# ChemComm

## COMMUNICATION

Check for updates

Cite this: DOI: 10.1039/d5cc01147g

## Light intensity-directed selective CO<sub>2</sub> photoreduction using iron(0)-zirconium dioxide photocatalyst<sup>†</sup>

Received 3rd March 2025, Accepted 9th May 2025

Tomoki Oyumi, ២ Ikki Abe, ២ Masahito Sasaki and Yasuo Izumi ២ \*

DOI: 10.1039/d5cc01147g

rsc.li/chemcomm

Selective photoreduction of CO<sub>2</sub> to CO, CH<sub>4</sub>, and C<sub>2,3</sub> paraffins was directed by increasing ultraviolet-visible light intensity over an Fe–ZrO<sub>2</sub> photocatalyst. Fe<sup>0</sup> nanoparticles sequentially reduced COH—transferred from the ZrO<sub>2</sub> surface—into CH<sub>x</sub> species and hydrocarbons, facilitated by light-induced heating to ~452 K.

Photocatalytic  $CO_2$  reduction establishes a novel C-neutral cycle and is considered a potential environmental solution for a sustainable society.<sup>1,2</sup> However, its near-term implementation is hindered by economic challenges, primarily due to the costs of photocatalysts and reactor design.<sup>3,4</sup> Among first-row transition metals, Fe is the most abundant and cost-effective. Consequently, Fe-based photocatalysts for  $CO_2$  photoreduction have been widely studied. However, nearly all reported systems employ Fe in the form of metal ions within metal–organic frameworks, covalent organic frameworks, porphyrins, or as Fe<sub>2</sub>O<sub>3</sub>, functioning primarily as redox mediators (Table S1, ESI<sup>†</sup>).<sup>5</sup>

In this study, a Fe<sup>0</sup> surface was evaluated as a CO<sub>2</sub> photoreduction catalyst for C<sub>1-3</sub> hydrocarbons (HCs) in combination with semiconductor ZrO<sub>2</sub>. An Fe<sub>3</sub>O<sub>4</sub>–ZrO<sub>2</sub> composite was synthesized *via* a liquid-phase reduction method, using Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O as the precursor and reducing it at 973 K under H<sub>2</sub> to obtain the Fe<sup>0</sup> (7.5 wt%)–ZrO<sub>2</sub>-973R photocatalyst. The valence state and coordination of Fe were monitored during synthesis using X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS).

This approach facilitated the formation of bifunctional sites—O vacancies ( $V_0^{\bullet\bullet}$ ) on the ZrO<sub>2</sub> surface<sup>3,6–9</sup> and Fe<sup>0</sup> nanoparticles—enabling the selective photogeneration of CO and C<sub>1–3</sub> HCs from CO<sub>2</sub>. At a ultraviolet-visible (UV-Vis) light intensity of 110 mW cm<sup>-2</sup>, using <sup>13</sup>CO<sub>2</sub> and H<sub>2</sub> gases with the Fe<sup>0</sup> (7.5 wt %)–ZrO<sub>2</sub>-973R photocatalyst, both <sup>13</sup>CO and <sup>13</sup>CH<sub>4</sub>

were gradually generated over the first 5 h of photoreaction (Table 1a). However, beyond this period, <sup>13</sup>CO formation became predominant (>99 mol% selectivity; entry a'), as subsequent reaction steps from CO did not proceed (Scheme 1a). The steady photogeneration of CO was significantly faster than that observed with ZrO<sub>2</sub> alone (Table S2a, ESI<sup>†</sup>), <sup>6–8</sup> confirming the active role of the Fe<sup>0</sup> surface, but the selectivity change after 5 h seemed due to strong CO<sub>2</sub> adsorption on it in CO<sub>2</sub> photoreduction (see below).

