

Article

Micro-Structure Engineering in Pd-InO_x Catalysts and Mechanism Studies for CO₂ Hydrogenation to Methanol

Fengwang Zhao ^{1,†}, Gemeng Liang ^{2,†} , Xiaoli Yang ^{1,*}, Yang Lei ³ , Fayi Jin ¹, Leilei Xu ⁴, Chuanhui Zhang ¹ , Wei Jiang ¹, Haoxi Ben ^{1,*} and Xingyun Li ^{1,*} 

¹ State Key Laboratory of BioFibers and Eco-Textiles, Institute of Materials for Energy and Environment, College of Materials Science and Engineering, Qingdao University, Qingdao 266071, China; zhaofengwangedu@163.com (F.Z.)

² Hubei Key Laboratory of Coal Conversion and New Carbon Materials, School of Chemical Engineering & Advanced Materials, University of Adelaide, Adelaide, SA 5000, Australia

³ School of Chemistry and Chemical Engineering, Wuhan University of Science and Technology, Wuhan 430081, China

⁴ Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, Joint International Research Laboratory of Climate and Environment Change (ILCEC), Collaborative Innovation Centre of the Atmospheric Environment and Equipment Technology, School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, China

* Correspondence: xlyang@qdu.edu.cn (X.Y.); benhaoxi@qdu.edu.cn (H.B.); xingyun_2008@qdu.edu.cn (X.L.)

† These authors contribute equally to this manuscript.

Abstract: Significant interest has emerged for the application of Pd-In₂O₃ catalysts as high-performance catalysts for CO₂ hydrogenation to CH₃OH. However, precise active site control in these catalysts and understanding their reaction mechanisms remain major challenges. In this investigation, a series of Pd-InO_x catalysts were synthesized, revealing three distinct types of active sites: In-O, Pd-O(H)-In, and Pd₂In₃. Lower Pd loadings exhibited Pd-O(H)-In sites, while higher loadings resulted in Pd₂In₃ intermetallic compounds. These variations impacted catalytic performance, with Pd-O(H)-In catalysts showing heightened activity at lower temperatures due to the enhanced CO₂ adsorption and H₂ activation, and Pd₂In₃ catalysts performing better at elevated temperatures due to the further enhanced H₂ activation. In situ DRIFTS studies revealed an alteration in key intermediates from *HCOO over In-O bonds to *COOH over Pd-O(H)-In and Pd₂In₃ sites, leading to a shift in the main reaction pathway transition and product distribution. Our findings underscore the importance of active site engineering for optimizing catalytic performance and offer valuable insights for the rational design of efficient CO₂ conversion catalysts.

Keywords: carbon dioxide; indium oxide; defect engineering; intermetallic compounds



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1. Introduction

The hydrogenation of carbon dioxide (CO₂) to methanol (CH₃OH) represents a crucial catalytic process, pivotal in addressing environmental concerns and fostering sustainable chemical production. This process provides a viable solution for utilizing CO₂, a significant greenhouse gas [1], while also contributing to the production of CH₃OH, a versatile chemical feedstock with a wide range of industrial applications [2,3]. However, this process presents formidable challenges, considering the ultra-stable C=O bond in CO₂ [4–6]. Meanwhile, the reverse water–gas shift reaction (RWGS), wherein CO₂ reacts with hydrogen for producing water, redirects the reaction towards the undesired production of carbon monoxide (CO) rather than CH₃OH.

To address the above issue, indium oxide (In₂O₃) based catalysts have recently garnered widespread attention due to their exceptional productivity for CH₃OH [7]. Nonetheless, pure In₂O₃ exhibits insufficient adsorption capacity for reaction gases, leading to suboptimal reaction efficiency [2]. Additionally, the instability of the In₂O₃ structure results

in a rapid deactivation of catalysts. Consequently, numerous researchers have explored surface modifications of In_2O_3 to enhance its activity and stability by altering its active sites. For instance, Liu et al. demonstrated the introduction of new active sites through nitrogen doping, resulting in a great enhancement of reaction activity and catalytic stability of In_2O_3 [8]. Recent discoveries have revealed that the interface sites between Pd and In_2O_3 catalysts are more active for the activation of H_2 [9]. Ge et al. reported the notable improvement for CO_2 hydrogenation to CH_3OH by coupling highly dispersed Pd nanoparticles with In_2O_3 , delivering a methanol productivity of $0.89 \text{ g}_{\text{MeOH}} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$ [10]. However, it is noteworthy that various catalytic sites may co-exist in addition to the Pd- In_2O_3 interfaces in the Pd/ In_2O_3 system. For example, metal Pd might tend to form large particles, exacerbating the competitive RWGS reaction, and leading to the increase in CO byproduct [11].

