

Catalysis Science & Technology

Accepted Manuscript

View Article Online View Journal

This article can be cited before page numbers have been issued, to do this please use: L. Zhang, L. Li, Y. Cao, Y. Xiong, S. Wu, J. Sun, C. Tang, F. Gao and L. Dong, *Catal. Sci. Technol.*, 2015, DOI:



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/catalysis

Catalysis Science & Technology Accepted Manuscript

Graphical Abstract



The promotional effect of SnO₂ in Ce/TiO₂ catalyst for NH₃-SCR reaction.

Cite this: DOI: 10.1039/c0xx00000x

ARTICLE TYPE

www.rsc.org/xxxxxx

Promotional effect of doping SnO₂ into TiO₂ over CeO₂/TiO₂ catalyst for the selective catalytic reduction of NO by NH₃

Lei Zhang^a, Lulu Li^a, Yuan Cao^a, Yan Xiong^a, Shiguo Wu^a, Jingfang Sun^b, Changjin Tang^{a*}, Fei Gao^b, Lin Dong^{a,b*}

s Received (in XXX, XXX) Xth XXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX DOI: 10.1039/b000000x

Abstract: Ti_xSn_{1-x}O₂ was prepared by co-precipitation method, and a series of CeO₂/Ti_xSn_{1-x}O₂ samples were prepared to investigate the effect of doping SnO₂ into TiO₂ for the selective catalytic reduction of NO by NH₃. The results of catalytic tests suggested that the catalyst with the optimal mole ratio (Ti:Sn=1:1) exhibited the best catalytic performances. Moreover, the NO removal efficiency of CeO₂/Ti_{0.5}Sn_{0.5}O₂ was higher than that of CeO₂/TiO₂. The obtained samples were characterized by BET, XRD, H₂-TPR, XPS, NH₃-TPD and *in situ* DRIFT. The results revealed that the introduction of SnO₂ resulted in the formation of rutile style Ti_{0.5}Sn_{0.5}O₂ solid solution with larger specific surface area and better thermal stability. The interactions between CeO₂ and Ti_{0.5}Sn_{0.5}O₂ support could improve the redox ¹⁵ performance of catalyst, which was beneficial to enhance catalytic activity at low temperature. Furthermore, doping SnO₂ enhanced surface acid sites and weakened the adsorption of nitrates, which played an important role in the process of catalytic reaction. Finally, *in situ* DRIFT demonstrated that the competition adsorption happened between bridging nitrates and gas NH₃ and the selective catalytic reduction of NO by NH₃ proceeded mainly via the Eley–Rideal mechanism over Ce/TiO₂ and ²⁰ Ce/Ti_{0.5}Sn_{0.5}O₂.

1. Introduction

Published on 07 January 2015. Downloaded by University of Massachusetts - Boston on 11/01/2015 08:22:37.

Nitrogen oxides (NO_x) are responsible for acid rain, photochemical smog and ozone depletion threatening ecological ²⁵ environment and human health.¹ Stringent environmental legislation has been made across the world to regulate the emission standard of NO_x from stationary sources (such as coal– fired power plants) and mobile sources (such as vehicle exhaust). The selective catalytic reduction of NO_x by NH₃ (NH₃–SCR) is a

³⁰ kind of high efficient deNO_x technology for the emission reduction of NO_x from coal-fired power plants.² The industrial catalysts for NH₃-SCR process are based on TiO₂-supported V₂O₅-WO₃ and/or V₂O₅-MoO₃ oxides for their high NO_x removal efficiency at 300-400 °C and excellent resistance to SO₂

- ³⁵ poisoning. However, V–W(Mo)/TiO₂ catalyst will be gradually replaced for some practical problems: the toxicity of active component V₂O₅, narrow operation temperature window and poor N₂ selectivity at higher temperature.^{3–5} In addition, anatase TiO₂ as catalyst carrier is easy to suffer from the crystal transformation
- ⁴⁰ to form rutile TiO₂ when temperature is over 600 °C, which results in the decrease of surface area and catalytic activity.^{6, 7} Nowadays, researches about non–vanadium–SCR catalysts

mainly including Fe, Cu, Mn, Ce based catalysts. In addition, the structures and components of catalysts usually influence the NH₃–SCR operation temperature window and the resistance of H₂O and/or SO₂.^{7, 8} It is worth noting that CeO₂–TiO₂ based catalysts may be a potential replacement of V₂O₅/WO₃–TiO₂ catalyst for its excellent NO conversion, high N₂ selectivity at ⁵⁰ medium–high temperature and environmentally–benign characteristic.^{9–11}

mainly focus on transition metal and rare earth metal catalysts

SnO₂ is a wide band gap n-type semiconducting metal oxide^{12, 13} and can form oxygen vacancies,^{14, 15} which is widely used in gas sensors, transparent conductors and catalysis. SnO₂ has a rutile– ⁵⁵ style structure (P42/mnm) as same as rutile TiO₂. It is reported that SnO₂ can be doped into TiO₂ to form rutile Ti_xSn_{1-x}O₂ solid solution with high surface area and excellent thermal stability.¹⁶, ¹⁷ Meanwhile, our previous studies^{18–20} suggest that supported Ti_{0.5}Sn_{0.5}O₂ solid solution based catalysts showed excellent NO ⁶⁰ removal efficiency over both three-way catalysts (TWC) and NH₃-SCR catalysts. Recently, Chang *et.al*²¹ reported that adding SnO₂ to MnO_x-CeO₂ could improve the catalytic activity at low temperature and SO₂ resistance in NH₃-SCR reaction.

In this work, we attempt to substitute $Ti_{0.5}Sn_{0.5}O_2$ solid solution for TiO_2 over CeO_2/TiO_2 to prepare $CeO_2/Ti_{0.5}Sn_{0.5}O_2$ by an impregnation method. Catalytic performance evaluation suggests that $CeO_2/Ti_{0.5}Sn_{0.5}O_2$ displayed higher NO removal rate than CeO₂/TiO₂ within the whole temperature range. Therefore, we focus on investigating the promotional effect of doping SnO₂ into TiO₂ on NH₃–SCR performances over CeO₂/TiO₂. To elucidate the functions of Ti_{0.5}Sn_{0.5}O₂ in NH₃–SCR reaction, textural ⁵ structure, surface acidity, redox performance and surface component of samples have been explored by BET, XRD, *in situ* DRIFT, H₂–TPR, NH₃–TPD and XPS.

