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## Introduction

Vehicular engines operating under lean burn conditions are effective for fuel cost improvement and environmental protection. Under these excess oxygen conditions, however, the  $NO_x$  components cannot be efficiently removed by a traditional three-way catalyst, which is effective only under stoichiometric conditions. Developing new technologies to eliminate  $NO_x$  emission from lean-burn exhaust has, therefore, attracted much attention in environmental catalysis. One of the most promising technologies is  $NO_x$  storage reduction (NSR, also known as lean  $NO_x$  trap, LNT), which was first developed by Toyota Corporation in the 1990s.<sup>1–4</sup> Generally, NSR is an inherently transient operation in which the gases fed to the



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Pt/BaO/CeO<sub>2</sub> catalysts derived from CeO<sub>2</sub> nanomaterials with shapes of rods, cubes, and particles were investigated for NO<sub>v</sub> storage/reduction. Catalytic tests were performed in a transient flow reactor system. A series of characterization techniques including XRD, TEM, XPS, EXAFS, NO<sub>x</sub>-TPD, H<sub>2</sub>-TPR and in situ DRIFTS were conducted to investigate the electrical, chemical, and structural properties. The NO<sub>x</sub> storagereduction performance ranked by the  $CeO_2$  support was nanorods > nanoparticles > nanocubes. Amazingly, the CeO2-nanorod based NSR catalyst possessed a superior NOx storage capacity (NSC) of 913.8  $\mu$ mol NO<sub>x</sub> g<sub>cat</sub><sup>-1</sup> at 350 °C in the absence of H<sub>2</sub>O and CO<sub>2</sub>, which almost reached the theoretical value. Even under harsh lean-rich cycling conditions (90 s vs. 6 s) and a high GHSV of 360 000 h<sup>-1</sup>, the nanorodbased catalyst also showed the best reduction efficiency, affording ~ 99% NO<sub>x</sub> conversion levels from 200 °C to 400 °C under the conditions without H<sub>2</sub>O and CO<sub>2</sub>. The morphology of ceria has significant influences on the selectivity of ammonia, and on the H<sub>2</sub>O and CO<sub>2</sub> tolerance during the NSR process. For the first time, a close linear correlation was drawn between the NO<sub>x</sub> storage capacity and the amount of oxygen vacancies of NSR catalysts. Over the NSR catalysts, oxygen vacancies play a crucial role in anchoring Pt. Meanwhile, H<sub>2</sub>-TPR results showed that the number of active surface oxygen species trapped in oxygen vacancies was closely related to the NSC value. This suggests that the oxygen vacancies on the NSR surface govern the NO<sub>x</sub> storage capacity by creating efficient sites or channels for the formation of nitrate and its further transformation to Ba-based storage sites. These findings may be fundamental for designing ceria-based NSR catalysts with better performance.

> catalysts are periodically switched between fuel-lean and fuelrich streams. Under lean conditions, NO is oxidized to more active NO<sub>2</sub> followed by storage on the catalyst; under a subsequent fuel-rich atmosphere, the stored NO<sub>x</sub> is reduced and thus the active sites are released for the next cycle.<sup>4,5</sup> Storage periods of 1-2 min followed by rich phases of several seconds are typically used in real engines;<sup>3</sup> however, many studies on NSR catalysts have used long rich regeneration periods compared to those of real systems. Consequently, minimizing the duration of the rich phase without decreasing  $NO_x$  conversion is highly desired for avoiding excessive fuel consumption. In principle, a NSR catalyst should consist of three major components: (1) noble metals (Pt, Pd), for NO oxidation/reduction; (2) alkali metal or alkaline earth metal compounds (e.g. Ba), for NO<sub>x</sub> sorption; (3) a high-surface-area support (e.g.  $Al_2O_3$ ).<sup>3,6</sup>

> Ceria (CeO<sub>2</sub>) has been regarded as one of the most significant components in many catalytic systems due to its unique redox properties and high oxygen storage capacity (OSC), releasing/taking up oxygen through redox processes involving the Ce<sup>4+</sup>/Ce<sup>3+</sup> couple.<sup>7</sup> Moreover, several features of CeO<sub>2</sub> appear to be beneficial for NSR reactions: sustaining high metal dispersion, promoting the water-gas shift reaction and steam

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reforming reaction, and providing surface basicity to benefit the formation of carbonates.<sup>7-9</sup> With these in mind, CeO<sub>2</sub> has been used as either an additive or support, and its role varies according to research focus.<sup>10-21</sup> As for NSR catalysts containing BaO, Casapu et al.<sup>22</sup> found that ceria serving as a support significantly improved the NO<sub>x</sub> storage capacity (NSC), due to the high instability of BaCeO<sub>3</sub> in the presence of NO<sub>2</sub>/H<sub>2</sub>O or CO<sub>2</sub> at 300-500 °C. Compared with conventional Pt/BaO/Al<sub>2</sub>O<sub>3</sub> catalysts, a higher NO<sub>x</sub> storage capacity and better regeneration behaviour were also observed for Pt/ BaO/CeO<sub>2</sub> (or Pt/BaO/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) at low temperatures by Shi et al.,13 which was attributed to enhanced Pt dispersion and improved redox properties due to ceria introduction (or modification). It has also been found<sup>23</sup> that the addition of CeO<sub>2</sub> to Pt/Al<sub>2</sub>O<sub>3</sub> helped maintain metallic Pt dispersion on Al<sub>2</sub>O<sub>3</sub> and introduce more NO<sub>x</sub> adsorption sites, finally relating to the enhanced NSC. Indeed, the strong metal-support interaction (SMSI) between noble metals and ceria has been recognized as an important factor that affects both the microstructure and redox properties of ceria-based catalysts.7,24,25

The design and fabrication of catalytic materials with desired performance are key issues in heterogeneous catalysis. Recently, the structure-sensitive behaviour of nanosized ceria systems has attracted significant attention owing to their unique catalytic properties, and fruitful results have been achieved in catalytic applications such as CO oxidation,<sup>26-28</sup> water-gas shift reaction,<sup>29</sup> CO<sub>2</sub> reforming,<sup>30</sup> NO reduction<sup>31,32</sup> and ethanol reforming.33 Si et al.29 have found that gold supported on CeO<sub>2</sub> nanorods and nanopolyhedra exhibited higher activity for the water-gas shift reaction than that supported on nanocubes, due to the higher levels of defects in the former two. As for the preferential CO oxidation in H<sub>2</sub>rich gas, Yi et al.<sup>34</sup> confirmed that the catalytic activity of Au/ CeO<sub>2</sub> catalysts varied as a function of the CeO<sub>2</sub> nanomaterial support as follows: nanorods > nanopolyhedra > nanocubes. More recently, higher activity was achieved for  $MnO_x/$ ZrO<sub>2</sub>-CeO<sub>2</sub> in the selective catalytic reduction of NO by using ZrO<sub>2</sub>-CeO<sub>2</sub> nanorods as a support compared with that using nanocubes and nanopolyhedra.<sup>31</sup> Further results revealed by XPS, Raman, HRTEM, and kinetic measurements demonstrated that the excellent catalytic activity of the nanorod catalyst could be attributed to adsorbed surface oxygen and oxygen vacancies associated with ZrO<sub>2</sub>-CeO<sub>2</sub> nanorods' exposed (110) and (100) planes. The achievements mentioned above confirmed that the activity of CeO2-based catalysts is often shape-dependent, creating a guideline for designing catalysts with high efficiency, and also for revealing the structure-activity relationship.