Meanwhile, Pd can also form alloys with other metals, resulting in the tailored active site for CO_2 hydrogenation reactions. Bowker et al. reported that ZnO-supported Pd-Zn alloys with optimized particle size and surface structure demonstrated a high performance to activate CO_2 with CO_2 conversion of 11% and methanol selectivity of 60%, at conditions of 250°C and 20 bar [12]. Song et al. used SiO_2 as support for Pd-Cu alloy particles. With the optimization of Pd/(Pd + Cu) atomic ratios, it was found that Pd(0.34)-Cu/ SiO_2 was most active with CH_3OH yield of $0.31 \mu\text{mol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{s}^{-1}$ [13]. Additionally, Pd-In alloy may be simultaneously created, which may also shine for CO_2 hydrogenation to CH_3OH [14]. These complex multi-structures might complicate the reaction route, incubating different intermediates, which makes it difficult to achieve a clear understanding of the reaction mechanism [15–17]. Thus, engineering specific active sites and exploring the structure–function relationship is crucial, albeit challenging for the development of advanced Pd/ In_2O_3 catalyst [14,18].

In this study, Pd- InO_x catalysts with tailor-orchestrated structures were precisely designed and synthesized. The cryogenic activity has great advantages over existing work. Combined (in situ) characterizations were systematically conducted to shed light on the reaction intermediates and reaction pathways. These findings provide valuable insights into the catalytic mechanism of InO_x -based catalysts, offering guidance for the rational design and development of catalysts for CO_2 hydrogenation to CH_3OH .

2. Results and Discussion

2.1. Structure Characterization of Pd- InO_x

The synthesis of InO_x with varying Pd contents was achieved using a two-step method. Analysis by ICP-AES revealed the actual Pd content in 0.4Pd- InO_x and 1.2Pd- InO_x are 0.40 wt.% and 1.28 wt.%, respectively (Table S1), consistent with the theoretical values. N_2 adsorption–desorption isotherms in Figure 1a indicate that the specific surface area of all samples is below $11 \text{ m}^2 \cdot \text{g}^{-1}$, as summarized in Table S1. XRD analysis depicted the presence of the h- In_2O_3 phase (JCPDS 04-005-4422) in all InO_x and Pd- InO_x samples before calcination (Figure 1b). Upon subsequent calcination and reduction of these samples, a coexistence of h- In_2O_3 and c- In_2O_3 phases (JCPDS 97-001-4388) was observed over pure InO_x and 0.4Pd- InO_x samples, indicating a crystal transition of In_2O_3 (Figure 1c) while only the h- In_2O_3 phase was observed in 1.2Pd- InO_x . Moreover, no diffraction peaks associated with Pd were discernible in the 0.4Pd- InO_x sample, indicating highly dispersed Pd on the InO_x substrate [19]. In contrast, diffraction peaks corresponding to the Pd_2In_3 intermetallic compound were evident (JCPDS 97-064-0231) in the 1.2Pd- InO_x sample. The interaction between Pd and In in Pd_2In_3 might prevent the crystal transition of h- In_2O_3 into the c- In_2O_3 phase [20,21].

