Activity and hydrothermal stability of CeO$_2$–ZrO$_2$–WO$_3$ for the selective catalytic reduction of NO$_x$ with NH$_3$

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ABSTRACT

A series of CeO$_2$–ZrO$_2$–WO$_3$ (CZW) catalysts prepared by a hydrothermal synthesis method showed excellent catalytic activity for selective catalytic reduction (SCR) of NO with NH$_3$ over a wide temperature of 150–550°C. The effect of hydrothermal treatment of CZW catalysts on SCR activity was investigated in the presence of 10% H$_2$O. The fresh catalyst showed above 90% NO$_x$ conversion at 201–459°C, which is applicable to diesel exhaust NO$_x$ purification (200–440°C). The SCR activity results indicated that hydrothermal aging decreased the SCR activity of CZW at low temperatures (below 300°C), while the activity was notably enhanced at high temperature (above 450°C). The aged CZW catalyst (hydrothermal aging at 700°C for 8 hr) showed almost 80% NO$_x$ conversion at 229–550°C, while the V$_2$O$_5$–WO$_3$/TiO$_2$ catalyst presented above 80% NO$_x$ conversion at 308–370°C. The effect of structural changes, acidity, and redox properties of CZW on the SCR activity was investigated. The results indicated that the excellent hydrothermal stability of CZW was mainly due to the CeO$_2$–ZrO$_2$ solid solution, amorphous WO$_3$ phase and optimal acidity. In addition, the formation of WO$_3$ clusters increased in size as the hydrothermal aging temperature increased, resulting in the collapse of structure, which could further affect the acidity and redox properties.

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Introduction

The NO$_x$ from diesel engines poses a serious problem to the environment and human health (Yu et al., 2015). With increasingly stringent NO$_x$ emission legislation, extensive efforts are being made to find ways to eliminate NO$_x$ from diesel engines. Among the NO$_x$ removal technologies, selective catalytic reduction (SCR) has been successfully applied to reduce NO$_x$ by NH$_3$ (Zhang et al., 2011). Typically, the main industrial SCR catalysts are V$_2$O$_5$/WO$_3$ (MoO$_3$)/TiO$_2$ and Fe-zeolite catalysts (Chapman, 2011; Iwasaki et al., 2008). The vanadium-based catalysts can dramatically remove NO$_x$ and be effectively regenerated (Tang et al., 2007). However, some drawbacks of these catalysts exist that impede wide application, including a narrow reaction temperature window (300–400°C), the inherent toxicity of vanadium oxides and the formation of N$_2$O at high temperatures (Xu et al., 2014; Yang et al., 2011). The Fe-zeolite catalysts show excellent NH$_3$-SCR performance at high temperatures (300–600°C), but inferior SCR activity at low temperature and poor hydrothermal stability are still serious problems (Brandenberger et al., 2010). To avoid these problems, new efficient catalysts are urgently needed.

Currently, one of the challenges for the diesel engine application of SCR catalysts is their durability under hydrothermal conditions. Although a large number of catalysts have been
employed in NH₃-SCR, no suitable catalyst has been found for diesel de-NOₓ abatement. It is fundamentally difficult to control NOₓ emissions from diesel engines because the temperature of NOₓ emitted from diesel engine is 200-440°C (Kim et al., 2012). In addition, SCR catalysts are often exposed to high hydrothermal temperatures (above 650°C) during soot oxidation processes in upstream DPFs (Zheng and Keith, 2004). Therefore, considerable efforts have been devoted to developing efficient SCR catalysts with excellent hydrothermal stability for application in diesel engines. TiO₂-based catalysts easily undergo a phase transition above 600°C, leading to deactivation (Shan et al., 2012). Zeolite-based catalysts are not suitable as diesel catalysts due to their instability under hydrothermal conditions (Metkar et al., 2012). Consequently, high hydrothermal durability and high-temperature catalytic activity are crucial for practical implementation with diesel engines.