To the best of our knowledge, however, there has been little information concerning the morphology effect of  $CeO_2$ nanomaterials on the activity of  $CeO_2$ -supported NSR catalysts under cyclic lean-rich conditions. To highlight this issue, herein, nanosized ceria with the shapes of rods, cubes, and particles was synthesized and used as a support for Pt/ BaO/CeO<sub>2</sub> catalysts. Catalytic tests were performed in a transient flow reactor system and a series of characterization techniques including XRD (powder X-ray diffraction), TEM (transmission electron microscopy), XPS (X-ray photoelectron spectra), EXAFS (extended X-ray absorption fine structure), NO<sub>x</sub>-TPD (NO<sub>x</sub> temperature programmed desorption), H<sub>2</sub>-TPR (H<sub>2</sub> temperature programmed reduction) and *in situ* DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) were conducted to investigate the electrical, chemical, and structural properties. Even under harsh lean-rich cycling operation (90 s *vs.* 6 s) and a high GHSV of 360 000 h<sup>-1</sup>, it was found that superior NO<sub>x</sub> storage-reduction performance was achieved on the CeO<sub>2</sub>-nanorod supported NSR catalyst, which was attributed to the higher numbers of oxygen vacancies in the exposed (110) and (100) planes of ceria.

## Experimental

#### **Catalyst preparation**

Preparation of different shaped CeO<sub>2</sub> nanomaterials. The CeO<sub>2</sub> nanorods and nanocubes were prepared by a hydrothermal method modified on the basis of previous studies.<sup>26,30,35</sup> Specifically, 6.9 mmol of cerium nitrate (AR grade, Tianjin Fuchen Chemical Reagent Factory, China) and specific amounts of NaOH (AR grade, Sinopharm Chemical Reagent Beijing Co., Ltd., China, 0.375 mol for nanorods, 0.75 mol for nanocubes) were dissolved in 30 ml and 50 ml of deionized water, respectively. Then the mixture was stirred for 60 min to obtain a purple slurry and subsequently transferred into a Teflon-lined stainless autoclave at a temperature of 100 °C and held for 12 h for nanorods (for nanocubes, this process was performed at 180 °C for 24 h). The fresh precipitates were thoroughly washed with deionized water and anhydrous ethanol (AR grade, Sinopharm Chemical Reagent Beijing Co., Ltd., China) to remove any possible ionic remnants. The solid obtained was dried at 60 °C in air for 24 h and calcined at 550 °C for 4 h in air.

The CeO<sub>2</sub> nanoparticles were prepared *via* a traditional precipitation method: 6.9 mmol of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was dissolved in 30 ml of deionized water, and then 50 ml of 0.01 mol L<sup>-1</sup> NaOH solution was dropped into the above solution with vigorous stirring. After 60 min of stirring, the mixture was transferred into a water bath kettle at 30 °C for 12 h. The fresh precipitates were washed with deionized water and anhydrous ethanol, dried at 60 °C in air for 24 h and calcined at 550 °C for 4 h in air.

Catalyst preparation. The NSR catalysts were synthesized by an impregnation method using nanosized CeO<sub>2</sub> materials as supports. First, the CeO<sub>2</sub> (nanoparticles, nanocubes, or nanorods) was impregnated in a Ba(CH<sub>3</sub>COO)<sub>2</sub> (AR grade, Sinopharm Chemical Reagent Beijing Co., Ltd., China) solution. After stirring for 60 min, the excess water was removed in a rotary evaporator at 50 °C. The samples were then dried at 120 °C overnight and calcined at 500 °C for 3 h in air. Subsequently, Pt was loaded on the surface of Ba/CeO<sub>2</sub> by the same procedure using PtCl<sub>4</sub> as a precursor. The catalysts prepared with CeO<sub>2</sub> nanoparticles, nanocubes, and nanorods are hereafter denoted as Pt/BaO/CeO<sub>2</sub>-NP, Pt/BaO/CeO<sub>2</sub>-NC, and Pt/BaO/CeO<sub>2</sub>-NR, respectively, with a nominal Ba loading of 8 wt% and a value of 1 wt% for Pt loading.

#### Characterization

Powder X-ray diffraction (XRD) patterns were measured on a PANalytical X'Pert PRO X-ray diffractometer (Netherlands, Cu  $K_{\alpha}$  as radiation source,  $\lambda = 0.154$  nm).

The specific surface areas of the catalysts were obtained at -196 °C over the whole range of relative pressures, using a Quantachrome Quadrasorb SI-MP. Prior to N<sub>2</sub> physisorption, the catalysts were degassed at 300 °C for 5 h. Specific surface areas were calculated from these isotherms by applying the BET equation in the 0.05-0.3 partial pressure range. The component contents of catalysts were analyzed using an inductively coupled plasma instrument (OPTMIA 2000DV) with a radial view of the plasma. All samples were dissolved using a strong acid solution before testing. Transmission electron microscopy (TEM) images with low magnification were obtained on a Hitachi H-7500 transmission electron microscope (Hitachi) with an acceleration voltage of 80 kV. Highresolution transmission electron microscopy (HR-TEM) images were obtained on a JEOL JEM 2010 TEM with 200 kV acceleration voltage. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDS) elemental mapping were performed on a probe Cs-corrected JEOL JEM-ARM 200 F operated at 200 kV.

X-ray photoelectron spectra (XPS) measurements were recorded in a scanning X-ray microprobe (PHI Quantera, ULVAC-PHI, Inc.) using Al  $K_{\alpha}$  radiation. Binding energies were calibrated using the C 1 s peak (BE = 284.8 eV) as standard.

Extended X-ray absorption fine structure (EXAFS) measurements were carried out on the XAFS station in 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF) operating at about 150 mA and 2.2 GeV. Data were analyzed using the program REX2000 (Rigaku Co.). The EXAFS oscillation  $\chi(k)$  was extracted using spline smoothing with a Cook-Sayers criterion,<sup>36</sup> and the filtered  $k^3$ -weighted  $\chi(k)$  was Fourier transformed into *R* space (*k* range: 3–12 Å<sup>-1</sup> for Pt-L<sub>III</sub> EXAFS). In the curve fitting step of Pt-L<sub>III</sub> EXAFS, the back-scattering amplitude and phase shift were calculated using FEFF8.4.<sup>37</sup>

NO<sub>x</sub> temperature programmed desorption (NO<sub>x</sub>-TPD) experiments were performed in a Micromeritics AutoChem II 2920 apparatus, equipped with a computer-controlled CryoCooler, a thermal conductivity detector (TCD), and a quadrupole mass spectrometer (MKS Cirrus). The samples were first pre-reduced with 10% H<sub>2</sub>/Ar at 450 °C for 30 min, and cooled down to room temperature. After purging with He for 30 min, the gas was switched to NO<sub>2</sub> adsorption for 60 min. After He flow for another 30 min, the temperature was increased to 900 °C at a heating rate of 10 °C min<sup>-1</sup>, and the signal of NO (m/z = 30) was recorded simultaneously. To

avoid the influence of  $H_2O$ , a cold trap was set before the MS detector.

 $H_2$  temperature programmed reduction ( $H_2$ -TPR) was performed in the same instrument as the NO<sub>x</sub>-TPD. The 100 mg samples were pretreated at 450 °C in a flow of air (50 mL min<sup>-1</sup>) for 30 min and cooled down to room temperature. Then reduction profiles were obtained by passing a flow of 10%  $H_2$ /Ar through the sample at a rate of 50 mL min<sup>-1</sup>, during which the temperature was increased from 50 to 950 °C at a ramp rate of 10 °C min<sup>-1</sup>.

In situ DRIFTS experiments were performed on an FTIR spectrometer (Nicolet Nexus 670) equipped with a smart collector and an MCT/A detector cooled with liquid nitrogen. Prior to each experiment, the sample was pretreated with 3%  $H_2/N_2$  at 450 °C for 1 h, and then cooled down to the specified temperature. A mixture containing 500 ppm NO and 8%  $O_2$  at a total flow rate of 300 mL min<sup>-1</sup> was employed to investigate the behavior of the NSR catalyst for NO<sub>x</sub> storage, while a stream of 3%  $H_2$  was used to measure the activity of ad-NO<sub>x</sub> over the Pt/Ba/CeO<sub>2</sub> catalyst. All spectra presented here were recorded by accumulating 30 scans with a resolution of 4 cm<sup>-1</sup>.

