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Novel cerium–tungsten mixed oxide catalyst for the selective catalytic reduction of NO_x with NH₃[†]

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A novel Ce–W mixed oxide catalyst prepared by homogeneous precipitation method presented nearly 100% NO_x conversion in a wide temperature range from 250 to 425 °C for the selective catalytic reduction of NO_x with NH₃ under an extremely high GHSV of 500 000 h^{−1}.

NO_x abatement from diesel engine exhaust remains one of the major challenges in environmental catalysis.¹ Selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) is one of the most promising technologies for NO_x removal from diesel engines. The NH₃-SCR catalysts for industrial application are mainly V₂O₅–WO₃ (MoO₃)/TiO₂, which have been widely used for the NO_x removal from stationary sources and introduced into the market for diesel vehicles.² However, some inevitable problems with this catalyst system still remain, such as the toxicity of vanadium species, the rapid decrease of SCR activity together with low N₂ selectivity at high temperatures, and the high conversion of SO₂ to SO₃. Metal-exchanged zeolites, especially Fe-ZSM-5, have been studied extensively for reducing NO_x from diesel engines in recent years.^{3,4} However, the low SCR activity at low temperatures and the poor hydrothermal stability at high temperatures restrained their practical applications.³ Thus, great efforts have been made to develop environmentally-benign NH₃-SCR catalysts, with high SCR activity and N₂ selectivity in a wide temperature range, for controlling the NO_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 NH₃-SCR catalysts. MnO_x–CeO₂ mixed oxide was reported by Qi *et al.*⁵ as a superior catalyst for the low-temperature NH₃-SCR reaction. A WO₃/CeO₂–ZrO₂ catalyst reported by Li *et al.*⁶ annealed at 800 °C still showed high NH₃-SCR activity. In our previous study, we have developed a highly effective Ce/TiO₂ catalyst prepared by impregnation method.⁷ The deactivation mechanism of this catalyst by SO₂ was fully investigated using various methods.⁸ Afterwards,

Gao *et al.*⁹ 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 CeO₂/TiO₂ 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 V₂O₅/TiO₂ catalyst for NH₃-SCR. Chen *et al.*¹⁰ found that the doping of tungsten to CeO₂/TiO₂ could induce a strong interaction between Ce and W, thus resulting in enhanced catalytic activity for NH₃-SCR reaction.

Previous studies have already revealed that the well dispersion of active components (such as CeO₂ and WO₃) is very important for the enhancement of NH₃-SCR activity of cerium based oxides.^{7,9,10} 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 NH₃-SCR activity, high N₂ 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_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_aW_bO_x, where “a/b” denotes the Ce/W molar ratio, such as Ce₂W₁O_x, CeW₁O_x and Ce₁W₂O_x calcined at 500 °C for 5 h and CeW₁O_x-800 calcined at 800 °C for 1 h for the thermal stability test. Pristine CeO_x and WO_x were also prepared as reference samples using the same method. For comparison, the conventional 4.5% V₂O₅–10% WO₃/TiO₂ 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 NH₃, 5 vol% O₂, 5 vol% CO₂ (when used) and 5 vol% H₂O (when used), balance N₂, and 500 mL min^{−1} total flow rate. Different GHSV were obtained by changing the catalyst volume. The effluent gas, including NO, NH₃, NO₂ and N₂O, was continuously analyzed by an online NEXUS 670-FTIR spectrometer equipped with a gas cell with 0.2 dm³ volume. The FTIR spectra were collected after 1 h when the

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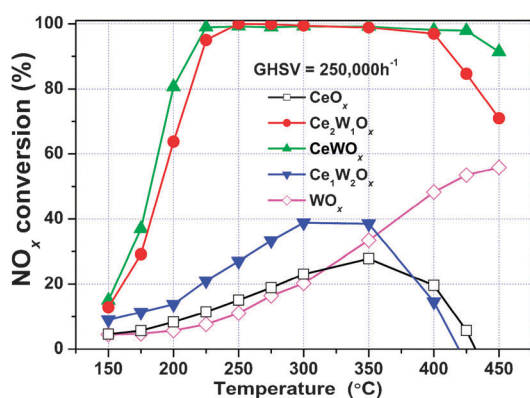


Fig. 1 NH_3 -SCR activity of $\text{Ce}_a\text{W}_b\text{O}_x$ serial catalysts under GHSV of $250\,000\text{ h}^{-1}$.