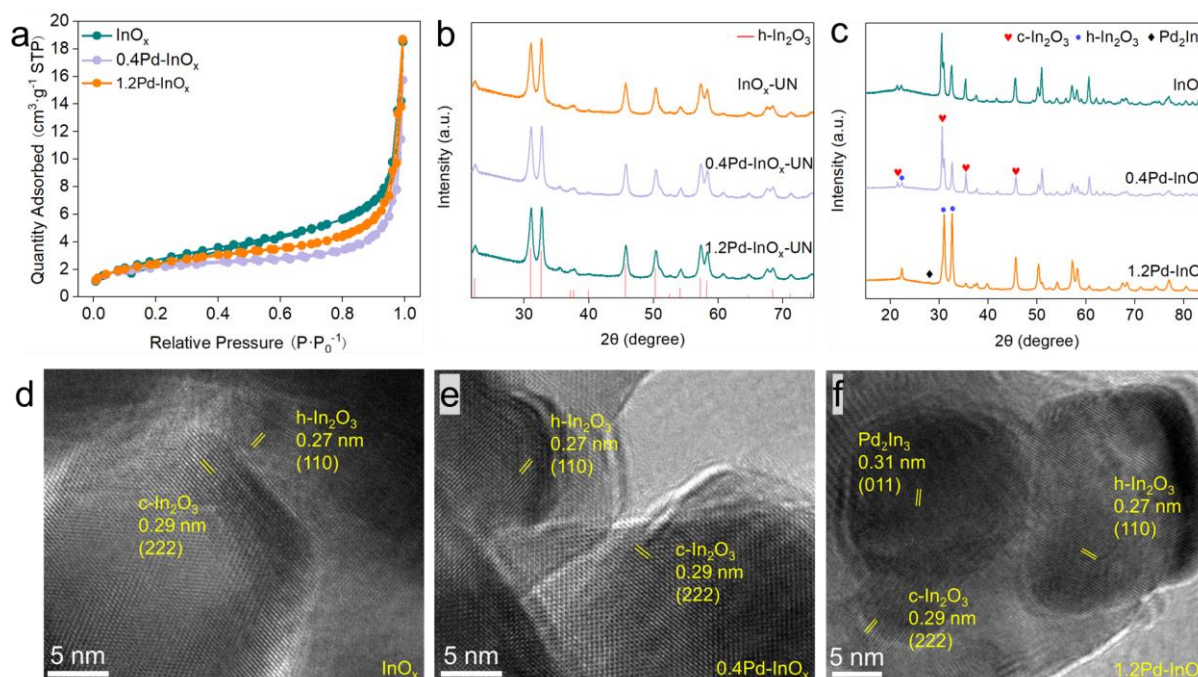


Figure 1. (a) N₂ adsorption–desorption isotherms, XRD patterns of different samples before (b) and after (c) calcination and reduction. HR-TEM images of (d) InO_x, (e) 0.4Pd-InO_x and (f) 1.2Pd-InO_x.

SEM images revealed a bulky shape for the catalysts, while EDS mapping demonstrated the uniform distribution of In, O and Pd atoms in all xPd-InO_x samples (Figures S1 and S2). We further investigated the elemental distribution in the material using STEM-EDX. The distribution of elements in InO_x (Figure S3) and 0.4Pd-InO_x (Figure S4) is uniform, with no large aggregates observed, which confirms the evenly dispersed state of Pd in 0.4Pd-InO_x, while for the sample of 1.2Pd-InO_x, distinct Pd heterogeneous particles are observed (Figure S5). Combined with the XRD results, it can be inferred that Pd₂In₃ is formed for the sample of 1.2Pd-InO_x. (HR-TEM) analysis revealed inter-planar distances of 0.27 nm and 0.29 nm over InO_x (Figure 1d) and 0.4Pd-InO_x (Figure 1e), corresponding to the (110) facet of h-In₂O₃ and (222) facet of c-In₂O₃, respectively. These characterizations underscore that InO_x and 0.4Pd-InO_x constitute a homogeneous structure composed of c-In₂O₃ and h-In₂O₃. Additionally, a distinct inter-planar distance of 0.31 nm was observed in 1.2Pd-InO_x, corresponding to the (011) crystal plane of Pd₂In₃ (Figure 1f). It suggests that higher loading of Pd leads to some Pd interacting with In to form Pd₂In₃ intermetallic compounds. The SAED pattern of Pd-InO_x is shown in Figure S6, consisting of polycrystalline diffraction rings. From the innermost to the outermost ring, they are indexed as (011), (−130) of Pd₂In₃, respectively. The SAED values are in good agreement with XRD results, further confirming the presence of Pd₂In₃ in 1.2Pd-InO_x.

2.2. The Structure–Function Relationship

To further investigate the structural states of these catalysts, H₂-TPR experiments were conducted on the fresh catalysts. From Figure 2a, peaks at 200–300 °C (as indicated by the red heart) is observed in the curves of all catalysts contributed to the formation of oxygen vacancy on the In₂O₃ surface, resulting in the reduced state of InO_x. Further, compared to InO_x, the area of this peak becomes stronger over 0.4Pd-InO_x and 1.2Pd-InO_x. It suggests the promoted surface reduction of InO_x facilitated by the interaction with Pd [22]. Additionally, a new peak at higher temperatures (300–400 °C) over 1.2Pd-InO_x is formed. It may be attributed to the presence of Pd₂In₃ intermetallic compounds [23,24], which also suggested that the Pd₂In₃ intermetallic compounds significantly benefit the activation of hydrogen.