#### Catalytic activity measurements

NO<sub>x</sub> storage capacity experiment. NO<sub>x</sub> uptake experiments were carried out under fuel-lean conditions as a function of temperature. Before each experiment, the catalyst was pretreated in 3% H<sub>2</sub>/N<sub>2</sub> for 1 h at 450 °C, and then cooled to the desired temperature. A mixture of 500 ppm NO, 8% O<sub>2</sub>, 1% CO<sub>2</sub> (if used), and 2% H<sub>2</sub>O (if used) at a total flow rate of 300 mL min<sup>-1</sup> was used to simulate the fuel-lean exhaust, using N<sub>2</sub> as a balance gas. The outlet NO<sub>x</sub> (NO + NO<sub>2</sub>) concentration was monitored by a chemiluminescence detector (ECO Physics CLD 62). The outlet NH<sub>3</sub> was analyzed using a chemiluminescence detector (ECO Physics CLD 822).

Cyclic NO<sub>x</sub> storage reduction tests. NSR cyclic measurements were conducted with 100 mg of catalyst using a fixedbed quartz reactor. The reactor was connected to a pneumatically actuated four-way valve, which provides quick switching between the lean and rich atmospheres. Constant flows (300 mL min<sup>-1</sup>) of 500 ppm NO + 8% O<sub>2</sub> + 1% CO<sub>2</sub> (if used) + 2% H<sub>2</sub>O (if used) and 500 ppm NO + 3% H<sub>2</sub> + 1% CO<sub>2</sub> (if used) + 2% H<sub>2</sub>O (if used) were introduced alternately, during which a lean period of 90 s and a rich period of 6 s were performed between 200 °C and 400 °C. The NO<sub>x</sub> conversion was averaged over 20 lean/rich cycles to give a mean value according to the following formula:

NO<sub>x</sub> conversion(%) = 
$$\frac{\text{NO}_{x,\text{in}} - \text{NO}_{x,\text{out}}}{\text{NO}_{x,\text{in}}} \times 100\%.$$

The NH<sub>3</sub> selectivity was calculated by the following formula:

$$NH_3$$
 selectivity =  $\frac{NH_{3,out}}{NO_{x,in} - NO_{x,out}} \times 100\%$ .

## **Results and discussion**

#### Structural features of nanoceria and Pt/BaO/CeO2 catalysts

The morphology of CeO<sub>2</sub> nanomaterials and corresponding NSR catalysts was characterized by TEM and HRTEM (Fig. 1 and S1<sup>†</sup>). As shown in Fig. S1a,<sup>†</sup> the CeO<sub>2</sub> nanoparticles (denoted as CeO<sub>2</sub>-NP hereafter) displayed a mean diameter of around 9 nm. HRTEM images (Fig. 1a) further revealed that the CeO<sub>2</sub>-NP were dominated by (111) planes together with small amounts of (100) planes, exhibiting interplanar spacings of 0.31 and 0.27 nm, respectively. This feature indicates that CeO<sub>2</sub> nanoparticles were in the form of a truncated octahedron enclosed by eight (111) and six (100) planes, with the structural model presented in the insert of Fig. 1a.38,39 As shown in Fig. S1b,<sup>†</sup> the CeO<sub>2</sub> nanocubes (CeO<sub>2</sub>-NC), with an inhomogeneous grain size ranging from 10-50 nm, were mostly well-developed. Calculating for 200 nanocubes from the HRTEM images, the average size of ca. 0.27 nm was obtained. An interplanar spacing of 0.27 nm implies that the CeO<sub>2</sub> nanocubes are enclosed by six polar (100) planes, showing a cubic structure (Fig. 1b). The CeO<sub>2</sub> nanorods (CeO<sub>2</sub>-NR) had a mean diameter of 8.1 nm and a length from 40-110 nm (Fig. S1c<sup>†</sup>). Fig. 1c-d depicts the HRTEM image of CeO<sub>2</sub>-NR combined with a fast Fourier transform (FFT) analysis. According to the FFT analysis, three kinds of lattice fringe directions attributed to (111), (002), and (220) were observed for the nanorods, which have respective interplanar spacings of 0.31, 0.27, and 0.19 nm in the HRTEM image. The nanorods show a 1D growth structure with a preferred growth direction along [110], and are enclosed by (110) and (100) planes.



Fig. 1 HRTEM images of CeO<sub>2</sub>-NP (a), CeO<sub>2</sub>-NC (b), and CeO<sub>2</sub>-NR (c), FFT analysis of (c) (d); HAADF-STEM EDS elemental mapping images of Pt/BaO/CeO<sub>2</sub>-NP (e), Pt/BaO/CeO<sub>2</sub>-NC (f), and Pt/BaO/CeO<sub>2</sub>-NR (g).

After the deposition of Ba and Pt, it can be clearly seen from Fig. S1d-f<sup>†</sup> that the three different CeO<sub>2</sub> nanomaterials maintained their original crystal shapes, while no structural features of Pt and Ba can be observed. With this in mind, elemental maps were measured by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Fig. 1e–g), revealing that the active components of Pt and Ba were highly dispersed on all three NSR catalysts.

The specific surface areas of CeO<sub>2</sub> nanomaterials and corresponding NSR catalysts are listed in Table 1. Pure CeO<sub>2</sub> nanoparticles had the largest surface area (134.9 m<sup>2</sup> g<sup>-1</sup>), while the CeO<sub>2</sub> nanocubes gave the lowest value of 26.5 m<sup>2</sup> g<sup>-1</sup>. After deposition of Pt and BaO, the surface areas of Pt/BaO/CeO<sub>2</sub>-NP, Pt/BaO/CeO<sub>2</sub>-NR, and Pt/BaO/CeO<sub>2</sub>-NC decreased to 115.7, 84.2, and 20.0 m<sup>2</sup> g<sup>-1</sup>, respectively. The ICP-OES data (Table 1) showed that the contents of the active components had no significant difference among the NSR catalysts, all of which were close to the nominal values (1% Pt and 8% BaO).

The crystal structures of the different shaped samples were investigated by XRD and shown in Fig. 2. The diffraction peaks at 28.5, 33.0, 47.5, 56.3, 59.1, 69.4, 76.7, 79.1 and 88.4° could be ascribed to the fluorite structure of ceria (JCPDS no. 43-1002), while no peaks from Pt species were observed in any of the samples, indicating high dispersion and further confirming the results of the elemental maps. Using the Scherrer equation for the peak due to the (111) plane, the CeO<sub>2</sub> sizes of CeO<sub>2</sub> nanomaterials and corresponding NSR catalysts were calculated (Table 1), giving values in good agreement with the results of the HRTEM. In every Bacontaining sample, XRD analysis confirmed the decomposition of Ba(CH<sub>3</sub>COO)<sub>2</sub> into crystalline BaCO<sub>3</sub> (JCPDS no. 44-1487) during catalyst calcination, in agreement with previous results.<sup>13</sup>

#### **Catalytic performance**

 $NO_x$  storage performance. The  $NO_x$  breakthrough curves versus time of Pt/BaO/CeO2-NP, Pt/BaO/CeO2-NC and Pt/BaO/ CeO<sub>2</sub>-NR at different temperatures are recorded as shown in Fig. S2.† As soon as the lean feed was switched from the bypass loop to the catalysts, the  $NO_x$  concentration in the outlet dropped sharply from 500 ppm to 0 ppm, followed by a complete uptake process. With increasing time, the outlet NO<sub>x</sub> concentration gradually increased and a saturation state was achieved slowly by the end of 3600 s. The areas between the inlet feed and the breakthrough curves represent the NO<sub>x</sub> storage capacities (NSC), which were calculated and summarized in Fig. 3. It was apparent that Pt/BaO/CeO<sub>2</sub>-NR showed much larger NSC than Pt/BaO/CeO2-NP and Pt/BaO/CeO2-NC at all temperatures tested. Specifically, Pt/BaO/CeO2-NR presented the highest NO<sub>x</sub> storage capacity at 350 °C, affording about 913.8  $\mu$ mol g<sub>cat</sub><sup>-1</sup>, which approached the theoretical NO<sub>x</sub> storage capacity (937.4  $\mu$ mol g<sub>cat</sub><sup>-1</sup>, see the ESI†).