In stark contrast, increasing the irradiated light intensity to 322 mW cm<sup>-2</sup> shifted the Fe<sup>0</sup>–ZrO<sub>2</sub>-973R photocatalyst from selective two-electron reduction to <sup>13</sup>CO to predominant eight-electron reduction to <sup>13</sup>CH<sub>4</sub> production (>95 mol% selectivity; Table 1b). This shift occurred because the hydrogenation steps from CO proceeded rapidly under higher light intensity, facilitating the sequential reduction from CO<sub>2</sub> to CO and ultimately to CH<sub>4</sub>. From a practical perspective, however, the <sup>13</sup>CH<sub>4</sub> light-induced synthesis using Fe<sup>0</sup>–ZrO<sub>2</sub> requires further improvement, as photocatalytic activity declined after 5 h of photoreaction—more so than under 110 mW cm<sup>-2</sup> irradiation (Table 1a' and b'). As no CH<sub>x</sub> species were observed in the Fourier transform infrared (FTIR) spectrum under the conditions, this deactivation was attributed to Fe<sup>0</sup> surface poisoning by strongly adsorbed CO<sub>2</sub> (Scheme 1b).

To enhance the stability of the Fe<sup>0</sup>–ZrO<sub>2</sub>-973R photocatalyst, the irradiated light intensity was further increased to 472 mW cm<sup>-2</sup>. Under these conditions, the <sup>13</sup>CH<sub>4</sub> formation rate reached 170 µmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> with >71 mol% selectivity, accompanied by <sup>13</sup>CO formation at 69 µmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> (>28 mol% selectivity) over 5 h of photoreaction (Fig. 1A and Table 1c). Over time, <sup>13</sup>CH<sub>4</sub> formation exhibited a turning point at ~5 h of photoreaction (Fig. 1A), attributed to partial Fe<sup>0</sup> site poisoning by intermediate species such as HCO<sub>2</sub> and CH<sub>x</sub>. Beyond this period, the <sup>13</sup>CH<sub>4</sub> formation rate stabilized at 20 µmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> with >49 mol% selectivity (Table 1c' and Scheme 1c). Under the steady conditions, CO<sub>2</sub> blocking on Fe<sup>0</sup> sites should be less effective in contrast to the status under 110–322 mW cm<sup>-2</sup> irradiation. This time-dependent product distribution confirmed a consecutive



View Article Online

Department of Chemistry, Graduate School of Science, Chiba University, Yayoi 1-33, Inage-ku, Chiba 263-8522, Japan. E-mail: yizumi@faculty.chiba-u.jp

<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Lists of reported photoand thermal catalysts, experimental details, photocatalytic time course, X-ray diffraction, and optical, X-ray absorption, and FTIR spectroscopy of photocatalyst and surface species. See DOI: https://doi.org/10.1039/d5cc01147g

Table 1  $CO_2$  photoreduction outcomes using Fe (7.5 wt%)–ZrO<sub>2</sub> prereduced at 973 K in the presence of either H<sub>2</sub> or H<sub>2</sub>O

Entry	Reactant	Reductant	Light intensity (mW)	Stage of reaction test (h)	Formation rate ( $\mu$ mol h <sup>-1</sup> g <sub>cat</sub> <sup>-1</sup> )				
					<sup>13</sup> CO	$^{13}\mathrm{CH}_4$	$^{13}C_{2}H_{6}$	$^{13}C_{3}H_{8}$	$O_2$
a	$^{13}CO_2$ (2.3 kPa)	H <sub>2</sub> (21.7 kPa)	$110 \text{ cm}^{-2}$	0-5	3.7	3.8	0.052	0.018	< 0.002
a′	2( )	2( )		5-48	3.7	< 0.002	< 0.002	< 0.002	
b			$322 \text{ cm}^{-2}$	0-5	2.4	45	0.20		
b′				5-48	1.7	1.1	0.036		
с			$472 \text{ cm}^{-2}$	0-5	69	170	2.1	0.30	
$\mathbf{c}'$				5-48	18	20	2.3	0.56	
c″				(20-48)	(2.7)	(16)	(2.6)	(0.70)	
d			$1510 \text{ cm}^{-2}$	0-5	35	40	0.26	< 0.002	< 0.002
d′			(with water bath)	5-48	5.2	0.41	0.037		
					CO	$CH_4$	$C_2H_6$	$C_3H_8$	$O_2$
e	CO <sub>2</sub> (95 kPa)	H <sub>2</sub> O (70 mL)	367 per cell	0-5	12	< 0.002	< 0.002	-5 8	64
e′	2 ( )	2 ( )	1	5-48	8.5	0.86			9.0



