

Synthesis of Cr/Ce_xZr_{1-x}O₂ and its Performance in Catalytic Oxidation NO

Wei Cai and Qin Zhong

Abstract—Cr/Ce_xZr_{1-x}O₂ catalysts were prepared by impregnation method and used for catalytic oxidation of NO. The effects of preparation conditions including the various Ce/Zr of the support, the loading of active component, calcination temperature, and operating conditions as reaction temperature, O₂ and NO concentration, gas hour space velocity for catalytic oxidation were investigated. The results showed that 7%Cr/Ce_{0.14}Zr_{0.86}O₂ which was calcined at 400 °C showed optimal catalytic oxidation activity. And O₂ was important for the NO adsorption over the Cr/Ce_xZr_{1-x}O₂ catalysts.

Index Terms—Ceria-zirconia solid solution; catalytic oxidation; NO.

I. INTRODUCTION

Nitrogen oxides (NO_x) which mainly comes from mobile and stationary combustion sources have direct impact on the global environment and human health through the formation of photochemical smog and the acid deposition. Extensive studies on the NO_x catalytic elimination has been carried out in recent years [1-3]. Selective catalytic reduction (SCR) with ammonia is a popular choice for NO_x reduction in stationary sources since 1970s, and nowadays also some applications for mobile sources have been developed [4-8]. Although these SCR processes appear effective and established, there still remain several problems, such as a large reactor volume, the reductant ammonia, etc.; moreover, the ammonia reacts with sulfur dioxide to generate ammonium sulfite, which will block the pore of catalysts. In addition, the process is not available to NO of low concentrations [9]. Selective catalytic oxidation (SCO) of NO in the flue gas is potentially an ideal technology, and considerable interest has recently been taken in the process of developing catalysts for oxidizing NO into NO₂. Because NO₂ is easier to be removed by absorption than NO, especially, the maximum absorption efficiency could be achieved at the proper ratio of NO/NO_x (NO/NO_x = 50~60%) [10], and after that, the mixed gas production (NO + NO₂) is absorbed by lime, NaOH or ammonia.

Ceria-based materials are effective for the oxidation for its excellent ability of releasing or storing oxygen. S.Y. Christou et al [11] found that bulk oxygen and chemical adsorbed oxygen can exchange in the mutual transformation of Ce⁴⁺ and Ce³⁺, thus activating the oxygen and generating oxygen vacancies. However, it is easily susceptible to sintering at high temperatures [12,13], thereby reducing the specific surface area and the exchange between Ce⁴⁺ and Ce³⁺. It has

been found that the thermal stability, oxygen storage capacity and redox property of CeO₂ can be improved by doping Zr⁴⁺ ions [14,15], thus Ce_{1-x}Zr_xO₂ solid solution shows a good catalytic activity in the oxidation. Moreover, chromium (Cr⁶⁺) metal oxides are very effective in oxidation reaction process for its strong oxidizing property. Hence it can be used as the active site to absorb the acid gas NO.

In this study, several Ce/Zr and various Cr loading catalysts were prepared by impregnation method (the supports were prepared by simple hydration) and the influence of Ce/Zr, Cr loading, the calcination temperature, the O₂ and NO concentration in the reactant gas, and the gas hourly space velocity (GHSV) on the NO conversion were investigated to find the best preparation conditions of the catalysts and the best operating condition.

II. EXPERIMENTAL

A. Catalyst Preparation

The supports were synthesized by a simple hydration and then Cr/Ce_xZr_{1-x}O₂ catalysts were synthesized by impregnation method. The starting materials were cerium(III) nitrate, zirconium(IV) oxychloride, chromium(III) nitrate. First cerium nitrate and zirconium oxychloride were dissolved in de-ionized water on the basis of Ce/Zr=4, 1.5, 0.25 (mass ratio, coded as C4Z, CZ, CZ4 respectively), refluxed in water bath (T=60 °C), dried in oven (T=120 °C) overnight. The supports were obtained after calcination under air at 500 °C for 6 h. Then the Cr species were loaded on the support by impregnation method. The CrO_x loading amount was 5%, 7%, 10% (mass percent of the support, coded as 05Cr, 07Cr, 10Cr respectively). Chromium nitrate and the support were dissolved in de-ionized water, reflux in water bath (T=60 °C), drying in oven (T=120 °C) overnight. Finally, the mixture was calcined under air at 400 °C, 500 °C and 600 °C (coded as -400, -500, -600 respectively) for 6 h with the heating rate of 2 °C/min to obtain the catalysts. The catalysts supported on CeO₂ and ZrO₂ were also prepared to make comparison (the CrO_x loading amount was 10%).

