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Ce and Zr Modified WO_3-TiO_2 Catalysts for Selective Catalytic Reduction of NO_x by NH_3

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Abstract: A series of Ce and/or Zr modified WO_3-TiO_2 catalysts were synthesized by the impregnation method, which were employed for NH_3-SCR reaction. The T_{50} contour lines of NO_x were used to quickly optimize catalyst composition, the Ce20Zr12.5WTi catalyst was considered to be the optimization result, and also exhibited excellent NH_3-SCR activity and thermal stability with broad operation temperature window, which is a very promising catalyst for NO_x abatement from diesel engine exhaust. The excellent catalytic performance is associated with the formation of Ce-Zr solid solution. The introduction of Zr to CeWTi catalyst facilitated the redox of Ce^{4+}/Ce^{3+} and the formation of more acid sites, more Ce^{3+} ions, more oxygen vacancies, larger quantities of surface adsorbed oxygen species and NH_3, which were beneficial for the excellent selective catalytic reduction (SCR) performance.

Keywords: NH_3-SCR; nitrogen oxides; Ce-Zr solid solution; T_{50} contour line

1. Introduction

Nitrogen oxides (NO_x) resulting from automobiles are major air pollutants, which can cause acid rain, photochemical smog, haze, ozone depletion and direct damages to the respiratory systems of human bodies. Great efforts have been made to the development and application of available technologies for the control of NO_x emissions [1,2]. Among these technologies, selective catalytic reduction of NO_x with NH_3 (NH_3-SCR) has been widely used and considered one of the most effective approaches for NO_x control in diesel vehicles.

The commercial catalyst used for the NH_3-SCR process is V_2O_5-WO_3/TiO_2 [3]. However, the toxicity of vanadium species and the narrow operation temperature window restrains the practical application of the V-based catalysts for diesel. Therefore, great efforts have been made to develop an environmentally-benign selective catalytic reduction (SCR) catalyst with high deNO_x performance.

CeO_2-based oxides have attracted increasing attention due to the excellent redox properties shifting between Ce^{3+} and Ce^{4+} [4–6]. Among all the CeO_2-based catalysts, CeO_2/WO_3-TiO_2 catalyst exhibits excellent SCR performance, with high SCR activity and N_2 selectivity, and broad operation temperature window [7–15]. However, in practical applications the low-temperature catalytic activity of the catalyst was still relatively low. Moreover, the thermal stability of the CeO_2/WO_3-TiO_2 catalyst was also not satisfied. The problems mentioned above restrained the application of CeO_2/WO_3-TiO_2 in diesel engine exhaust after treatment. From a research aspect, the relationship between the structure and activity of this catalyst has been studied thoroughly, so the modification of the catalyst has become a research hotspot on this basis, including the enhancement of redox properties and acidity.

It is well-known that ZrO_2 is usually combined with CeO_2 to form the Ce-Zr oxide catalyst, which has shown a great performance in three-way catalyst (TWC), diesel oxidation catalyst (DOC), and SCR applications. ZrO_2 can increase the reducibility, surface acidity and stability of CeO_2 [16–18]. These properties are important factors for catalytic performance in SCR. It is worth nothing that the Zr modified active site of the Ce catalyst CeO_2-ZrO_2/WO_3-TiO_2 has not been reported yet.

In this current work, a series of Ce and Zr modified CeO_2-ZrO_2/WO_3-TiO_2 catalysts were prepared by the impregnation method, and their deNO_x performance was evaluated in a simulated real engine exhaust (Composed of NH_3, NO_x, CO, CO_2, C_3H_6, H_2O, O_2 and N_2). The T_{50} contour lines of NO_x were used to quickly optimize the catalyst composition. Based on this characterization, the essence of the activity enhancement arising from the Ce and Zr introduction and the active species for the reaction were proposed and discussed in detail.