 $\begin{array}{l} \mbox{Scheme 1} & \mbox{Temporary and steady CO}_2 \mbox{ photoreduction pathways directed} \\ \mbox{by irradiated light intensity (110-472 mW cm^{-2}) using the Fe^0 (7.5 wt%)- $ZrO_2-973R$ photocatalyst in presence of H_2 ((a)-(c) and (c')) or H_2O (a). \\ \end{array}$ 

reaction pathway: CO<sub>2</sub> reduction to CO, followed by CH<sub>4</sub> formation, and subsequent conversion to C<sub>2,3</sub> hydrocarbons. Between 20 and 48 h of photoreaction, the <sup>13</sup>CH<sub>4</sub> formation rate remained stable (>73 mol% selectivity), while <sup>13</sup>C<sub>2</sub>H<sub>6</sub> and <sup>13</sup>C<sub>3</sub>H<sub>8</sub> selectivity significantly increased to 15 mol% (total formation rate: 3.3 µmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>), effectively suppressing initial <sup>13</sup>CO production (Table 1c" and Scheme 1c'). Notably, no C<sub>2</sub>H<sub>4</sub> or C<sub>3</sub>H<sub>6</sub> was detected. Furthermore, photocatalytic activity could be restored by a 1-h evacuation at 10<sup>-6</sup> Pa under light, reactivating the consecutive reduction process from CO to CH<sub>4</sub> (Fig. 1B).

The other photocatalytic test was using CO<sub>2</sub> (2.3 kPa), H<sub>2</sub> (21.7 kPa), and the light irradiation at 1510 mW cm<sup>-2</sup>, but the quartz reactor was cooled with water bath (Table 1d–d' and Chart S1, ESI†). The <sup>13</sup>CO and <sup>13</sup>CH<sub>4</sub> formation rates were 24–51% of corresponding rates without water cooling until 5 h of reaction (Table 1c and c'), while the decline after 5 h was more significant, especially for <sup>13</sup>CH<sub>4</sub> formation, strongly suggesting that charge separation in/on ZrO<sub>2</sub> owing to light proceeded CO<sub>2</sub> reduction while Fe nanoparticle surface at lower temperature in thermal equilibrium with ZrO<sub>2</sub>, reactor, and 2.5 L of water was deactivated for subsequent multiple hydrogenation earlier by adsorbed species, *e.g.* CO<sub>2</sub>. The increase of water temperature was minimal: from 295.2 to 295.5 K during the photocatalytic test for 48 h (Chart S1, ESI†).



**Fig. 1** (A) and (B) Time course of  ${}^{13}$ CO,  ${}^{13}$ CH<sub>4</sub>,  ${}^{12}$ CH<sub>4</sub>,  ${}^{13}$ C<sub>2</sub>H<sub>6</sub>, and  ${}^{13}$ C<sub>3</sub>H<sub>8</sub> formation using Fe<sup>0</sup> (7.5 wt%)–ZrO<sub>2</sub>-973R,  ${}^{13}$ CO<sub>2</sub> (2.3 kPa), H<sub>2</sub> (21.7 kPa), and UV-Vis light irradiation at 472 mW cm<sup>-2</sup>. (B) Comparison with the reactivation test (filled symbols) after 1 h of catalyst evacuation under UV-Vis light irradiation at the 5-h mark.

Steady photocatalytic CO<sub>2</sub> reduction was also achieved using H<sub>2</sub>O as the reductant instead of H<sub>2</sub> under UV-Vis light irradiation at 367 mW per cell. CO was continuously generated at a rate of 12–8.5 µmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> (Table 1e and e'), proceeding more rapidly than the multiple hydrogenation steps required for CH<sub>4</sub> formation over Fe<sup>0</sup> (selectivity <9.2 mol%; Scheme 1a and Fig. S1, ESI†). This was attributed to the predominant presence of H<sub>2</sub>O rather than H at the Fe<sup>0</sup> surface, which favored CO generation over further hydrogenation to CH<sub>4</sub>.

