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1 **Reverse Oxygen Spillover Triggered by CO Adsorption on**
2 **Sn-doped Pt/TiO₂ for Low-Temperature CO Oxidation**

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20 **Abstract:**

21 The spillover of oxygen species is fundamentally important in redox reactions, but the spillover
22 mechanism has been less understood compared to that of hydrogen spillover. Herein Sn is doped
23 into TiO₂ to activate low-temperature (<100 °C) reverse oxygen spillover in Pt/TiO₂ catalyst,
24 leading to CO oxidation activity much higher than that of most oxide-supported Pt catalysts. A
25 combination of near-ambient-pressure X-ray photoelectron spectroscopy, *in situ* Raman/Infrared
26 spectroscopies, and ab initio molecular dynamics simulations reveal that the reverse oxygen
27 spillover is triggered by CO adsorption at Pt²⁺ sites, followed by bond cleavage of Ti-O-Sn
28 moieties nearby and the appearance of Pt⁴⁺ species. The O in the catalytically indispensable Pt-O
29 species is energetically more favourable to be originated from Ti-O-Sn. This work clearly depicts
30 the interfacial chemistry of reverse oxygen spillover that is triggered by CO adsorption, and the
31 understanding is helpful for the design of platinum/titania catalysts suitable for reactions of
32 various reactants.

33
34 **Keywords:** reverse oxygen spillover, near-ambient-pressure XPS, AIMD, platinum, CO oxidation

35
36 **1. Introduction**

37 Platinum group metals supported on oxides are widely used in environmental catalysis,
38 electrocatalysis, and energy-related hydrogenation processes¹⁻⁴. To understand the mechanisms,
39 interfacial chemistry of catalytic reactions over noble metals is of great importance in the
40 development of catalytic science. The concept of strong metal support interaction (SMSI) effect
41 has been widely used to describe and/or interpret phenomena of electronic interaction, as well as
42 the stabilization/destabilization of metals on support materials^{5,6}. For instance, Ding et al.⁷
43 synthesized single-atom Pt/CeO₂ catalysts via oxidative and non-oxidative dispersions, and found
44 significant differences in the CO catalytic oxidation activity of single-atom Pt in different
45 coordination environments. Another important concept is the transport of adsorbates and/or
46 intermediates through metal-support interfaces, known as spillover of active species, such as
47 hydrogen and oxygen entities. For hydrogen spillover, the fundamentals have been well
48 documented⁸ and widely applied in catalyst design^{9,10}. By contrast, much less attention has been

49 given to oxygen spillover, and the related information are limited.

50 Recently reverse oxygen spillover (ROS) has opened new opportunities in improving the
51 activity, selectivity and stability of the catalyst systems with Ce-based supports due to the
52 excellent oxygen mobility of ceria. For example, Hensen and co-workers¹¹ investigated the
53 interfacial dynamics of Pd-CeO₂ catalyst in CO oxidation, and found that the surface oxidized Pd
54 species showed high resistance against sintering ascribable to extent ROS, whereas the ionic Pd
55 species in a Pd-CeO₂ system without ROS underwent swift reduction and agglomeration. Also, by
56 varying the particle size of CeZrO₄ support of the Co/Ce-Zr catalysts, Hensen et al.¹² observed
57 facile formation of oxygen vacancies ascribable to ROS, and upon CO/CO₂ exposure the filling of
58 vacancies by oxygen atoms via oxygen spillover. The migration of oxygen species enables the
59 stabilization of cobalt metal nanoparticles and CO₂ activation, thus playing essential roles in
60 various CO₂ hydrogenation reactions. Theoretical calculations were also employed to investigate
61 the ROS in CeO₂-based catalysts. Combining DFT predictions and resonant photoelectron
62 spectroscopy, Vayssilov et al.¹³ proposed that the ROS process occurred on nanostructured ceria
63 rather than on bulk ceria. In their study, a model Pt-CeO₂-film catalyst was designed and the
64 generation of Ce³⁺ was used to indirectly indicate the transfer of O from support to the active Pt
65 sites. It should be noted that the spillover of oxygen species is fast and its rate can compete with
66 the rate of reaction. Therefore, the direct observation of such a phenomenon is difficult and
67 challenging.

68 Because the oxygen mobility of TiO₂ is much lower than that of CeO₂, systemic ROS study on
69 Pt/Titania catalyst is extremely rare despite the related catalytic behavior is known. By a potential
70 dynamic sweep method¹⁴, Lin studied oxygen spillover and back spillover over Pt/TiO₂ working
71 electrode. It was found that the transport of oxygen species is brought about not only on the
72 surface but also significantly in the TiO₂ crystal lattice. Nevertheless, only current-potential
73 profiles of Pt/TiO₂ electrode were reported and the related interface chemistry was not illustrated
74 in detail. More importantly, the effect of electricity introduction into the system cannot be ignored,
75 making the information obtained by electrochemical methods, to a certain extent, irrelevant to
76 thermocatalysis. Therefore, it is appropriate despite challenging to activate the ROS process in
77 TiO₂-based supports and to understand the ROS dynamics of Pt/Titania interfaces in

78 heterogeneous catalysis.

79 Since SnO₂ possess a similar structure as rutile TiO₂¹⁵, doping Sn will not change significantly
80 the bulk construction but create asymmetric oxygens (M₁-O-M₂) in TiO₂. Such altering of oxygen
81 symmetry probably increases its mobility and thus benefits to the ROS process. Therefore, in the
82 present work, we modulated the rutile TiO₂ by Sn doping to activate the oxygen in TiO₂ support,
83 and illustrated the rich interfacial chemistry of reverse oxygen spillover from Sn-doped TiO₂
84 (SnTiO₂) to Pt sites in low-temperature (100 °C) CO oxidation. Comparing with the reference
85 catalysts, namely, anatase-supported and rutile-support Pt (denoted herein as Pt/TiO₂-A and
86 Pt/TiO₂-R, respectively), the fabricated Pt/SnTiO₂ was intrinsically 6–12 times more active and
87 there was no sight of deactivation in a test of seven days, based on the USDRIVE's protocol¹⁶ in
88 the presence of 10% H₂O and 100 ppm SO₂. The revealed interface chemistry suggested that the
89 reverse oxygen spillover was triggered by CO adsorption on Pt sites followed by the appearance
90 of Pt⁴⁺ species. With the cleavage of Ti-O-Sn bonds in the vicinity of CO-adsorbed Pt sites, there
91 is the availability of O species and the formation of catalytically indispensable Pt-O sites. The
92 revealed reactant-adsorption-triggered characteristics of interfacial reverse oxygen spillover can
93 help understand the mechanistic aspects of catalytic reactions that are different in reactants, as
94 well as those of photo-electrocatalytic nature such as oxygen evolution and reduction reactions.

95 **2. Results**

96 **2.1 CO oxidation performance**

97 The absence of heat and mass transfer limitations was verified by Mears criterion¹¹
98 (Supplementary Note 1 and Supplementary Fig. S1). The H₂ pretreatment temperature and the
99 valence of Pt were discussed by Supplementary Note 2 and Supplementary Figs. S2-3. As
100 displayed in Supplementary Fig. S4, the Pt/Sn_xTi_{1-x}O₂ catalysts exhibited satisfactory CO
101 oxidation activities with T₉₀ < 120 °C. Specifically, Pt/Sn_{0.2}Ti_{0.8}O₂ showed the highest activity
102 with CO conversion of ~100% at 120 °C, meeting the guideline of “90% conversion of all criteria
103 pollutants at 150 °C” proposed by the U.S. Department of Energy¹⁷. Fig. 1a shows that the CO
104 oxidation activity of Pt/Sn_{0.2}Ti_{0.8}O₂ obviously better than those of Pt/TiO₂-R and Pt/TiO₂-A with
105 the same Pt loading (0.5 wt%), indicating that Sn doping plays a critical role in promoting
106 low-temperature CO oxidation over the Pt/Sn_{0.2}Ti_{0.8}O₂ catalyst. A comparison between Fig. 1a and

107 Supplementary Fig. S5a revealed that a moderate H₂ reduction (5% H₂, 300°C) of the catalysts
108 resulted in obvious improvement of CO oxidation activities over the Pt/Sn_{0.2}Ti_{0.8}O₂ catalyst,
109 whereas over Pt/TiO₂-R and Pt/TiO₂-A the improvement was less obvious. A possible reason is
110 that the reaction pathways for CO oxidation over Pt/Sn_{0.2}Ti_{0.8}O₂ and Pt/TiO₂ catalysts are different
111 (vide infra).