Ceria-based catalysts have attracted more attention due to their advantageous redox properties. However, a major drawback of pure CeO₂ is that it is largely deactivated at high temperature due to poor thermostability (Fornasiero et al., 1999). However, the thermal stability can be promoted by the addition of other metal oxides into CeO₂ (Casapu et al., 2011). Currently, Ce-Zr mixed oxides are a key component for NH₃-SCR catalysts because of their favorable attributes, such as high-temperature phase stability, good redox properties, and acidity (Marcotte et al., 2011). Tungsten trioxide (WO₃), as an important catalyst promoter, not only acts as an acidic component, but also functions as a stabilizer for catalysts. Li et al. (2008) reported that 80% NOₙ conversion was obtained at 325–500°C over a WO₃/CeO₂–ZrO₂ catalyst prepared by a wet impregnation method after hydrothermal treatment. In this study, the CeO₂–ZrO₂–WO₃ catalyst prepared by a hydrothermal method was found to present rather good activity at 201–459°C. Compared with V₂O₅–WO₃/TiO₂ catalysts, the CZW catalyst exhibits exceptional activity, superior N₂ selectivity and excellent hydrothermal stability even under an extremely high hydrothermal temperature (700°C) for 96 hr, making it a promising catalyst for NOₓ abatement from diesel engine exhaust. To analyze the cause of hydrothermal aging, the catalysts were characterized by powder X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), infrared spectroscopy of adsorbed pyridine (Py-IR), raman spectra (RS), X-ray photoelectron spectrum (XPS), and temperature-programmed reduction with hydrogen (H₂-TPR) techniques.

1. Experimental studies

1.1. Catalyst preparation

The samples were synthesized by a hydrothermal method. All chemicals were of analytical grade. The precursors zirconium nitrate pentahydrate (0.01 mol), cerium nitrate hexahydrate (0.01 mol), ammonium metatungstate hydrate (0.6491 g), acrylic acid (0.03 mol), and glucose (0.05 mol) were mixed in an aqueous solution. Afterwards, an ammonia solution (25 wt.%) was added dropwise into the solution with vigorous stirring until the pH reached 10. Subsequently, the mixture was stirred for 5 hr at room temperature. Then the blend was transferred into a Teflon-lined, stainless steel autoclave and heated at 160°C for 72 hr. The obtained precipitates were filtrated and washed, followed by drying at 80°C for 12 hr and calcining at 550°C for 5 hr. The catalysts were denoted as CZW.

To comprehensively evaluate the high temperature catalytic performance and hydrothermal stability, the CZW catalysts were studied after hydrothermal aging at different temperatures (600, 700, 800, and 900°C) for 8 hr in the presence of 10 vol.% H₂O. The samples were correspondingly denoted as CZW-6-8, CZW-7-8, CZW-8-8, and CZW-9-8. In order to study the durability of CZW catalysts, the samples were also investigated after hydrothermal aging at 700°C for different times (24, 48, and 96 hr) in 10 vol.% H₂O. The samples were denoted as CZW-7-24, CZW-7-48, and CZW-7-96.

1.2. Characterization

XRD patterns were recorded by an X-ray diffractometer (s-7000, Shimadzu, Japan) between 10 and 70° 2θ at a step of 2°/min using Cu Kα radiation operating at 30 kV and 30 mA to determine the crystal structure. Raman spectra were measured on a Renishaw-2000 Raman spectrometer (Renishaw-2000, Renishaw, UK) at a resolution of 2 cm⁻¹ by using the 514.5 nm line of an Ar ion laser as the excitation source.

XPS analysis was employed using an ULVAC PHI 5000 Versa Probe-II equipment (PHI 5000 Versa Probe-II, ULVAC, Japan) operating at 10⁻⁸ Pa with Al Kα radiation (1486.6 eV). The observed spectra were corrected using the C 1 s binding energy value at 284.8 eV.

