The Remarkable Improvement of a Ce–Ti based Catalyst for NO<sub>x</sub> Abatement, Prepared by a Homogeneous Precipitation Method

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The selective catalytic reduction (SCR) of NO<sub>x</sub> by NH<sub>3</sub> (NH<sub>3</sub>-SCR) over V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub> (MoO<sub>3</sub>)/TiO<sub>2</sub> has been widely used for the removal of NO<sub>x</sub> emissions from stationary sources, especially for coal-fired power plants. Additionally, NH<sub>3</sub>-SCR is thought to be one of the most promising technologies for NO<sub>x</sub> elimination from diesel engines, which has attracted considerable attention under the effect of more and more strict legislation for NO<sub>x</sub> emissions. Some inevitable problems (especially the toxicity of active vanadium species) have restrained the practical applications of traditional vanadium-based catalysts for NO<sub>x</sub> abatement from diesel engine exhaust. The exhaust gas temperature from a diesel engine is mainly in the range of 200–350 °C. However, zeolite-based NH<sub>3</sub>-SCR catalysts often present insufficient activity at low temperatures, as well as the recently reported WO<sub>3</sub>/CeO<sub>2</sub>–ZrO<sub>2</sub> catalyst, when NO<sub>x</sub> mainly consists of NO. 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 NH<sub>3</sub>-SCR catalyst.

We have presented the NH<sub>3</sub>-SCR activity of a Ce/TiO<sub>2</sub> catalyst prepared by using an impregnation method and investigated the deactivation mechanism of this catalyst by SO<sub>2</sub>. Gao et al. studied the activity of CeO<sub>2</sub>–TiO<sub>2</sub> catalyst prepared by sol–gel method for NH<sub>3</sub>-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 CeO<sub>2</sub> on TiO<sub>2</sub> is very important for the improvement of NH<sub>3</sub>-SCR activity. 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<sub>x</sub> conversions and N<sub>2</sub> selectivity over Ce<sub>x</sub>TiO<sub>y</sub>(500) (x = 0.1, 0.2, 0.5, 1.0) are presented in Figure 1. Ce<sub>0.1</sub>TiO<sub>500</sub> showed relatively low activity in the low temperature range from 125 to 225 °C and high activity, also excellent N<sub>2</sub> selectivity, in the high temperature range from 350 to 450 °C. As the Ce loading was increased, both Ce<sub>0.2</sub>TiO<sub>500</sub> and Ce<sub>0.5</sub>TiO<sub>500</sub> presented enhanced low temperature activity in comparison with Ce<sub>0.1</sub>TiO<sub>500</sub>, while the high temperature NO<sub>x</sub> 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<sub>x</sub> conversion in the low temperature range. Pure TiO<sub>2</sub> showed no SCR activity below 400 °C, and pure CeO<sub>2</sub> showed limited low temperature activity, which indicated a significant synergistic effect between CeO<sub>2</sub> and TiO<sub>2</sub> in NH<sub>3</sub>-SCR reaction.

