WO_3/CeO_2-ZrO_2, a promising catalyst for selective catalytic reduction (SCR) of NO_x with NH_3 in diesel exhaust

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A WO_3/CeO_2-ZrO_2 catalyst system was discovered for selective catalytic reduction of NO_x with NH_3; the catalyst (10 wt% WO_3 loading) showed nearly 100% NO_x conversion in a temperature range of 200–500 °C, at a space velocity of 90 000 h^{-1} in a simulated diesel exhaust containing 550 ppm NO_x ($NO : NO_2$ feed ratio at 1.0), 10 vol% H_2O and 10 vol% CO_2; the catalyst also exhibited high temperature stability.

In light of the impending emission standards, interest in reducing NO_x emissions of diesel powered vehicles has increased significantly in recent years. The most efficient technology to remove NO_x from stationary sources is the selective catalytic reduction (SCR) of NO_x by ammonia ($4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$). V_2O_5-WO_3/TiO_2 (anatase) has been a well-known SCR catalyst for stationary NO_x reduction and shows optimum performance in a narrow temperature window (300–400 °C).[1] As a mobile power source, a diesel engine operates at more dynamic windows for temperature and flow. Reduction of NO_x emissions from a diesel engine requires a highly efficient catalyst operating over a temperature range of 200–500 °C, capable of high space velocity. Under certain circumstances such as diesel particulate filter (DPF) regeneration, the diesel exhaust gas temperature can go even higher temperature to above 740 °C.[2] Furthermore, vanadia has a rather low melting point (690 °C) and there is a toxicological concern if vanadia is discharged from the tail pipe. Hence, extensive efforts have been made over the past decade to develop non-vanadium catalysts for NO_x SCR using NH_3. Long and Yang[3] reported that the addition of a small amount ($\leq$ 2 wt%) of CeO_2 to Fe-TiO_2-PILC catalyst increased the catalyst activity (by 35%) within the range 250–450 °C. Other supported transition metal oxides have been studied extensively in SCR, such as $Fe_2O_3/WO_3/ZrO_2$,[4] CeO_2-zeolite,[5] Fe-ZSM-5,[6,7] MnO_x-CeO_2[8] and Fe-Ce-ZSM-5.[9] They showed various activities under different conditions.

Ceria has been one of the main components in automotive three-way catalysts. It provides oxygen storage capability through redox cycling between the trivalent and tetravalent oxidation states of the Ce ions. However, pure ceria is not suitable for the applications due to its high reduction temperature (700 °C) and loss of surface area due to sintering. By adding zirconium oxide into ceria, the oxygen storage capacity (OSC) and the thermal stability of CeO_2 were significantly improved.[10]

Recently, we studied CeO_2-ZrO_2 based catalysts for selective catalytic reduction of NO_x with NH_3. Six transition metal oxides (WO_3, MoO_3, Mn_2O_3, CrO_3, Fe_2O_3 and Co_2O_3) were deposited on CeO_2-ZrO_2 and their catalytic activities were tested, respectively. Among these catalysts, the WO_3/CeO_2-ZrO_2 catalyst showed the highest conversion efficiency at 250–500 °C with nearly 100% N_2 selectivity at a high space velocity of 90 000 h^{-1} when the simulated exhaust gas contains 550 ppm of NO_x with the $NO : NO_2$ feed ratio at 1.0, 10 vol% H_2O, 10 vol% CO_2 and balance N_2. Due to the high temperature of the diesel exhaust during regeneration of DPF, the thermal stability of an SCR catalyst is critical to withstand the harsh environment. All the catalysts were annealed in air for 1 hour at 800 °C and then their SCR activities were tested.

