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# Hydroxyl-oxygen vacancy synergy over $\text{In}_2\text{O}_3$ – $\text{ZrO}_2$ catalysts: mechanistic insights into $\text{CO}_2$ hydrogenation to methanol†

Xia Li,<sup>‡a</sup> Zixia Feng,<sup>‡b</sup> Hanjun Lu,<sup>a</sup> Xinlin Hong,<sup>‡a</sup> Guangchao Li<sup>‡\*abcde</sup> and Shik Chi Edman Tsang<sup>b</sup>

The synergistic interplay between oxygen vacancies ( $\text{O}_\text{V}$ ) and hydroxyl species in  $\text{In}_2\text{O}_3$ – $\text{ZrO}_2$  catalysts plays a crucial role in steering  $\text{CO}_2$  hydrogenation pathways, however, the atomic-scale interactions between these features have remained elusive. In this study, we engineered  $\text{In}_2\text{O}_3$ – $\text{ZrO}_2$  solid solutions via  $\text{ZrO}_2$  aerogel phase modulation and thoroughly elucidated the surface chemistry using advanced experimental techniques, including solid-state NMR, *in situ* DRIFTS, and adsorption studies. The results demonstrate that three distinct hydroxyl site types on the catalyst's surface (terminal hydroxyls ( $\mu_1$ -OH), bridged hydroxyls ( $\mu_2$ -OH), and triply bridging hydroxyls ( $\mu_3$ -OH)) are in close spatial proximity. Besides,  $\mu_2$ -OH and  $\mu_3$ -OH are particularly susceptible to dihydroxylation, a process that facilitates the generation of  $\text{O}_\text{V}$  that serve as anchoring sites for  $\text{CO}_2$ . These hydroxyl-vacancy ensembles effectively promote  $\text{CO}_2$  activation to carbonate/bicarbonate species, which then undergo selective hydrogenation to methanol via a formate-mediated pathway, thus establishing a self-sustaining catalytic cycle. This work clarifies the cooperative role of vacancy coordination and hydroxyl chemistry in  $\text{CO}_2$  activation and provides a mechanistic guide for the rational design of bimetallic oxide catalysts for  $\text{CO}_2$  hydrogenation to methanol.

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## 1 Introduction



Guangchao Li

Dr Guangchao Li obtained his PhD in physical chemistry in 2021 at the University of Chinese Academy of Sciences (UCAS). He was a visiting PhD student at the University of Oxford (2019–2021). Later, he worked as a postdoctoral researcher at the Hong Kong Polytechnic University (PolyU). Since 2023, he has worked as a research assistant professor in the Department of Applied Biology and Chemical Technology at PolyU. His current

research interests focus on the characterization and application of porous materials in energy conversion.

Since the inception of the “methanol economy” and “liquid sunshine”,  $\text{CO}_2$  hydrogenation to methanol has emerged as a pivotal technology for fossil fuel substitution strategies.<sup>1–4</sup> Bimetallic oxide catalysts, particularly those combining redox-active and structural-stabilizing components, have shown significant advantages in optimizing  $\text{CO}_2$  activation kinetics and methanol selectivity. These benefits arise from their synergistic interfacial interactions and tailored electronic configurations.<sup>5,6</sup> However, the atomistic mechanisms driving these processes, particularly defect-mediated catalysis, remain poorly understood due to the inherent complexity of these systems. This complexity necessitates the use of model catalysts to understand underlying structure–activity relationships. This knowledge deficit motivates focused investigation of the  $\text{In}_2\text{O}_3$ – $\text{ZrO}_2$  system, where interfacial oxygen vacancies emerge as

<sup>a</sup>College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China. E-mail: hongxl@whu.edu.cn

<sup>b</sup>Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hong Kong 999077, China. E-mail: guangchao.li@polyu.edu.hk

<sup>c</sup>The Hong Kong Polytechnic University Shenzhen Research Institute, The Hong Kong Polytechnic University, Shenzhen 518057, China

<sup>d</sup>PolyU-Daya Bay Technology and Innovation Research Institute, The Hong Kong Polytechnic University, Huizhou 516000, China

<sup>e</sup>Research Institute of Advanced Manufacturing (RIAM), Research Centre for Resources Engineering towards Carbon Neutrality (RCRE), The Hong Kong Polytechnic University, Hong Kong 999077, China

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‡ These authors contributed to this paper equally.

catalytic linchpins linking macroscopic performance to atomic-scale phenomena.

Early studies on pure  $\text{In}_2\text{O}_3$  revealed oxygen vacancies as critical for  $\text{CO}_2$  activation, with the coordination environments governing product selectivity.<sup>7</sup> Triple-coordinated vacancies on specific crystal planes (e.g., c- $\text{In}_2\text{O}_3(111)$ ) promote methanol formation *via*  $\text{HCOO}^*$  stabilization, whereas double-coordinated vacancies favour CO production through C–O bond cleavage.<sup>8</sup> This reactivity highlights that vacancy geometry, not merely concentration, is the primary structural factor determining the selectivity of  $\text{CO}_2$  hydrogenation pathways.<sup>9</sup> Since doping  $\text{ZrO}_2$  brings additional complexity, there is an ongoing debate about the origin of the reactive oxygen vacancies.<sup>10,11</sup> Blum *et al.* attributed these vacancies to a partial reduction of  $\text{In}_2\text{O}_3$  at the  $\text{In}_2\text{O}_3/\text{m-ZrO}_2$  interface.<sup>12</sup> While Müller *et al.* demonstrated that the  $\text{In-O}_\text{V}\text{-Zr}$  structure, formed by the solvation of  $\text{In}^{3+}$  into the  $\text{ZrO}_2$  lattice, serves as the true reactive centre.<sup>13</sup> Furthermore, Gong *et al.* reported that electron transfer modulates the electronic properties of the active sites, enhancing the selectivity toward methanol in ways that transcend the influence of vacancy concentration alone.<sup>14</sup> These findings challenge the simple vacancy-centred model, underscoring the multifaceted nature of catalytic selectivity in these systems.

Further investigations reveal that the surface chemical complexity of  $\text{In}_2\text{O}_3\text{-ZrO}_2$  catalysts arises not only from the dynamic evolution of oxygen vacancies but also from the diversity of surface hydroxyl species.<sup>15</sup> Metal oxides inherently host a variety of hydroxyl groups, including terminal hydroxyls ( $\mu_1\text{-OH}$ ), doubly bridged hydroxyls ( $\mu_2\text{-OH}$ ), and triply bridged hydroxyls ( $\mu_3\text{-OH}$ ), whose stability and reactivity are governed by their local coordination environments.<sup>16</sup> Under thermal pretreatment and hydrogenation conditions, weakly bound hydroxyl groups are selectively destabilized *via* dehydration or heterolytic  $\text{H}_2$  dissociation, thereby revealing distinct  $\text{O}_\text{V}$  configurations.<sup>17</sup> Moreover, the catalytic behaviour varies significantly among these hydroxyl groups. Previous studies have shown that the  $\text{In}_2\text{O}_3\text{-x(OH)}_y$  surface is mainly composed of terminally bonded  $\text{In-OH}\cdots\text{In}$  and bridged  $\text{In-OH}\rightarrow\text{In}$  species, with only the former exhibiting the active frustrated Lewis pair (FLP) feature. This FLP efficiently dissociates  $\text{H}_2$  and directs the selective conversion of  $\text{CO}_2$  into CO.<sup>18–20</sup> This finding suggests that different hydroxyl-vacancy combinations exhibit conformational specificity in regulating the reaction pathways. Nevertheless, there is still a gap in the understanding of the mechanistic details within the more complex  $\text{In}_2\text{O}_3\text{-ZrO}_2$  solid solution system.

In this work, we synthesized a series of composite supports containing monoclinic zirconia and tetragonal zirconia phases by heat treating  $\text{ZrO}_2$  aerogel precursor. Subsequently,  $\text{In}_2\text{O}_3$  was doped onto these supports to obtain  $\text{In}_2\text{O}_3\text{-ZrO}_2$  catalysts featuring diverse hydroxyl sites. By employing magic-angle spinning solid-state nuclear magnetic resonance (MAS SSNMR), *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and chemical adsorption analysis techniques, we thoroughly investigated the surface chemical environment of the  $\text{In}_2\text{O}_3\text{-ZrO}_2$  catalysts and elucidated the

synergistic interaction between hydroxyl groups and oxygen vacancies in the activation of  $\text{CO}_2$  molecules. Our findings revealed that double and triple-coordinated  $\text{O}_\text{V}$ , especially those in the  $\text{In-O}_\text{V}\text{-Zr}$  configuration, serve as critical sites for  $\text{CO}_2$  adsorption and activation. Moreover, hydroxyl groups adjacent to these asymmetric oxygen vacancies further stabilized  $\text{CO}_2$  and facilitated subsequent hydrogenation processes. These insights provide an understanding of the reaction mechanism underlying  $\text{CO}_2$  hydrogenation over bimetallic oxide catalysts.

