**Novel cerium–tungsten mixed oxide catalyst for the selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3}†**

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A novel Ce–W mixed oxide catalyst prepared by homogeneous precipitation method presented nearly 100% NO\textsubscript{x} conversion in a wide temperature range from 250 to 425 °C for the selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3} under an extremely high GHSV of 500 000 h\textsuperscript{−1}. NO\textsubscript{x} abatement from diesel engine exhaust remains one of the major challenges in environmental catalysis. Selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3} (NH\textsubscript{3}-SCR) is one of the most promising technologies for NO\textsubscript{x} removal from diesel engines. The NH\textsubscript{3}-SCR catalysts for industrial application are mainly V\textsubscript{2}O\textsubscript{5}–WO\textsubscript{3} (MoO\textsubscript{3})/TiO\textsubscript{2}, which have been widely used for the NO\textsubscript{x} removal from stationary sources and introduced into the market for diesel vehicles. However, some inevitable problems with this catalyst system still remain, such as the toxicity of vanadium species, the rapid decrease of SCR activity in high space velocity. The Ce–W mixed oxide catalyst could be a very competitive catalyst for practical application in controlling the NO\textsubscript{x} emission from diesel engines.

Recently, cerium based oxides with high oxygen storage capacity and excellent redox property attracted much attention for their use as NH\textsubscript{3}-SCR catalysts. MnO\textsubscript{x}–CeO\textsubscript{2} mixed oxide was reported by Qi et al. as a superior catalyst for the low-temperature NH\textsubscript{3}-SCR reaction. A WO\textsubscript{3}/CeO\textsubscript{2}–ZrO\textsubscript{2} catalyst reported by Li et al. annealed at 800 °C still showed high NH\textsubscript{3}-SCR activity. In our previous study, we have developed a highly effective Ce/TiO\textsubscript{2} catalyst prepared by impregnation method. The deactivation mechanism of this catalyst by SO\textsubscript{2} was fully investigated using various methods. Afterwards, Gao et al. concluded that the strong interaction between ceria and titania as well as the highly dispersed nanocrystalline ceria should be the reason for the good performance of CeO\textsubscript{2}/TiO\textsubscript{2} catalyst prepared by single step sol–gel method. Tungsten is widely used as a modifier to improve the activity and widen the operation temperature window of V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalyst for NH\textsubscript{3}-SCR. Chen et al. found that the doping of tungsten to CeO\textsubscript{2}/TiO\textsubscript{2} could induce a strong interaction between Ce and W, thus resulting in enhanced catalytic activity for NH\textsubscript{3}-SCR reaction.

Previous studies have already revealed that the well dispersion of active components (such as CeO\textsubscript{2} and WO\textsubscript{3}) is very important for the enhancement of NH\textsubscript{3}-SCR activity of cerium based oxides. Homogeneous precipitation, characterized by a highly uniform increase in the pH of metal salts solution, is a convenient catalyst preparation method that can produce highly dispersed mixed metal oxides. In this study, we report a superior Ce–W mixed oxide catalyst prepared by homogeneous precipitation method using urea as precipitator, which presented excellent NH\textsubscript{3}-SCR activity, high N\textsubscript{2} selectivity, broad operation temperature window and extremely high resistance to space velocity. The Ce–W mixed oxide catalyst could be a very competitive catalyst for practical application in controlling the NO\textsubscript{x} emission from diesel engines.

The serial Ce–W mixed oxide catalysts were prepared by homogeneous precipitation method using cerium nitrate and ammonium tungstate as precursors. The detailed preparation procedures are described in ESI and the resulting catalysts are denoted as Ce\textsubscript{x}W\textsubscript{y}O\textsubscript{z}, where “a/b” denotes the Ce/W molar ratio, such as Ce\textsubscript{1}W\textsubscript{1}O\textsubscript{z}–6, CeWO\textsubscript{z} and Ce\textsubscript{1}W\textsubscript{2}O\textsubscript{z} calcined at 500 °C for 5 h and CeWO\textsubscript{z}–800 calcined at 800 °C for 1 h for the thermal stability test. Pristine CeO\textsubscript{2} and WO\textsubscript{3} were also prepared as reference samples using the same method. For comparison, the conventional 4.5% V\textsubscript{2}O\textsubscript{5}–10% WO\textsubscript{3}/TiO\textsubscript{2} and 7% Fe-ZSM-5 catalysts were also prepared. The SCR activity tests were carried out in a fixed-bed quartz flow reactor with following reaction conditions: 500 ppm NO, 500 ppm NH\textsubscript{3}, 5 vol% O\textsubscript{2}, 5 vol% CO\textsubscript{2} (when used) and 5 vol% H\textsubscript{2}O (when used), balance N\textsubscript{2}, and 500 mL min\textsuperscript{−1} total flow rate. Different GHSV were obtained by changing the catalyst volume. The effluent gas, including NO, NH\textsubscript{3}, N\textsubscript{2}O, was continuously analyzed by an online NEXUS 670-FTIR spectrometer equipped with a gas cell with 0.2 dm\textsuperscript{3} volume. The FTIR spectra were collected after 1 h when the...
The SCR reaction reached a steady state, and the NO\textsubscript{x} conversion and N\textsubscript{2} selectivity were calculated accordingly.\textsuperscript{11,12}