The effects of UV-Vis light irradiation on the  $Fe^0$ – $ZrO_2$ -973R photocatalyst were investigated. In the UV-Vis absorption spectra of the  $Fe_3O_4$ – $ZrO_2$  sample (Fig. S2b, ESI†), two absorption shoulders at 410 and 525 nm, attributed to  $Fe^{2+}$  and  $Fe^{3+}$  ions, were observed, whereas  $ZrO_2$  alone exhibited no visible light absorption (spectrum a). This spectral profile was consistent with the reported absorption spectrum of  $Fe_3O_4$ .<sup>10</sup> Upon H<sub>2</sub> treatment at 973 K, absorption extended across the entire visible region

(spectrum c), and the spectrum remained similar after 48 h of photocatalytic <sup>13</sup>CO<sub>2</sub> reduction (spectrum d), confirming the formation and stability of Fe<sup>0</sup> nanoparticles, which facilitated multiple hydrogenation steps from CO/COH species (Scheme 1c and c'). The Fe valence state assignments were corroborated by changes in the XANES spectrum, aligning with those of standard Fe<sup>0</sup> and Fe<sub>3</sub>O<sub>4</sub> (Fig. S3A(c) and (d), ESI<sup>+</sup>).<sup>11</sup> EXAFS Fourier transform analysis of Fe<sup>0</sup>–ZrO<sub>2</sub>-973R revealed interatomic pairs characteristic of Fe<sup>0</sup> (Fig. S4, ESI<sup>+</sup>), while X-ray diffraction showed an Fe (011) peak overlapping with peaks corresponding to monoclinic ZrO<sub>2</sub> (Fig. S5, ESI<sup>+</sup>), further supporting the formation of Fe<sup>0</sup> active sites in the Fe<sup>0</sup>–ZrO<sub>2</sub>-973R photocatalyst.

The fluorescence emission spectra of  $Fe^0$ – $ZrO_2$ -973R were measured under excitation at 200 nm (Fig. S6, ESI†), a wavelength corresponding to an energy higher than the band gap of  $ZrO_2$ (Fig. S2a, ESI†). The spectrum exhibited both an interband excitation–deexcitation peak centered at 367 nm (spectrum a) and intraband transition peaks associated with impurity levels, such as O vacancies and Hf (0.55 wt%) in/on  $ZrO_2$ , appearing at 451, 468, 481, 491, 528, and 623 nm. These emissions were significantly suppressed upon the addition of  $Fe_3O_4$  and further reduced with  $Fe^0$  nanoparticles (spectra b and c), indicating effective trapping of excited electrons at the conduction band (CB) of  $ZrO_2$ .

Next, the reaction pathway from  $CO_2$  to CO and HCs is considered. The role of  $V_0^{\bullet\bullet}$  sites on the  $ZrO_2$  surface in  $CO_2$ adsorption and its subsequent photoreduction to OCOH and COH species was analyzed using density functional theory (DFT) calculations.<sup>9</sup> The population of surface  $V_0^{\bullet\bullet}$  sites was evaluated to one per 44 nm<sup>2</sup> based on <sup>13</sup>CO<sub>2</sub> exchange amount with preadsorbed <sup>12</sup>CO<sub>2</sub> on  $V_0^{\bullet\bullet}$  site (0.070 µmol; Table S3g and Fig. S7, ESI†). The population of surface  $V_0^{\bullet\bullet}$  sites seems not vary much before and after photocatalytic test based on essentially negligibly-changing UV-visible and XRD data (Fig. S2c, d and S5a, b, ESI†). Consequently, this study focuses on the critical steps enabling transient or sustained  $C_{1-3}$  photogeneration (Scheme 1b and c), specifically the conversion of COH and/ or CO into  $C_{1-3}$  HCs over the Fe<sup>0</sup> surface.

