Effect of Cerium Precursor on the Performance of Pure CeO₂ Catalysts for Selective Catalytic Reduction of NO with NH₃

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Pure CeO₂ catalysts were prepared from different cerium precursors and their activities for selective catalytic reduction of NO with NH₃ were investigated in the presence of O₂. The results showed that the catalysts prepared from cerium nitrate have better selective catalytic reduction performance and SO₂ resistance. As can be seen from the BET, XRD, TPR, TPD and XPS results, the good performance of the catalysts prepared from cerium nitrate should be resulted from large surface area, good redox ability, high NH₃ adsorption capacity and enrichment of Ce³⁺ on the surface accompanied by an increase of active oxygen content.

Key Words: CeO₂, Citric acid method, Selective catalytic reduction.

INTRODUCTION

NO_x emitted from stationary sources such as coal-fired power plants and incinerators has caused serious environmental problems. And selective catalytic reduction process has been used to remove NO_x from power plants for several decades¹. Now, the V₂O₅/TiO₂ catalysts have been widely employed in power plants and perform well in the temperature range of 300-400 °C^{2,3}. But the drawbacks of this kind catalyst such as formation of N₂O at high temperature^{4,5}, emission of vanadia⁵ would cause secondary pollution. Therefore, developing new selective catalytic reduction catalyst has drawn much interest during the past years⁷⁻⁹.

CeO₂ has been usually used as the active component of selective catalytic reduction catalyst due to its oxygen storage and redox properties⁷. The redox shift between Ce⁴⁺ and Ce³⁺ of CeO₂ can promote NO oxidation to NO₂, which is beneficial to selective catalytic reduction reaction. As such, CeO₂ has been widely used as key component of selective catalytic reduction catalyst for NO_x removal such as CeO₂/TiO₂⁶, CeO₂/Al₂O₃¹⁰, CeO₂/zeolite¹¹, Mn-Ce/TiO₂¹². It had been reported that ceria based catalyst has great resistance to SO₂ and H₂O poisoning in selective catalytic reduction reaction^{11,13}.

However, few reports have focused on the reduction of NO by NH₃ over pure CeO₂ catalysts. In this work, we prepared pure CeO₂ catalysts from different cerium precursors by using the citric acid method. Then the activities of these catalyst

samples for selective catalytic reduction of NO with NH₃ were tested in the presence of O₂. Moreover, the crystalline structures and surface properties of these catalyst samples were characterized by XRD, BET, TPR, TPD and XPS methods to investigate the precursor effect.

EXPERIMENTAL

Catalyst preparation: The catalyst samples were prepared by using the citric acid method¹⁴. Cerium nitrate and citric acid were mixed under vigorous stirring and the mole ratio of citric acid to cerium nitrate was kept at 1.0. After the mixture was stirred at room temperature for 1 h, the solution was dried at 100 °C, forming a porous, foam-like solid. Then the foam-like precursor was calcined in air at 550 °C for 6 h. The catalyst samples using cerium acetate as the cerium precursor were prepared by the same procedure. The catalysts were denoted as CeO₂-CN and CeO₂-CA respectively. CN represented cerium nitrate and CA represented cerium acetate.

Catalytic activity evaluation: Selective catalytic reduction of NO with NH₃ was carried out in a fixed-bed quartz reactor (19 mm i.d.) at 150-350 °C, with 1 g catalyst of 60-100 mesh. All experiments were performed under atmosphere pressure. The typical reactant gas composition was as follows: 600 ppm NO, 600 ppm NH₃, 5 % O₂, balanced with Ar. The flow rate of reactant gas was kept at 1 L/min with a gas hourly space velocity of 28,000 h⁻¹. The concentrations of NO in the

inlet and outlet of the reactor were continuously measured by a flue gas analyzer (Model 60i, Thermo Fisher Scientific Inc.).

Catalyst characterization: The textural properties of the catalysts samples were measured by N_2 adsorption/desorption at -196°C with a surface area and pore size analyzer (3 H-2000 PS4, Beishide Instrument Co. Ltd.). Then the specific surface areas and pore volumes of the catalyst samples could be calculated by using the BET (Brunauer-Emmett-Teller) method based on the obtained adsorption-desorption isotherms.

X-ray diffraction (Rigaku/max2550pc, $\text{CuK}\alpha$ radiation) was used to determine the crystal phase of catalyst samples. Scans were taken over a 2θ range of 20 – 80° with a step size of 0.02° .

Temperature programmed reductions (TPR) (Quantachrome Autosorb-1C-VP) were used to compare the reduction temperatures of the catalyst samples prepared from different cerium precursors. The H_2 consumption was measured with an analysis gas of 10 % He/Ar and heating rate of $10^\circ\text{C}/\text{min}$, from 100 to 900°C .

