Significant Improvement of Thermal Stability for CeZrPrNd Oxides Simply by Supercritical CO$_2$ Drying

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Abstract

Pr and Nd co-doped Ce-Zr oxide solid solutions (CZPN) were prepared using co-precipitation and microemulsion methods. It is found that only using supercritical CO$_2$ drying can result in a significant improvement of specific surface area and oxygen storage capacity at lower temperatures for CZPN after aging at 1000°C for 12 h in comparison with those using conventional air drying and even supercritical ethanol drying. Furthermore, the cubic structure was obtained in spite of the fact that the atomic ratio of Ce/(Ce+Zr+Pr+Nd) is as low as 29%. The high thermal stability can be attributed to the loosely aggregated morphology and the resultant Ce enrichment on the nanoparticle surface, which are caused by supercritical CO$_2$ drying due to the elimination of surface tension effects on the gas-liquid interface.

Introduction

Cerium dioxide (CeO$_2$) is an indispensable oxygen storage capacity (OSC) material in three-way catalysts (TWCs), which work close to stoichiometric conditions so as to eliminate simultaneously CO, NO$_x$, and hydrocarbons contained in automotive exhausts [1]. This is due to the ability of CeO$_2$ to store and release oxygen under lean and rich conditions respectively, according to the unique redox behavior between Ce$^{4+}$ and Ce$^{3+}$. However, the increasingly stringent standards for the automotive emissions have set new challenges for the development of more thermally stable oxygen storage materials which can withstand temperatures at or above 1000°C for long periods of time [2]. The current TWCs are based on Ce-Zr oxide solid solutions (CZ) [3]. Generally, two strategies were adopted to improve the thermal stability of CZ. One approach is doping with other metal ions into the ceria lattice. Therein, Al [4] and Pr/Nd [5] are mostly used. The composite oxides of Al$_2$O$_3$ and CZ in intervening layers on a nanometer scale show higher surface area and OSC after heat treatment at 1000°C due to the role of so-called “diffusion barrier” of Al$_2$O$_3$; however, the presence of bulk alumina and/or CeAlO$_3$, which are deleterious to the OSC, was generally concomitant [2]. Comparatively, the doping of Pr or Nd causes the lattice deformation of the tetragonal Zr-rich mixed oxides to form a pseudocubic structure and prevents the phase segregation after calcinations at 1050°C for 5 h [5]. In view of these facts, it is preferred that the CZ is first doped with Pr/Nd and then suspended with Al$_2$O$_3$, and finally washcoated on the honeycomb.

The other approach to improve thermal stability of CZ is changing preparation methods, which include co-precipitation, sol–gel, solution combustion, surfactant-assisted and microemulsion [6]. However, the drying method used to remove solvents of the wet precipitates, which would affect many important powder properties, for example, the homogeneity, the size of the agglomerates/aggregates and the extent of agglomeration/aggregation, is scarcely studied. Often this process is carried out conventionally in air/vacuum, which results in particle agglomerates by the capillary attraction because of the existence of the liquid to vapor phase transformation of the solvent. To solve this problem, supercritical ethanol drying technology was reported for the preparation of La-doped CZ, which shows better thermal stability [higher surface areas and larger OSCs] in comparison with the conventional drying techniques [7,8]. The authors attributed this to the elimination of vapor–liquid interface in the process of supercritical drying. However, the following questions still exist: (1) drastic conditions are required (critical point of ethanol: 243°C, 6.3 MPa). The same case applies to using supercritical water [9,10]; (2) the structure is tetragonal (The molar ratio of Ce/Zr equals to 1/4). It is well known that preserving the cubic c phase is beneficial for the OSCs and catalytic activity, while the appearance of the tetragonal t phase is detrimental [11,12]. Looking for milder reaction conditions, supercritical CO$_2$ can be used as an alternative due to its easily accessible critical point (31°C, 7.4 MPa) and nontoxic, nonflammable, inexpensive and recyclable nature. Indeed, a lot of materials including CeO$_2$ [13], CeO$_2$–Al$_2$O$_3$ [14] and ZrO$_2$ [15–17] have been prepared using the supercritical CO$_2$ process. Unfortunately, the only paper concerning CZ prepared by supercritical CO$_2$ drying reported the experimental temperature and pressure are 455°C and 19.5 MPa, respectively [18]. It is unimaginable that the temperature is so much higher than the critical point of CO$_2$.