The oxidation of NO to  $NO_2$  is regarded as a key step in the NO trapping process, during which platinum plays a

Table 1	Specific surface area,	active component l	oading, and	I particle size (D)	) of CeO <sub>2</sub>	nanomaterials and P	t/BaO/CeO <sub>2</sub> sa	mples
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Catalyst	Surface area $(m^2 g^{-1})$	Pt loading (%)	BaO loading (%)	$D^{a}$ (nm)	$CeO_2$ size <sup>b</sup> (nm)
CeO <sub>2</sub> -NP	134.9	_	_	_	11.2
Pt/BaO/CeO2-NP	115.7	1.07	7.50	$8.8 \pm 2.4$	11.3
CeO <sub>2</sub> -NC	26.5	_		_	33.3
Pt/BaO/CeO2-NC	20.0	0.92	7.33	$26.9 \pm 13.7$	33.1
CeO <sub>2</sub> -NR	103.6	_	_	_	12.3
Pt/BaO/CeO <sub>2</sub> -NR	84.2	1.01	7.82	$(8.1 \pm 1.4) \times (40 - 110)$	12.2

<sup>*a*</sup> Caculated for 200 CeO<sub>2</sub> nanomaterials from the HRTEM images. <sup>*b*</sup> Caculated based on the CeO<sub>2</sub> diffraction peak at  $2\theta$  = 28.5° by applying the Scherrer equation.

significant role.<sup>40–42</sup> Fig. S3<sup>†</sup> compares the molecular ratio of NO<sub>2</sub>/(NO + NO<sub>2</sub>) over the series of Pt/BaO/CeO<sub>2</sub> catalysts at the end of the storage process, where the NO<sub>2</sub>/NO<sub>x</sub> ratio reached a steady state. For a given NSR catalyst, a gradually increased NO<sub>2</sub>/(NO + NO<sub>2</sub>) always relates to an increase in the NSC value within the temperature range of 200–350 °C, confirming the key role of NO oxidation.

The effects of CO<sub>2</sub> and H<sub>2</sub>O on the NO<sub>x</sub> storage process were investigated over all the NSR catalysts, with the results shown in Fig. S4.† Introducing of 1% CO<sub>2</sub> and 2% H<sub>2</sub>O into the feed gas decreased the NO<sub>x</sub> storage capacity, while the extent of NSC reduction was quite different among the tested NSR samples. Over Pt/BaO/CeO<sub>2</sub>-NP and Pt/BaO/CeO<sub>2</sub>-NC, drastic decreases in NSC values were observed within the whole temperature range if compared with those in the absence of H<sub>2</sub>O and CO<sub>2</sub>. In the presence of H<sub>2</sub>O and CO<sub>2</sub>, in contrast, Pt/BaO/CeO<sub>2</sub>-NR still presented a relatively high NO<sub>x</sub> storage capacity. At the temperature of 350 °C, Pt/BaO/ CeO<sub>2</sub>-NR afforded about 713.6 µmol NO g<sub>cat</sub><sup>-1</sup>, which is nearly 80% of that without H<sub>2</sub>O and CO<sub>2</sub>.

Dynamic  $NO_x$  storage and reduction performance. The  $NO_x$  removal efficiency is not only concerned with the storage capacity in the lean phase, but also related to the reduction of trapped  $NO_x$  during the rich phase. Minimizing the duration of the rich phase can improve the fuel efficiency, so a

rich regeneration time of several seconds is typically used in real systems.<sup>33</sup> However, many studies use a longer rich period compared to those of real engines. In this study, the  $NO_x$  removal efficiency was investigated under harsh cycling conditions, with a lean period of 90 s and a rich period of 6 s at a quite high gas hourly space velocity (GHSV) of 360 000  $h^{-1}$ .

Fig. 4a–c depicts the evolution of  $NO_x$  in the outlet feed over twenty lean/rich cycles for all NSR catalysts at temperatures between 200 and 400 °C. The averaged twenty-cycle NO<sub>x</sub> conversion values over Pt/BaO/CeO2-NP, Pt/BaO/CeO2-NC and Pt/BaO/CeO2-NR are compared in Fig. 4d. On Pt/BaO/CeO2-NR, it was easy to see that the outlet NO<sub>r</sub> breakthrough was close to 0 ppm during all the cycles performed at 200 °C and 400 °C. At other temperatures,  $NO_x$  spilled out still maintained relatively low values (10-60 ppm) at the end of the lean durations. This indicates that Pt/BaO/CeO2-NR possessed the highest catalytic performance, obtaining nearly 100% NO<sub>x</sub> conversion from 200 °C to 400 °C. Similarly, the NO<sub>x</sub> removal efficiency of Pt/BaO/CeO<sub>2</sub>-NP was quite high, reaching 93.5% at all temperatures. For the Pt/BaO/CeO2-NC catalyst, however, the outlet NO<sub>x</sub> breakthrough increased significantly (to 100 ppm at 200 °C) during the first cycle. And even worse, much more NOx spilled out and reached around 400 ppm after 5 cycles, presenting extremely low NO<sub>x</sub> removal.



Fig. 2 XRD patterns of  $\text{CeO}_2$  nanomaterials and  $\text{Pt/BaO/CeO}_2$  samples.



**Fig. 3** NO<sub>x</sub> storage capacities (NSC) tested at different temperatures over Pt/BaO/CeO<sub>2</sub> catalysts.



Fig. 4 Evolutions of  $NO_x$  concentrations under cyclic lean-rich conditions at different temperatures on Pt/BaO/CeO<sub>2</sub>-NP (a), Pt/BaO/CeO<sub>2</sub>-NC (b), and Pt/BaO/CeO<sub>2</sub>-NR (c); average NO<sub>x</sub> conversion over all NSR catalysts under cyclic lean-rich conditions at different temperatures (d).

Ammonia, as the main by-product of the NSR process, was also measured under cyclic lean-rich conditions, with the results shown in Fig. S5 and Table S1.<sup>†</sup> Obviously, the three NSR catalysts show quite different features of NH<sub>3</sub> release. Over Pt/BaO/CeO<sub>2</sub>-NP, the selectivity to NH<sub>3</sub> decreased monotonically with a rise in temperature, changing from 52.8% at 200 °C to 0.88% at 400 °C. In the whole temperature range, Pt/BaO/CeO<sub>2</sub>-NC exhibited much higher production of NH<sub>3</sub> than Pt/BaO/CeO<sub>2</sub>-NP, particularly at temperatures above 250 °C. Among the tested NSR catalysts, interestingly, Pt/BaO/ CeO<sub>2</sub>-NR shows the lowest NH<sub>3</sub> selectivity, exhibiting the lowest value of 0.74% at 300 °C and the highest one of 11.54% at 200 °C.

