁻¹, [SO2] = 0.02 vol%, [H2O] = 5 vol%.

Figure 4(a) showed the apparent toxicity of 5 vol% H2O at 300 °C to the catalysts. The activity of R1.0CZ stabilized at about 35% after 7 h with water supply. After cutting water injection for 1 h, the activity of the catalysts returned to the original level quickly, indicating that the poison of water to the catalysts was reversible. One reason that water deactivated the catalysts should be the competition adsorption with NO and O2 [14]. Another reason may be that the strong oxidation ability to NO of the catalysts led to the production of a large amount of NO2. Then NO2 and H2O generated nitrates, which covered the surface and blocked the pores of the catalysts [15]. Although it was found from figure 3(d) that the addition of Ru helped to weaken the hydroscopicity of catalysts, the oxidation activity of the catalysts to NO was also increased, leading to the formation of more nitrates. Therefore, although the activity of Ru-doped catalysts fell much more, it was still higher than Ru-free catalysts. The effects of 0.02 vol% SO2 on the catalysts at 300 °C can be seen from figure 4(b). After injecting 0.02 vol% SO2 for 24 h, the activity of the catalysts continued to decline. Especially R1.0CZ, the activity dropped to about half of the initial value. Then, the catalysts were heated at 350 °C for 1 h to regenerated. The activity of the catalysts partially recovered, but still cannot return to the original level, indicating that the toxic effect of SO2 on catalysts was irreversible. The toxic effects of SO2 on catalysts were mainly due to the competitive adsorption with O2, NO and the formation of sulfate species [16].

As can be seen from figure 4(c), after 12 h, the activity of R1.0CZ was above 40%, and the decline rate of activity was obviously slower than before. After heating at 350 °C for 1 h, the activity of the catalysts still cannot return to the original level, indicating that the toxicity was still irreversible [17]. However, adding 0.02 vol% SO2 and 5 vol% H2O at the same time had less toxic effects on the catalysts than adding SO2 alone. The addition of H2O and SO2 can form sulfates which weakened the competitive adsorption effects. This indirectly reflected that the main reason for the deactivation of the catalysts was that SO2 and H2O competed to adsorb on the active sites of the catalysts, which was consistent with the findings of peng et al [18].

In order to study the further mechanism of catalyst deactivation, the fresh and toxic catalysts were characterized by FT-IR. In figure 4(d), the vibration adsorptions at a wave number of 1671 cm⁻¹ corresponded to the absorption peak of H2O. Two separated bands at 1420 cm⁻¹ and 1265 cm⁻¹ were assigned to nitrates, which were shown in both fresh and toxic catalysts. The difference revealed that the toxic catalyst had a band at 1078 cm⁻¹ which corresponded to sulfates. The band at 1163 cm⁻¹ was assigned to SO2 adsorbed on the surface of the catalyst. This result further proved that one of the causes of catalyst deactivation is the formation of sulfates [16].

4. Conclusions

In this study, the catalysts were all prepared by coprecipitation method. The effects of Ru doping on the oxidation activity of catalysts were investigated and the reaction of catalysts with SO2 and H2O was also discussed. The following conclusions can be drawn:

(1) The NO conversion rate of R0.5CZ reached 40% at 300 °C, and the effective temperature window for fast SCR was from 300 °C to 350 °C. And the activity of catalysts increased, with the addition of ruthenium.

(2) The activity of R0.5CZ stabilized at about 30% after 7 h with water supply. After injecting 0.02 vol% SO2 for 24 h, the activity of the catalysts continued to decline, especially R1.0CZ, the activity dropped to about half of the original. Finally, after 12 h of simultaneous injection of SO2 and H2O, the activity of R0.5CZ decreased less than 10%. The catalysts were proved to have some resistance to SO2 and H2O.

(3) The mechanism of catalyst deactivation was demonstrated, and it was found that the main reasons were competitive adsorption and sulfate formation, which were also confirmed by FT-IR. The “fast SCR” could improve the reaction rate of SCR, save the amount of catalysts and reduce the volume of reactor. This could control pollutants in exhausted gas of vessels and other mobile pollution.
sources with narrow space effectively, and let the exhausted gas meet the emission standards while obtaining the same energy.

5. References

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