Ce and Zr Modified WO₃-TiO₂ Catalysts for Selective Catalytic Reduction of NOₓ by NH₃

Wenyi Zhao 1, Zhaoqiang Li 1,*, Yan Wang 1, Rongrong Fan 1, Cheng Zhang 1, Yu Wang 1, Xin Guo 1, Rong Wang 1 and Shule Zhang 2,*

1 National Engineering Research Center of Rare Earth Metallurgy and Functional Materials, Baotou Research Institute of Rare Earths, Baotou 014030, China; zhaowybrire@163.com (W.Z.); wy_brire@163.com (Y.W.); fanrong0419@163.com (R.F.); zhangchengbrire@163.com (C.Z.); wydyxl01@sina.com (Y.W.); gxbtctxiyj@163.com (X.G.); xtywangrong@163.com (R.W.)
2 School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China
* Correspondence: li_brire@163.com (Z.L.); shulezhang@163.com (S.Z.); Tel.: +86-472-517-9281 (Z.L.); +86-025-8431-5517 (S.Z.)

Received: 21 August 2018; Accepted: 3 September 2018; Published: 5 September 2018

Abstract: A series of Ce and/or Zr modified WO₃-TiO₂ catalysts were synthesized by the impregnation method, which were employed for NH₃-SCR reaction. The T₅₀ contour lines of NOₓ were used to quickly optimize catalyst composition, the Ce₂₀Zr₁₂.₅W₁ catalyst was considered to be the optimization result, and also exhibited excellent NH₃-SCR activity and thermal stability with broad operation temperature window, which is a very promising catalyst for NOₓ 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 Ce⁴⁺/Ce³⁺ and the formation of more acid sites, more Ce³⁺ ions, more oxygen vacancies, larger quantities of surface adsorbed oxygen species and NH₃, which were beneficial for the excellent selective catalytic reduction (SCR) performance.

Keywords: NH₃-SCR; nitrogen oxides; Ce-Zr solid solution; T₅₀ contour line

1. Introduction

Nitrogen oxides (NOₓ) 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 NOₓ emissions [1,2]. Among these technologies, selective catalytic reduction of NOₓ with NH₃ (NH₃-SCR) has been widely used and considered one of the most effective approaches for NOₓ control in diesel vehicles.

The commercial catalyst used for the NH₃-SCR process is V₂O₅-WO₃/TiO₂ [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 deNOₓ performance.

CeO₂-based oxides have attracted increasing attention due to the excellent redox properties shifting between Ce³⁺ and Ce⁴⁺ [4–6]. Among all the CeO₂-based catalysts, CeO₂/WO₃-TiO₂ catalyst exhibits excellent SCR performance, with high SCR activity and N₂ 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 CeO₂/WO₃-TiO₂ catalyst was also not satisfied. The problems mentioned above restrained the application of CeO₂/WO₃-TiO₂ 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, CO, CO$_2$, C$_3$H$_6$, H$_2$O, 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 Ce$_{20}$Zr$_{12.5}$WTi catalyst possesses the lowest $T_{50}$. Moreover, the Ce$_{20}$Zr$_{12.5}$WTi displayed an excellent catalytic performance from 200 to 500 $^{\circ}$C, as presented in Figure 1b.

![Figure 1.](image)

The optimal catalyst Ce$_{20}$Zr$_{12.5}$WTi 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-Ce$_{20}$Zr$_{12.5}$WTi-550 $^{\circ}$C-200 h and Aged-Ce$_{20}$Zr$_{12.5}$WTi-650 $^{\circ}$C-100 h catalysts, the average NO$_x$ conversion decreased by 3 and 4.86%, respectively, which suggested that the Ce$_{20}$Zr$_{12.5}$WTi possess high thermal stability.
Figure 2. \( \text{NO}_x \) 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 \( \theta \approx 28.8, 33.2 \) and \( 56.5^\circ \) 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 \( \theta \) 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.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>BET Surface Area (m$^2$.g$^{-1}$)</th>
<th>Total Pore Volume (cm$^3$.g$^{-1}$)</th>
<th>Average Pore Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WTi</td>
<td>80.32</td>
<td>0.2874</td>
<td>125.3</td>
</tr>
<tr>
<td>Ce20WTi</td>
<td>46.93</td>
<td>0.1685</td>
<td>109.0</td>
</tr>
<tr>
<td>Ce20Zr12.5WTi</td>
<td>58.34</td>
<td>0.1513</td>
<td>86.04</td>
</tr>
</tbody>
</table>

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](image_url)  
**Figure 4.** X-ray photoelectron spectroscopy (XPS) spectra of Ce3d for CexZryWTi catalysts.