2. Experimental

2.1. Catalyst preparation

¹⁰ A series of $Ti_x Sn_{1-x}O_2$ solid solution (*x* is molar ratio) were prepared by a co-precipitation method. An ethanol and water mixed solution containing required amounts of TiCl₄ and SnCl₄ was precipitated by ammonium hydroxide under vigorous stirring (pH \approx 9.0). The precipitate was washed with deionized water ¹⁵ until no Cl⁻ could be detected by 1.0 mol·L⁻¹ AgNO₃ solution, then dried at 110 °C for 12 h and calcined at 550 °C for 4 h in flowing air.

Both anatase TiO₂ (denoted as TiO₂–A) and rutile TiO₂ (denoted as TiO₂–R) were prepared by TiCl₄ dropwise into ethanol in an ²⁰ ice-water bath under stirring. The differences were that TiO₂–A was obtained by adding appropriate amount of NH₃·H₂O until the pH value was 9.0 while TiO₂–R was obtained by adding appropriate amount of H₂O (pH < 1.0). Furthermore, SnO₂ was prepared by the same procedure as anatase TiO₂ and SnCl₄ was ²⁵ used as the precursor. The precipitate was washed with distilled water to be free of chloride, then dried at 110 °C for 12 h and

calcined at 500 °C for 4 h in flowing air. A series of $yCeO_2/Ti_xSn_{1-x}O_2$ (denoted as yCe/Ti_xSn_{1-x} , and "y" is the mass fraction of CeO₂ in sample) and CeO₂/TiO₂ (using ³⁰ anatase TiO₂ as support, denoted as Ce/Ti) were prepared by incipient wetness impregnation with the solution of Ce(NO₃)₃·6H₂O. The samples were vigorously stirred for 1 h and then evaporated at 100 °C until achieving a paste, which was dried at 110 °C overnight and then calcined in a muffle stove at ³⁵ 500 °C for 4 h in flowing air. For $yCe/Ti_{0.5}Sn_{0.5}$, the CeO₂ loading

was 5%, 10%, 15% and 20 wt.% respectively. For Ce/Ti and Ce/Sn samples, the CeO₂ loading was fixed at 10 wt.%.

2.2. Catalyst characterization

X-ray powder diffraction (XRD) patterns were collected using a ⁴⁰ Philips X'pert Pro diffractometer with Ni-filtered CuK α 1 radiation (0.15408 nm). The X–ray tube was operated at 40 kV and 40 mA. Average crystallite size was calculated by Debye– Scherrer equation.²²

Specific surface areas of samples were measured by nitrogen 45 adsorption at 77 K on a Micrometrics ASAP–2020 analyzer by the Brunauer–Emmet–Teller (BET) method. Before each adsorption measurement, about 0.1 g of the sample was degassed in a N₂/He mixture at 300 °C for 4 h.

- X-ray photoelectron spectroscopy (XPS) experiments were ⁵⁰ performed on a PHI 5000 Versa Probe high performance electron spectrometer, using monochromatic Al K α radiation (1486.6 eV) operating at an accelerating power of 15 kW. Before the measurement, the sample was outgassed at room temperature in a UHV chamber (< 5×10⁻⁷ Pa). The sample charging effects were ⁵⁵ compensated by calibrating all binding energies (BE) with the
- adventitious C 1s peak at 284.6 eV. This reference gave BE

H₂-temperature programmed reduction (H₂-TPR) was carried out in a quartz U-tube reactor connected to a TCD with H₂-Ar ⁶⁰ mixture (7% H₂ by volume) as reductant. 50 mg of the sample was used for each measurement. Before switching to the H₂-Ar stream, the sample was pre-treated in a N₂ stream at 200 °C for 1 h. TPR started from room temperature to 850 °C at a rate of 10 °C ·min⁻¹.

65 The in situ DRIFT experiments were performed on a Nicolet Nexus 5700 FTIR spectrometer by using a diffuse reflectance attachment (HARRICK) equipped with a reaction cell (ZnSe windows). The number of scans was 32 at a resolution of 4 cm⁻¹ and the spectra were presented as Kubelka-Munk function 70 referred to background spectra of sample recorded in N₂. The powder sample was used (ca. 25 mg) and pre-treated in N2 at 400 °C for 1 h prior to adsorption experiments. The reaction conditions as follows: 500 ppm NH₃, 500ppm NO, 5 vol.% O₂, N₂ balance and 100 ml·min⁻¹ flow rate. For each sample, the 75 NH₃/(NO + O₂) were adsorbed for 45 min to steady state at required temperature. Afterwards, (1) the sample was purged by N₂ for 10 min, then spectra were recorded in pure N₂ stream at a desired temperature by the heating rate of 10 °C min⁻¹; (2) the sample was purged by N_2 for 10 min, then passing (NO + ⁸⁰ O₂)/NH₃ into the gas chamber to react with the pre-adsorbed

NH₃/NO_x species.

NH₃--temperature programmed desorption (NH₃--TPD) experiments were carried out on a multifunction chemisorption analyzer with a quartz U--tube reactor, detected by a thermal so conductivity detector (TCD). About 0.1 g of the sample was pretreated by high purified N₂ (40 ml·min⁻¹) at 450 °C for 1 h. After pre-treatment, the sample was saturated with 1 vol.% NH₃ (10 ml·min⁻¹) at 100 °C for 1 h and subsequently flushed with high purified N₂ at the same temperature for 1 h to remove gaseous on and weakly adsorbed NH₃, then the sample was heated to 600 °C

¹⁰ and weakly adsorbed NH₃, then the sample was heated to 600 °C at a rate of 10 °C·min⁻¹ in the flowing high purified N₂ (40 ml·min⁻¹).