SCR reaction reached a steady state, and the NO_x conversion and N_2 selectivity were calculated accordingly.^{11,12}

Fig. 1 shows the NH_3 -SCR activity of $\text{Ce}_a\text{W}_b\text{O}_x$ catalysts under a fixed GHSV of $250\,000\text{ h}^{-1}$. Without W doping, the pristine CeO_x showed rather poor SCR activity in the whole temperature range with the maximum NO_x conversion of 26%. With the Ce/W molar ratio being 2 : 1, the operation temperature window of $\text{Ce}_2\text{W}_1\text{O}_x$ catalyst was greatly broadened, with 100% NO_x conversion from 250 to 400°C . This result indicates that a synergistic effect for the NH_3 -SCR reaction might exist between Ce and W species. For the CeWO_x catalyst, both the low temperature SCR activity ($<250^\circ\text{C}$) and high temperature SCR activity ($>400^\circ\text{C}$) were further improved to a certain extent. Decreasing the Ce/W molar ratio to 1 : 2 in $\text{Ce}_1\text{W}_2\text{O}_x$ catalyst led to a severe decline of NO_x conversion in the whole temperature range, which was probably due to the decrease of active cerium sites in catalyst. The pristine WO_x 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_3 -SCR activity of CeWO_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_x conversion curve slightly shifted to high temperature and nearly 100% NO_x conversion could still be achieved in a wide temperature range from 250 to 425°C under a rather high

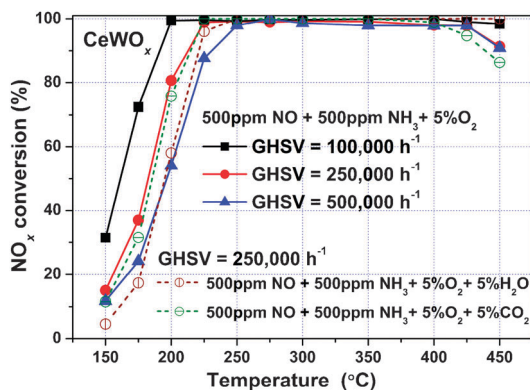


Fig. 2 NH_3 -SCR activity of CeWO_x catalyst under different GHSV and in the presence of $\text{H}_2\text{O}/\text{CO}_2$ under GHSV of $250\,000\text{ h}^{-1}$.

GHSV of $500\,000\text{ h}^{-1}$, suggesting that this novel CeWO_x 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_2 and H_2O on the SCR activity of CeWO_x are also shown in Fig. 2. The presence of 5 vol% CO_2 had no significant influence on SCR activity. Comparatively, in the presence of 5 vol% H_2O the NO_x conversion curve only shifted *ca.* 15°C to high temperature. The decrease of NO_x conversion below 225°C is mainly due to the blocking of active sites by H_2O , and the increase of NO_x conversion above 400°C is mainly associated with the inhibition effect of H_2O on the unselective oxidation of NH_3 . We also tested the NH_3 -SCR activity of CeWO_x in the coexistence of CO_2 and H_2O (Fig. S1†), which suggested that no synergistic inhibition effect on the SCR activity was present between CO_2 and H_2O .

To better evaluate the NH_3 -SCR performance of CeWO_x catalyst, we also carried out the comparative SCR activity test over $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ and Fe-ZSM-5 catalysts (Fig. 3). The CeWO_x catalyst showed much higher SCR activity in the whole temperature range than $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$, together with much better N_2 selectivity. The broad operation temperature window and less formation of nitrogenous by-products are important characteristics of CeWO_x catalyst for its practical utilization. Compared with a Fe-ZSM-5 catalyst which has been industrially and commercially used for NH_3 -SCR of NO_x from diesel engines, the operation temperature window of the CeWO_x catalyst is nearly 100°C lower under the same GHSV, with similar N_2 selectivity above 95% in the whole temperature range. Even after high temperature calcination at 800°C , the low temperature activity of CeWO_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_x catalyst ($70.5\text{ m}^2\text{ g}^{-1}$) is much larger than those of pristine CeO_x ($46.1\text{ m}^2\text{ g}^{-1}$) and WO_x ($6.1\text{ m}^2\text{ g}^{-1}$) 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_x catalyst greatly lowered the cerianite CeO_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

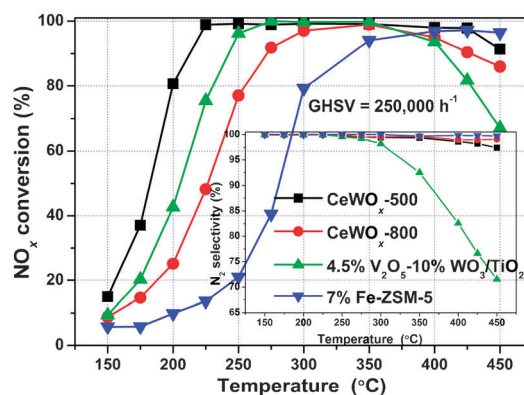


Fig. 3 Comparison of NH_3 -SCR activity and N_2 selectivity (inserted) of CeWO_x catalyst (calcined at 500 and 800°C) with those of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ and Fe-ZSM-5 catalysts under GHSV of $250\,000\text{ h}^{-1}$.

