

Supplementary Material (ESI) for Catalysis Science & Technology  
This journal is (c) The Royal Society of Chemistry 2015

## **A high-efficiency CeWO<sub>x</sub> catalyst for the selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub>**

Wenpo Shan,<sup>a\*</sup> Yang Geng,<sup>a</sup> Xiaoling Chen,<sup>a</sup> Nan Huang,<sup>a</sup> Fudong Liu<sup>b</sup> and Shijian Yang<sup>a</sup>

<sup>a</sup> School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, PR China

<sup>b</sup> Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley 94720, California, United States

\*Corresponding author. Tel: 86-18012920637; Fax: 86-25-84315173;  
E-mail address: wenposhan@hotmail.com

Electronic Supplementary Information

### **S1 Preparation of Ce-W oxide by citric acid method**

In order to further evaluate the activity of CeWO<sub>x</sub> catalyst prepared by homogeneous precipitation method, a Ce-W oxide catalyst was prepared by citric acid method<sup>S1-4</sup> as a reference material.

Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and (NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41</sub>, with a Ce/W molar ratio of 1:1, were dissolved in citric acid solution. The mole ratio of citric acid to metal components (the total mole of Ce and W) was 1.0. The above mixture was stirred at room temperature for 1 hour. Then, it was dried at 100 °C, resulting in a porous, foam-like solid. The foam-like precursor was calcined at 500 °C for 5 h in air condition. The obtained catalyst was denoted as Ce-W oxide\_citric acid.

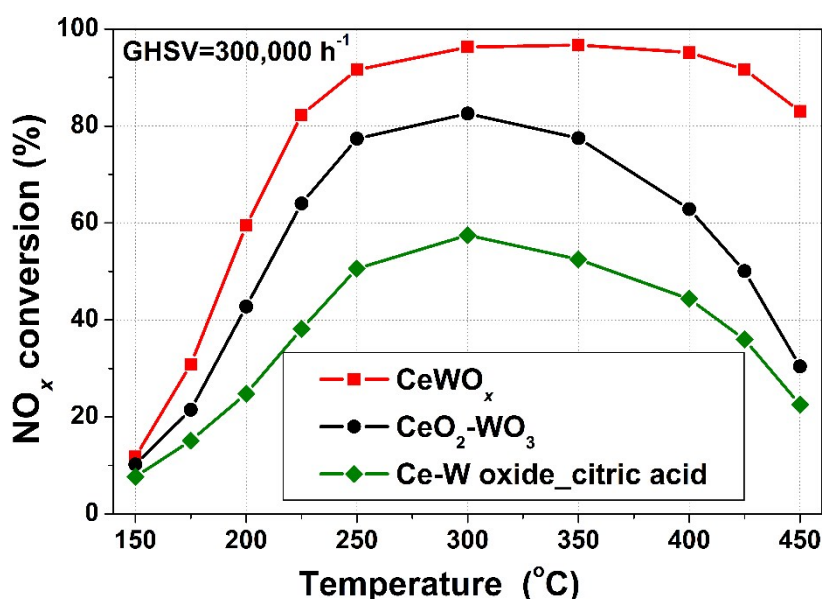
In this study, a V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst with 1 wt.% V<sub>2</sub>O<sub>5</sub> and 10 wt.% WO<sub>3</sub> was also prepared as a reference material.

The V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst was prepared by conventional impregnation method using NH<sub>4</sub>VO<sub>3</sub> and (NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41</sub> as precursors, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O as solubility promoter, and TiO<sub>2</sub> (P25) as support. After impregnation, the excess water was removed in a rotary evaporator at 60 °C. The sample was dried at 100 °C overnight and then calcined at 500 °C for 5h in air condition.

## S2 NH<sub>3</sub>-SCR activity of the Ce-W oxide\_citric acid

The NO<sub>x</sub> conversion over the Ce-W oxide\_citric acid under a high GHSV of 300,000 h<sup>-1</sup> was shown in Fig. S1.