112 In agreement with the CO oxidation activities, the activation energies (E_a) over all the
113 Pt/Sn_xTi_{1-x}O₂ catalysts (especially for Pt/Sn_{0.2}Ti_{0.8}O₂) were lower than those over Pt/TiO₂-R and
114 Pt/TiO₂-A (Supplementary Fig. S6). Moreover, the E_a of the catalysts without H₂ pretreatment
115 (Supplementary Fig. S5b) were obviously higher than those of the catalysts with H₂ pretreatment
116 (Supplementary Fig. S6), suggesting that the H₂ reduction treatment could optimize the active sites
117 and accelerate the CO oxidation process. Even compared with reported Pt-based catalysts¹⁸⁻⁴³, the
118 Pt/Sn_{0.2}Ti_{0.8}O₂ catalyst is much lower in E_a value, except in cases such as 1% wt Pt/CNT-600 and
119 0.70% wt Pt_{NPs}/TiO_{2-x} (Supplementary Fig. S7 and Supplementary Table S1). Through calculation,
120 the turnover frequency of CO conversion over Pt sites (TOF_{Pt}) of Pt/Sn_{0.2}Ti_{0.8}O₂ is 0.30 s⁻¹ at
121 100 °C (Fig. 1b), exhibiting a level comparable to those of the superior Pt-based catalysts¹⁸⁻⁴³ (Fig.
122 1c and Supplementary Table S1). Meanwhile, the reaction order of CO and O₂ during CO catalytic
123 oxidation over Pt/Sn_{0.2}Ti_{0.8}O₂, Pt/TiO₂-R and Pt/TiO₂-A were all slightly higher than 0
124 (Supplementary Fig. S8), indicating that CO oxidation over these three Pt-based catalysts follow
125 the Mars-van Krevelen (MvK) mechanism, which is typical for reducible oxide-based catalysts¹¹.
126 Additionally, the partial orders of CO (or O₂) were approximately 0, highlighting the weakened
127 kinetic relevance of CO (or O₂) adsorption/activation over Pt/Sn_{0.2}Ti_{0.8}O₂, Pt/TiO₂-R and
128 Pt/TiO₂-A²².

129 On top of the superior CO oxidation performance, the Pt/Sn_{0.2}Ti_{0.8}O₂ catalyst shows a
130 satisfactory sulfur resistance ability, giving 100% CO conversion in a span of 7 days even in the
131 presence of 10% H₂O and 100 ppm SO₂ (Fig. 1d), demonstrating that Pt/Sn_{0.2}Ti_{0.8}O₂ could operate
132 reasonably well under complicated conditions harsher than those of USDRIVE's protocol¹⁶. One
133 plausible explanation for the enhanced sulfur resistance is that the introduction of Sn doping
134 results in a notable modification of the coordination environment of Ti within the support structure,
135 thereby influences the interaction between the active Pt site and the support, leading to improved

136 sulfur resistance⁴⁴. Moreover, harsh pre-treatment process (e.g., hydrothermal aging by 10% H₂O
137 at 750 °C for 9 h) could not impair the performance of Pt/Sn_{0.2}Ti_{0.8}O₂, which still exhibited CO
138 conversion of ~100% at 200 °C (Supplementary Fig. S9). To sum up, by doping a proper content
139 of Sn into the titania of TiO₂-supported Pt catalyst, excellent CO oxidation activity as well as
140 sulfur resistance ability under complicated conditions could be acquired.

141 **2.2 Catalyst Structure**

142 A series of analyses were conducted to characterize the microstructure of Pt/Sn_xTi_{1-x}O₂,
143 Pt/TiO₂-R and Pt/TiO₂-A. The X-ray diffraction (XRD) patterns (Supplementary Fig. S10) suggest
144 that the reflection peaks of Pt/Sn_xTi_{1-x}O₂ and Pt/TiO₂-R catalysts could be assigned to rutile TiO₂
145 (JCPDS: #21-1276), whereas those of Pt/TiO₂-A to anatase TiO₂ (JCPDS: #21-1272). No
146 reflections corresponded to Pt species could be observed plausibly due to the low content and well
147 dispersion of Pt species on the support. Further Rietveld refinements of the XRD patterns
148 (Supplementary Fig. S11 and Supplementary Table S2) suggest that the doped Sn was embedded
149 in the TiO₂ crystal structure with the substitution of Ti in an appropriate theoretical dosage.
150 Interestingly, despite different in phase structure, the Pt/Sn_xTi_{1-x}O₂ and Pt/TiO₂-A catalysts are
151 similar in texture parameters (Supplementary Fig. S12 and Supplementary Table S3).

152 The microchemical state was studied by X-ray absorption near edge spectroscopy (XANES). As
153 shown in Fig. 2a, the peaks at 530.6 eV and 533.3 eV of O K-edge XANES spectra could be
154 assigned to the *T*_{2g} and *E*_g states of TiO₂^{45,46}. The O K-edge XANES spectra of Pt/TiO₂-R and
155 Pt/TiO₂-A correspond well to that of TiO₂, whereas the O K-edge XANES spectrum of
156 Pt/Sn_{0.2}Ti_{0.8}O₂ is more distorted¹, suggesting the doped Sn could significantly change the
157 electronic interactions between oxygen and metal. Fig. 2b gives the XANES spectra of Pt L₃-edge
158 over Pt/Sn_{0.2}Ti_{0.8}O₂, Pt/TiO₂-R and Pt/TiO₂-A, and the reference spectra of Pt and PtO₂ are shown
159 in Supplementary Fig. S13a. The Pt L₃-edge XANES spectra of Pt/Sn_{0.2}Ti_{0.8}O₂, Pt/TiO₂-R and
160 Pt/TiO₂-A are almost identical. However, the edge position and edge jump of Pt/Sn_{0.2}Ti_{0.8}O₂ are
161 both slightly lower than those of Pt/TiO₂-R and Pt/TiO₂-A, indicating a slightly more reduced Pt
162 state for Pt/Sn_{0.2}Ti_{0.8}O₂^{47,48}. A similar conclusion can be drawn from the data of *k*² weighted
163 Fourier transform-extended X-ray absorption fine structure (FT-EXAFS) shown in Fig. 2c and
164 Supplementary Fig. S13b, Supplementary Fig. S14 and Supplementary Table S4. All the samples

165 contained a strong peak at $\sim 1.8 \text{ \AA}$ ascribable to Pt–O bond in $\text{PtO}_x^{48,49}$, among which that of
166 $\text{Pt/Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$ is the shortest. In addition, the intensities of the Pt–O peaks of $\text{Pt/Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$,
167 $\text{Pt/TiO}_2\text{-R}$ and $\text{Pt/TiO}_2\text{-A}$ (Supplementary Fig. S14) are all much weaker than that of reference
168 PtO_2 (Supplementary Fig. S13b); with due consideration to the weaker absorption edge intensity
169 and shorter Pt–O bond length, it is deduced that the Pt valence of all the samples is lower than that
170 of PtO_2 . It is noted that there is weak Pt–O–Sn bonding at $\sim 3.0 \text{ \AA}$ of $\text{Pt/Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$ (Fig. 2c),
171 suggesting interaction feasibility of Pt with the $\text{Sn}_x\text{Ti}_{1-x}\text{O}_2$ support. The Pt–O environments of the
172 $\text{Pt/Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$ were more disorder in comparison to that of $\text{Pt/TiO}_2\text{-R}$ and $\text{Pt/TiO}_2\text{-A}$. Moreover,
173 although Pt–Pt bond was taken into consideration when fitting the data, the low Pt–Pt coordination
174 number ($\text{CN} < 2$, see Supplementary Table S4) for all the samples suggested the extremely low
175 metallic nature of Pt presumably due to the moderate reduction conditions ($300 \text{ }^\circ\text{C}$ and $5\% \text{ H}_2$),
176 which are consistent with the results of XPS characterizations (vide infra).

177 The scanning electron microscopic (SEM) images of $\text{Pt/Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$, $\text{Pt/TiO}_2\text{-R}$ and $\text{Pt/TiO}_2\text{-A}$
178 (Supplementary Fig. S15) display micro morphologies of particle accumulation. The average
179 particle size of $\text{Pt/Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$ is similar to that of $\text{Pt/TiO}_2\text{-A}$, but smaller than that of $\text{Pt/TiO}_2\text{-R}$.
180 High resolution transmission electron microscopic (HR-TEM) images (Supplementary Fig. S16)
181 reveal that the exposed crystal planes of $\text{Pt/Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$ and $\text{Pt/TiO}_2\text{-R}$ are mainly the (110) planes
182 of rutile TiO_2 , whereas the major exposed planes of $\text{Pt/TiO}_2\text{-A}$ are the (101) planes of anatase TiO_2 .
183 Energy dispersive X-ray spectrometry (EDX) mapping (Supplementary Fig. S17) was conducted
184 to investigate the element distribution of $\text{Pt/Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$ and $\text{Pt/TiO}_2\text{-R}$. Obviously, there is even
185 dispersion of Sn, Ti and O elements, but Pt was hardly observed in the mapping due to its low
186 amount (0.5 wt%). To directly observe the microstate of loaded Pt species, we employed spherical
187 aberration-corrected scanning transmission electron microscopy (SAC-STEM). The high angle
188 annular dark field (HAADF) and the corresponding bright field (HAABF) images are shown in
189 Fig. 2d and Supplementary Fig. S18. It should be noted that the Pt species in $\text{Pt/Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$ are
190 hardly observed directly by the SAC-STEM images because of the closeness in atomic numbers
191 between Sn (50) and Pt (78). However, we could still observe the microstate of Pt species by
192 comparing the HAADF and HAABF images, which are circled in Fig. 2d and Supplementary Fig.
193 S18. The Pt species in all the samples were in the form of nano clusters, and the average diameter

194 of the Pt clusters in Pt/Sn_{0.2}Ti_{0.8}O₂, Pt/TiO₂-R and Pt/TiO₂-A was 1.2, 1.8 and 0.9 nm, respectively.