## 2 Results and discussion

### 2.1 Catalytic performance for $\text{CO}_2$ hydrogenation

Mixed-crystal supports with varying proportions of m- $\text{ZrO}_2$  and t- $\text{ZrO}_2$  were prepared by calcining amorphous zirconia at 300, 400, 600, and 800 °C. Afterwards, four catalysts, designed as 10In400Zr300, 10In300Zr400, 10In300Zr600, and 10In300Zr800, were synthesized by wet impregnation with indium contents confirmed by ICP-OES (see full description in the Experimental section and Table S1, ESI†). It is noteworthy that the relative content of m- $\text{ZrO}_2$  in the catalyst increased with increasing calcination temperature of the supports (Table S1†). The  $\text{CO}_2$  hydrogenation performance for these catalysts was evaluated over a temperature range of 250–310 °C at 5 MPa, enabling direct comparison with previous reports on  $\text{In}_2\text{O}_3\text{-ZrO}_2$  catalysts. Prior to testing, all the catalysts were reduced at 350 °C in 10%  $\text{H}_2/\text{Ar}$  for 1 h unless otherwise noted. No methanol is formed from pure  $\text{ZrO}_2$ , and the space-time yield ( $\text{STY}_{\text{Methanol}}$ ) of bare  $\text{In}_2\text{O}_3$  is only  $104.3 \text{ mg g}_{\text{cat}}^{-1} \text{ h}^{-1}$ , which is significantly lower than that of 10In300Zr400 ( $302 \text{ mg g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ) at 300 °C, 5 MPa,  $12\,000 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$  (Fig. S1 and Table S2†). Additionally, the  $\text{In}_2\text{O}_3\text{-ZrO}_2$  catalyst synthesized *via* the one-step hydrothermal method performs worse than 10In300Zr400. This may be mostly In doped in  $\text{ZrO}_2$ , which is detrimental to methanol synthesis (Fig. S2 and S5†). Due to the competitive relationship between methanol synthesis and the reverse water-gas shift reaction,  $\text{CO}_2$  conversion and methanol selectivity show a seesaw effect with increasing temperature (Fig. 1a).<sup>21</sup> Whereas, the process of increasing temperature promotes the activation of reactants and intermediates and exhibits higher  $\text{STY}_{\text{Methanol}}$  (Fig. 1d). Moreover, the methanol yield is almost unchanged for up to 106 h, which is indicative of exceptional catalyst stability under prolonged reaction conditions (Fig. 1e).

Fig. 1b illustrates the variability in catalytic activity among the four catalysts examined at 290 °C. The results indicate that the catalyst labelled 10In300Zr800 exhibits almost no activity. In contrast, 10In300Zr400 shows superior catalytic performance at this temperature, achieving 83% methanol selectivity and 8%  $\text{CO}_2$  conversion. Interestingly, as the m- $\text{ZrO}_2$  content in the support increases (Table S1†), the selectivity of the  $\text{In}_2\text{O}_3\text{-ZrO}_2$  catalyst correspondingly improves. This enhancement in selectivity may be attributed to increased electron transfer between  $\text{In}_2\text{O}_3$  and  $\text{ZrO}_2$ . To further investigate the relationship between methanol selectivity and m- $\text{ZrO}_2$  content, an identical mass fraction of indium was doped onto both m- $\text{ZrO}_2$  and t- $\text{ZrO}_2$  supports. Subsequently, the heterogeneous support prepared *via* the one-pot method was simulated by physical



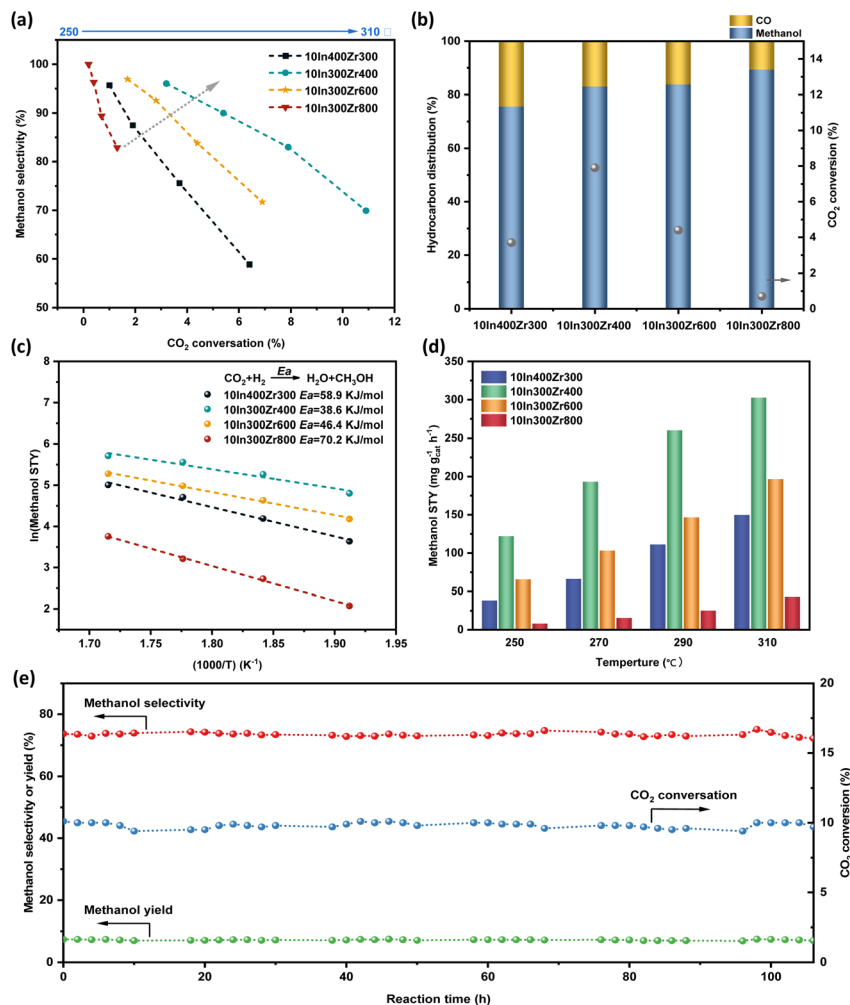


Fig. 1 Catalytic performance of 10In400Zr300, 10In300Zr400, 10In300Zr600, and 10In300Zr800 in the CO<sub>2</sub> hydrogenation reaction. (a) The correlation between methanol selectivity and CO<sub>2</sub> conversion at different reaction temperatures (for the same catalyst, each data point represents a temperature, 250, 270, 290 and 310 °C in that order), (b) CO<sub>2</sub> conversion and product distribution, (c) Arrhenius plots for the methanol synthesis reaction kinetics and the corresponding activation energy (*E<sub>a</sub>*) calculations by using Arrhenius equation. (d) Relationship between the space-time yield (STY) of methanol and the reaction temperature. (e) Long-term TOS testing of 10In300Zr400. Reaction conditions: 0.1 g catalyst, GHSV = 12 000 mL g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, 5 MPa, 310 °C, H<sub>2</sub>/CO<sub>2</sub> = 3.

mixing to facilitate a comparative analysis (Fig. S2 and S3†). Testing under identical conditions confirmed that methanol selectivity positively correlates with the m-ZrO<sub>2</sub> content. Furthermore, the apparent activation energy (*E<sub>a</sub>*) of the methanol synthesis reaction was calculated using the Arrhenius equation (Fig. 1c). The result indicates that the apparent activation energy of the 10In300Zr400 (38.6 kJ mol<sup>-1</sup>) is noticeably lower than that of 10In400Zr300 (58.9 kJ mol<sup>-1</sup>), 10In300Zr600 (46.4 kJ mol<sup>-1</sup>), and 10In300Zr800 (70.2 kJ mol<sup>-1</sup>), also showing a similar trend as CO<sub>2</sub> conversion. Thus, the above results indicate that 10In300Zr400 is most effective at lowering the energy barrier of the methanol synthesis and driving CO<sub>2</sub> into methanol.