2. Results and Discussion

2.1. Catalytic Activity

Considering the complex composition of the Ce*x*Zr*y*WTi catalyst, lots of experiments were generally required to optimize the content. In this study, a method of "prediction verification" was used to optimize the contents of Ce, Zr, and WTi, with an aim to decrease the amount of optimization experiments. Based on the preliminary activity test, a coarse optimization zone was predicted with the calculated contour lines of T_{50} (Temperature corresponding to NO_x conversion of 50%). Subsequently, around the coarse optimization zone, verification experiments were carried out to verify and adjust the zone. Through the cycle of "prediction-verification-reprediction", the amount of optimization experiments could be controlled at a relatively low level. In this work, optimization was achieved after 13 experiments, as shown in Figure 1a. Among all the Ce*x*Zr*y*WTi catalysts, the WTi catalyst shows the lowest catalytic activity, when Zr was added to WTi, the catalytic activity enhanced to a limited extent. But when Ce or Ce & Zr was introduced into WTi, the catalytic activity increased largely. The Ce20Zr12.5WTi catalyst possesses the lowest T_{50}. Moreover, the Ce20Zr12.5WTi displayed an excellent catalytic performance from 200 to 500 °C, as presented in Figure 1b.

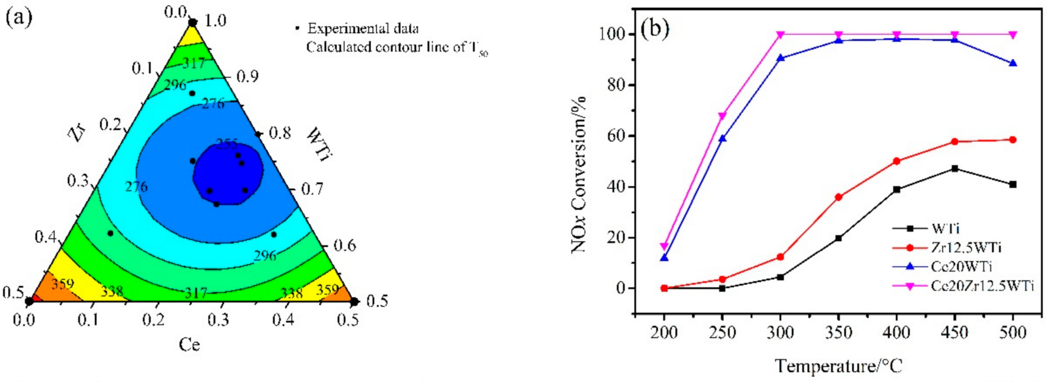

Figure 1. (**a**) T_{50} contour lines of NO_x and (**b**) NO_x conversion of 200–500 °C over Ce*x*Zr*y*WTi catalysts.

The optimal catalyst Ce20Zr12.5WTi was thermally aged at different situations and then deNO_x performance was tested, as exhibited in Figure 2. Compared with the fresh sample, the SCR activity of aged samples only decreased to a limited extent. For the Aged-Ce20Zr12.5WTi-550 °C-200 h and Aged-Ce20Zr12.5WTi-650 °C-100 h catalysts, the average NO_x conversion decreased by 3 and 4.86%, respectively, which suggested that the Ce20Zr12.5WTi possess high thermal stability.

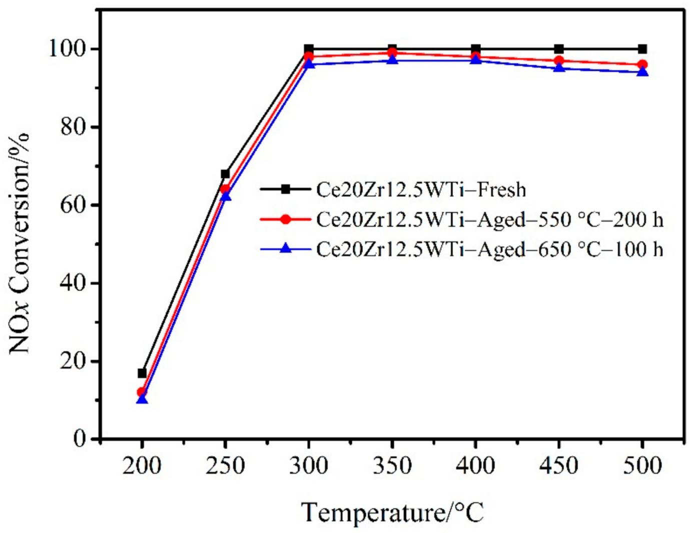

Figure 2. NO_x conversion of fresh and aged Ce20Zr12.5WTi catalyst.