In the initial 2 lean/rich cycles (Fig. 4b), it is clear that the NO<sub>x</sub> conversion over Pt/BaO/CeO<sub>2</sub>-NC was well related to the NSC value. As cycles continued, however, the  $NO_x$  was not fully trapped under lean conditions, and was not further reduced during the rich phase. Such gradual deactivation with time on stream was more pronounced within the temperature range of 300-400 °C (Fig. 4b), which was also indicated by the average  $NO_x$  conversion over 20 lean/rich cycles (Fig. 4d). This result indicates that, in our case, the  $NO_x$  removal efficiency under a large scale is not only concerned with the storage capacity under lean conditions, but also related to the reduction efficiency for the trapped  $NO_x$  during the rich phase. Under rich conditions, the consumption of H<sub>2</sub> was involved in the reduction of released NO<sub>x</sub> and residual oxygen species on the catalyst surface. Because of a long lean period (90 s) and a short rich period (6 s), the residual oxygen on the surface would increase gradually with an increase in cyclic operation, reducing of which needs a greater amount of H<sub>2</sub> if compared with the initial several cycles.<sup>43</sup> As a result, the amount of  $H_2$  for the reduction of trapped  $NO_x$ decreased with time going on, leading to the partial regeneration of the storage sites in the rich phase and a decrease in NO<sub>x</sub> storage under lean conditions. A slightly decrease in NO<sub>x</sub> conversion was also observed on Pt/BaO/CeO<sub>2</sub>-NR and Pt/BaO/CeO2-NP during the lean-rich cycling operation, particularly at the temperature of 300 °C (Fig. 4). A further intensive study will be performed to reveal the temperature and sample shape dependency of the  $NO_x$  conversion over Pt/ BaO/CeO<sub>2</sub>.

The formation of ammonia and its reaction pathway for the NSR process have been intensively investigated by Courtois and co-workers.<sup>16,44</sup> Over Pt/BaO/Al<sub>2</sub>O<sub>3</sub>, it was proposed that the NH<sub>3</sub> formation rate *via* NO<sub>x</sub> reduction by H<sub>2</sub>, is higher that the NH<sub>3</sub> reaction rate with NO<sub>x</sub> to form N<sub>2</sub>, leading to NH<sub>3</sub> emission during the NSR process when H<sub>2</sub> is employed as a reductant.<sup>44</sup> When Pt/BaO/Al<sub>2</sub>O<sub>3</sub> is modified with an optimal amount of Ce, interestingly, the ammonia selectivity significantly decreased, attributed to the promotion of ammonia oxidation into N<sub>2</sub> *via* the available oxygen at the catalyst surface.<sup>16</sup> Among the three NSR catalysts, in our case, Ce XPS and H<sub>2</sub>-TPR results (in the following section) indicated that the greatest amount of surface active oxygen trapped by oxygen vacancies was available from Pt/BaO/CeO<sub>2</sub>- NR. Such active oxygen from ceria possibly enhances the ammonia oxidation to produce  $N_2$ . As a consequence, a low  $NH_3$ selectivity was achieved on Pt/BaO/CeO<sub>2</sub>-NR due to the high amount of active oxygen trapped by oxygen vacancies, in accordance with the results of previous studies.<sup>16,44</sup>

The influences of CO<sub>2</sub> and H<sub>2</sub>O on the NSR performance under lean-rich cycling operation were also evaluated, with the results shown in Fig. S6.<sup>†</sup> Similar to the NO<sub>x</sub> storage process, an inhibition effect of H<sub>2</sub>O and CO<sub>2</sub> on NO<sub>x</sub> conversion was also observed over all the samples. Among the tested NSR catalysts, Pt/BaO/CeO<sub>2</sub>-NR showed the highest NO<sub>x</sub> removal efficiency, exceeding 80% in the temperature range of 200–350 °C.

#### Thermal stabilities of the stored $NO_x$

The  $NO_x$  storage features and thermal stabilities of the  $NO_x$ stored on Pt/BaO/CeO2-NP, Pt/BaO/CeO2-NC and Pt/BaO/ CeO2-NR were compared by TPD experiments after NO2 adsorption at room temperature (Fig. 5). Because NO<sub>2</sub> is easily dissociated to the NO ionization fragment under our MS conditions, the signal of NO<sub>2</sub> (m/z = 46) in our experiment was very weak and the main signal was NO (m/z = 30).<sup>43</sup> Clearly, Pt/BaO/CeO<sub>2</sub>-NR showed the largest amount of desorbed NO, while the amount of desorbed NO of Pt/BaO/CeO2-NP was approximately the same as that of Pt/BaO/CeO<sub>2</sub>-NC. This was consistent with the NO<sub>x</sub> storage capacity as presented in Fig. 3. It is noteworthy that Pt/BaO/CeO2-NC exhibits the lowest amount of desorbed NO at temperatures below 350 °C, while the strongest peak is centered at much higher temperature than for the other two catalysts. This result clearly shows that the ad-NO<sub>x</sub> on Pt/BaO/CeO<sub>2</sub>-NC possesses high stability, benefiting for NO storage at high temperatures. As a result, a larger NSC value was obtained over this catalyst at a temperature of 400 °C (Fig. 3). On the other hand, the ad-NO<sub>x</sub> with high stability makes against its release under fuel-rich conditions, thus lowering NO<sub>x</sub> conversion over Pt/BaO/CeO<sub>2</sub>-NC (Fig. 4).



Fig. 5 NO<sub>x</sub>-TPD profiles of the NSR catalysts.

#### Chemical states and oxygen vacancies

XPS analysis was performed to verify the state of Pt and Ce on the surface of the NSR catalysts. Fig. S7<sup>†</sup> shows the Pt 4f XPS spectra of fresh Pt/BaO/CeO2 catalysts, and those reduced by H<sub>2</sub> (hereafter denoted as Pt/BaO/CeO<sub>2</sub>-R), considering that the samples were pre-treated by H<sub>2</sub> before activity measurement. The binding energies of the individual peaks of the Pt 4f spectra are summarized in Table S2.† According to previous studies,<sup>45,46</sup> the peaks at 72.5 (4f7/2) and 75.8 eV (4f5/2) should belong to PtO while those at 74.1 (4f7/2) and 77.5 eV (4f5/2) can be attributed to PtO2. It could be concluded that platinum on all the three NSR catalysts was present in the form of PtO and PtO2. In addition to the peaks belonging to PtO and PtO<sub>2</sub>, the H<sub>2</sub>-treated NSR catalysts also showed peaks at 71.0 (4f7/2) and 74.2 eV (4f5/2) corresponding to Pt<sup>0</sup>. Thus the reduced NSR catalysts contained metallic Pt and Pt oxides.

The EXAFS of Pt-L<sub>III</sub> edges were also measured over all the samples (Fig. S8<sup>†</sup>). The results of curve-fitting analysis of the EXAFS are summarized in Table S3.† In the Fourier transform spectrum of Pt foil, the peak at 2.77 Å is assigned to the Pt-Pt bond. As for the reference sample of PtO<sub>2</sub>, the peaks at 2.02 and 3.10 Å are assigned to the Pt-O and Pt-O-Pt bonds, respectively. Interestingly, only the intense peak at 2.00 Å corresponding to the Pt-O bond was observed over the fresh NSR catalysts. The formation of defined Pt-O-Ce bonds, as reported in the references,47,48 which may inhibit the sintering of Pt could not be observed in our Pt/BaO/CeO2 catalysts, in agreement with previous studies.49,50 Moreover, Pt-Pt or Pt-O-Pt peaks could not be observed in all the NSR catalysts, suggesting that there are no large Pt metal or oxide particles. In other words, highly dispersed Pt oxides were present on the surface of the CeO<sub>2</sub> supports, in agreement with the elemental mapping images. Generally, Pt<sup>0</sup> is considered to be the active site for the catalytic reaction. Therefore, the EXAFS of Pt-L<sub>III</sub> edges over the reduced NSR catalysts were also presented. After H<sub>2</sub> reduction at 450 °C, the Pt-O peak decreased significantly compared with the fresh catalysts. In addition, the Pt-Pt peak could be observed in the reduced catalysts. These results suggested that all of the Pt species were reduced from Pt4+ to Pt0 and Pt2+, further confirming the XPS results.