Total acidity was measure by a temperature programmed desorption (TPD) of ammonia using a custom-made thermal conductivity detector (TCD) setup (TP-5000, Xianquan, China) using 50 mg catalyst sample. The samples were preheated to 500°C in pure He flow for 1 h. Then the catalyst samples were cooled down to room temperature in pure He and then saturated for 0.5 h with a stream of pure NH_3 (flow rate = $1\text{ mL}/\text{min}$). After saturation, the catalysts were flushed in a pure He flow for 0.5 h at 100°C . Finally, the temperature programmed desorption of NH_3 was performed in pure He stream (flow rate = $30\text{ mL}/\text{min}$) with a heating rate of $10^\circ\text{C}/\text{min}$ from 100 to 850°C .

XPS measurements were made using an AXIS-NOVA (Kratos, Inc.). A monochromatic $\text{AlK}\alpha$ (1486.6 eV) X-ray source and 40 eV of analyzer pass energy were used under ultra-high vacuum conditions ($5.2 \times 10^{-9}\text{ Torr}$).

RESULTS AND DISCUSSION

Catalytic activity of pure CeO_2 catalysts: The activity of the pure CeO_2 catalysts prepared from the two kinds of cerium precursors with the variation of reaction temperature is presented in Fig. 1. It is clear that $\text{CeO}_2\text{-CN}$ shows higher NO conversion than $\text{CeO}_2\text{-CA}$ over the entire temperature range tested. In addition, the change of the catalytic activity shows a parabola curve with increasing reaction temperature. And the highest NO conversion is 73.3 %, that is to say, the catalytic activity of pure CeO_2 catalysts is not very high. The similar phenomena was also observed by Gu *et al.*¹³. The maximum NO conversion of pure CeO_2 catalyst samples used in their work was only about 36 %. The difference in NO conversion of our work and Gu *et al.*¹³ may be caused by different preparation method and experimental conditions. The maximum NO conversions for the two catalysts appear at about 250°C , but when the reaction temperature exceeds 250°C , NO conversion would decrease with increasing reaction temperature. This may be attributed to an increase of energy below 250°C and the reduction of activated NH_3 amount caused by unselective oxidation of NH_3 by O_2 at high temperature¹⁵.

Fig. 1. NO conversion at different reaction temperatures for the two catalysts; Reaction conditions: $[\text{NO}]=[\text{NH}_3]=600\text{ ppm}$, $[\text{O}_2]=5\%$, balance Ar, total flow rate = $1\text{ L}/\text{min}$, GHSV = $28,000\text{ h}^{-1}$

Effect of SO_2 on the catalytic activity of pure CeO_2 catalysts: It is well known that SO_2 has strong inhibition effect on the catalytic activity^{6,16}. Thus the effect of SO_2 on the catalytic activity of pure CeO_2 catalysts was investigated in this study. The results are shown in Fig. 2. When 200 ppm SO_2 was added into the reactant gas stream, the NO conversion of $\text{CeO}_2\text{-CN}$ catalyst decreased from 62 % to 50 % in 3 h, after SO_2 was turned off, NO conversion increased from 50 % to 56.9 % in 3 h. As for $\text{CeO}_2\text{-CA}$, the effect of SO_2 on its catalytic activity was similar with that of $\text{CeO}_2\text{-CN}$. But the deactivation effect caused by SO_2 is more obvious compared with $\text{CeO}_2\text{-CN}$. Therefore, it can be concluded that the catalyst prepared from cerium nitrate has good SO_2 resistance performance. This may be caused by the different cerium species state on the surface of the two CeO_2 catalysts. It could also be seen from Fig. 2, NO conversion over the two samples recovered obviously after SO_2 was cut off, nearly restoring to the original level, which might be due to the increase of active oxygen species or enhancement of NH_3 chemical adsorption¹³.

Fig. 2. Effect of SO_2 on the catalytic activity of pure CeO_2 catalysts; Reaction conditions: $[\text{NO}]=[\text{NH}_3]=600\text{ ppm}$, $[\text{SO}_2]=200\text{ ppm}$, reaction temperature = 200°C , $[\text{O}_2]=5\%$, balance Ar, total flow rate = $1\text{ L}/\text{min}$, GHSV = $28,000\text{ h}^{-1}$

BET and XRD measurements: The textural properties of the pure CeO₂ catalysts prepared from the two kinds of cerium precursors are listed in Table-1. As can be seen from Table-1, there are great differences in the textural properties of the two pure CeO₂ catalyst samples. The surface area and total pore volume of CeO₂-CN are much larger than that of CeO₂-CA, which is helpful to enhancing its catalytic activity.