195 It is generally accepted that the CO oxidation process over various reducible supported Pt
196 catalysts follows a MvK reaction mechanism⁵⁰. The CO adsorbed on Pt nano clusters reacts with
197 active lattice oxygen species (O_{latt}) of the supports, and there is no involvement of competitive
198 adsorption between CO and O₂^{19,25}. Therefore, a transient CO oxidation study without continuous
199 O₂ supply was conducted at 100 °C; thus the amount of CO₂ generation could represent the
200 available amount of active O. Meanwhile, the variation of CO concentration during the study was
201 recorded. As shown in Fig. 2e, the amounts of CO₂ generation follow a decreasing order of
202 Pt/Sn_{0.2}Ti_{0.8}O₂ > Pt/TiO₂-A > Pt/TiO₂-R, suggesting that Pt/Sn_{0.2}Ti_{0.8}O₂ has the highest amount of
203 active O_{latt}. A similar order was observed when the study was conducted at 200 °C (see
204 Supplementary Fig. S19), suggesting that Pt/Sn_{0.2}Ti_{0.8}O₂ is the highest in terms of the availability
205 of active O disregard of the variation of reaction temperature. Interestingly, the results of O₂
206 temperature-programmed desorption (O₂-TPD) over the three catalysts reveal that the extents of
207 O₂ desorption follow a decreasing order of Pt/TiO₂-A > Pt/Sn_{0.2}Ti_{0.8}O₂ > Pt/TiO₂-R (Fig. 2f),
208 implying that Pt/TiO₂-A has the highest amount of active oxygen. The implication differs from
209 that of transient CO oxidation study (Fig. 2e). To explain the inconsistency, it is assumed that there
210 was *in situ* generation of active O species when Pt/Sn_{0.2}Ti_{0.8}O₂ was exposed to CO, and these *in*
211 *situ* generated O species upon CO introduction cannot be measured by O₂-TPD study. Therefore, a
212 series of *in situ* studies were performed to verify this assumption.

213 **2.2 Existence of reverse O spillover**

214 *In situ* near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) is an effective
215 technique to investigate the chemical behavior of catalyst surfaces. The *in situ* NAP-XPS Pt 4f
216 spectra were recorded at 100 °C of the reduced samples and after it were exposed to O₂, CO+O₂,
217 and CO in turn. It should be noted that the Ti 3s satellite (at ~75 eV) overlaps with the Pt 4f peaks,
218 causing complication in the deconvolution of the Pt 4f profiles in cases such as Pt/Sn_{0.2}Ti_{0.8}O₂,
219 Pt/TiO₂-R, and Pt/TiO₂-A catalysts^{48,51}. Therefore, the peak area ratio of Pt 4f_{5/2} to 4f_{7/2} was strictly
220 fixed as 3 : 4, and the full width of half maximum (FWHM) of all the Pt²⁺ and Pt⁴⁺ peaks was set
221 to be identical during the deconvolution process. In Fig. 3, the peaks at ~72.2 eV and ~74.8 eV
222 could be assigned to 4f_{7/2} and 4f_{5/2} signals of Pt²⁺ species, whereas the peaks at ~74.4 eV and ~77.8

223 eV to $4f_{7/2}$ and $4f_{5/2}$ signals of Pt^{4+} species, respectively⁴⁸. There was no detection of peaks
224 attributable to metallic Pt species in the entire *in situ* NAP-XPS study. After moderate H_2
225 pretreatment, only Pt^{2+} species could be observed (Fig. 3a), indicating that the Pt species on the
226 surface of $Pt/Sn_{0.2}Ti_{0.8}O_2$ was mainly PtO. Moreover, no Pt^{4+} species could be observed after
227 further O_2 treatment, suggesting that the PtO was stable upon the O_2 exposure. However, there
228 was the generation of Pt^{4+} species upon the introduction of $CO+O_2$ over $Pt/Sn_{0.2}Ti_{0.8}O_2$, and the
229 Pt^{4+} species existed only in the presence of CO. It should be emphasized that CO is a reducing gas,
230 and could be oxidized to CO_2 by the O_{latt} of $Pt/Sn_{0.2}Ti_{0.8}O_2$ without the introduction of gaseous O_2
231 (see Fig. 2e). In Fig. 3a, the oxidation of Pt^{2+} to Pt^{4+} occurred concurrently with CO oxidation,
232 implying that there was first the transfer of O_{latt} species to Pt sites, and then the oxidation of CO to
233 CO_2 by the O_{latt} species at the Pt sites. However, when O_{latt} species transferred to Pt sites, the
234 decrease of valence state of Ti and Sn species was hardly observed by the *in situ* NAP-XPS
235 technique due to the content difference of about 2 orders of magnitude between Pt and carrier
236 elements (Ti, Sn and O) (see Supplementary Note 3). As for Pt/TiO_2 -R and Pt/TiO_2 -A, only Pt^{2+}
237 species could be observed upon all the exposures (Fig. 3b and c), suggesting the absence of
238 reverse O spillover (ROS) over Pt/TiO_2 -R and Pt/TiO_2 -A. The overall results evidence that the
239 doped Sn promoted the migration of O_{latt} in the TiO_2 support, leading to the occurrence of the
240 ROS process upon CO introduction.

241 Raman spectra were also *in situ* recorded at 100 °C after the reduced catalysts were exposed to
242 O_2 , $CO+O_2$, and CO in turn. As shown in Fig. 3d and e, the Raman spectra of $Pt/Sn_{0.2}Ti_{0.8}O_2$ and
243 Pt/TiO_2 -R both exhibit three peaks at ~ 604 , ~ 422 and ~ 251 cm^{-1} , ascribable to the A_{1g} and E_g
244 vibration modes and the second-order effect (SOE) of rutile TiO_2 , respectively⁵². Interestingly, the
245 A_{1g} and E_g vibration modes of $Pt/Sn_{0.2}Ti_{0.8}O_2$ shift to lower wavenumbers after exposure to
246 $CO+O_2$, and more obviously with the sole introduction of CO. The A_{1g} vibration mode is derived
247 from the symmetric stretching of O-Ti(Sn)-O in the (110), ($\bar{1}10$) and (001) plane, and the E_g
248 vibration mode represents asymmetric bending of O-Ti(Sn)-O in the (110) plane. The shifts to
249 lower wavenumbers of A_{1g} and E_g vibration modes indicate weakened bond strength of
250 O-Ti(Sn)-O⁵², implying higher mobility of O_{latt} in TiO_2 , thereby contributing to the ROS during
251 CO oxidation on the surface of $Pt/Sn_{0.2}Ti_{0.8}O_2$ catalyst. In the cases of Pt/TiO_2 -R, there was no

252 obvious change of peak positions with the introduction of CO, indicating that there is no
253 Raman-visible change of O-Ti-O bond strength. As for Pt/TiO₂-A (Fig. 3f), the peaks at 636, 513
254 and 396 cm⁻¹ were assigned to the vibration modes of *E_g*, *A_{1g}/B_{1g}* doublet and *B_{1g}*, respectively⁵³.
255 The signal positions of these vibration modes also remain unchanged when Pt/TiO₂-A was
256 exposed to CO, indicating that the O-Ti-O bond strength also kept unchanged during the CO
257 oxidation reaction at 100 °C.

258 Spectra of diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) were *in situ*
259 recorded at 30–100 °C after having the Pt-based catalysts exposed to CO+O₂ (Fig. 4). There was
260 the appearance of three peaks at 2172, 2117, and ~2065 cm⁻¹ after the exposure. The peaks at 2172
261 cm⁻¹ and 2117 cm⁻¹ were assigned to gaseous and weakly adsorbed CO, and the peaks at ~2065
262 cm⁻¹ to adsorbed CO on semi-oxidized Pt species (Pt^{δ+}-CO)^{11,43,54,55}, which are sensitive to factors
263 such as Pt dispersion, Pt microstructure (i.e., steps, crystal planes and so on) and charge transfer
264 nearby the Pt sites⁴⁸. At higher temperature, more Pt sites would participate in the reaction cycle of
265 CO catalytic oxidation. Thus, the average valence state of Pt should decrease with increasing
266 reaction temperature, leading to deviation of Pt^{δ+}-CO infrared peak. As shown in Fig. 4a–c, when
267 the reaction temperature was increased from 30 to 100 °C, the peaks of Pt^{δ+}-CO over Pt/TiO₂-R
268 and Pt/TiO₂-A shifted to lower wavenumbers, while an opposite trend was observed over
269 Pt/Sn_{0.2}Ti_{0.8}O₂, which could be caused by ROS. To verify this conception, *in situ* NAP-XPS
270 spectra were acquired under the same reaction conditions of the DRIFTS experiments. As shown
271 in Fig. 4d–f, only Pt/Sn_{0.2}Ti_{0.8}O₂ possessed the Pt⁴⁺ species after the introduction of CO+O₂, and
272 the Pt⁴⁺ content increased with the increase of reaction temperature, suggesting that ROS was
273 more significant with the increase of CO oxidation rate over Pt/Sn_{0.2}Ti_{0.8}O₂.

274 **2.4 The ROS investigated by AIMD**

275 The configurations of Pt/Sn_{0.2}Ti_{0.8}O₂ and Pt/TiO₂-R employed in Density Functional Theory
276 (DFT) simulation were obtained from an *ab initio* molecular dynamics (AIMD) simulation
277 combined with geometrical optimization (see Supplementary Note 4, Supplementary Figs. S20–21,
278 and Supplementary Table S5). Then the charge density difference study was performed on
279 Pt/Sn_{0.2}Ti_{0.8}O₂ and Pt/TiO₂-R with the loading of Pt₄O₄ clusters (Supplementary Fig. S22) and the
280 adsorption of CO (Fig. 5a and b). The loading of Pt₄O₄ clusters led to an increase of charge

281 density of O in Sn-O-Ti around Pt, which was further enhanced after the subsequent adsorption of
282 CO over Pt/Sn_{0.2}Ti_{0.8}O₂ (Fig. 5a and Supplementary Fig. S22a). The increase of charge density of
283 O suggests an increase of O mobility, benefiting the ROS in Pt/Sn_{0.2}Ti_{0.8}O₂ during CO oxidation
284 reaction. As for Pt/TiO₂-R, there is no obvious change of “O” charge density in the Ti-O-Ti around
285 Pt upon the loading of Pt₄O₄ clusters as well as upon the adsorption of CO (Fig. 5b and
286 Supplementary Fig. S22b).

