Influence of tin doping on the activity and mechanism of 1 CeO₂ catalyst for selective catalytic reduction of NO_x with 2 NH₃ 3 Jingsong Zhou^{1*}, Yanping Du^{2*}, Yuqing Qiao¹, Fei Zhou³, Zhou Liu⁴, Zhibo Xiong^{1**}, Mengqi 4 5 Liu⁵, Wei Lu¹ 6 (1. School of Energy and Power Engineering, University of Shanghai for Science & Technology, Shanghai, 200093, China 7 2. School of Engineering, Lancaster University, Lancaster, LA1 4YW, UK 8 3. Jiangsu Guoxin Research Institute Co., Ltd., Nanjing 210000, Jiangsu, China 9 4. Jiangsu Guoxin Jingjiang Power Co. Ltd., Jingjiang 214500, Jiangsu, China 10 5. School of Physics and Technology, University of Jinan, Jinan, 250022, China) 11 Abstract: 12 Herein, the gelatin bio-template sol-gel self-combustion was confirmed to fabricate fluorite 13 structured CeO₂ catalyst with a high crystallinity, although the doping of Sn improved its 14 NH₃-SCR activity at medium-low temperatures due to the incorporating into the lattice of 15 crystals. Furthermore, this doping restricted the growth of both SnO₂ and CeO₂ crystals in the 16 mixed oxide catalyst and enlarged the BET surface area of CeO_2 catalyst. Moreover, $Ce_4Sn_2O_2$ 17 presented the best catalytic performance mainly attributed to the largest low-temperature reactive 18 oxygen species and weak acid sites. DFT calculations demonstrated that the doping of Sn 19 induced new reactive sites formed on the $CeO_2(111)$ surface and reduced the total energy barrier 20 of NH₃-SCR reaction. Furthermore, the doping of Sn changed the reaction path, and the 21 decomposition process of NH4NO2 intermediate was the found as rate determining step for the 22 NH_3 -SCR reaction over Sn-CeO₂ (111), which was different from the activation of NH_3 species on CeO₂ (111). 23 24 Keywords: NO_x reduction, Catalyst, Cerium oxide, gelatin bio-template, Sn-doping, Promotional effect 25

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29 1. Introduction

30 As one of the main pollutants from mobile and stationary sources, large emissions of 31 nitrogen oxides can cause severe environmental problems, including acid rain, greenhouse effect 32 and particulate matter pollution [1], and many technologies have been developed and applied to control the emission of NO_x [2]. Among them, selective catalytic reduction with ammonia 33 34 (NH₃-SCR) has attracted large attention due to high de-nitrification efficiency [3], and V2O5-WO3(MoO3)/TiO2 catalysts have been widely used in commercial applications with a high 35 36 NH₃-SCR activity in the temperature window of 300-400 °C [4]. Nonetheless, there are some 37 problems to be overcome further in the industrial applications, including the bio-toxicity of vanadium species, the poisoning of alkali metal, the catalytic conversion of partial SO_2 to SO_3 at 38 39 high-temperature and so on [5]. Therefore, it is necessary to develop new non-toxic catalysts 40 with a wide active temperature window suitable for multi-condition environments.

41 Due to the unique 4f orbitals of cerium atom, CeO_2 exhibits excellent redox properties via the switching of Ce³⁺/Ce⁴⁺, and thus cerium-based catalysts have attracted attention owing to the 42 43 strong oxygen storage capacity. However, the weak surface acid sites restrict the NH₃-SCR 44 activity of single cerium oxide catalyst [6]. Therefore, many metal oxides have been doped to 45 optimize the surface acid sites of CeO₂ catalyst, and a series of cerium-based mixed oxide catalysts, including Mn-Ce/TiO₂ [7], Ce-W@TiO₂ [8], CeO₂/MnO_x [9] and so on, have been 46 47 developed and present good NH₃-SCR activity. Different from these doped metal oxides, SnO₂ 48 exhibits similar redox properties to CeO_2 via the conversion of Sn^{4+}/Sn^{2+} [10], and Ce-Sn binary 49 catalysts have been applied in various catalytic fields such as NO_x reduction [11], CO oxidation 50 [12], soot combustion [13], Electro-oxidation [14], diesel exhaust treatment [15], gas sensors [16] 51 and photo-catalytic degradation [17], etc. Li et al. pointed out that the Ce-Sn mixed oxide 52 catalysts synthesized via an inverse co-precipitation method achieved over 90% of NO_x reduction at 250-400 °C under a gas hourly space velocity (GHSV) of 20,000 h⁻¹ 53 54 [18]. Furthermore, the doped Sn species has also been regarded to induce an electron transfer between Ce³⁺ and Sn⁴⁺, which contributes to enhancing the oxygen adsorption capacity and 55 56 NH₃-SCR activity of cerium oxide catalyst. However, the preparation methods may affect the 57 interaction of Ce and Sn species and the catalytic performance of cerium-tin mixed oxide. Zhang 58 et al. proposed that compared to co-precipitation, the synthesized H-CeSnTiO_x-E catalyst via the

59 solvothermal method presented a larger specific surface area and more crystal defects, thereby 60 exhibited a good NH₃-SCR activity at medium-low temperatures [19]. Zhao et al. found that the 61 synthesized CeO₂-SnO₂ catalysts via hydrothermal method exhibited superior redox performance 62 and lager acid sites than the catalyst prepared by co-precipitation, and the former also presented stronger resistance to K poisoning [20]. Meanwhile, Ferenc Martinovic pointed out that the 63 64 CeO₂-SnO₂ catalyst synthesized via the co-precipitation method showed good NH₃-SCR activity 65 as a nitrate donor, which also provided more active intermediates for the oxidation of 66 hydrocarbons [21]. Owing to simplicity, low-cost, environmental friendliness and specific structure morphology, the bio-templates, including cotton, eggshells, wood and willow catkins, 67 68 have been widely used to fabricate porous nano-materials, which present good activity in many 69 catalytic fields [22].

70 As a denatured product of collagen, gelatin is the main structural protein in animal skin and 71 bone connective tissue and is composed of one single chain of three amino acid chains existing in collagen [23]. Furthermore, there exist various functional groups (e.g., -CO-NH₂, -COOH, 72 73 -NH₂) for the amino acids of gelatin, which can coordinate and chelate with numerous metal ions 74 well [24]. Thus, gelatin renders suitable as a structural directing agent and bio-template to 75 synthesize the nano-materials with large specific surface area and porous structure. For instance, 76 Shen et al. reported that the synthesized nano Y-Al₂O₃ material through the gelatin bio-template 77 method had a high specific surface area of $262 \text{ m}^2/\text{g}$ with an average pore diameter of 6.3 nm 78 [25]. Additionally, a star-shaped zinc oxide (ZnO) had been prepared via the hydrothermal 79 method with gelatin as the bio-template, and it was found that the gelatin not only served as a 80 soft biological template to restrict the growth of ZnO nanorods, but also performed as a guiding 81 agent for assembly to convert nanorods into star shaped nanostructures [26]. Therefore, the 82 application of gelatin bio-template might regulate the pore-structure or/and other properties of 83 cerium-based catalyst, which play an important role in the NH₃-SCR reaction.