## 2.2 Catalyst structure characterization

It is well known that the crystalline phase of ZrO<sub>2</sub> can undergo transformation in response to changes in the external

environment, particularly temperature fluctuations, as evidenced by TG-DSC, XRD and Raman profiles (Fig. S4–S8†).<sup>14,22</sup> Previous studies have demonstrated that surface hydroxyl condensation drives the phase evolution of ZrO<sub>2</sub>. The strong peak at 355 °C observed in the DSC curves is directly associated with the condensation of surface hydroxyls, which facilitates the transformation of a-ZrO<sub>2</sub> to t-ZrO<sub>2</sub>.<sup>23,24</sup> In contrast, the weak peak at 481 °C corresponds to the phase change from t-ZrO<sub>2</sub> to m-ZrO<sub>2</sub>.<sup>25</sup> Raman spectroscopy with 532 nm excitation was performed on four In<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> samples. As shown in Fig. S8,† the appearance of Raman peaks at 146 and 269 cm<sup>-1</sup> correspond to the bulk of t-ZrO<sub>2</sub>, whereas the m-ZrO<sub>2</sub> exhibits distinct Raman peaks at 178, 192, 333, and 378 cm<sup>-1</sup>.<sup>22</sup> The 10In400Zr300 sample displays a dominant tetragonal phase. Notably, the intensity of the monoclinic phase (178 cm<sup>-1</sup>) increases with higher calcination temperatures, reflecting a gradual phase transition from t-ZrO<sub>2</sub> to m-ZrO<sub>2</sub>. These

spectral trends align with the XRD result, corroborating the structural evolution of the  $\text{ZrO}_2$  support. Moreover, upon doping with 10 wt% In, the diffraction peaks corresponding to the (101) crystal plane (at  $\sim 30.2^\circ$ , PDF#88-1007) of both fresh and spent 10In300Zr400 shift towards higher angles relative to those of Zr400. This shift indicates the incorporation of In into the  $\text{ZrO}_2$  lattice, resulting in the formation of  $\text{InZrO}_x$  solid solution (Fig. 2a).<sup>13,26</sup> Based on the Scherrer equation, the calculated particle sizes of 10In300Zr400 and 10In400Zr300 are in the range of 9–10 nm (Table S2†). The observed difference in catalytic activity between the two catalysts indicates that the crystal size has a relatively minor effect on the overall performance.

Although  $\text{In}_2\text{O}_3$  diffraction signals are obscured due to peak overlap with  $\text{t-ZrO}_2$ , aberration-corrected HAADF-STEM images enable clear visualization of its distribution and structure. On 10In300Zr400 catalyst,  $\text{In}_2\text{O}_3$  is well dispersed, likely facilitated by the abundant surface hydroxyl groups (Fig. 2b, c and S9†).<sup>15,27</sup> Images acquired at higher magnification of 10In300Zr400 reveal that the In atom is positioned at the top of the Zr atomic column in the form of brighter spots (Figure S10†). This observation aligns with the XRD results, confirming that some of the indium is embedded in zirconium oxide in the form of single atoms.<sup>28,29</sup> Moreover, the existence of indium single atoms is still observed on the spent catalysts, suggesting that this structure was extremely stable under high reaction temperatures.

Additionally,  $\text{H}_2$ -TPR measurements were performed to evaluate the  $\text{H}_2$  dissociation behaviour, which further

elucidated the  $\text{In}_2\text{O}_3$  morphology across the four  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  catalysts (Fig. 2d and 5d). Compared with pure  $\text{In}_2\text{O}_3$ , the reduction peaks of the  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  catalysts shift to higher temperatures, indicating a strong metal-support interaction (SMSI) between  $\text{ZrO}_2$  and  $\text{In}_2\text{O}_3$ . This interaction promotes the partial reduction of  $\text{In}_2\text{O}_3$ , resulting in a more stable In–O–Zr structure and smaller  $\text{In}_2\text{O}_3$  particles.<sup>30</sup> Also, the higher the proportion of m- $\text{ZrO}_2$  in the carrier, the lower the surface reduction temperature of  $\text{In}_2\text{O}_3$ . XPS analysis of the In 3d and Zr 3d spectra further supports these findings. Previous studies have shown that t- $\text{ZrO}_2$  and m- $\text{ZrO}_2$  have different electron transfer ability to  $\text{In}_2\text{O}_3$ , where the interfacial electron transfer from m- $\text{ZrO}_2$  to In–O–In is stronger.<sup>14,31</sup> In this study, we also observed that the binding energy of In exhibits a shift toward lower values, whereas the binding energy of Zr demonstrates a shift toward to higher values with increasing m- $\text{ZrO}_2$  content (Fig. 2e and f). This change suggests that the high electron density of  $\text{In}_2\text{O}_3$  may contribute to the methanol selectivity. Moreover, although the  $\text{H}_2$  dissociation ability of 10In300Zr400 is not the highest among the samples, its  $\text{H}_2$  consumption is considerably greater than that of other systems, which promotes the formation of oxygen vacancies (Table S3†). These oxygen vacancies are essential for the effective activation and dissociation of  $\text{H}_2$  and  $\text{CO}_2$ , as will be discussed in detail below.

### 2.3 Identification of surface hydroxyls and oxygen vacancies

The spatial configuration of the surface hydroxyls, which act as a key bridge between the catalyst crystal and the oxygen

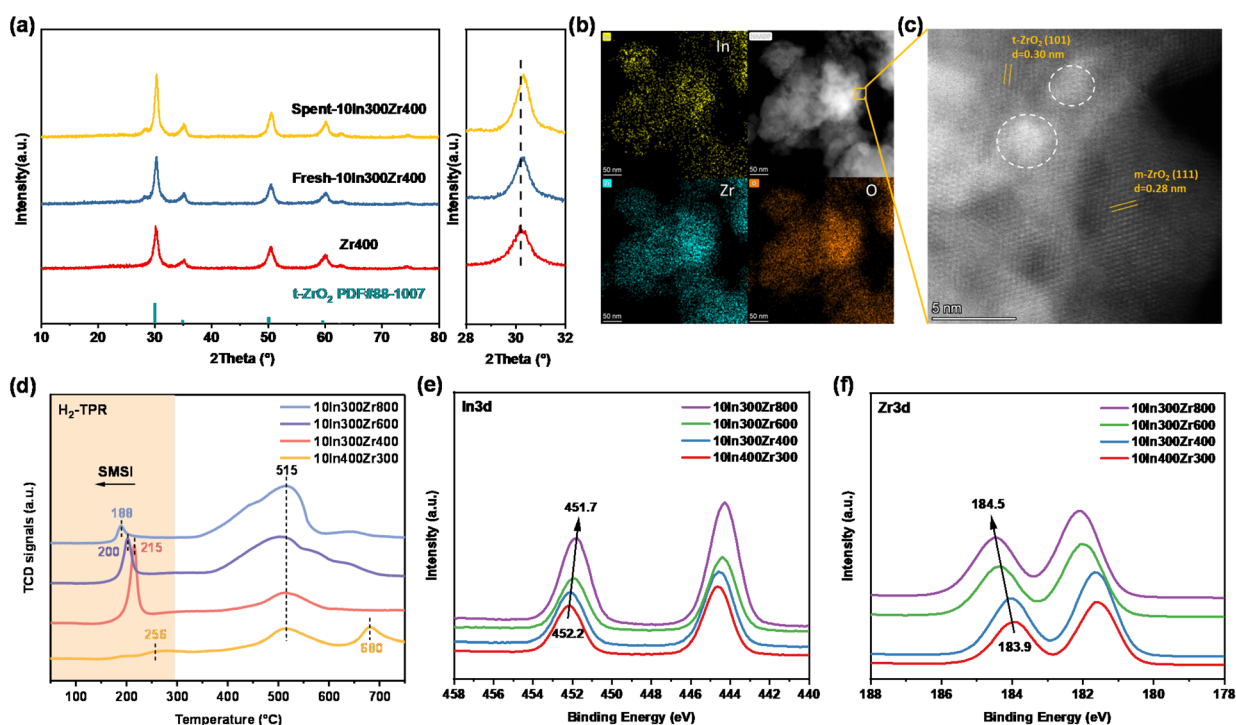


Fig. 2 Structural characterization and electronic effects. (a) XRD patterns of Zr400, fresh-10In300Zr400 and spent-10In300Zr400. (b) EDX elemental mapping and (c) HAADF-STEM images of fresh-10In300Zr400. (d)  $\text{H}_2$ -TPR profiles of the  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  catalysts. XPS profiles of (e) In 3d and (f) Zr 3d for reduced 10In300Zr400.



vacancies, directly affects the exposure of the active sites.  $^1\text{H}$  MAS SSNMR experiments were conducted to bring out the detailed structural information on the surface hydroxyls of  $\text{In}_2\text{O}_3$ , different crystalline  $\text{ZrO}_2$ , and the corresponding  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  catalysts. As illustrated in Fig. 3a and S11,<sup>†</sup>  $\text{In}_2\text{O}_3$ ,  $\text{ZrO}_2$ , and  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  catalysts possess three types of surface hydroxyls. Within the range of 0–10 ppm, characteristic peaks of the surface hydroxyls emerge, with chemical shifts at 0–1.5 ppm, 1.6–3.8 ppm, and 3.9–5.0 ppm corresponding to the terminal hydroxyls ( $\mu_1$ -OH), doubly bridged hydroxyls ( $\mu_2$ -OH), and triply bridged hydroxyls ( $\mu_3$ -OH), respectively (Fig. 3b).<sup>16,32</sup> The signals in the high-frequency regions (5.1–8.5 ppm) are attributed to the overlapping resonance of  $\mu_2$ -OH and  $\mu_3$ -OH, which contribute to the formation of extensive hydrogen-bonding networks. This spatial proximity is corroborated by the 2D  $^1\text{H}$ - $^1\text{H}$  homonuclear correlation SSNMR spectra (Fig. 3c, S13–S15<sup>†</sup>), where strong diagonal peaks reveal the mutual interactions among  $\mu_1$ -OH,  $\mu_2$ -OH, and  $\mu_3$ -OH. Additionally,

both  $\text{In}_2\text{O}_3$  and  $\text{ZrO}_2$  exhibit a  $\mu_2$ -OH characteristic peak at 3.2 ppm, however, in the  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  system, a new peak appears at 2.0 ppm. This observation suggests a significant alteration in the hydroxyl coordination environment, attributable to the formation of an In-O(H)-Zr heterointerface. Combining XRD and aberration-corrected HAADF-STEM results, it is inferred that the dissolution of In species onto the  $\text{ZrO}_2$  surface leads to a partial reorganization of  $\mu_3$ -OH groups. This reorganization results in the formation of an In-O(H)-Zr structure characterized by bimetallic coordination, directly contributing to a reduction in the  $\mu_3$ -OH content in the composite catalyst and an increase in the ratio of  $\mu_2$ -OH groups. These findings confirm the critical role of surface hydroxyls in stabilizing the active indium species and in determining their spatial distribution.