Temperature-programmed reduction (TPR) experiments for the CZW powders were carried out in a conventional gas chromatograph (GC-9750, FULI Analytical Instrument Co. Ltd., China) with 0.05 g of catalysts. The H₂-TPR experiments were performed from 100 to 890°C with a heating rate of 10°C/min under 1 atm. H₂/Ar flow. The nature of acid sites over the samples was studied by Py-IR based on the fact that pyridine molecules adsorbed on different acid sites displayed characteristic vibration bands. The spectra were recorded with 4 cm⁻¹ spectral resolution on a Nicolet Nexus 470 spectrometer (Nexus 470, Nicolet, USA) equipped with a deuterated triglycine sulfate (DTGS) detector by signal averaging 64 scans. The spectra were recorded at 25, 100, and 200°C.

HR-TEM with high magnification was performed on a JEOL JEM-2100 analytical transmission electron microscope (JEOL-2100, JEOL, USA). Before the HR-TEM test, the samples were dispersed in high-purity ethanol for 15 min, and deposited onto copper-grid-supported amorphous carbon films, then the impregnated mesh was dried in air before TEM analysis.

1.3. Catalytic activity measurement

The NH₃-SCR activity measurements were carried out in a fixed-bed quartz reactor (8 mm i.d.) with 0.4 mL catalysts of 60–80 mesh. The experiments were performed under atmospheric pressure at 150–550°C and the gas flow was monitored by mass flow meters (Beijing Sevenstar Electronics, Beijing, China). The typical composition of inlet gas was 0.06% NH₃, 0.06% NO, 5 vol.% O₂, and N₂ as the balance gas at a flow rate of 400 mL/min, which corresponded to a GHSV (gas hourly space velocity) of 60,000 hr⁻¹. The concentration of NOₓ was continuously detected by a flue gas analyzer (ECOM-J2KN,
RBR, Germany). The N₂O was analyzed by a gas chromatograph (GC-9750, FULI Analytical Instrument Co. Ltd., China) on two parallel columns linked to a thermal conductivity detector and electron capture detector, respectively. A Porapak Q column was used for N₂O and a 5 Å molecular sieve column for N₂. To minimize the influence of gas adsorption on the catalyst samples, test data were measured after the reactions had achieved steady state.

2. Results and discussion

2.1. Catalytic activity

The activities of the CZW catalysts are exhibited in Fig. 1. As shown in Fig. 1a, a decrease in low-temperature activity was observed for all CZW catalysts after hydrothermal aging, while the performance of the aged CZW catalysts was dramatically enhanced at high temperature (above 400°C). The NOₓ conversion of CZW was noticeably different after hydrothermal aging at various temperatures. It has been reported that the NOₓ conversion is increased at high temperature (above 500°C) for hydrothermally aged NiₓSC catalysts (Shi et al., 2013). The phenomena implied that the hydrothermal treatment could decrease SCR catalytic activity at low temperature and enhance high-temperature performance. For aged CZW catalysts, the CZW-6-8 sample exhibited 74% NOₓ conversion at 219–527°C. More than 74% NOₓ conversion was obtained over the CZW-7-8 catalyst in the wide temperature range of 225–550°C. With the increase of hydrothermal aging temperature (800 and 900°C), the catalytic activity decreased significantly. Above 74% NOₓ conversion was achieved at 300–525°C over the CZW-9-8 catalyst. Therefore, the CZW-7-8 catalyst showed the best performance over the whole temperature range. It could be seen from Fig. 1b that nearly 100% NOₓ conversion was obtained with the CZW-7-8 catalyst at 250–525°C. With increasing hydrothermal aging time, no evident decrease of activity was observed. Hence, the results indicated that the CZW catalysts showed considerable tolerance to hydrothermal shock at high temperature.