2.2. X-ray Diffraction (XRD) and Brunauer-Emmett-Teller (BET) Analysis

The XRD patterns of Ce*x*Zr*y*WTi catalysts are presented in Figure 3a. For the WTi catalyst, all the main diffraction peaks were in good agreement with those of anatase TiO_2. No peaks attributed to WO_3 were detected, indicating that WO_3 existed as a high dispersion or amorphous species at the support. When Ce or Ce & Zr was added into WTi, the main characteristic peaks belong to anatase TiO_2, at the same time, weak peaks at $2\theta \approx 28.8, 33.2$ and 56.5° were detected, which could be attributed to cubic CeO_2. Generally, it is thought that the high dispersion of the active component is beneficial to catalytic activity; however, the Ce modified catalysts possessed high SCR performance when CeO_2 aggregated on the WTi support. Therefore, Ce species were active sites of the catalyst. Moreover, the catalytic activity of Zr12.5WTi catalyst was similar to WTi and much lower than that for the Ce modified catalyst, which also implied that the Ce species were the main active sites. In addition, as shown in Figure 3b, for Ce20Zr12.5WTi sample, the diffraction peaks of CeO_2 shift to a higher 2θ position when compared with Ce20WTi. This observation implied that the relatively smaller Zr^{4+} has been incorporated into the lattice of CeO_2 and formed Ce-Zr solid solution.

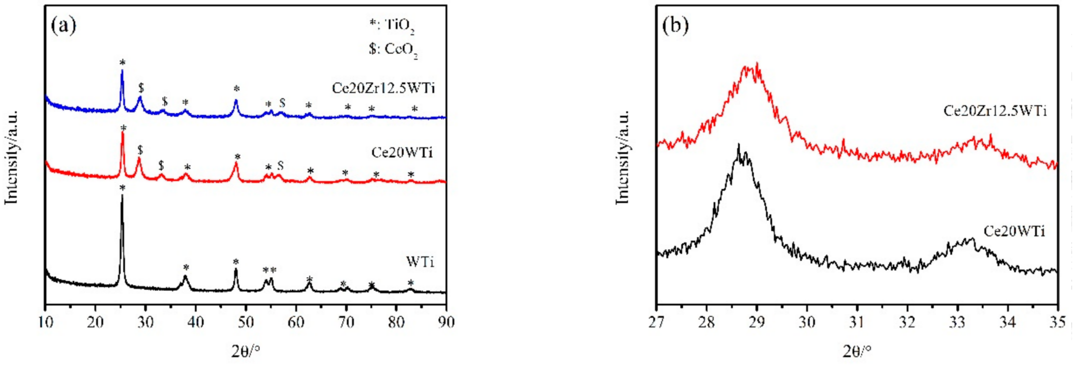

Figure 3. X-ray diffraction (XRD) patterns of Ce*x*Zr*y*WTi catalysts: (**a**) full patterns; (**b**) enlarged part to show the shift of the peaks for CeO_2 (111) and (200) reflections.

The BET surface area, total pore volume, and average pore diameter of the catalysts are summarized in Table 1. It can be seen that the introduction of Ce and Ce & Zr to WTi causes the decrease in surface area. However, the surface area of Ce20Zr12.5WTi catalyst was larger than that of Ce20WTi. It could be due to the formation of the Ce-Zr solid solution between CeO_2 and ZrO_2 according to the XRD results.

Table 1. The texture properties of the Ce*x*Zr*y*WTi catalysts.