By analysing the ratio of various hydroxyl groups in  $^1\text{H}$  MAS SSNMR and the total amount of acid sites obtained from  $\text{NH}_3$ -TPD measurements, we accurately calculated the specific

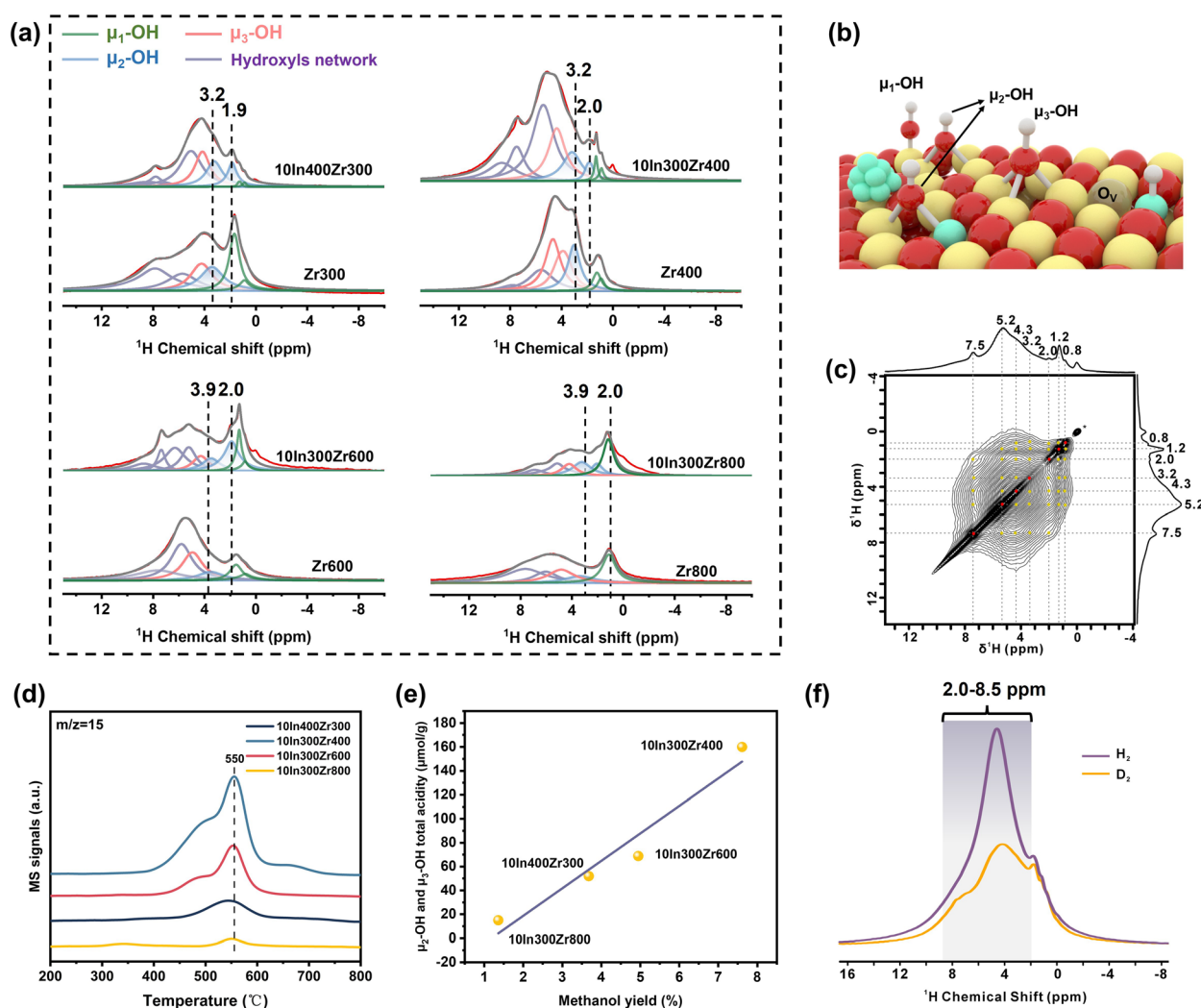


Fig. 3 Characterization of surface hydroxyl configurations and their structure-activity correlations. (a)  $^1\text{H}$  MAS SSNMR spectra of  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  catalysts and  $\text{ZrO}_2$  supports, (b) schematic representation of the three types of surface hydroxyls, (c) 2D  $^1\text{H}$ - $^1\text{H}$  homonuclear correlation SSNMR spectra of 10In300Zr400, (d)  $\text{NH}_3$ -TPD profiles of  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  catalysts, (e) the proportion of  $\mu_2$ -OH and  $\mu_3$ -OH total acidity and methanol yield for  $\text{CO}_2$  hydrogenation over  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  catalysts, (f)  $^1\text{H}$  MAS SSNMR spectra of  $\text{H}_2$ - $\text{D}_2$  exchange experiment for 10In300Zr400. Reaction condition: 0.1 g catalyst, GHSV = 12 000  $\text{mL g}_{\text{cat}}^{-1} \text{h}^{-1}$ , 5 MPa, 310  $^\circ\text{C}$ ,  $\text{H}_2/\text{CO}_2 = 3$ .

concentrations of different hydroxyl species in the catalysts. Upon analysing the  $\text{NH}_3$ -TPD profile through peak fitting (as detailed in Fig. 3d and Table S4†), a volcanic-like relationship emerges between the total acidity of the  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  catalysts and their monoclinic phase content, with the catalyst labelled 10In300Zr400 possessing the highest concentration of acid sites ( $182 \mu\text{mol g}^{-1}$ ). When correlating the total acidity of the catalysts with the methanol yield, a positive correlation trend akin to that between oxygen vacancy concentration and methanol yield is observed, which points to a link between oxygen vacancies and surface hydroxyls (Fig. S16†). Intriguingly, the total  $\mu_2$ -OH and  $\mu_3$ -OH concentrations of four  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  catalysts show regular variations:  $10\text{In}300\text{Zr}400 > 10\text{In}300\text{Zr}600 > 10\text{In}400\text{Zr}300 > 10\text{In}300\text{Zr}800$ , and this order coincides with a significant linear correlation with their methanol yield (Fig. 3e). Taking this into account, it is reasonable to speculate that  $\mu_2$ -OH and  $\mu_3$ -OH may be the active site for methanol synthesis. To confirm this point, we adsorbed  $\text{H}_2$  on the catalyst surface and then switched  $\text{D}_2$  to exchange the surface hydrogen species to obtain the  $^1\text{H}$  SSNMR spectra (Fig. 3f). Our results show that a significant attenuation of both  $\mu_2$ -OH and  $\mu_3$ -OH signals in the 2.0–8.5 ppm region after  $\text{D}_2$  treatment suggests that the two types of hydroxyl groups are highly reactive. In corroboration with this, O 1s XPS analysis shows a decrease in the hydroxyl group fraction after the reduction treatment and an increase in the oxygen vacancy fraction. Therefore, we propose that  $\mu_2$ -OH and  $\mu_3$ -OH are structural precursors of the

active site, which may be generated by dehydroxylation to oxygen vacancies during the reaction process.