Fig. 1c presents a comparison between the CZW catalyst and a commercial vanadium-based catalyst (V₅O₂-WO₃/TiO₂). After aging at 700°C for 8 hr, a decrease in SCR performance was observed at 150–250°C for the CZW catalyst. Interestingly, the CZW-7-8 catalyst exhibited a dramatic increase in NOₓ conversion at high temperature (450–550°C) when compared with fresh CZW catalyst. However, substantial differences were observed for the V₅O₂-WO₃/TiO₂ catalyst after hydrothermal aging at 700°C for 8 hr (denoted as V₅O₂-WO₃/TiO₂-7-8). Above 80% NOₓ conversion was obtained at 259–482°C over the fresh V₅O₂-WO₃/TiO₂ catalyst. The V₅O₂-WO₃/TiO₂-7-8 catalyst showed a significant decrease in the NOₓ conversion at low temperatures (150–300°C) and was even worse at high temperatures (400–550°C). Furthermore, the NOₓ conversion at 308–370°C for the V₅O₂-WO₃/TiO₂-7-8 catalyst was only a little over 80%. Brandenberger et al. (2010) reported that the catalytic activity of a Fe-ZSM-5 catalyst aged at 650°C for 8 hr decreased rapidly at low temperatures (<350°C) and 70% NOₓ conversion was obtained at 360°C. Ye et al. (2012) found that the performance of an aged Cu/ZSM-5 catalyst decreased dramatically, and 60% NOₓ conversion was reached at 400°C. By comparison, the CZW catalyst possessed superior hydrothermal stability.

Fig. 1 - Catalytic activity of (a) fresh and aged CeO₂-ZrO₂-WO₃ (CZW) catalysts and (b) CZW catalysts aged at 700°C for different hydrothermal times for SCR of NOₓ with NH₃; (c) a comparison of NOₓ conversion between CZW catalyst and V₅O₂-WO₃/TiO₂ catalysts. Reaction conditions: 0.06% NO, 0.06% NH₃, 5% O₂, balance N₂ gas hourly space velocity (GHSV) = 60,000 hr⁻¹. CZW-m-n and V₅O₂-WO₃/TiO₂-m-n refer to CZW and V₅O₂-WO₃/TiO₂ catalysts aged at m × 100°C in the presence of 10 vol.% H₂O for n hr.
2.2. N₂ selectivity

The N₂ selectivity and N₂O outlet concentration of the CZW catalysts are presented in Fig. 2. From Fig. 2a, the N₂ selectivity of the CZW catalysts was more than 91%. Regarding the N₂O outlet concentration, the CZW-9-8 catalyst exhibited the largest N₂O concentration, especially at high temperatures (above 500°C). However, the maximum N₂O concentration was merely 28 × 10⁻⁶ at 550°C over the CZW-9-8 sample. Consequently, the CZW catalyst possessed superior N₂ selectivity. As shown in Fig. 2b, with increasing hydrothermal aging time, the N₂ selectivity showed almost no change; furthermore, more than 96% N₂ selectivity was obtained for all the CZW catalysts. The phenomena further confirmed that the CZW catalyst possessed excellent hydrothermal stability.

2.3. XRD analysis

XRD patterns of CZW samples in the 2θ range of 10–70° are shown in Fig. 3. The XRD pattern of the fresh sample was consistent with the characteristic peaks of cubic CeO₂ (PDF: 65-5923), and WO₃ species and phase-separated ZrO₂ were not detected (Fig. 3a). This indicated that the CZW catalysts consisted of CeO₂–ZrO₂ solid solutions (Si et al., 2010; Lee et al., 2014). For the aged CZW catalysts, both CeO₂ and ZrO₂ phases could be observed from the diffractograms. The intensities of CeO₂ and ZrO₂ lines were weak for the CZW-6-8 catalyst, but the characteristic peaks for both phases intensified and narrowed with an increase in hydrothermal aging temperature, which implied that hydrothermal treatment at high temperature could result in phase segregation and crystal agglomeration. It was reported that a proper amount of CeO₂ could enhance thermal stabilization, and the CeO₂–ZrO₂ mixed oxides possessed a similar mechanism to prevent the sintering process of catalysts (Wu et al., 2004). In addition, the characteristic peaks of CeO₂ and ZrO₂ shifted to higher 2θ positions with an increase in hydrothermal aging temperature, which would be caused by lattice contraction (Guo et al., 2014). The phenomenon implied that the microscopic structure of CZW catalysts underwent changes at high hydrothermal aging temperatures. In order to further investigate the influence of hydrothermal treatment on the microstructure of CZW, the Scherrer formula was utilized to calculate the grain size of ceria in CZW catalysts, and the average grain size of ceria in catalyst are as follows: CZW (26 nm); CZW-6-8 (11 nm); CZW-7-8 (23 nm); CZW-8-8 (36 nm); CZW-9-8 (56 nm); CZW-7-24 (40 nm); CZW-7-48 (46 nm); and CZW-7-96 (57 nm). It was clear that the average grain size was influenced by the hydrothermal aging temperature and time. Furthermore, no separate WO₃ species were detected for the aged samples, indicating that WO₃ existed as amorphous species on the surface of the CZW catalysts. As shown in Fig. 3b, compared with the weak diffraction peaks of CZW-7-8 samples, sharp peaks were observed for aged samples (CZW-7-24, CZW-7-48 and CZW-7-96) due to the sintering of crystallites. Nevertheless, no obvious phase change was noticed besides the change in peak intensities, which indicated that the CZW catalysts exhibited excellent tolerance to hydrothermal shock at 700°C. The results further confirmed that the microstructure of CZW possessed superior hydrothermal stability.

