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# Structural transformation and redox chemistry of Pd/CeO<sub>2</sub> during SO<sub>2</sub>-induced sulfurization: an *in situ* XAFS study

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*In situ* X-ray absorption fine structure (XAFS) spectroscopy was employed to elucidate the structural evolution of Pd/CeO<sub>2</sub> catalysts during SO<sub>2</sub>-induced sulfurization. Linear combination fitting of Ce L<sub>3</sub>-edge XANES spectra quantified the Ce<sup>4+</sup> → Ce<sup>3+</sup> transformation, revealing fundamentally different sulfurization mechanisms for bare *versus* Pd-promoted CeO<sub>2</sub>. At 500 °C, bare CeO<sub>2</sub> exhibited surface-limited sulfurization with Ce<sup>3+</sup>/(Ce<sup>3+</sup> + Ce<sup>4+</sup>) reaching 0.18, while Pd/CeO<sub>2</sub> achieved 0.68, demonstrating bulk oxygen participation. Temperature-dependent measurements (200–500 °C) confirmed thermal activation of the sulfurization process, with higher temperatures enabling deeper lattice penetration. Complementary Pd L<sub>3</sub>-edge XANES revealed that Pd maintained its oxidized state throughout SO<sub>2</sub> exposure, excluding PdS formation. S K-edge analysis confirmed exclusive SO<sub>4</sub><sup>2-</sup> formation *via* direct oxidation without intermediate species. These findings establish that Pd catalyzes oxygen mobility within the CeO<sub>2</sub> lattice, transforming sulfurization from a surface-confined to a bulk-accessible process while preserving the fluorite structure. The resulting cerium sulfate oxide (Ce<sub>2</sub>O<sub>2</sub>SO<sub>4</sub>) exhibits enhanced stability against re-oxidation in Pd/CeO<sub>2</sub>, contrasting with the partial reversibility observed for bare CeO<sub>2</sub>.

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## 1. Introduction

Pd catalysts are key materials for purifying exhaust gases from factories and vehicles.<sup>1–4</sup> These gases contain air pollutants and harmful compounds, such as NO<sub>x</sub>, CO, and hydrocarbons. Regulations on these compounds are becoming increasingly stringent worldwide to achieve a sustainable society. Generally, platinum-group metal (PGM) catalysts are used to oxidize or reduce harmful compounds to non-toxic substances. There is a strong need to reduce the amount of PGM used because they are scarce and expensive. Therefore, the activity of PGM catalysts must be improved. It has been reported that Pd has better thermal durability than Pt.<sup>1,5–7</sup> Various oxides, such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and TiO<sub>2</sub>, have been used as supports for Pd catalysts. CeO<sub>2</sub> has excellent redox properties and improves CO oxidation activity at low temperatures when used as a supporting material for Pd catalysts. Therefore, CeO<sub>2</sub>-supported Pd catalysts (Pd/CeO<sub>2</sub>) are frequently used for oxidation reactions.

Catalyst poisoning by sulfur-containing substances (*e.g.*, SO<sub>2</sub> and H<sub>2</sub>S) poses a critical challenge in exhaust gas purification. SO<sub>2</sub>, ubiquitously emitted from both stationary and mobile sources, can be converted to H<sub>2</sub>S under reducing conditions, creating multiple pathways for sulfur poisoning. This sulfur exposure severely deteriorates the performance of Pd catalysts.<sup>8–12</sup> Therefore, developing Pd catalysts with both high activity and enhanced sulfur tolerance is imperative. A thorough understanding of the sulfur poisoning mechanism is essential for the rational design of such S-tolerant catalysts.

It has been reported that treatment of supported Pd catalysts with SO<sub>2</sub> generally leads to a significant decrease in catalytic activity, primarily due to palladium sulfidation and a reduction in catalyst surface area.<sup>11,13–16</sup> The effects of SO<sub>2</sub> treatment on the properties of CeO<sub>2</sub> have also been investigated.<sup>17–19</sup> When CeO<sub>2</sub> undergoes sulfurization, oxygen vacancies are introduced, resulting in the reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup>. Sulfurized CeO<sub>2</sub> formed by SO<sub>2</sub> treatment exhibits enhanced oxygen storage capacity and high activity for the reduction of nitrogen oxides by ammonia.<sup>20</sup>

Although Pd/CeO<sub>2</sub> catalysts suffer from activity deterioration in the presence of SO<sub>2</sub>, Hilaire *et al.* reported that SO<sub>2</sub> poisoning, under alternating CO and O<sub>2</sub> pulse conditions, unexpectedly increased the amount of oxygen that could be transferred to and from the catalyst across the entire temperature range examined.<sup>21</sup> These findings highlight the complex

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ity of sulfur poisoning behavior in CeO<sub>2</sub>-supported Pd catalysts. Despite these insights, most previous investigations have been conducted under *ex situ* conditions or have focused solely on catalytic performance evaluation. Consequently, the real-time structural evolution of Pd/CeO<sub>2</sub> during SO<sub>2</sub> exposure and the specific role of Pd in promoting CeO<sub>2</sub> sulfurization remain insufficiently understood. Addressing these knowledge gaps is essential for developing sulfur-tolerant Pd-based catalysts.

In this study, we employed *in situ* XAFS measurements under controlled SO<sub>2</sub> gas flow to capture the dynamic structural changes of both Pd and CeO<sub>2</sub> components in real time. This approach enables us to directly observe the sequential transformation of Ce oxidation states (Ce<sup>4+</sup> to Ce<sup>3+</sup>) during SO<sub>2</sub> exposure, simultaneously monitor the chemical state of Pd species to clarify whether PdSO<sub>4</sub> or PdS formation occurs under our reaction conditions, quantitatively determine the Ce<sup>3+</sup>/Ce<sup>4+</sup> ratio evolution as a function of time and temperature, and elucidate the promotional effect of Pd on CeO<sub>2</sub> sulfurization through comparative studies of Pd/CeO<sub>2</sub> versus bare CeO<sub>2</sub>. Our *in situ* approach, combined with complementary *ex situ* characterization (XRD, STEM-EDS, XPS), provides unprecedented insights into the sulfurization mechanism and helps explain the paradoxical enhancement of oxygen storage capacity reported by Hilaire *et al.* This mechanistic understanding is crucial for designing next-generation sulfur-tolerant catalysts.

Unlike previous studies that primarily relied on *ex situ* characterization or focused on catalytic performance under SO<sub>2</sub> exposure, our work provides the first comprehensive *in situ* XAFS investigation of Pd/CeO<sub>2</sub> sulfurization under controlled reaction conditions. This real-time approach enables direct observation of Ce oxidation state evolution and Pd speciation during SO<sub>2</sub> treatment, revealing the mechanistic role of Pd in promoting bulk oxygen mobility and irreversible sulfate formation. By combining Ce L<sub>3</sub>-, Pd L<sub>3</sub>-, and S K-edge analyses with complementary structural characterization, we uncover a fundamental shift in sulfurization behavior—from surface-limited in bare CeO<sub>2</sub> to bulk-accessible in Pd/CeO<sub>2</sub>—thus offering unprecedented insights into the design of sulfur-tolerant Pd-based catalysts.

## 2. Experimental

### 2.1 Catalyst preparation

Pd/CeO<sub>2</sub> catalysts were prepared by the impregnation method. CeO<sub>2</sub> (JRC-CEO-5, Catalysis Society of Japan, 99.98% purity) was used as the support. The pore volume of JRC-CEO-5 CeO<sub>2</sub> determined by N<sub>2</sub> adsorption was 0.24 mL cm<sup>-3</sup> g<sup>-1</sup>. An aqueous solution of tetraamminepalladium(II) nitrate, [Pd(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub> (10 wt% in H<sub>2</sub>O, Sigma-Aldrich Japan, purity: 99.99%) was added dropwise to CeO<sub>2</sub> powder. The amount of [Pd(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub> solution was adjusted to achieve a Pd loading of 1 wt%. The impregnation was carried out in a water bath at 60 °C, followed by thorough mixing and drying. The

precursor was dried at 100 °C overnight, calcined in air at 400 °C for 2 h, and subsequently reduced under a 5% H<sub>2</sub>-N<sub>2</sub> flow at 200 °C for 1 h. The final Pd loading was 1 wt%.