Considering the excellent SCR activity in the main temperature range of diesel engine exhaust (200–350 °C), we chose Ce<sub>0.2</sub>TiO<sub>500</sub> and Ce<sub>0.5</sub>TiO<sub>500</sub> 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 50000 to 100000 h<sup>−1</sup>, the NO<sub>x</sub> conversion over Ce<sub>0.2</sub>TiO<sub>500</sub> showed an obvious decrease, both in the low and high temperature range, accompanied by a decrease of N<sub>2</sub> selectivity above 300 °C. However, the change of GHSV showed only a relatively slight influence on Ce<sub>0.5</sub>TiO<sub>500</sub> in comparison with Ce<sub>0.2</sub>TiO<sub>500</sub>; the influence occurred only in the low temperature range. We further increased the GHSV to 150000 h<sup>−1</sup> and found that the NO<sub>x</sub> conversion and N<sub>2</sub> selectivity over Ce<sub>0.2</sub>TiO<sub>500</sub> at high temperatures still showed no obvious decrease, although the NO<sub>x</sub> conversion at low temperatures decreased further.
In comparison with pure TiO$_2$(500) and CeO$_2$(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 TiO$_2$ and CeO$_2$ crystallization in the homogeneous precipitation process.$^{[12]}$ The BET surface area increased sharply from 127.6 m$^2$g$^{-1}$ for pure TiO$_2$(500) to 198.8 m$^2$g$^{-1}$ for Ce$_{0.1}$TiO$_x$(500), but decreased continuously with the further increases of the Ce/Ti molar ratio. The Ce$_x$Ti$_{1-x}$ 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 TiO$_2$(500) and CeO$_2$(500). The X-ray diffraction (XRD) analysis revealed that there was no cubic CeO$_2$ 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 CeO$_2$ 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 TiO$_2$ in the catalysts calculated by using the Scherrer equation gradually 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$_2$(400) and Ce$_{0.2}$TiO$_2$(500) on NO$_x$ conversion and N$_2$ selectivity from 125 to 400 °C, whereas Ce$_{0.2}$TiO$_2$(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 CeO$_2$ phase observed in Ce$_{0.2}$TiO$_2$(600) in the XRD analysis (see Figure S3). The Ce$_{0.2}$TiO$_2$(500) catalyst was also tested in the presence of CO$_2$, H$_2$O, and SO$_2$, respectively (see Figure 5). The addition of 5 vol.% CO$_2$ 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.% H$_2$O 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 H$_2$O on the unselective oxidation of NH$_3$. This finding could be verified by the decrease of NH$_3$ conversion and enhancement of N$_2$ selectivity in the SCR reaction over Ce$_{0.2}$TiO$_2$(500) in the presence of H$_2$O (see Figure S4). We also tested the NO$_x$ conversion of a 4.5%V$_2$O$_5$-10%WO$_3$/TiO$_2$ catalyst in the presence of 5 vol.% H$_2$O for comparison. We can see that, Ce$_{0.2}$TiO$_2$(500) catalyst presented very similar catalytic activity to the V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst. Addition of 100 ppm SO$_2$ 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 SO$_2$ poisoning.

The catalyst prepared by homogeneous precipitation method in this study presented significantly enhanced catalytic properties.
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/TiO2)39 and sol–gel (CeTi(SG))10 methods. Normalized by BET surface areas, the SCR reaction rates of Ce0.2TiO2 (500) were higher than that over 20% Ce/TiO2 in the low temperature range. For example, the reaction rates of Ce0.2TiO2(500) and 20% Ce/TiO2 were 1.55 x 10−9 and 1.10 x 10−9 mol·m−2·s−1 at 175 °C, respectively. To further investigate the reason for the enhancement of SCR activity, we measured the separate NO oxidation activity over Ce0.2TiO2(500) and compared the result with that over 20% Ce/TiO2. As shown in Figure 6, Ce0.2TiO2(500) presented a much higher NO oxidation capability than the 20% Ce/TiO2 catalyst. We have already noticed that the addition of NO2 to the feeding gas could significantly enhance the low temperature NOx conversion over Ce–Ti mixed oxide catalysts (see Figure 5). Therefore, the enhanced low temperature activity might be associated with the effect of “fast SCR”. Many studies have shown that, if the SCR catalyst can oxidize NO to NO2 in situ, its low temperature SCR activity will be significantly enhanced, owing to the occurrence of a “fast SCR” reaction.11,12,16 Though the NO conversion in NO oxidation reaction is limited, during SCR process the produced NO2 contributes to the “fast SCR” reaction even before desorption when NH3 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 NH3-SCR activity and N2 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 CeO2 on TiO2, 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 NH3-SCR performances are under way.

Experimental Section

The Ce–Ti mixed oxide catalyst was prepared by homogeneous precipitation method. The aqueous solutions of Ce(NO3)3·6H2O and Ti(SO4)2·12H2O were mixed with required molar ratios (Ce/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 Ce0.2TiO2(T) for which T denotes the Ce/Ti molar ratio and T denotes the calcination temperature. Pure CeO2 and TiO2 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 NO2), 500 ppm NH3, 5 vol. % O2, 5 vol. % CO2 (when used), 5 vol. % H2O (when used), 100 ppm SO2 (when used), balance N2, and GHSV = 50 000 h−1.

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

$$\text{N}_2 \text{ selectivity} = \frac{[\text{N}_2]_{\text{out}} - [\text{NO}]_{\text{out}} + [\text{N}_2]_{\text{in}}}{[\text{NO}]_{\text{in}} + [\text{NH}_3]_{\text{in}}} \times 100\%$$ \hspace{1cm} (2)

A Quantachrome Autosorb-1C instrument was used to measure the N2 adsorption–desorption isotherms at −196 °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 CuKα (λ = 0.15406 nm) radiation. The TEM images were obtained using an H-7500 (Hitachi) instrument. The accelerating voltage for the microscope was 80 kV.

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