2.4. HR-TEM results

The general morphologies and microstructures of the fresh CZW and aged CZW catalysts hydrothermal aging at 700°C were investigated by HR-TEM and representative images are shown in Fig. 4. From Fig. 4a, b, and c, it was clear that the lattice fringes of CZW catalyst became increasingly distinct with an increase in hydrothermal aging time, indicating high crystallinity. As shown in Fig. 4a, the average particle size for fresh CZW samples was about 19 nm. A slight increase in the crystallite size was noticed after hydrothermal treatment at 700°C (Fig. 4b and c). The grain size increased from 19 to 30 nm for the CZW-7-8 sample and from 30 to 37 nm for the CZW-7-96 sample with increasing hydrothermal aging time, respectively. The phenomena demonstrated that the aged CZW crystals agglomerated to some extent at high temperatures. In addition, WO₃ particles were not observed in the images of aged CZW catalysts. In brief, the HR-TEM results implied that the morphology of the samples was only slightly affected by hydrothermal

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Fig. 2 – N₂O formation and N₂ selectivity over (a) CZW catalysts aged at different temperatures and (b) CZW catalysts aged at 700°C for different hydrothermal aging times. CZW–m–n refers to Fig. 1. CZW: CeO₂–ZrO₂–WO₃.
Therefore, the CZW catalyst possessed excellent hydrothermal stability.

2.5. Raman results

The Raman spectra of CZW catalysts are shown in Fig. 5. For aged CZW catalysts, a strong band observed at ~465 cm$^{-1}$ could be due to the F$_{2g}$ Raman-active mode of the fluorite type lattice, which can be attributed to a symmetric breathing mode of the oxygen atoms around cerium ions (Wang et al., 2014). The Raman bands of the samples became noticeably broader with an increase in hydrothermal aging temperature, which might be related to morphology and grain size (Spanier et al., 2001). With an increase in hydrothermal aging temperatures, new bands (146 and 267 cm$^{-1}$) appeared, which were ascribed to tetragonal ZrO$_2$, and the bands for monoclinic ZrO$_2$ were located around 334 and 386 cm$^{-1}$. The band intensities strengthened with increasing hydrothermal aging temperature. The phenomena implied that the crystallinity of CZW particles increased and the phase separation of CeO$_2$ and ZrO$_2$ phases was observed with an increase in hydrothermal aging temperature. The presence of the broad band at 618 cm$^{-1}$ was
assigned to the longitudinal optical (LO) mode of ceria, which originated from the relaxation of symmetry rules (Reddy et al., 2005); oxygen vacancies were responsible for the emergence of this band. This indicated that the CZW catalysts formed a CeO$_2$–ZrO$_2$ solid solution by substitution of Zr into the CeO$_2$ lattice under high hydrothermal aging temperature conditions. The band (~310 cm$^{-1}$) could be attributed to the displacement of oxygen atoms from their ideal fluorite lattice positions (Vidal et al., 2000), which confirmed the presence of a CeO$_2$–ZrO$_2$ solid solution in the aged samples. For the CZW-8-8 and CZW-9-8 catalysts, the CeO$_2$ peak was sharper and new bands appeared at 815, 925, and 944 cm$^{-1}$, which were observed in spectra of various tungsten trioxide hydrates (Nonaka et al., 1993; Sadek et al., 2009). This was due to better crystallization of the samples at higher hydrothermal aging temperature. From Fig. 5b, it could be seen that all aged samples subjected to hydrothermal aging at 700°C for different times showed similar profiles except for differences in intensity. This implied that the CZW catalysts possessed a stable structure and excellent resistance to hydrothermal treatment at high temperatures. On the basis of the XRD and Raman results, the formation of a CeO$_2$–ZrO$_2$ solid solution might effectively stabilize the cubic structure and significantly enhance the structural homogeneity of the CZW catalyst.