2.3. Catalytic performance test

Catalytic reaction was performed in a fixed-bed quartz reactor ⁹⁵ tube. The reaction condition were: 500 ppm NO, 500 ppm NH₃, 5 vol.% O₂, 100 ppm SO₂ (when used), 5 vol.% H₂O (when used), balance N₂ and the gas flow rate of 100ml·min⁻¹, GHSV was 90,000 h⁻¹. Prior to catalytic test, the sample was pre-treated in N₂ at 200 °C for 1 h. The effluent gases including NO, NH₃, NO₂, ¹⁰⁰ and N₂O were continuously analysed by an online Nicolet IS10 spectrometer equipped with a gas cell. IR Data were collected at required temperature with keeping reaction for 15 min to reach a steady state. The NO conversion and N₂ selectivity were calculated by the following equations:

¹⁰⁵ NO conversion (%) =
$$\frac{[NO]_{in} - [NO]_{out}}{[NO]_{in}} \times 100$$

N₂ selectivity (%)

$$=\frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}} - [\text{NO}_2]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}} \times 100$$

3. Results and discussion

55

3.1. Catalytic performances evaluation

3.1.1. Effect of doping SnO₂ on catalytic activity over Ce/Ti Firstly, the influence of Ti/Sn mole ratio on NO conversion over Ce/Ti_xSn_{1-x} samples was investigated. Herein, the loading of 5 CeO₂ was fixed at 10 wt.%. As shown in Fig. S1, the order of catalytic activity followed Ce/Ti_{0.5}Sn_{0.5} > Ce/Ti_{0.75}Sn_{0.25} > Ce/Ti_{0.9}Sn_{0.1} > Ce/Ti_{0.95}Sn_{0.05} > Ce/Ti_{0.25}Sn_{0.75}. The results of catalytic activities indicated that Ce/Ti_xSn_{1-x} samples exhibited the optimal NO conversion when the molar ratio of Ti/Sn was

- ¹⁰ 1:1. So a series of y/Ce/Ti_{0.5}Sn_{0.5} samples were prepared, and comparative studies between Ce/Ti_{0.5}Sn_{0.5} (Ce/TiSn for short) and Ce/Ti samples were conducted to elucidate the effect of doping SnO₂ on NH₃–SCR performances.
- Fig. 1 showed the NO conversion as a function of temperature for ¹⁵ NH₃–SCR over Ce/TiSn, Ce/Ti, Ce/Sn, TiSn support and CeO₂. It could be seen that Ce/Sn, TiSn solid solution and CeO₂ exhibited much poor catalytic activity. In contrast, Ce/Ti displayed better catalytic activity with over 90% NO conversion between 300 °C and 400 °C while Ce/TiSn samples had the best catalytic activity
- ²⁰ with more than 88% NO conversion from 250 °C to 450 °C in the present experimental conditions. The order of catalytic activity followed Ce/TiSn > Ce/Ti > Ce/Sn > CeO₂> TiSn, indicating the sample with triple components had the best catalytic activity. Based on the above results, doping SnO₂ into TiO₂ was beneficial

Published on 07 January 2015. Downloaded by University of Massachusetts - Boston on 11/01/2015 08:22:37.

- $_{25}$ to improve the catalytic activity of Ce/Ti, and the promotional effect was possible related to the interactions among CeO₂, SnO₂ and TiO₂. It is worth noting that the loading amounts of CeO₂ for Ce/TiSn had little effect on catalytic activity. Thus, it is rational to choose the 10Ce/TiSn sample as a represent to investigate the
- ³⁰ promotional effect of SnO₂ on CeO₂/TiO₂. Fig. S2 indicated that the N₂ selectivity of Ce/TiSn and Ce/Ti was more than 95% in the entire temperatures. In addition, as shown in Fig.S3, when 10Ce/TiSn was calcined at 750 °C for 4 h, although the catalytic activity of 10Ce/TiSn decreased, its catalytic activity was much ³⁵ higher than that of Ce/Ti calcined at 750 °C, which indicated that

Ce/TiSn had better thermal stability than Ce/Ti.

100 TiSn 5Ce/TiSn 10Cc/TiSn 80 15Ce/TiSn v 20Ce/TiSn Ce/Ti conversion% 60 -0 CeO 40 NO NO 20 150 200 250 300 350 400 450 Temperature/°C

Fig. 1 NO conversion of CeO2, TiSn, Ce/Sn, Ce/Ti, and Ce/TiSn samples.

3.1.2. NO + O_2 reaction on 10Ce/TiSn and Ce/Ti

⁴⁰ As reported elsewhere, $^{23-26}$ the oxidation of NO to NO₂ over catalysts (such as V₂O₅–WO₃/TiO₂ and Fe–zeolite catalysts) could improve the low temperature NH₃–SCR activity by the "fast SCR" reaction route as following:

 $\mathrm{NO} + \mathrm{NO}_2 + 2\mathrm{NH}_3 \rightarrow 2\mathrm{N}_2 + 3\mathrm{H}_2\mathrm{O}$

⁴⁵ In order to investigate the influence of doping SnO₂ on NH₃–SCR catalytic activities at low temperature, NO oxidation reaction was

conducted in the range from 150 to 450 °C. As shown in Fig. 2, the NO conversion of 10Ce/TiSn was higher than that of Ce/Ti at the same reaction temperature. It seemed that NH₃–SCR ⁵⁰ proceeded more easily via the "fast SCR" reaction route over 10Ce/TiSn. Possible reasons for improving the "fast SCR" reaction by doping SnO₂ would be discussed combined with the results of XPS and H₂–TPR.







Fig. 3 5 vol.% H₂O and/or 100 ppm SO₂ resistance testing over Ce/Ti and 10Ce/TiSn.