More information on the density of oxygen vacancies is unravelled in the O 1s spectra by XPS. As shown in Fig. 4a, the broad peak of the O 1s spectra can be deconvoluted into three different components. The peak at the lower binding energy (529.8 eV) is associated with the lattice oxygen of  $\text{ZrO}_2$  ( $\text{O}_\text{L}$ ). The two peaks centered at ca. 531.2 eV and 532.4 eV originate from O atoms in the proximity of an oxygen vacancy ( $\text{O}_\text{V}$ ) and the chemisorbed oxygen species related to the surface hydroxyls ( $^*\text{OH}$ ). The ratio of  $\text{O}_\text{V}/(\text{O}_\text{L} + \text{O}_\text{V} + \text{OH})$  and  $\text{OH}/(\text{O}_\text{L} + \text{O}_\text{V} + \text{OH})$  reflects the density of surface oxygen vacancies and the surface hydroxyls, respectively.<sup>30,33</sup> It is worth noting that doping In on Zr400 increases the concentration of  $\text{O}_\text{V}$  without changing  $^*\text{OH}$  concentration, regarded as interfacial oxygen vacancies formed *via* the penetration of In into  $\text{ZrO}_2$ . Also, after reducing 10In300Zr400 by  $\text{H}_2$ , the oxygen vacancy concentration is increased from 21.4% to 26.9%, while the hydroxyl group concentration is decreased from 11.3% to 9.26% (Fig. S17†). Thus, some of the oxygen vacancies on the catalyst surface are derived from the oxidation of surface hydroxyls. Surface oxygen vacancies, as electron-rich centres, can effectively activate  $\text{CO}_2$  molecules, and are usually regarded as important active sites for methanol synthesis by  $\text{CO}_2$  hydrogenation. Systematic comparison of the composition–performance relationships among different catalyst systems revealed that  $\text{O}_\text{V}$  and OH concentrations in reduced catalysts follow the order

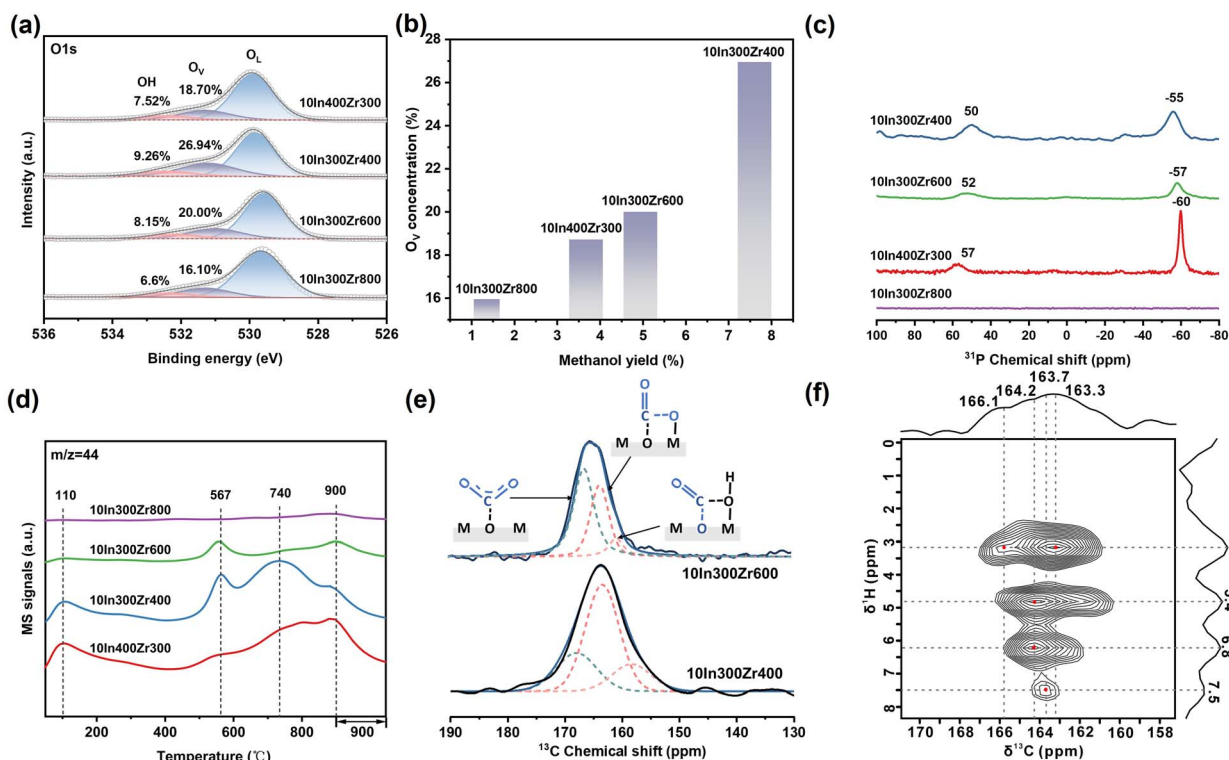


Fig. 4 Characterization for revealing the relationship between oxygen vacancies and  $\text{CO}_2$  activation. (a) Deconvoluted O 1s XPS spectra  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  catalysts, (b) the proportion of  $\text{O}_\text{V}$  concentration and methanol yield for  $\text{CO}_2$  hydrogenation over  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  catalysts, (c)  $^{31}\text{P}$  MAS SSNMR spectra of TMP adsorbed on  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  catalysts, (d)  $\text{CO}_2$ -TPD profiles of  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  catalysts, (e)  $^{13}\text{C}$  MAS NMR spectra of  $\text{CO}_2$  adsorbed on 10In300Zr400 and 10In300Zr600. (f)  $^{13}\text{C}$ - $^1\text{H}$  heteronuclear correlation MAS SSNMR spectra of 10In300Zr400.

10In300Zr400 > 10In300Zr600 > 10In400Zr300 > 10In300Zr800, both exhibiting linear correlations with methanol synthesis activity (Fig. 4b and S18†). This result aligns with Liu *et al.*'s study,<sup>15</sup> where air plasma treatment enhanced the hydrophilicity of ZrO<sub>2</sub>. In the highly hydrophilic 1% Ru/DBD-ZrO<sub>2</sub> catalyst, CO<sub>2</sub> is captured at oxygen vacancies, and the H atoms from surface OH\* combine with CO<sub>2</sub> to form HCO<sub>3</sub>\* intermediates, which further convert to HCOO\*. Although their work focused on CO<sub>2</sub> hydrogenation to CO, we propose that oxygen vacancies and hydroxyl groups serve as critical active sites and descriptors for catalyst structure–activity relationships, given the established role of formate as a key intermediate in methanol synthesis.

SSNMR is a powerful technique for the characterization of active sites on the solid materials.<sup>34–36</sup> As the TMP molecule is highly alkaline, TMP-assisted <sup>31</sup>P MAS SSNMR analysis was adopted to distinguish the acid sites over the catalysts.<sup>37</sup> Previous studies have shown that TMP is more sensitive to Lewis acidity than Brønsted acidity, and the signal ranging from –30 to –58 ppm is attributed to TMP binding onto the LAS.<sup>38</sup> Fig. 4c shows that for all catalysts except 10In300Zr800, two peaks are observed at –50 to –60 ppm and 40 to 60 ppm, respectively. The signals at –60, –57, and –55 ppm are assigned to Lewis acid sites in 10In400Zr300, 10In300Zr600, and 10In300Zr400, respectively. Apparently, 10In300Zr400 exhibits stronger Lewis acidity than both 10In300Zr600 and 10In400Zr300, which aligns with the increased oxygen vacancy concentration observed in the O 1s spectra. The signal in the positive chemical shift range corresponds to TMPO, formed by the reaction between TMP and lattice oxygen, indicating that the In<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> catalyst readily forms more oxygen vacancies.<sup>39</sup>

To investigate the effect of Lewis acidity/basicity of In<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> catalysts on the CO<sub>2</sub> adsorption and activation, the CO<sub>2</sub>-TPD measurement was performed, as CO<sub>2</sub> molecules could bind strongly to FLP. The signals of CO<sub>2</sub> were collected by the mass spectrometer. As shown in Fig. 4d, CO<sub>2</sub> desorption peaks can be divided into three regions, 0–200 °C, 200–400 °C, and 400–900 °C, which are attributed to weak, medium-strong, and strong basic sites, respectively. In the temperature range below 400 °C, the two signals correspond to the physically adsorbed CO<sub>2</sub> and CO<sub>2</sub> adsorbed on the weakly basic site, like surface hydroxyls.<sup>40,41</sup> In the high temperature range of 400–900 °C, three consecutive desorption peaks at around 560, 740, and 900 °C are observed for all catalysts. These peaks are assigned to CO<sub>2</sub> adsorbed as bidentate carbonates (b-CO<sub>3</sub><sup>2–</sup>) and monodentate carbonates (m-CO<sub>3</sub><sup>2–</sup>) on the strongly basic sites (O<sub>V</sub>).<sup>42</sup> Compared with the CO<sub>2</sub>-TPD profiles of pure ZrO<sub>2</sub>, we noticed that a larger peak area in the high temperature region for 10In300Zr400, which indicates that the oxygen vacancy concentration is elevated after doping with In, and this result is also evidenced by H<sub>2</sub>-TPR and O 1s XPS (Fig. S19†). Analogously, the existence of more surface oxygen vacancies on 10In300Zr400 is further verified. To explore the effect of H<sub>2</sub> pretreatment on the surface properties of the catalysts, the In<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> catalysts were exposed to H<sub>2</sub> and Ar atmospheres at 350 °C for reduction and heat treatment, respectively (Fig. S20†). Obviously, after treatment with H<sub>2</sub>, the signal intensities in the low-temperature

region (<200 °C) decrease while the peak in the high-temperature region increases, suggesting that H<sub>2</sub> reduction creates more oxygen vacancies by removing the surface hydroxyls.