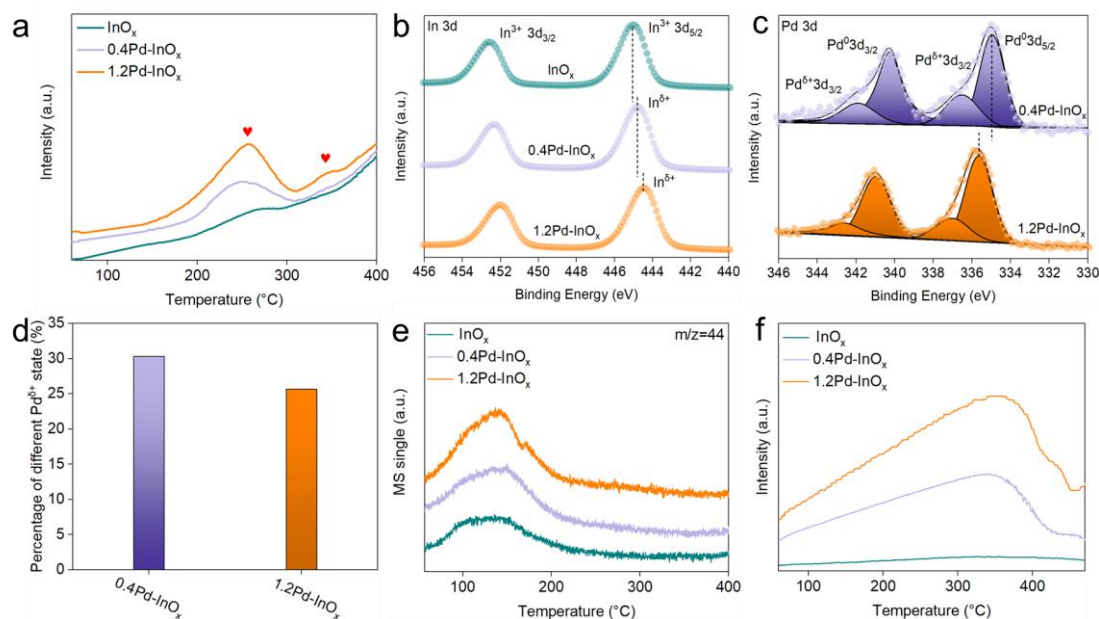


Figure 2. (a) H₂-TPR. The heart symbol represents the peak center. (b) Deconvolution of Pd 3d XPS spectra and (c) In 3d XPS spectra. (d) Percentage of different Pd^{δ+} states. (e) CO₂-TPD and (f) H₂-TPD of different samples.

XPS analysis was carried out to characterize the surface chemical information of the catalysts after reduction. The full XPS spectrum proved clearly the presence of In, O, and Pd as displayed in Figure S7. The In 3d spectra exhibit binding energies consistent with In³⁺ over InO_x (Figure 2b) [25,26], while Pd 3d signals could be deconvoluted into four peaks corresponding to Pd^{δ+} and metallic Pd⁰ (Figure 2c) [27,28]. Notably, compared to pure In₂O₃, a slight shift towards lower binding energy for In 3d XPS peak was observed for 0.4Pd/InO_x, indicating a reduced valence state [29]. Previous studies have indicated that the incorporation of Pd in oxides may result in the formation of Pd-O(H)-M bonds [30], while the presence of Pd^{δ+} species in the Pd 3d XPS spectra (Figure 2c) may offer evidence for the existence of Pd-O(H)-In structures for Pd/InO_x [31]. It is interesting to find the relative content of Pd^{δ+} decreased as the content of Pd increased to 1.2 wt.% (Figure 2d); however, the 3d_{5/2} of In further shifted to a lower binding energy (444.4 eV). This suggests the formation of another chemical bond over 1.2Pd/InO_x, possibly attributed to the formation of Pd₂In₃ intermetallic compound on the surface [18,32]. Thus, Pd species tend to form highly dispersed Pd-O(H)-In sites on the sample surface at a low Pd loading, while partly forming Pd₂In₃ sites at high Pd loading, resulting in a surface where Pd-O(H)-In and Pd₂In₃ synergistically co-existence. Moreover, the presence of these active sites may alter the adsorption properties and reaction pathway, influencing the catalytic performance of CO₂ hydrogenation. Further detailed investigations are required to elucidate these effects.

CO₂-TPD analysis reveals a low-temperature desorption peak for all catalysts, with the desorption temperature remaining unchanged but the peak area slightly increasing with more Pd loadings (Figure 2e) [33]. This phenomenon indicates similar adsorption strength but a slightly enhanced adsorption capacity for Pd/InO_x [34,35], which may be due to the beneficial effect of Pd-O(H)-In and Pd₂In₃ for the CO₂ adsorption. It can be observed that after the formation of Pd₂In₃, an overlapping CO₂ desorption peak appears at 171 °C, which may be attributed to the change in the CO₂ desorption pattern caused by the formation of Pd₂In₃ [36]. The H₂-TPD analysis could demonstrate the catalyst's capability for dissociating and activating H₂. On pure InO_x, there is virtually no desorption peak, indicating a weak adsorption and activation capacity for H₂ on the pure In-O bonds. As the Pd loading increases, the desorption peak area for xPd-InO_x enhances at elevated temperatures (300–400 °C), as depicted in Figure 2f. In comparison, the peak area for 1.2Pd-InO_x is greater than that for 0.4Pd-InO_x. Considering the formation of Pd-O(H)-In