60 3.1.3. Effect of H₂O and/or SO₂ on catalytic activity over 10Ce/TiSn and Ce/Ti

The actual working conditions of coal fired plants usually contained a certain amount of SO₂ and H₂O, thus it was necessary to investigate the influence of SO2 and H2O on SCR activities of 65 catalysts.²⁷ All tests were carried out at 300 °C. As shown in Fig. 3. 5 vol.% H₂O had basically no influence on the activity of 10Ce/TiSn with keeping nearly 100% NO conversion in the whole testing. When 100 ppm SO₂ was injected, the NO conversion of 10Ce/TiSn slowly decreased with the increase of 70 time and maintained ca. 81% after 24 h. Meanwhile, NH₃-SCR in the presence of 100 ppm SO₂ was measured over Ce/Ti as a comparison, and NO conversion decreased from ca. 94% to ca. 62% after 24 h. Thus, it indicated that doping SnO₂ into TiO₂ could improve the SO₂ resistance of Ce/Ti. When both SO₂ and 75 H₂O were introduced, the NO conversion of 10Ce/TiSn was lower than that of only adding SO₂ in the whole testing. In terms of the accelerated deactivation of catalyst influenced by H₂O, two possible reasons could be proposed. On one hand, NH₄HSO₄ could be more easily formed in the presence of SO₂ and H₂O than ⁸⁰ only introducing SO₂, which led to the deactivation of catalysts.²⁸

On the other hand, active sites could be occupied by the adsorbed H₂O as a consequence of the competitive adsorption of NH₃ and H₂O, which resulted in the reversible deactivation of catalysts.²⁹ Thus, catalysts were easier to be deactivated by introducing both ⁵ SO₂ and H₂O comparing to only introducing SO₂. Interestingly, it could be seen that NO conversion could recover up to ca. 96%

when cutting off SO₂ and H₂O over 10Ce/TiSn (the inset in Fig. 3), which indicated that the deactivation in the coexistence of SO₂ and H₂O was reversible over Ce/TiSn. As reported elsewhere, ^{30, 31}

¹⁰ the NH₃–SCR activity could be regenerated automatically after cutting off SO₂ and H₂O over $Ce_{0.2}W_{0.2}TiO_x$ or Fe–Mn/TiO₂ catalysts.

3.2. Structural characterization (XRD and BET)

As shown in Fig. S4, $Ti_x Sn_{1-x}$ (x=0-1) samples were rutile-style 15 structure (PDF 77-0450 for pure SnO₂ and PDF 78-1510 for pure TiO₂). With the increase of Ti/Sn mole ratio, diffraction peak gradually shifted to lower angle (the effective ionic radius $r(\text{Sn}^{4+})$) $= 0.069 \text{ nm} > r(\text{Ti}^{4+}) = 0.0605 \text{ nm})$ comparing to TiO₂-R, indicating that Sn⁴⁺ had been successfully incorporated into the 20 lattice of TiO₂ to form TiSn solid solution maintaining the rutilestyle structure, which was in agreement with the literatures.^{16, 22,} ³² When CeO₂ was supported and the loading amount of CeO₂ was less than 10 wt.%, as shown in Fig. 4, only the peaks related to TiSn support were detected, which indicated that CeO₂ was 25 dispersed on the surface of TiSn support or its particle size was smaller than the detection limit of XRD. When CeO₂ loading was more than 15 wt.%, the peaks at 28.6° and 47.6° ascribed to CeO₂ phase were emerged. Combined with the results of catalytic activity, it could be seen that crystalline CeO₂ over Ce/TiSn 30 catalyst had little effect on catalytic performance. In addition, diffraction peaks of TiSn became significantly broader than those of pure TiO₂ and SnO₂, indicating the smaller size of crystallite for TiSn as summarized in Table 1. Meanwhile, the specific surface area of TiSn solid solution was much larger than those of $_{35}$ pure TiO₂ and SnO₂, which suggested that the introduction of SnO₂ improved the textural structure of TiO₂.



Fig. 4 XRD results of supports and catalysts.

3.3. Surface component and chemical states (XPS)

⁴⁰ XPS was performed to illustrate the surface component and chemical state of elements in Ce/Ti and 10Ce/TiSn samples. The CeO₂ spectrum was composed of two multiplets (v and u) by Gaussian–Lorentz fitting procedure with the assignment defined in Fig. 5 of Ce 3d spectra. The bands labelled u stand for $3d_{3/2}$ ⁴⁵ spin–orbit states and those labelled v represented $3d_{5/2}$ states. The bands labelled as u' and v' were ascribed to the primary photoemission of Ce³⁺ and the other six bands labelled as u'' and v''', u'' and v'', u and v were assigned to Ce^{4+,33} Ce³⁺ content could be estimated by the formula:³⁴

• Ce(III)%=
$$\frac{100 \times \left[S(u')+S(v')\right]}{\Sigma \left[S(u)+S(v)\right]}\%$$

Table 1 The textural data of supports and catalysts

Sample	BET surface area/m ² ·g ⁻¹	Crystallite size/nm	a=b /nm	c/nm
TiO ₂ –A	54.2	22.6	-	-
TiO ₂ –R	19.5	33.9	0.4602	0.2972
SnO_2	30.5	22.3	0.4692	0.3151
$Ti_{0.5}Sn_{0.5}O_2$	86.4	10.2	0.4640	0.3058
10Ce/TiSn	75.6	-	-	-
Ce/Ti	47.3	-	-	-



⁵⁵ As listed in Table 2, the relative content of Ce³⁺ increased from 17.0% in Ce/Ti to 35.1% in 10Ce/TiSn. Meanwhile, in terms of Sn 3d, it can be seen that the bands of 10Ce/TiSn shifted to lower binding energy comparing to these of pure SnO₂, indicating that part of low valence tin species existed over 10Ce/TiSn sample.
⁶⁰ However, the binding energies of Ti 2p for Ce/Ti and 10Ce/TiSn samples kept unchanged. Thus, the increase of Ce³⁺ over 10Ce/TiSn sample could be due to the synergetic interaction of CeO₂ and SnO₂ via the redox equilibrium of 2Ce⁴⁺ + Sn²⁺ ↔ 2Ce³⁺ + Sn⁴⁺, as reported by the previous studies.^{35, 36} In

addition, For the XPS spectra of O1s, the band of O' at 531.2 eV could be assigned to surface adsorbed oxygen species and the band of O" at 529.8 eV could be ascribed to lattice oxygen.³⁷ From data listed in Table 2, the relative content of O' over s 10Ce/TiSn was larger than that of Ce/Ti sample, which indicated that more surface adsorbed oxygen species were formed over 10Ce/TiSn sample. Therefore, in NH₃–SCR reaction, the synergetic interaction between CeO₂ and SnO₂ was beneficial to activate O₂ molecular to react with NO, which could improve the ¹⁰ "fast–SCR" route over Ce/TiSn.