### 2.2 Catalyst characterization

X-ray diffraction (XRD) patterns were recorded using a RINT 2200 diffractometer (Rigaku, Japan) with Cu K $\alpha$  radiation ( $\lambda$  = 1.54 Å) at 40 kV and 20 mA, with a step rate of 2° min<sup>-1</sup>. Temperature-programmed reduction with H<sub>2</sub> (H<sub>2</sub>-TPR) was performed using a BEL-CAT instrument (Microtrac BEL). Samples (0.10 g) were pretreated in air at 350 °C for 1 h, then heated from 50 to 950 °C at 5 °C min<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) was carried out using a Kratos ESCA-3400 spectrometer (AXIS-165, KRATOS, Japan) with an Al K $\alpha$  source. X-ray fluorescence (XRF) spectra were obtained using a ZSX Primus IV/RX9 instrument (Rigaku).

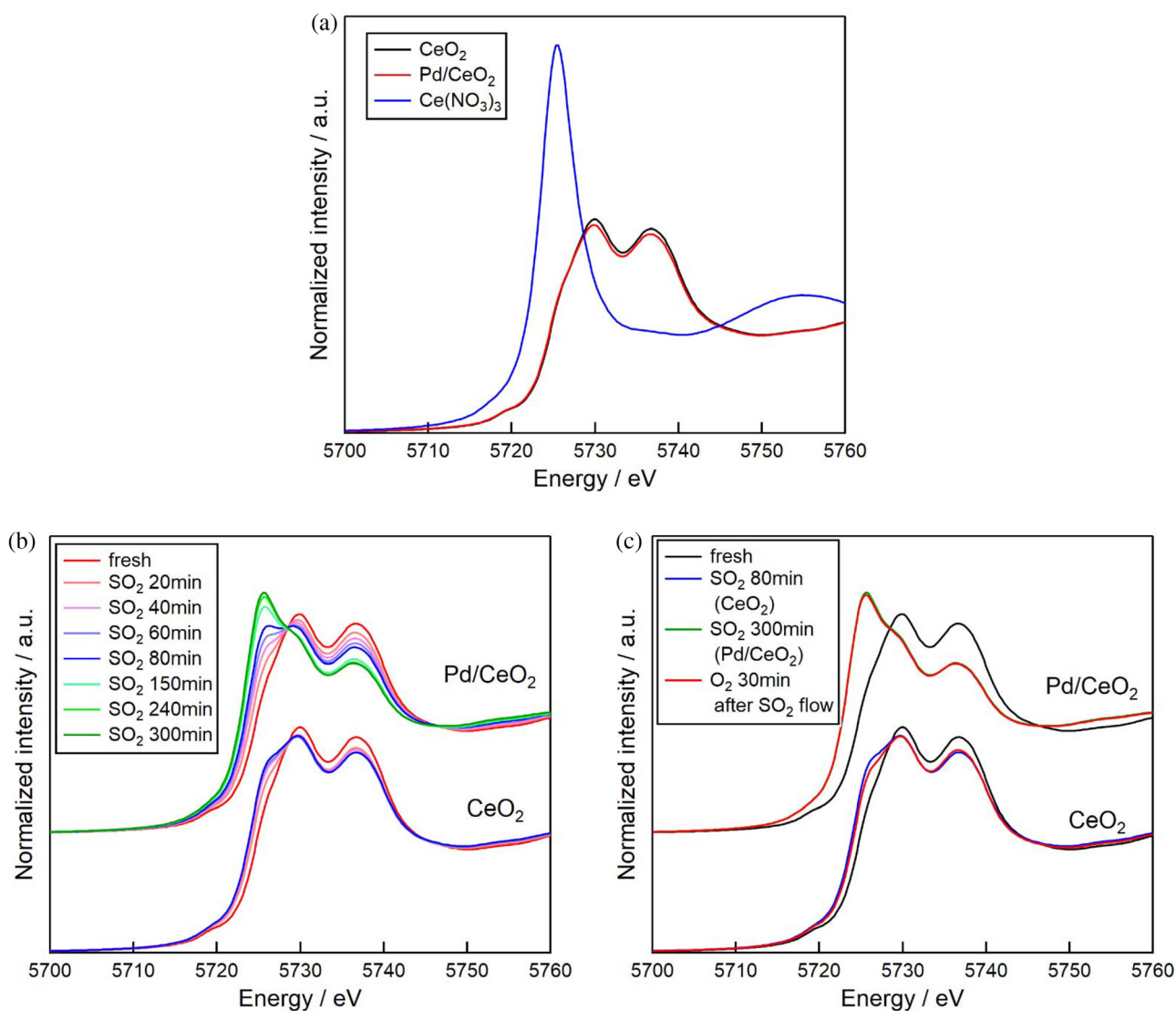
### 2.3 *In situ* XAFS measurements

XAFS measurements were conducted at the Kyushu Synchrotron Light Research Center (SAGA-LS), beamline BL06 (Saga, Japan). The storage ring energy was 1.4 GeV, and a Si (111) double-crystal monochromator was employed. Ce L<sub>3</sub>-edge spectra were collected in transmission mode, while S K-edge and Pd L<sub>3</sub>-edge spectra were recorded in fluorescence mode. For *in situ* measurements, catalysts were mixed with boron nitride, pressed into 10 mm diameter disks, and placed in a glass cell (Fig. S1). The samples were heated to the reaction temperature under a 500 ppm SO<sub>2</sub>-N<sub>2</sub> flow (100 mL min<sup>-1</sup>), then measured at room temperature. Subsequently, the catalysts were reoxidized in O<sub>2</sub> at 500 °C and re-measured. Additional measurements were performed at 200 °C and 400 °C under the same conditions. XAFS data analysis was carried out using the Athena software package.<sup>22</sup> CeO<sub>2</sub> (JRC-CEO-5, Catalysis Society of Japan, 99.98% purity) and Ce (NO<sub>3</sub>)<sub>3</sub> (Kojundo Chemical Lab. Co., Ltd, 99.9% purity) were used as reference samples.

## 3. Results and discussion

### 3.1 Structural changes in CeO<sub>2</sub> support induced by SO<sub>2</sub> treatment

Fig. 1 presents the *in situ* Ce L<sub>3</sub>-edge XANES spectra of CeO<sub>2</sub> and Pd/CeO<sub>2</sub> during SO<sub>2</sub> treatment at 500 °C. In the fresh samples, characteristic peaks corresponding to quasi-atomic Ce 2p<sub>3/2</sub> → 5d<sub>5/2,3/2</sub> electronic transitions<sup>23–25</sup> were observed at 5730 and 5737 eV, confirming the predominance of Ce<sup>4+</sup> in both materials. The similarity between the spectra of Pd/CeO<sub>2</sub> and bare CeO<sub>2</sub> indicates that Pd loading did not alter the initial oxidation state of Ce. Upon exposure to SO<sub>2</sub>, both samples exhibited a gradual decrease in peak intensities at 5730 and 5737 eV, accompanied by a shift of the absorption edge (Fig. 1(b)). Notably, Pd/CeO<sub>2</sub> displayed more pronounced spectral changes, including the emergence of a distinct peak at 5726 eV characteristic of Ce<sup>3+</sup>, demonstrating that Pd significantly enhances CeO<sub>2</sub> reduction under SO<sub>2</sub>. The presence of



**Fig. 1** *In situ* Ce L<sub>3</sub>-edge XANES spectra of CeO<sub>2</sub> and Pd/CeO<sub>2</sub> at 500 °C. (a) Fresh samples before SO<sub>2</sub> exposure. (b) Under SO<sub>2</sub> flow (500 ppm, 100 mL min<sup>-1</sup>) for up to 300 min. (c) After switching to O<sub>2</sub> flow at 500 °C following SO<sub>2</sub> treatment.

isosbestic points in both samples confirms direct conversion of Ce<sup>4+</sup> to Ce<sup>3+</sup> without detectable intermediates.