### 2.6. XPS analysis

To further gain a better understanding of the chemical state of all elements on the catalysts’ surfaces, the surface atomic concentrations and valence states of elements in the CZW catalysts were investigated by XPS. The surface atomic concentrations of Ce, Zr, W, and O were measured and are shown in Table 1. The CZW catalyst had the highest relative surface concentration of Ce atoms (44.51%). The surface concentration of Ce atoms was dramatically decreased on the surface of aged CZW catalysts. However, the concentrations of Zr and W atoms were increased after hydrothermal aging treatment. This indicated that hydrothermal treatment led to the agglomeration of CZW particles, which was consistent with the results of XRD.

The chemical states of elements could be identified from the XPS results. Fig. 6 shows the spectra of the Ce 3p region for CZW catalysts. 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 (Gao et al., 2010). The bands labeled u’ and v’ were assigned to the electronic state corresponding to Ce$^{3+}$, while the peaks labeled u, u”, v, v” and v‴ represented Ce$^{4+}$ ions. For the aged CZW catalysts, the Ce 3d binding energies all shifted to higher values.

### Table 1 – Surface atomic concentration of the CZW catalysts by the XPS results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface atomic concentration (at.%)</th>
<th>Ce</th>
<th>Zr</th>
<th>W</th>
<th>O</th>
<th>Ce$^{3+}$/Ce$^{4+}+Ce^{3+}$</th>
<th>O$<em>{\alpha}$(O$</em>{\alpha}$+O$_{\beta}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZW</td>
<td></td>
<td>44.51</td>
<td>4.49</td>
<td>1.54</td>
<td>49.46</td>
<td>14.8</td>
<td>30.5</td>
</tr>
<tr>
<td>CZW-6-8</td>
<td></td>
<td>25.34</td>
<td>15.20</td>
<td>5.5</td>
<td>53.96</td>
<td>15.8</td>
<td>27.2</td>
</tr>
<tr>
<td>CZW-7-8</td>
<td></td>
<td>21.52</td>
<td>14.54</td>
<td>6.26</td>
<td>57.68</td>
<td>16.4</td>
<td>24.2</td>
</tr>
<tr>
<td>CZW-8-8</td>
<td></td>
<td>22.34</td>
<td>11.46</td>
<td>5.72</td>
<td>60.47</td>
<td>18.4</td>
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</tr>
<tr>
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<td>15.43</td>
<td>6.99</td>
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<td>18.2</td>
<td>18.1</td>
</tr>
<tr>
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<td></td>
<td>31.20</td>
<td>7.29</td>
<td>5.90</td>
<td>55.61</td>
<td>14.2</td>
<td>25.3</td>
</tr>
</tbody>
</table>

CZW-m-n refers to CZW catalysts aged at m × 100°C in the presence of 10 vol.% H$_2$O for n hr. O$_{\alpha}$: chemisorbed oxygen; O$_{\beta}$: lattice oxygen; XPS: X-ray photoelectron spectrum; CZW: CeO$_2$–ZrO$_2$–WO$_3$. 

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**Fig. 5** – Raman spectra of (a) fresh and aged CZW catalysts and (b) CZW catalysts aged for different hydrothermal aging times. CZW: CeO$_2$–ZrO$_2$–WO$_3$. 

