

The Remarkable Improvement of a Ce–Ti based Catalyst for NO_x Abatement, Prepared by a Homogeneous Precipitation Method

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The selective catalytic reduction (SCR) of NO_x by NH₃ (NH₃-SCR) over V₂O₅–WO₃ (MoO₃)/TiO₂, has been widely used for the removal of NO_x emissions from stationary sources, especially for coal-fired power plants.^[1–3] Additionally, NH₃-SCR is thought to be one of the most promising technologies for NO_x elimination from diesel engines, which has attracted considerable attention under the effect of more and more strict legislation for NO_x emissions.^[4–6] Some inevitable problems (especially the toxicity of active vanadium species) have restrained the practical applications of traditional vanadium-based catalysts for NO_x abatement from diesel engine exhaust. The exhaust gas temperature from a diesel engine is mainly in the range of 200–350 °C.^[7] However, zeolite-based NH₃-SCR catalysts often present insufficient activity at low temperatures, as well as the recently reported WO₃/CeO₂-ZrO₂ catalyst, when NO_x mainly consists of NO.^[4] Recently, a Ce–Ti based catalysts, with high activity in the temperature range of 275–400 °C, has been reported as a potential substitution for toxic vanadium-based NH₃-SCR catalyst.^[8–10]

We have presented the NH₃-SCR activity of a Ce/TiO₂ catalyst prepared by using an impregnation method,^[8] and investigated the deactivation mechanism of this catalyst by SO₂.^[11] Gao et al.^[9,10] studied the activity of CeO₂–TiO₂ catalyst prepared by sol–gel method for NH₃-SCR. Nevertheless, the reported Ce–Ti based catalysts still have some problems in practical use, such as the narrow operation temperature window and poor activity in the low temperature range.

Previous studies have shown that catalyst preparation methods can significantly influence the catalytic performance of Ce–Ti based catalysts, and a good dispersion of active component CeO₂ on TiO₂ is very important for the improvement of NH₃-SCR activity.^[8–10] Homogeneous precipitation, characterized by a highly uniform increase in the pH of metal salts solution achieved by thermal decomposition of some organic alkali, is a suitable catalyst preparation method that can produce highly dispersed mixed metal oxides. In this study, we report a significant improvement of Ce–Ti based catalyst prepared by a homogeneous precipitation method using urea as precipitator.

NO_x conversions and N₂ selectivity over Ce_aTiO_x(500) (*a* = 0.1, 0.2, 0.5, 1.0) are presented in Figure 1. Ce_{0.1}TiO_x(500) showed

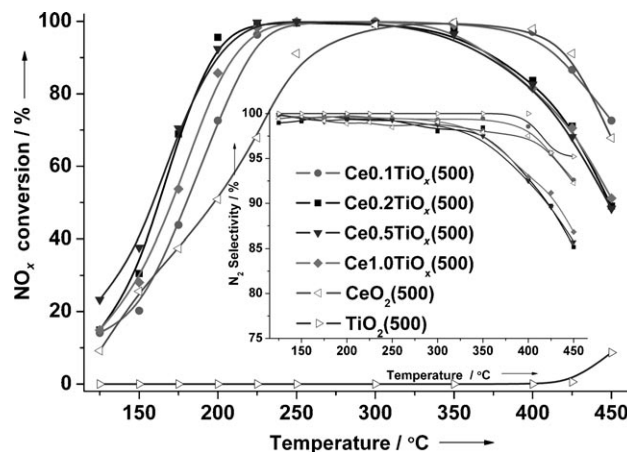


Figure 1. NO_x conversions and N₂ selectivity (inserted) over catalysts with different Ce/Ti molar ratios (GHSV = 50 000 h⁻¹).

relatively low activity in the low temperature range from 125 to 225 °C and high activity, also excellent N₂ selectivity, in the high temperature range from 350 to 450 °C. As the Ce loading was increased, both Ce_{0.2}TiO_x(500) and Ce_{0.5}TiO_x(500) presented enhanced low temperature activity in comparison with Ce_{0.1}TiO_x(500), while the high temperature NO_x conversions decreased to a certain extent. However, further increase of the Ce loading to Ce/Ti = 1.0 resulted in a decrease in the NO_x conversion in the low temperature range. Pure TiO₂ showed no SCR activity below 400 °C, and pure CeO₂ showed limited low temperature activity, which indicated a significant synergistic effect between CeO₂ and TiO₂ in NH₃-SCR reaction. NH₃ was almost completely consumed over Ce_{0.2}TiO_x(500) and Ce_{0.5}TiO_x(500) with no considerable slip above 200 °C (see Figure S1 in the Supporting Information).