The determination of specific reaction steps helps reveal the NH₃-SCR mechanism, which also plays an important role on the development of novel catalysts. For example, Liu et al. conducted the density functional theory (DFT) calculation to determine the entire NH₃-SCR cycle process of the Ce-Ti catalyst and investigated the inhibitory effects of K poisoning on the formation of Brønsted acid sites of catalyst and the continuous dehydrogenation of NH₃ on the 89 CeO₂/TiO₂ catalyst surface [27]. Furthermore, the NH₃-SCR reaction mechanism of the 90 tungsten-doped CeO₂ (W-CeO₂) catalyst had also been studied through DFT calculations and a 91 comprehensive catalytic cycle was outlined by highlighting the dominant position of the 92 Langmuir-Hinshelwood (L-H) mechanism in the entire NH₃-SCR process. Therefore, DFT 93 calculation is an effective computational tool to reveal the NH₃-SCR mechanism of catalysts 94 [28]. Meanwhile, there are relatively few studies on using DFT calculations to reveal the 95 mechanism of Ce-Sn mixed oxide catalyst.

96 In this study, gelatin bio-template was firstly used to fabricate cerium-tin mixed oxide 97 catalyst for NH₃-SCR reaction via the sol-gel self-combustion method, and the influence of Sn-doping on the activity and physical-chemical properties of CeO₂ catalyst was also 98 99 investigated. The results indicate that the gelatin bio-template sol-gel self-combustion method 100 contributes to fabricating the high crystallite of fluorite structure CeO₂, and the doping of Sn 101 exhibits a good promotional effect on the NH₃-SCR activity of the as-fabricated CeO₂ 102 catalyst. Furthermore, DFT calculations were performed to reveal the NH₃-SCR mechanisms 103 over both fluorite-structured CeO₂ (111) and Sn-CeO₂ (111) models herein. This study provides 104 experimental and theoretical guidance for the development of cerium-based catalyst for NH₃-SCR reactions. 105

106 2. Experimental sections

107 2.1 Catalyst preparation, characterization and activity evaluation

108 Cerium nitrate (Ce(NO₃)₃·6H₂O, AR), stannous chloride (SnCl₂·2H₂O, AR) and gelatin (AR) 109 were used as the precursors and bio-template, which were purchased from Sinopharm Group 110 Chemical reagent Co., LTD without further treatment. The synthesis of cerium-tin mixed oxide 111 catalyst via the gelatin bio-template sol-gel self-combustion method is listed as follows: a certain 112 amount of gelatin, Ce(NO₃)₃·6H₂O and SnCl₂·2H₂O were dissolved sequentially in 10 ml 113 de-ionized water to obtain a mixed solution. After being magnetically stirred at room temperature 114 for 4 h, the obtained uniform mixed solution was then stirred in a 50 °C water bath until the magnetic rotor stopped rotating, and then was further dried at a 30 °C water bath for 12 h. Finally, 115 116 the obtained gelatin gel was ignited at 500 °C in a muffle furnace, and then the powder after 117 ignition was calcined at 550 °C for 5 h to obtain the cerium-tin mixed oxide catalyst. For 118 simplicity, the synthesized catalysts are labeled as CeO₂, Ce₄Sn₂O₂, Ce₃Sn₃O₂, Ce₂Sn₄O₂ and

SnO₂ by controlling the added amount of Ce(NO₃)₃·6H₂O and SnCl₂·2H₂O in the above mixed
solution based on different molar ratios.

A series of characterization methods, including X-ray diffraction (XRD), N₂ adsorption desorption, hydrogen temperature programmed reduction (H₂-TPR), Raman, Inductively Coupled Plasma (ICP-AES), X-ray photoelectron spectroscopy (XPS) and ammonia temperature-programmed desorption (NH₃-TPD) were adopted to study the influence of Sn-doping on the physical-chemical properties of CeO₂ catalyst prepared by the gelatin bio-template sol-gel self-combustion method. And the detailed testing process is given in supporting information (SI).

128 The NH₃-SCR activity of catalyst was measured in a fixed-bed quartz tube reactor at 129 200~500 °C using 0.6 g sample. The typical reaction gases are composed of 500 ppm NH₃, 500 ppm NO, 5 vol.% O2 and 99.999 vol.% N2 as the balance gas. The total rate of reaction gas was 130 131 2000 mL/min corresponding to a GHSV of 200,000 mL/(g·h). After the reaction system reached 132 the stable state, the concentrations of NO_x at the inlet and outlet were measured using a flue gas 133 analyzer (Model 60i, ThermoFisher Scientic Co. Ltd, USA). The conversion of NO_x was 134 calculated according to the following equation: NO_x conversion(%) =(1-[NO_x]_{out}/[NO_x]_{in})×100% 135 (1), where $[NO_x]_{out}$ and $[NO_x]_{in}$ represent the outlet and inlet concentrations of NO_x $(NO_x = NO + NO_2)$, respectively. 136

137 2.2 DFT calculation method

138 In this study, DFT calculations were performed using the Dmol3 package within Materials Studio 2020. To enhance the computational accuracy, the generalized gradient approximation 139 (GGA) with the Perdew-Burke-Ernzernhof (PBE) functional, augmented with a U_{eff} = 5 eV 140 141 correction for the orbitals of Ce 4f, was employed to treat the electronic exchange-correlation 142 energy functional [29]. A double numerical basis set with polarization functions (DNP) was 143 utilized, and the k-points in the Brillouin zone were set to 4x4x4. The convergence criterion for self-consistent field iterations was set to 1.0×10^{-6} [30]. To accelerate the convergence, a smearing 144 145 width of 0.01 Ha was adopted. During the geometry optimization, the convergence criteria for 146 the model energy, gradients and maximum displacements were set to 1.0×10^{-5} Ha, 0.002 Ha/Å 147 and 0.005 Å with an orbital cutoff radius of 5.8 Å, respectively. The complete LST/QST method 148 was employed for searching transition states [31]. The adsorption energy (E_{ads}) was calculated

- 149 using the following equation:
- 150 $E_{ads} = E_{(adsorbate+adsorbent)} E_{adsorbate} E_{adsorbent}$ (2)
- 151 where $E_{(adsorbate+adsorbent)}$ is the total energy of the adsorbent-adsorbate system, $E_{adsorbate}$ and
- 152 $E_{adsorbent}$ are the energies of adsorbate and adsorbent alone, respectively.
- 153 The oxygen vacancy energy (E_{vac}) was calculated using the following equation
- 154 $E_{vac} = E_{(adsorbent-vac)} 1/2E_{(O_2)} E_{adsorbent}$ (3)
- where $E_{(adsorbent-vac)}$ is the energy of oxygen vacancies on the surface of the model, $E_{(O_2)}$ is the energy of gaseous O₂ molecules.
- 157 The energy barrier, representing the energy that must be overcome during a chemical158 reaction, was calculated using the equation:

$$159 \qquad E_{\text{nergy barrier}} = E_{\text{TS}} - E_{\text{IS}} \tag{4}$$

where E_{TS} and E_{IS} are the energies of the transition state and the initial state during the
 reaction, respectively.