Fig. 6a–c shows the Ce 3d XPS spectra of the pure  $\text{CeO}_2$  nanomaterials and the NSR catalysts, together with the corresponding peak fitting results. The v', and u' peaks correspond to  $\text{Ce}^{3+}$ ; while v, v", v", u, u", and u" are contributed by  $\text{Ce}^{4+}$ .<sup>51–53</sup> The peak positions for all the samples are listed in Table S4.<sup>†</sup> The  $\text{Ce}^{3+}$  concentration in the  $\text{CeO}_2$  nanomaterials and corresponding NSR catalysts was calculated by analysis of the integrated peak area, with the equation shown as follows:

$$\left[\operatorname{Ce}^{3+}\right] = \frac{A_{v'} + A_{u'}}{A_{v'} + A_{u'} + A_{v'} + A_{v''} + A_{u''} + A_{u''} + A_{u'''}},$$

where  $A_i$  is the integrated area of peak "i".



Fig. 6 Ce 3d XPS spectra of three different shaped CeO<sub>2</sub> (a), Pt/BaO/CeO<sub>2</sub> (b), and Pt/BaO/CeO<sub>2</sub>-R (c).

As we all know, once  $Ce^{3+}$  appears in fluorite-structure ceria, oxygen vacancies will be produced by the transformation of  $Ce^{4+}$  to  $Ce^{3+}$ ,  $4Ce^{4+} + O^{2-} \rightarrow 2Ce^{4+} + 2Ce^{3+} + \Box + 0.5O_2$  (where  $\Box$  presents an empty position).<sup>54</sup> The higher the  $Ce^{3+}$  concentration in these materials is, the more oxygen

vacancies are formed. Fig. 6 summarizes the concentrations of  $Ce^{3+}$  present in the CeO<sub>2</sub> nanomaterials and corresponding NSR catalysts. The results showed that the concentration of oxygen vacancies in the CeO<sub>2</sub> nanorods was much higher than that in the other two CeO<sub>2</sub> nanomaterials. The addition of Ba and Pt components increased the Ce<sup>3+</sup> contribution on the NSR catalysts, except for Pt/BaO/CeO<sub>2</sub>-NC. A similar result was also observed over Ag/CeO<sub>2</sub> by Chang *et al.*, in which the Ag–CeO<sub>2</sub> interaction affected the concentration and structure of oxygen vacancies in the CeO<sub>2</sub> support.<sup>55</sup>

As reported in the literature,<sup>56</sup> the presence of Ce<sup>4+</sup> can be estimated by the high binding energy band u". The proportions of the relative intensity of the u" peak over all the samples are shown in Table S4.† The H<sub>2</sub> treatment decreased the proportion of Ce<sup>4+</sup>, indicating the decrease in the surface content of Ce<sup>4+</sup>. In other words, the reduced NSR catalysts had a higher amount of Ce<sup>3+</sup>. Moreover, the proportions of the relative intensity of the u" peak on the reduced Pt/BaO/ CeO<sub>2</sub>-NP, Pt/BaO/CeO<sub>2</sub>-NC, and Pt/BaO/CeO<sub>2</sub>-NR were 13.4%, 14.3%, and 12.7%, respectively, indicating that the surface content of Ce<sup>4+</sup> on Pt/BaO/CeO<sub>2</sub>-NR was the lowest, in agreement with the concentrations of Ce<sup>3+</sup>.

Among all the NSR catalysts, the amount of Ce3+ in the nanorod-based sample was the highest, which indicates a strong interaction between active components and CeO<sub>2</sub>-NR. XPS measurements were also carried out to identify the surface concentrations of Ce<sup>3+</sup> on the reduced catalysts. As shown in Fig. 6, the surface concentrations of Ce<sup>3+</sup> as percent of the total Ce on the reduced Pt/BaO/CeO2-NP, Pt/BaO/CeO2-NC, and Pt/BaO/CeO<sub>2</sub>-NR were 15.2, 14.9, and 16.8%, respectively, indicating that higher concentrations of oxygen vacancies were created by H<sub>2</sub> pre-treatment. Theoretical calculation predicted that<sup>57</sup> the formation of oxygen vacancies on the  $CeO_2$  (110) plane is much more favourable than those on the (100) and (111) planes. As shown in Fig. 1, the CeO<sub>2</sub> nanorods were enclosed by the (110) and (100) facets, while the nanoparticles and nanocubes mainly exposed  $\{(100) + (111)\}$ and (100), respectively. As a result, it is reasonable that the Pt/BaO/CeO2-NR catalyst exhibits a higher concentration of oxygen vacancies than the other two.

As reported by Lavalley *et al.*,<sup>58</sup> methanol adsorbed on the surface of CeO<sub>2</sub> prefers to dissociate into methoxy species and H<sup>+</sup>. In that case, the methoxy species adsorbed on the potential redox sites of CeO<sub>2</sub> exhibits the feature band around 970–1085 cm<sup>-1</sup>. As a result, the methanol adsorption technique provides a useful method for revealing the amount or states of oxygen vacancies.<sup>59</sup> With this in mind, the IR spectra of Pt/BaO/CeO<sub>2</sub>-R (H<sub>2</sub> pretreatment) were recorded during flowing methanol (Fig. S9†).

Within the region of  $\nu$ (C–O), four bands grow conjointly at 1006, 1032, 1052, and 1114 cm<sup>-1</sup> during the introduction of methanol, assignable to on-top methoxy (1006 cm<sup>-1</sup>), bridging methoxy (1032 and 1052 cm<sup>-1</sup>), and three-coordinate methoxy (1114 cm<sup>-1</sup>), respectively.<sup>60</sup> After exposure of methanol for 30 min, the intensity of methoxy species was stable for all the samples. Based on the spectra at 30 min, the

amount of redox sites on Pt/BaO/CeO<sub>2</sub>-R was calculated from the integral area of 970–1085 cm<sup>-1</sup> per gram of catalyst, and the results are shown in Table S5.† Obviously, the integral area relating to the redox sites on Pt/BaO/CeO<sub>2</sub>-NR was much higher than the other two, indicating a higher concentration of oxygen vacancies, and further confirming the results of Ce 3d XPS.

#### **Redox properties**

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Fig. S10<sup>†</sup> shows the H<sub>2</sub>-TPR profiles of pure nano-CeO<sub>2</sub> with different shapes. All the CeO<sub>2</sub> samples exhibited a broad reduction peak at 200-500 °C and a high-temperature reduction peak above 600 °C, attributed to surface and bulk ceria reduction, respectively.<sup>7</sup> Fig. 7 illustrates the H<sub>2</sub>-TPR profiles and corresponding fitting results of the NSR catalysts with different shaped CeO<sub>2</sub> serving as supports. The peak at temperatures below 300 °C can be assigned to the combined reduction of PtO<sub>x</sub> and its neighbouring surface ceria. This surface ceria (denoted as promoted surface ceria hereafter) was intimately in contact with PtO<sub>x</sub>, the reduction of which was attributable to the abstraction of O<sup>2-</sup> by hydrogen and facilitated by the presence of platinum.61,62 Another peak was observed at an intermediate temperature (ca. 570 °C), resulting from the reduction of surface ceria that was more remote from the platinum. In other words, the peak at the intermediate temperature originates from O<sup>2-</sup> abstraction from surface ceria that is not in direct contact with Pt. Finally, a hightemperature peak was observed at ca. 750 °C, due to the reduction of bulk ceria to Ce<sup>3+</sup>.<sup>61,62</sup> If compared with the pure nano-CeO<sub>2</sub>, the reduction of surface ceria occurs at a much lower temperature after loading of Pt and BaO, but the peak intensity significantly changed depending on the shape of CeO<sub>2</sub>. This indicates that the morphology of nanoscale ceria has a great influence on the synergistic interaction between platinum and ceria nanostructures (possibly via H<sub>2</sub> spillover).