3.4. Redox performances (H₂-TPR)

Published on 07 January 2015. Downloaded by University of Massachusetts - Boston on 11/01/2015 08:22:37.

In NH₃-SCR reaction, the reaction temperature window of NO removal rate largely depended on the redox properties of catalyst. Therefore, the influence of doping SnO₂ on the reducibility 15 performance of Ce/Ti was investigated by H₂-TPR. As shown in Fig. 6, pure CeO₂ displayed two peaks at ca. 500 and 780 °C, which could be respectively assigned to surface oxygen and bulk lattice oxygen reduction.³⁸⁻⁴⁰ In terms of pure SnO₂, a strong reduction peak located at 630 °C could be ascribed to the 20 reduction of Sn⁴⁺ to metal Sn.^{35, 41} In addition, TiSn solid solution displayed the similar redox behaviour as pure SnO_2 . The peak α of Ce/Ti could be ascribed to the dispersed CeO₂, and peak β was due to the reduction of bulk TiO2.^{42, 43} With regard to Ce/TiSn, peak α (150–500 °C) could be ascribed to the reduction of surface 25 species including Ce⁴⁺ or/and Sn⁴⁺ and peak β (above 500 °C) could be due to the reduction of bulk species including bulk TiSn and CeO₂. Compared with Ce/Ti and TiSn samples, peaks α and β of Ce/TiSn samples shifted to the lower temperature, it could be explained that the interaction between CeO₂ and SnO₂ evidenced 30 by XPS could improve the redox properties of Ce/TiSn. Considering the results of $NO + O_2$ reaction, it could be deduced that the better redox properties of Ce/TiSn promoted the occurrence of "fast-SCR" reaction and enhanced the NO removal

35 Table 2 The fitting data of XPS over Ce/Ti and 10Ce/TiSn.

rate at low temperature over Ce/TiSn.

Sample	Ce ³⁺ /(Ce ³⁺ +Ce ⁴⁺)/%	O'/(O' +O'')/%
Ce/Ti	17.0	23.9
10Ce/TiSn	35.1	39.5



3.5. Surface molecular adsorption (in situ DRIFT)

40 3.5.1. NH₃ adsorption–desorption

In order to investigate the differences of NH₃ adsorption behaviours over the samples induced by doping SnO₂, the DRIFT spectra of NH₃ adsorption-desorption were recorded from 150 to 350 °C. NH₃ adsorption results of pure TiO₂ and TiSn solid 45 solution were respectively shown in Fig. 7a and 7b. The triplet peaks in the range of 3100-3400 cm⁻¹ could be assigned to the N-H stretching vibration of coordinated NH₃, the peaks in the range of 1660-1680 cm⁻¹ and 1490-1450 cm⁻¹ could be ascribed to ionic NH₄⁺ bounded to Brønsted acid sites (denoted as B acids), so and the peaks in the range of 1610-1580 cm⁻¹ and 1160-1220cm⁻¹ could be assigned to the coordinated NH₃ bounded to Lewis acid sites (denoted as L acids).44,45 It could be seen that B acids totally desorbed after the temperature exceeded 300 °C and L acids still exhibited even at 350 °C, which indicated that L acid 55 sites were stronger acid sites than B acid sites over Ce/Ti and 10Ce/TiSn. Compared with pure TiO₂, the peaks of L acids at 1160–1220 cm⁻¹ obviously were widened in the range from 1100 cm⁻¹ to 1300 cm⁻¹ and the intensity of B acids at 1490–1450 cm⁻¹ increased over TiSn solid solution. It was reported that peak of L $_{60}$ acid appeared at about 1240–1250 cm $^{-1}$ for pure SnO $_2$ ⁴⁶ and Shen et.al⁴⁷ also found that a new peak of L acid at 1195 cm⁻¹ appeared for NH₃ adsorption over SnO₂/Al₂O₃ compared with pure Al₂O₃. Thus, L acid sites consisted of not only NH₃ bounded to TiO₂ at ca. 1180 cm⁻¹ but also NH₃ bounded to SnO₂ at ca. 1220 cm⁻¹ 65 over Ce/TiSn. It could be seen that doping SnO₂ into TiO₂ could enhance the sort and amount of acid sites over TiO2. As shown in Fig. 7c and 7d, Ce/Ti and 10Ce/TiSn respectively exhibited a similar spectrum as the corresponding support. By carefully comparing to pure supports, the peaks of NH₃ adsorption over 70 Ce/Ti and 10Ce/TiSn shifted to higher wavenumbers, implying that the adsorption behaviour of NH₃ was influenced probably by the interaction between CeO₂ and supports.



75 Fig. 7 In situ DRIFT spectra of NH₃ adsorption–desorption over TiO₂ (a), TiSn (b), Ce/Ti (c) and 10Ce/TiSn (d).

3.5.2. NO + O₂ adsorption-desorption

NO + O₂ adsorption–desorption spectra were recorded from 150 ⁸⁰ to 400 °C to investigate the adsorption differences of nitrogen oxides between Ce/Ti and 10Ce/TiSn samples. It was reported that IR active modes of nitrates adsorbed on metal oxides are located in 1650–1500 cm⁻¹ and 1300–1200 cm^{-1.48} As shown in Fig. 8a for Ce/Ti sample, different kinds of surface nitrate species formed during the process of NO + O₂ desorption. According to 5 the change regulation of peak intensity and precious studies, the

- peaks at 1616, 1579 and 1230 cm⁻¹ could be attributed to bridging nitrates (including bridging monodentate and bridging bidentate nitrates as shown in Fig. S5), the peaks at 1554 and 1245 cm⁻¹ could be ascribed to chelating bidentate nitrates, the peaks at
- ¹⁰ 1510 and 1286 cm⁻¹ could be assigned to monodentate nitrates, and the peak at 1351 cm⁻¹ could be due to free nitrate ions.⁴⁸ Raising the temperature from 150 to 400 °C, the intensity of monodentate nitrates continuously decreased and totally eliminated at 350 °C. Similarly, the peaks of bidentate nitrates 15 also decreased but still existed at 400 °C. However, the intensity of bridging nitrates increased firstly and then decreased. All the results indicate that the transformation from monodentate nitrates to bridging nitrates occurred during the process of thermal desorption, and the order of thermal stability for these nitrate 20 species followed bridging nitrates > bidentate nitrates > monodentate nitrates. In terms of 10Ce/TiSn sample shown in Fig. 8b, the peaks at 1612, 1575 and 1232 cm^{-1} , 1545 and 1250 cm⁻¹, 1510 and 1280 cm⁻¹ could be respectively assigned to bridging nitrates, chelating bidentate nitrates and monodentate 25 nitrates. The intensity of all peaks uniformly decreased with the increase of temperature and completely disappeared at 400 °C, which indicated that nitrate species over 10Ce/TiSn were continuously desorbing and the desorption of nitrate species over 10Ce/TiSn was easier than that of Ce/Ti. Our previous study 30 suggested that the adsorption of NO_x species on the surface of SnO₂ was considerably weak.³⁵ Based on the present results, it could be seen that doping SnO₂ resulted in weakening the adsorption ability of nitrate species over Ce/TiSn.