- 162 3. Results and discussions
- 163 3.1 NH₃-SCR activity and Catalyst characterization
- 164 3.1.1 Catalytic performance and XRD pattern

Fig.1 presents the effect of Sn-doping on the NH₃-SCR activity and XRD pattern of CeO₂ 165 166 catalyst prepared via the gelatin bio-template sol-gel self-combustion method. As depicted in 167 Fig.1(A), the fabricated CeO_2 catalyst presents poor NH₃-SCR activity, and its conversions of NO_x at 450-500 °C are even lower than zero, which might be attributed to the catalytic oxidation 168 169 of NH₃ to NO_x over CeO₂ catalyst at high temperatures [32]. This demonstrates that highly 170 crystalline fluorite structure CeO₂ crystals might be formed in the as-fabricated CeO₂ 171 catalyst. Similarly, the as-fabricated SnO₂ catalyst via this method also shows poor NH₃-SCR 172 activity. However, the doping of Sn improves the NH₃-SCR activity of CeO₂ catalyst effectively, and the suitable molar ratio of Sn/Ce is 2:4. Furthermore, the as-fabricated Ce₄Sn₂O_z catalyst 173 achieves higher than 80% of NOx reduction within the temperature range of 350-450 °C under a 174 175 high GHSV of 200,000 mL/(g·h), which is higher than the reported Ce/Sn-based catalyst 176 summarized in the Table S1 in Supporting Information. The results of XRD pattern in Fig.1(B) indicate that high crystalline crystals of SnO₂ and fluorite-structured CeO₂ are formed in the 177

as-fabricated cerium-tin mixed oxide catalysts. This indicates that the gelatin bio-template 178 179 sol-gel self-combustion method is beneficial in synthesizing the high crystalline metal oxide 180 catalysts. However, the doping of Sn restricts the crystallization and growth of fluorite structure 181 CeO₂, and the as-fabricated Ce₄Sn₂O_z, Ce₃Sn₃O_z and Ce₂Sn₄O_z catalysts also present weaker XRD pattern of tin oxide crystal than that of SnO₂ catalyst. Furthermore, the doping of Sn makes 182 183 the diffraction peaks of fluorite structure CeO₂ crystals shift towards higher angles, suggesting 184 the formation of Ce-Sn solution in the cerium-tin mixed oxide catalysts due to the incorporation 185 of Sn species into the lattice of fluorite structure CeO₂. According to the detected XRD patterns, the inter-planar spacing, lattice parameters and crystallite sizes of fluorite structure CeO₂ and 186 SnO₂ for the as-fabricated cerium-tin mixed oxide catalysts are given in Table S2 based on their 187 prominent lattice diffraction peaks located at about 28.5 ° and 26.6 °, respectively. It can be 188 found that the doping of Sn leads to a slight decrease in the lattice parameters of fluorite-189 190 structured CeO₂, indicating partial substitution of Ce with Sn atom, especially for the 191 as-fabricated Ce₄Sn₂O_z catalyst. Furthermore, this catalyst presents the smallest crystallite sizes of both SnO_2 and fluorite structure CeO₂ compared with Ce₃Sn₃O_z and Ce₃Sn₃O_z, which implies 192 193 Ce and Sn species has the best interaction, and excessive tin is not conducive to the substitution 194 of Ce and the formation of Ce-Sn solid solution.



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199 3.1.2 Raman spectra

Raman spectroscopy was employed to further investigate the effect of Sn-doping on the microstructure of CeO₂ catalyst and the results are shown in Fig.2. The as-fabricated catalysts 202 exhibit the distinct Raman characteristic band at 466 cm⁻¹, which is attributed to the oxygen 203 breathing frequency (F_{2g} mode) around Ce⁴⁺ ions in cubic fluorite CeO₂ [33], and a new Raman 204 band appears at 464 cm⁻¹ for the as-fabricated cerium-tin mixed oxide catalysts after the doping of Sn, which indicates that Sn atoms might be doped into the lattice of cubic fluorite CeO₂ and 205 results in the lattice distortion. Furthermore, the enhancement of Sn/Ce molar ratio from 2:4 to 206 207 4:2 decreases the intensity of Raman peak at 464 cm⁻¹, but the full width at half maximum of this 208 peak increases, suggesting that the doping of Sn is indeed conducive to refine the particle size of 209 cubic fluorite CeO₂, which is consistent with the results of XRD pattern. Additionally, the Raman band at approximately 630 cm⁻¹ attributed to Sn-O species was detected for the as-fabricated 210 $Ce_4Sn_2O_z$, $Ce_3Sn_3O_z$ and $Ce_4Sn_2O_z$ catalysts, especially the former, which show that more Ce-Sn 211 212 solid solution is formed in $Ce_4Sn_2O_z$ catalyst [34].



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Fig.2 The Raman spectra of the as-fabricated cerium-tin mixed oxide catalysts.

215 3.1.3 N₂ adsorption-desorption

216 Fig.3(A) depicts the N_2 adsorption-desorption isotherms of the as-fabricated cerium-tin 217 mixed oxide catalysts measured at liquid nitrogen temperature. It can be found that according to 218 IUPAC classification, the as-fabricated catalysts exhibit a typical Type IV adsorption-desorption 219 isotherm, indicating the presence of meso-porous structure. Furthermore, the hysteresis loops of 220 the N_2 adsorption-desorption isotherms are a typical H3 type, suggesting the presence of slit-like pore structure for the catalysts [35]. It should be mentioned that the hysteresis loop closing point 221 222 (p/p_0) of Ce₄Sn₂O_z catalyst at low pressure is lower than those of the other as-fabricated 223 catalysts. This indicates that more micro/meso-pores are formed in it. The BJH pore size

224 distributions in Fig.3(B) illustrates that the as-fabricated CeO₂ catalyst has a broad pore size 225 distribution of 2-80 nm with two peaks located at around 3-4 and 20-40 nm. Furthermore, the doping of Sn contributes to increasing the meso-porous formed in the as-fabricated CeO₂ 226 catalyst. Especially, $Ce_4Sn_2O_z$ exhibits the largest meso-pores of 3-6 nm. The cumulative pore 227 volumes in Fig.S1 also demonstrate that the doping of Sn increases the pore volume of CeO₂ 228 catalyst, especially the pore volume lower than 30 nm. In addition, Ce₄Sn₂O_z presents an 229 appropriate ratio of micropores (<2 nm), mesopores (2-50 nm) and macropores (>50 nm), which 230 231 had been considered as an important reason for the high NH₃-SCR activity of iron-titanium mixed oxide catalyst [36]. As shown in Table 1, the doping of Sn is advantageous in increasing 232 the BET surface area and pore volume of the as-fabricated CeO₂ catalyst, and Ce₄Sn₂O_z has the 233 234 minimum average pore diameter and maximum S_{BET} , which might be an important reason for its 235 best NH₃-SCR activity compared with the other catalysts in this study.



237 Fig.3 The N₂ adsorption-desorption isotherms (A) and pore size distributions (B) of the as-fabricated cerium-tin

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Table 1 The structural parameters of the as-fabricated cerium-tin mixed oxide catalysts

mixed oxide catalysts.

	BET surface area ^a	Pore volume ^b	Pore diameter ^c		
Samples	(m ² /g)	(cm ³ /g)	(nm)		
CeO ₂	24.2	0.066	9.8		
Ce ₄ Sn ₂ O _z	54.4	0.127	8.0		
Ce ₃ Sn ₃ O _z	37.9	0.111	9.8		
$Ce_2Sn_4O_z$	31.3	0.089	9.0		
SnO ₂	22.8	0.027	9.9		

- a BET surface area
- 241 ^b BJH desorption pore volume
- ^c BJH desorption pore diameter
- 243 3.1.4 XPS spectra and ICP