287 An AIMD simulation was conducted to further illustrate the ROS process. A CO molecule was
288 adsorbed on the Pt sites of Pt/Sn_{0.2}Ti_{0.8}O₂ and Pt/TiO₂-R. Because the relatively short time scale of
289 AIMD (20 ps in this study), the sampling of AIMD is only suitable to fast events of low-energy
290 barrier, and the observation of slow processes is excluded. Therefore, raising the simulation
291 temperature can result in quick exploration of a large number of phase spaces, and thus the AIMD
292 simulation temperature was performed at 700 K (427 °C), which is slightly lower than the
293 synthesis temperature of SnTiO₂ support⁵⁶. Fig. 5c and d show the variation of atomic distance
294 between Ti and O (Ti-O), Sn and O (Sn-O), and Pt and O (Pt-O) as a function of simulation time
295 over Pt/Sn_{0.2}Ti_{0.8}O₂ and Pt/TiO₂-R. The atomic distance of Ti-O, Sn-O and Pt-O stays at 2~3 Å
296 during the first 6 ps of AIMD simulation (Fig. 5c), indicating that the O in Sn-O-Ti kept bonding
297 with the Pt of Pt₄O₄ clusters. Then, the atomic distance of Ti-O and Sn-O quickly increased at 6~9
298 ps, while the atomic distance of Pt-O remained unchanged. The result indicates cleavage of Ti-O
299 and Sn-O bonds in Sn-O-Ti, subsequently leading to the reverse flow of O towards the Pt sites.
300 Finally, such structure remained stable to the end of the AIMD simulation. The whole AIMD
301 simulation process of Pt/Sn_{0.2}Ti_{0.8}O₂ can be directly seen in the Supplementary Movie 1, which
302 shows that the ROS only occurred in the Pt site bonded with CO, whereas the other Pt sites stayed
303 intact. This explains why the ROS process only occurred when CO was introduced, which is in
304 accordance with the results of *in situ* NAP-XPS and transient CO oxidation studies (Fig. 2e and
305 Fig. 3a). As for Pt/TiO₂-R (Fig. 5d and Supplementary Movie 2), the atomic distance of Pt-O
306 quickly increased in the first 6 ps, and then stayed at 3~4 Å to the end of AIMD simulation,
307 whereas the atomic distances of the two Ti-O bonds in Ti-O-Ti remained unchanged during the
308 whole AIMD simulation. This means cleavage of Pt-O bond, while the Ti-O-Ti kept intact,
309 indicating that there was no occurrence of ROS over Pt/TiO₂-R.

310 The cycles of complete CO oxidation reaction over Pt/Sn_{0.2}Ti_{0.8}O₂ and Pt/TiO₂-R were
 311 simulated by Vienna Ab-initio Simulation Package (VASP), and the oxidation routes were based
 312 on the AIMD simulation, which were named as CO oxidation by ROS (configurations I-VIII in Fig.
 313 5e) and CO oxidation by O_{latt} (configurations i-vii in Fig. 5e). Additionally, the route of CO
 314 oxidation by O_{latt} over Pt/Sn_{0.2}Ti_{0.8}O₂ was presented as a reference. It should be noted that these
 315 reaction routes followed the MvK mechanism, and other reaction mechanisms were not
 316 considered because O₂ could not be adsorbed at or around the Pt clusters of Pt/Sn_{0.2}Ti_{0.8}O₂ and
 317 Pt/TiO₂-R (Supplementary Fig. S23). As for the route of CO oxidation by O_{latt}, CO was first
 318 adsorbed on the Pt site (i→ii). Then, CO was oxidized by the O_{latt} near Pt to generate adsorbed
 319 CO₂ (ii→ts-1→iii). With the subsequent desorption of surface CO₂, an oxygen vacancy (V_O) was
 320 left on the surface (iii→iv). The V_O was filled by an oxygen molecule (iv→v). Another CO
 321 molecule was adsorbed on the Pt site near the adsorbed O₂ (v→vi), and subsequently oxidized by
 322 the O atom of O₂ to generate surface CO₂ (vi→ts-2→vii). Finally, the surface CO₂ was released,
 323 and the catalyst surface was restored to its original state (vii→i). The energy barrier of CO
 324 oxidation by O_{latt} over Pt/Sn_{0.2}Ti_{0.8}O₂ was 0.90 eV, which was slightly higher than that over
 325 Pt/TiO₂-R (0.84 eV). Such result was inconsistent with the activity results (Fig. 1a and b),
 326 indicating that CO should be oxidized following a different reaction route over Pt/Sn_{0.2}Ti_{0.8}O₂. As
 327 for the route of CO oxidation by the O comes from the ROS process, CO was also adsorbed on the
 328 Pt site (I→II). Then, the Sn-O and Ti-O bonds in Sn-O-Ti near the Pt-CO site were broken, and
 329 the O atom migrated to the Pt clusters (II→TS-1→III, i.e. ROS process) and left an V_O next to Sn
 330 and Ti on the support. Then the adsorbed CO was oxidized by the O in Pt cluster to generate
 331 adsorbed CO₂ (III→TS-2→IV). With the desorption of CO₂, the residual V_O next to Pt was filled
 332 by an O atom transferred through ROS (IV→V). The O atom transferred through ROS could
 333 oxidize CO following another reaction cycle. The V_O next to Sn and Ti on the support was filled
 334 by an O₂ molecule (V→VI), and the subsequent reaction route (VI→VII→TS-3→VIII→I) was the
 335 same as that of CO oxidation by O_{latt} (v→vi→ts-2→vii→i). The results of this DFT simulation
 336 show that the energy barrier of CO oxidation by ROS over Pt/Sn_{0.2}Ti_{0.8}O₂ was 0.69 eV, which was
 337 lower than that of CO oxidation by O_{latt} (0.90 eV), suggesting that CO oxidation by the O atom
 338 transferred through ROS is probably more preferred over Pt/Sn_{0.2}Ti_{0.8}O₂. In addition, the energy

339 barrier of CO oxidation by ROS over Pt/Sn_{0.2}Ti_{0.8}O₂ (0.69 eV) was lower than that of CO
340 oxidation by O_{latt} over Pt/TiO₂-R (0.84 eV), indicating that CO was more easily oxidized by
341 Pt/Sn_{0.2}Ti_{0.8}O₂, which was in accord with the activity results (Fig. 1a and b).

342 **3. Discussion**

343 In this study, Sn was doped into TiO₂ to induce ROS in Pt/Sn_{0.2}Ti_{0.8}O₂. With the Pt/TiO₂-R and
344 Pt/TiO₂-A catalysts as references, the Pt/Sn_{0.2}Ti_{0.8}O₂ catalyst exhibited much higher CO catalytic
345 oxidation activity, demonstrating that low-temperature CO oxidation on Pt/Sn_{0.2}Ti_{0.8}O₂ was
346 energetically more favorable via the ROS route.

347 The reaction orders of CO and O₂ over Pt/Sn_{0.2}Ti_{0.8}O₂, Pt/TiO₂-R and Pt/TiO₂-A were all
348 slightly higher than 0, which pointed to the MvK mechanism, typical of catalysts based on
349 reducible oxides. This result was further verified by DFT simulation, which suggests that O₂ could
350 not be directly adsorbed at or around the Pt clusters of Pt/Sn_{0.2}Ti_{0.8}O₂ and Pt/TiO₂-R. Accordingly,
351 the reactivity of the active lattice oxygen was studied by a transient CO oxidation without the
352 presence of gaseous O₂. The results reveal that Pt/Sn_{0.2}Ti_{0.8}O₂ contained higher amount of active
353 lattice oxygen, but it cannot be characterized by O₂-TPD. Therefore, the idea of “*in situ* generation
354 of active O species upon CO introduction” over Pt/Sn_{0.2}Ti_{0.8}O₂ was conceived.