To identify the active sites responsible for these reaction steps, Fe K-edge EXAFS measurements were conducted on the Fe<sup>0</sup>–ZrO<sub>2</sub>-973R photocatalyst under CO<sub>2</sub> and H<sub>2</sub> exposure. Unexpectedly, ~20% of the Fe<sup>0</sup> sites reduced at 973 K were oxidized upon reaction with CO<sub>2</sub> in the dark, as indicated by EXAFS analysis (Fig. 2A, 0 min). The spectral fit, obtained by convolving standard XANES spectra for Fe<sup>0</sup> and FeO with an 8:2 mixing ratio (Fig. S3B(d), ESI†), aligned with the EXAFS data. This oxidation is attributed to the formation of an Mshaped Fe<sup>2+</sup>–O–C(==Fe<sup>0</sup>)–O–Fe<sup>2+</sup> species upon CO<sub>2</sub> adsorption on Fe. DFT calculations further support the energetic stability of this species on the Fe<sup>0</sup> (111) surface, with an adsorption energy of 0.92 eV and a Bader charge of +0.352 on Fe bonded to O, consistent with prior studies.<sup>12</sup> At this stage, CO did not desorb spontaneously from Fe surface and was not detected.

Upon UV-Vis light irradiation, the Fourier transform of EXAFS spectra (Fig. 2A, 0 min) showed that the Fe–O and Fe $\cdots$ Fe peaks corresponding to FeO were rapidly replaced by



**Fig. 2** Time-dependent Fourier transform of Fe K-edge EXAFS for Fe<sup>0</sup> (7.5 wt%)–ZrO<sub>2</sub>–973R under CO<sub>2</sub> (2.3 kPa), H<sub>2</sub> (21.7 kPa), and UV-Vis light irradiation (322 mW cm<sup>-2</sup>). (A) During 75 min of illumination, (B) after the light was turned off, and (C) corresponding time-dependent evolution of the Debye–Waller factor for the Fe–Fe interatomic pair.

a metallic Fe–Fe peak at 0.21 nm (phase shift uncorrected; Fig. 2A, 12 min). This transformation indicates the reduction of  $Fe^{2+}$  in the M-shaped  $Fe^{2+}$ –O–C(= $Fe^{0}$ )–O–F $e^{2+}$  species.

In the FTIR spectrum of Fe<sup>0</sup>–ZrO<sub>2</sub>-973R under <sup>13</sup>CO<sub>2</sub> and H<sub>2</sub> (Fig. S8, ESI<sup> $\dagger$ </sup>), shoulder peaks at 1584, 1396, and 1217 cm<sup>-1</sup> corresponded to  $\nu_{as}(OCO)$ ,  $\nu_{s}(OCO)$ , and  $\delta(OH)$  bending vibrations, respectively, were attributed to monodentate and bridging bicarbonate species adsorbed on the surface.<sup>6-8</sup> In contrast, the broader peaks centered at 1538 and 1261 cm<sup>-1</sup> were tentatively assigned  $\nu_{\rm as}$ (OCO) and  $\nu_{\rm s}$ (OCO) stretching vibrations of bidentate carbonate species on ZrO<sub>2</sub>,<sup>13</sup> as well as the M-shaped Fe–O–C(=Fe<sup>0</sup>)–O–Fe species proposed earlier, adsorbed at various sites on the Fe<sup>0</sup> surface. This assignment aligns with DFT-calculated O-C-O bond angles of  $122^{\circ}$ . Upon UV-Vis light irradiation (265 mW cm<sup>-2</sup>), the peak associated with <sup>13</sup>CO<sub>2</sub> and H<sub>2</sub> adsorption negatively shifted by 41 cm<sup>-1</sup>. This shift was attributed to the reduction of Fe<sup>2+</sup> to Fe<sup>0</sup> via electron transfer from ZrO<sub>2</sub> CB to Fe, followed by electron injection into the  $\sigma^*$  orbitals of C-O bonds, facilitating bond weakening and activation under UV-Vis illumination, in consistent with the reduction from Fe<sup>2+</sup> to Fe<sup>0</sup> upon the light irradiation based on EXAFS (Fig. 2A).