Quantitative analysis of the Ce oxidation states was performed using two complementary approaches. First, the XANES spectra were deconvoluted using arctangent and Gaussian functions (Fig. 2), yielding four components: peaks A, B, and D (Ce<sup>4+</sup>) and peak C (Ce<sup>3+</sup>). The Ce<sup>3+</sup>/(Ce<sup>3+</sup>+Ce<sup>4+</sup>) ratio was calculated from the integrated peak areas. In pristine CeO<sub>2</sub>, Ce<sup>3+</sup> arises from intrinsic oxygen vacancies; however, its absolute concentration depends significantly on preparation conditions and fitting procedures.<sup>26–28</sup> To validate these results, linear combination fitting (LCF) analysis was conducted using CeO<sub>2</sub> and Ce(NO<sub>3</sub>)<sub>3</sub> as Ce<sup>4+</sup> and Ce<sup>3+</sup> references, respectively (Fig. 3). While this method cannot quantify intrinsic Ce<sup>3+</sup> in pure CeO<sub>2</sub>, it provides reliable assessment of SO<sub>2</sub>-induced changes. The temporal evolution of Ce<sup>3+</sup>/(Ce<sup>3+</sup>+Ce<sup>4+</sup>)

ratios (Fig. 4) was monitored throughout SO<sub>2</sub> exposure and subsequent O<sub>2</sub> reoxidation. For bare CeO<sub>2</sub>, measurements were taken at 0, 20, 40, 60, and 80 min under SO<sub>2</sub> flow, followed by O<sub>2</sub> treatment at 500 °C. For Pd/CeO<sub>2</sub>, data points were collected at 0, 20, 40, 60, 80, 150, 240, and 300 min during continuous SO<sub>2</sub> exposure, after which the gas was switched to O<sub>2</sub> for reoxidation. These time intervals correspond exactly to the horizontal axis in Fig. 4, ensuring direct comparison between the two catalysts. Bare CeO<sub>2</sub> reached a plateau at Ce<sup>3+</sup>/(Ce<sup>3+</sup>+Ce<sup>4+</sup>) = 0.18 after 60 min, whereas Pd/CeO<sub>2</sub> continued reducing to Ce<sup>3+</sup>/(Ce<sup>3+</sup>+Ce<sup>4+</sup>) = 0.68 after 300 min, highlighting the catalytic role of Pd in CeO<sub>2</sub> sulfuration.

Upon switching from SO<sub>2</sub> to O<sub>2</sub> flow at 500 °C, the XANES spectra revealed distinct re-oxidation behaviors (Fig. 1(c)). Bare CeO<sub>2</sub> exhibited partial recovery of the Ce<sup>4+</sup> state, as evidenced by the diminished Ce<sup>3+</sup> peak intensity, indicating reversible

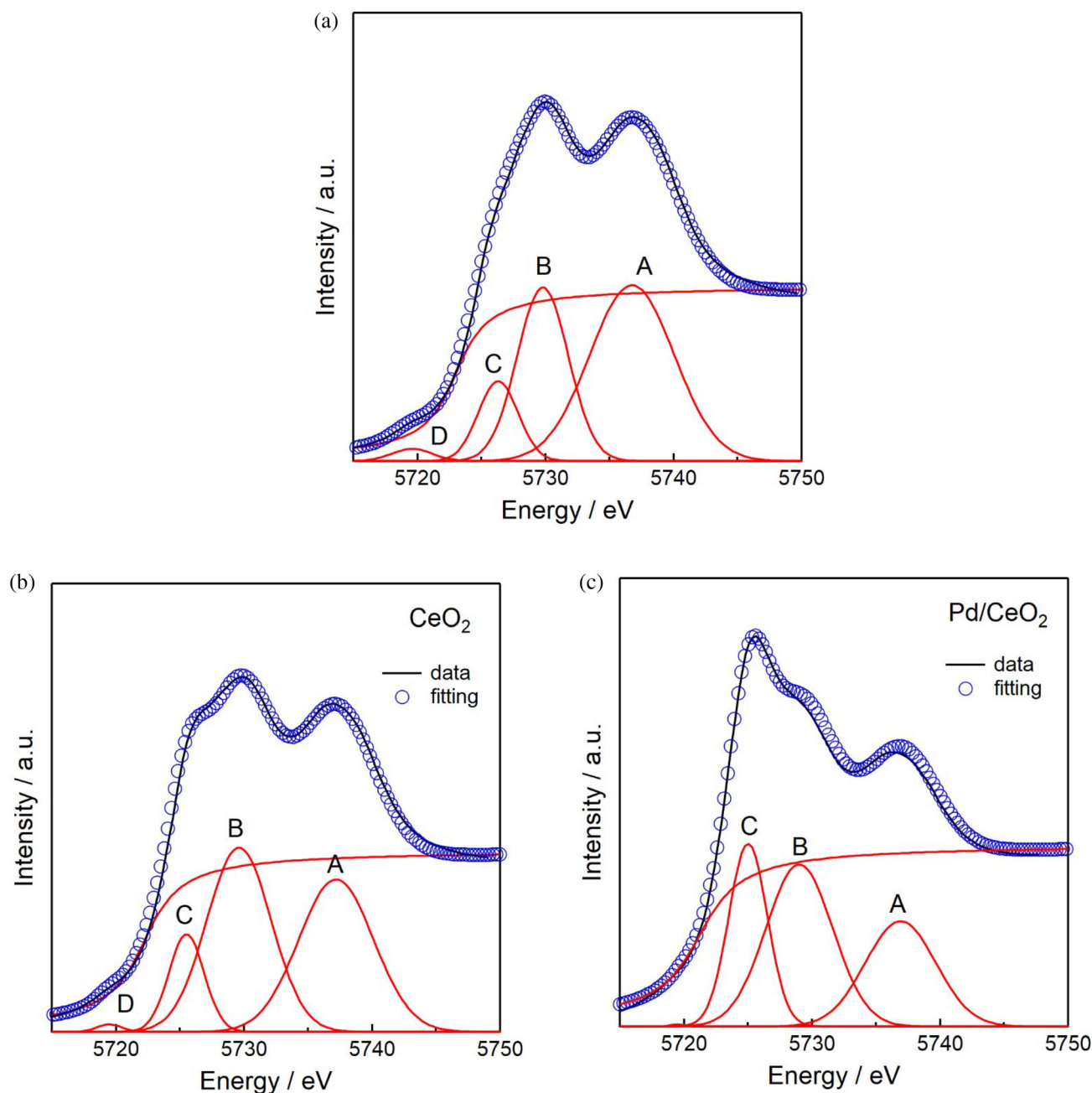
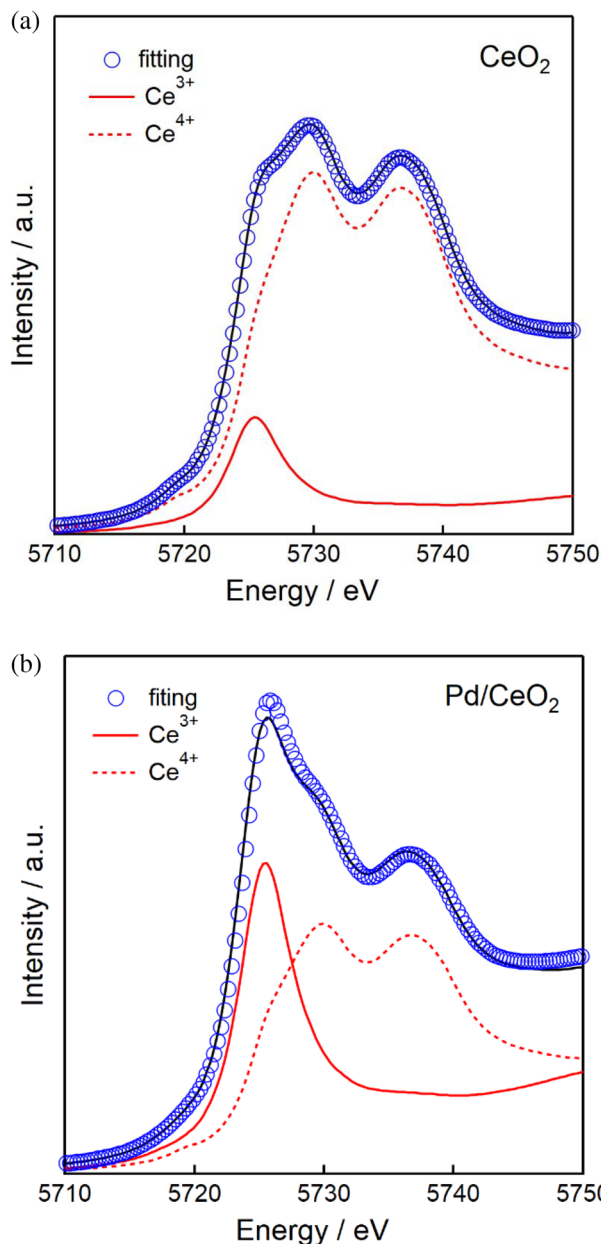