355 The assumption of CO-induced ROS was systematically investigated by a series of *in situ*
356 studies. The *in situ* NAP-XPS spectra suggest that Pt²⁺ was the major Pt species of Pt/Sn_{0.2}Ti_{0.8}O₂,
357 Pt/TiO₂-R and Pt/TiO₂-A after the moderate reduction, but only on Pt/Sn_{0.2}Ti_{0.8}O₂ catalyst that the
358 generation of Pt⁴⁺ species was observed when it was exposed to CO or CO+O₂. Three possibilities
359 may lead to the formation of Pt⁴⁺ on Pt/Sn_{0.2}Ti_{0.8}O₂: (i) Pt²⁺ captures gaseous O₂ thus being
360 oxidized into Pt⁴⁺; (ii) Pt²⁺ donates electron to the support, therefore resulting in Pt⁴⁺ formation;
361 (iii) lattice O in the support migrates to the vicinity of Pt²⁺ (i.e. the ROS process), causing the
362 oxidation of Pt²⁺ to Pt⁴⁺. *In situ* NAP-XPS results (Fig. 3a) indicate that Pt⁴⁺ was not observed
363 when Pt/Sn_{0.2}Ti_{0.8}O₂ was exposed to O₂ alone, eliminating the first possibility. Regarding the
364 second possibility, it is well-known that Pt clusters supported on stoichiometric TiO₂ donate
365 electrons to the support, and the Pt clusters draw electrons from the reduced TiO₂. Therefore,
366 when reducing gas CO is introduced, Pt should receive electrons from the support, resulting in
367 lower Pt valence. However, NAP-XPS (Fig. 3a) shows that when reducing gas CO was introduced,

368 Pt^{2+} on the surface of $\text{Pt}/\text{Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$ is oxidized to Pt^{4+} , indicating that electron transfer between
369 Pt and the support cannot result in the Pt^{4+} formation. Therefore, the ROS process induced by CO
370 adsorption should be the cause of the oxidation of Pt^{2+} to Pt^{4+} . *In situ* Raman studies showed that
371 there was weakening of O-Ti(Sn)-O bond strength, demonstrating higher mobility of surface O_{latt}
372 when CO was introduced onto $\text{Pt}/\text{Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$. The *in situ* DRIFTS spectra indicated that the
373 average valence state of Pt over $\text{Pt}/\text{Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$ obviously increases with rising reaction
374 temperature. The result was further verified by the *in situ* acquired NAP-XPS spectra conducted
375 under reaction conditions. Such results reveal that ROS over $\text{Pt}/\text{Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$ became more
376 significant with increasing CO oxidation rate. Overall, the doped Sn promoted the mobilities of
377 O_{latt} in support, facilitating the ROS process upon CO introduction. This conclusion substantiates
378 the “*in situ* generation of active O species” assumption over the $\text{Pt}/\text{Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$ catalyst.

379 The fundamental details of ROS process were further investigated by DFT simulations.
380 Structure optimization suggests that the Pt_4O_4 clusters tended to connect with Sn-O-Ti through the
381 O site in Sn-O-Ti. The charge density of O in these Sn-O-Ti bonds increased after the loading of
382 Pt_4O_4 clusters as well as the subsequent adsorption of CO. We speculated that the increased charge
383 density promoted the mobility of the O in Sn-O-Ti, resulting in the occurrence of ROS in
384 $\text{Pt}/\text{Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$ during CO oxidation reaction. Reaction cycle simulations show that over
385 $\text{Pt}/\text{Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$, the energy barrier of CO oxidation directly by lattice O was higher than that by the
386 O species derived from the ROS process, suggesting that the latter is more preferred for CO
387 oxidation over $\text{Pt}/\text{Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$ as depicted in Fig. 6. A detailed visible depiction of the ROS process
388 can be found in the Supplementary Movies 1 and 2 of AIMD simulations.

389 Overall, we activated the low temperature reverse oxygen spillover on Titania-supported
390 Platinum catalyst by introducing Sn into TiO_2 support, and further demonstrated the existence and
391 mechanistic route of reverse oxygen spillover in low-temperature CO oxidation by a combination
392 of experimental and theoretical studies. The revealed interfacial dynamics in reverse oxygen
393 spillover fills the gaps of interfacial chemistry of adsorbates and/or intermediate transport through
394 metal-support interfaces, and allows deeper fundamental understanding of catalytic reactions
395 involving oxygen, and hence improvement of catalyst design for technologically relevant redox
396 reactions. We speculate the strategy to improve the oxygen mobility of support, such as the

397 construction of asymmetric oxygens ($M_1\text{-O-M}_2$) or doping secondary metals with weak M-O bond,
398 probably is particularly effective to promote ROS. Looking forward, we anticipate that the
399 reactant-adsorption-triggered characteristics of oxygen spillover will arouse further investigations
400 on the mechanistic effect of microstructures (such as size of active sites, nature of supports, degree
401 of O charging) and reactants (such as hydrocarbons, H_2O and SO_2), finding more potential
402 applications in thermo-, photo- and electro-catalysis.

403

404 **Methods**

405 **Synthesis of materials**

406 The $\text{Sn}_x\text{Ti}_{1-x}\text{O}_2$ supports (where x represents the molar ratio of $\text{Sn}/(\text{Sn}+\text{Ti})$) were synthesized by
407 a co-precipitation method using $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$ and $\text{Ti}(\text{SO}_4)_2$ as precursors⁵⁷. First, $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$ and
408 $\text{Ti}(\text{SO}_4)_2$ were dissolved in deionized water. Then, standard ammonia solution (25 wt%) was
409 added into the solution until pH 10 to induce the co-precipitation of Sn and Ti ions. The
410 precipitates were filtered out and washed by deionized water until neutral. The obtained materials
411 were dried at 105 °C for 12 h and subsequently calcined at 500 °C for 4 h in air with a heating rate
412 of 2 °C/min. The reference anatase TiO_2 was prepared by the same method but without
413 $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$, and was denoted as $\text{TiO}_2\text{-A}$ due to its anatase crystallite. A rutile TiO_2 (Aladdin,
414 99.99%) was directly employed as another reference sample, and was denoted as $\text{TiO}_2\text{-R}$.

415 All the $\text{Pt}/\text{Sn}_x\text{Ti}_{1-x}\text{O}_2$ and Pt/TiO_2 catalysts were prepared by the impregnation method using
416 platinum nitrate ($\text{Pt}(\text{NO}_3)_2$) solution as metal source. First, commercial solution of $\text{Pt}(\text{NO}_3)_2$
417 (Aladdin, 18.02% of Pt) was diluted to 0.01g Pt/mL. Then 1.0 mL of the diluted $\text{Pt}(\text{NO}_3)_2$ solution
418 was added into 2 g of support (TiO_2 or $\text{Sn}_x\text{Ti}_{1-x}\text{O}_2$) with vigorous stirring at room temperature. The
419 obtained samples of 0.5 wt% Pt loading were dried at 105 °C for 12 h, and then calcined at 500 °C
420 for 1 h in air with a heating rate of 2 °C/min. Finally, the $\text{Pt}/\text{Sn}_x\text{Ti}_{1-x}\text{O}_2$ and Pt/TiO_2 catalysts were
421 treated in 5% H_2/N_2 at 300 °C for 1 h.

422 **CO oxidation performance**

423 The performance of catalysts (100 mg, 40–60 mesh) in CO oxidation was evaluated using a
424 fixed-bed quartz micro-reactor. The typical reaction condition was as follows: 1% CO, 1% O_2 , and
425 N_2 as balance gas with a total flow rate of 100 $\text{mL}\cdot\text{min}^{-1}$, corresponding to a gas hourly space

426 velocity (GHSV) of 60 000 mL g_{cat}⁻¹ h⁻¹. The concentrations of CO and CO₂ in the inlet and outlet
427 streams were measured by an infrared gas analyzer (Gasmeter Dx-4000). The CO conversion was
428 calculated based on the following equation:

$$429 \quad X_{CO} = \frac{C_{COin} - C_{COout}}{C_{COin}} \times 100\% \quad (1)$$

430 where, X_{CO} is CO conversion, C_{COin} and C_{COout} are the concentrations of CO in the inlet and outlet.

431 The specific reaction rates and TOF of CO oxidation at different temperatures over the catalysts
432 were measured under different conditions, keeping CO conversion below 20% by varying the
433 GHSV (to suppress the influence of inner and external diffusion).

434 The reaction rate k ($\mu\text{mol g}^{-1} \text{s}^{-1}$) can be calculated by assuming ideal gas behavior:

$$435 \quad k = \frac{X_{CO} \cdot F_{CO}}{W} \times 100\% \quad (2)$$

436 where, X_{CO} is CO conversion, F_{CO} ($\mu\text{mol s}^{-1}$) is molar gas flow rate of CO, and W (g) is the mass
437 of catalyst in the fixed-bed reactor.

438 The catalytic velocities were determined by a turnover frequency of CO conversion over Pt sites
439 (TOF_{Pt} (s^{-1})), which can be obtained by the following equation:

$$440 \quad \text{TOF}_{Pt} = \frac{X_{CO} \cdot F_{CO}}{N_{Pt}} \times 100\% \quad (3)$$

441 where, X_{CO} is CO conversion (< 20%), F_{CO} ($\mu\text{mol s}^{-1}$) is molar gas flow rate of CO, and N_{Pt} (μmol)
442 is the total number of Pt atoms on the catalyst. It should be noted that all the catalysts used in this
443 study contained 0.5 wt% Pt. Moreover, all Pt atoms were considered when calculating TOF_{Pt} to
444 enable a fair comparison of catalyst activity under the same Pt usage.

445 The apparent activation energies (E_a (kJ mol^{-1})) over the catalysts were calculated at CO
446 conversion lower than 20% according to the Arrhenius equation.

447 **Characterization**

448 **Transient CO oxidation** was tested in a fixed-bed quartz micro-reactor. The reduced catalysts
449 were loaded into the reactor and heated to the reaction temperature under N₂ without any further
450 pretreatment. The reaction temperature was fixed at 100 or 200 °C with a CO concentration of 1%
451 and N₂ as the balance gas, without the supply of O₂. The gas flow rate was set to 100 mL·min⁻¹
452 with a GHSV of 60,000 mL g_{cat}⁻¹ h⁻¹. The infrared gas analyzer (Gasmeter Dx-4000) was utilized to

453 measure the concentrations of CO and CO₂ in both the inlet and outlet streams.

454 **N₂ physisorption** was measured at liquid nitrogen temperature by a micromeritics ASAP 2460
455 instrument in the static mode. Before measurement, the catalysts were degassed at 250 °C for 4 h.
456 The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) equation. The pore
457 volumes and average pore diameters were determined using the Barrett-Joyner-Halenda (BJH)
458 method based on the N₂ adsorption-desorption isotherms.