and Pd_2In_3 active sites within the Pd-InO_x catalyst, this finding may corroborate that the Pd-O(H)-In site plays a more significant role in facilitating H_2 activation at lower temperature [9], whereas Pd_2In_3 is more favorable for H_2 activation at higher temperatures [14]. This is in agreement with the H_2 -TPR results. It is to be mentioned that a minor desorption peak observed at approximately 436°C for 1.2Pd-InO_x may be ascribed to the spillover of H_2 from Pd_2In_3 to the support [37].

2.3. Catalytic Performance for CO_2 Hydrogenation

Under reaction conditions of 5 MPa and a gas hourly space velocity (GHSV) of $3000\text{ mL}\cdot\text{gcat}^{-1}\cdot\text{h}^{-1}$, CO_2 hydrogenation experiments were conducted. As shown in Figures 3a and S8, the catalytic performance varies significantly among these three catalysts. At 200°C , the CO_2 conversion rate of InO_x is only 1.28%. In contrast, for 0.4Pd-InO_x and 1.2Pd-InO_x , the CO_2 conversion rates at 200°C are 3.66% and 4.04%, respectively. It implies the promoted role of Pd-O(H)-In sites and Pd_2In_3 sites in CO_2 conversion. Interestingly, the change in the CO_2 conversion rate with the increase in reaction temperature differed obviously for these catalysts. For InO_x , the CO_2 conversion rate improved from 1.28% at 200°C to 4.20% at 300°C , while 0.4Pd-InO_x demonstrates a slight CO_2 conversion rate increase to 4.56% at 300°C . Prominently, for 1.2Pd-InO_x , its CO_2 conversion rate increased notably at elevated temperatures, reaching 6.69% at 300°C . These differences are attributed to the varied active sites over these catalysts [5,33].

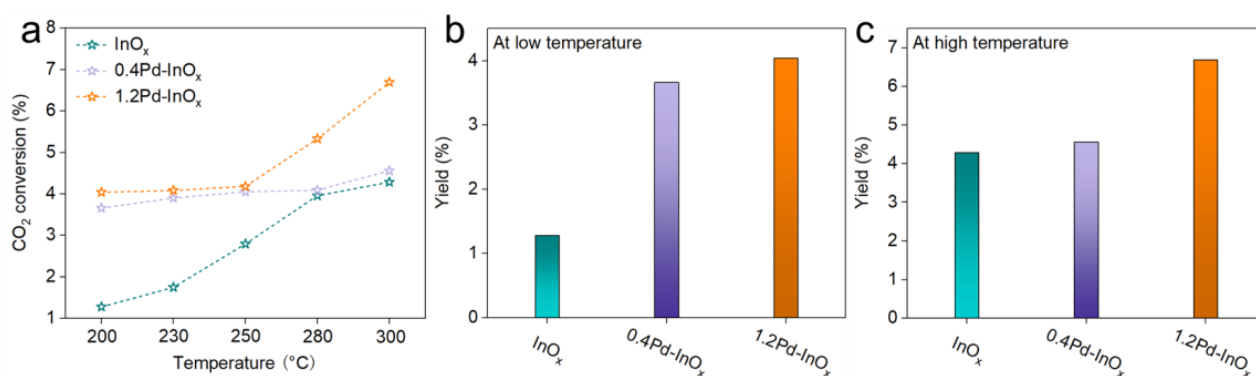


Figure 3. (a) CO_2 conversion. Methanol yield of different samples at (b) 200°C and (c) 300°C . Reaction condition: 5 MPa, $\text{CO}_2/\text{H}_2 = 1/3$, and $3000\text{ mL}\cdot\text{gcat}^{-1}\cdot\text{h}^{-1}$.