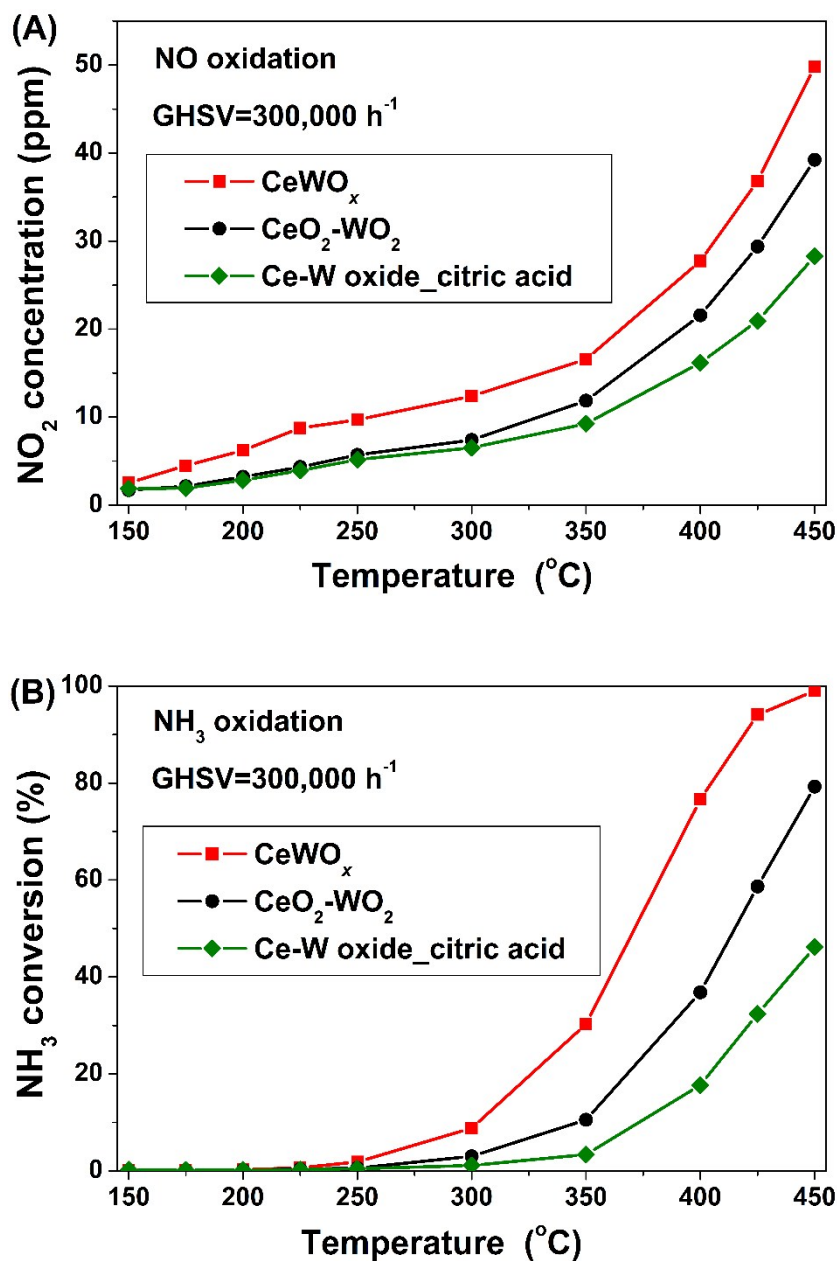
Compared with the CeWO<sub>x</sub> (prepared by homogeneous precipitation method) and CeO<sub>2</sub>-WO<sub>3</sub> (prepared by solution evaporating method), the Ce-W oxide\_citric acid catalyst prepared by citric acid method showed clearly lower SCR activity in the whole temperature range.



**Fig. S1** NO<sub>x</sub> conversions over the catalysts. Reaction conditions: [NO] = [NH<sub>3</sub>] = 500 ppm, [O<sub>2</sub>] = 5 vol.%, N<sub>2</sub> balance and GHSV = 300,000 h<sup>-1</sup>.

## S3 Separated NO/NH<sub>3</sub> oxidation over the Ce-W oxide\_citric acid

The NO<sub>2</sub> production during the separated NO oxidation and the NH<sub>3</sub> conversion during separated NH<sub>3</sub> oxidation over the Ce-W oxide\_citric acid catalyst were shown in Fig. S2(A) and Fig. S2(B), respectively. Both the NO<sub>2</sub> production and NH<sub>3</sub> conversion over the Ce-W oxide\_citric acid catalyst were lower than those over the other two catalysts, which might be associated with the relatively low NH<sub>3</sub>-SCR activity of the Ce-W oxide\_citric acid.



**Fig. S2** (A) NO<sub>2</sub> productions during separate NO oxidation reaction and (B) NH<sub>3</sub> conversions during separate NH<sub>3</sub> oxidation reaction over the catalysts. Reaction conditions: (A) [NO] = 500 ppm, (B) [NH<sub>3</sub>] = 500 ppm, [O<sub>2</sub>] = 5 vol.%, N<sub>2</sub> balance and GHSV = 300,000 h<sup>-1</sup>.