Catalysts	**BET Surface Area ($m^2 \cdot g^{-1}$)**	**Total Pore Volume ($cm^3 \cdot g^{-1}$)**	**Average Pore Diameter (nm)**
WTi	80.32	0.2874	125.3
Ce20WTi	46.93	0.1685	109.0
Ce20Zr12.5WTi	58.34	0.1513	86.04

2.3. X-ray Photoelectron Spectroscopy (XPS) Results

Figure 4 displays the XPS spectra of Ce 3d for Ce20WTi and Ce20Zr12.5WTi catalyst. It was reported that two sets of spin-orbital multiplets for Ce, designated u and v, corresponded to the $3d_{3/2}$ and $3d_{5/2}$ contributions, respectively [19]. The sub-bands labelled u′ and v′ represent the $3d^{10}4f^1$ initial electronic state corresponding to Ce^{3+}, and the sub-bands labelled u, u″, u‴, v, v″, and v‴ represent the $3d^{10}4f^0$ state of Ce^{4+} [20]. As shown in Table 2, the presence of Ce^{3+} could create a charge imbalance, oxygen vacancies, unsaturated chemical bonds that generated additional chemisorbed oxygen on the catalyst surface, which could improve the SCR activity [21,22].

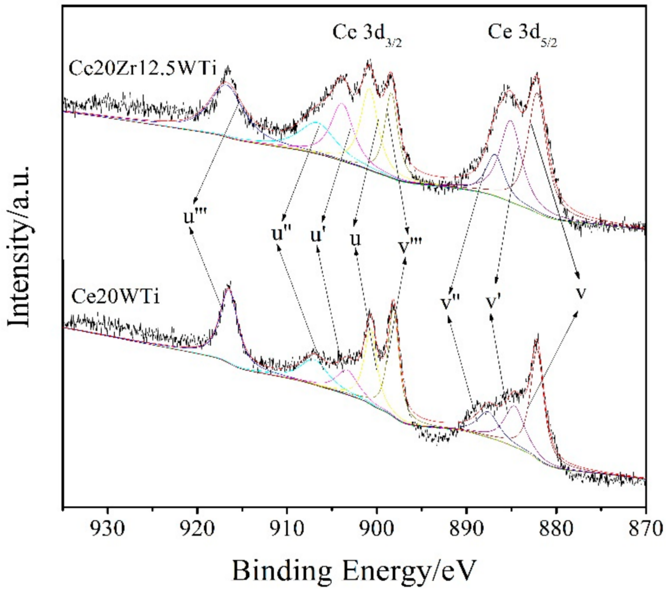

Figure 4. X-ray photoelectron spectroscopy (XPS) spectra of Ce3d for Ce*x*Zr*y*WTi catalysts.

The O 1s XPS spectra for Ce*x*Zr*y*WTi catalysts are exhibited in Figure 5. They are composed of two overlapping peaks, which correspond to two different kinds of oxygen species. The subband with a binding energy of ~529.9 eV contributes to the lattice oxygen (denoted as O_β). The peak at the binding energy of ~531.3 eV was attributed to surface adsorbed oxygen (denoted by O_α) such as O_2^- or O^- [23]. The $O_\alpha/(O_\alpha + O_\beta)$ ratio varied as follows: Ce20Zr12.5WTi > Ce20WTi > WTi, as presented in Table 2. This trend was consistent with the Ce^{3+} ratio of the catalyst. Surface adsorbed oxygen (O_α) is reported to be more active in oxidation reactions due to its higher mobility than lattice oxygen (O_β) [24]. A high O_α ratio is thought to be beneficial for the NO oxidation in the SCR reaction [25,26], thereby improving the activity of the catalysts.