First, the catalyst support CeO_2-ZrO_2 mixed oxides were prepared by homogeneous precipitation. Ammonium cerium nitrate $(NH_4)_2Ce(NO_3)_6$, zirconium nitrate and 3 mol L^{-1} urea solution were mixed in the desired mole ratios (Ce : Zr : urea = 1 : 1 : 20). The resultant solution was heated to boiling temperature under stirring until coprecipitation was observed. The above mixture was aged at boiling temperature for 2 hours and was then cooled down to room temperature while stirring. The precipitation was filtered and washed with deionized water, and a cream-like solid was obtained. The solid was calcined at 500 °C for 2 hours in a muffle oven. The powder was denoted as CZ. The mixed oxide was pressed, ground and sieved to 20–30 mesh. Then, incipient wetness impregnation was carried out for MO_x/CeO_2-ZrO_2 (M: W, Mo, Mn, Cr, Fe or Co). The desired amount of ammonium metatungstate $(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$, ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and transition metal (Mn, Cr, Fe or Co) nitrate precursor solutions was added to 10 wt% of MO_x on CeO_2-ZrO_2 oxide, respectively. The obtained solid samples were first dried at room temperature for 6 hours, at 120 °C for 3 hours, heated at 500 °C for 2 hours and annealed at 800 °C in air for 1 hour and then denoted M/CZ catalyst.

SCR catalytic activity was tested under the following conditions: 1 ml sample (*ca.* 1.5 g), 550 ppm NO, 550 ppm NH_3, 6% O_2, 10% CO_2, 10% water vapor, balance N_2, 1500 ml min^{-1} total flow rate and GHSV = 90 000 h^{-1} (ambient conditions), as simulated for diesel exhaust gas.

The reactor system was heated to 80 °C to prevent formation and deposition of ammonium nitrate. The gas

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composition (NO, NO_2, N_2O, NH_3, CO_2) was continually monitored by an FT-IR gas analyzer (Nicolet 5700 with DTGS detector with 2 m-path gas cell) and recorded by a computer. A cold trap was installed before the exhaust gas was introduced into the analyzer to eliminate water effects on the analyzer.

The NO conversion activities of the MO_x/CeO_2-ZrO_2 catalysts prepared in the present study are shown in Fig. 1. Among the six catalysts W/CZ had the highest NO conversion at almost all temperatures tested. 60% NO conversion was obtained at 250 °C. As the temperature increased, NO conversion moved up significantly, achieving more than 90% at 350–500 °C. The decrease in activity at high temperature for some catalysts can be attributed to a decrease in selectivity, due to the competing reaction of ammonia oxidation, characteristic of most SCR catalysts.[11] The rank of maximum activity for the catalysts was as follows: W (91%) > Mo (85%) > Mn (45%) > Cr (38%) > Fe (27%) > Co (8%). It is well known that the redox properties and acidity of a V_2O_5-WO_3/TiO_2 catalyst are necessary for the SCR reaction; the redox properties are the key factors controlling the reactivity of the catalysts at low temperature, whereas the acid properties are expected to play a role in the SCR reaction at high temperature.[12] Similarly, as the same kind of oxide-type catalyst, W/CZ catalysts (the BET surface of W/CZ is 33 m^2 g^{-1}) may have the better combination of the acid properties and redox properties in the SCR process.

In order to better evaluate the W/CZ catalyst, we compared it with three kinds of commercial V–W–Ti (L, M and H) catalysts which have different vanadia loadings for low, medium and high temperature process. Fig. 2 shows a comparison of NO conversion on the W/CZ catalyst and three commercial V–W–Ti catalysts after being annealed in air for 1 hour at 800 °C. W/CZ showed the highest NO conversion in the tested temperature range, in spite of a higher space velocity. It is noteworthy that V–W–Ti (L) had the highest NO conversion (>90% at 250–425 °C) without annealing, while it had little NO conversion after annealing at 800 °C. It is well known that the interaction between the titania support and vanadium is the important factor in the SCR reaction. As mentioned before, the melting point of vanadia is only 690 °C. After annealing, surface area loss due to melting of vanadia and/or loss of vanadia due to evaporation contribute to activity loss.[13] Anatase sintering and anatase-to-rutile phase transition should also contribute to the deactivation of the V–W–Ti catalysts.[14]

