

Selective Catalytic Reduction of NO by NH₃ Over Ceria: Effect of Calcination Temperature on the Activity of Catalysts

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Ceria was investigated as a catalyst for selective catalytic reduction of NO by NH₃. The ceria catalysts were prepared by citric acid method with different calcination temperature. Experimental results showed that the selective catalytic reduction activity of ceria catalyst decreases with increasing calcination temperature within the reaction temperature range of 150-350 °C. As can be seen from the characterization results of BET, XRD, temperature programmed reduction, total programmed desorption and XPS, the best selective catalytic reduction performance of ceria catalyst calcinated at 350 °C may be resulted from its large surface area, good redox ability, strong NH₃ adsorption capacity and high concentration of active oxygen species on the surface of this catalyst.

Keywords: Selective catalytic reduction, CeO₂, NO, NH₃.

INTRODUCTION

Selective catalytic reduction (SCR) of NO_x with NH₃ is the most effective process for removing NO_x from coal-fired power plants. The commercial catalysts such as V₂O₅/TiO₂ and V₂O₅-WO₃/TiO₂¹ are not environmental friendly due to the formation of N₂O² and toxicity of vanadia³. Therefore, it is necessary to develop new selective catalytic reduction catalysts with high activity for NO removal.

Due to its high oxidation storage capacity, *d*-electron orbital, good sulfur-resistance and excellent redox properties⁴, CeO₂ has drawn much attention for SCR of NO in recent years. Shen *et al.*⁵ found that the selective catalytic reduction of NO over CeO₂/Al₂O₃ may be an oxidation-reduction process. Gao *et al.*⁶ reported that preparation method had great impact on the SCR performance of CeO₂/TiO₂ catalyst. And the experimental results of Gu *et al.*³ showed that surface sulfation could enhance the SCR activity of CeO₂.

The literatures mentioned above focused on the SCR performance of CeO₂ over some supports. However, effect of preparation conditions on the SCR performance of pure CeO₂ has not been found in the literature. Therefore, the influence mechanism of calcination temperature on the SCR activity of pure CeO₂ catalyst is the objective of the present study.

EXPERIMENTAL

Catalyst preparation: The CeO₂ catalysts were prepared by citric acid method⁷. Cerium nitrate and citric acid were mixed with a mole ratio of cerium nitrate to citric acid of 1.0. The mixture mentioned above was stirred at room temperature for 1 h. Then the solution was dried at 100 °C, forming a porous and foamy solid. Then the foam-like precursor was calcinated at a desired temperature for 6 h. And the catalyst samples were denoted as CeO₂(y), where y represented the calcination temperature.

Catalytic activity test: The SCR activities of the catalysts were measured in a fix-bed flow reactor (i.d. 19 mm). Four gas streams: 600 ppm NO, 600 ppm NH₃, 5 % O₂ and pure Ar in balance were used to simulated the flue gas. In all the experimental runs, the total gas flow rate was kept at 1 L/min over a certain amount of catalyst sample (60-100 mesh) corresponding to a gas hourly space velocity (GHSV) of 28,000 h⁻¹. During the experiments, the concentrations of NO and NO₂ were continuously monitored by a flue gas analyzer (Model 60i, Thermo Fisher Scientific Inc.).

Characterization of catalyst: Brunauer-Emmett-Teller (BET) surface area was measured by N₂ adsorption/desorption at -196 °C with a surface area and pore size analyzer (3H-2000PS4, Beishide Instrument Co. Ltd.).

X-Ray diffraction (Rigaku/max2550pc, $\text{CuK}\alpha$ radiation) was used to analyze the crystal structure of the catalysts, with a scan range of $20\text{--}80^\circ$ and a step size of 0.02° .

Temperature programmed reduction (H_2 -TPR) experiments were carried out using a Quantachrome Autosorb-1C-VP Analyzer to study the redox behaviour of the catalyst samples prepared at different calcination temperatures. 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 $150\text{--}850^\circ\text{C}$.