Fig. 8 In situ DRIFT spectra of NO + O₂ adsorption–desorption over Ce/Ti (a) and 10Ce/TiSn (b).



Fig. 9 In situ DRIFT spectra of NO + O_2 reaction with pre–adsorbed NH₃ over Ce/Ti (a) and 10Ce/TiSn (b) at 250 °C.



NH₃ was pre-adsorbed over Ce/Ti and 10Ce/TiSn samples for 1 h

followed by N₂ purging, and then NO and O₂ were introduced and the DRIFT spectra were collected as a function of time. The results of Ce/Ti sample were shown in Fig. 9a. The peaks at 1601 45 and 1178 cm⁻¹ due to L acids and the peaks of N–H stretching vibration in the range of 3100-3400 cm⁻¹ decreased with the increase of time and disappeared after 20 min. With the consumption of adsorbed NH₃, the peak at 1621 cm⁻¹ due to bridging nitrates and 1558 cm⁻¹ due to bidentate nitrates 50 appeared. It implied that NH₃ coordinated with L acid sites was the active species and the reaction between pre-adsorption NH₃ and NO + O₂ proceeded by Eley-Rideal (E-R) mechanism. As shown in Fig. 9b, the adsorption behaviours of 10Ce/TiSn were similar to those of Ce/Ti sample. The peaks of L acids at 1602 55 and 1188 cm⁻¹ gradually disappeared accompanying with the appearance of nitrate species, which indicates that E-R mechanism could proceed over 10Ce/TiSn sample. As reported elsewhere,44, 49 NH3-SCR process mainly followed E-R mechanism over tungsten or manganese modified Ce/TiO2 based 60 catalysts, and the reaction between adsorbed NH₃ species and NO gas was a key intermediate reaction. In addition, it is worth noting that the peaks of N-H stretching vibration in 3100-3400 cm⁻¹ and the peak at 1188 cm⁻¹ due to L acid mostly disappeared after 15min, and the consumption rate of NH₃ over 10Ce/TiSn 65 was faster than that of Ce/Ti, indicating that doping SnO₂ into TiO₂ promoted the activation of NH₃.



Fig. 10 In situ DRIFT spectra of NH₃ reaction with pre–adsorbed NO + O_2 over Ce/Ti (a) and 10Ce/TiSn (b) at 250 °C.

70 3.5.4. NH₃ adsorption after pre-adsorption NO + O₂

NO and O2 were pre-adsorbed over Ce/Ti and 10Ce/TiSn samples for 1 h followed by N₂ purging, NH₃ was introduced and the DRIFT spectra were recorded as a function of time. In terms of Ce/Ti shown in Fig. 10a, bridging nitrates at 1609, 1578 and ⁷⁵ 1238 cm⁻¹ and chelating bidentate nitrates at 1561 and 1257 cm⁻¹ formed. After injecting NH₃ for 10 min, L acids at 1600 and 1182 cm⁻¹ formed with N-H stretching peaks in the range of 3100- 3400 cm^{-1} . In the meantime, the peaks at 1506 and 1288 cm⁻¹ due to monodentate nitrates formed and the intensity of bidentate so nitrates at 1561 and 1257 cm⁻¹ increased with the intensity of bridging nitrates at 1609, 1578 and 1238 cm⁻¹ decreasing. NO + O₂ adsorption-desorption has demonstrated that the order of thermal stability followed bridging nitrates > bidentate nitrates > monodentate nitrates over Ce/Ti sample. Therefore, the 85 possibility that the disappearance of bridging nitrates was caused by thermal desorption could be ruled out. In addition, surface adsorption was saturated over the samples for 1 h NO+O₂ preadsorption judged from the DRIFT intensity of nitrate species. Thus, it could be deduced that competition adsorption happened 90 between bridging nitrates and gas NH₃. Combined with DRIFT results, it could be proposed that one NH3 molecular could snatch

an adsorption site from bridging nitrates to form one L acid, and then bridging nitrates transformed to monodentate and chelating bidentate nitrates over Ce/Ti as shown in Fig. S5. With regard to 10Ce/TiSn (in Fig. 10b), NH₃ adsorption resulted in the ⁵ disappearance of bridging nitrates at 1603, 1571 and 1231 cm⁻¹ after 10 min. Meanwhile the broad and asymmetric peaks at 1545 and 1255 cm⁻¹ including in monodentate and chelating bidentate nitrates increased. Thus, it could be seen that competition adsorption as shown in Fig. S5 also happened over 10Ce/TiSn

- ¹⁰ sample. It was worth noting that the competition adsorption over Ce/Ti and 10Ce/TiSn was beneficial to form L acids, which guaranteed the successful proceeding of NH₃-SCR reaction by E-R mechanism. After injecting NH₃ for 10 min, although L acids at 1597 and 1189 cm⁻¹ formed, the intensities of both nitrate spaces and NH bounded to L acids kent unchanged over Ce/Ti
- ¹⁵ species and NH₃ bounded to L acids kept unchanged over Ce/Ti and 10Ce/TiSn samples, indicating the adsorbed nitrate species could not react with the adsorbed NH₃ species. Therefore, NH₃– SCR reaction could not proceed by Langmuir–Hinshelwood (H– L) mechanism over Ce/Ti and 10Ce/TiSn.
- ²⁰ From the above results of *in situ* DRIFT, doping SnO₂ influenced the adsorption behaviors of both ammonia and nitrate species. Comparing to Ce/Ti sample, the adsorption behaviors over Ce/TiSn sample were characterized as following: 1. increasing the sorts of L acid sites; 2. weakening the adsorption of nitrates;
- ²⁵ 3. improving the activation of NH₃. *In situ* DRIFT results demonstrated that NH₃–SCR reaction proceeded by E–R mechanism over the studied samples, since the adsorption of nitrate species was weakened over Ce/TiSn by doping SnO₂, L acid sites were not easily blocked by nitrate species and could be ³⁰ highly effective to activate NH₃.