B. Catalytic Activity Tests

The catalytic oxidation of NO was performed in a fixed-bed flow micro-reactor at atmospheric pressure. Typically, 300 mg sample (sieve fraction of 40~60 mesh) was placed in a quartz reactor (6.8 mm i.d.), the reactant gas mixture (390 ppm NO, 8% O₂, N₂ balance) was fed to the reactor with a total flow rate of 100 mL/min, corresponding to a gas hour space velocity (GHSV) of 20000 mL/(h·g). The steady-state tests were conducted isothermally every 50 °C

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from 150 °C to 400 °C and the gas products (after 90 min reaction) were analyzed by a Ecom-JZKN flue gas analyzer (Germany). The compositions in the outlet gas were NO and NO₂ only. The NO conversion is defined as:

$$\text{NO conversion} = \frac{\text{NO}_{(\text{inlet})} - \text{NO}_{(\text{outlet})}}{\text{NO}_{(\text{inlet})}} \times 100\%$$

III. RESULTS AND DISCUSSION

A. Catalytic Activity Tests

The catalytic activity of various Ce/Zr catalysts is shown in Fig. 1. CeO₂ support exhibits much lower activity (<25%) for NO oxidation, and the NO conversion increased with the increasing of temperature. The result explained that CeO₂ supported catalyst reflected activity at high temperature. It was obvious that 10CrCZ4 showed the best activity at 150~400 °C and the oxidation efficiency reached 59.35% at 300 °C. The NO conversion on catalysts all reached highest at 300 °C except CeO₂. The conversion decreased slowly as the result of the decomposition of NO₂ at 350~400 °C. However, the oxidation efficiency of 10CrCZ4 was much more higher.

Fig. 2 shows the catalytic activity of various Cr loading catalysts. It is obvious that the 07CrCZ4 shows the best activity at 300 °C. The oxidation efficiency reaches 62.18%. However, we can confirm from the Fig. 2 that the difference of oxidation efficiency between the different Cr loading is not obvious than the difference of oxidation efficiency between the various Ce/Zr. The fact explains that the Ce/Zr plays the important role in this oxidation.

The oxidation efficiency of the catalysts with different calcination temperatures is shown in Fig. 3. It is clear that the catalyst calcined at 400 °C exhibits the best oxidation efficiency, which reaches 62.33% at 300 °C. Obviously, the difference between the calcination temperatures of 400 °C and 500 °C is not distinct. However, keeping on rising the calcination temperature will lead the obvious decreases in oxidation efficiency. Above all, the best preparation conditions of the catalyst are that the Ce/Zr was 0.25, the Cr loading was 7% in mass percent and the calcination temperature was 400 °C.

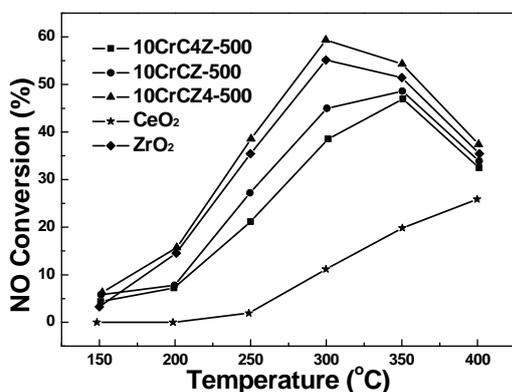


Fig. 1. NO conversion of 10%Cr/Ce_xZr_{1-x}O₂ catalysts with various Ce/Zr. Reaction conditions: 390 ppm NO, 8% O₂, N₂ as balance gas, GHSV=20000 mL/(h·g).