Meanwhile, high-resolution 1D <sup>13</sup>C MAS SSNMR and 2D <sup>13</sup>C–<sup>1</sup>H Heteronuclear Correlation (HETCOR) MAS SSNMR spectra have been utilized to precisely elucidate the adsorption behaviour and structure of CO<sub>2</sub> over the catalyst surface. In general, the electron-rich oxygen atoms in the CO<sub>2</sub> molecule are anchored by Lewis acids (O<sub>V</sub>) and are immobilized on the catalyst surface in the form of bidentate carbonates (b-CO<sub>3</sub><sup>2–</sup>) and monodentate carbonates (m-CO<sub>3</sub><sup>2–</sup>). As depicted in Fig. 4e, three <sup>13</sup>C signals are observed in the 158–175 ppm region after introducing <sup>13</sup>CO<sub>2</sub> to In<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub>. The peaks from 158 to 162 ppm, 163 to 167 ppm, and 167 to 171 ppm correspond to bicarbonate, bidentate carbonate, and monodentate carbonate, respectively.<sup>43</sup> Furthermore, the 2D <sup>13</sup>C–<sup>1</sup>H HETCOR MAS SSNMR experiments reveal the spatial proximity of the adsorbed <sup>13</sup>CO<sub>2</sub> and the three surface hydroxyls (Fig. 4f and S21†). Apparently, the b-CO<sub>3</sub><sup>2–</sup> species in the 163–167 ppm regime exhibits strong interactions with structural hydroxyl groups of μ<sub>2</sub>-OH and μ<sub>3</sub>-OH, as well as their associated hydrogen-bonding network. No correlation peak corresponding to an interaction with μ<sub>1</sub>-OH is observed. Therefore, we conclude that μ<sub>2</sub>-OH and μ<sub>3</sub>-OH adjacent to O<sub>V</sub> act synergistically as proton donors to promote CO<sub>2</sub> protonation to HCO<sub>3</sub><sup>–</sup> on the one hand, and by stabilizing b-CO<sub>3</sub><sup>2–</sup> through the O–H...O bond on the other, thereby providing an optimized microenvironment for CO<sub>2</sub> hydrogenation.

## 2.4 Investigation of the reaction mechanism

*In situ* DRIFTS measurements were conducted to elucidate the synergistic effect of surface hydroxyls and oxygen vacancies in methanol synthesis. Fig. 5a presents the real-time monitoring of the catalytic process over the 10In300Zr400 catalysts under programmed temperature conditions. When the test temperature is controlled at 100 °C, a broad absorption band in the range of 1660 and 1200 cm<sup>–1</sup> is observed, which can be attributed to the formation of carbonate or bicarbonate species. Specifically, the peaks at 1276, 1300, 1662 cm<sup>–1</sup> and 1508, 1335 cm<sup>–1</sup> are assigned to bidentate carbonate species (b-CO<sub>3</sub><sup>2–</sup>) and monodentate carbonate (m-CO<sub>3</sub><sup>2–</sup>), respectively. In addition, peaks at 1446 and 1624 cm<sup>–1</sup> correspond to bidentate bicarbonate species (b-HCO<sub>3</sub><sup>–</sup>).<sup>44</sup> These findings suggest that CO<sub>2</sub> is predominantly adsorbed on the reduced catalyst as carbonates and bicarbonates, consistent with CO<sub>2</sub>-TPD and <sup>13</sup>C MAS SSNMR results. Moreover, linearly adsorbed CO (2077 cm<sup>–1</sup>) is also observed at 100 °C, which may originate from the dissociation of carbonates induced by surface oxygen vacancies, as supported by the literature.<sup>42</sup> As the temperature increases, the band of carbonate species and bicarbonate species gradually diminish, while new spectral features emerge. These new features correspond to the formation of bidentate formates (b-HCOO\*, 1392, 1376, 1592 cm<sup>–1</sup>) and methoxy (CH<sub>3</sub>O\*, 1046 and 1140 cm<sup>–1</sup>).<sup>45,46</sup> Notably, upon reaching 250 °C, the HCOO\* absorption peak intensity markedly increases, while the HCOO\*/CH<sub>3</sub>O\* ratio initially rise but



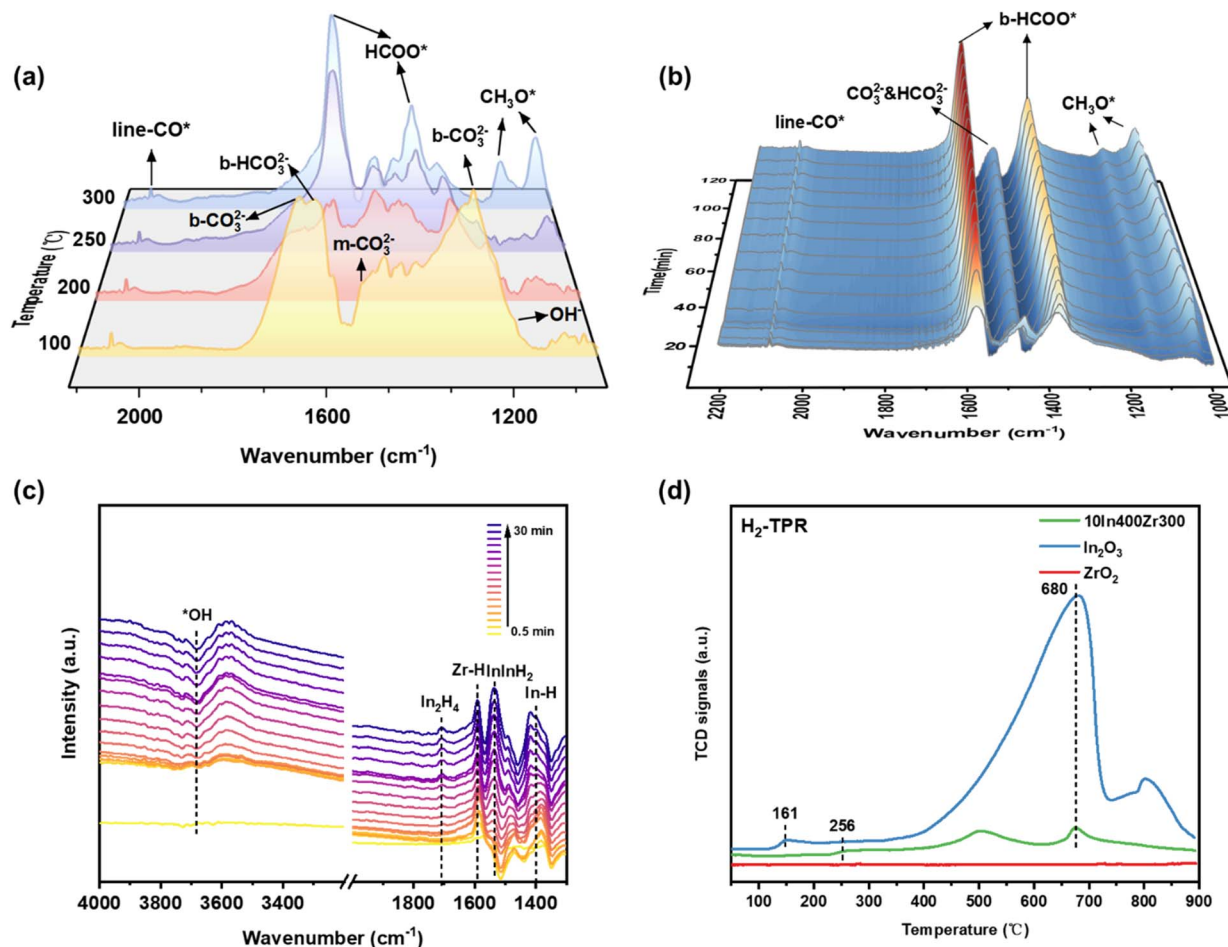


Fig. 5 *In situ* DRIFTS spectra of  $\text{CO}_2 + \text{H}_2$  reaction in the range of  $1000\text{--}2200\text{ cm}^{-1}$  over  $10\text{In}300\text{Zr}400$  catalyst. (a) DRIFTS spectra at different temperatures ( $100\text{--}300\text{ }^\circ\text{C}$ ) after reacting for 1 h; (b) time-resolved DRIFTS spectra at a reaction temperature of  $300\text{ }^\circ\text{C}$ ; (c) DRIFTS spectra of  $\text{H}_2$  reduction at  $350\text{ }^\circ\text{C}$ ; (d)  $\text{H}_2$ -TPR profiles of  $\text{ZrO}_2$ ,  $\text{In}_2\text{O}_3$ ,  $10\text{In}400\text{Zr}300$ .

subsequently decline, suggesting that  $\text{HCOO}^*$  acts as a key intermediate in the  $\text{CO}_2$  hydrogenation pathway, with its conversion to  $\text{CH}_3\text{O}^*$  requiring a high activation energy barrier (Fig. S22†). Furthermore, time-resolved DRIFTS analysis at  $300\text{ }^\circ\text{C}$  captures the dynamic behaviour of reaction intermediates (Fig. 5b). Initially observed carbonate and bicarbonate species, analogous to those at  $100\text{ }^\circ\text{C}$ , show rapid intensity decay within 10 minutes, while  $\text{HCOO}^*$  and  $\text{CH}_3\text{O}^*$  species progressively increase, indicating the conversion of carbonate/bicarbonate to formate on the  $\text{In}_2\text{O}_3\text{--ZrO}_2$  catalysts.