Sample	Weak acids $S_{\alpha}/a.u.$	Strong acids S _β /a.u.	Total acids $S_{\alpha} + S_{\beta}/a.u.$
TiO ₂ –A	6630	14038	20668
TiSn	7889	20224	28113
Ce/Ti	3756	9885	13461
10Ce/TiSn	5922	14597	20519

3.6. Surface acidities (NH₃-TPD)

- NH₃-TPD was carried out to further investigate the effect of ³⁵ doping SnO₂ on acid properties over the samples. As shown in Fig. 11, all the TPD curves could be fitted into peak α and peak β indicating two different kinds of acid species. NH₃ adsorption DRIFT had displayed that B acids totally desorbed at 300 °C and L acids still exhibited even at 350 °C, thus peak α for weak acid
- ⁴⁰ could be ascribed to B acid and peak β for strong acid could be assigned to L acid. As listed in Table 3, the amount of L acid was higher than that of B acid for all the samples. Meanwhile, the total acid amount of TiSn solid solution was larger than that of pure TiO₂, which indicated that surface acid sites of TiO₂ were
- ⁴⁵ added by doping SnO₂ due to the increase of specific surface area and the new added acid sites on SnO₂. When loading CeO₂ on TiO₂ and TiSn solid solution, the total acid amount of Ce/Ti and Ce/TiSn decreased compared with pure supports because of the decrease of specific surface area. Thus, NH₃-TPD results

⁵⁰ indicated that doping SnO₂ into TiO₂ could enhance the amount of acid sites over Ce/Ti sample.



Fig. 11 NH₃-TPD results of supports and catalysts.

4. Conclusions

ss Based on the all above results and discussion, Ce/TiSn sample exhibited better catalytic performances than Ce/Ti sample by doping SnO₂ into TiO₂, the reasons as following:

1. Rutile Ti_{0.5}Sn_{0.5}O₂ solid solution prepared by co–precipitation method displayed more excellent texture structure than pure ⁶⁰ anatase or rutile TiO₂, including larger specific surface area and better thermal stability in NH₃–SCR reaction.

2. H₂-TPR and XPS suggested that doping SnO_2 into TiO_2 improved the redox ability of Ce/TiO₂ and enhanced the interaction between CeO₂ and TiSn support, which contributed to ⁶⁵ the "fast-SCR" route and promoted the deNO_x activity at low temperature.

3. *In situ* DRIFT results suggested that competition adsorption happened between bridging nitrates and gas NH₃ and NH₃–SCR reaction proceeded by the Eley–Rideal mechanism over Ce/Ti ⁷⁰ and Ce/TiSn. Doping SnO₂ not only improved L acid sites to activate NH₃ but also weakened the adsorption ability of nitrates, which was conductive to push forward NH₃–SCR reaction by Eley–Rideal mechanism. In addition, NH₃–TPD demonstrated that the amount of acid sites increased by doping SnO₂.

75 Acknowledgements

The financial supports of the National Natural Science Foundation of China (Nos. 21303082, 21273110), Doctoral Fund of Ministry of Education of China (No. 2013009111005) and Sinopec Shanghai Research Institute of Petrochemical Technology are gratefully acknowledged.

Notes and references

^aKey Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, P. R. China

- 85 ^bJiangsu Key Laboratory of Vehicle Emissions Control, Center of Modern Analysis, Nanjing University, Nanjing 210093, PR China Corresponding author:
- *Fax:* +86 25 83317761; *Phone:* +86 25 83592290
- Address: Hankou Road 22#, Nanjing, Jiangsu province, P. R. China, 90 210093
- E-mail address: <u>donglin@nju.edu.cn</u> (L. Dong); <u>tangcj@nju.edu.cn</u> (C. J. Tang)

Published on 07 January 2015. Downloaded by University of Massachusetts - Boston on 11/01/2015 08:22:37