The temperature programmed desorption (NH_3 -TPD) was performed a custom-made thermal conductivity detector (TCD) setup (TP-5000, Xianquan, China) using 50 mg catalyst sample. At the start of the experiment, the samples should be pretreated in pure He at 500°C for 1 h. Subsequently, 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 mL/min. After saturation, the catalysts were flushed in a pure He flow for 0.5 h at 100°C . Finally, the TPD of NH_3 was performed in pure He stream (flow rate = 30 mL/min) with a heating rate of $10^\circ\text{C}/\text{min}$ from $125\text{--}825^\circ\text{C}$.

XPS (Kratos, Inc.) with $\text{AlK}\alpha$ ($h\nu = 1486.6\text{ eV}$) as the excitation source was used to determine the binding energies of Ce 3d and O1s. The C1s line at 284.6 eV was taken as a reference for the binding energy calibration.

RESULTS AND DISCUSSION

Catalytic performance: Fig. 1 shows the SCR performance of CeO_2 catalysts. As can be seen from Fig. 1, the calcination temperature influences the SCR activity significantly. The SCR performance of CeO_2 catalysts decreases with increasing calcination temperature. In addition, when reaction temperature is below 250°C , NO conversion increases with increasing reaction temperature; but when reaction temperature exceeds 250°C , it would decrease with increasing reaction temperature, which may be due to an increase of surface energy below 250°C and the oxidation of NH_3 to NO at high temperature⁵.

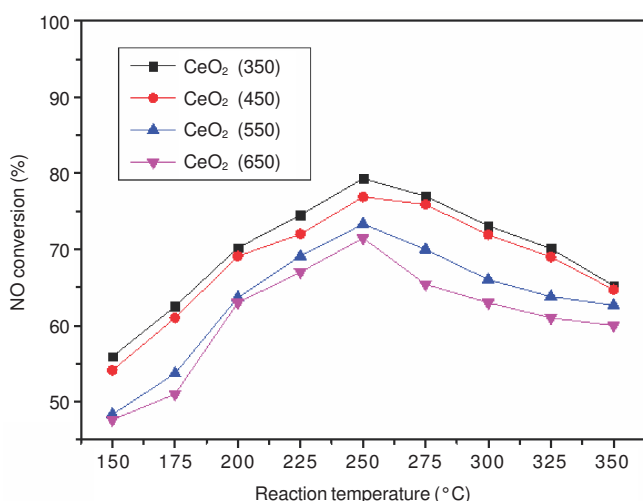


Fig. 1. NO conversion as a function of reaction temperature for different catalysts. Reaction conditions: $[\text{NO}] = \text{NH}_3 = 600\text{ ppm}$, $[\text{O}_2] = 5\%$, balance Ar, total flow rate = 1 L/min, GHSV = $28,000\text{ h}^{-1}$

BET measurements: To find out the relation between the calcination temperature and the textural properties of CeO_2

catalysts, N_2 -adsorption experiment was conducted. The textural properties of CeO_2 catalysts examined in this work are listed in Fig. 2. As shown in Fig. 2, the surface area and total pore volume of CeO_2 catalyst samples decrease with increasing calcination temperature, which may be caused by the pore collapse during calcination process. The large surface area and pore volume are helpful to enhancing the SCR activity of CeO_2 catalyst. However, it seems that there is no correlation between the average pore diameter and SCR activity.

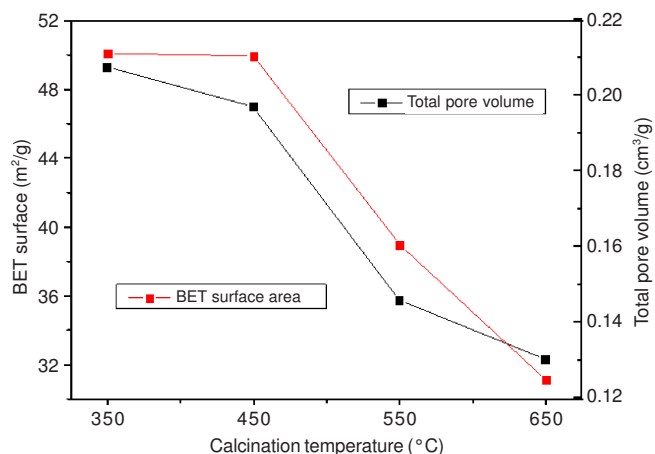


Fig. 2. Effect of calcination temperature on the textural properties of CeO_2 catalysts