The improvement of thermal stability is reflected in high surface areas and high porosity at high temperatures, which are desired...
for practical applications taking into consideration the potential kinetic advantages. In this paper, Pr and Nd co-doped CZ (CZPN) was prepared using co-precipitation (CO) and microemulsion (ME) methods followed by drying at 100°C in air, and co-precipitation followed by supercritical CO₂ drying (CO–SC) and microemulsion followed by supercritical CO₂ drying (ME–SC) (50°C, 15 MPa). Surprisingly, after aging at 1000°C for 12 h, the significant improvement of surface areas and OSCs at lower temperatures were obtained for both SC samples in comparison with those using supercritical ethanol and conventional drying. Furthermore, the cubic structure was obtained in spite of the fact that the atomic ratio of Ce/(Ce + Zr + Pr + Nd) is as low as 29% in CZPN (The actual contents of Ce, Zr, Pr and Nd were determined by X-ray fluorescence spectrometry (XRF) and are given in Table 1, nearly in accordance with the nominal values, suggesting that the drying method cannot change the compositions). The schematic representation of the general synthesis steps to produce thermally stable CZPN is shown in Figure 1.

Materials and Methods

Synthesis

CZPN mixed oxides were prepared by co-precipitation (CO), microemulsion (ME), co-precipitation followed by supercritical CO₂ (CO–SC) and microemulsion followed by supercritical CO₂ (ME–SC). In the as-prepared samples, the atom ratios of Ce, Pr and Nd to Zr are 0.51, 0.12 and 0.12, respectively. In the CO synthesis, NH₃·H₂O (25%) and H₂O₂ were dropped into a stoichiometric solution (0.2 mol/L) of Ce(NO₃)₃·6H₂O, Zr(NO₃)₄·3H₂O, Pr(NO₃)₃·6H₂O and Nd(NO₃)₃·6H₂O under vigorous agitation and then the resultant precipitate was aged in air for 24 h at room temperature and pressure. After filtration, the aerogels were dried at 100°C overnight and calcined at 1000°C for 12 h in air. In the ME synthesis [19], the microemulsion (I) of Ce(NO₃)₃·6H₂O, Zr(NO₃)₄·3H₂O, Pr(NO₃)₃·6H₂O and Nd(NO₃)₃·6H₂O, polyethylene glycol octylphenyl ether (as surfactant), cyclohexane (as oil phase) and 1-hexanol (as cosurfactant) was prepared; the microemulsion (II) of ammonia, polyethylene glycol octylphenyl ether, cyclohexane, 1-hexanol and hydrogen peroxide (as oxidant) was prepared; the reverse microemulsion (I) was mixed with (II) to react. The aerogels were filtered, washed and dried overnight at 100°C and calcined at 1000°C for 12 h in air. In the SC processes, water in the aerogels was first exchanged with anhydrous ethanol. Then the cake was loaded in a stainless-steel reactor to supercritical CO₂ drying (15 MPa at 30°C in order to insure the homogenous phase of CO₂ and ethanol and thus eliminate the gas-liquid interface [20]) and maintained under flow for 5 h. After that, the pressure was slowly released. Finally, the aerogels were calcined at 1000°C for 12 h in air.

Characterization

The elemental compositions were measured by XRF (ARL–9800, Switzerland). X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max–2500/PC diffractometer employing Cu Kα radiation (l = 1.5418 Å) operating at 50 kV and 200 mA. A Le Bail method was used for the profile fitting of the XRD patterns. Raman spectra were measured using a Raman spectroscope (HR800) with a CCD camera. The 632.8 nm line of a He–Ne laser was used to simulate the Raman spectra. The measurements were carried out with a microscope by using a

Table 1. Textural properties and compositions.

| Samples | BET surface area (m²/g) | Pore volume (cm³/g) | Average pore diameter (nm) | Unit cell parameter (Å) | Unit cell volume (Å³) | Crystallite size (nm) | Ce/Zr/Pr/Nd (molar) |
|---------|------------------------|--------------------|---------------------------|------------------------|-----------------------|----------------------|---------------------|
| CO      | 9.71 (9.71)             | 0.025 (naught)     | 9.5                       | 5.273(3)               | 146.72(1)            | 9.53                 | 26.3/59.9/7.3/6.5  |
| CO–SC   | 52.4 (47.7)             | 0.379 (0.0022)     | 25.5                      | 5.274(2)               | 146.72(1)            | 8.43                 | 33.4/48.1/9.1/0.9  |
| ME      | 29.4 (27.4)             | 0.135 (0.0008)     | 15.3                      | 5.272(1)               | 146.56(7)            | 12.17                | 27.9/58.0/7.4/6.7  |
| ME–SC   | 63.3 (56.3)             | 0.479 (0.0032)     | 26.5                      | 5.272(1)               | 146.51(8)            | 8.57                 | 33.4/51.6/7.9/7.1  |

| Samples | at-plot external surface area; | bt-plot micropore volume; | Calculated standard deviations from Le Ball fitting are given in parentheses. |