#### S4 NO<sub>x</sub>-TPD of the Ce-W oxide\_citric acid

The NO<sub>x</sub>-TPD profile of the Ce-W oxide\_citric acid catalyst was shown in Fig. S3.

Just a  $\text{NO}_x$  peak due to the desorption of physisorbed  $\text{NO}_x$  was clearly observed over  $\text{Ce-W}$  oxide\_citric acid catalyst, and almost no  $\text{NO}_x$  peak associated with the decomposition of chemisorbed  $\text{NO}_x$  species was detected. In addition, no  $\text{NO}_2$  desorption was observed over the  $\text{Ce-W}$  oxide\_citric acid.

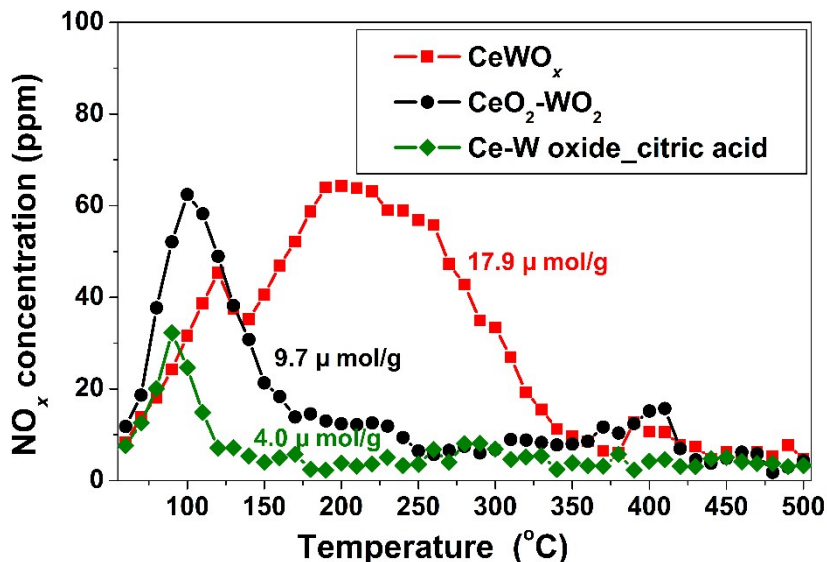


Fig. S3  $\text{NO}_x$ -TPD profiles of the catalysts.

#### S5 Influences of $\text{H}_2\text{O}$ on the activities of $\text{CeWO}_x$ and $\text{CeO}_2\text{-WO}_3$ catalysts

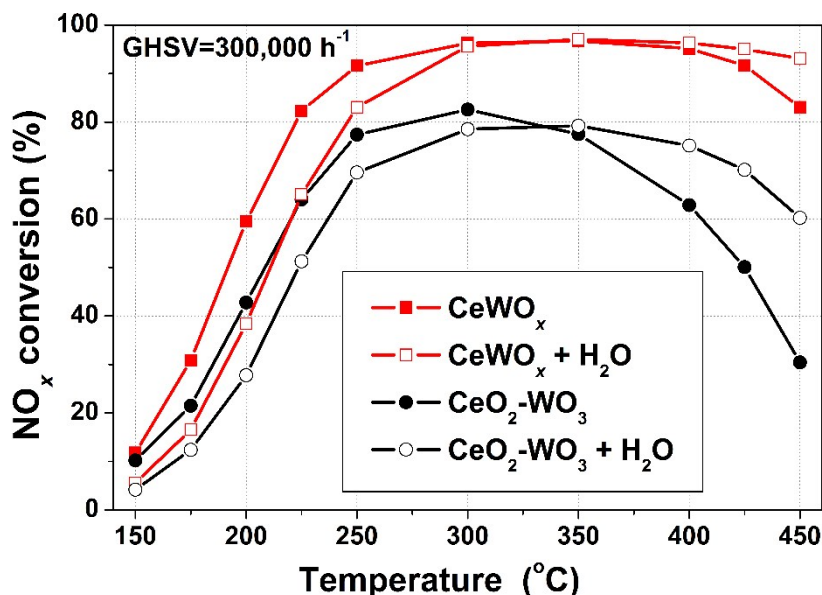


Fig. S4 Influence of  $\text{H}_2\text{O}$  on the  $\text{NO}_x$  conversions over the  $\text{CeWO}_x$  and  $\text{CeO}_2\text{-WO}_3$  catalysts. Reaction conditions:  $[\text{NO}] = [\text{NH}_3] = 500$  ppm,  $[\text{O}_2] = 5$  vol.%,  $[\text{H}_2\text{O}] = 5$  vol.% (when used), balance  $\text{N}_2$  and  $\text{GHSV} = 300,000$   $\text{h}^{-1}$ .