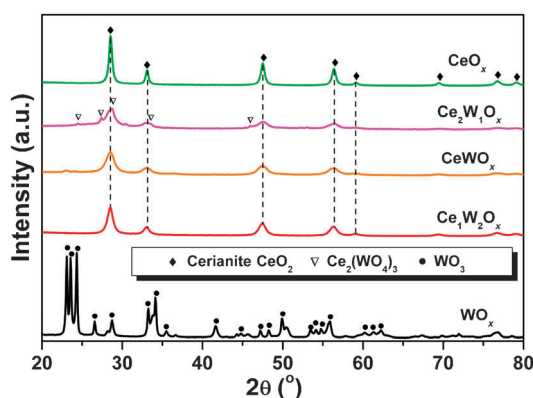


Fig. 4 XRD patterns of $\text{Ce}_a\text{W}_b\text{O}_x$ serial catalysts.

CeO_2 is the active phase in $\text{CeO}_2/\text{TiO}_2$ catalyst.^{7,9} According to the XRD and Raman results in this study, we can deduce that the main active phase in $\text{Ce}_a\text{W}_b\text{O}_x$ is also small CeO_2 crystallite, and the formation of highly dispersed CeO_2 and WO_3 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. S3†): $\text{Ce}_2\text{W}_1\text{O}_x > \text{CeWO}_x > \text{Ce}_1\text{W}_2\text{O}_x$, confirming that the catalyst with the most abundant CeO_2 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 NO_2 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 N_2 selectivity by supplying large adsorption capacity of NH_3 and suppressing the unselective catalytic oxidation of NH_3 to N_2O or NO_x ,¹³ which is consistent with the separate NH_3 oxidation results in Fig. S5.† Therefore, the Ce–W mixed oxide catalyst could present excellent

NH_3 -SCR activity and N_2 selectivity simultaneously in a wide temperature range.

We also measured the XPS of Ce 3d (Fig. S6†), which showed that the $\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$ ratio on CeWO_x (37.2%) was much higher than that on CeO_x (7.8%), indicating the presence of more surface oxygen vacancies on CeWO_x . The O 1s XPS (Fig. S7†) indeed showed that much more surface adsorbed oxygen (O_2) was present on CeWO_x than those on CeO_x and WO_x , 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 CeWO_x greatly enhanced the NH_3 adsorption (e.g. 1668 and 1419 cm^{-1} of NH_4^+ , 1591 and 1190 cm^{-1} of NH_3), yet showed no obvious inhibition on NO_x 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 CeO_x and CeWO_x cannot explain the discrepancy of the reactant adsorption ability, thus some synergistic effect must exist between Ce and W. Moreover, the adsorbed NH_3 species (*i.e.* ionic NH_4^+ and coordinated NH_3) and adsorbed NO_x species (*i.e.* bridging nitrate and monodentate nitrate) on CeWO_x surface were both reactive to each other, contributing to the total De NO_x efficiency. From this point of view, the coexistence of Ce and W species with synergistic effect in CeWO_x is crucial for achieving high NH_3 -SCR performance.

In conclusion, a novel Ce–W mixed oxide catalyst prepared by homogeneous precipitation method showed excellent NH_3 -SCR activity and high N_2 selectivity with a broad operation temperature window and extremely high resistance to space velocity. The CeWO_x catalyst showed much higher SCR activity and N_2 selectivity than $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$ 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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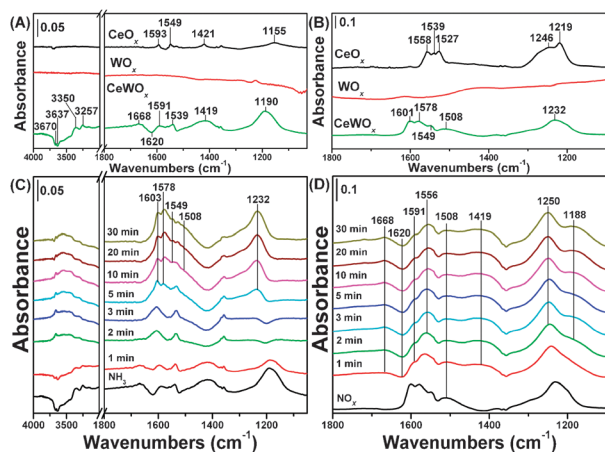


Fig. 5 *In situ* DRIFTS of (A) NH_3 adsorption, (B) $\text{NO} + \text{O}_2$ adsorption, (C) $\text{NO} + \text{O}_2$ reacted with pre-adsorbed NH_3 species, and (D) NH_3 reacted with pre-adsorbed NO_x species at 200 °C on CeWO_x catalyst. (Detailed assignments of infrared bands were described in ESI†).