To obtain a more comprehensive understanding of the reaction trend, the yields of CH_3OH were calculated. According to the curves, the yield change was divided into the low-temperature region ($200\text{--}250^\circ\text{C}$) and the high-temperature region ($250\text{--}300^\circ\text{C}$). The InO_x catalyst, with limited activation capability for H_2 , yields less than 2% in the lower-temperature region (Figure 3b). With the increase in Pd loading, the yields increase to over 3% for 0.4Pd-InO_x and 1.2Pd-InO_x catalysts. This might be attributed to the enhanced CO_2 and H_2 adsorption capability, especially for the H_2 adsorption capability at lower temperatures due to the formation of Pd-O(H)-In sites. However, in the higher-temperature region, the yield of 1.2Pd-InO_x reached over 6%, much higher than the yields of InO_x (4.25%) and 0.4Pd-InO_x (4.28%) (Figure 3c). The more favorable reaction of 1.2Pd-InO_x at high temperatures may be due to the formation of Pd_2In_3 which greatly enhances its ability to adsorb and dissociate H_2 at high temperatures. These phenomena illustrate that the varied active sites might play different roles in the reaction intermediates and pathways, which will be further discussed. We provide a comparison of the performance of Pd-based catalysts in Table S2.

2.4. Reaction Mechanisms

The activation pathways for CO_2 and H_2 to produce CH_3OH were well established by the previous reports [38]. Initially, CO_2 adsorbs onto the sample surface, forming $^*\text{CO}_2$,

which then reacts with lattice oxygen (O_{lattice}) or dissociated hydrogen (*H) to produce either $^*CO_3^{2-}$ or $^*HCO_3^-$. Subsequently, CH_3OH is generated through two possible pathways. The first pathway involves the formation of *CO intermediate, generated via the RWGS routes involving carboxyl (*COOH) species. This intermediate is then hydrogenated to produce CH_3OH . The second pathway entails the formation of formate (*HCOO) intermediates through the hydrogenation of CO_2 , ultimately leading to the production of CH_3OH through C-O bond cleavage and *HCO or *H_2CO intermediates (referred to as the formate pathway).

To elucidate the effect of varied active sites on intermediate evolution, in situ DRIFTS studies were conducted on InO_x (Figure 4a), $0.4Pd-InO_x$ (Figure 4b), and $1.2Pd-InO_x$ (Figure 4c). $^*CO_3^{2-}$ at 1456 and 1520 cm^{-1} and $^*HCO_3^-$ at 1650 cm^{-1} are observed on InO_x [39,40]. Subsequently, formate at 1559 and 1683 cm^{-1} , as well as *COOH at 1540 and 1637 cm^{-1} , are detected with time on stream [31,38], along with a small amount of *CO at 2077 cm^{-1} [8,41]. In comparison to InO_x , the initial area of CO_3^{2-} and HCO_3^- is significantly higher for $0.4Pd-InO_x$ and $1.2Pd-InO_x$, which may be due to the enhancement of CO_2 adsorption caused by the presence of $Pd-O(H)-In$ sites. Furthermore, a new peak corresponding to the adsorption of *COOH at the interface appears at 1758 cm^{-1} , and the proportion of *CO and *COOH intermediates increases, as shown in Figure 5a and Table S3. This suggests that the appearance of $Pd-O(H)-In$ sites alters the main reaction pathway transition, initiating the conversion of the key intermediate in CH_3OH synthesis from *HCOO to *COOH and *CO [15,29]. This likely occurs because the formation of $Pd-O(H)-In$ modulates the catalyst's activation capability concerning *H [42]. H_2 undergoes rapid activation at $Pd-O(H)-In$ sites, subsequently converting to *COOH intermediates on the surface [43]. For $1.2Pd-InO_x$ that contained Pd_2In_3 sites, the peak intensity of $^*HCO_3^-$ initially increases and then decreases. It indicates that the modulation of H_2 adsorption and dissociation capability by Pd_2In_3 renders the catalyst more favorable for the transition from $^*HCO_3^-$ to other intermediates (Figure 5b).

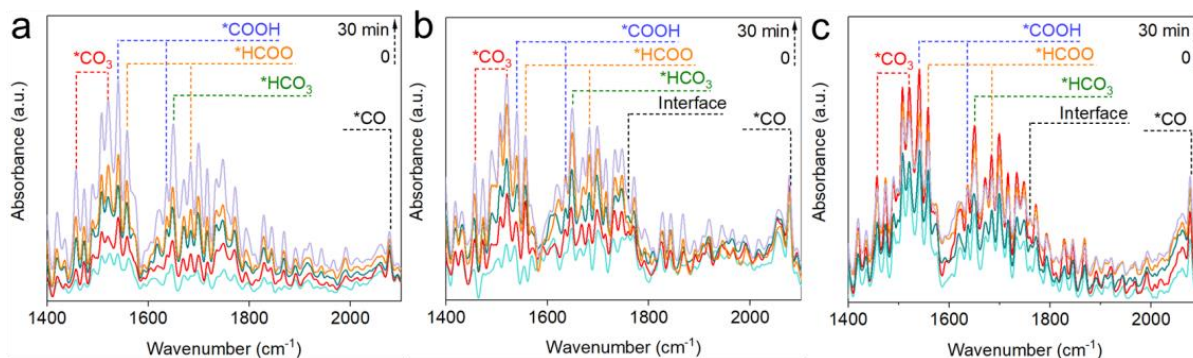


Figure 4. (a) In situ DRIFT spectra of InO_x , (b) $0.4Pd-InO_x$, and (c) $1.2Pd-InO_x$. Reaction conditions: $200\text{ }^{\circ}C$, $CO_2/H_2 = 1/3$, $10\text{ mL}\cdot\text{min}^{-1}$, and 0.1 MPa .