During the H<sub>2</sub>-TPR experiments, the total H<sub>2</sub> consumption was measured, with a value of 110.8 µmol for Pt/BaO/CeO2-NP, 123.6 µmol for Pt/BaO/CeO2-NC, and 158.8 µmol for Pt/ BaO/CeO<sub>2</sub>-NR. Based on the fitting results of the H<sub>2</sub>-TPR, the H<sub>2</sub> consumption due to the reduction of the total surface ceria for all three NSR catalysts is given in Table S6 (ESI<sup>+</sup>). The proportions of promoted surface ceria were calculated (the area under the relevant TPR curve divided by the area under all the surface-related curves), giving 13% for Pt/BaO/ CeO2-NP, 3.3% for Pt/BaO/CeO2-NC and 14.5% for Pt/BaO/ CeO<sub>2</sub>-NR. This demonstrates that the interaction between platinum and CeO2-NR is stronger than that with CeO2-NP and CeO<sub>2</sub>-NC. The morphology of nanoscale ceria, therefore, influences the synergistic interaction between platinum and ceria nanostructures. It is worth noting that a sharp peak due to PtO<sub>x</sub> reduction was observed for all the NSR catalysts, showing the good dispersion of  $PtO_x$  and further confirming the results of elemental maps. The proportions of PtO<sub>x</sub> reduction were also calculated, with a value of 13.7% for Pt/BaO/



Fig. 7  $H_2$ -TPR profiles of the NSR catalysts based on the different shaped CeO<sub>2</sub> (a), and fitting results for nanoparticle (b), nanocube (c), and nanorod (d) based catalysts, respectively.

CeO<sub>2</sub>-NP, 8.2% for Pt/BaO/CeO<sub>2</sub>-NC, and 20.0% for Pt/BaO/CeO<sub>2</sub>-NR (Table S6<sup>†</sup>). Over the nanorod-supported sample, meanwhile, the reduction of PtO<sub>x</sub> occurred at 137 °C, 76 °C lower than that of Pt/BaO/CeO<sub>2</sub>-NP. This result reveals that more Pt species are available on the surface of Pt/BaO/CeO<sub>2</sub>-NR, which also exhibits a higher reducibility. As a result, it is reasonable that Pt/BaO/CeO<sub>2</sub>-NR is more active for NO oxidation than the other two NSR catalysts (Fig. S3<sup>†</sup>).

As suggested by Fridell and co-workers,<sup>63</sup> the adsorption of NO<sub>2</sub> and its further transformation into surface nitrates involve the oxidation of the surface or oxygen species by NO<sub>2</sub> to produce NO. It means that, in turn, the reducibility of the NSR catalysts or the availability of active oxygen species plays a crucial role in NO<sub>2</sub> adsorption and storage. Over the Pt/ BaO/CeO<sub>2</sub> catalysts presented here, these properties were closely related to the oxygen vacancies on the ceria surface as confirmed by Fig. 6 and 7. Pt/BaO/CeO<sub>2</sub>-NP and Pt/BaO/CeO<sub>2</sub>-NC exhibit a similar concentration of oxygen vacancies (15.2% for Pt/BaO/CeO<sub>2</sub>-NP and 14.9% for Pt/BaO/CeO<sub>2</sub>-NC), thus giving a similar amount of desorbed NO in TPD (Fig. 5).

#### Reaction sites and reaction testing by in situ DRIFTS

In Fig. 8, in situ DRIFTS show the evolution of surface species during the NO<sub>x</sub> storage and reduction process at 350 °C. After exposing the Pt/BaO/CeO2-NP catalyst to a NO/O2/N2 mixture for 40 s (Fig. 8a), two bands were observed at 1020 and 1294 cm<sup>-1</sup>, which were assigned to the symmetric and asymmetric stretching modes of -NO2 due to bidentate nitrate species adsorbed on Ba sites.<sup>10</sup> Meanwhile, another significant band attributed to monodentate nitrate on ceria was observed at 1538 cm<sup>-1</sup>.<sup>23</sup> With increasing exposure time, bands at 816 and 1770 cm<sup>-1</sup> appeared and their intensities gradually increased, indicating the formation of bulk nitrate associated with Ba.<sup>64,65</sup> Along with the formation of nitrates, two negative bands appeared at 863 and 1750 cm<sup>-1</sup>, originating from the decomposition of surface barium carbonate.<sup>23</sup> As time passed, a shoulder was observed at 1349 cm<sup>-1</sup> which was assigned to free nitrate ions.<sup>66</sup> When the gas feed was switched to a rich atmosphere (Fig. 8b), the bands at 1538, 1349, 1294, and 1020 cm<sup>-1</sup> disappeared in the first 20 seconds, indicating the high activity of surface nitrates and nitrate ions. In contrast, the bands at 1770 and 816 cm<sup>-1</sup> decreased gradually, disappearing after 5 min of reduction, suggesting that the bulk nitrates are not as active as those adsorbed on the surface.

The same experiments were carried out on Pt/BaO/CeO<sub>2</sub>-NC, with the corresponding DRIFT spectra shown in Fig. 8c and d. The NO<sub>x</sub> storage process on Pt/BaO/CeO<sub>2</sub>-NC was similar to that on Pt/BaO/CeO<sub>2</sub>-NP, except that the intensity of the peak assignable to nitrate ions (1349 cm<sup>-1</sup>) was much stronger than that on the nanoparticle supported catalyst. Under rich conditions, the nitrates adsorbed on Pt/BaO/CeO<sub>2</sub>-NC displayed a significantly lower activity for reaction with H<sub>2</sub>, compared with that on Pt/BaO/CeO<sub>2</sub>-NP. Notably, in the first 20 s of H<sub>2</sub> flow, the intensities of the IR bands due



Fig. 8 In situ DRIFTS studies of storage (a, c, e) and reduction (b, d, f,) process at 350 °C for Pt/BaO/CeO<sub>2</sub>-NP, Pt/BaO/CeO<sub>2</sub>-NC and Pt/BaO/CeO<sub>2</sub>-NR.

to nitrates adsorbed on the surface of Pt/BaO/CeO<sub>2</sub>-NC (1538, 1294, and 1024 cm<sup>-1</sup>) and free nitrate (1349 cm<sup>-1</sup>) only decreased slightly, disappearing after introduction of H<sub>2</sub> for 1 min. As a result, it is reasonable that Pt/BaO/CeO<sub>2</sub>-NC exhibits low activity for NO<sub>x</sub> conversion under lean-rich cyclic conditions as shown in Fig. 4.

Obviously, bidentate nitrates on Ba sites (1020 and 1294 cm<sup>-1</sup>) and monodentate nitrate on Ce sites (1538 cm<sup>-1</sup>) were also formed on the surface of the Pt/BaO/CeO<sub>2</sub>-NR catalyst (Fig. 8e). By comparing the intensities of the bands due to the two nitrate species, we can easily conclude that the Pt/BaO/CeO<sub>2</sub>-NR catalyst possesses more adsorption sites available for NO<sub>x</sub> storage than Pt/BaO/CeO<sub>2</sub>-NP and Pt/BaO/CeO<sub>2</sub>-NC. This conclusion was further confirmed by the appearance of a shoulder peak at 1230 cm<sup>-1</sup> assigned to bridged bidentate nitrites on Ba or Ce sites, while it was not observed in Fig. 8a and c.<sup>67</sup> Also, bulk nitrates (816 and 1770 cm<sup>-1</sup>) and free ions (1349 cm<sup>-1</sup>) were observed after feeding of NO + O<sub>2</sub> for 10 min.

When Pt/BaO/CeO<sub>2</sub>-NR was exposed to a reducing atmosphere (Fig. 8f), the bands at 1538, 1294, 1230, and 1020  $\text{cm}^{-1}$  decreased sharply, indicating the high activity of surface nitrates and nitrate ions. After 40 s of reduction, few Published on 05 January 2016. Downloaded by RESEARCH CENTRE FOR ECO-ENVIRONMENTAL SCIENCES, CAS on 03/06/2016 08:57:10.

adsorbed species remained on Pt/BaO/CeO<sub>2</sub>-NR, further demonstrating its high  $NO_x$  removal efficiency as shown in Fig. 4c.