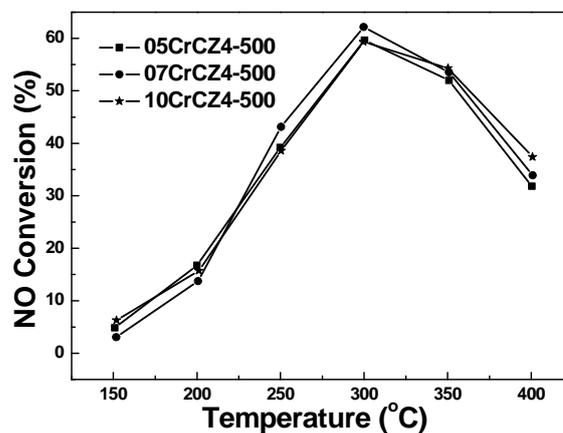


Fig. 2. NO conversion of Cr/Ce_{0.14}Zr_{0.86}O₂ catalysts with various Cr loading. Reaction conditions: 390 ppm NO, 8% O₂, N₂ as balance gas, GHSV=20000 mL/(h·g).

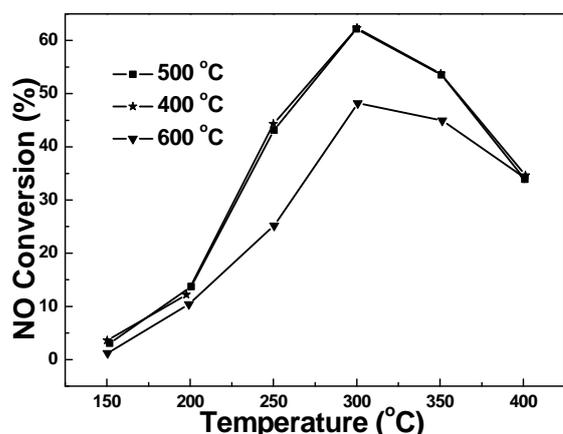


Fig. 3. NO conversion of 10CrCZ4 catalysts with various calcination temperatures. Reaction conditions: 390 ppm NO, 8% O₂, N₂ as balance gas, GHSV=20000 mL/(h·g).

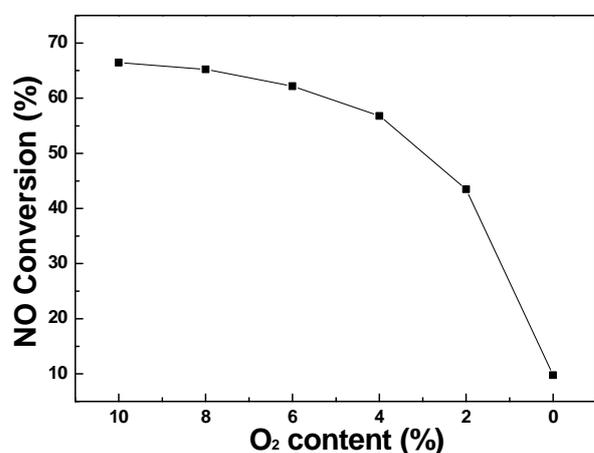


Fig. 4. The effect of O₂ concentration on NO conversion of 07CrCZ4-400. Reaction conditions: 390 ppm NO, N₂ as balance gas, GHSV=20000 mL/(h·g), T=300°C.

B. Effect of O₂ and NO Concentration on NO Conversion

It was known from previous studies [16] that O₂ had significant effect on NO oxidation. In this paper, the effect of O₂ concentration on NO conversion of 07CrCZ4-400 has been studied and shows in Fig. 4. The NO conversion is stable as the O₂ concentration in 10%-6% and the conversion decreases slightly when the O₂ concentration is 4%. At low O₂ concentration, the NO conversion decreases sharply to 43.51% and 9.75% when the O₂ concentration is 2% and 0%,

respectively. The reason of this result is that O_2 promotes the NO adsorption over 07CrCZ4-400 so that the NO concentration of outlet of fixed-bed flow reactor decreases.