Considering the excellent SCR activity in the main temperature range of diesel engine exhaust (200–350 °C), we chose Ce_{0.2}TiO_x(500) and Ce_{0.5}TiO_x(500) for further examination with a higher gas hourly space velocity (GHSV) to find out the optimal Ce/Ti molar ratio (Figure 2). As the GHSV was increased from 50 000 to 100 000 h⁻¹, the NO_x conversion over Ce_{0.5}TiO_x(500) showed an obvious decrease, both in the low and high temperature range, accompanied by a decrease of N₂ selectivity above 300 °C. However, the change of GHSV showed only a relatively slight influence on Ce_{0.2}TiO_x(500) in comparison with Ce_{0.5}TiO_x(500); the influence occurred only in the low temperature range. We further increased the GHSV to 150 000 h⁻¹ and found that the NO_x conversion and N₂ selectivity over Ce_{0.2}TiO_x(500) at high temperatures still showed no obvious decrease, although the NO_x conversion at low temperatures decreased further.

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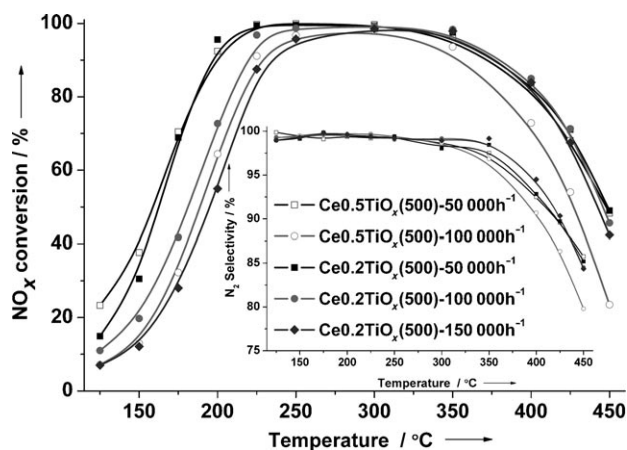


Figure 2. NO_x conversions and N₂ selectivity (inserted) over Ce_{0.2}TiO_x(500) and Ce_{0.5}TiO_x(500) under different GHSV.

In comparison with pure TiO₂(500) and CeO₂(500), the mixed oxide catalysts with different Ce/Ti molar ratios showed increased BET surface areas (see Table S1), which were attributed to the inhibition of the individual TiO₂ and CeO₂ crystallization in the homogeneous precipitation process.^[12] The BET surface area increased sharply from 127.6 m²g⁻¹ for pure TiO₂(500) to 198.8 m²g⁻¹ for Ce_{0.1}TiO_x(500), but decreased continuously with the further increases of the Ce/Ti molar ratio. The Ce–Ti mixed oxide catalysts prepared by means of the homogeneous precipitation method clearly presented larger surface areas than those of previously reported catalysts.^[8,9] The variation of pore volume of the catalysts followed the same trend as that for the BET surface area. In addition, the pore diameters of the mixed oxide catalysts were all between those of pure TiO₂(500) and CeO₂(500). The X-ray diffraction (XRD) analysis revealed that there was no cubic CeO₂ phase in Ce_{0.1}TiO_x(500) and Ce_{0.2}TiO_x(500), indicating that the Ce exists as a highly dispersed or amorphous species (see Figure 3). As the Ce loading was increased, the cubic CeO₂ phase became apparent in Ce_{0.5}TiO_x(500) and Ce_{1.0}TiO_x(500). With the increase of Ce/Ti molar ratios, the average crystallite sizes of anatase TiO₂ in the catalysts calculated by using the Scherrer equation gradually