Fig. 2 Ce L<sub>3</sub>-edge XANES spectra and peak fitting for Ce oxidation states. (a) Fresh CeO<sub>2</sub>. (b) CeO<sub>2</sub> after 80 min under SO<sub>2</sub> flow at 500 °C. (c) Pd/CeO<sub>2</sub> after 300 min under SO<sub>2</sub> flow at 500 °C.

reduction of surface sites. In contrast, Pd/CeO<sub>2</sub> showed no spectral changes during O<sub>2</sub> treatment, demonstrating that Pd stabilizes the sulfurized state and prevents re-oxidation. The absence of re-oxidation also excludes the formation of bulk Ce<sub>2</sub>O<sub>3</sub> during SO<sub>2</sub> treatment, as Ce<sub>2</sub>O<sub>3</sub> would readily re-oxidize to CeO<sub>2</sub> under these oxidizing conditions.

Fig. 5 presents the *in situ* Ce L<sub>3</sub>-edge EXAFS spectra of CeO<sub>2</sub> and Pd/CeO<sub>2</sub> collected at 500 °C under SO<sub>2</sub> flow. Both samples initially displayed characteristic coordination shells: Ce–O at 2.0 Å and Ce–(O)–Ce at 3.5 Å (phase uncorrected). Progressive

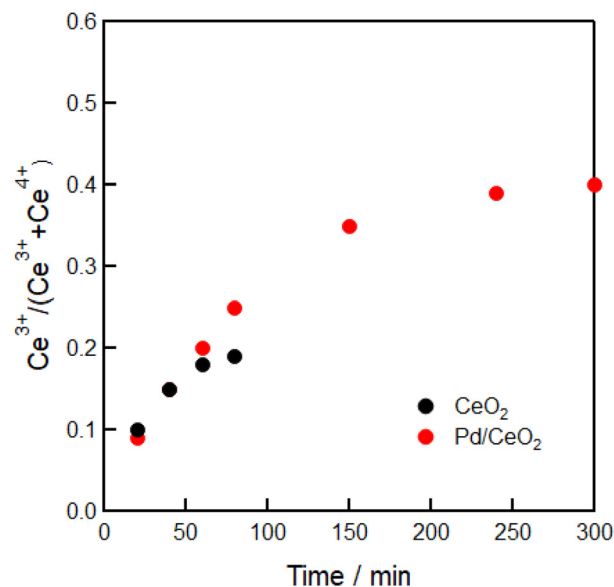
SO<sub>2</sub> exposure induced time-dependent attenuation of both peaks, reflecting the disruption of local structural order in the CeO<sub>2</sub> lattice. Notably, after 40 min of SO<sub>2</sub> treatment, Pd/CeO<sub>2</sub> exhibited significantly greater structural disorder than bare CeO<sub>2</sub>, as evidenced by the more pronounced reduction in Ce–O and Ce–(O)–Ce peak intensities. Subsequent O<sub>2</sub> treatment revealed contrasting structural recovery behaviors. While bare CeO<sub>2</sub> showed partial restoration of the Ce–O coordination shell, consistent with the Ce<sup>3+</sup> → Ce<sup>4+</sup> re-oxidation observed in XANES (Fig. 1), Pd/CeO<sub>2</sub> remained structurally unchanged.



**Fig. 3** Linear combination fitting (LCF) of Ce L<sub>3</sub>-edge XANES spectra using CeO<sub>2</sub> and Ce(NO<sub>3</sub>)<sub>3</sub> references. (a) CeO<sub>2</sub> after 80 min SO<sub>2</sub> exposure at 500 °C. (b) Pd/CeO<sub>2</sub> after 300 min SO<sub>2</sub> exposure at 500 °C.

This irreversibility demonstrates that Pd not only accelerates CeO<sub>2</sub> sulfuration but also stabilizes the resulting disordered structure against re-oxidation, likely through the formation of stable sulfate species at the Pd–CeO<sub>2</sub> interface.

The temperature dependence of SO<sub>2</sub>-induced CeO<sub>2</sub> reduction was investigated systematically (Fig. 6). At 400 °C, the Ce L<sub>3</sub>-edge XANES spectra exhibited a characteristic red-shift of the absorption edge accompanied by diminished Ce<sup>4+</sup> peak intensity, confirming partial reduction to Ce<sup>3+</sup>. The presence of clear isosbestic points demonstrated that direct Ce<sup>4+</sup> → Ce<sup>3+</sup> conversion occurred without intermediates, similar to the

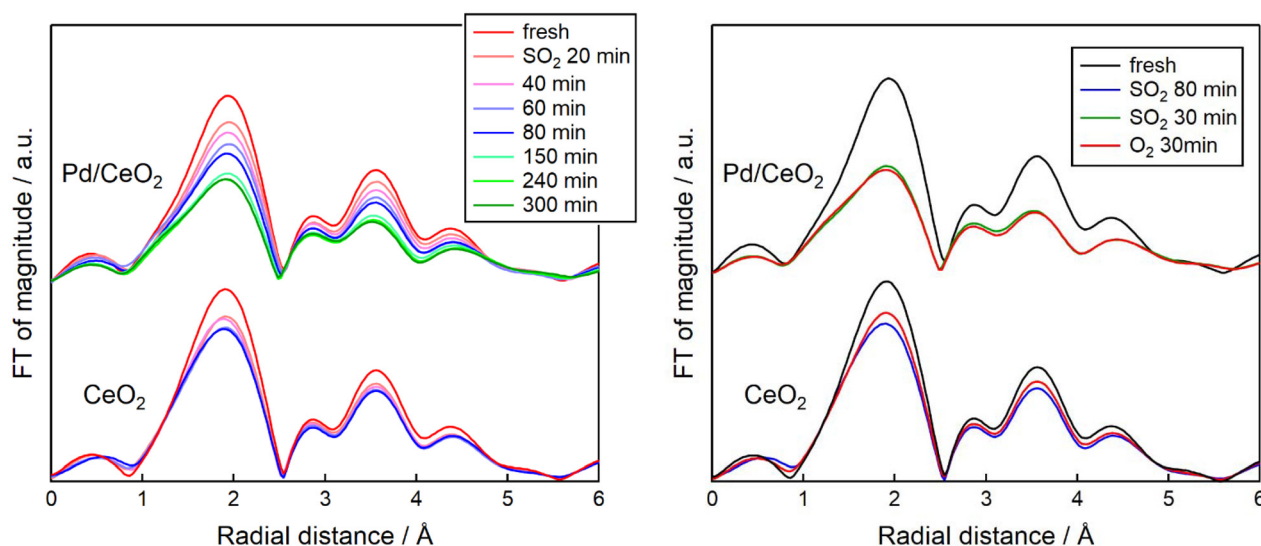


**Fig. 4** Time-dependent evolution of Ce<sup>3+</sup>/(Ce<sup>3+</sup> + Ce<sup>4+</sup>) ratio for bare CeO<sub>2</sub> and Pd/CeO<sub>2</sub> during SO<sub>2</sub> exposure at 500 °C, followed by O<sub>2</sub> re-oxidation. CeO<sub>2</sub> was measured at 0, 20, 40, 60, and 80 min under SO<sub>2</sub> flow, then switched to O<sub>2</sub> at 500 °C. Pd/CeO<sub>2</sub> was measured at 0, 20, 40, 60, 80, 150, 240, and 300 min under SO<sub>2</sub> flow, followed by O<sub>2</sub> treatment at 500 °C.