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indicated that the hydrothermal treatment procedure led to interactions effect between Ce, Zr, and W oxides. This result was also consistent with the Ce 3d peaks of ceria-zirconia (Ricote et al., 2006). The phenomena demonstrated that the aged CZW samples maintained the CeO₂–ZrO₂ solid solution under the hydrothermal treatment. Compared with the fresh CZW catalyst, it was obvious that the relative peak intensity of the Ce 3d peaks dramatically decreased after hydrothermal treatment. The relative content of Ce^{3+}/(Ce^{3+}+Ce^{4+}) over various catalysts is listed in Table 1. It can be seen that the percent of Ce^{3+} was increased with an increase in hydrothermal aging temperature. This result was consistent with the results from the H₂-TPR analysis discussed below.

The photoelectron spectra obtained from the fresh and aged samples in the O 1 s region are shown in Fig. 6. The oxygen in the catalysts could be categorized into two types of species: lattice oxygen (529.2–530.3 eV, denoted as O_β) and chemisorbed oxygen (531.3–532.3 eV, denoted as O_α) (Li et al., 2011). It had been reported that the chemisorbed oxygen (O_α) could be regarded as the most active oxygen, which was associated with a significant improvement in oxidation reactions, and a high ratio of O_α/(O_α+O_β) on the catalyst surface was closely correlated with excellent SCR activity (Liu et al., 2013). With an increase in the aging temperature, the O_α/(O_α+O_β) ratio varied as follows: CZW > CZW-6-8 > CZW-7-96 > CZW-7-8 > CZW-8-8 > CZW-9-8. This trend was consistent with the NH₃-SCR activity over the whole temperature range. Meanwhile, this could confirm that a low concentration of surface chemisorbed oxygen resulted in a less reactive oxidation process, which would decrease the low-temperature activity (below 275°C). Furthermore, the binding energy (BE) of O_α peaks tended to shift towards higher BE (approximately 0.5–1.3 eV) over aged CZW catalysts. This shift was related to the partial conversion of Ce^{4+} into Ce^{3+} species.

The Zr 3d binding energies of the CZW catalysts are exhibited in Fig. 6. The Zr 3d spectra showed a doublet corresponding to Zr 3d⁵/₂ at ~184.4 eV and Zr 3d₃/₂ at ~182.1 eV, which was assigned to quadrivalent zirconium (Picasso et al., 2007). As for aged CZW samples, the intensity of Zr 3d peaks increased with an increase in aging temperature. This implied that the sintering of zirconium occurred during the aging process, resulting in the formation of more oxidized zirconium species. It is worth noting that the Zr 3d intensity of CZW-7-96 became much weaker than that of CZW-7-8, indicating that the aging of the CZW catalyst at 700°C for a long time was beneficial to the dispersion of Zr species. Furthermore, a shift of these peaks to higher BE values was found, which was associated with the formation of Zr(IV) species bound to more electron attractive species, as reported in the literature (Younes et al., 2003).

2.7. Redox property analysis

The reducibility of catalysts was investigated by H₂-TPR experiments. Fig. 7 exhibited the H₂-TPR profiles of the CZW samples. Roh et al. (2001) reported that no reduction peak could be observed over pure ZrO₂ below 900°C. The reduction peaks of the surface oxygen species (Ce⁴⁺–O–Ce⁴⁺) and the bulk oxygen species (Ce³⁺–O–Ce⁴⁺) of pure ceria were centered at 509 and 812°C, respectively (Damyanova et al., 2002). From Fig. 7a, a reduction peak was observed centered at 700°C over the CZW, CZW-6-8, and CZW-7-8 samples, which might be attributed to the stronger interaction between CeO₂ and ZrO₂. As for CZW-8-8 and CZW-9-8 catalysts, two reduction peaks were clearly observed. The other peaks appearing at high temperature were assigned to the reduction of Ce³⁺–O–Ce⁴⁺. Furthermore, with an increase in hydrothermal aging temperature from 600 to 900°C, the intensity of the reduction peak of Ce⁴⁺–O–Ce⁴⁺ species decreased, while that of Ce³⁺–O–Ce⁴⁺ species bound to more electron attractive species, as reported in the literature (Younes et al., 2003).
species increased. This proved that much more bulk ceria in
the form of bigger crystals existed for the aged CZW samples
at high temperature, which contributed to the disappearance
of surface oxygen species. In addition, the peak of fresh CZW
was broader and more intense than that of aged samples. This
confirmed that the number of surface oxygen species dra-
matically decreased after the hydrothermal treatment at high
temperature. The phenomenon was in accord with the results
of XPS. Furthermore, the onset reduction temperature in CZW-
7-8 was the lowest among the CZW samples, suggesting that
hydrothermal treatment at 700°C was beneficial to redox ability.
Therefore, the relationship between redox ability and hydro-
thermal aging time at 700°C was investigated (Fig. 7b). It could
be noted that the onset and maximum temperatures for the
reduction peaks showed no significant changes. As the hydro-
thermal aging time went up, the intensity of peak in the
CZW-8-8 became slightly broader than the other samples.
These results demonstrated that the CZW catalysts possessed
excellent redox properties and high hydrothermal stability.