H<sub>2</sub>O can significantly influence the catalytic performance of the NH<sub>3</sub>-SCR catalysts.<sup>S5-7</sup> Therefore, the effects of H<sub>2</sub>O on the NO<sub>x</sub> conversions over the CeWO<sub>x</sub> and CeO<sub>2</sub>-WO<sub>3</sub> catalysts were tested under a GHSV of 300,000 h<sup>-1</sup> (Fig. S4). The existence of 5% H<sub>2</sub>O induced a decrease of low temperature activity while an enhancement of high temperature activity. Over 80% of NO<sub>x</sub> conversion could still be obtained from 250 to 450 °C over the CeWO<sub>x</sub> catalyst.

### S6 Activity comparisons among CeWO<sub>x</sub>, CeO<sub>2</sub>-WO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>

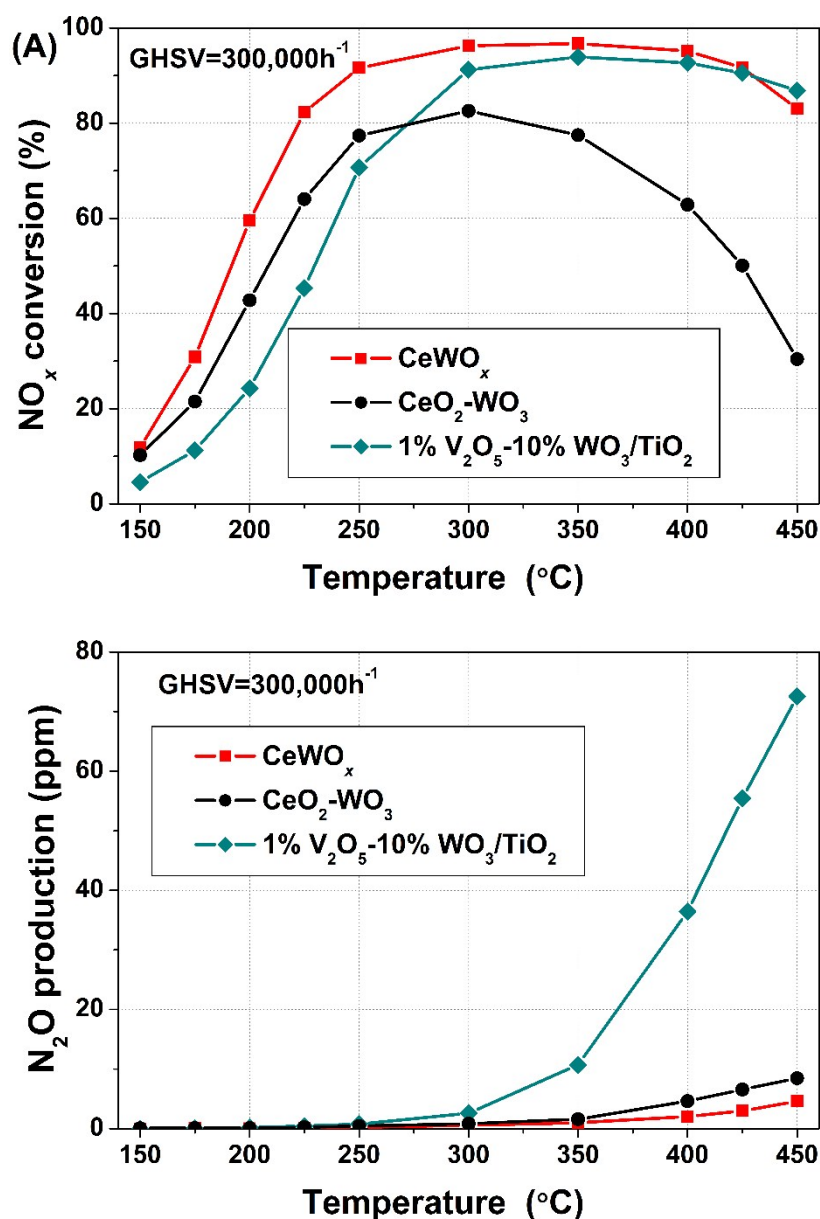
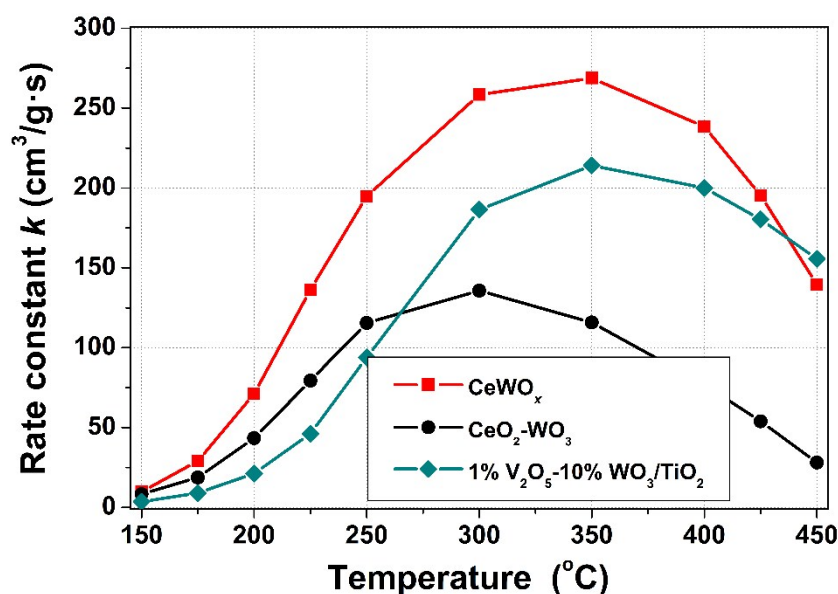