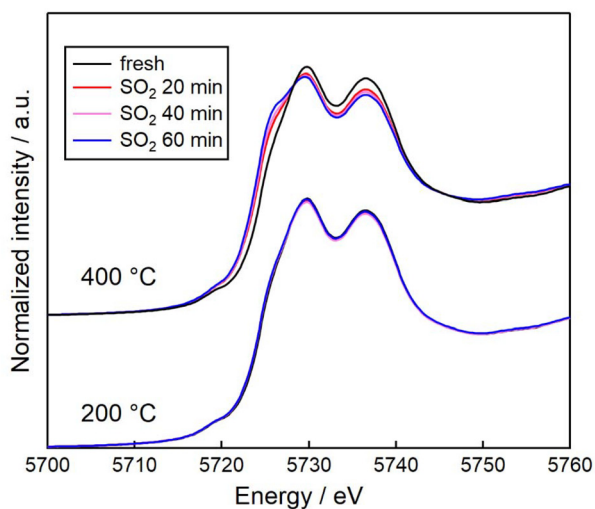
500 °C treatment. However, quantitative analysis revealed a lower Ce<sup>3+</sup>/(Ce<sup>3+</sup> + Ce<sup>4+</sup>) ratio compared to 500 °C, establishing a positive correlation between reaction temperature and reduction extent. At 200 °C, minimal spectral changes were observed even after prolonged SO<sub>2</sub> exposure, suggesting that sulfuration was confined to the outermost surface layer under these mild conditions. These results demonstrate that CeO<sub>2</sub> sulfuration exhibits strong thermal activation, with higher temperatures required to enable SO<sub>2</sub> penetration beyond the surface region into the bulk lattice.

To elucidate the role of Pd in CeO<sub>2</sub> reduction, comparative H<sub>2</sub>-reduction experiments were conducted at 600 °C (Fig. 7(a)). This temperature was selected based on established H<sub>2</sub>-TPR profiles showing distinct reduction regimes: surface oxygen removal (50–600 °C) and bulk oxygen extraction (600–950 °C).<sup>29,30</sup> Therefore, treatment at 600 °C enables selective monitoring of surface reduction processes. Both CeO<sub>2</sub> and Pd/CeO<sub>2</sub> exhibited comparable shifts in their absorption edges during H<sub>2</sub> treatment, with linear combination fitting revealing identical Ce<sup>3+</sup> formation (15% conversion from Ce<sup>4+</sup>) in both samples. This equivalence contrasts sharply with the SO<sub>2</sub>-treatment results, where Pd dramatically enhanced CeO<sub>2</sub> reduction. The absence of Pd promotion under H<sub>2</sub> indicates that the catalytic effect is specific to SO<sub>2</sub>-mediated reduction pathways, suggesting fundamentally different mechanistic routes for H<sub>2</sub> versus SO<sub>2</sub> reduction of CeO<sub>2</sub>.

The structural consequences of H<sub>2</sub> reduction were examined *via in situ* Ce L<sub>3</sub>-edge EXAFS (Fig. 7(b)). Both CeO<sub>2</sub> and Pd/CeO<sub>2</sub> displayed comparable attenuation of Ce–O and Ce–



**Fig. 5** *In situ* Ce  $L_{3}$ -edge EXAFS spectra of  $\text{CeO}_2$  and  $\text{Pd/CeO}_2$  during  $\text{SO}_2$  exposure at 500 °C.  $\text{CeO}_2$  measured at 0, 20, 40, 60, and 80 min;  $\text{Pd/CeO}_2$  measured at 0, 20, 40, 60, 80, 150, 240, and 300 min under  $\text{SO}_2$  flow (500 ppm, 100 mL  $\text{min}^{-1}$ ).



**Fig. 6** Ce  $L_{3}$ -edge XANES spectra of  $\text{CeO}_2$  and  $\text{Pd/CeO}_2$  under  $\text{SO}_2$  flow (500 ppm, 100 mL  $\text{min}^{-1}$ ) at 200 °C and 400 °C. Measurements taken at 0, 20, 40, and 60 min.

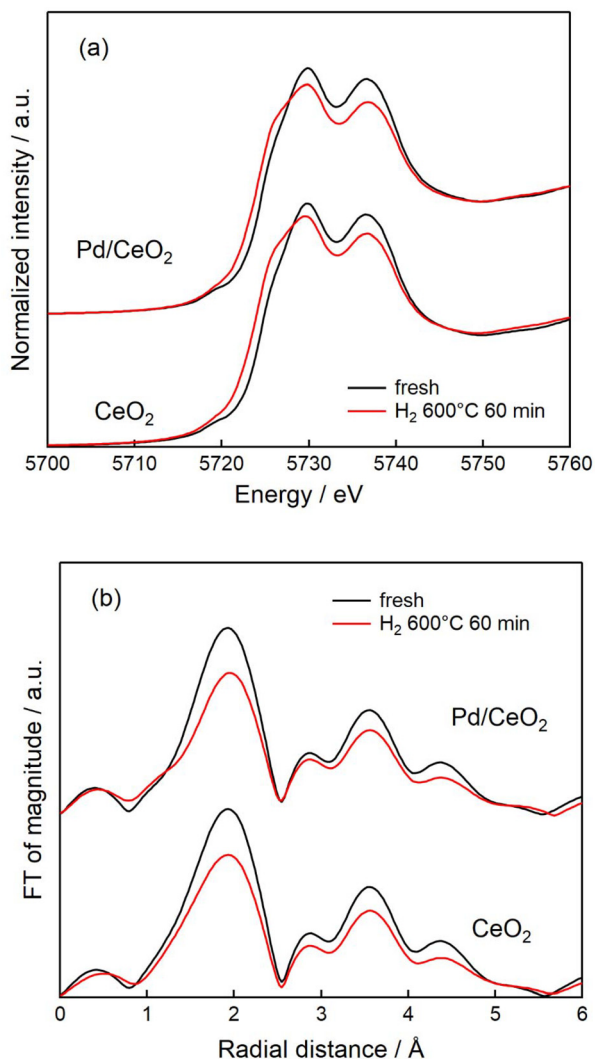
(O)–Ce coordination peaks at 600 °C, indicating similar degrees of local structural disorder upon surface oxygen removal. The equivalent post-reduction peak intensities confirm that while Pd accelerates the kinetics of  $\text{CeO}_2$  reduction under certain conditions, it does not alter the final structural state of  $\text{H}_2$ -reduced  $\text{CeO}_2$ . This observation further supports that the promotional effect of Pd is reaction-specific rather than a general enhancement of  $\text{CeO}_2$  reducibility.