XRD analysis: Fig. 3 shows the XRD patterns of the CeO_2 catalysts calcinated at different temperatures. As indicated in Fig. 3, the calcination temperature has great impact on the diffraction intensity of CeO_2 peaks. Although there are several small peaks are apparent for crystalline CeO_2 in $\text{CeO}_2(350)$, the intensity of the bands was relatively low. Therefore, it could be concluded that CeO_2 is dispersed well in this sample. Therefore, highly dispersed CeO_2 crystallite in $\text{CeO}_2(350)$ may be another reason for its high SCR activity.

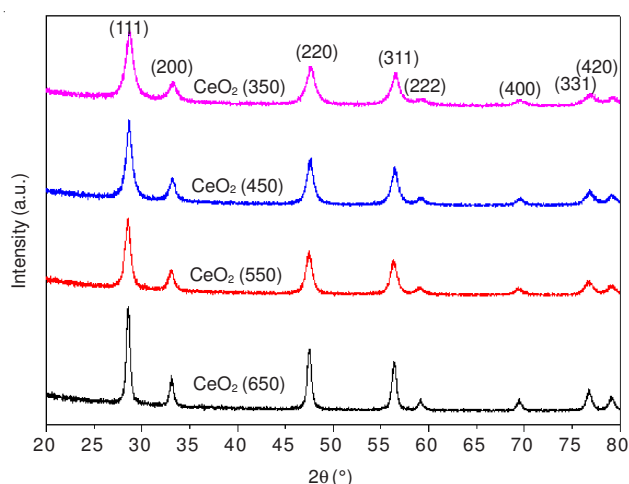


Fig. 3. XRD patterns of the CeO_2 catalysts calcinated at different temperature

Temperature programmed reduction (TPR) analysis: It is well known that the redox ability of catalysts has great impact on its SCR performance because is bound up with redox cycle⁸. H_2 -TPR analysis was used to study the redox ability of the

CeO₂ catalysts calcinated at different temperature. The results are shown in Fig. 4. As illustrated in Fig. 4, there are two peaks for the four catalyst samples. The first peak between 400-500 °C could be assigned to the reduction of the surface oxygen of stoichiometric ceria of type^{9,10} Ce⁴⁺-O-Ce⁴⁺. Second peak around 800 °C should be caused by the formation of Ce₂O₃⁹. In addition, the peaks in the profile of CeO₂ (350) are much broader and more intensive than that in the profile the other catalyst samples. It was also found that the initial reduction peak temperature of CeO₂ (350) is lower than that of other catalyst samples. And the main reduction peaks of the other catalyst samples shift to higher temperature. Thus CeO₂ (350) shows the best redox property among the four catalysts, which is helpful to enhance its SCR performance.

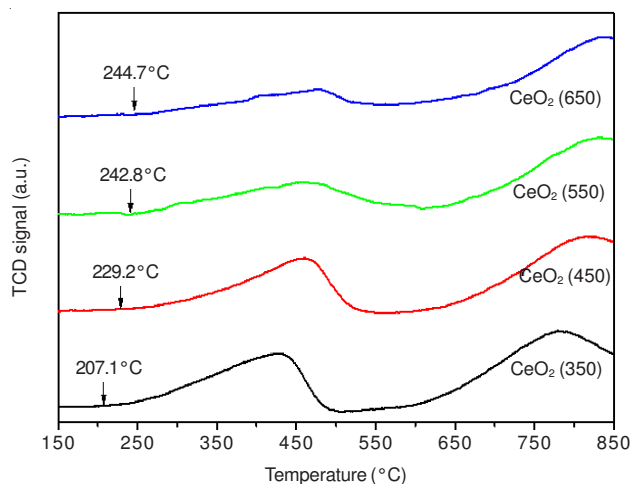


Fig. 4. H₂-TPR profiles of the CeO₂ catalysts calcinated at different temperature

