High Performance of NO Oxidation Over Co/Zr0.2Ce0.8O2 Catalysts Prepared by One-pot Method

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Abstract. Cobalt supported on Zr0.2Ce0.8O2 with different cobalt loading for catalytic oxidation of NO to NO2 were prepared by the one-pot method using citric acid as complexing agent. The samples were characterized by XRD, H2-TPR, O2-TPD and NO-TPD and the catalytic performance was investigated. The results showed that the Co/Zr0.2Ce0.8O2 catalyst containing 10 wt.% of Co3O4 exhibited excellent activity at a wide temperature window ranged from about 240 ℃ to 380 ℃ with NO conversion above 50%. The high catalytic performance of Co/Zr0.2Ce0.8O2 samples should be attributed to the active component related with cobalt species.

1. Introduction
The high DeNOx conversion rate in the fast SCR process can be achieved by using an oxidation catalyst at upstream of the SCR unit so as to convert ca. 50% of NO to NO2 and this indirectly enables to reduce the SCR catalyst volume [1]. Therefore, NO2 plays a decisive role in increasing SCR reaction rate for exhaust gas. Various types of catalysts have been used for NO oxidation to NO2. Among them, Pt-based materials are traditional catalysts due to their high catalytic performance. However, the drawbacks such as high cost and limited availability of most precious metals are obstacles to their large-scale industrial application.

Nowadays, ceria-zirconia solid solution has been widely utilized not only as catalytic supports but also as active catalysts due to its excellent redox property, significant thermal stability and catalytic activity [2]. Therefore, ceria-zirconia mixed oxides have been studied in many fields, such as soot oxidation[3, 4], carbon dioxide reforming [5], VOC combustion [6] and CO oxidation[7].

In the present work, cobalt, which was verified as an active component in many oxidation reactions[8-10], was supported on ceria-zirconia solid solution and Co/Zr0.2Ce0.8O2 catalysts with different cobalt loading were prepared using citric acid as complexing agent. One-pot method was employed as it is a facile and rapid method. The catalytic performance of samples for NO oxidation to NO2 was investigated. Previous literatures [3, 11] reported that catalysts with cerium-rich formulation had more active than that with zirconium-rich in oxidation reactions, so Zr0.2Ce0.8O2 was employed as supports here. The results showed that the Co/Zr0.2Ce0.8O2 catalyst with ≥ 5 wt.% loading exhibited high catalytic activity, the NO conversion above 50% was obtained over Co/Zr0.2Ce0.8O2 catalyst containing 10 wt.% of Co3O4 at a wide temperature window ranged from about 240 oC to 380 oC.
2. Experimental

2.1. Catalyst preparation

Co/Zr0.2Ce0.8O2 catalysts with various cobalt loading were prepared from the corresponding nitrates by one-pot method using citrate acid as complex agent. The stoichiometric nitrate precursors and citric acid were separately dissolved under stirring to give a clear homogeneous solution. After 2h constant stirring, the mixed solution was subsequently placed in water bath at 60 °C. The obtained gel was dried at 120 °C for 12h followed by calcination at 500 °C for 4h in air. The prepared catalysts referred to xCo/ZC (x = 0, 1, 5, 10), where x is the theoretical concentration of Co3O4 (wt.%).

2.2. Catalyst characterization

X-ray diffraction patterns were measured on a Beijing Purkinjie general instrument XD-3 X-ray diffraction with Cu-Kα radiation at 35 kV (λ = 0.15418 nm) and 20 mA. The samples were scanned at 2° ranging from 5° to 80° with a 0.02° step size. Temperature-programmed reduction was carried out on a Quanta Chembet (3000) system equipped with a thermal conductivity detector (TCD). Typically, 100 mg of sample was loaded in a quartz reactor and heated from room temperature to 800 °C at a rate of 10 °C/min under 5 vol.% H2/Ar at a total flow of 70 mL/min.

Temperature-programmed desorption (TPD) was carried out on automated chemisorptions analyzer (Quantochrome Instruments). About 200 mg of sample was used. After O2 (or NO) saturation in 1h, the gas was switched to He for 0.5 h. Subsequently, TPD was performed by ramping the temperature at 10 °C/min to 800 °C in He (70 mL/min). Desorption of O2 (or NO) was detected by a thermal conductivity detector (TCD).

The BET surface areas of catalysts were determined by N2 physisorption by on a V-Sorbet 2800S automated gas sorption apparatus at -196 °C. Before the BET measurement, the samples were evacuated at 200 °C for 12 h to desorb moisture adsorbed on the surface and inside the porous network.