Figure 1. The schematic representation of the synthesis steps to produce thermally stable CZPN. doi:10.1371/journal.pone.0088236.g001

Figure 2. XRD patterns of CO, CO–SC, ME and ME–SC. doi:10.1371/journal.pone.0088236.g002
×50 objective lens (focus diameter larger than 1 micron) and the data are recorded in a backscattering geometry. The Brunauer–Emmett–Teller (BET) surface area and pore structure were measured by N2 adsorption/desorption using a Micromeritics 2020M instrument. Before N2 physisorption, the sample was outgassed at 300°C for 5 h. Field-emission scanning electron microscopy (FESEM) was conducted on a JEOL SU70. Transmission electron microscopy (TEM) equipped with selective area electron diffraction (SAED) was conducted on a JEOL JEM–2010 microscope at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) data were obtained on an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al Kα radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charge effects, the binding energies were calibrated using the C 1s hydrocarbon peak at 284.80 eV.

Performance Studies

Temperature-programmed reduction with H2 (H2–TPR) experiments were performed in a quartz reactor with a thermal conductivity detector (TCD) to monitor the H2 consumed. A 50 mg sample was pretreated in situ at 500°C for 1 h in a flow of O2 and cooled to room temperature in the presence of O2. TPR was conducted at 10°C/min up to 900°C in a 30 mL/min flow of 5 vol.% H2 in N2. After the first cycle, the sample was cooled to room temperature in the H2/N2 mixture. The sample was then reoxidized at 500°C for 1 h in O2 and cooled to room temperature in O2, and then a second TPR run was conducted. Similar consecutive TPR runs were carried out three times. To quantify the total amount of H2 consumed, CuO was used as a calibration reference. The total OSC was measured at low temperatures (200°C) and high temperatures (700°C). In respect of the former, the 50 mg sample was first reduced at 550°C in 5 vol.% H2 in N2 flow for 40 min. After cooling down to 200°C in He flow, the high-purity O2 pluses were injected up to the breakthrough point and the O2 consumption was measured. As to the latter, the H2 consumption was measured. The 50 mg sample was first oxidized at 500°C in O2 flow for 30 min. After heating up to 700°C in He flow, the high-purity H2 pluses were injected up to the breakthrough point.

Results and Discussion

Although the atomic ratio of Ce/(Ce+Zr+Pr+Nd) equals 29%, the XRD patterns of all CZPN samples (Figure 2) show a cubic fluorite structure and no peak splitting that would indicate the presence of two phases could be detected. The peaks are symmetrical, suggesting sample homogeneity. Single-phase and homogeneous materials are preferred to phase-segregated ones (for example CZ–0.75 in Figure S1) since it is believed that this results in better thermal stability and redox properties [2]. The unit cell parameters (a) derived from Le Bail fitting of XRD (Table 1, Figure S2 and Table S1) is nearly the same, in agreement with the formation of a solid solution. However, the crystallite sizes calculated according to Scherrer equation for SC samples are lower than those using conventional drying. This suggests that
supercritical CO$_2$ prevents particle agglomeration and coarsening. A smaller particle size increases the solubility of zirconia in cubic ceria, which is beneficial to the OSC [21]. Moreover, the grain size influences the defect formation energy, and in particular the concentration of oxygen vacancies. That is, the smaller the grain size, the more the oxygen vacancy and the oxygen release ability [5].