Temperature programmed desorption analysis: Fig. 5 shows the ammonia desorption profiles of the CeO₂ catalysts. As can be seen from Fig. 5, there are several peaks in the NH₃-TPD spectra of CeO₂(350) and CeO₂(450) ranging within 125-700 °C. These peaks could be attributed to the successive desorption of ammonia physisorbed or chemisorbed¹¹. And the desorption peaks centered at *ca.* 800 °C are related to the existence of strong acid sites. Furthermore, the NH₃ desorption peaks of CeO₂ (350) are more intensive and broader than that of the other catalyst samples. Besides that, the NH₃ desorption peak of CeO₂(350) appears at the lowest temperature compared with that of the other catalyst samples. That is to say, CeO₂ (350) has strong NH₃ adsorption capacity. It has been recognized that the surface acidity plays a critical role in SCR reaction¹². Thus the strong NH₃ adsorption capacity of CeO₂ (350) has a great contribution to its high SCR activity.

XPS analysis: Fig. 6 shows the chemical states of the elements on the surface of the catalyst determined by XPS analysis. In the XPS spectra of Ce 3d, the peaks 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⁺^{1,13}. It is obvious that Ce (350) has the highest surface Ce³⁺ content among the four catalyst samples. On one hand, the increase of Ce³⁺ content would lead to the generation of more oxygen vacancies in the catalyst. On the other hand, oxygen vacancies could promote the enrichment of gaseous oxygen on the surface of catalyst.

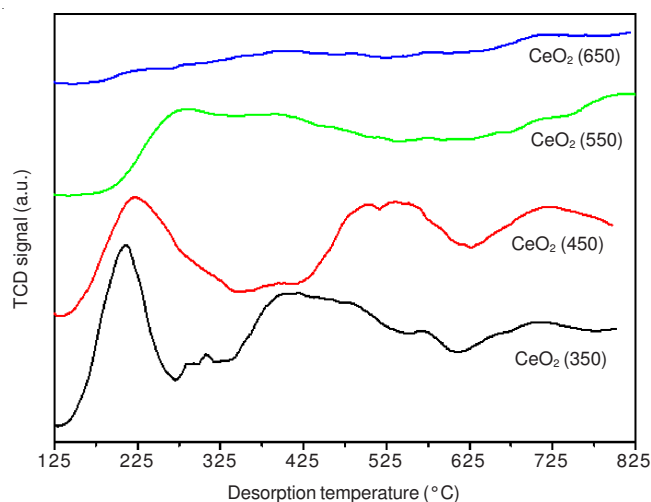


Fig. 5. NH₃-TPD profiles of the CeO₂ catalysts calcinated at different temperature

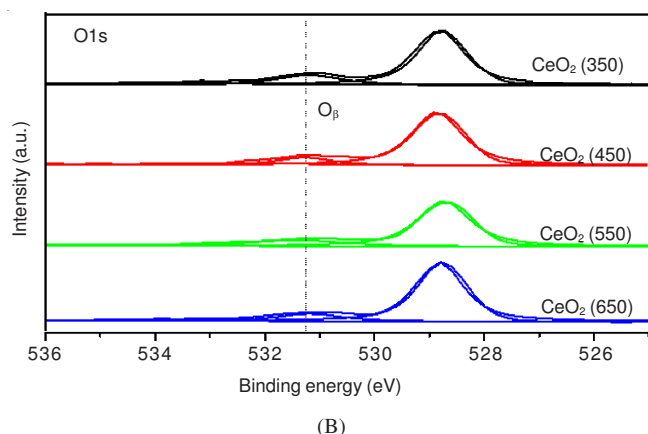
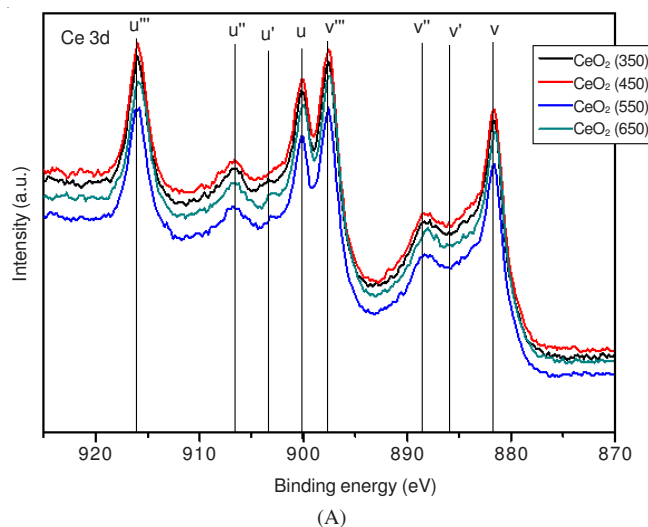