459 **XRD** patterns were recorded over D8 Advance X-ray diffractometer (Bruker AXS company)
460 using Cu K_α radiation. The pattern was recorded in the 2θ range of 5–90° with a speed of 1.5°/min
461 and a step size of 0.02°. The operating voltage and current was 40 kV and 40 mA, respectively.
462 Rietveld refinements of all XRD patterns were performed by the GSAS software package.

463 **O₂-TPD** study was conducted on a chemisorption analyzer (Micromeritics, AutoChem 2920
464 ThermoStar). In a quartz reactor, the catalyst sample was pretreated at 300 °C in 2% O₂/He for 1 h.
465 Then, the catalyst was cooled to 50 °C in a flow of 2% O₂/He for 30 min. Then the weakly
466 adsorbed O species were purged by pure He for 30 min, and the temperature was subsequently
467 increased to 800 °C with continuous introduction of He at a rate of 10 °C min⁻¹. The desorption of
468 O₂ was recorded using a thermal conductivity detector (TCD).

469 **SEM and TEM** images were observed by ZEISS GEMINISEM 500 electron field emission
470 scanning electron microscope at 30 kV, and JEM 2100F microscope operating at 200 kV,
471 respectively.

472 **In situ NAP-XPS** spectra were recorded by a SPECS-AU190069 instrument. The instrument
473 was equipped with an advanced multi-stage differential pumping system and static voltage lens,
474 which can be used in ultra-high vacuum (1×10⁻⁹ mbar) with gases of 0–5 mbar. All spectra were
475 collected by using monochromatized Al K_α irradiation (1486.6 eV), which was generated by 50 W
476 of excitation source power in an Al anode (SPECS XR-50). The generated X-ray spot was about
477 0.3 mm in diameter, close to the aperture of the nozzle. The reaction pressure was kept at 1 mbar
478 by a pressure reducing valve. The powder sample was pressed into a smooth sheet, and was fixed
479 on a special sample table that can be heated during reaction. An electron flood gun was equipped
480 to compensate the charging of catalysts during measurements.

481 **In situ DRIFTS** study was carried out on a Nicolet iS50 FTIR spectrometer equipped with a

482 DRIFTS cell and a highly sensitive MCT detector. The DRIFTS spectra were collected by
483 accumulating 64 scans with a spectral resolution of 4 cm^{-1} . To exclude the influence of moisture
484 and impurities, the catalyst was pretreated at $300\text{ }^{\circ}\text{C}$ in $5\%\text{H}_2/\text{He}$ for 1 h before each test, then
485 purged with pure He for 1 h. After the pretreatment, the catalyst was cooled to a designated
486 temperature. The spectrum was collected after the introduction of $1\%\text{ CO}$ and $1\%\text{ O}_2$ with N_2
487 balance for 30 min.

488 ***In situ* Raman** study was conducted by a Horiba LabRAM HR Evolution instrument equipped
489 with 532 nm laser source (Ventus LP 532), Synapse Charge Coupled Device (CCD) detector, and
490 *in situ* cell reactor (Linkam CCR1000). The catalyst was pretreated at $300\text{ }^{\circ}\text{C}$ in $5\%\text{H}_2/\text{N}_2$ for 1 h
491 before each test, then purged with pure N_2 for 1 h. After the pretreatment, the catalyst was cooled
492 to $100\text{ }^{\circ}\text{C}$ for spectrum collection. The Raman spectra were collected by accumulating 8 scans
493 with acquisition time of 6 s. Then, $1\%\text{ CO}$ and/or $1\%\text{ O}_2$ with N_2 balance were introduced, and the
494 corresponding Raman spectra were recorded after 30 min of reaction.

495 **SAC-STEM** image was observed by using a JEM ARM200F transmission electron microscope
496 operating at 200 kV , which was equipped with a probe corrector, a high-angle annular dark-field
497 detector, and a EDX detector.

498 **XANES and EXAFS** were conducted at Singapore Synchrotron Light Sources. The radiation
499 was monochromatized by a Si (111) double crystal monochromator, and the results were processed
500 by employing the Athena software.

501 **DFT simulation**

502 The slab models were designed rationally. First, because the HR-TEM images indicate that the
503 (110) plane of rutile was the main exposed plane of $\text{Pt}/\text{Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$ and $\text{Pt}/\text{TiO}_2\text{-R}$, we employed
504 the (110) plane of rutile TiO_2 as substrate with a $[5\times 3]$ supercell and three stoichiometric TiO_2
505 layers (approximately $15\text{ \AA}\times 20\text{ \AA}\times 9\text{ \AA}$). Second, since the SAC-STEM images and XPS results
506 suggest that the Pt species on the support was in the form of PtO nano clusters, a Pt_4O_4 cluster was
507 placed on this (110) plane of rutile TiO_2 to simulate the configuration of $\text{Pt}/\text{TiO}_2\text{-R}$. Then, 20% of
508 Ti atoms in the configuration of $\text{Pt}/\text{TiO}_2\text{-R}$ was randomly replaced by Sn atoms to simulate the
509 configuration of $\text{Pt}/\text{Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$. All these slab models were separated by a vacuum of 15 \AA .

510 AIMD simulation was performed using the CP2K package. The generalized-gradient

511 approximation (GGA) with spin-polarized Perdew–Burke–Ernzerh (PBE) functional was used to
512 describe the exchange–correlation energy. A double-z Gaussian basis sets with an auxiliary plane
513 wave basis set (cutoff energy of 500 Rydberg) was used to expand the wavefunctions. All AIMD
514 simulations were conducted by sampling the canonical ensemble with Nose–Hoover thermostats
515 and a time step of 1 fs. Because of the relatively short time scale of AIMD (10–20 ps in this study),
516 the sampling of AIMD was only applied to extremely fast events of low energy barrier, and the
517 observation of slow processes was excluded. Hence a large number of phase spaces could be
518 explored quickly by enhancing the simulation temperature, and thus the AIMD simulation
519 temperature was set at 700 K, slightly lower than the temperature adopted for the calcination of
520 the samples⁵⁶. The configurations of Pt/Sn_{0.2}Ti_{0.8}O₂ and Pt/TiO₂-R first underwent an AIMD
521 simulation of 10 ps to ensure the stabilization of these configurations. Then, the configurations at
522 2, 4, 6, 8 and 10 ps of AIMD simulation were set as initial structure and optimized by VASP to
523 obtain the most stable configurations of Pt/Sn_{0.2}Ti_{0.8}O₂ and Pt/TiO₂-R. Finally, a CO molecule was
524 adsorbed on the configurations of Pt/Sn_{0.2}Ti_{0.8}O₂ and Pt/TiO₂-R to undergo an AIMD simulation of
525 20 ps to investigate the reverse O spillover during CO oxidation reaction.

526 The geometrical optimization and transition state (TS) retrievals were performed by VASP with
527 projected augmented wave (PAW). The PBE functional was used in the GGA with the Hubbard
528 model, which was expanded on a plane wave basis with 400 eV of kinetic cutoff energy. The U_{eff}
529 (i.e., $U-J$) of Ti⁵⁸, Sn⁵⁹, and Pt⁶⁰⁻⁶² were set at 4.5, 5.0, and 9.0 eV, respectively. The gamma point
530 (i.e., 1×1×1) of the K-point was employed due to the large sizes of these configurations. The SCF
531 tolerance and maximum atomic force were set at 10⁻⁶ eV and 0.02 eV/Å during geometrical
532 optimization. The transition state was roughly estimated by the CI-NEB (climbing the
533 image-nudged elastic band) method. Then the roughly converged transition state was precisely
534 optimized by the Dimer method.

535 **Data availability**

536 The data that support the findings of this study are included in the published article (and its
537 Supplementary Information) or available from the corresponding author upon reasonable request.

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685 **Author contributions**

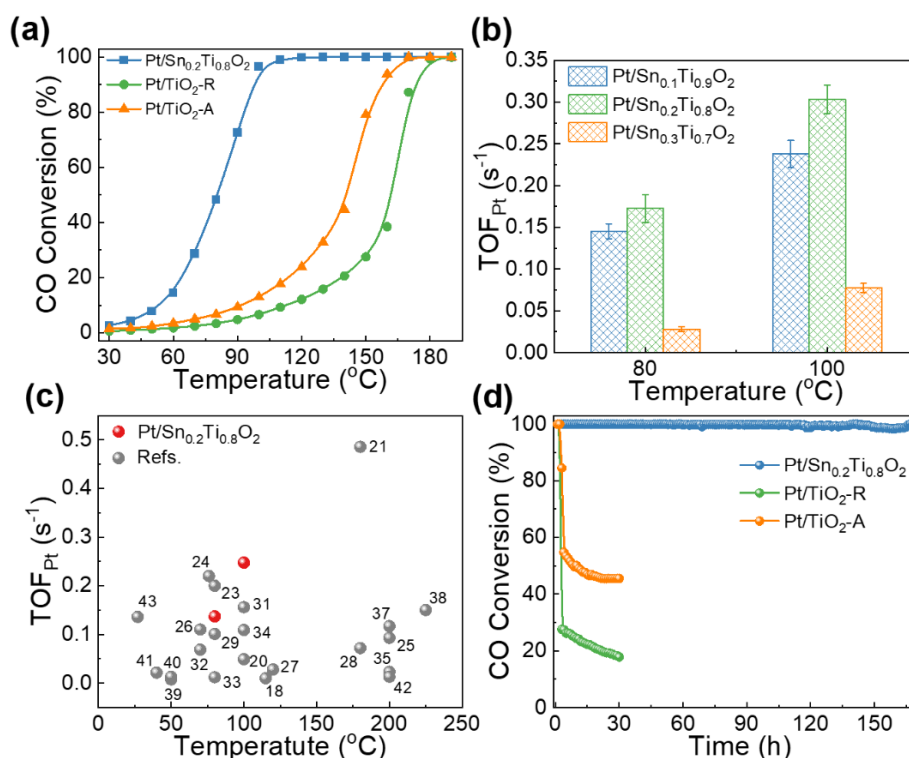
686 J.J. C. and S.C. X. proposed idea and wrote the paper. J.J. C. and J.H. Li. supervised the whole
687 work. S.C. X. performed DFT simulation. H.Y. L. and J.Q. S. performed all the experiments

688 except *in situ* DRIFTS. L. O. and F. M. designed the *in situ* DRIFTS and modified the manuscript.
689 J.X. M., H. L. and Z.J. G. modified the manuscript. All the authors discussed the results and
690 commented on the manuscript.