The phase composition was further investigated by Raman spectroscopy (Figure 3). The band observed at $\sim$463 cm$^{-1}$ can be assigned to the symmetric breathing mode of the O atoms around each Ce$^{4+}$ because that is the only allowed Raman mode with F$_{2g}$ symmetry in metal oxides with a fluorite structure [22]. The peaks become broader for ME and ME–SC, which can be explained by serious lattice distortions due to the incorporation of Pr, Nd and Zr into cubic CeO$_2$ (c phase) [22]. However, the coexistence of the 463 cm$^{-1}$ peak coupled with a peak at $\sim$300 cm$^{-1}$ suggests the presence of pseudocubic phase ($\epsilon'$ which contains c and $\ell'$) for CO and CO–SC [21]. The $\ell'$ phase is a tetragonal metastable phase; however, it does not show any tetragonality (the axial ratio equals to 1) and thus is indistinguishable by XRD from the c phase [11]. Based on Raman spectra, it can be concluded that a more homogeneous structure was obtained in ME and ME–SC in comparison with CO and CO–SC. In addition, the peak at $\sim$594 cm$^{-1}$ is characteristic of oxygen vacancies in the cubic lattice [22], which is generated by incorporation of hetero atoms.

For TWC application, besides the homogeneity of the mixed oxide, textural stability is fairly important. Pr and Nd co-doping did improve the BET surface area (Table 1 and Table S2). Furthermore, the BET surface areas and pore volumes for SC samples are much larger than those using conventional drying.

Figure 5. SEM images (a); TEM and HRTEM images (b) as well as the corresponding SAED patterns (insets) for CO, CO–SC, ME and ME–SC. doi:10.1371/journal.pone.0088236.g005
(Table 1) and supercritical ethanol drying (Figure S3 and Table S2). In the case of CO samples, the surface area of CO–SC is 5.4 times as large as that of CO, while the pore volume is 15.2 times as large as that of CO. As for ME samples, the surface area and pore volume for ME–SC are 2.2 and 3.5 times as large as those of ME, respectively.

The negligible pore for CO (Table 1 and Figure 4) suggests the complete sintering by high-temperature aging. The adsorption-desorption isotherms of ME (Figure 4a) show type IV isotherm (IUPAC classification) with type H1 hysteresis loop, which is associated with pores known to consist of agglomerates, and hence narrow pore distributions and smaller pore sizes were formed (Figure 4b). The isotherms of CO–SC and ME–SC (Figure 4a) comply with type II with a type H3 hysteresis loop in the relative pressure (p/p0) range of 0.8–1.0, which is observed with aggregates of plate-like particles giving rise to slit-shaped pores [23]. This corresponds to a shift in the pore size distribution to higher pore diameters and the presence of macropores (>50 nm). As shown in Figure 4b, there were two pore size distributions: one small peak centered at 2.4 nm and one strong and broad peak centered at about 50 nm. In addition, the t-plot micropore volumes for SC samples are much larger than those of CO and ME though the values are extremely low. All these facts confirm the more loose texture for the SC samples due to the absence of surface tension in supercritical CO2, which is the reason for the wide pore size distribution and the increase in surface areas [24].

The morphology is first checked by FESEM (Figure 5a). The sintering and aggregation of primary particles were severe for CO and thus negligible pores were formed. In the case of ME, the situation is improved partially. The interstitial space among nanoparticles in the agglomeration constitutes mesopores. As expected in Figure 1, the loosely aggregated morphology was obtained for both CO–SC and ME–SC, which is attributed to the weak interaction between the oxide nanoparticles during the supercritical drying process [9,10]. The morphology observation is direct evidence of the loose aggregate structures for CO–SC and ME–SC.

The primary particles of CZPN around 10 nm can be distinguished by TEM images (Figure 5b), consistent with the XRD results (Table 1). The corresponding SAED patterns and high resolution TEM (HRTEM) reinforced the cubic structure. It is reported that the higher the surface area, the larger the number of surface sites the sample can provide, and thus the better the catalytic activities the sample will have. In this paper, H2–TPR and total OSCs were used to evaluate the performance.

As shown in Figure 6a, only one broad peak was observed for all CZPN samples. In contrast, CeO2 shows two peaks centered at about 500°C and 800°C, which can be assigned to the reduction of surface oxygen and lattice oxygen, respectively [25]. Furthermore, both CO–SC and ME–SC show lower peak temperatures and higher H2 consumption than CO and ME, respectively (Table 2). This is clearly demonstrated by the initial H2 consumption rate per gram of samples where reduction is less than 5% (Figure 6b) [26]. These facts suggest that the CZPN samples prepared by SC possess a higher redox property than those prepared by the conventional drying method. Furthermore, as shown in Figure S4 and Table S3, the cyclic TPR profile characteristics were almost reproducible, indicating that the oxidative-reductive reaction is reversible. The improved reducibility was displayed by the total OSC data (Table 2). The OSCs for CO–SC and ME–SC are higher than that for CO and ME, respectively. This improvement is remarkable especially at lower temperatures (200°C). From Table 2, it is also observed that the OSCs at 200°C and BET surface areas have the same tendency, suggesting that the redox activity is dependent on surface areas at lower temperatures, because the increase in surface area means increasing the amount of exposed coordinately structural oxygen ions at the surface. However, the OSCs at 700°C are not greatly different from one another, which show the same tendency with H2 consumed. This