2.3. Catalytic measurements

The catalytic tests were carried out in a continuous fixed-bed quartz tubular microreactor (i.d. 6.8 mm) at atmospheric pressure. Typically, 0.3 g catalyst (sieve fraction, 40-60 mesh) was packed in the reactor bed, the reactant gas mixture (400 ppm NO, 8% O2, N2 balance) was fed to the reactor with a total flow rate of 100 mL min⁻¹, corresponding to a gas hour space velocity (GHSV) of 30 000 h⁻¹. The steady-state tests were conducted isothermally every 50 °C from 200 °C to 400 °C and the gas products (after 90 min reaction) were analyzed by an Ecom-JZKN flue gas analyzer (Germany). The NO conversion is defined as:

\[ X(\%) = \frac{(NO_{in} - NO_{out})}{NO_{in}} \times 100 \]  

3. Results and Discussions

3.1. Catalyst characterization (BET and XRD)

XRD patterns of calcined samples in the 2θ range of 10–80° are shown in Figure 1. All samples exhibited four well-defined peaks associated with typical cubic phase CeO2. However, after doping of cobalt, the peaks in cobalt-contained samples were broadened with the increasing of cobalt loading, suggesting that the particle sizes of catalysts decreased. No apparent cobalt phases were detected on cobalt-contained samples, which suggested that fine dispersion of Co3O4 particles on the surface or cobalt related species might be incorporated into the Ce-Zr solid solution.

The BET surface areas of the catalysts are summarized in Table 1. It was seen that the doping of cobalt had obvious effect on BET surface area. The specific surface area of xCo/ZC decreased with the loading of cobalt probably due to the coverage of cobalt species on the surface of catalysts. The same results also was obtained by Gawade [12].
Figure 1. XRD patterns of \( x\text{Co/ZC} \).

Table 1. BET surface area of the catalysts.

| Samples | BET surface area (m\(^2\)g\(^{-1}\)) |
|---------|-------------------------------------|
| ZC      | 45.1                                |
| 1Co/ZC  | 44.1                                |
| 5Co/ZC  | 30.7                                |
| 10Co/ZC | 30.4                                |

3.2. \( H_2\)-TPR

The reduction characteristics of Co supported catalysts and ZC support are shown in Figure 2. For ZC support, only one reduction peak at about 600 °C ascribed to the surface reduction of CeO\(_2\) was observed. After the addition of Co to the ZC mixed oxide, the reducibility of \( x\text{Co/ZC} \) samples was improved substantially by shifting peaks to a much lower temperature range due to the higher reducibility of Co species than CeO\(_2\) as well as the mutual interaction between Ce and Co, which facilitated the reducibility of each metal oxide. For lower cobalt content catalyst, 1Co/ZC as well as ZC support, presented only one overlapped peak, which could be correlated to the reduction of cobalt and surface cerium species. The weakly resolved reduction features observed over 1Co/ZC catalyst could be due to low cobalt concentration [12]. While for 5Co/ZC catalyst, three distinct reduction features at 300 °C, 440 °C and 600 °C were observed. The first reduction peaks at about 300 was assigned to the reduction of Co\(_3\)O\(_4\) to CoO whereas the second peak at around 440 °C could be attributed to the overlapped reductions of CoO to Co and surface CeO\(_2\) to Ce\(_2\)O\(_3\) [13]. The third reduction feature at about 600 °C was probably ascribed to the reduction of surface CeO\(_2\) to Ce\(_2\)O\(_3\), as the reduction of lattice oxygen in bulk CeO\(_2\) with the maximum temperature of the peak at around 800 °C is not affected by the presence of cobalt species [14]. The reduction features of 10Co/ZC was similar with that of 5Co/ZC, however the H\(_2\) consumption was increased due to the increasing content of cobalt and the reduction peaks were shifted to higher temperature corresponding to 5Co/ZC. The results suggested that cobalt species were well-dispersed on the ceria-zirconia system and cobalt was able to improve the reducibility of ceria.
3.3. NO-TPD
The TPD profiles of NO on the xCo/ZC were shown in Figure 3. As the temperature increased from 50 to 700 °C, NO desorption was observed on these catalysts. The NO desorption patterns recorded for 1Co/ZC and ZC were spread in the similar range of around 130–550 °C. However, the cobalt-free sample, ZC, desorbed small amount of NO in comparison with the cobalt-contained sample, 1Co/ZC. As displayed in Figure 3, the desorption intensity of 1Co/ZC was stronger than that of ZC. Furthermore, it was worth to note that the addition of cobalt to the Zr-Ce solid solution led to shift desorption features towards lower temperature and the intensity of desorption peaks increased as the Co loading increases. Thus, we could conclude that NO adsorption was associated with the cobalt species and more loading of cobalt in Zr-Ce system was beneficial for the adsorption-desorption of NO. It facilitated the catalytic oxidation of NO over the Co/ZC catalysts.