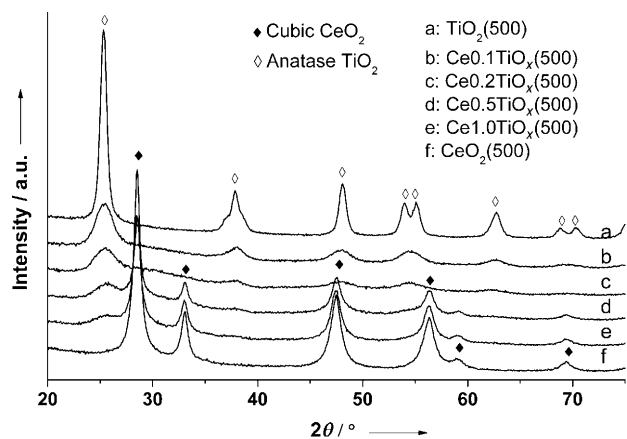


Figure 3. XRD profiles of catalysts with different Ce/Ti molar ratios.

increase, corresponding to the decrease of BET surface areas (see Table S1).

Based on the above results, we chose 0.2 as the optimal Ce/Ti molar ratio and further investigated the effect of calcination temperature (see Figure 4). There was no significant difference between Ce_{0.2}TiO_x(400) and Ce_{0.2}TiO_x(500) on NO_x conversion

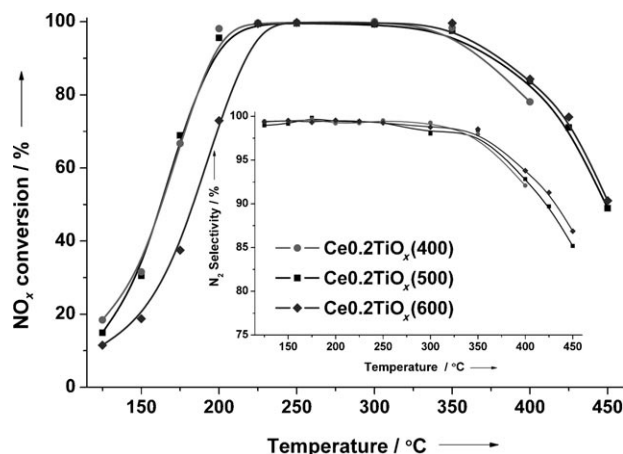


Figure 4. NO_x conversions and N₂ selectivity (inserted) over catalysts with different calcination temperature (GHSV = 50 000 h⁻¹).

and N₂ selectivity from 125 to 400 °C, whereas Ce_{0.2}TiO_x(600) clearly showed lower NO_x conversions in the low temperature range. The decrease of low temperature activity with the increased calcination temperature might be associated with the sintering effect, which has been confirmed by the transmission electron microscopy (TEM) analysis (see Figure S2). In addition, the BET surface area sharply decreased when the calcination temperature increased from 500 to 600 °C (see table S1). Nevertheless, there was still no cubic CeO₂ phase observed in Ce_{0.2}TiO_x(600) in the XRD analysis (see Figure S3).

The Ce_{0.2}TiO_x(500) catalyst was also tested in the presence of CO₂, H₂O, and SO₂, respectively (see Figure 5). The addition of 5 vol.% CO₂ to the feeding gas induced a slight decrease of low temperature (< 200 °C) activity and a slight increase of high temperature (> 300 °C) activity. The addition of 5 vol.% H₂O to the feeding gas markedly decreased the NO_x conversion below 225 °C, mainly due to the blocking of some active sites. However, a wider temperature range of 100% NO_x conversion from 225 to 425 °C was achieved, owing to the inhibition effect of H₂O on the unselective oxidation of NH₃. This finding could be verified by the decrease of NH₃ conversion and enhancement of N₂ selectivity in the SCR reaction over Ce_{0.2}TiO_x(500) in the presence of H₂O (see Figure S4). We also tested the NO_x conversion of a 4.5%V₂O₅-10%WO₃/TiO₂ catalyst in the presence of 5 vol.% H₂O for comparison. We can see that, Ce_{0.2}TiO_x(500) catalyst presented very similar catalytic activity to the V₂O₅-WO₃/TiO₂ catalyst. Addition of 100 ppm SO₂ to the feeding gas at 300 °C led to almost no change of NO_x conversion over the catalyst in 24 h, indicating a high resistance to SO₂ poisoning.