Table 2. H2–TPR and total OSC results.

| Samples  | Peak Temperature (°C) | H2 consumed | 200°C | 700°C |
|----------|-----------------------|-------------|-------|-------|
| CO       | 603                   | 20.6 (1193.5) | 42.2 (122.2) | 236 (683.7) |
| CO–SC    | 588                   | 21.6 (1251.4) | 108.9 (315.5) | 245 (709.7) |
| ME       | 606                   | 23.4 (1355.7) | 75.3 (218.1)  | 273 (790.8) |
| ME–SC    | 586                   | 24.3 (1407.9) | 124.6 (360.9) | 295 (853.1) |

aμmol O2/g sample; b μmol O2/g CeO2.

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suggests that the H$_2$–TPR peak can be attributed to the reduction of lattice oxygen species, which may need to be reoxidized at higher temperatures [27].

According to XPS compositional analysis (Table 3 and Figure S5), it is deduced that the SC process may bring about Ce enrichment, high adsorbed oxygen (O$_1$ and O$_2$) and Ce$_{5+}$/Ce percentage on the surface, which is attributed to the high dispersion of nanoparticles. This should be another reason why the SC samples possess higher OSCs at lower temperatures in comparison with those using conventional drying method in air, because it is testified that only the Ce$_{3+}$/Ce$_{4+}$ plays the role of active redox couple in the Pr-doped CeZr (Ounce totally reduced, Pr$_{3+}$ is difficult to be reoxidized [28]) and Nd-doped CeZr (Nd is a trivalent cation [29]) samples. As confirmed by XPS (Figure S5), both Pr and Nd are in the valence of +3.

In conclusion, the cubic Pr and Nd co-doped Ce–Zr oxide solid solutions were prepared by co-precipitation and microemulsion methods. The samples dried using supercritical CO$_2$ show the significant improvement of specific surface areas and OSCs at lower temperatures after aging at 1000°C for 12 h in comparison with those using conventional air drying and even supercritical ethanol drying. Supercritical CO$_2$ drying can result in the loose aggregated morphology due to the elimination of surface tension effects on the gas-liquid interface and the resultant Ce enrichment on the nanoparticle surfaces.

**Supporting Information**

**Figure S1 XRD pattern of CZe-0.75 (the molar ratio of Ce/Zr is 0.75) prepared by co-precipitation, conventional air drying and calcination at 1000°C for 12 h in air.**

**Table 3.** XPS analysis results.

| Sample  | Ce   | Zr   | Pr   | Nd   | O$_{1s}$ (%) | Ce$_{5+}$/Ce (%) |
|---------|------|------|------|------|--------------|-----------------|
| CO      | 27.65| 54.87| 7.98 | 9.49 | 22.45        | 47.36           |
| CO-SC   | 34.83| 41.57| 13.28| 10.32| 30.81        | 57.85           |
| ME      | 27.85| 52.86| 10.95| 8.33 | 24.44        | 52.55           |
| ME-SC   | 31.05| 47.79| 12.63| 8.45 | 30.34        | 57.09           |

*a*Adsorbed oxygen/(Adsorbed and lattice oxygen, Figure S5c). doi:10.1371/journal.pone.0088236.t003