The influence of NO concentration on NO conversion of 07CrCZ4-400 is shown in Fig. 5. The oxidation efficiency decreases with the increasing of NO concentration. However, the conversion decreases slightly before the NO concentration is 480 ppm. And the conversion almost keeps a constant while the NO concentration increases from 480 ppm to 570 ppm. Then the oxidation efficiency decreases sharply to 42.54% while the NO concentration is 660 ppm. The reason for this result is that the adsorption of NO reaches saturation while the NO concentration is too high to reducing the remained active site on the surface of the catalysts, thus leading to reduce the adsorbed amount of O_2 . Moreover, the driving force of the reaction increases with the increasing of NO concentration, but the amount of NO to be resolved also increases. And the final result leads to this phenomenon.

C. Effect of GHSV on NO Conversion

The space velocity is very important for practical applications. Fig. 6 is catalytic activity of 07CrCZ4-400 in a range of GHSV from 12,000 to 30,000 mL/(h·g). As shown in Fig. 6, the NO conversion increased clearly as GHSV decreased. However, the oxidation efficiency increases slightly while the GHSV decreases from 20,000 to 12,000 mL/(h·g). When the GHSV reached 12,000 mL/(h·g), 07CrCZ4-400 has an excellent NO conversion that was 59.17% at 300 °C.

IV. CONCLUSION

The $Cr/Ce_xZr_{1-x}O_2$ catalysts have a good performance on NO oxidation efficiency. And the above mentioned results showed that 7%Cr/ $Ce_{0.14}Zr_{0.86}O_2$ which was calcined at 400 °C showed optimal catalytic oxidation activity. The oxidation efficiency at 300 °C reaches 62.18% under the conditions of that GHSV=20,000 mL/(h·g), the O_2 concentration is 8% and the NO concentration is 390 ppm. O_2 is important for the NO adsorption over the $Cr/Ce_xZr_{1-x}O_2$ catalysts and the NO concentration is not suitable too high to reducing the active sites on the catalysts, thus decreasing the adsorbed amount of O_2 .

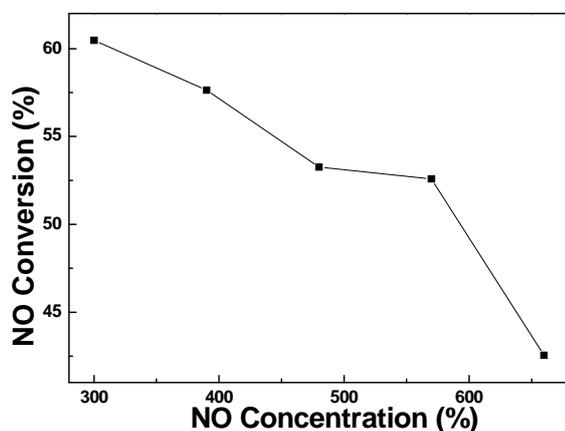


Fig. 5. The effect of NO concentration on NO conversion of 07CrCZ4-400. Reaction conditions: 8% O_2 , N_2 as balance gas, GHSV=20000 mL/(h·g), T=300 °C.

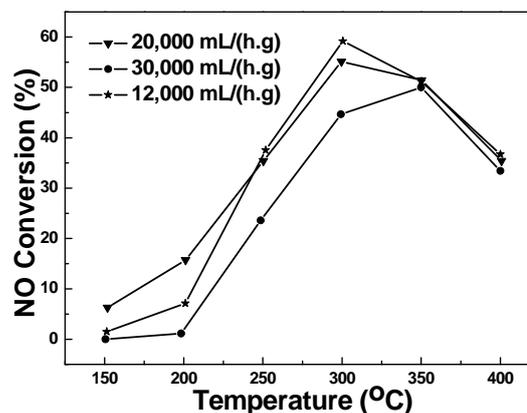


Fig. 6. The catalytic activity of 07CrCZ4-400 in a range of GHSV from 12,000 to 20,000 mL/(h·g). Reaction conditions: 390 ppm NO, 8% O_2 , N_2 as balance gas.

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- Denitration Technology and Engineering Applications in Power Plant Flue Gas. Beijing: Keqin Sun, Qin Zhong, Chemical Industry Press, 2007.
- Desulfurization System Design, Construction and Operation In Power Plant Flue Gas. Beijing: Keqin Sun, Qin Zhong, Chemical Industry Press, 2005.

Currently, he is interesting in studying how to removal the mercury in the gas and at the same time to removal NO_x with the way of SCR.

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