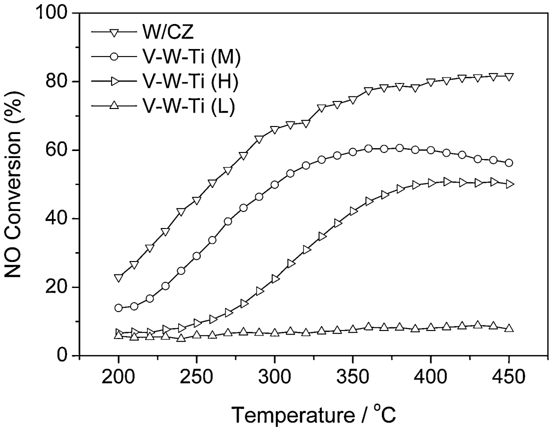

Fig. 2 Comparison with three kinds of commercial V–W–Ti catalysts. Reaction conditions: 1 g catalyst (20–30 mesh), total flow rate = 1500 ml min^{-1}, 550 ppm NO, 550 ppm NH_3, 6 vol% O_2, 10 vol% CO_2, 10 vol% H_2O, N_2 balance, heating rate = 2 °C min^{-1}, GHSV = 56 250 h^{-1} (V_2O_5-WO_3/TiO_2) and GHSV = 135 000 h^{-1} (WO_3/CeO_2-ZrO_2).

Results of the NO conversion as a function of temperature over various loadings of WO_3/CeO_2-ZrO_2 mixed oxide catalysts are given in Fig. 3. In order to investigate the thermal stability of xW/CZ catalysts (x denotes wt% WO_3/CZ), the annealing time was 4 hours at 800 °C in air. Interestingly, 10W/CZ catalyst showed the highest activity. The higher and lower WO_3 loadings resulted in low conversions. This phenomenon indicates that the amount of tungsta has a significant impact on SCR activity. It is reported that 0.8 mmol /(100 m^2 CZ) or 185 mg of WO_3 on 1 g of CZ with a specific surface area of 100 m^2 g^{-1} is just enough to form a complete

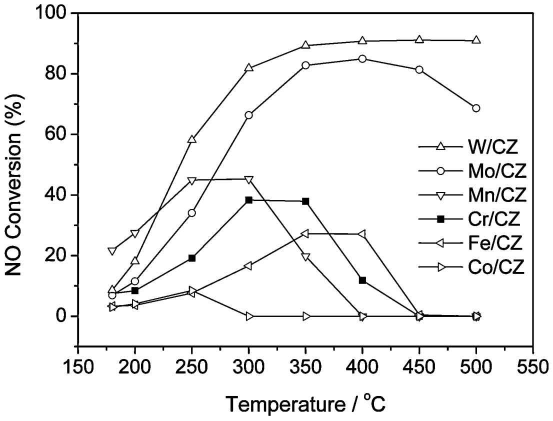

Fig. 1 NO conversion as a function of temperature over various MO_x/CeO_2-ZrO_2 mixed oxide catalysts. Reaction conditions: 1 ml catalyst, total flow rate = 1500 ml min^{-1}, 550 ppm NO, 550 ppm NH_3, 6 vol% O_2, 10 vol% CO_2, 10 vol% H_2O, N_2 balance and GHSV = 90 000 h^{-1}.

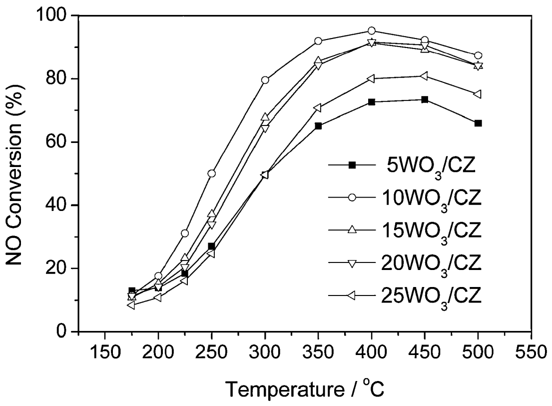

Fig. 3 NO conversion as a function of temperature over various loading WO_3/CeO_2-ZrO_2 mixed oxide catalysts. Reaction conditions: 1 ml catalyst, total flow rate = 1500 ml min^{-1}, 550 ppm NO, 550 ppm NH_3, 6 vol% O_2, 10 vol% CO_2, 10 vol% H_2O, N_2 balance and GHSV = 90 000 h^{-1}.