The comparative analysis of  $\text{H}_2$  and  $\text{SO}_2$  reduction provides critical mechanistic insights into Pd's catalytic role. For bare  $\text{CeO}_2$ ,  $\text{SO}_2$  treatment at 500 °C yielded  $\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$  ratios identical to those achieved by  $\text{H}_2$  reduction at 600 °C, demon-

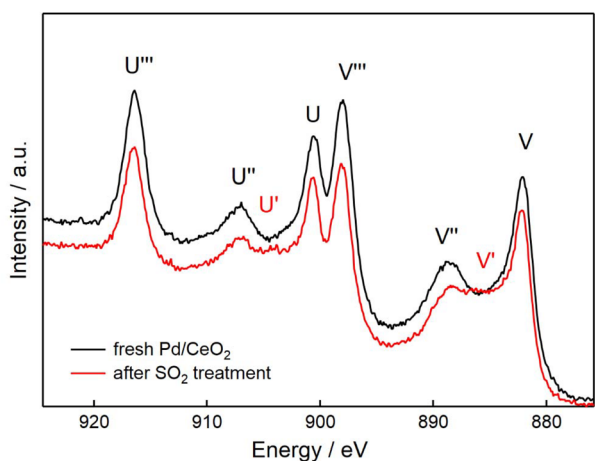
strating that  $\text{SO}_2$ -induced sulfate formation is confined to surface oxygen sites. This surface-limited reaction persisted even under prolonged  $\text{SO}_2$  exposure, indicating an intrinsic barrier to bulk sulfurization in unpromoted  $\text{CeO}_2$ . In stark contrast,  $\text{Pd/CeO}_2$  under  $\text{SO}_2$  treatment surpassed the  $\text{H}_2$ -induced reduction threshold, unequivocally demonstrating  $\text{SO}_2$  access to bulk oxygen sites. This fundamental difference reveals that Pd not only accelerates surface sulfurization kinetics but, more importantly, enables  $\text{SO}_2$  penetration into the  $\text{CeO}_2$  bulk lattice. The mechanism likely involves Pd-mediated oxygen mobility enhancement or the creation of preferential  $\text{SO}_2$  diffusion pathways at the Pd– $\text{CeO}_2$  interface, fundamentally altering the sulfurization process from a surface-limited to a bulk-accessible reaction.

Surface chemical states were characterized by XPS to complement the bulk-sensitive XAFS measurements (Fig. 8). The Ce 3d spectra exhibited the characteristic multiplet structure with V ( $3d_{5/2}$ ) and U ( $3d_{3/2}$ ) components and their satellites (V', V'', V''', U', U'', U''').<sup>31–34</sup> Fresh samples displayed predominantly  $\text{Ce}^{4+}$ -associated features, while  $\text{SO}_2$ -treated  $\text{Pd/CeO}_2$  showed pronounced enhancement of the  $\text{Ce}^{3+}$  markers (U' and V' peaks).<sup>31,34</sup> Quantitative deconvolution yielded  $\text{Ce}^{3+}/\text{Ce}^{4+} = 0.31/0.69$ , in reasonable agreement with the XANES-derived values. Given the XPS probing depth of approximately 2 nm in  $\text{CeO}_2$ ,<sup>38,39</sup> these results confirm substantial  $\text{Ce}^{3+}$  enrichment within the near-surface region. The coexistence of  $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$  in this shallow sampling volume indicates incomplete surface sulfurization, suggesting either heterogeneous reaction sites or equilibrium between sulfurized and pristine surface domains.

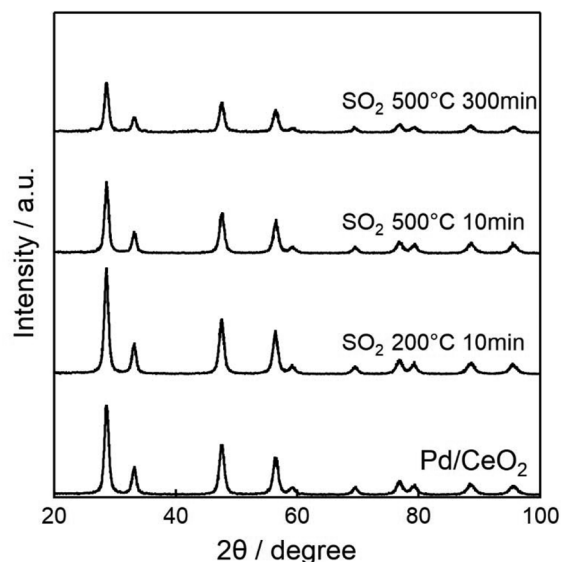
XRD analysis was employed to assess crystallographic changes induced by  $\text{SO}_2$  treatment (Fig. 9). Fresh  $\text{Pd/CeO}_2$  exhibited characteristic reflections of the fluorite structure at  $2\theta = 28, 33, 47, 56, 59, 69, 76, 79, 88,$  and  $95^\circ$ , consistent with



**Fig. 7** (a) Ce  $L_{3}$ -edge XANES and (b) EXAFS spectra of  $\text{CeO}_2$  and Pd/ $\text{CeO}_2$  during  $\text{H}_2$  reduction at 600 °C (5%  $\text{H}_2$ - $\text{N}_2$  flow, 100 mL  $\text{min}^{-1}$ ). Measurements taken after 60 min of  $\text{H}_2$  exposure.



**Fig. 8** XPS spectra of Pd/ $\text{CeO}_2$  before and after  $\text{SO}_2$  treatment at 500 °C (500 ppm  $\text{SO}_2$ , 100 mL  $\text{min}^{-1}$ , 300 min). Spectra show Ce 3d multiplet structure and changes in  $\text{Ce}^{3+}/\text{Ce}^{4+}$  ratio upon sulfuration.



**Fig. 9** XRD patterns of Pd/ $\text{CeO}_2$  before and after  $\text{SO}_2$  exposure at 500 °C (500 ppm  $\text{SO}_2$ , 100 mL  $\text{min}^{-1}$ , 300 min). Fluorite structure reflections are retained with intensity attenuation, indicating increased disorder without phase transformation.

cubic  $\text{CeO}_2$  ( $Fm\bar{3}m$ ).<sup>35</sup> The absence of Pd or PdO reflections confirms high metal dispersion on the  $\text{CeO}_2$  support. Following  $\text{SO}_2$  treatment, the fluorite reflections showed reduced intensities while maintaining their positions, with no emergence of new phases. This intensity attenuation without peak shifting or phase transformation indicates partial amorphization or increased structural disorder rather than formation of crystalline sulfate phases. The preservation of the fluorite framework despite  $\text{SO}_2$ -induced reduction aligns with the EXAFS observations of decreased local ordering while maintaining the basic  $\text{CeO}_2$  structure.

In this study, the Pd/ $\text{CeO}_2$  catalyst was subjected to calcination in air at 400 °C, followed by reductive activation under 5%  $\text{H}_2/\text{N}_2$  at 200 °C. To properly interpret the sulfuration behavior of Pd/ $\text{CeO}_2$ , it is important to consider the extent to which these thermal and reductive treatments may influence the  $\text{CeO}_2$  support itself. Because the  $\text{CeO}_2$  used in this work had already undergone high-temperature calcination at 600 °C prior to catalyst preparation, an additional calcination at 400 °C is unlikely to induce further structural modifications. Thus, the only treatment step that may affect the bare support is the mild reduction at 200 °C. According to previous  $\text{H}_2$ -TPR studies,  $\text{CeO}_2$  exhibits negligible reduction at 200 °C, with only minimal  $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$  conversion and insignificant oxygen-vacancy formation.<sup>29</sup> These findings indicate that such mild reductive pre-treatment does not meaningfully alter the intrinsic redox properties of  $\text{CeO}_2$ . In contrast,  $\text{H}_2$ -TPR measurements demonstrate that the incorporation of Pd markedly enhances the reducibility of surface lattice oxygen in  $\text{CeO}_2$ . Therefore, the possibility that this Pd-induced increase in oxygen mobility facilitates the reaction with  $\text{SO}_2$  cannot be excluded.