Fig. S5 (A) NO<sub>x</sub> conversions and (B) N<sub>2</sub>O productions over the catalysts. Reaction conditions: [NO]=[NH<sub>3</sub>]=500 ppm, [O<sub>2</sub>]=5vol.%, N<sub>2</sub> balance and GHSV=300,000 h<sup>-1</sup>.

Under the same GHSV condition of 300,000 h<sup>-1</sup>, the NH<sub>3</sub>-SCR activity of CeWO<sub>x</sub> was clearly higher than that of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> (Fig. S5A). In addition, the N<sub>2</sub>O production over the CeWO<sub>x</sub> and CeO<sub>2</sub>-WO<sub>3</sub> catalysts were both much lower than that over V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> (Fig. S5B). Therefore, the CeWO<sub>x</sub> is a very promising catalyst for the NO<sub>x</sub> abatement by NH<sub>3</sub>-SCR.



**Fig. S6** Comparison of the first-order reaction rate constants over the catalysts.

Reaction conditions: [NO] = [NH<sub>3</sub>] = 500 ppm, [O<sub>2</sub>] = 5 vol.%, N<sub>2</sub> balance and GHSV = 300,000 h<sup>-1</sup>.

To furtherly compare the NH<sub>3</sub>-SCR activities between these catalysts, the first-order reaction rate constants were calculated by assuming plug flow reactor and no mass transfer limitation, according to:  $k = -V/W \times \ln(1-X)$ , where  $k$  was the mass based reaction rate constant [cm<sup>3</sup>/(g s)],  $V$  was the volume flow rate (cm<sup>3</sup>/s),  $W$  was the catalyst mass (g), and  $X$  was the NO conversion. The calculated reaction rate constants were shown in Fig. S6. We can see that, the reaction rate constants of CeWO<sub>x</sub> were obviously high than those of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>, except for those at 450 °C. When the reaction rate constants of CeWO<sub>x</sub> were compared with those of CeO<sub>2</sub>-WO<sub>3</sub>, the differences between the constants of the two catalysts at low temperatures (below 250 °C) were probably due to the difference between their BET surface areas (69.9 m<sup>2</sup>/g of

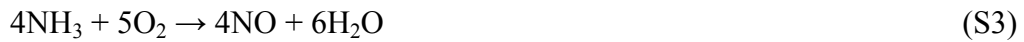
CeWO<sub>x</sub> and 39.8 m<sup>2</sup>/g of CeO<sub>2</sub>-WO<sub>3</sub>). At high temperatures (above 300 °C), the differences between the constants of the two catalysts were much larger, so there might be some other reasons besides the surface area for the difference of the constants.