The XPS technique was used to further study the influence of Sn-doping on the atomic 244 245 concentrations and the chemical states of species on the surface of CeO₂ catalyst, and the results 246 are given in Fig.4 and Table 2. According to the de-convoluted XPS spectra of Ce 3d using a 247 Gaussian-Lorentzian function in Fig.4(A), it can be found that the Ce 3d XPS spectra of catalysts can be fitted into eight peaks, which are assigned to the $3d^{10}4f^1$ initial electronic state of $Ce^{3+}(u)$ 248 and v'), and the 3d¹⁰4f⁰ electronic state of Ce⁴⁺ ions (u, u", u", v, v" and v") [37], respectively. And 249 the doping of Sn makes the binding energies of peaks attributed to Ce³⁺ and Ce⁴⁺ shift to higher 250 energy. This confirms the interaction of cerium and tin species again. However, this doping 251 decreases the molar ratio of $Ce^{3+}/(Ce^{3+}+Ce^{4+})$ on the surface of CeO_2 catalyst, although the 252 presence of Ce3+ had been generally considered to result in the charge imbalance, oxygen 253 vacancies and unsaturated chemical bonds via the switching of Ce³⁺/Ce⁴⁺ [38]. Furthermore, the 254 255 enhancement of Sn-doping molar ratio from 2:4 to 4:2 further decreases the surface molar ratio of Ce³⁺/(Ce³⁺+Ce⁴⁺) from 21.4% to 19.4%. As a result, the doping of Sn might restrict the redox 256 cycle of Ce^{3+}/Ce^{4+} on the as-fabricated CeO_2 catalyst surface. It is worth mentioning that 257 Ce₄Sn₂O_z presents larger surface concentrations of Ce³⁺ or/and Ce⁴⁺ than CeO₂ catalyst (Table 258 259 2). This indicates that the doped Sn can combine with the oxygen species from the surface of 260 CeO₂ catalyst via the formation of Ce-O-Sn bond on the Ce₄Sn₂O_z surface, which also decreases 261 the surface concentration of total oxygen.

262 The XPS spectra of O 1s in Fig.4(B) demonstrates the presence of chemically adsorbed 263 water (O_{α}), active oxygen/hydroxyls (O_{β}) and lattice oxygen (O_{γ}) on the surface of cerium-tin 264 mixed oxide catalysts [39]. Compared to SnO₂ catalyst, CeO₂ exhibits lower binding energies of O_{α} , O_{β} and O_{γ} , and the doping of Sn further decreases the values of these three binding energies, 265 266 indicating a significant change in the electron cloud density around the O atoms on the CeO_2 267 catalyst surface, and new Ce-O-Sn bond might be formed on the catalyst surface. Furthermore, the doping of Sn improves the molar ratio of $(O_{\alpha}+O_{\beta})/(O_{\alpha}+O_{\beta}+O_{\gamma})$ on the CeO₂ catalyst surface, 268 and this promotional effect further increases with the enhancement of Sn-doping amount. It is 269

270 generally believed that the presence of Ce^{3+} contributes to the formation of O_{α} and O_{β} , which is 271 the important reason for high NH₃-SCR activity of cerium-based catalyst [40]. Interestingly, the 272 as-fabricated SnO₂ catalyst exhibits larger surface molar ratio of $(O_{\alpha}+O_{\beta})/(O_{\alpha}+O_{\beta}+O_{\gamma})$ than the 273 CeO₂ catalyst. This demonstrates that the redox cycle of Sn²⁺/Sn⁴⁺ also contributes to the 274 formation of active surface oxygen. Furthermore, the fabrication of Ce-O-Sn bond increases the 275 surface O_β concentration of CeO₂ catalyst.

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Table 2 The compositions of the as-fabricated cerium-tin mixed oxide catalysts

Samples -	Atomic Concentrations (%)						Mass Concentrations(%) ^b			
	Ce ³⁺	Ce ⁴⁺	Ce _{total}	Sn	Οα	O_{β}	\mathbf{O}_{γ}	Ototal ^a	Ce	Sn
CeO ₂	5.1	17.8	22.9	-	2.8	18.0	56.3	77.1	-	-
Ce ₄ Sn ₂ O _z	5.7	20.8	26.5	6.1	3.9	32.4	31.1	67.4	63.6	16.1
Ce ₃ Sn ₃ O _z	4.1	16.3	20.4	10.6	12.3	28.5	28.2	69.0	54.2	25.8
Ce ₂ Sn ₄ O _z	3.6	14.9	18.5	13.1	11.6	35.3	21.5	68.4	47.5	31.3
SnO_2	-	-	-	27.1	5.4	22.2	45.3	72.9	-	-

 $277 \qquad {}^{a}O_{total} = O_{\alpha} + O_{\beta} + O_{\gamma}$

^bCalculated by ICP







Fig.4 Ce 2p (A) and O 1s (B) XPS spectra of the as-fabricated cerium-tin mixed oxide catalysts.

The XPS spectra of Sn 3d in Fig.S2 confirms the presence of both Sn⁴⁺ and Sn²⁺ species on the surface of cerium-tin mixed oxide catalysts with two XPS peaks belonging to Sn 3d 5/2 and Sn 3d 3/2, separately [41]. Meanwhile, the formed interaction of cerium and tin leads to a reduction of their binding energies. Theoretically, the active surface oxygen O_{β} helps to promote the catalytic oxidation of NO to NO₂ by adsorbing onto the surface defective sites of catalyst due 286 to high mobility, thereby enhancing the fast-SCR reaction [42]. However, $Ce_4Sn_2O_2$ has lower 287 surface concentrations of total oxygen and O_{β} than Ce₃Sn₃O_z and Ce₂Sn₄O_z catalysts, and this 288 pattern is inconsistent with their NH₃-SCR activity at medium-low temperature. Furthermore, the 289 ICP results of $Ce_4Sn_2O_z$, $Ce_3Sn_3O_z$ and $Ce_2Sn_4O_z$ catalysts in Table 2 show that the calculated 290 mass concentrations of Ce/Sn (molar ratio) are higher than the theoretical values, which might be 291 attributed to the specific valences of both Ce and Sn elements in the as-fabricated cerium-tin 292 mixed oxide catalysts or/and their limited solid solution states, confirming the good interaction 293 of Ce and Sn in the composite catalysts. Therefore, it can be deduced that the promotional effect of the active surface oxygen O_β from Ce^{3+}/Ce^{4+} and Sn^{2+}/Sn^{4+} redox cycles and Ce-O-Sn bonds is 294 different for the NH₃-SCR activity of cerium-tin mixed oxide catalyst. In addition, excessive tin 295 296 is adverse to the NH₃-SCR activity of catalyst although it further contributes to increasing the 297 concentration of O_{β} on the CeO₂ catalyst surface.

298 3.1.5 H₂-TPR

299 It is widely accepted that the surface redox properties have a profound impact on the 300 NH₃-SCR activity of catalyst. Herein, H₂-TPR had been carried out to investigate the influence 301 of Sn-doping on the redox property of the as-fabricated CeO₂ catalyst. As depicted in Fig.5, there exists a broad peak of hydrogen consumption for CeO2 catalyst at the temperature range of 302 200-900 °C with three reduction peaks located at approximately 428 °C, 476 °C and 778 °C. And 303 304 these reduction peaks are attributed to the reduction of surface and sub-surface oxygen species of 305 fluorite-structured CeO₂ and the reduction of oxygen in the bulk CeO₂, respectively. Meanwhile, 306 SnO₂ catalyst presents a sharper broad reduction peak at 400-850 °C, which is assigned to the 307 reduction of SnO_2 to Sn [43]. This indicates that SnO_2 has stronger performance of oxygen supply than CeO₂ catalyst via the redox cycle of Sn^{4+}/Sn^{2+} , but the activity of its supplied oxygen 308 309 is lower than the latter due to higher reduction temperature. Furthermore, as shown in Fig.5(B), 310 the doping of Sn increases the H₂ consumption of CeO₂ catalyst, and the enhancement of Sn/Ce 311 molar ratio from 2:4 to 4:2 makes the strongest reduction peak of cerium-tin mixed oxide catalyst shift to higher temperature. However, Ce4Sn2Oz presents larger H2 consumption at the 312 313 reduction temperature of 200-530 °C than Ce₃Sn₃Oz and Ce₂Sn₄Oz catalysts (Fig.S3), indicating 314 the best performance in supplying reactive oxygen species at medium-low temperatures. This confirms the inference about the different effect of the surface active oxygen induced by 315

316 Ce^{4+}/Ce^{3+} and Sn^{4+}/Sn^{2+} redox cycles and Ce-O-Sn bonds on the NH₃-SCR activity of cerium-tin



consumption.