Based on the phenomenon, distinct active sites might induce different reaction pathways, as summarized in Figure 6 [24]. On the InO_x surface, CO_2 and H_2 were activated on $In-O$, generating small amounts of $^*CO_3^{2-}$ and $^*HCO_3^-$, which are then hydrogenated to form *HCOO , leading to CH_3OH production primarily through the formate pathway [2,44]. With the formation of $Pd-O(H)-In$ interfacial sites on $0.4Pd-InO_x$, the initial peak area of $^*HCO_3^-$ and $^*CO_3^{2-}$ increases. Subsequently, a larger number of *COOH and *CO intermediates are formed as H_2 is more readily activated over $Pd-O(H)-In$ sites, leading to CH_3OH synthesis through the reverse water-gas pathway [45]. After the formation of Pd_2In_3 sites over $1.2Pd-InO_x$, H_2 becomes more accessible to be activated compared to when only $Pd-O(H)-In$ sites are present [42]. It could be further observed that the content of $^*HCO_3^-$ intermediates shows a trend of initially increasing and then decreasing, which aids in the continued conversion of $^*HCO_3^-$ to *COOH and *CO , further hydrogenating to produce CH_3OH .

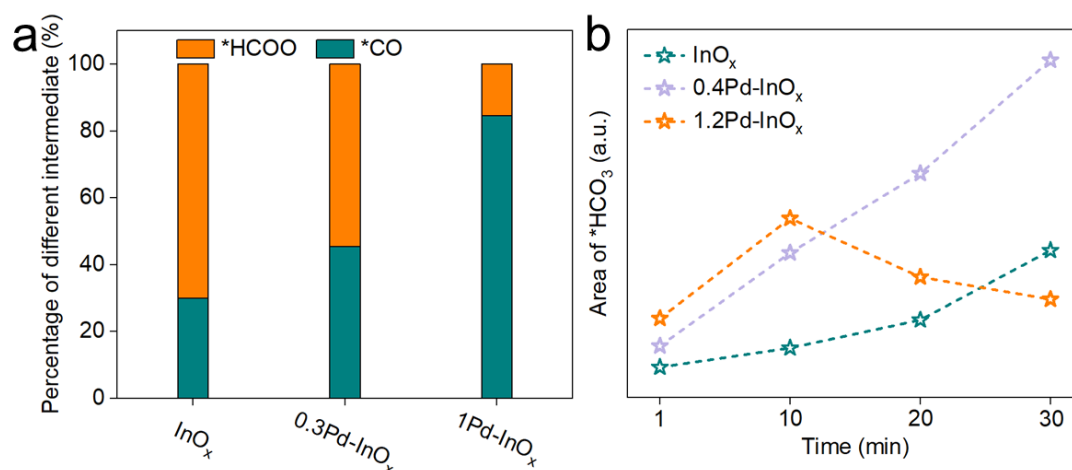


Figure 5. (a) Percentage of different intermediates over the xPd/InO_x catalysts calculated by in situ DRIFT. (b) The trend of in situ DRIFT peak area changes for *HCO₃[−].