### S7 Analysis of the N<sub>2</sub>O formation over CeWO<sub>x</sub> and CeO<sub>2</sub>-WO<sub>3</sub> catalysts

The main reaction over that catalysts under NH<sub>3</sub>-SCR condition is the standard SCR reaction:



At high temperature region, two side reactions, non-selective catalytic reduction reaction (NSCR reaction, reaction S2) and catalytic oxidation of NH<sub>3</sub> (C-O reaction, reaction S3), will appear simultaneously:<sup>S8,S9</sup>



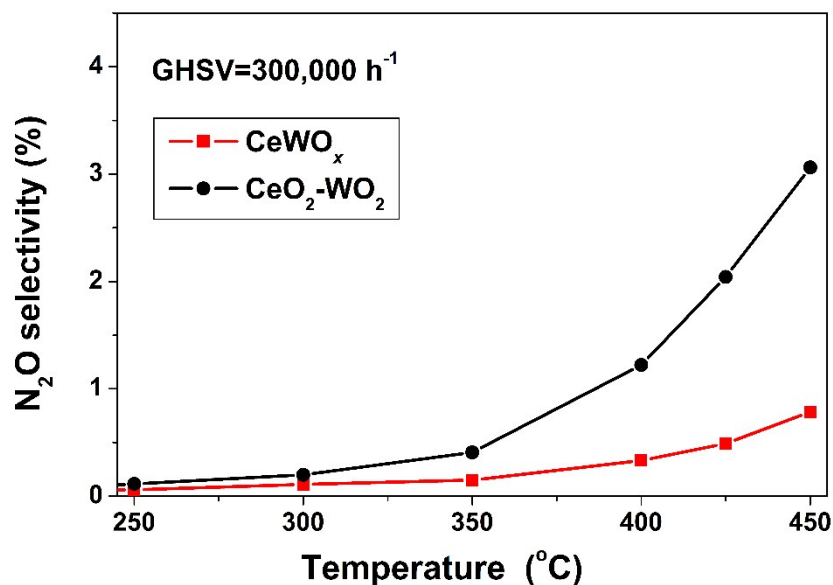
The NSCR reaction can be represented by the N<sub>2</sub>O formation. On the other hand, the SCR reaction can be represented by the N<sub>2</sub> formation, while the N<sub>2</sub> formation was calculated by the following equation:

$$N_2 \text{ formation} = ([\text{NO}_x]_{in} + [\text{NH}_3]_{in} - [\text{NO}_x]_{out} - [\text{NH}_3]_{out} - 2[\text{N}_2\text{O}]_{out})/2 \quad (\text{S4})$$

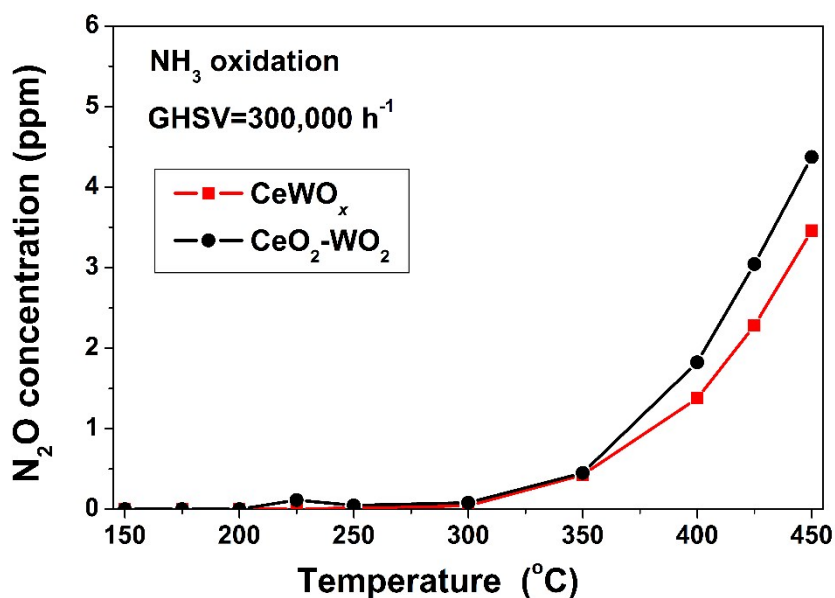
To investigate the reason for the less amount of N<sub>2</sub>O formation over CeWO<sub>x</sub> than that over CeO<sub>2</sub>-WO<sub>3</sub> during SCR activity test, the N<sub>2</sub>O selectivity was calculated by the following equation:

$$N_2\text{O selectivity} = \frac{2[\text{N}_2\text{O}]_{out}}{([\text{NO}_x]_{in} + [\text{NH}_3]_{in} - [\text{NO}_x]_{out} - [\text{NH}_3]_{out})} \times 100\% = 1 - N_2 \text{ selectivity} \quad (\text{S5})$$

The calculated results of the N<sub>2</sub>O selectivity were shown in Fig. S7. The N<sub>2</sub>O selectivity over CeWO<sub>x</sub> was clearly lower than that over CeO<sub>2</sub>-WO<sub>3</sub>. Compared with CeO<sub>2</sub>-WO<sub>3</sub>, the CeWO<sub>x</sub> remarkably enhanced SCR reaction, and thus depressed the NSCR reaction due to the competition between the two reactions. Therefore, the N<sub>2</sub>O formation over CeWO<sub>x</sub> was relatively low.