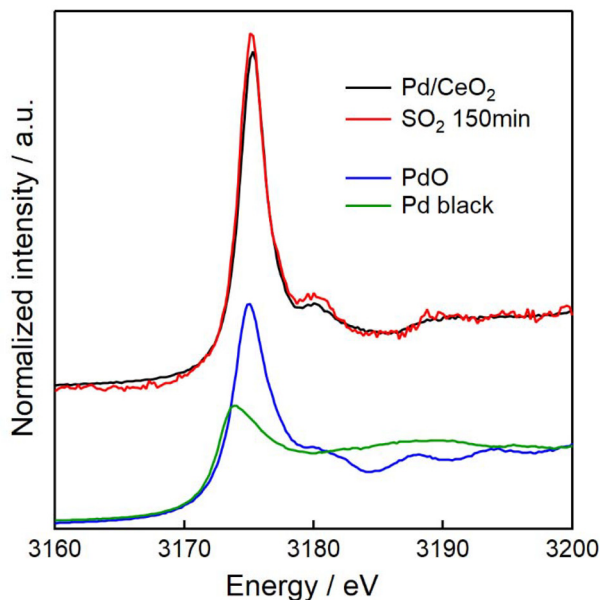
### 3.2 Changes in Pd on catalysts and the structure of sulfur species formed by SO<sub>2</sub>

The Pd-CeO<sub>2</sub> interface plays a crucial role in catalytic performance, particularly for CO oxidation, where Pd deposition on CeO<sub>2</sub> dramatically enhances activity.<sup>29,36,37</sup> Since the Pd oxidation state directly governs interfacial reactivity, we monitored Pd speciation during SO<sub>2</sub> exposure using *in situ* Pd L<sub>3</sub>-

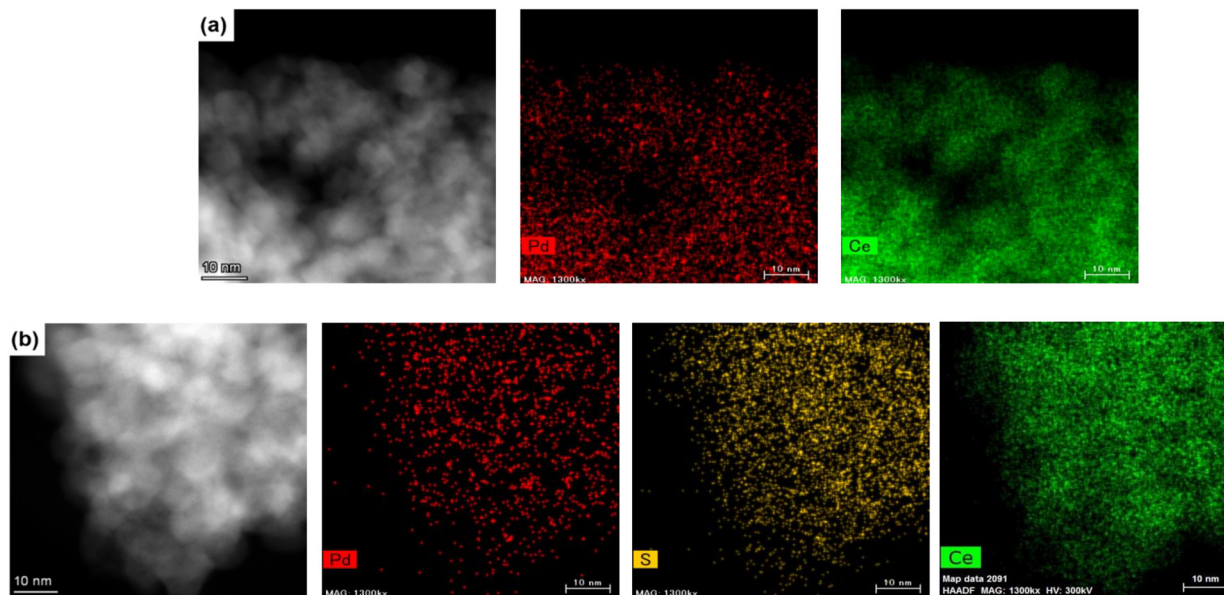
edge XANES (Fig. 10). The Pd L<sub>3</sub>-edge spectra, originating from 2p<sub>3/2</sub> → 4d electronic transitions and thus sensitive to d-electron occupancy, remained invariant throughout SO<sub>2</sub> treatment at 500 °C. This spectral stability definitively excludes Pd reduction to metallic Pd<sup>0</sup> or conversion to PdS, indicating that Pd maintains its oxidized state despite the strongly reducing SO<sub>2</sub> atmosphere. This resistance to reduction contrasts markedly with the facile CeO<sub>2</sub> reduction observed under identical conditions, suggesting that SO<sub>2</sub> preferentially interacts with the CeO<sub>2</sub> support rather than the supported Pd species.

STEM-EDS mapping provided direct visualization of Pd dispersion and sulfur distribution before and after SO<sub>2</sub> treatment at 500 °C (Fig. 11). Fresh Pd/CeO<sub>2</sub> exhibited uniformly dispersed Pd nanoparticles with a mean diameter of ~3 nm and absence of large aggregates (>30 nm), consistent with the XRD results showing no detectable Pd or PdO reflections. Following SO<sub>2</sub> treatment, Pd maintained its original particle size distribution, demonstrating remarkable resistance to sintering under sulfurizing conditions. Critically, EDS mapping revealed homogeneous sulfur distribution across the entire catalyst surface, confirming uniform CeO<sub>2</sub> sulfurization rather than localized sulfate formation. This comprehensive surface sulfurization, combined with stable Pd dispersion, indicates that SO<sub>2</sub> interacts primarily with the CeO<sub>2</sub> support while leaving the metal nanoparticles structurally intact.

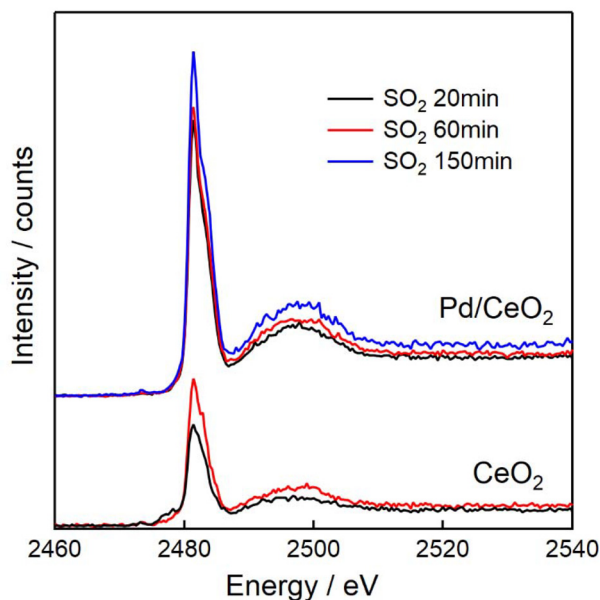
Sulfur speciation during SO<sub>2</sub> treatment was monitored *via in situ* S K-edge XANES spectroscopy (Fig. 12). Both CeO<sub>2</sub> and Pd/CeO<sub>2</sub> developed a dominant peak at 2.482 keV, characteristic of SO<sub>4</sub><sup>2-</sup> species, which intensified over 60 min before reaching steady state. For bare CeO<sub>2</sub>, a transient feature at 2.479 keV indicated initial SO<sub>2</sub> adsorption, which subsequently oxidized to S<sup>6+</sup> within 60 min. In contrast, Pd/CeO<sub>2</sub> exclusively



**Fig. 10** *In situ* Pd L<sub>3</sub>-edge XANES spectra of Pd/CeO<sub>2</sub> during SO<sub>2</sub> exposure at 500 °C (500 ppm SO<sub>2</sub>, 100 mL min<sup>-1</sup>) for up to 300 min. Spectra confirm Pd remains in oxidized state throughout sulfurization.



**Fig. 11** STEM-EDS mapping of Pd/CeO<sub>2</sub> before and after SO<sub>2</sub> exposure at 500 °C (500 ppm SO<sub>2</sub>, 100 mL min<sup>-1</sup>, 300 min). (a) Fresh sample showing uniform Pd dispersion (~3 nm). (b) After SO<sub>2</sub> treatment, Pd particle size remains unchanged; sulfur is homogeneously distributed across the surface.