317 mixed oxide catalyst in the section of XPS spectra.

Fig.5 H₂-TPR profiles of the as-fabricated cerium-tin mixed oxide catalysts (A) Full spectrum and (B) H₂

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321 3.1.6 NH₃-TPD

As reported, the acid sites play an important role on the NH₃-SCR reaction due to the 322 pivotal step of NH₃ adsorption over the acid sites of catalyst, and the strength of acidity is closely 323 correlated with the NH₃-SCR activity [20]. As shown in Fig.6(A), it can be found that the 324 325 as-fabricated CeO₂ catalyst exhibits a broad peak of NH₃ desorption at the temperature range of 326 100-500 °C, which is stronger than that of SnO₂, indicating the presence of more acid sites on the 327 CeO_2 catalyst surface. Interestingly, as shown in Fig.6(B), the doping of Sn increases the intensity of NH3 desorption below 200 °C, which is attributed to the desorbed NH3 species from 328 329 weak acid sites [44]. Meanwhile, this promotional effect gradually decreases with the increasing of Sn/Ce molar ratio from 2:4 to 4:2, which is in accordance with the medium-low temperature 330 NH₃-SCR activity of the cerium-tin mixed oxide catalysts. And the strongest weak acid sites 331 might be an important reason for the best NH₃-SCR activity of Ce₄Sn₂O_z catalyst. 332

Therefore, the doped tin species can incorporate into the lattice of fluorite structure CeO₂ accompanied with the formation of Ce-O-Sn bond in the as-fabricated CeO₂ catalyst, which restricts the growth of both SnO₂ and fluorite structure CeO₂ crystals in the cerium-tin mixed oxide catalyst. This doping also optimizes the pore structure of CeO₂ catalyst and results in a significant change of the electron cloud density around the O atoms on the CeO₂ catalyst surface due to the fabrication of Ce-O-Sn bond, which also effectively increases the molar ratio of $(O_{\alpha}+O_{\beta})/(O_{\alpha}+O_{\beta}+O_{\gamma})$. However, the influence of the chemically adsorbed oxygen (O_{α}) from 340 Ce^{4+}/Ce^{3+} and Sn^{4+}/Sn^{2+} redox cycles and Ce-O-Sn bond is different for the NH₃-SCR activity of 341 cerium-tin mixed oxide catalyst, and the as-fabricated $Ce_4Sn_2O_2$ provides the largest 342 low-temperature reactive oxygen species and weak acid sites, thereby presents the best 343 medium-low temperature NH₃-SCR activity.



344

345 Fig.6 NH₃-TPD profiles of the as-fabricated cerium-tin mixed oxide catalysts (A), and the corresponding NH₃

346

desorption amount (B).

347 3.2 DFT calculation

348 3.2.1 Fabrication and optimization of $CeO_2(111)$ and $Sn-CeO_2(111)$ models

349 Based on the results of XRD pattern in section 3.1.1, the predominant exposed crystal facet 350 of fluorite structure CeO_2 is (111) for the as-fabricated CeO_2 catalyst in this study, which had 351 also been established as the relatively most stable exposed facet of fluorite structure CeO_2 in 352 previous research [32]. Consequently, a CeO₂ (111) model with a 3x3 supercell, consisting of 353 nine atomic layers arranged in a tri-layer (C-O-Ce) structure, encompassing 81 atoms, was 354 employed. A vacuum layer of 15 Å perpendicular to the model surface was introduced to isolate 355 the atoms from the upper unit cell. Furthermore, due to the incorporation of Sn into the lattice of fluorite structure CeO2 in the as-fabricated cerium-tin mixed oxide catalyst, the substitution of 356 357 one Ce atom with Sn on the surface of the above $CeO_2(111)$ model was constructed to study the influence of tin doping (designated as Sn-CeO₂ (111)). In these two models, the bottom layer 358 atoms were fixed and the remaining atoms were relaxed during the DFT calculation. The 359 geometrically optimized CeO₂(111) and Sn-CeO₂(111) models are depicted in Fig.S4. 360

361 3.2.2 Effect of Sn-doping on the surface acid sites and oxygen vacancies of CeO_2 (111)

362 The influence of Sn-doping on the cell structure of CeO_2 (111) is illustrated in Fig.S5, and it

363 can be observed that the doping of Sn atom leads to a notable change of the local environment around Ce atoms on the surface of fluorite-structured CeO₂, and cause rise of the lattice 364 365 distortions and disruptions in the periodic structure of CeO₂. Specifically, the length of the formed bond of Sn-O on the Sn-CeO₂ (111) surface is 2.11 Å, which is shorter than that of Ce-O 366 bond (2.36 Å). Furthermore, the length of the Ce-O bond adjacent to the doped Sn atom stretches 367 368 to 2.45 Å, and this stretching change of the length of Ce-O-Sn bond is mainly attributed to the 369 larger electronegativity of Sn atom than Ce atom, which causes the shifting of the bonded 370 oxygen atoms towards the side of the doped Sn atom. Additionally, the lattice distortions induced 371 by Sn-doping contribute to the observed shifts in the diffraction peaks of fluorite-structured CeO₂ 372 crystals for the as-fabricated Ce₄Sn₂O₂ catalyst compared to CeO₂ catalyst.

373 Due to the dominant role of NH₃ adsorption for the NH₃-SCR reaction, it is imperative to 374 further investigate the influence of Sn-doping on the adsorption capabilities of NH₃ species over 375 the CeO_2 (111) surfaces via DFT calculation. In order to pinpoint the optimal adsorption sites of 376 NH₃ species on the catalysts surface, four distinct L-acid sites, including the Sn site (Set1), a Ce 377 site far from Sn (Set2), a Ce site adjacent to Sn (Set3), and a Ce atom adsorption site even further 378 from Sn (Set4) were selected on the surface of Sn-CeO₂ (111). Additionally, an H atom can be 379 adsorbed onto an O atom adjacent to Set1, which serves as a proton-donating B-acid site. For the fluorite-structured $CeO_2(111)$, the Ce site corresponding to the position of Set1 is chosen as the 380 381 L-acid site, while the B-acid site is positioned identically to that of $Sn-CeO_2$ (111), and the 382 calculated adsorption sites and energies of NH₃ species on the catalysts surface are shown in 383 Fig.7. From Fig.7(A), it can be found that the resulting chemical adsorption bond of NH₃ species 384 on Set1 of Sn-CeO₂(111) is the shortest (2.36 Å), indicating a strong interaction between the 385 adsorbate and adsorbent. Meanwhile, the adsorption energy of NH₃ species on Set1(-1.31 eV) is 386 also lower than those on the other three L-acid sites, which suggests that the reactive ammonia 387 species should preferentially adsorb on the Sn atom surface during the NH₃-SCR reaction over 388 Sn-CeO₂ (111). However, the adsorption energy of NH₃ on the L-acid site of CeO₂ (111) is 389 merely -0.41 eV, which is much higher than the adsorption energy on its Set1 site and the 390 adsorption values on the L-acid sites of Sn-CeO₂ (111), which indicates that the strength of 391 L-acid sites is relatively weak for pure CeO_2 catalyst, and it is challenging for the adsorption of 392 NH₃ species at medium-low temperature [41]. Fig.7(B) gives the influence of Sn-doping on the adsorption of NH₃ species over the Brønsted acid (B-acid) sites of CeO₂ (111), and the adsorption energy of NH₃ species on the B-acid sites of Sn-CeO₂ (111) is close to the adsorption value on that of CeO₂ (111), indicating no influence of Sn doping on the B-acid sites of CeO₂ catalyst, which is consistent with the characterized NH₃-TPD spectra in section 3.1.6. Therefore, the doped tin not only acts as a novel more potential reactive metal site, but also improves the L-acid sites of CeO₂ (111) due to the interaction of Sn and Ce atoms.