**Fig. S7** N<sub>2</sub>O selectivity over the CeWO<sub>x</sub> and CeO<sub>2</sub>-WO<sub>3</sub> catalysts. Reaction conditions: [NO] = [NH<sub>3</sub>] = 500 ppm, [O<sub>2</sub>] = 5 vol.%, balance N<sub>2</sub> and GHSV = 300,000 h<sup>-1</sup>.

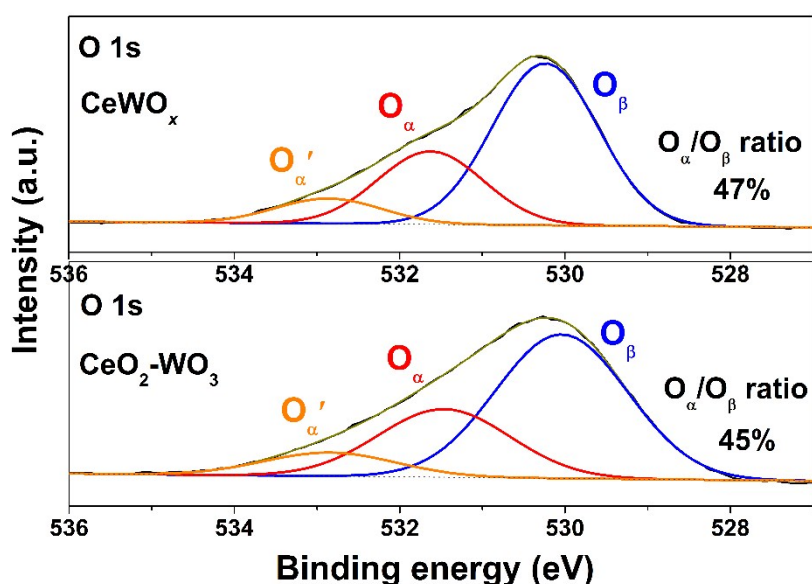


**Fig. S8** N<sub>2</sub>O formation during separate NH<sub>3</sub> oxidation reaction over CeWO<sub>x</sub> and CeO<sub>2</sub>-WO<sub>3</sub> catalysts. Reaction conditions: [NH<sub>3</sub>] = 500 ppm, [O<sub>2</sub>] = 5 vol.%, N<sub>2</sub> balance and GHSV = 300,000 h<sup>-1</sup>.



At high temperature, the C-O reaction could significantly contribute to NO formation. Previous studies on the reaction mechanism of NH<sub>3</sub> oxidation at high temperature have identified NO as an important intermediate: (1) NH<sub>3</sub> is first oxidized to NO by O<sub>2</sub> (C-O reaction), and then (2) the NO react with adsorbed NH<sub>3</sub> species to form N<sub>2</sub> (iSCR reaction) or N<sub>2</sub>O (NSCR reaction).<sup>S10-13</sup> During the separated NH<sub>3</sub> oxidation, although the NH<sub>3</sub> oxidation ability of CeWO<sub>x</sub> was obviously higher than that of CeO<sub>2</sub>-WO<sub>3</sub>, the formed N<sub>2</sub>O over CeWO<sub>x</sub> was lower (Fig. S8). This result also indicated that the enhanced SCR reaction over CeWO<sub>x</sub> depressed the formation of N<sub>2</sub>O through NSCR reaction.

### S8 XPS results of O 1s of CeWO<sub>x</sub> and CeO<sub>2</sub>-WO<sub>3</sub> catalysts



**Fig. S9** XPS results of O 1s of the CeWO<sub>x</sub> and CeO<sub>2</sub>-WO<sub>3</sub> catalysts.

The XPS results of O 1s of the CeWO<sub>x</sub> and CeO<sub>2</sub>-WO<sub>3</sub> catalysts are shown in Fig. S9. The peak of O 1s was fitted into three sub-bands by searching for the optimum combination of Gaussian bands with correlation coefficients ( $r^2$ ) above 0.99. The sub-bands at 530.0-530.3 eV could be attributed to the lattice oxygen O<sup>2-</sup> (denoted as O<sub>β</sub>). Two shoulder sub-bands at 531.4-531.6 eV and 532.8-532.9 eV are assigned to the surface adsorbed oxygen (denoted as O<sub>α</sub>), such as the O<sub>2</sub><sup>2-</sup> and O<sup>-</sup> belonging to defect-oxide or hydroxyl-like group, and chemisorbed water (denoted as O<sub>α'</sub>), respectively.<sup>S14-</sup>