The O 1s XPS spectra for CexZryWTi 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$_{\beta}$). The peak at the binding energy of ~531.3 eV was attributed to surface adsorbed oxygen (denoted by O$_{\alpha}$) 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$_{\alpha}$) is reported to be more active in oxidation reactions due to its higher mobility than lattice oxygen (O$_{\beta}$) [24]. A high O$_{\alpha}$ 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 CeZryWTi catalysts.

Table 2. The XPS results of the CeZryWTi catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Ce(^{3+})/(Ce(^{3+}) + Ce(^{4+}))</th>
<th>O(<em>{\alpha})/(O(</em>{\alpha}) + O(_{\beta}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>WTi</td>
<td>–</td>
<td>23.2%</td>
</tr>
<tr>
<td>Ce20WTi</td>
<td>19.1%</td>
<td>28.8%</td>
</tr>
<tr>
<td>Ce20Zr12.5WTi</td>
<td>26.5%</td>
<td>35.4%</td>
</tr>
</tbody>
</table>

2.4. \(\text{H}_2\)-Temperature Programed Reduction (\(\text{H}_2\)-TPR) and \(\text{NH}_3\)-Temperature Programed Desorption (\(\text{NH}_3\)-TPD) Analysis

The redox properties of the catalyst were characterized by \(\text{H}_2\)-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 \(\text{H}_2\)-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 \(\text{NH}_3\) on the surface acid sites of catalysts are generally viewed as the primary processes in \(\text{NH}_3\)-SCR of NO\(_x\). \(\text{NH}_3\)-TPD was performed to investigate the surface acid amount and strength of the CeZryWTi catalysts as shown in Figure 7. All the catalysts exhibited three broad \(\text{NH}_3\) 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 \(\text{NH}_3\) desorption amount increased from 83 µmol·g\(^{-1}\) to 212 µmol·g\(^{-1}\). Moreover, for the Ce & Zr modified WTi catalyst, the amounts of the acid site were further enhanced (410 µmol·g\(^{-1}\)). Consequently, the simultaneous introduction of Ce and Zr to WTi catalyst brought more active \(\text{NH}_3\) adsorbed species, which is believed to be significantly beneficial to SCR reaction.
3. Materials and Methods

3.1. Catalyst Preparation

A series of CeO\(_2\)-ZrO\(_2\)/WO\(_3\)-TiO\(_2\) (denoted as CexZryWTi; \(x\) 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\(_3\))\(_3\)-6H\(_2\)O, Zr(NO\(_3\))\(_4\)-5H\(_2\)O (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\(_3\))\(_3\)-6H\(_2\)O and Zr(NO\(_3\))\(_4\)-5H\(_2\)O 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\(_2\)O/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\(_2\)O/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 Ka 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·min⁻¹. A mixture gas consisting of H₂ and Ar with H₂ content of 10 vol.% was used as reductant at a flow rate of 50 mL·min⁻¹. Before detection by the TCD, the gas was purified by a trap containing CaO + NaOH materials in order to remove the H₂O and CO₂.

NH₃ temperature programmed desorption (NH₃-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·min⁻¹ for 1 h, the samples were cooled down to 50 °C and saturated with 1% NH₃ 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·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 NH₃, 12% O₂, 5% H₂O, 200 ppm CO, 4.5% CO₂, 50 ppm C₃H₆, and N₂ 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, NO₂, and O₂ 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 NOₓ conversion was calculated accordingly [3], whereas NOₓ = NO + NO₂.

\[
\text{NO}_x \text{ conversion} = \frac{[\text{NO}_x]_{\text{inlet}} - [\text{NO}_x]_{\text{outlet}}}{[\text{NO}_x]_{\text{inlet}}} \times 100\% \quad (1)
\]

4. Conclusions

In this work, Ce and/or Zr was introduced to WO₃-TiO₂ oxides by the impregnation method. And their deNOₓ 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 WO₃-TiO₂. In a wide temperature range 300–500 °C, 100% NOₓ 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 Ce⁴⁺/Ce³⁺ and formation of a larger amount of oxygen vacancies, larger quantities of surface adsorbed oxygen species (O₂⁻ and O¹⁻), more Ce³⁺ ions and more acid sites. And the surface adsorbed oxygen are the principal active oxygen species and
beneficial for NO oxidation to NO₂. Therefore, surface adsorbed oxygen species, together with the improved redox properties and more acid sites were responsible for the excellent SCR performance.

**Author Contributions:** Conceptualization, Z.L.; Investigation, R.F.; C.Z.; Y.W. (Yu Wang) and X.G.; Data Curation, Y.W. (Yan Wang); Writing-Review & Editing, S.Z.; Supervision, R.W.; Project Administration, W.Z.

**Funding:** This research was funded by the Science and Technology Projects of China Northern Rare Earth (Group) High-tech Co., Ltd. (Grant No. BFXT-2018-D-1) and Natural Science Foundation of Inner Mongolia (Grant No. 2017MS0209).

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

**References**