400 Fig.7 Effect of Sn-doping on NH₃ adsorption performance (A), (B) and oxygen vacancies (C) on the CeO₂ (111)
401 surface.

399

402 Generally, the defects of oxygen vacancy have been considered to play an important role in 403 the NH₃-SCR reaction due to the promotional effect on the formation of chemically adsorbed 404 oxygen. Consequently, the formation energies of oxygen vacancies over the CeO_2 (111) and 405 $Sn-CeO_2(111)$ models were calculated to elucidate the effect of Sn-doping on the formation of 406 surface oxygen vacancy defects of CeO_2 catalyst. According to the results in Fig.7(C), it can be 407 found that the doping of Sn reduces the formation energy of oxygen vacancies on the CeO_2 (111) 408 surface from 1.42 eV to 0.77 eV. This indicates that the surface lattice oxygen of CeO₂ (111) 409 becomes more unstable by doping Sn atom, which helps to induce oxygen 410 vacancies. Subsequently, these excited vacancies are filled by the gas-phase oxygen molecules, leading to an enhancement of chemically adsorbed oxygen on the catalyst surface. This 411

412 observation aligns well with the conclusion drawn from XPS spectra of Section 3.1.4, which

413 reinforces the notion that the doping of Sn facilitates the formation of oxygen vacancies on the

414 as-fabricated CeO₂ catalyst surface due to the formation of Ce-O-Sn bond.

415 3.2.3 Influence of Sn-doping on the NH_3 -SCR reaction steps of CeO_2 (111)

Due to the advantages to reveal the specific reaction intermediates of NH₃-SCR reaction,
DFT calculations were employed to explore the influence of Sn-doping on the NH₃-SCR
mechanism of fluorite structure CeO₂ (111).

419 *Reaction Step I*: NH₃ adsorption and decomposition

420 Generally, the agent of NH₃ is firstly adsorbed on the surface L-acid sites of catalyst, and 421 then the adsorbed NH_3 species undergoes dehydrogenation activation to form an adsorbed NH_2 422 intermediate before initiating the catalytic cycle of NO_x reduction [45]. Therefore, the simulation 423 of the adsorption and decomposition of NH₃ species over the surfaces of CeO₂ (111) and Sn-CeO₂ (111) were conducted via DFT calculations, and the adsorption energies of the 424 425 corresponding intermediates and transition states during this reaction are depicted in Fig.8. As 426 mentioned in Fig.7(A), the adsorption energy of NH_3 species on the L-acid site of CeO_2 (111) is 427 -0.41 eV (IM2' in Fig.8). Subsequently, a high energy barrier of 1.62 eV must be overcome to 428 break an N-H bond and then the dissociated H atom adsorbs on a lattice oxygen far from the L-acid site of CeO₂ (111), forming -OH (IM3' in Fig.8). This means that the dissociation process 429 430 of NH₃ is difficult to occur on the surface of CeO_2 (111), which hinders the starting of the 431 NH₃-SCR reaction cycle and is the determining rate step. However, the doping of Sn atom 432 effectively reduces this energy barrier of NH₃ activation process on the surface of CeO₂ (111), 433 and only 0.17 eV and 0.8 eV are required to surpass this transition state (TS1 in Fig.8) and 434 complete the dehydrogenation activation on the $Sn-CeO_2(111)$ surface, respectively. Therefore, 435 the doping of Sn atom significantly reduces the reaction activation energy for the activation of 436 NH_3 species on the surface of $CeO_2(111)$ and enhances the oxidative dehydrogenation capability 437 of catalyst, promoting the initiation of NH₃-SCR catalytic cycle over Sn-CeO₂ (111). This is a 438 crucial factor for the better de-nitration performance of $Ce_4Sn_2O_z$ compared to fluorite structure 439 CeO₂ catalyst at medium-low temperature. Furthermore, the dissociated H atom on the surface of 440 $Sn-CeO_2(111)$ could adsorb and migrate to a lattice oxygen adjacent to the doped Sn atom, but not the O atom far from the active site of CeO₂ (111). This further confirms that the doping of Sn 441

442 atom contributes to facilitating the cleavage of N-H bond and the formation of O-H bond on the





444

445

Fig.8 Energy profile of reaction step I over the surface of CeO₂ (111) and Sn-CeO₂ (111).

446 *Reaction Step II*: Formation and decomposition of intermediate NH₂NO

447 With respect to the E-R and L-H mechanisms for the NH₃-SCR reaction, the activated NH₃ species in step I reacts with gas-phase NO and adsorbed NO species to form the intermediate of 448 449 NH₂NO, respectively. Therefore, the Step II reaction pathway of E-R mechanism over CeO₂(111) 450 was firstly calculated and proposed. As illustrated in Fig.S6, a stable intermediate NH₂NO^{*} 451 adsorbed on the lattice oxygen of $CeO_2(111)$ is formed by the reaction between the generated 452 NH₂^{*} specie in Step I and the gas-phase NO through an N-N bond (IM4'). This process is nearly 453 energy barrier-less. Subsequently, another dehydrogenation reaction undergoes and the detached 454 H atom adsorbs on an adjacent lattice oxygen. This step is also nearly unhindered, but the 455 configuration and adsorption site of newly formed intermediate NHNO^{*} (IM5' in Fig.S6) shifts to Ce site. And then, the two H atoms left on CeO₂(111) surface after the preceding reactions of 456 457 two-step dehydrogenation migrate and combine with a lattice oxygen to form H_2O^* (IM6' in Fig S6). After the desorption of H₂O into the flue gas, an oxygen vacancy is created at the original 458 459 lattice oxygen site of CeO₂ (111). This process requires a transition state (TS3' in Fig.S6) with an 460 energy barrier of -1.63 eV. And then, NHNO (IM7' in Fig.S6) undergoes an isomerization process and facilitates the formation of surface oxygen vacancy by breaking the bonds of N-O 461 and N-H. In the meantime, the formed N₂ desorbs into the flue gas with a new Brønsted acid site 462 (IM8' in Fig.S6) fabricated on the surface of $CeO_2(111)$, because the O atom from gas-phase O_2 463 refills this oxygen vacancy, and the H atom combines with the surface lattice oxygen to form 464