691 **Competing Interests**

692 The authors declare no competing interests.

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Fig. 1 | CO oxidation performance over Pt/Sn_{0.2}Ti_{0.8}O₂, Pt/TiO₂-R and Pt/TiO₂-A

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pretreated with 5% H₂ at 300 °C for 1 hour. a, CO conversion plots under steady-state

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feed of “1% CO, 1% O₂, N₂ balance” and GHSV of 60 000 ml·g_{cat}⁻¹·h⁻¹. **b**, Turnover

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frequencies of CO oxidation over Pt sites (TOF_{Pt}) measured at 80 °C and 100 °C with CO

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conversion below 20%. The error bars represent standard deviations. **c**, Comparison of

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TOF_{Pt} between Pt/Sn_{0.2}Ti_{0.8}O₂ and the Pt-based catalysts in reported references. **d**, Long

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term test of sulfur resistance in CO oxidation. Reaction conditions: reaction feed of 1% CO,

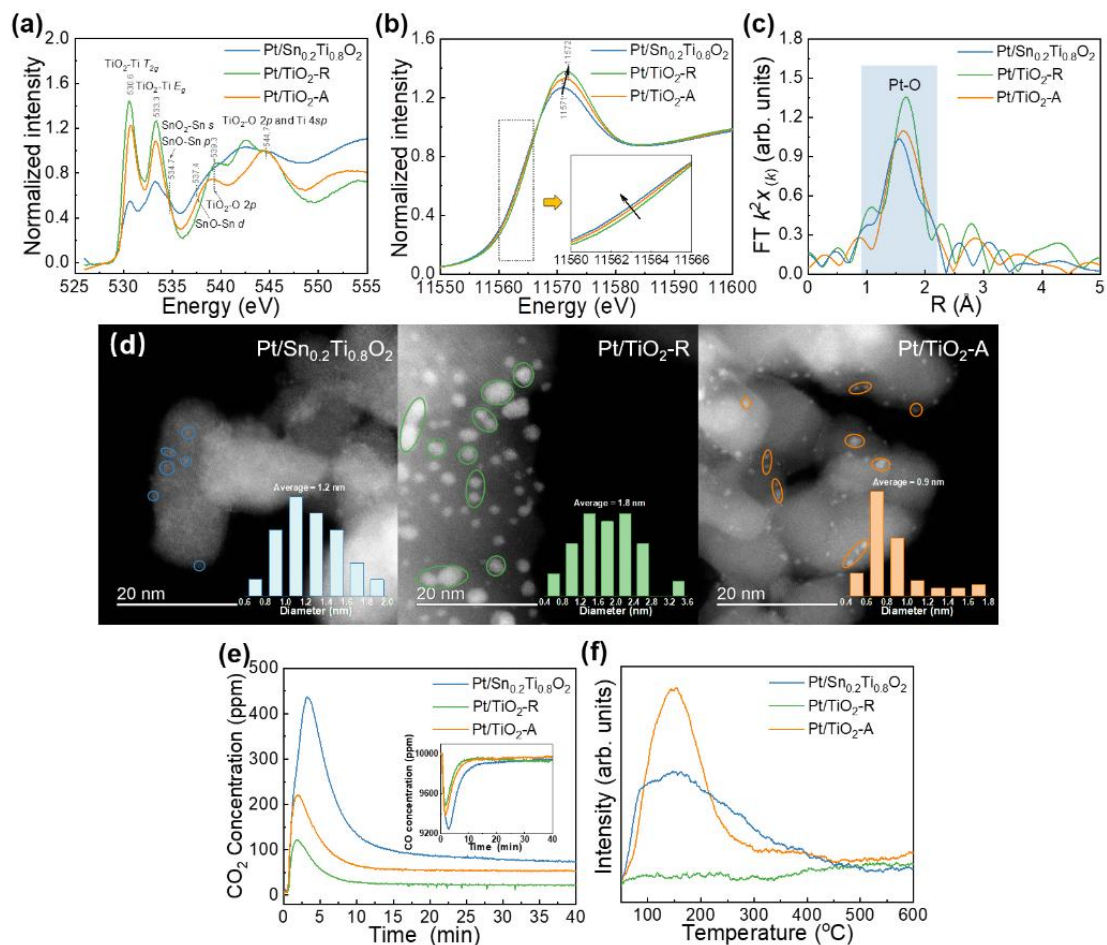
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1% O₂, 10% H₂O, 100 ppm SO₂, N₂ balance; GHSV of 60 000 ml·g_{cat}⁻¹·h⁻¹; and reaction

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temperature of 240 °C.

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Fig. 2 | Static characterization of Pt/Sn_{0.2}Ti_{0.8}O₂, Pt/TiO₂-R and Pt/TiO₂-A pretreated

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with 5% H₂ at 300 °C. a, XANES spectra of O K-edge. b, XANES spectra of Pt L₃-edge. c,

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Magnitude component of the k² weighted FT-EXAFS data of Pt L₃-edge. d, SAC-STEM

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HAADF images; inset shows the particle size distribution of Pt clusters. e, CO₂ generation

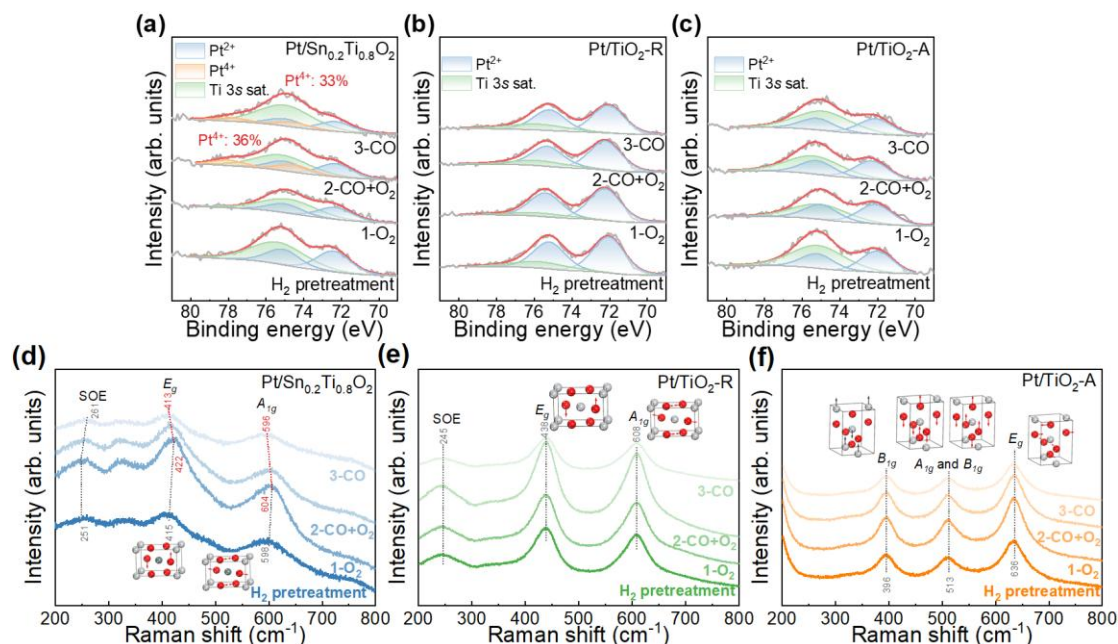
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and corresponding CO concentration (inset) as a function of time during the transient CO

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oxidation without O₂ supply (1% CO/N₂) at 100 °C. f, O₂-TPD profiles.