Samples	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)	Mean crystallite size of CeO ₂ (nm)
CeO ₂ -CN	38.96	0.1458	18.97	13.9
CeO ₂ -CA	8.29	0.0529	25.54	15.4

Fig. 3 shows the XRD patterns of the pure CeO₂ catalysts prepared from the two kinds of cerium precursors. As shown in Fig. 2, the diffraction intensity of CeO₂-CN sample is much weaker than that of CeO₂-CA, indicating that CeO₂-CN has a lower CeO₂ crystallinity. The mean crystallite size of CeO₂ was calculated using Scherrer equation. And the results are given in Table-1. It is obvious that CeO₂-CN has smaller mean crystallite size of CeO₂, which is consistent with XRD intensity. Thus, highly dispersed CeO₂ crystallite in CeO₂-CN catalyst might partly contribute to its high activity.

Fig. 3. XRD profiles of the pure CeO₂ catalysts

Temperature programmed reductions analysis: H₂-TPR analysis was performed to evaluate the reducibility of pure CeO₂ catalysts. And the redox ability can be reflected from the reduction peak temperature, lower reduction peak temperature means stronger redox ability¹⁷. As illustrated in Fig. 4, there are two peaks for CeO₂-CN and CeO₂-CA respectively. The first peak at 479.6 °C for CeO₂-CN could be assigned to the reduction of the surface oxygen of stoichiometric ceria of type Ce⁴⁺-O-Ce⁴⁺^{18,19}. And the second peak at 841.2 °C should be caused by the formation of Ce₂O₃¹⁸. In addition, the peaks are much broader and more intensive than that of CeO₂-CA. Also, it was found that the initial reduction peak temperature of CeO₂-CN is lower than that of CeO₂-CA. And the main reduction peaks of CeO₂-CA shift to higher

Fig. 4. H₂-TPR profiles of the pure CeO₂ catalysts

temperature. Thus CeO₂-CN shows a better redox property than CeO₂-CA, which is helpful to enhance its selective catalytic reduction performance.

Temperature programmed desorption analysis: Temperature programmed desorption experiments of NH₃ has been carried out to investigate the adsorption of NH₃ on the catalysts. The results are shown in Fig. 5. As can be seen from Fig. 5, there are two main peaks in the profiles of both CeO₂-CN and CeO₂-CA, indicating the presence of several adsorbed species with different thermal stability on the surface of the catalysts. As for CeO₂-CN, the two broad overlapped desorption peaks are centered at 288.5 °C and 401.6 °C respectively. These peaks are mainly corresponded to the successive desorption of ammonia physisorbed to weak acid sites and likely linked to Brönsted acid sites²⁰. And the desorption peak centered at 713.8 °C in the profile of CeO₂-CA could be assigned to the existence of strong acid sites²¹. Furthermore, the NH₃ desorption peaks of CeO₂-CN is much broader and more intensive than that of CeO₂-CA. Therefore, CeO₂-CN shows stronger NH₃ adsorption capacity than CeO₂-CA. And the improvement in NH₃ adsorption capacity is believed to be beneficial to selective catalytic reduction reaction²².

Fig. 5. NH₃-TPD profiles of the pure CeO₂ catalysts

XPS analysis: XPS analysis was carried out to determine the chemical states of the elements on the surface of the catalysts. And the XPS spectra of Ce 3d and O 1s are shown in Fig. 6. According to the study of Burroughs *et al.*²³, XPS peaks in Fig. 6 (1) denoted as u, u', u'' and v, v', v'' could be assigned to Ce⁴⁺ state while u' and v' peaks could be attributed to Ce³⁺. As can be seen from Fig. 6 (1), the intensities of Ce⁴⁺ characteristic peaks in the spectra of CeO₂-CA is more intensive than that of CeO₂-CN. But the characteristic peaks attributed to Ce³⁺ in the spectra of CeO₂-CN seems more obvious. The increase of Ce³⁺ concentration is helpful to the migration of oxygen from bulk to the surface, which can promote the activation and transportation of active oxygen species on the surface of catalyst samples. As a result, CeO₂-CN shows better selective catalytic reduction activity than CeO₂-CA.

Fig. 6. (1) Ce 3d, (2) O 1s XPS spectra of (a) CeO₂-CN (b) CeO₂-CA

The O 1s spectra are illustrated in Fig. 6 (2). As shown in Fig. 6 (2), the peak due to chemisorbed oxygen O_β (531.3-531.9 eV)²⁴ in the spectra of CeO₂-CN is much broader and more intensive than that in the spectra of CeO₂-CA, which means a higher concentration of chemisorbed oxygen in CeO₂-

CA. It has been reported that chemisorbed oxygen is the most active oxygen in selective catalytic reduction reaction²⁵. Therefore, the high surface chemisorbed oxygen in the CeO₂-CN catalyst sample could also increase its selective catalytic reduction activity.

Conclusion

The catalyst prepared from cerium acetate shows better catalytic activity and SO₂ resistance compared from the catalyst prepared from cerium nitrate. The better performance of CeO₂-CN might be attributed to its large surface area, good redox ability, high NH₃ adsorption capacity, enrichment of Ce³⁺ on the surface accompanied by an increase of active oxygen content.

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