465 O-H as an H^{*} reactive center for Brønsted acid sites. An energy barrier of 0.41 eV is required to be overcome to complete the process of TS4'. For comparison, the reaction pathways of Step II 466 467 on Sn-CeO₂(111) are also calculated and proposed. As depicted in Fig.9, analogous to the N-N 468 bond coupling on the surface of $CeO_2(111)$, gas-phase NO directly reacts with the adsorbed NH_2 on the Sn-CeO₂ surface via Step I to generate NH₂NO. However, the formed NH₂NO does not 469 470 exist on the catalyst surface stably, which immediately dehydrogenates to a stable intermediate 471 NHNO^{*} adsorbed on the active site of Sn (IM4 in Fig.9). Furthermore, this dehydrogenation 472 process is energy barrier-less, which is lower than that of NH₂NO dehydrogenation on the CeO₂ (111) surface, suggesting that the doping of Sn atom contributes to enhancing the oxidative 473 474 dehydrogenation capability of CeO₂ (111). It should be mentioned that the subsequent 475 decomposition of NHNO^{*} intermediate over Sn-CeO₂ (111) is completely different from that on CeO₂ (111), even if this intermediate could stabilize on their surfaces. Firstly, the H atom bonded 476 477 to the N atom in IM4 migrates to the O atom adjacent to the N atom, forming a hydroxyl group 478 (-OH) and stably adsorbing NHNOH on the Ce active site of Sn-CeO₂ (111) (IM5 in 479 Fig.9). Meanwhile, this migrating H atom cannot present on the surface of fluorite structure 480 CeO₂ and thus NHNOH is unstable over it, which might be attributed to the alteration of doped 481 Sn atom on the electronic cloud density around the active sites of original fluorite structure CeO_2 , enabling the stable bonding of NHNOH to the surface of Sn-CeO₂ (111). And a high energy 482 483 barrier of 1.29 eV is required to be overcome for this process. Subsequently, the N-O bond in 484 IM5 breaks, forming free -OH and N₂ species, and then the dissociated hydroxyl combines with 485 an adsorbed H atom on the surface of Sn-CeO₂ (111) to form H₂O (IM6 in Fig.9). Finally, a 486 leftover H atom adsorbs on the Ce atom adjacent to Sn atom after the dissociation of the formed 487 N₂ and H₂O from the surface of catalyst, serving as a Brønsted acid site for the subsequent 488 NH₃-SCR reactions. In addition, an energy barrier of 0.57 eV needs to be overcome for this 489 process (TS3 in Fig.9), releasing a heat of 2.30 eV. Different from the Step II reaction pathway of 490 CeO₂ (111), a novel reaction pathway for the gradual decomposition of the NHNO species into 491 N_2 and H_2O is facilitated for Sn-CeO₂ (111), and this process involves a shorter route, fewer 492 reactive intermediates and a significantly lower activation energy of 1.29 eV compared to that of 493 CeO₂ (111) (2.37 eV). Furthermore, the released heat during this process is also higher for Sn-CeO₂ (111). Consequently, this reaction pathway over Sn-doped CeO₂ (111) exhibits a clear 494

thermodynamic advantage [46].

Furthermore, the L-H mechanisms on both $Sn-CeO_2$ (111) and CeO_2 (111) were also 496 497 calculated and are depicted in Fig S7. As illustrated in Fig S7(B), the adsorbed NH_3 on the 498 surface of Sn-CeO₂ (111) activates and then decomposes into the adsorbed NH₂ and H on the 499 catalyst surface (IM1" in Fig S7(B)). At the same time, NO species are adsorbed onto the lattice 500 oxygen adjacent to the Sn atom, forming surface nitrite species (IM2" in 501 Fig.S7(A)). Subsequently, the intermediate of NHNO₂* forms via the N-N bond between the 502 adsorbed NH₂ and NO₂ species (IM3" in Fig.S7(B)), and a significantly high energy barrier of approximately 1.97 eV needs to be overcome for this process, which is higher than the energy 503 504 barriers of all transition states involved in the above Step II reaction pathways. This suggests that 505 the E-R mechanism dominates in the NH₃-SCR reaction of Sn-CeO₂ (111). Furthermore, as shown in Fig.S7(A), the formation of $NHNO_2^*$ intermediate from the adsorbed NH_2 and NO_2 506 507 species needs an energy input of 2.47 eV to traverse for CeO_2 (111), which is also higher than the 508 energy barriers required for the transition states in the E-R reaction pathways. This indicates that 509 the E-R mechanism also dominates in the NH₃-SCR reaction of CeO₂ (111).







Fig.9 Energy profile of reaction step II over the surface of Sn-CeO₂ (111).

The calculated results of reaction step II demonstrate that a new B-acid site is formed due to the leave of an active H^* atom on the surface lattice oxygen of both CeO₂ (111) and Sn-CeO₂ (111). And the subsequent removal of H^* from the catalysts surface becomes crucial for realizing the entire NH₃-SCR cycle. Previous studies on the NH₃-SCR mechanisms by *in situ* DRIFTS showed that various ammonium nitrite species were formed on the catalyst surface after introducing NH₃, NO and O₂ into the reaction chamber, which gradually decomposed into

Reaction Step III: Formation and decomposition of intermediate NH₄NO₂

⁵¹²

519 nitrogen and water during the subsequent reactions [47]. However, there is no consensus on the 520 decomposition mechanism of ammonium nitrite (NH4NO2) on the catalyst surface. Herein, a possible decomposition pathway of NH4NO2 over CeO2 (111) and Sn-CeO2 (111) is proposed 521 through DFT computational simulations. As illustrated in Fig.10, the calculated decomposition 522 process of NH₄NO₂ on the surface of CeO₂ (111) is described as follows: the NH₄ intermediate is 523 524 firstly formed on the catalyst surface due to the adsorption of NH₃ on the B-acid site via IM10' 525 reaction, and subsequently reacts with gas-phase NO to form NH₄NO₂ via IM11' reaction (an 526 exothermic reaction, releasing approximately 1.08 eV of energy). And then, the bonds of N-O 527 and N-H in NH4NO2 break and recombine to form a new N-N bond, while the dissociated H 528 atom adsorbs onto the surface lattice oxygen of catalyst, resulting in the stable intermediate 529 cis-NHNOH (IM12'). This step requires overcoming an energy barrier of 1.19 eV and releases 0.32 eV of energy. Subsequently, cis-NHNOH undergoes isomerization and converts to 530 trans-NHNOH by rotating the position of the H atom (IM13' in Fig 10). This process has a 531 relatively low energy barrier and occurs easily. And then, the N-O and N-H bonds in 532 533 trans-NHNOH break, forming N₂ and the adsorbed -OH and H species, which further recombine 534 to form H_2O (IM14' in Fig.10). Finally, the formed H_2O and N_2 dissociate into the surrounding gaseous environment and the step III reaction on CeO₂ (111) is over. This step requires a 535 transition state (TS7' in Fig.10) and releases a significant amount of heat of approximately 2.32 536 eV. As evidenced from the above calculation, relatively low activation energy barriers need to be 537 538 overcome for the decomposition process of NH_4NO_2 on CeO_2 (111), which suggests that the 539 proposed reaction pathway is reasonable herein.

540 From Fig.10, it can also be found that $Sn-CeO_2$ (111) presents a similar step III reaction to 541 CeO₂ (111) with identical intermediate configurations and corresponding adsorption sites, but 542 has different energies of intermediates and transition states. Notably, the transition state of TS4 in 543 the reaction step III is the rate-determining step of the entire NH₃-SCR reaction cycle over 544 Sn-CeO₂ (111) (Fig.S8), with a reaction energy barrier of 1.53 eV. Furthermore, apart from the rate-determining step, the energy barriers of the remaining transition states over Sn-CeO₂ (111) 545 546 are lower and the released energy is also larger compared to that of CeO_2 (111) during the step III 547 reaction, suggesting a pronounced thermodynamic advantage for this step on Sn-CeO₂ (111).



548 549

Reaction coordinate

Fig.10 Energy profile of reaction step III over the surface of CeO₂ (111) and Sn-CeO₂ (111).