The catalyst prepared by homogeneous precipitation method in this study presented significantly enhanced catalytic

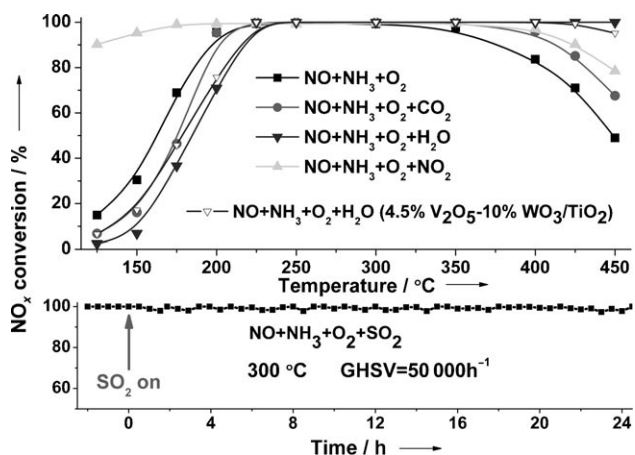


Figure 5. Influence of CO_2 , H_2O , SO_2 , and NO_2 on NO_x conversion in the NH_3 -SCR reaction over $\text{Ce}_{0.2}\text{TiO}_x(500)$ and the comparison of NO_x conversions over $\text{Ce}_{0.2}\text{TiO}_x(500)$ and a V_2O_5 - WO_3/TiO_2 catalyst. Reaction conditions: 500 ppm NO (or 250 ppm NO and 250 ppm NO_2), 500 ppm NH_3 , 5 vol.% O_2 , 5 vol.% CO_2 (when used), 5 vol.% H_2O (when used), 100 ppm SO_2 (when used), balance N_2 , and $\text{GHSV} = 50\,000\text{ h}^{-1}$.

activity, especially in the low temperature range (see Figure S5) in comparison with the previously reported Ce–Ti based catalysts, prepared by impregnation (20% Ce/TiO_2)^[8] and sol–gel ($\text{CeTi}(\text{SG})$)^[10] methods. Normalized by BET surface areas, the SCR reaction rates over $\text{Ce}_{0.2}\text{TiO}_x(500)$ were higher than that over 20% Ce/TiO_2 in the low temperature range. For example, the reaction rates of $\text{Ce}_{0.2}\text{TiO}_x(500)$ and 20% Ce/TiO_2 were 1.55×10^{-9} and $1.10 \times 10^{-9}\text{ mol s}^{-1}\text{ m}^{-2}$ at 175 °C, respectively. To further investigate the reason for the enhancement of SCR activity, we measured the separate NO oxidation activity over $\text{Ce}_{0.2}\text{TiO}_x(500)$ and compared the result with that over 20% Ce/TiO_2 . As shown in Figure 6, $\text{Ce}_{0.2}\text{TiO}_x(500)$ presented a much higher NO oxidation capability than the 20% Ce/TiO_2 catalyst. We have already noticed that the addition of NO_2 to the feeding gas could significantly enhance the low temperature NO_x conversion over Ce–Ti mixed oxide catalysts (see Figure 5). Therefore, the enhanced low temperature activity might be as-

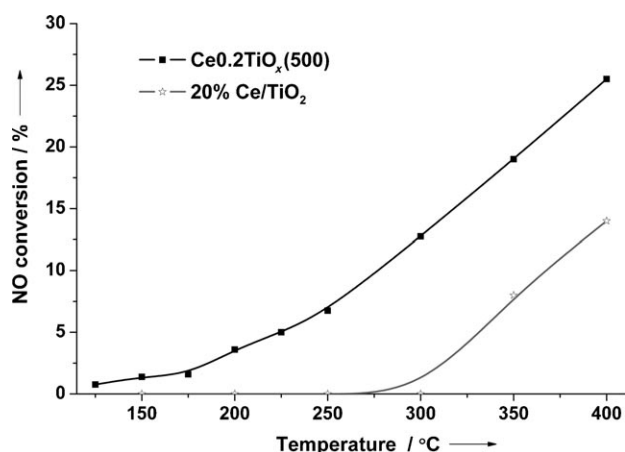


Figure 6. Comparison of separate NO oxidation activity over $\text{Ce}_{0.2}\text{TiO}_x(500)$ prepared by homogeneous precipitation method and 20% Ce/TiO_2 prepared by impregnation method^[8] (reaction conditions: $[\text{NO}] = 500\text{ ppm}$, $[\text{O}_2] = 5\text{ vol.}\%$, balance N_2 , and $\text{GHSV} = 50\,000\text{ h}^{-1}$).

sociated with the effect of “fast SCR”. Many studies have shown that, if the SCR catalyst can oxidize NO to NO_2 in situ, its low temperature SCR activity will be significantly enhanced, owing to the occurrence of a “fast SCR” reaction.^[13,15] Though the NO conversion in NO oxidation reaction is limited, during SCR process the produced NO_2 contributes to the “fast SCR” reaction even before desorption when NH_3 existed, resulting in a significant enhancement of SCR activity at low temperature.