2.8. Py-IR analysis

During operation of diesel engines, SCR-DeNO\textsubscript{x}
catalysts have been found to be gradually deactivated and even completely
deactivated due to masking of the acid sites (Lin et al., 2007).
Herein, the pyridine adsorption infrared spectra of different
CZW were measured to investigate the surface acidity for the
hydrothermally aged catalysts after vacuum treatment at room
temperature and 200°C, respectively. As shown in Fig. 8, IR bands
at 1440 and 1490 cm\textsuperscript{-1} were respectively assigned to the
adsorption of pyridine coordinated on Lewis (L) acid sites and
Brönsted (B) acid sites (Zhang et al., 2008, 2009). At room
temperature, the intensity of L acid sites decreased with an
increase in hydrothermal aging temperature. Furthermore, both
bands dramatically changed as temperature rose to 200°C. From
Fig. 8b, it is apparent that the B acid site (1540 cm\textsuperscript{-1}) appeared on
the CZW sample. In addition, the intensity of the L acid sites
band was much weaker than that in Fig. 8a, and the peak even
disappeared for CZW-8-8 and CZW-9-8. However, no obvious

Fig. 7 – H\textsubscript{2}-TPR profiles of (a) the fresh and aged CZW catalysts and (b) CZW catalysts aged for different hydrothermal aging
time. H\textsubscript{2}-TPR: temperature-programmed reduction with hydrogen; CZW: CeO\textsubscript{2}–ZrO\textsubscript{2}–WO\textsubscript{3}.

Fig. 8 – Py-IR (infrared spectroscopy of adsorbed pyridine) spectra of CZW catalysts degassed at (a) room temperature and (b)
200°C. CZW: CeO\textsubscript{2}–ZrO\textsubscript{2}–WO\textsubscript{3}.
changes were observed with an increase in hydrothermal aging time. These indicated that the acid strength of the L and B sites was weak and medium respectively, but the weak L acid sites were dominant. In addition, the hydrothermal temperature significantly affected the amount and type of acid sites, but the hydrothermal time had little influence on the acidity. It was reported that the amounts of L and B acid sites were closely related to NO\textsubscript{x} conversion (Ma et al., 2012). In other words, the increase of the number of weak and medium acid sites improved the reactivity of CZW catalysts for the adsorption of ammonia, which was beneficial to ammonia oxidation, and then led to excellent catalytic activity in the NH\textsubscript{3}-SCR reaction, especially low-temperature activity. This was consistent with the activity results.

3. Conclusions

In summary, the CZW catalyst exhibited high performance and superior hydrothermal stability at high temperature. The catalytic activity results revealed that the CZW catalyst hydrothermally aged at 700°C in the presence of 10% H\textsubscript{2}O showed over 90% NO\textsubscript{x} conversion (Ma et al., 2012). In other words, the increase of weak and medium acid sites improved the reactivity of CZW catalysts for the adsorption of ammonia, which was beneficial to ammonia oxidation, and then led to excellent catalytic activity in the NH\textsubscript{3}-SCR reaction, especially low-temperature activity. This was consistent with the activity results.

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