Reaction Step IV: O_v formation and catalyst recovery

551 Fig.11 depicts the intermediates and their corresponding energies involved in the final step 552 of the entire NH₃-SCR cycle for CeO_2 (111) and Sn-CeO₂ (111). After the reaction of step III, two adsorbed H* atoms remain on the surface of CeO₂ (111) (IM15` in Fig.11) and one H* atom 553 migrates to the lattice oxygen, forming an H-O bond, which reacts with the other adsorbed H* 554 atom to form the H₂O species (IM16' in Fig.11). This process requires an energy barrier of 2.06 555 556 eV to traverse a high-energy transition state (TS8' in Fig.11). And then, the formed H_2O 557 molecule dissociates into the surrounding gaseous environment, leaving behind an oxygen vacancy (IM17' in Fig.11) and generating two Ce³⁺ ions on the surface of fluorite structure 558 CeO₂. Due to the excellent oxygen migration capability of Ce^{3+}/Ce^{4+} ion pair, the gas-phase O₂ 559 molecules from the surrounding environment can be adsorbed onto this formed oxygen vacancy, 560 561 reforming the Ce-O-Ce bond of adjacent Ce species and re-oxidizing Ce^{3+} back to Ce^{4+} [48]. This contributes to returning CeO_2 (111) to the original physicochemical state before the NH₃-SCR 562 563 reaction and rejuvenates it (IM18' in Fig.11). Therefore, the gas-phase O_2 molecules from the surrounding environment can re-oxidize and regenerate the active sites of cerium-based catalyst 564 565 during the NH₃-SCR reaction. From Fig.11, it can also be found that the doping of Sn atom does not affect this step reaction of CeO_2 (111), but decreases the corresponding reaction activation 566 energies and energy barriers of transition states within this reaction step. Furthermore, the 567 achievement of a lower-energy transition state (TS7 in Fig.11) during the migration process of 568 active H* atom can be attributed to the superior de-hydroxylation capability of Sn-CeO₂ (111) 569 compared with CeO_2 (111). 570





Fig.11 Energy profile of reaction step IV over the surface of CeO₂(111) and Sn-CeO₂(111)

573 3.2.4 Influence of Sn-doping on the NH₃-SCR reaction mechanism of CeO₂(111)

574 According to the different active sites of NH₃ species pre-adsorption during the NO reduction process, as shown in Fig.S8, the NH₃-SCR cycle reaction pathways on CeO₂(111) and 575 $Sn-CeO_2(111)$ surfaces can be divided into two parts: the reaction part on L-acid sites and that 576 on B-acid sites, respectively. Specifically, the reaction pathway of NH₃ species adsorbed on 577 578 L-acid sites can be regarded as the first stage reduction process of NO, and the activation of NH₃ is a prerequisite for initiating the entire NH₃-SCR reaction cycle. Through in situ DRIFTs 579 580 experiments, Mu et al. found that the introduced NH₃ could immediately decompose into NH₂ 581 and NH species which were adsorbed on the surface reaction active sites of $CeSnO_x/TiO_2-E$ 582 catalyst [49], and the formed NH2NO has been verified as one of critical intermediates in the 583 NH₃-SCR reaction [50]. In this DFT calculation, NH₃ species are initially adsorbed on the Ce or Sn sites of catalysts and then activated into NH2, which subsequently react with gaseous NO to 584 form NH₂NO or NHNO intermediates on the surface of CeO₂ (111) or Sn-CeO₂ (111) via E-R 585 586 mechanism, respectively. And the formed intermediate of NH₂NO eventually decomposes into N2 and H2O. However, the dissociation of N2 and H2O results in about a new B-acid site 587 fabricated on the catalysts surface due to a leftover H atom adsorbing onto the Ce site of CeO2 588 589 (111) or/and Sn-CeO₂(111), thereby initiates the second stage reduction of NO via the reaction 590 pathway of NH₃ species attached to the B-acid sites, where the formed NH₄ species react with 591 the adsorbed NO on the catalysts surface to produce NH₄NO₂ [51]. And then the intermediate of 592 NH₄NO₂ ultimately decomposes into N₂ via the break of N-O and N-H bonds in trans-NHNOH

593 with two adsorbed H* atoms left on the catalysts surface. Among them, an adsorbed H* atom 594 migrates to the lattice oxygen of catalysts to fabricate the adsorbed -OH, which further 595 recombines with the other H* atom to form H2O. Furthermore, the dissociation of H2O brings about an surface oxygen vacancy of catalyst, which is finally refilled by the gas-phase O_2 and the 596 597 catalysts of CeO₂(111) or/and Sn-CeO₂(111) return to the original physicochemical state before the NH₃-SCR reaction [52]. However, the doping of Sn regulates the rate determining step of 598 NH₃-SCR reaction for CeO₂(111), and the decomposition process of the intermediate NH₄NO₂ is 599 600 the rate determining step for the NH_3 -SCR reaction of Sn-CeO₂(111), rather than the activation 601 of NH₃ species. Furthermore, Sn-doping also decreases the energy barrier of the rate determining step for the NH₃-SCR reaction of CeO₂ (111), and the NH₃-SCR reaction steps over Sn-CeO₂ 602 (111) are all exothermic reactions with higher released heat than the activation energy required 603 604 for the corresponding reaction. This makes easy occurrence of the NH₃-SCR reaction on the surface of $Sn-CeO_2$ (111) compared to CeO_2 (111). Therefore, the incorporation of Sn 605 significantly alters the intrinsic physicochemical properties of CeO₂ (111), and brings about the 606 607 thermodynamic and kinetic advantages for the NH₃-SCR reaction of cerium-tin mixed oxide 608 catalyst. Finally, the main E-R mechanisms for the NH₃-SCR reaction of CeO₂ (111) and $Sn-CeO_2$ (111) are given in Fig.13 for comparison. 609

610



611

Fig.12 The main and top views of intermediates during the calculated reaction pathways over CeO₂(111) (A)

613







Fig.13 Complete E-R catalytic mechanism of NOx reduction over CeO₂ (111) and Sn-CeO₂ (111).

616 4. Conclusion

The doping of Sn contributes to improving the NH₃-SCR activity of the as-fabricated 617 618 cerium oxide catalyst via the gelatin template sol-gel self-combustion method by incorporating into the lattice of fluorite-structured CeO2 crystals, which restricts the growth of both SnO2 and 619 CeO₂ crystals in the cerium-tin mixed oxide catalyst. Furthermore, this doping optimizes the 620 pore structure of CeO2 catalyst and effectively increases the surface molar ratio of 621 622 $(O_{\alpha}+O_{\beta})/(O_{\alpha}+O_{\beta}+O_{\gamma})$. Moreover, Ce₄Sn₂O_z presents the best NH₃-SCR activity at medium-low 623 temperature, which is mainly attributed to the largest low-temperature reactive oxygen species 624 and weak acid sites. DFT calculations demonstrate that the doping of Sn helps provide new 625 reactive sites on the surface of $CeO_2(111)$ catalysts and reduces the total energy barrier for the 626 NH_3 -SCR reaction. Furthermore, the doping of Sn changes the reaction path of NO_x reduction, and the decomposition process of the intermediate NH₄NO₂ is the rate determining step for the 627 628 NH_3 -SCR reaction over Sn-CeO₂(111), which is different from the activation of NH_3 species on 629 CeO₂(111). Finally, the NH₃-SCR mechanisms of both CeO₂ (111) and Sn-CeO₂ (111) are 630 proposed.

631 CRediT authorship contribution statement

Jingsong Zhou and Yanping Du: Writing-original draft, Methodology and Validation. Yuqing Qiao, Fei Zhou
and Zhou Liu: Experiment and Methodology. Zhibo Xiong: Conceptualization, Funding acquisition,
Writing-review & editing. Mengqi Liu and Wei Lu: Investigation, Supervision and editing.

635 Declaration of Competing Interest

636 The authors declare that they have no known competing financial interests or personal relationships that637 could have appeared to influence the work reported in this paper.

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641 Appendix A. Supporting information

- 642 Supplementary data associated with this article can be found in the online version.
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