To further elucidate the hydrogen dissociation mechanism on the  $\text{In}_2\text{O}_3\text{--ZrO}_2$  catalyst, we also conducted *in situ* DRIFTS experiments under hydrogen-rich conditions at  $350\text{ }^\circ\text{C}$  and 1 MPa. As illustrated in Fig. 5c, upon exposure to a hydrogen atmosphere, the characteristic peak corresponding to surface hydroxyls ( $\text{OH}^*$ ,  $3684\text{ cm}^{-1}$ ) on the  $10\text{In}300\text{Zr}400$  catalyst demonstrates a progressive intensity reduction. Meanwhile, distinct shifts at  $1707$ ,  $1584$ ,  $1533$ , and  $1390\text{ cm}^{-1}$  appear, which can be assigned to the intermediate  $\text{In}_2\text{H}_4$ ,  $\text{Zr-H}$ ,  $\text{InInH}_2$ , and  $\text{InH}$  species.<sup>47</sup> Previous studies have demonstrated that molecular hydrogen preferentially adsorbs on the  $\text{In}_2\text{O}_3$  surface, where it readily undergoes heterolytic dissociation to form indium

hydride species.<sup>19</sup> This preferential adsorption behaviour is supported by both theoretical calculations and surface characterization techniques.<sup>7,48</sup> In contrast,  $\text{H}_2$ -TPR has revealed that  $\text{ZrO}_2$  exhibits a strong tendency to interact with carbon-based species rather than hydrogen molecules, indicating its limited capability for hydrogen dissociation under similar conditions (Fig. 5d).<sup>49,50</sup> These collectively suggest that while hydrogen molecules remove surface hydroxyls, they simultaneously generate electron-rich  $\text{InH}$  species on the indium oxide surface. Accordingly,  $\text{Zr-H}$  species are likely formed through a hydrogen spillover mechanism from the adjacent  $\text{In}_2\text{O}_3$  surface, rather than through direct dissociation on  $\text{ZrO}_2$ .<sup>11</sup> This hydrogen migration phenomenon is consistent with the well-documented surface mobility of hydrogen atoms in mixed oxide systems.

## 2.5 Discussion on hydroxyl-oxygen vacancy synergy

Based on the experimental results discussed above, Fig. 6 illustrates the proposed surface chemical environment of the  $\text{In}_2\text{O}_3\text{--ZrO}_2$  catalyst and delineates the synergistic mechanism between hydroxyl groups and oxygen vacancies in the activation of  $\text{CO}_2$  molecules. The crystalline phase of  $\text{ZrO}_2$  is usually



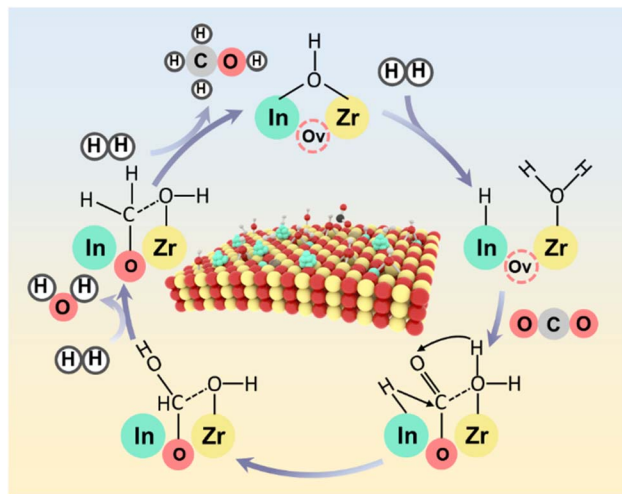


Fig. 6 Schematic representation of CO<sub>2</sub> hydrogenation to methanol over In<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> catalysts.

closely related to the distribution of surface hydroxyls. We found that 400 °C approaches the critical phase transition temperature of ZrO<sub>2</sub>, and calcination at temperatures above this threshold enables the formation of mixed-crystalline supports. The 10In300Zr400 catalyst constructed on mixed-crystalline ZrO<sub>2</sub> by low-temperature calcination is enriched with a higher O<sub>v</sub> concentration at the interface while simultaneously maintaining a greater density of surface hydroxyls. According to XPS and XRD results, the more severe lattice mismatch between the mixed-crystalline ZrO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub>, which creates a greater number of interfacial oxygen vacancies than in pure t-ZrO<sub>2</sub>.<sup>28</sup> Compared to the physical mixed system with the same mixed-crystal composition, the catalysts synthesised by the one-pot method exhibit higher CO<sub>2</sub> conversion than, confirming that *in situ* construction of interfacial oxygen vacancies is the key to the formation of active sites (Fig. S2†). The atomic-level dispersion of In<sub>2</sub>O<sub>3</sub> is promoted through surface hydroxyls and strong metal-support interactions, thereby increasing the number of active sites. However, further elevation of calcination temperatures leads to particle coarsening and reduced hydroxyl group concentration, resulting in a reduction of hydroxyl-oxygen vacancy active sites and a decline in catalytic performance. During CO<sub>2</sub> hydrogenation, H<sub>2</sub> preferentially dissociates at In-containing structural sites, such as In nanoclusters and the In–O(H)–Zr structure. This process exposes oxygen vacancies that exist in double- and triple-bridged coordination environments. These oxygen vacancies function as strong Lewis acid sites, anchoring the oxygen atoms of CO<sub>2</sub>, while the neighbouring μ<sub>2</sub>-OH/μ<sub>3</sub>-OH network forms FLP sites through hydrogen bonding. This synergistic interaction promotes the formation of carbonate and bicarbonate in a locally polar environment. The CO<sub>2</sub> species stabilized by the hydroxyl network are activated in the presence of the In–H active site, leading to directed hydrogenation to methanol *via* formate intermediate. Throughout the reaction, the depleted hydroxyl groups and oxygen vacancies are dynamically regenerated by

surface remodelling under reaction conditions, thereby creating a hydroxyl-oxygen vacancy synergistic catalytic cycle.

### 3 Conclusions

In summary, a straightforward In<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> model catalyst was utilized to investigate the distribution of surface hydroxyls and to elucidate the synergistic interactions and transformations between oxygen vacancies and surface hydroxyls in CO<sub>2</sub> hydrogenation to methanol. Among the catalysts tested—10In400Zr300, 10In300Zr400, 10In300Zr600, and 10In300Zr800—the 10In300Zr400 catalyst exhibits a higher concentration of surface hydroxyls and oxygen vacancies. Under the operating conditions of 300 °C, 5 MPa, and 12 000 mL g<sub>cat</sub><sup>−1</sup> h<sup>−1</sup>, it achieved superior methanol synthesis activity (302 mg g<sub>cat</sub><sup>−1</sup> h<sup>−1</sup>). Structural characterization and mechanistic studies revealed that the FLP sites formed by surface hydroxyls and oxygen vacancies, act as centres for stabilizing CO<sub>2</sub>, providing an abundant carbon source for the formation of methanol synthesis intermediates, HCOO\* and CH<sub>3</sub>O\*. Overall, this work reinterprets the physicochemical behaviour of small molecule reactants on the catalyst surface from an acid–base perspective, offering novel insights for designing catalysts with high-density active interfacial sites for enhanced performance.

### Data availability

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

### Author contributions

Xia Li: data curation, software, formal analysis, writing—original draft, writing—review & editing. Zixia Feng: investigation, data curation, formal analysis, resources, methodology. Hanjun Lua: investigation, formal analysis. Xinlin Hong: writing—review & editing, guiding the project. Guangchao Li: writing—review & editing, guiding the project. Shik Chi Edman: discussion.

### Conflicts of interest

There are no conflicts to declare.

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### Notes and references

- 1 G. A. Olah, *Angew. Chem., Int. Ed.*, 2005, **44**, 2636–2639.