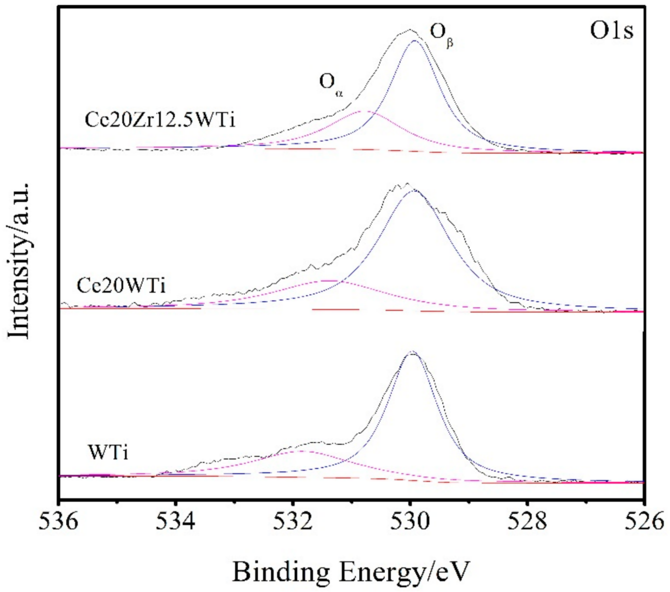

Figure 5. XPS spectra of O 1s core level for Ce*x*Zr*y*WTi catalysts.

Table 2. The XPS results of the Ce*x*Zr*y*WTi catalysts.

Catalysts	Ce^3+/(Ce^{3+} + Ce^{4+})	O_α/(O_α + O_β)
WTi	–	23.2%
Ce20WTi	19.1%	28.8%
Ce20Zr12.5WTi	26.5%	35.4%

2.4.H_2-Temperature Programed Reduction (H_2-TPR) and NH_3-Temperature Programed Desorption (NH_3-TPD) Analysis

The redox properties of the catalyst were characterized by H_2-TPR, as presented in Figure 6. For the WTi catalyst, the peaks at 605 and 693 °C were associated with the multi-stage reduction process from WO_3 to WO_2 via two non-stoichiometric WO*x* oxides [27,28]. For Ce20WTi and Ce20Zr12.5WTi catalyst, the peaks at 556 and 544 °C could be assigned to the reduction of surface Ce^{4+} to Ce^{3+}, while the peaks at 732 and 717 °C might be attributed to the reduction of bulk CeO_2 [29,30]. It can also be seen that H_2-TPR of Ce^{4+} and W^{6+} overlapped on the two catalysts between the temperature range of WO*x* reduction. In addition, the CeO_2 reduction peaks of the two Ce contained catalysts were most obvious, which implied that the active sites of the catalysts were CeO_2 species. It is worth noting that the reduction peaks of CeO_2 in Ce20Zr12.5WTi moved to lower temperature compared to that of the Ce20WTi catalyst, which indicated that the addition of Zr facilitated the redox property of the catalyst. Namely, Ce and Zr formed solid solution, which lead to an increase of redox property, which was beneficial to SCR activity.

Besides the redox property, surface acidity is another critical factor during the SCR process. The chemisorption and activation of NH_3 on the surface acid sites of catalysts are generally viewed as the primary processes in NH_3-SCR of NO_x. NH_3-TPD was performed to investigate the surface acid amount and strength of the Ce*x*Zr*y*WTi catalysts as shown in Figure 7. All the catalysts exhibited three broad NH_3 desorption peaks at 150–350, 350–500, and 500–800 °C, which are attributed to the weak, medium and strong acid sites, respectively [25,30]. When Ce was introduced to WTi, the NH_3 desorption amount increased from 83 $\mu mol \cdot g^{-1}$ to 212 $\mu mol \cdot g^{-1}$. Moreover, for the Ce & Zr modified WTi catalyst, the amounts of the acid site were further enhanced (410 $\mu mol \cdot g^{-1}$). Consequently, the simultaneous introduction of Ce and Zr to WTi catalyst brought more active NH_3 adsorbed species, which is believed to be significantly beneficial to SCR reaction.