**References**

1. Kaspar J, Fornasiero P, Graziani M (1999) Use of CeO$_2$-based oxides in the three-way catalysis. Catal Today 50: 285–298.
2. Kaspar J, Fornasiero P (2003) Nanostructured materials for advanced automotive de-pollution catalysts. J Solid State Chem 171: 19–29.
3. Sugiuira M (2003) Oxygen storage materials for automotive catalysts: ceria-zirconia solid solutions. Catal Surv Asia 7: 77–87.
4. Morikawa A, Suzuki T, Kanazawa T, Kikuta K, Suda A, et al. (2008) A new concept in high performance ceria-zirconia oxygen storage capacity material with Al$_2$O$_3$ as a diffusion barrier. Appl Catal B: Environ 78: 132–137.
5. Wu XD, Wu XD, Liang Q, Fan J, Wang D, et al. (2007) Structure and oxygen storage capacity of Pr/Nd doped CeO$_2$–ZrO$_2$ mixed oxides. Solid State Sci 9: 636–643.
6. Zhang ZL, Zhang XY, Mu ZG, Yu PF, Ni XZ, et al. (2007) Synthesis and catalytic properties of Ce$_{x}$Zr$_{1-x}$O$_2$ solid solutions in the oxidation of soluble organic fraction from diesel engines. Appl Catal B: Environ 76: 335–347.
7. Wang QY, Li GF, Zhao B, Zhou RX (2010) Synthesis of La modified ceria-zirconia solid solution by advanced supercritical ethanol drying technology and its application in Pt-only three-way catalyst. Appl Catal B: Environ 100: 516–528.
14. Chen J, Wang R, Zhang J, He F, Han S (2005) Effects of preparation methods on properties of Ni/CeO$_2$–Al$_2$O$_3$ catalysts for methane reforming with carbon dioxide. J Mol Catal A: Chem 235: 302–310.

15. Ward DA, Ko EI (1993) Synthesis and structural transformation of zirconia aerogels. Chem Mater 5: 936–969.

16. Sui R, Rikadhe AS, Charpentier PA (2006) Direct synthesis of zirconia aerogel nanoarchitecture in supercritical CO$_2$. Langmuir 22: 4390–4396.

17. Ye L, Qiu W, Li H, Zhao A, Cai T, et al. (2013) Preparation and characterization of ZrCO/C composite aerogels. J Sol-Gel Sci Technol 65: 130–139.

18. Gennari FC, Ramos AC, Condon A, Montini T, Bengio S, et al. (2011) Hydrogen interaction with Pt/Ce$_{0.8}$Zr$_{0.2}$O$_2$ nanocomposites prepared by microemulsion, coprecipitation and supercritical CO$_2$ treatment. Appl Catal A: Gen 398: 123–133.

19. Wang XH, Lu GZ, Guo Y, Xue YY, Jiang LZ, et al. (2007) Structure, thermal-stability and reducibility of Ni-doped Ce-Zr-O solid solution. Catal Today 126: 412–419.

20. Shimoyama Y, Ogata Y, Ishihara R, Iwai Y (2010) Drying processes for preparation of titania aerogel using supercritical carbon dioxide. Chem Eng Res Des 88: 1427–1431.

21. Zhang F, Chen CH, Hanson JC, Robinson RD, Herman IP, et al. (2006) Phases in ceria-zirconia binary oxide (1–x)CeO$_2$–xZrO$_2$ nanoparticles: The effect of particle size. J Am Ceram Soc 89: 1028–1036.

22. Zhang ZL, Han D, Wei SJ, Zhang YX (2010) Determination of active site densities and mechanisms for soot combustion with O$_2$ on Fe-doped CeO$_2$ mixed oxides. J Catal 276: 16–23.

23. Sing KSW, Everett DH, Haul RAW, Moscou L, Piretti RA, et al. (1985) Reporting physiosorption data for gas/solid systems with special reference to the determination of surface area and porosity. Pure Appl Chem 57: 603–619.

24. Wang QY, Zhao B, Li GF, Zhou RX (2010) Application of rare earth modified Zr-based ceria-zirconia solid solution in three-way catalyst for automotive emission control. Environ Sci Technol 44: 3870–3875.

25. Li P, Xin Y, Li Q, Wang ZP, Zhang ZL, et al. (2012) Ce-Ti amorphous oxides for selective catalytic reduction of NO with NH$_3$: confirmation of Ce–O–Ti active sites. Environ Sci Technol 46: 9600–9605.

26. Ye Q, Yan LN, Wang HP, Cheng SY, Wang D, et al. (2012) Enhanced catalytic performance of rare earth-doped Ca/H-Sep for the selective catalytic reduction of NO with C$_2$H$_4$. Appl Catal A: Gen 42: 49–56.

27. Kastner J, Monte RD, Fornasiero P, Graziani M, Bradshaw H, et al. (2001) Dependency of the oxygen storage capacity in ceria-zirconia solid solutions upon textural properties. Top Catal 16–17: 83–87.

28. Putna ES, Vohs JM, Gorte RJ, Graham GW (1998) An examination of praseodymia as an oxygen-storage component in three-way catalysts. Catal Lett 54: 17–21.

29. Yamazaki S, Matsui T, Ohshima T, Arita Y (2000) Defect structures in doped CeO$_2$ studied by using XAFS spectrometry. Solid State Ionics 136–137: 913–920.