Fig. 6. XPS spectra of the CeO₂ catalysts calcinated at different temperature

As a result, CeO₂ (350) catalyst shows a good SCR activity due to the activation and transportation of active oxygen species in SCR reaction.

It was widely accepted that the surface chemisorbed oxygen O^β(531.3-531.9 eV)¹⁴ was the most active oxygen in SCR reaction. As can be seen from Fig. 6(B), the high concentration of surface chemisorbed oxygen in CeO₂ (350) catalyst may be another reason for its high SCR activity.

Conclusion

Effect of calcination temperature on the SCR performance of CeO₂ catalyst was investigated. And the catalyst calcinated at 350 °C shows the highest NO conversion. The characterization results indicate that large surface area, good redox ability, high NH₃ adsorption capacity and high concentration of surface chemisorbed oxygen might be the main reasons for the excellent SCR performance of this catalyst.

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REFERENCES

1. X. Gao, Y. Jiang, Y. Zhong, Z. Luo and K. Cen, *J. Hazard. Mater.*, **174**, 734 (2010).
2. W. Shan, F. Liu, H. He, X. Shi and C. Zhang, *Catal. Today*, **184**, 160 (2012).
3. T. Gu, Y. Liu, X. Weng, H. Wang and Z. Wu, *Catal. Commun.*, **12**, 310 (2010).
4. M. Adamowska, A. Krzton, M. Najbar, P. Da Costa and G. Djéga-Mariadassou, *Catal. Today*, **137**, 288 (2008).
5. Y. Shen, S. Zhu, T. Qiu and S. Shen, *Catal. Commun.*, **11**, 20 (2009).
6. X. Gao, Y. Jiang, Y. Fu, Y. Zhong, Z. Luo and K. Cen, *Catal. Commun.*, **11**, 465 (2010).
7. G. Qi and R.T. Yang, *Chem. Commun.*, **39**, 848 (2003).
8. N.Y. Topsoe, H. Topsoe and J.A. Dumesic, *J. Catal.*, **151**, 226 (1995).
9. S. Damyanova, C.A. Perez, M. Schmal and J.M.C. Bueno, *Appl. Catal. A: Gen.*, **234**, 271 (2002).
10. B. Murugan and A.V. Ramaswamy, *J. Phys. Chem. C*, **112**, 20249 (2008).
11. H. Wang, X. Chen, X. Weng, Y. Liu, S. Gao and Z. Wu, *Catal. Commun.*, **12**, 1042 (2011).
12. L. Lietti, I. Nova, G. Ramis, L. Dall'Acqua, G. Busca, E. Giamello, P. Forzatti and F. Bregani, *J. Catal.*, **187**, 419 (1999).
13. P. Burroughs, A. Hamnett, A.F. Orchard and G. Thornton, *J. Chem. Soc. Dalton Trans.*, **17**, 1686 (1976).
14. M. Kang, E.D. Park, J.M. Kim and J.E. Yie, *Appl. Catal. A: Gen.*, **327**, 261 (2007).