Fig. 1 shows the NH\textsubscript{3}-SCR activity of Ce\textsubscript{1}W\textsubscript{2}O\textsubscript{x} serial catalysts under a fixed GHSV of 250 000 h\textsuperscript{-1}. Without W doping, the pristine CeO\textsubscript{2} showed rather poor SCR activity in the whole temperature range with the maximum NO\textsubscript{x} conversion of 26%. With the Ce/W molar ratio being 2 : 1, the operation temperature window of Ce\textsubscript{2}W\textsubscript{1}O\textsubscript{6} catalyst was greatly broadened, with 100% NO\textsubscript{x} conversion from 250 to 400 °C. This result indicates that a synergistic effect for the NH\textsubscript{3}-SCR reaction might exist between Ce and W species. For the CeWO\textsubscript{x} catalyst, both the low temperature SCR activity (< 250 °C) and high temperature SCR activity (> 400 °C) were further improved to a certain extent. Decreasing the Ce/W molar ratio to 1 : 2 in Ce\textsubscript{1}W\textsubscript{2}O\textsubscript{6} catalyst led to a severe decline of NO\textsubscript{x} conversion in the whole temperature range, which was probably due to the decrease of active cerium sites in catalyst. The pristine WO\textsubscript{3} sample also showed poor SCR activity, indicating again that the coexistence of Ce and W species is very important for the promotion of SCR activity.

Fig. 2 shows the NH\textsubscript{3}-SCR activity of CeWO\textsubscript{x} catalyst under different GHSV. Obviously, the increase of GHSV only resulted in some decrease of low temperature SCR activity, but no clear influence on high temperature SCR activity. The NO\textsubscript{x} conversion curve slightly shifted to high temperature and nearly 100% NO\textsubscript{x} conversion could still be achieved in a wide temperature range from 250 to 425 °C under a rather high GHSV of 500 000 h\textsuperscript{-1}, suggesting that this novel CeWO\textsubscript{3} catalyst is highly resistant to the large space velocity, which is crucial for its application in diesel vehicles with limited space on board. The effects of CO\textsubscript{2} and H\textsubscript{2}O on the SCR activity of CeWO\textsubscript{x} are also shown in Fig. 2. The presence of 5 vol% CO\textsubscript{2} had no significant influence on SCR activity. Comparatively, in the presence of 5 vol% H\textsubscript{2}O the NO\textsubscript{x} conversion curve only shifted ca. 15 °C to high temperature. The decrease of NO\textsubscript{x} conversion below 225 °C is mainly due to the blocking of active sites by H\textsubscript{2}O, and the increase of NO\textsubscript{x} conversion above 400 °C is mainly associated with the inhibition effect of H\textsubscript{2}O on the unselective oxidation of NH\textsubscript{3}. We also tested the NH\textsubscript{3}-SCR activity of CeWO\textsubscript{x} in the coexistence of CO\textsubscript{2} and H\textsubscript{2}O (Fig. S1†), which suggested that no synergistic inhibition effect on the SCR activity was present between CO\textsubscript{2} and H\textsubscript{2}O.

To better evaluate the NH\textsubscript{3}-SCR performance of CeWO\textsubscript{x} catalyst, we also carried out the comparative SCR activity test over V\textsubscript{2}O\textsubscript{5}–WO\textsubscript{3}/TiO\textsubscript{2} and Fe-ZSM-5 catalysts (Fig. 3). The CeWO\textsubscript{x} catalyst showed much higher SCR activity in the whole temperature range than V\textsubscript{2}O\textsubscript{5}–WO\textsubscript{3}/TiO\textsubscript{2}, together with much better N\textsubscript{2} selectivity. The broad operation temperature window and less formation of nitrogenous by-products are important characteristics of CeWO\textsubscript{x} catalyst for its practical utilization. Compared with a Fe-ZSM-5 catalyst which has been industrially and commercially used for NH\textsubscript{3}-SCR of NO\textsubscript{x} from diesel engines, the operation temperature window of the CeWO\textsubscript{x} catalyst is nearly 100 °C lower under the same GHSV, with similar N\textsubscript{2} selectivity above 95% in the whole temperature range. Even after high temperature calcination at 800 °C, the low temperature activity of CeWO\textsubscript{x} was still much higher than that of Fe-ZSM-5, indicating its high resistance to the thermal shock, which is also very important for practical use.