In conclusion, a Ce–Ti mixed oxide catalyst prepared by a homogeneous precipitation method presented excellent NH_3 -SCR activity and N_2 selectivity, broad operation temperature window, and high GHSV resistance. Comparison with previously reported Ce–Ti based catalysts prepared by means of impregnation and sol–gel methods revealed that the catalyst in this study has significantly improved low temperature SCR activity, which is mainly attributed to the better dispersion of CeO_2 on TiO_2 , larger surface area, and enhanced low temperature NO oxidation activity. Further optimization of this catalyst and the investigation on the promotion effect of low temperature NH_3 -SCR performances are under way.

Experimental Section

The Ce–Ti mixed oxide catalyst was prepared by homogeneous precipitation method. The aqueous solutions of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ti}(\text{SO}_4)_2$ were mixed with required molar ratios ($\text{Ce}/\text{Ti} = 0.1, 0.2, 0.5,$ and 1.0). Excessive urea aqueous solution was then added into the mixed solution, with an urea/(Ce+Ti) molar ratio of 23:1. The solution was heated to 90 °C and held there for 8 h with vigorous stirring. After filtration and washing with deionized water, the resulting precipitant was dried at 100 °C overnight and subsequently calcined at a certain temperature (400, 500, or 600 °C) for 5 h in air. The catalysts were denoted as $\text{Ce}_a\text{TiO}_x(T)$ for which a denotes the Ce/Ti molar ratio and T denotes the calcination temperature. Pure CeO_2 and TiO_2 were also prepared by using the same method.

The SCR activity measurements were performed in a fixed-bed quartz flow reactor, which contained 0.6 mL catalyst (60–80 mesh, about 0.45 g) at atmospheric pressure. The reaction conditions were as follows: 500 ppm NO (or 250 ppm NO and 250 ppm NO_2), 500 ppm NH_3 , 5 vol.% O_2 , 5 vol.% CO_2 (when used), 5 vol.% H_2O (when used), 100 ppm SO_2 (when used), balance N_2 , and 500 mL min^{-1} total flow rate, yielding a GHSV of 50 000 h^{-1} . Different GHSV were achieved by changing the volume of catalyst, that is, 0.3 mL catalyst for a GHSV = 100 000 h^{-1} and 0.2 mL catalyst for a GHSV = 150 000 h^{-1} . The effluent gas, including NO, NH_3 , NO_2 , and N_2O was continuously analyzed by using an online NEXUS 670-FTIR spectrometer equipped with a gas cell with 0.2 dm^3 volume. The spectra were collected after 1 h after the SCR reaction had reached a steady state. NO_x conversion and N_2 selectivity were calculated by using Equations (1) and (2):^[14,15]

$$\text{NO}_x \text{ conversion} = \left(1 - \frac{[\text{NO}]_{\text{out}} + [\text{NO}_2]_{\text{out}}}{[\text{NO}]_{\text{in}} + [\text{NO}_2]_{\text{in}}} \right) \times 100\% \quad (1)$$

$$\text{N}_2 \text{ selectivity} = \frac{[\text{NO}]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}_2]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}]_{\text{in}} + [\text{NH}_3]_{\text{in}}} \times 100\% \quad (2)$$

A Quantachrome Autosorb-1C instrument was used to measure the N_2 adsorption–desorption isotherms at $-196\text{ }^\circ\text{C}$. The surface areas were determined by BET equation in 0.05–0.35 partial pressure range. The pore volumes and average pore diameters were

determined by using the BJH method from the desorption branches of the isotherms. Powder XRD measurements were performed by using a computerized PANalytical X'Pert Pro diffractometer with $\text{Cu}_{\text{K}\alpha}$ ($\lambda = 0.15406$ nm) radiation. The TEM images were obtained by using an H-7500 (Hitachi) instrument. The accelerating voltage for the microscope was 80 kV.

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