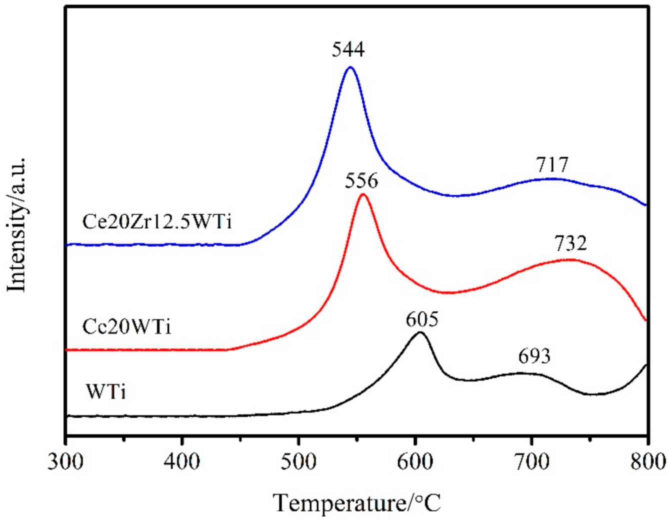

Figure 6. H_2-TPR profiles of Ce*x*Zr*y*WTi catalysts.

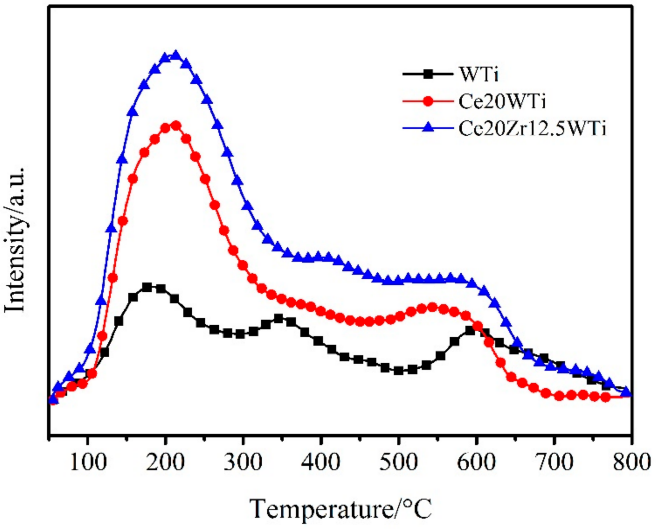

Figure 7. NH_3-TPD profiles of Ce*x*Zr*y*WTi catalysts.

3. Materials and Methods

3.1. Catalyst Preparation

A series of CeO_2-ZrO_2/WO_3-TiO_2 (denoted as Ce*x*Zr*y*WTi; *x* and *y* represents the weight percent of CeO_2 and ZrO_2, respectively; the WO_3-TiO_2 content is 100-*x*-*y*) catalysts were prepared by the impregnation method. $Ce(NO_3)_3 \cdot 6H_2O$, $Zr(NO_3)_4 \cdot 5H_2O$ (Sinopharm Chemical Reagent Corp., Beijing, China) and WO_3-TiO_2 (Cristal Corp., Thann, France) (WO_3: 10 wt %) were used for the experiment. Firstly, a given amount of $Ce(NO_3)_3 \cdot 6H_2O$ and $Zr(NO_3)_4 \cdot 5H_2O$ was dissolved in deionized water and mixed with WO_3-TiO_2 powders. The mixture was stirred for 30 min, then exposed to ultrasonic energy for 2 h, dried at 110 °C overnight, and calcined at 550 °C for 3 h in static air.

The fresh Ce20Zr12.5WTi catalyst was thermally aged in 10% H_2O/air at 550 °C for 200 h and named as Ce20Zr12.5WTi-Aged-550 °C-200 h. Similarly, the Ce20Zr12.5WTi-Aged-650 °C-100 h catalyst was obtained by treating the fresh catalyst in 10% H_2O/air at 650 °C for 100 h.

3.2. Catalyst Characterization

XRD measurement was carried out on an X′ pert Pro diffractometer (Panalytical Corp., The Netherlands) operating at 40 mA and 40 kV with Cu *Kα* radiation. The 2θ data from 10° to 90° were collected with the step size of 0.03°.

The BET surface area was measured at –196 °C on an ASAP 2050 physical adsorption instrument (Micromeritics Corp., Norcross, GA, USA) by using the nitrogen adsorption method. The samples were pretreated in a vacuum at 300 °C for 4 h before experiments. The surface area was determined by BET method in 0–0.3 partial pressure range.