The broad peak centered at 1497 cm<sup>-1</sup> disappeared within 4 min under vacuum and UV-Vis light irradiation, likely due to  $CO_2$  desorption, suggesting that  $CO_2$  and carbonate species are not direct intermediates in  $C_{1-3}$  HC formation. In contrast, the conversion of adsorbed  $CO_2$  on the  $ZrO_2$  surface to COH species appears to be the rate-limiting step, as only methane ( $\nu_3$  peak at 3010 cm<sup>-1</sup>) was detected alongside adsorbed  $CO_2$  and bicarbonate species.

To elucidate the energetic origins of the multiple hydrogenation steps in which COH and/or CO species migrate over the Fe<sup>0</sup> surface to form HCs, the Fe–Fe coordination number was determined *via* EXAFS as 5.3, corresponding to a surface dispersion of 0.95.<sup>14</sup> In the correlated Debye model, the Debye temperatures of bulk and surface Fe (vertical motion) are reported as 467 K<sup>15</sup> and 225 K,<sup>16</sup> respectively. Using multiple scattering calculation code FEFF<sup>17</sup> and plane-wave EXAFS analysis code XDAP,<sup>18</sup> the local Fe site temperature during CO<sub>2</sub> photoreduction was experimentally monitored. Upon UV-Vis light irradiation, the Fe site temperature rapidly increased to ~452 ( $\pm$ 35) K as hot spot due to light absorption and remained nearly constant at thermal equilibrium with the supporting ZrO<sub>2</sub> and the EXAFS cell both at ~295 K (Fig. 2C, left).

When the light was turned off, the heat generated by light energy dissipated, and the Fe site temperature returned to 296 K (Fig. 2C, right). This observation confirms that the selective formation of  $C_{1-3}$  HCs in this study resulted from a two-step process: (i) CO<sub>2</sub> reduction to COH/CO *via* charge separation in ZrO<sub>2</sub><sup>3,6–8</sup> and (ii) subsequent multiple hydrogenation of CO/COH on the Fe<sup>0</sup> surface, which was maintained at ~452 K due to light absorption.

Thermal CO<sub>2</sub> hydrogenation and Fischer–Tropsch synthesis of HC(s) using Fe-based catalysts typically require reaction temperatures above 548 K (Table S4, ESI<sup>†</sup>) to achieve HC formation rates comparable to the Fe site temperature (~452 K, Fig. 2C) and the observed rate of 0.24 mmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> (Table 1c) in this study. Under CO<sub>2</sub> photoreduction conditions, Fe sites remained exclusively in the Fe<sup>0</sup> state (Fig. 2A and B), whereas thermal CO<sub>2</sub> reduction commonly involves Fe oxides and carbides (Table S4, ESI<sup>†</sup>). While the initial reduction of the first O atom in CO<sub>2</sub> over Fe<sup>0</sup> surfaces<sup>19</sup> typically requires high temperatures (>548 K),<sup>20</sup> this study demonstrates that the first reduction step was instead facilitated by charge separation at V<sub>0</sub><sup>--</sup> sites on the ZrO<sub>2</sub> surface under light irradiation, enabling the reaction:

$$\operatorname{CO}_2(a)\operatorname{V}_{O}^{\bullet\bullet} + \operatorname{H}^+ + \operatorname{e}^- \to \operatorname{OCOH}(a)\operatorname{V}_{O}^{\bullet\bullet} \to \operatorname{O} + \operatorname{COH}$$
(1)

as previously reported.<sup>9</sup> This step was particularly effective at lower light intensities (110–322 mW cm<sup>-2</sup>; Table 1a–b') in the presence of neighboring Fe<sup>0</sup> nanoparticles. The subsequent hydrogenation pathway, where COH migrates to Fe<sup>0</sup> and undergoes further reduction to  $C_{1-3}$  HCs, is likely a common feature in both thermal (Table S4, ESI†) and photo (~452 K, Fig. 2C) reactions, regardless of whether H<sub>2</sub> or H<sub>2</sub>O serves as the reductant.