Looking back at the NO<sub>x</sub> storage behavior (Fig. 8a, c, and e), one can easily find that, within the initial 2 min over all the NSR catalysts, the nitrates adsorbed on the surface sites of Ba (1020 and 1294 cm<sup>-1</sup>) and Ce (1538 cm<sup>-1</sup>) were predominant. This means that, in our lean (90 s)–rich (6 s) cyclic conditions, the availability of surface Ba and Ce sites is crucial for NO<sub>x</sub> storage.

# Relationship between the properties of the catalysts and catalytic performance

Even though all Pt/BaO/CeO<sub>2</sub> samples had almost the same Ba and Pt loadings, their catalytic performance for the NSR process was strongly dependent on the shape of the ceria support. The nanoparticle-based NSR catalyst exhibits a much larger BET surface area than the nanorod-related one (Table 1), while the former shows a significantly lower NSC value than the latter (Fig. 3). Also, under lean–rich conditions, the activity of Pt/BaO/CeO<sub>2</sub>-NP for NO<sub>x</sub> conversion is poorer than Pt/BaO/CeO<sub>2</sub>-NR. These results show that the surface area of Pt/BaO/CeO<sub>2</sub> is not a determining factor for the NSR process. It also suggested that ceria can serve as a component for NO<sub>x</sub> storage, which was identified by our *in situ* DRIFTS measurements. As shown in Fig. S9,† however, the NO<sub>x</sub> storage capacity of ceria is marginal.

Previous studies showed that the oxidation of NO to NO<sub>2</sub> was crucial for the  $NO_x$  storage capacity, the occurrence of which was closely related to the presence of a noble metal. Combining the result of H<sub>2</sub>-TPR (Fig. 7 and Table S6<sup>†</sup>) with that of NSC (Fig. 3), the larger amount of the available Pt is, the higher the  $NO_x$  storage capacity is. Over  $CeO_2$  supported catalysts, experimental measurement and theoretical prediction confirmed that the oxygen vacancies are anchoring sites for the noble metal, creating a strong metal-support bond, thus enhancing the catalytic activity.9,68,69 If the results presented in Fig. 6 and 7 are taken into account, it is easy to find that the higher the concentration of  $Ce^{3+}$  is, the higher the availability of Pt is. These results mentioned above suggest that the oxygen vacancies play a key role in  $NO_x$  storage over Pt/BaO/CeO<sub>2</sub>. Furthermore, it is interesting to note that a good linear correlation between the Ce<sup>3+</sup> concentrations of reduced NSR catalysts and their NO<sub>x</sub> storage capacities was observed in the temperature range of 200-350 °C (Fig. 9a), indicating that oxygen vacancies may govern the process of  $NO_x$  storage. At temperatures above 350 °C, however, such a linear relationship was not observed between the Ce<sup>3+</sup> content and NSC value. Glancing at Fig. 5, one can easily find that the stored NO<sub>x</sub> begins to decompose at 350 °C, the occurrence of which gives a negative contribution to the NSC value of Pt/BaO/CeO2. As a result, a linear relationship was not obtained at the high temperature of 400 °C.

As described in the previous literature, the presence of  $Ce^{3+}$  is accompanied by the formation of oxygen vacancies on



**Fig. 9** The relationship between the concentration of  $Ce^{3+}$  measured by XPS and the NO<sub>x</sub> storage capacity of all the Pt/BaO/CeO<sub>2</sub> catalysts (a); the relationship between the H<sub>2</sub> consumption of surface CeO<sub>2</sub> measured by H<sub>2</sub>-TPR and the NO<sub>x</sub> storage capacity of all the Pt/BaO/CeO<sub>2</sub> catalysts (b).

the surface of ceria,<sup>54</sup> on which active oxygen (O\*) is created.<sup>70</sup> A linear relationship between the Ce<sup>3+</sup> concentration on the reduced NSR catalysts and the H<sub>2</sub> consumption of total surface CeO<sub>2</sub> (Fig. S12†) further suggests that the oxygen vacancies both neighbouring the Pt and far away from the Pt are active for oxygen activation.

Interestingly, there is a close linear correlation between the H<sub>2</sub> consumption of total surface CeO<sub>2</sub> and the NO<sub>x</sub> storage capacity of different shaped ceria-based catalysts at 200– 350 °C (Fig. 9b), revealing that the surface active oxygen trapped by oxygen vacancies plays a crucial role in the NO<sub>x</sub> storage process.

As presented in Fig. S11,<sup>†</sup> however, ceria only exhibits a marginal  $NO_x$  storage capacity even though it contains large amounts of oxygen vacancies. With this in mind, a question may arise: how does the oxygen species activated by oxygen vacancies on ceria govern the  $NO_x$  storage, which is mainly trapped on Ba sites?

Among the three NSR catalysts, Pt/BaO/CeO<sub>2</sub>-NR has the highest concentration of Ce<sup>3+</sup>, and the highest number of oxygen vacancies both neighbouring the Pt and far away from the Pt, creating the largest amount of active oxygen species (eqn (1)). The O\* species are active for NO<sub>2</sub> formation on the Pt sites (eqn (2))<sup>71</sup> and also for nitrate production (eqn (3)).<sup>72</sup> Considering that the Ba sites exhibit higher basicity than the Ce sites,<sup>73</sup> the produced nitrates are thus preferably stored on and/or transfer to the former, which has been established by Fig. S11 and 8.† This feature of nitrate adsorption also guarantees the availability of oxygen vacancies for further activation of O<sub>2</sub>, nitrate formation, and further transformation of nitrate.

$$2Pt \cdots Ce^{3^{+}} - \Box + O_2 \rightarrow 2Pt \cdots Ce^{4^{+}} - O^{*}$$
(1)

$$NO + Pt \cdots Ce^{4+} - O^* \rightarrow NO_2 + Pt + Ce^{3+} - \Box$$
 (2)

$$BaO + 2NO_2 + Ce^{4+} - O^* \rightarrow Ba(NO_3)_2 + Ce^{3+} - \Box$$
(3)

$$BaO + 2NO + 3Ce^{4+} - O^* \rightarrow Ba(NO_3)_2 + 3Ce^{3+} - \Box$$
(4)

where,  $Pt \cdots Ce^{3^+} \square$  represents the Pt sites neighbouring oxygen vacancies while  $Pt \cdots Ce^{4^+} - O^*$  means the active oxygen species adsorbed on  $Pt \cdots Ce^{3^+} \square$ .

## Conclusions

The CeO2-nanorod based NSR catalyst displayed an excellent NO<sub>x</sub> storage capacity that can reach as high as 913.8 µmol  $NO_x g_{cat}^{-1}$ , as well as high  $NO_x$  removal efficiency in periodically alternating lean-rich atmospheres (90 s vs. 6 s). During 20 lean-rich cycles of operation, an extraordinarily high  $NO_x$ conversion (>96.6%) was achieved on Pt/BaO/CeO2-NR in the temperature range 200-400 °C. During the cyclic operation, this catalyst also exhibits much lower selectivity to ammonia and higher tolerance of H<sub>2</sub>O and CO<sub>2</sub>. XPS measurements confirm the formation of oxygen vacancies on the surface of ceria and Pt/BaO/CeO2. A higher concentration of oxygen vacancies guarantees that large amounts of Pt species are available for NO oxidation to NO2 over Pt/BaO/CeO2, indicating the key role of oxygen vacancies in anchoring and dispersion of Pt. Over all the NSR catalysts, the concentration of Ce<sup>3+</sup> is linearly correlated with the  $NO_x$  storage capacity. This relationship reveals that the oxygen vacancies on the ceria surface govern the formation and/or transformation of nitrates via the reaction between NO (and/or NO<sub>2</sub>) and active O species created on oxygen vacancies. The superior activity of the CeO<sub>2</sub>-nanorod-supported NSR catalyst for NO<sub>x</sub> storage thus originates from the higher numbers of oxygen vacancies, located both neighbouring and far away from the Pt on the ceria surface.

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