X-ray photoelectron spectra (XPS) were recorded with a Thermo ESCALAB 250Xi spectrometer (ThermoFisher Scientific, Waltham, MA, USA) using Al *Kα* radiation (1486.6 eV). Binding energies of Ce 3d and O 1s were calibrated using C1s peak (B.E. = 284.6 eV) as standard. The catalysts' surface composition according to atomic ratios was calculated, and Shirley background and Gaussian-Lorentzian was used for peak analysis.

Temperature programmed reduction (TPR) was conducted on an AutoChem 2920 chemisorption analyzer (Micromeritics, Norcross, GA, USA) supplied by the Micromeritics Company. Each time, 100 mg of the sample was heated from room temperature to 800 °C at a rate of 10 $°C \cdot min^{-1}$. A mixture gas consisting of H_2 and Ar with H_2 content of 10 vol.% was used as reductant at a flow rate of 50 $mL \cdot min^{-1}$. Before detection by the TCD, the gas was purified by a trap containing CaO + NaOH materials in order to remove the H_2O and CO_2.

NH_3 temperature programmed desorption (NH_3-TPD) was conducted on an AutoChem 2920 chemisorption analyzer (Micromeritics, Norcross, GA, USA) supplied by the Micromeritics Company. After being pretreated at 350 °C in He flow at 200 $mL \cdot min^{-1}$ for 1 h, the samples were cooled down to 50 °C and saturated with 1% NH_3 until adsorption saturation, followed by He purging at the same temperature to remove physical absorption species. The desorption of nitrogen–containing species was then performed in the range of 50–800 °C at a speed of 10 $°C \cdot min^{-1}$.

3.3. Activity Evaluation

The catalytic performance of the catalysts was tested in a fixed-bed quartz reactor (I.D. = 6 mm) at atmospheric pressure. The reaction conditions were controlled as follows: 200 ppm NO, 200 ppm NH_3, 12% O_2, 5% H_2O, 200 ppm CO, 4.5% CO_2, 50 ppm C_3H_6, and N_2 as balance gas. The total flow rate and the gas hourly space velocity (GHSV) were 300 mL min^{-1} and 200,000 h^{-1}, respectively. The effluent gas, including NO, NO_2, and O_2 was continuously analyzed by an online flue gas analyzer. The results for the steady-state activity of catalysts were recorded after about 20 min at each temperature. The NO_x conversion was calculated accordingly [3], whereas NO_x = NO + NO_2.

$$NO_x \text{ conversion} = \frac{[NO_x]_{\text{inlet}} - [NO_x]_{\text{outlet}}}{[NO_x]_{\text{inlet}}} \times 100\% \quad (1)$$

4. Conclusions

In this work, Ce and/or Zr was introduced to WO_3-TiO_2 oxides by the impregnation method. And their deNO_x performances were evaluated in a simulated real diesel engine exhaust, in order to decrease the amount of optimization experiments, a method of "prediction verification" was used to optimize the contents of Ce, Zr and WTi. The simultaneous addition of Ce and Zr could improve SCR activity remarkably of the WO_3-TiO_2. In a wide temperature range 300–500 °C, 100% NO_x conversion was obtained at the high GHSV of 300,000 h^{-1} over the Ce20Zr12.5WTi catalyst, and also this catalyst exhibited high thermal stability. For the Ce and Zr modified WTi catalyst (Ce20Zr12.5WTi), Ce and Zr has formed a solid solution, which facilitates the redox of Ce^{4+}/Ce^{3+} and formation of a larger amount of oxygen vacancies, larger quantities of surface adsorbed oxygen species (O_2^- and O^-), more Ce^{3+} ions and more acid sites. And the surface adsorbed oxygen are the principal active oxygen species and beneficial for NO oxidation to NO_2. Therefore, surface adsorbed oxygen species, together with the improved redox properties and more acid sites were responsible for the excellent SCR performance.

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