- G. Liu and P.-X. Gao, Catal. Sci. Technol., 2011, 1, 552-568. 1
- 2 M. F. Fu, C. Li, P. Lu, L. Qu, M. Y. Zhang, Y. Zhou, M. G. Yu and Y. Fang, Catal. Sci. Technol., 2014, 4, 14-25.
- 53 G. Buscaa, L. Liettib, G. Ramisa and F. Berti, Appl. Catal. B: Environ., 1998, 18, 1-36.
- 1 P. Forzatti, Appl. Catal. A: Gen., 2001, 222 221-236.
- 5 P. G. Smirniotis, D. A. Pena and B. S. Uphade, Angew. Chem. Int. Ed., 2001, 40, 2479-2481.
- M. Suzana, P. Francisco and V. R. Mastelaro, Chem. Mater., 2002, 10 6 14, 2514-2518.
- 7 F. D. Liu, Y. B. Yu and H. He, Chem. Commun., 2014, 50, 8445-8463.
- 8 F. D. Liu, W. P. Shan, X. Y. Shi, C. B. Zhang and H. He, Chin. J. Catal., 2011, 32, 1113-1128. 15
 - 9 X. Gao, Y. Jiang, Y. Zhong, Z. Y. Luo and K. F. Cen, J. Hazard. Mater., 2010, 174, 734-739.
 - W. P. Shan, F. D. Liu, H. He, X. Y. Shi and C. B. Zhang, 10 ChemCatChem, 2011, 3, 1286-1289.
- 20 11 X. Gao, Y. Jiang, Y. C. Fu, Y. Zhong, Z. Y. Luo and K. F. Cen, Catal. Commun., 2010, 11, 465-469.
 - 12 Y. Wang, X. Jiang and Y. Xia, J. Am. Chem. Soc., 2003, 125, 16176-16177.
 - 13 K. Zakrzewska, Thin Solid Films, 2001, 391, 229-238
- 25 14 M. EpifaniJoan, D. Prades, E. Comini, E. Pellicer, M. Avella, P. Siciliano, G. Faglia, A. Cirera, R. Scotti, F. Morazzoni and J. R. Morante, J. Phys. Chem. C, 2008, 112, 19540-19546.
 - 15 L. Z. Liu, T. H. Li, X. L. Wu, J. C. Shen and P. K. Chu, J. Raman Spectrosc., 2012, 43, 1423-1426.
- 30 16 S. K. Kulshreshtha, R. Sasikala and V. Sudarsan, J. Mater. Chem., 2001, 11, 930-935.
 - 17 H. Uchiyama and H. Imai, Chem. Commun., 2005, 6014-6016.
- 18 L. H. Dong, L. L. Zhang, C. Z. Sun, W. J. Yu, J. Zhu, L. J. Liu, B. Liu, Y. H. Hu, F. Gao, L. Dong and Y. Chen, ACS Catal., 2011, 468-480. 35
- 19 C. Sun, L. Dong, W. Yu, L. Liu, H. Li, F. Gao, L. Dong and Y. Chen, J. Mol. Catal. A: Chem., 2011, 346, 29-38.
- 20 L. H. Dong, B. Zhang, C. J. Tang, B. Li, L. Y. Zhou, F. Z. Gong, B. Z. Sun, F. Gao, L. Dong and Y. Chen, Catal. Sci. Technol., 2014, 4, 482-493
- 21 H. Z. Chang, X. Y. Chen, J. H. Li, L. Ma, C. Z. Wang, C. X. Liu, J. W. Schwank and J. M. Hao, Environ. Sci. Technol., 2013, 47, 5294-5301
- 22 E. W. McFarland and H. Metiu, Chem. Rev., 2013, 113, 4391-4427.
- 45 23 C. Ciardelli, I. Nova, E. Tronconi, D. Chatterjee and B. Bandl-Konrad, Chem. Commun., 2004, 2718-2719.
- E. Tronconi, I. Nova, C. Ciardelli, D. Chatterjee and M. Weibel, J. 24 Catal., 2007, 245, 1-10.
- 25 A. Grossale, I. Nova, E. Tronconi, D. Chatterjee and M. Weibel, J. Catal., 2008, 256, 312-322.
- 26 A. Grossale, I. Nova and E. Tronconi, J. Catal., 2009, 265, 141-147. 27 R. K. Srivastava, C. A. Miller, C. Erickson and R. Jambhekar, J. Air
- Waste Manage., 2004, 54, 750-762. 28 Z. G. Huang, Z. P. Zhu and Z. Y. Liu, Appl. Catal. B: Environ., 2002,
- 39, 361-368. 29 C.-H. Lin and H. Bai, Ind. Eng. Chem. Res., 2004, 43, 5983-5988.
- W. Shan, F. Liu, H. He, X. Shi and C. Zhang, Appl. Catal. B: 30 Environ., 2012, 115-116, 100-106.
- 31 G. Qi and R. T. Yang, Appl. Catal. B: Environ., 2003, 44, 217-225.
- 60 32 X. Z. Ding, Z. A. Qi and Y. Z. He, NanoStruct. Mater., 1994, 4, 663-668.
- 33 S. Watanabe, X. L. Ma and C. S. Song, J. Phys. Chem. C, 2009, 113, 14249-14257
- 34 A. J. Silvestre, R. F. Rodríguez and E. A. Sepúlveda, J. Catal., 2002, 210, 127-136.
- 35 X. J. Yao, Y. Xiong, W. X. Zou, L. Zhang, S. G. Wu, X. Dong, F. Gao, Y. Deng, C. J. Tang, Z. Chen, L. Dong and Y. Chen, Appl. Catal. B: Environ., 2014, 144, 152-165.

- 36 T. Baidya, A. Gupta, P. A, Deshpandey, G. Madras and M. S. Hegde, J. Phys. Chem. C, 2009, 113, 4059-4068.
- 37 D. R. Sellick, A. Aranda, T. García, J. M. López, B. Solsona, A. M. Mastral, D. J. Morgan, A. F. Carley and S. H. Taylor, Appl. Catal. B: Environ., 2013, 132-133, 98-106.
- M. J. Sun, G. J. Zou, S. Xu and X. L. Wang, Mater. Chem. Phys., 38 75 2012, 134, 912-920.
- W. Miśta, M. A. Małecka and L. Kępiński, Appl. Catal. A: Gen., 39 2009, 368, 71-78.
- 40R. Qu, X. Gao, K. Cen and J. Li, Appl. Catal. B: Environ., 2013, 142-143.290-297.
- 80 41 X. J. Yao, C. J. Tang, Z. Y. Ji, Y. Dai, Y. Cao, F. Gao, L. Dong and Y. Chen, Catal. Sci. Technol., 2013, 3, 688-698.
- 42 P. R. Ettireddy, N. Ettireddy, S. Mamedov, P. Boolchand and P. G. Smirniotis, Appl. Catal. B: Environ., 2007, 76, 123-134.
- 43 S. Watanabe, X. L. Ma and C. S. Song, J. Phys. Chem. C, 2009, 113, 14249-14257.
- 44 L. Chen, J. H. Li and M. G. Fa, Environ. Sci. Technol., 2010, 44, 9590-9596.
- D. Wang, L. Zhang, K. Kamasamudram and W. S. Epling, ACS 45 Catal., 2013, 3, 871-881.
- 90 46 P. G. Harrisona and E. W. Thornton, J. Chem. Soc. Faraday Trans., 1975.71.1013-1020.
- 47 J. Y. Shen, R. D. Cortright, Y. Chen and J. A. Dumesic, Catal. Lett., 1994, 26, 247-257.
- 48 K. I. Hadjiivanov, Catal. Rev., 2000, 42, 71-144
- 95 49 Z. B. Wu, B. Q. Jiang, Y. Liu, H. Q. Wang and B. R. Jin, Environ. Sci. Technol., 2007, 41, 5812-5817.

8 | Journal Name, [year], [vol], 00-00