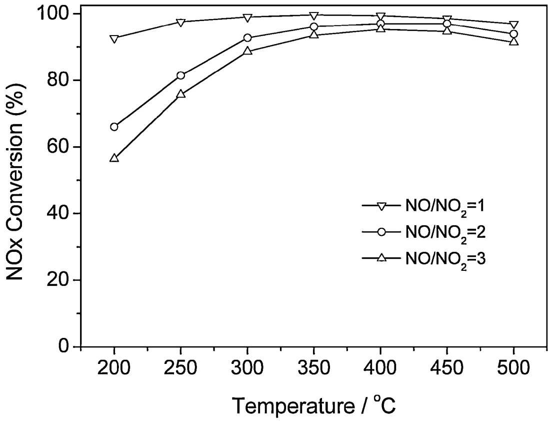

Fig. 4 Effect of NO : NO_2 molar ratio on NO_x conversion over 10 wt% WO_3/CeO_2-ZrO_2 catalyst. Reaction conditions: 1 ml catalyst, total flow rate = 1500 ml min^{-1}, 550 ppm NO_x (NO + NO_2), 550 ppm NH_3, 6 vol% O_2, 10 vol% CO_2, 10 vol% H_2O, N_2 balance and GHSV = 90 000 h^{-1}.

monolayer of WO_3 on CZ.[15] Thinking about different preparation methods of CZ (the BET surface of CZ is 94 m^2 g^{-1}), 10 wt% W/CZ may form monolayer WO_3 dispersion. At tungsten loadings below monolayer, the catalyst activity is enhanced with the increase of the tungsten loading. On the other hand, if the tungsten loading is increased above monolayer on the CZ, more WO_3 may lead to an agglomerate of dispersed WO_3, resulting in a decrease of the acidic sites, just as the conclusion reported by Natile *et al.*[16]

For the application of diesel NO_x SCR, NO_2 plays an important role for the emission reduction since it exists in real diesel exhaust, especially after DPF. We studied the impact of the NO : NO_2 molar ratio on the catalyst performance. Fig. 4 shows NO_x conversion efficiency at different NO : NO_2 molar ratios (1, 2 and 3) in the feed gas. The highest conversion efficiency was observed with a NO : NO_2 = 1 : 1 feed ratio. Noticeably, low temperature activity was enhanced much more than at high temperature. Koebel *et al.*[17] have found that NO_2 enhances the deNO_x efficiency over V_2O_5-WO_3/TiO_2 catalyst at low temperature and proposed the fast SCR process ($2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$). Ciardelli *et al.*[18] systematically studied NO : NO_2 feed ratios over a commercial V_2O_5-WO_3/TiO_2 catalyst in a wide range of temperatures, confirming that the best deNO_x efficiency is achieved with a 1 : 1 NO : NO_2 feed ratio. Similarly, fast SCR may exist over WO_3/CeO_2-ZrO_2 catalyst in our experiments. Further investigation on this phenomenon is warranted to optimize the WO_3/CeO_2-ZrO_2 catalyst for potential diesel SCR application.

In conclusion, we discovered a WO_3/CeO_2-ZrO_2 catalyst at about 10 wt% WO_3 loading that showed nearly 100% NO_x conversion in a temperature range of 200–500 °C at a high space velocity of 90 000 h^{-1} in a simulated diesel exhaust containing a NO : NO_2 feed ratio of 1.0, 10% H_2O and 10% CO_2. A synergetic effect between tungsta and ceria–zirconia promotes the SCR activity by ammonia. Characterization of the catalyst system is in progress to better understand the reaction mechanism. Further optimization of the catalyst is under way in our laboratory.

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