**Fig. 12** *In situ* S K-edge XANES spectra of CeO<sub>2</sub> and Pd/CeO<sub>2</sub> during SO<sub>2</sub> exposure at 500 °C (500 ppm SO<sub>2</sub>, 100 mL min<sup>-1</sup>) for up to 60 min. Spectra show formation of SO<sub>4</sub><sup>2-</sup> species; Pd/CeO<sub>2</sub> exhibits direct conversion without intermediate oxidation states.

formed SO<sub>4</sub><sup>2-</sup> without detectable intermediate oxidation states, suggesting that Pd facilitates direct SO<sub>2</sub> → SO<sub>4</sub><sup>2-</sup> conversion. These observations confirm that surface sulfate formation is the primary sulfurization pathway for both catalysts, with the key distinction being the reaction kinetics: Pd accelerates complete oxidation to sulfate while suppressing intermediate species formation. This direct sulfate formation mechanism explains the irreversible nature of Pd/CeO<sub>2</sub> sulfurization observed in the Ce L<sub>3</sub>-edge XANES studies.

Diffuse-reflectance FTIR spectra collected for CeO<sub>2</sub> and Pd/CeO<sub>2</sub> before and after sulfation exhibit a broad absorption band near 1200 cm<sup>-1</sup>, which is indicative of bulk-like sulfate species incorporated beneath the ceria surface (Fig. S2). This interpretation is consistent with previous findings showing that subsurface sulfate formation on ceria produces a broad feature around 1200 cm<sup>-1</sup>, whereas surface sulfate species generate sharper bands in the 1340–1400 cm<sup>-1</sup> region.<sup>38</sup> The predominance of the 1200 cm<sup>-1</sup> band under the present conditions suggests that sulfation proceeds through partial reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> and subsequent migration of sulfate into near-surface layers. The comparatively stronger intensity of this band on Pd/CeO<sub>2</sub> implies that palladium enhances the redox activity and oxygen mobility of the ceria support, thereby promoting the incorporation of sulfate species into subsurface sites.

Quantitative sulfur analysis by XRF provided further insights into the extent of sulfurization (Table 1). The Ce<sup>3+</sup>/(Ce<sup>3+</sup> + Ce<sup>4+</sup>) ratios were evaluated from these peak areas according to the reported literature. The Ce<sup>3+</sup>/(Ce<sup>3+</sup> + Ce<sup>4+</sup>) ratios were calculated from the integrated peak areas based on

**Table 1** Ce ion ratios calculated by linear combination fitting with standards and mol ratio of SO<sub>3</sub>/CeO<sub>2</sub> calculated by XRF

|   | LCF fitting      |                  | Curve fitting    |                  | SO <sub>3</sub> /CeO <sub>2</sub> |
|---|------------------|------------------|------------------|------------------|-----------------------------------|
|   | Ce <sup>3+</sup> | Ce <sup>4+</sup> | Ce <sup>3+</sup> | Ce <sup>4+</sup> |                                   |
| Fresh CeO <sub>2</sub>                    | 0.00             | 1.00             | 0.11             | 0.89             | —                                 |
| CeO <sub>2</sub> after SO <sub>2</sub>    | 0.15             | 0.85             | 0.14             | 0.86             | 0.09                              |
| CeO <sub>2</sub> after H <sub>2</sub>     | 0.15             | 0.85             | 0.13             | 0.87             | —                                 |
| Fresh Pd/CeO <sub>2</sub>                 | 0.02             | 0.98             | 0.12             | 0.88             | —                                 |
| Pd/CeO <sub>2</sub> after SO <sub>2</sub> | 0.40             | 0.60             | 0.28             | 0.72             | 0.24                              |
| Pd/CeO <sub>2</sub> after H <sub>2</sub>  | 0.15             | 0.85             | 0.13             | 0.87             | —                                 |

established methods reported in the literature.<sup>39</sup> The S/CeO<sub>2</sub> molar ratios were 0.24 for Pd/CeO<sub>2</sub> versus 0.09 for bare CeO<sub>2</sub>, demonstrating a 2.7-fold enhancement in sulfate formation with Pd promotion. This substantial difference correlates directly with the enhanced Ce<sup>4+</sup> → Ce<sup>3+</sup> reduction observed in XANES, confirming that Pd catalyzes both lattice oxygen extraction and subsequent sulfate formation. Notably, the Ce<sup>3+</sup>/S molar ratio was approximately 1.7 for both catalysts, suggesting a stoichiometric relationship independent of Pd presence. This invariant ratio indicates that each sulfate formation event consumes a consistent number of lattice oxygen atoms, likely following the reaction: 2CeO<sub>2</sub> + SO<sub>2</sub> → Ce<sub>2</sub>O<sub>3</sub> + SO<sub>4</sub><sup>2-</sup>. The preservation of the fluorite framework despite extensive oxygen removal and sulfate incorporation demonstrates remarkable structural resilience, with sulfate species presumably occupying oxygen vacancy sites or surface positions without disrupting the underlying crystal lattice.

The sulfurized cerium compounds formed require careful consideration of thermodynamic stability and experimental evidence. While Ce(SO<sub>4</sub>)<sub>2</sub> and Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> represent the thermodynamically stable phases, cerium uniquely does not form oxy-sulfate phases observed in other rare-earth elements.<sup>40</sup> Previous studies have identified cerium sulfate oxide (Ce<sub>2</sub>O<sub>2</sub>SO<sub>4</sub>) containing Ce<sup>3+</sup> as the primary product of CeO<sub>2</sub> sulfurization by SO<sub>2</sub>.<sup>41,42</sup> Our observed Ce<sup>3+</sup>/S ratio of ~1.7 closely approximates the theoretical value of 2.0 expected for Ce<sub>2</sub>O<sub>2</sub>SO<sub>4</sub> formation, strongly suggesting this phase as the dominant sulfurization product. The presence of isosbestic points during *in situ* XANES measurements provides definitive evidence for direct CeO<sub>2</sub> → Ce<sub>2</sub>O<sub>2</sub>SO<sub>4</sub> transformation without detectable intermediates, supporting a concerted mechanism where lattice oxygen removal and sulfate incorporation occur simultaneously. This direct conversion pathway, accelerated by Pd but maintaining the same stoichiometry, underscores the fundamental nature of the CeO<sub>2</sub>–SO<sub>2</sub> reaction.

## 4. Conclusions

This study employed comprehensive *in situ* XAFS spectroscopy combined with XRD and STEM-EDS characterization to elucidate the mechanistic pathways of SO<sub>2</sub>-induced structural transformations in Pd/CeO<sub>2</sub> catalysts. SO<sub>2</sub> treatment of bare CeO<sub>2</sub> at 500 °C induces surface-limited sulfurization with Ce<sup>4+</sup> → Ce<sup>3+</sup>

reduction reaching a plateau at  $Ce^{3+}/(Ce^{3+} + Ce^{4+}) = 0.18$ . The presence of Pd fundamentally alters this behavior, enabling  $SO_2$  penetration into the bulk lattice and achieving a  $Ce^{3+}/(Ce^{3+} + Ce^{4+})$  ratio of 0.68 after 300 min. This sulfurized state proves remarkably stable, showing no re-oxidation upon  $O_2$  exposure at 500 °C. Throughout the treatment, Pd remains oxidized and uniformly distributed without sintering, indicating that Pd promotes oxygen mobility rather than directly participating in sulfur chemistry. The primary product,  $Ce_2O_2SO_4$ , preserves the fluorite framework but exhibits diminished long-range order. These findings establish that Pd transforms the sulfurization mechanism from surface-limited to bulk-accessible while maintaining the structural architecture of  $CeO_2$ .

## Conflicts of interest

There are no conflicts of interest to declare.

## Data availability

The data supporting the findings of this study are available within the article and its supplementary information files. Additional raw data, including XAFS spectra, XRD patterns, and XPS measurements, are available from the corresponding author upon reasonable request. No restrictions apply to data sharing.

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