- 2 C. F. Shih, T. Zhang, J. Li and C. Bai, *Joule*, 2018, **2**, 1925–1949.
- 3 P. Gao, L. Zhang, S. Li, Z. Zhou and Y. Sun, *ACS Cent. Sci.*, 2020, **6**, 1657–1670.
- 4 H. Wang, X. Liu, P. Niu, S. Wang, J. Shi and L. Li, *Matter*, 2020, **2**, 1377–1413.
- 5 F. Tao, *Chem. Soc. Rev.*, 2012, **41**, 7977–7979.
- 6 X. Jiang, X. Nie, X. Guo, C. Song and J. G. Chen, *Chem. Rev.*, 2020, **120**, 7984–8034.
- 7 J. Ye, C. Liu, D. Mei and Q. Ge, *ACS Catal.*, 2013, **3**, 1296–1306.
- 8 S. Dang, B. Qin, Y. Yang, H. Wang, J. Cai, Y. Han, S. Li, P. Gao and Y. Sun, *Sci. Adv.*, 2020, **6**, eaaz2060.
- 9 W. Wang, K. Huo, Y. Wang, J. Xie, X. Sun, Y. He, M. Li, J. Liang, X. Gao, G. Yang, S. Lin, F. Cao, H. Jiang, M. Wu and N. Tsubaki, *ACS Catal.*, 2024, **14**, 9887–9900.
- 10 N. H. M. D. Dostagir, C. R. Tomuschat, K. Oshiro, M. Gao, J.-y. Hasegawa, A. Fukuoka and A. Shrotri, *JACS Au*, 2024, **4**, 1048–1058.
- 11 F. Gao, Y. Wang, Y. Zhao, K. Wang, W. Guo, Z. Sun, Y. Zhu, H. He, Y. Liu and Y. Cao, *ACS Catal.*, 2025, **15**, 2785–2795.
- 12 X. Zhang, A. V. Kirilin, S. Rozeveld, J. H. Kang, G. Pollefeyt, D. F. Yancey, A. Chojecki, B. Vanchura and M. Blum, *ACS Catal.*, 2022, **12**, 3868–3880.
- 13 A. Tsoukalou, P. M. Abdala, A. Armutlulu, E. Willinger, A. Fedorov and C. R. Müller, *ACS Catal.*, 2020, **10**, 10060–10067.
- 14 C. Yang, C. Pei, R. Luo, S. Liu, Y. Wang, Z. Wang, Z.-J. Zhao and J. Gong, *J. Am. Chem. Soc.*, 2020, **142**, 19523–19531.
- 15 M. Liu, R. Zou and C.-J. Liu, *Appl. Catal., B*, 2025, **360**, 124549.
- 16 Q. Han, P. Gao, L. Liang, K. Chen, A. Dong, Z. Liu, X. Han, Q. Fu and G. Hou, *Anal. Chem.*, 2021, **93**, 16769–16778.
- 17 L. Fu, Z. Qu, L. Zhou and Y. Ding, *ACS Sustain. Chem. Eng.*, 2024, **12**, 18412–18421.
- 18 G. C. Welch, R. R. S. Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124–1126.
- 19 K. K. Ghuman, L. B. Hoch, T. E. Wood, C. Mims, C. V. Singh and G. A. Ozin, *ACS Catal.*, 2016, **6**, 5764–5770.
- 20 R. Jing, X. Lu, J. Wang, J. Xiong, Y. Qiao, R. Zhang and Z. Yu, *Small*, 2024, **20**, 2310926.
- 21 S. Tada, S. Kayamori, T. Honma, H. Kamei, A. Nariyuki, K. Kon, T. Toyao, K.-i. Shimizu and S. Satokawa, *ACS Catal.*, 2018, **8**, 7809–7819.
- 22 M. Li, Z. Feng, P. Ying, Q. Xin and C. Li, *Phys. Chem. Chem. Phys.*, 2003, **5**, 5326–5332.
- 23 X. Guo, D. Mao, G. Lu, S. Wang and G. Wu, *Catal. Commun.*, 2011, **12**, 1095–1098.
- 24 Y. Wu, J. Chen, W. Hu, K. Zhao, P. Qu, P. Shen, M. Zhao, L. Zhong and Y. Chen, *J. Catal.*, 2019, **377**, 565–576.
- 25 Z. Yanwei, G. Fagherazzi and S. Polizzi, *J. Mater. Sci.*, 1995, **30**, 2153–2158.
- 26 T. Yan, N. Li, L. Wang, W. Ran, P. N. Duchesne, L. Wan, N. T. Nguyen, L. Wang, M. Xia and G. A. Ozin, *Nat. Commun.*, 2020, **11**, 6095.
- 27 H. Li, W. Wang, S. Xue, J. He, C. Liu, G. Gao, S. Di, S. Wang, J. Wang, Z. Yu and L. Li, *J. Am. Chem. Soc.*, 2024, **146**, 9124–9133.
- 28 M. S. Frei, C. Mondelli, A. Cesarini, F. Krumeich, R. Hauert, J. A. Stewart, D. Curulla Ferré and J. Pérez-Ramírez, *ACS Catal.*, 2019, **10**, 1133–1145.
- 29 H. Li, S. Di, P. Niu, S. Wang, J. Wang and L. Li, *Energy Environ. Sci.*, 2022, **15**, 1601–1610.
- 30 Y. Zhou, L. Liu, G. Li and C. Hu, *ACS Catal.*, 2021, **11**, 7099–7113.
- 31 C. Shen, K. Sun, R. Zou, Q. Wu, D. Mei and C. J. Liu, *Appl. Catal., B*, 2025, **361**, 124683.
- 32 J. Qin, Y. Long, F. Sun, P. P. Zhou, W. D. Wang, N. Luo and J. Ma, *Angew. Chem., Int. Ed.*, 2021, **61**, e202112907.
- 33 J. An, Y. Wang, J. Lu, J. Zhang, Z. Zhang, S. Xu, X. Liu, T. Zhang, M. Gocyla, M. Heggen, R. E. Dunin-Borkowski, P. Fornasiero and F. Wang, *J. Am. Chem. Soc.*, 2018, **140**, 4172–4181.
- 34 G. Li, C. Foo, X. Yi, W. Chen, P. Zhao, P. Gao, T. Yoskamtorn, Y. Xiao, S. Day, C. C. Tang, G. Hou, A. Zheng and S. C. E. Tsang, *J. Am. Chem. Soc.*, 2021, **143**, 8761–8771.
- 35 G. Li, T. Yoskamtorn, W. Chen, C. Foo, J. Zheng, C. Tang, S. Day, A. Zheng, M. M. J. Li and S. C. E. Tsang, *Angew. Chem., Int. Ed.*, 2022, **61**, e202204500.
- 36 G. Li, C. Foo, R. Fan, M. Zheng, Q. Wang, Y. Chu, J. Li, S. Day, P. Steadman, C. Tang, T. W. B. Lo, F. Deng and S. C. E. Tsang, *Science*, 2025, **387**, 388–393.
- 37 M. Wang, L. Zheng, G. Wang, J. Cui, G. L. Guan, Y.-T. Miao, J.-F. Wu, P. Gao, F. Yang, Y. Ling, X. Luo, Q. Zhang, G. Fu, K. Cheng and Y. Wang, *J. Am. Chem. Soc.*, 2024, **146**, 14528–14538.
- 38 D. Rivera-Barrera and J. C. Poveda-Jaramillo, *J. Solid State Chem.*, 2021, **294**, 121862.
- 39 Z. Zhang, J. Wu, Z. Feng, X. Xia, J. Wen, F. Wang, X. Ning, Y. Wen, X. Ke, H. Guan and L. Peng, *J. Phys. Chem. C*, 2024, **129**, 508–517.
- 40 S. Lu, H. Yang, Z. Zhou, L. Zhong, S. Li, P. Gao and Y. Sun, *Chin. J. Catal.*, 2021, **42**, 2038–2048.
- 41 R. Zou, C. Shen, K. Sun, X. Ma, Z. Li, M. Li and C.-J. Liu, *J. Energy Chem.*, 2024, **93**, 135–145.
- 42 C. Zhu, X. Wei, W. Li, Y. Pu, J. Sun, K. Tang, H. Wan, C. Ge, W. Zou and L. Dong, *ACS Sustain. Chem. Eng.*, 2020, **8**, 14397–14406.
- 43 Y. Fu, L. Zhang, B. Yue, X. Chen and H. He, *J. Phys. Chem. C*, 2018, **122**, 24094–24102.
- 44 C. Y. Regalado Vera, N. Manavi, Z. Zhou, L.-C. Wang, W. Diao, S. Karakalos, B. Liu, K. J. Stowers, M. Zhou, H. Luo and D. Ding, *Chem. Eng. J.*, 2021, **426**, 131767.
- 45 L. Liu, F. Cannizzaro, A. Kaychouhi, N. Kosinov and E. J. M. Hensen, *Chem. Eng. J.*, 2024, **494**, 153204.
- 46 A. R. Richard and M. Fan, *ACS Catal.*, 2017, **7**, 5679–5692.
- 47 L. Andrews and X. Wang, *Angew. Chem.*, 2004, **116**, 1738–1741.
- 48 Y. Dong, K. K. Ghuman, R. Popescu, P. N. Duchesne, W. Zhou, J. Y. Y. Loh, F. M. Ali, J. Jia, D. Wang, X. Mu, C. Kübel, L. Wang, L. He, M. Ghoussoub, Q. Wang, T. E. Wood, L. M. Reyes, P. Zhang, N. P. Kherani, C. V. Singh and G. A. Ozin, *Advanced Science*, 2018, **5**, 1700732.
- 49 E. L. Fornero, A. L. Bonivardi and M. A. Baltanás, *J. Catal.*, 2015, **330**, 302–310.
- 50 K. Li and J. G. Chen, *ACS Catal.*, 2019, **9**, 7840–7861.