The authors are grateful for the financial support from the Grant-in-Aid for Scientific Research B (24K01522, 20H02834, YI) from the Japan Society for the Promotion of Science. X-ray absorption experiments were performed with the approval of

the Photon Factory Proposal Review Committee (2024G067, 2022G527, 2021G546). The authors would like to thank Enago (www.enago.jp) for the language review.

#### Data availability

The supporting data have been included as part of the ESI.†

### Conflicts of interest

There are no conflicts to declare.

#### References

- 1 Y. Izumi, Coord. Chem. Rev., 2013, 257, 171-186.
- 2 Y. Izumi, in Advances in CO<sub>2</sub> Capture, Sequestration, and Conversion, ed. F. Jin, L.-N. He and Y. H. Hu, ACS Symposium Series, ACS Publications, 2015, ch. 1, vol. 1194, pp. 1–46.
- 3 T. Loumissi, R. Ishii, K. Hara, T. Oyumi, I. Abe, C. Li, H. Zhang, R. Hirayama, K. Niki, T. Itoi and Y. Izumi, *Angew. Chem., Int. Ed.*, 2024, **63**, e202412090.
- 4 J. Albero, Y. Peng and H. García, ACS Catal., 2020, 10, 5734-5749.
- 5 L. H. M. de Groot, A. Ilic, J. Schwarz and K. Wärnmark, J. Am. Chem.
- Soc., 2023, 145, 9369–9388.
  H. Zhang, T. Itoi, T. Konishi and Y. Izumi, Angew. Chem., Int. Ed., 2021, 60, 9045–9054.
- 7 H. Zhang, T. Itoi, K. Niki, T. Konishi and Y. Izumi, *Catal. Today*, 2020, 356, 544–556.
- 8 H. Zhang, T. Itoi, T. Konishi and Y. Izumi, J. Am. Chem. Soc., 2019, 141, 6292–6301.
- 9 K. Hara, M. Nozaki, T. Hirayama, R. Ishii, K. Niki and Y. Izumi, J. Phys. Chem. C, 2023, 127, 1776-1788.
- 10 A. Bouafia, S. E. Laouini, A. Khelef, M. L. Tedjani and F. Guemari, J. Cluster Sci., 2021, 32, 1033–1041.
- 11 Provided by Dr. Y. Niwa, High Energy Accelerator Research Organization.
- 12 C. R. Kwawu, R. Tia, E. Adei, N. Y. Dzade, C. R. A. Catlow and N. H. de Leeuw, *Phys. Chem. Chem. Phys.*, 2017, **19**, 19478–19486.
- 13 S. E. Collins, M. A. Baltanas and A. L. Bonivardi, J. Catal., 2004, 226, 410–421.
- 14 B. J. Kip, F. B. M. Duivenvoorden, D. C. Koningsberger and R. Prins, J. Catal., 1987, 105, 26–38.
- 15 American Institute of Physics Handbook, ed. D. E. Gray, B. H. Billings, H. P. R. Frederikse, D. F. Bleil, R. B. Lindsay, R. K. Cook, J. B. Marion, H. M. Crosswhite and M. W. Zemansky, McGraw-Hill, New York, USA, 1972, 3rd edn, pp. 4–115.
- 16 D. P. Jackson, Surf. Sci., 1974, 43, 431-440.
- 17 L. Ankudinov, B. Ravel, J. J. Rehr and S. D. Condradson, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1998, **58**, 7565–7576.
- 18 M. Vaarkamp, H. Linders and D. Koningsberger, XDAP Version 3.2.9, XAFS Services International, Woudenberg, The Netherlands, 2022.
- 19 L. Krauser, Q. W. Yang and E. V. Kondratenko, *ChemCatChem*, 2024, 16, e202301716.
- 20 C. R. Kwawu, A. Aniagyei, R. Tia and E. Adei, Mater. Renew. Sustainable Energy, 2020, 9, 4.