<sup>19</sup> The  $O_{\alpha}/O_{\beta}$  ratio of  $CeWO_x$  (47%) was higher than that of  $CeO_2-WO_3$  (45%), which means that the introduction of Ce indeed created more surface oxygen vacancies.  $O_{\alpha}$  is usually more reactive than  $O_{\beta}$  for oxidation reactions due to its higher mobility.<sup>S20</sup> Therefore, the relatively high  $O_{\alpha}/O_{\beta}$  ratio of  $CeWO_x$  would be beneficial for the activation of NO and  $NH_3$  in the SCR reaction, and thereby promote the  $NO_x$  conversion.

## References

- S1 C. H. Kim, G. Qi, K. Dahlberg and W. Li, *Science*, **327**, 1624-1627.
- S2 E. Arendt, A. Maione, A. Klisinska, O. Sanz, M. Montes, S. Suarez, J. Blanco and P. Ruiz, *Appl. Catal., A*, 2008, **339**, 1-14.
- S3 W. Yang, Q. Liu, W. Qiu, S. Lu and L. Yang, *Solid State Ionics*, 1999, **121**, 79-84.
- S4 G. Qi and R. T. Yang, *Chem. Commun.*, 2003, 848-849.
- S5 P. Hu, Z. Huang, W. Hua, X. Gu and X. Tang, *Appl. Catal., A*, 2012, **437-438**, 139-148.
- S6 J. Li, H. Chang, L. Ma, J. Hao and R. T. Yang, *Catal. Today*, 2011, **175**, 147-156.
- S7 Z. Huang, Z. Zhu and Z. Liu, *Appl. Catal., B*, 2002, **39**, 361-368.
- S8 S. Yang, Y. Liao, S. Xiong, F. Qi, H. Dang, X. Xiao and J. Li, *J. Phys. Chem. C*, 2014, **118**, 21500-21508.
- S9 I. Nova, D. Bounechada, R. Maestri, E. Tronconi, A. K. Heibel, T. A. Collins and T. Boger, *Ind. Eng. Chem. Res.*, 2010, **50**, 299-309.
- S10 J. Perez-Ramirez and E. V. Kondratenko, *Chem. Commun.*, 2004, 376-377.
- S11 Z. Qu, H. Wang, S. Wang, H. Cheng, Y. Qin and Z. Wang, *Appl. Surf. Sci.*, 2014, **316**, 373-379.
- S12 A. C. Akah, G. Nkeng and A. A. Garforth, *Appl. Catal., B*, 2007, **74**, 34-39.
- S13 L. Zhang and H. He, *J. Catal.*, 2009, **268**, 18-25.
- S14 J.-C. Dupin, D. Gonbeau, P. Vinatier and A. Levasseur, *Phys. Chem. Chem. Phys.*, 2000, **2**, 1319-1324.
- S15 D. Y. Yoon, E. Lim, Y. J. Kim, J. H. Kim, T. Ryu, S. Lee, B. K. Cho, I.-S. Nam, J. W. Choung and S. Yoo, *J. Catal.*, 2014, **319**, 182-193.

- S16 C. Zhang, C. Wang, W. Zhan, Y. Guo, Y. Guo, G. Lu, A. Baylet and A. Giroir-Fendler, *Appl. Catal., B*, 2013, **129**, 509-516.
- S17 Y. Zhang, Z. Qin, G. Wang, H. Zhu, M. Dong, S. Li, Z. Wu, Z. Li, Z. Wu, J. Zhang, T. Hu, W. Fan and J. Wang, *Appl. Catal., B*, 2013, **129**, 172-181.
- S18 Z.-Y. Tian, P. H. T. Ngamou, V. Vannier, K. Kohse-Höinghaus and N. Bahlawane, *Appl. Catal., B*, 2012, **117-118**, 125-134.
- S19 A. Machocki, T. Ioannides, B. Stasinska, W. Gac, G. Avgouropoulos, D. Delimaris, W. Grzegorzczuk and S. Pasieczna, *J. Catal.*, 2004, **227**, 282-296.
- S20 Z. Wu, R. Jin, Y. Liu, H. Wang, *Catal. Commun.*, 2008, **9**, 2217-2220.