The BET surface area of CeWO\textsubscript{x} catalyst (70.5 m\textsuperscript{2} g\textsuperscript{-1}) is much larger than those of pristine CeO\textsubscript{2} (46.1 m\textsuperscript{2} g\textsuperscript{-1}) and WO\textsubscript{3} (6.1 m\textsuperscript{2} g\textsuperscript{-1}) due to the formation of mixed oxide phase (Table S1†). Both the XRD analysis (Fig. 4) and Raman spectra (Fig. S2†) suggest that the coexistence of Ce and W species in the CeWO\textsubscript{x} catalyst greatly lowered the cerianite CeO\textsubscript{2} particle size (as indicated in Table S1†), and the tungsten species itself was mainly in an amorphous or highly dispersed state. It was reported that highly dispersed nanocrystalline
CeO₂ is the active phase in CeO₂/TiO₂ catalyst.⁷,⁹ According to the XRD and Raman results in this study, we can deduce that the main active phase in Ce₅W₆O₂₃ is also small CeO₂ crystallite, and the formation of highly dispersed CeO₂ and WO₃ crystallites by the coexistence of Ce and W could extensively increase the amount of active sites on catalyst surface. After normalization by BET surface area, the sequence of the SCR activity is as follows (Fig. S3⁹): Ce₅W₆O₂₃ > CeWO₃ > Ce₂WO₄, confirming that the catalyst with the most abundant CeO₂ crystallite exhibited the highest intrinsic activity. In addition, it was reported that the introduction of tungsten species to the catalyst could enhance the low temperature activity by promoting NO oxidation to NO₂ to facilitate the “fast SCR” reaction,¹⁰ which is in well accordance with the separate NO oxidation results in Fig. S4.† Furthermore, the tungsten species could also improve the high temperature activity and N₂ selectivity by supplying large adsorption capacity of NH₃ and suppressing the unselective catalytic oxidation of NH₃ to N₂O or NO,¹³ which is consistent with the separate NH₃ oxidation results in Fig. S5.† Therefore, the Ce–W mixed oxide catalyst could present excellent NH₃-SCR activity and N₂ selectivity simultaneously in a wide temperature range.

We also measured the XPS of Ce 3d (Fig. S6†), which showed that the Ce⁺/(Ce³⁺ + Ce⁴⁺) ratio on CeWO₃ (37.2%) was much higher than that on CeO₂ (7.8%), indicating the presence of more surface oxygen vacancies on CeWO₃. The O 1s XPS (Fig. S7†) indeed showed that much more surface adsorbed oxygen (O₁) was present on CeWO₃ than those on CeO₂ and WO₃, which is beneficial to the NO oxidation and facilitation of “fast SCR” reaction. As the in situ DRIFTS shown in Fig. 5, the inclusion of W species in CeWO₃ greatly enhanced the NH₃ adsorption (e.g. 1668 and 1419 cm⁻¹ of NH₄⁺, 1591 and 1190 cm⁻¹ of NH₃), yet showed no obvious inhibition on NO₃ adsorption (e.g. 1601 and 1232 cm⁻¹ of bridging nitrate, 1578 cm⁻¹ of bidentate nitrate, 1549 cm⁻¹ of monodentate nitrate). Only the difference in surface areas between CeO₂ and CeWO₃ cannot explain the discrepancy of the reactant adsorption ability, thus some synergistic effect must exist between Ce and W. Moreover, the adsorbed NH₃ species (i.e. ionic NH₄⁺ and coordinated NH₂) and adsorbed NO₃ species (i.e. bridging nitrate and monodentate nitrate) on CeWO₃ surface were both reactive to each other, contributing to the total DeNOₓ efficiency. From this point of view, the coexistence of Ce and W species with synergistic effect in CeWO₃ is crucial for achieving high NH₃-SCR performance.

In conclusion, a novel Ce–W mixed oxide catalyst prepared by homogeneous precipitation method showed excellent NH₃-SCR activity and high N₂ selectivity with a broad operation temperature window and extremely high resistance to space velocity. The CeWO₃ catalyst showed much higher SCR activity and N₂ selectivity than V₂O₅-WO₃/TiO₂ and presented a much higher low temperature SCR activity than Fe-ZSM-5, even after calcination at 800 °C. The excellent catalytic performance of the catalyst is attributed to a synergistic effect between Ce and W species. Further optimization of this catalyst and the reaction mechanism study are under way.

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Notes and references