3.4. O2-TPD
Generally, there are three kinds of active oxygen species: Oα, Oβ and Oγ on surface of ceria-zirconia mixed oxide. Oα species has a lower desorption temperature (<350 °C), which is assigned to the chemical adsorption oxygen; Oγ species has a higher desorption temperature (>750 °C), being assigned to the lattice oxygen. However, desorption temperature of Oβ species is between these two desorption temperatures, which is related with oxygen defect and is considered as partial crystal oxygen [15].

The O2-TPD curves of catalysts are depicted in Figure 4. For ZC and 5Co/ZC catalysts, two desorption regions could be observed, which matched up to the desorption temperature of Oα and Oβ species. In the case of 10Co/ZC sample, three desorption regions matched up to the desorption temperature of Oα, Oβ and Oγ species could be observed. However, it was found that cobalt species had negatively affected the adsorption capacity of O2. Apparently, the desorption amount of O2 decreased with the loading of cobalt. This was probably that cobalt species blocked the active sites related with the adsorption of O2 on the surface of ZC. The ranking in terms of desorbed oxygen quantity from the highest to lowest value was ZC > 5Co/ZC > 10Co/ZC, which indicated that ZC exhibited the highest capacity for adsorbed oxygen.

3.5. Catalytic test
Figure 5 shows the NO conversion as a function of temperature over xCo/ZC catalysts with difference cobalt-loadings during the oxidation of NO to NO2. It was seen that the Co-contained catalysts showed much higher activities for the oxidation reactions than the Co-free support, even though they have smaller surface area than ZC. This could be inferred that the cobalt species were the main active sites and they played a key role in the NO oxidation. Nevertheless, ZC, the Co-free sample had also catalytic activity towards NO oxidation, with the NO conversion reaching about 45% at the temperature of 350 °C. The reason for the catalytic activity of ZC catalyst was related to CeO2 with excellent exchanging oxygen ability which could be significantly improved by Zr4+ doping [16].
confirmed in the above discussion of O₂-TPD where among the investigated catalysts, ZC exhibited the highest capacity for adsorbed oxygen which was correlated with the oxidation reaction [4].

With the addition of cobalt to the Zr-Ce solid solution, a notable enhancement of the NO conversion could be observed. And the NO conversion for xCo/ZC catalysts increased with the increasing of cobalt loading, especially at temperature below 350 °C. The maximum NO conversion increased from about 56% to 76% when the mass percentage of cobalt increased from 1% to 10%. Meanwhile, the temperature of maximum activity shifted from 350 to 300 °C. Additionally, 10Co/ZC and 5Co/ZC exhibited higher activity in a wider temperature window with NO conversion above 50% with respect to 1Co/ZC. However, it was found that the difference in catalytic activity between 10Co/ZC and 5Co/ZC was not proportional with the difference in the content of cobalt and their catalytic activity was similar. This might be due to the probable presence of cobalt agglomerations because of large amount, which decreased the amount of cobalt interacting with NO.

This catalytic activity behavior mentioned above could be related with the characteristics of the cobalt coped catalysts such as reducibility and adsorption capacity of NO and O₂. The cobalt-contained catalysts showed higher reducibility and higher adsorption-desorption capacity for NO.

![Figure 4. O₂-TPD profiles of xCo/ZC.](image1)

Figure 4. O₂-TPD profiles of xCo/ZC.

Though the adsorption capacity for O₂ was negatively affected by the addition of cobalt, the rich ceria contained in support could make the oxygen easier mobility. These features were contributed to the high catalytic activity of NO oxidation for Co/ZC samples.

4. Conclusion

From the above discussions, we could deduce that the cobalt was the main active component in the NO oxidation to NO₂. The well-dispersed cobalt on the surface of catalysts facilitated the improvement in the catalytic activity. Relatively large amount of cobalt might partially aggregate, therefore decreasing the amount of cobalt interacting with NO. Among the catalysts investigated in the present work, 10Co/ZC showed the best performance for the NO oxidation and it had a wide temperature window ranged from about 240 °C to 380 °C, with NO conversion above 50%.

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