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Fig. 3 | *In situ* NAP-XPS and *in situ* Raman studies of Pt/Sn_{0.2}Ti_{0.8}O₂, Pt/TiO₂-R and

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Pt/TiO₂-A pretreated with 5% H₂ at 300 °C. a–c, *In situ* NAP-XPS Pt 4f spectra recorded

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at 100 °C after (a) Pt/Sn_{0.2}Ti_{0.8}O₂, (b) Pt/TiO₂-R and (c) Pt/TiO₂-A was exposed to 1 mbar

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of O₂, 0.5 mbar of CO with 0.5 mbar of O₂, and 1 mbar of CO in turn. d–f, *In situ* Raman

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spectra recorded at 100 °C after (d) Pt/Sn_{0.2}Ti_{0.8}O₂, (e) Pt/TiO₂-R and (f) Pt/TiO₂-A was

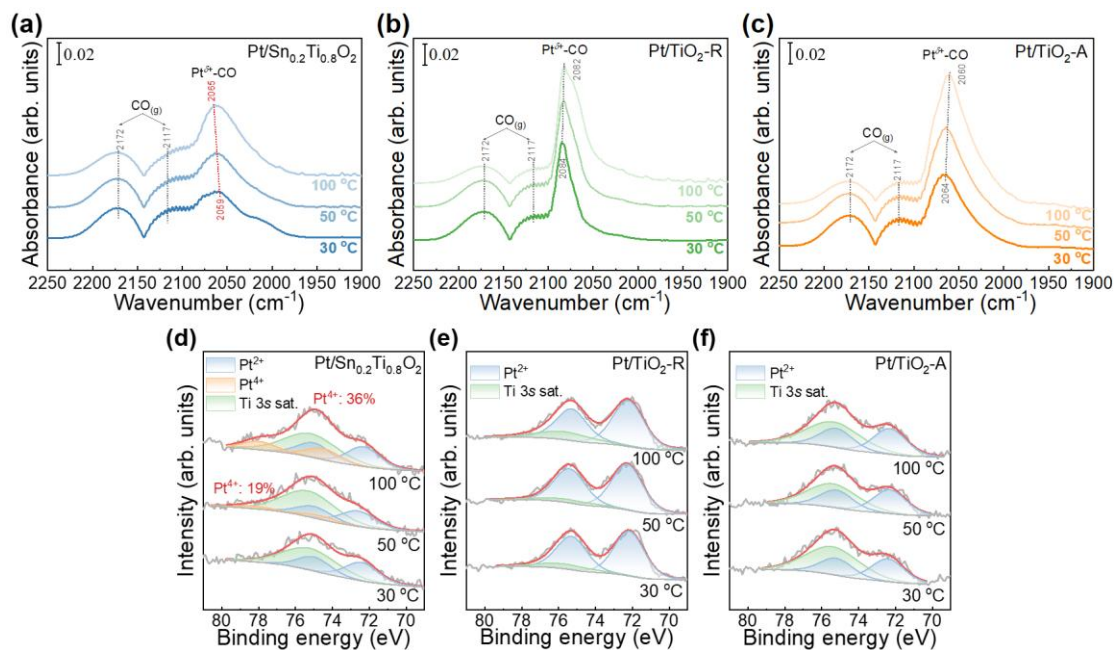
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exposed to 1% O₂, 1% CO + 1% O₂, and 1% CO in turn under ambient pressure. The term

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SOE means the second-order effect.

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Fig. 4 | *In situ* DRIFTS and *in situ* NAP-XPS spectra of Pt/Sn_{0.2}Ti_{0.8}O₂, Pt/TiO₂-R and

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Pt/TiO₂-A recorded at 30–100 °C after exposure to CO+O₂. a–c, *In situ* DRIFTS spectra

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recorded at 30–100 °C after (a) Pt/Sn_{0.2}Ti_{0.8}O₂, (b) Pt/TiO₂-R and (c) Pt/TiO₂-A was

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exposed to 1% CO + 1% O₂ at a designated temperature under ambient pressure. **d–f, *In***

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***in situ* NAP-XPS Pt 4f spectra recorded at 30–100 °C after (d) Pt/Sn_{0.2}Ti_{0.8}O₂, (e) Pt/TiO₂-R**

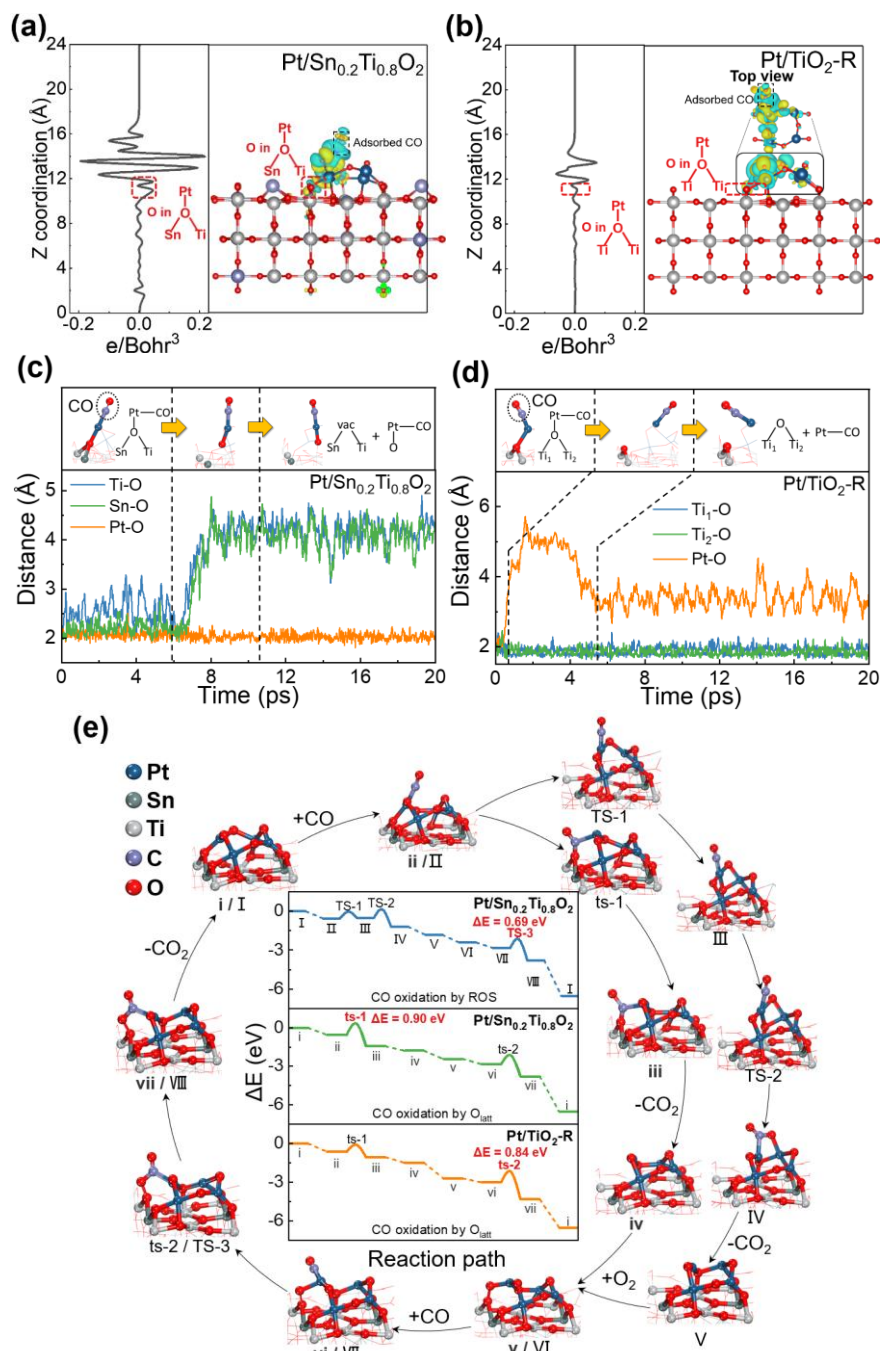
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and (f) Pt/TiO₂-A was exposed to 0.5 mbar of CO with 0.5 mbar of O₂ at a designated

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temperature.

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Fig. 5 | DFT simulations of CO oxidation over Pt/Sn_{0.2}Ti_{0.8}O₂ and Pt/TiO₂-R. a–b,

736 Charge density difference and the corresponding planar-average charge density analyses

737 of CO adsorption on (a) Pt/Sn_{0.2}Ti_{0.8}O₂, and (b) Pt/TiO₂-R. The charge density difference

738 was calculated by the equation $\Delta\rho = \rho_{AB} - \rho_A - \rho_B$, where A represents CO, and B represents

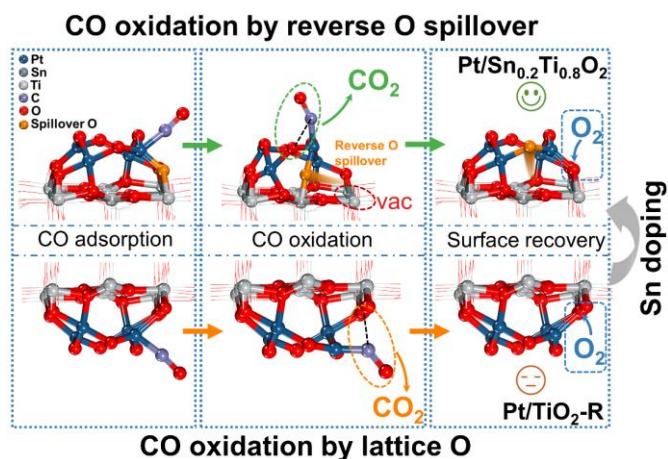
739 Pt/Sn_{0.2}Ti_{0.8}O₂ (a) or Pt/TiO₂-R (b) (Yellow represents increase of electron density, and

740 blue represents decrease of electron density). c–d, Atomic distance of Ti-O, Sn-O and

741 Pt-O as a function of simulated time during AIMD simulation over (c) Pt/Sn_{0.2}Ti_{0.8}O₂ and (d)

742 Pt/TiO₂-R. **e**, Energy profiles and configurations of CO oxidation reaction following the
743 pathway involving ROS (I-VIII) and that involving O_{latt} (i-vii).

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Fig. 6 | Schematic of CO oxidation on Pt/TiO₂ catalysts with and without reverse

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oxygen spillover. The upper part show CO is oxidized by reverse spillover O after Sn

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doping, and the lower part show CO is oxidized by lattice O without Sn doping.