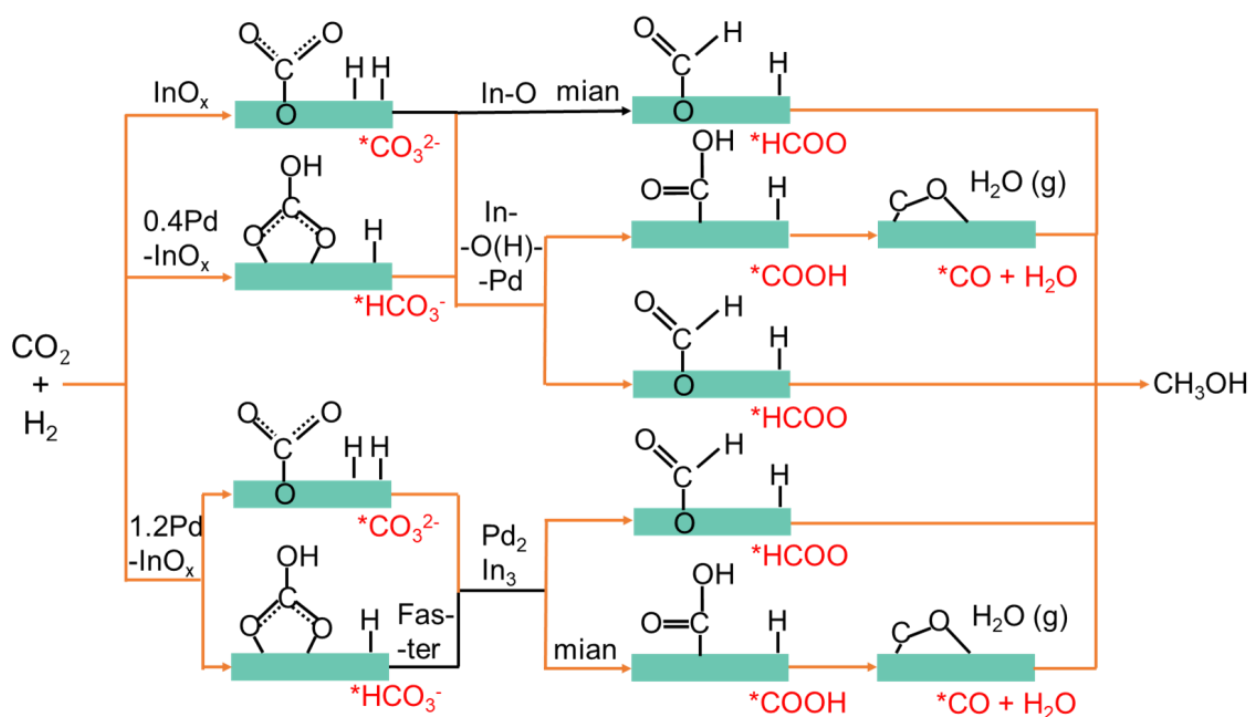


Figure 6. Possible reaction pathways corresponding to different active sites.

3. Experimental Section

3.1. Preparation of InO_x Catalysts

Firstly, 2.0 g of indium nitrate (99.99%, Macklin, Shanghai, China) was dissolved in a solution comprising 30 mL deionized (DI) water and 60 mL ethanol (AR, Sinopharm, Shanghai, China). Subsequently, 0.1 mL of nitric acid (AR, Sinopharm, Shanghai, China) was added. After complete dissolution, the obtained homogeneous solution was transferred into a Teflon-lined autoclave with a capacity of 200 mL and placed in an oven at 150 °C for 12 h. Upon naturally cooling down to room temperature, the resulting product was collected by centrifugation, washed with plenty of DI water and ethanol, and then dried at 60 °C overnight to obtain the InO_x-UN. The InO_x-UN was calcinated at 450 °C for 3 h in air to obtain the InO_x. Before characterizations and the catalytic applications, InO_x was reduced by H₂ at 380 °C for 120 min, except for H₂-TPR.

3.2. Preparation of Pd-InO_x Catalysts

The Pd-InO_x samples were synthesized using the impregnation method. The palladium nitrate solution (Pd 18.09 wt.% in nitric acid, Macklin, Shanghai, China) was diluted with DI water to a concentration of 5.04 g·L⁻¹, designated as solution A. Subsequently, 0.8 g of InO_x-UN (the precursor before reduction and roasting) was dispersed in 100 mL of ethanol under stirring, followed by the addition of 0.48 mL of solution A, which was stirred to dry at 70 °C. The resulting product was further dried overnight at 60 °C to obtain the 0.4Pd-InO_x-UN. The samples were calcinated at 450 °C for 3 h in air, denoted as 0.4Pd-InO_x (the number represented the weight percentage of Pd). 1.2Pd-InO_x was also prepared with a similar procedure to that of 0.4 Pd-InO_x but adding 1.60 mL of palladium nitrate solution. Before characterizations and the catalytic applications, the catalysts were reduced by H₂ at 380 °C for 120 min, except for H₂-TPR.

3.3. Catalyst Characterizations

The Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurements were carried out on an Avio 200 instrument (Thermo Electron Corporation, Massachusetts, USA). N₂ adsorption-desorption isotherms were measured on a Micromeritics ASAP 2460 (Micromeritics, Shanghai, China) at -196 °C. All the samples were outgassed at 150 °C overnight before the measurement. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method. Scanning and transmission analytical electron microscopy (STEM-EDX) was performed using the FEI Talos F200X (FEI, Hillsboro, UAS). High-resolution transmission electron microscopy (HR-TEM) and selected area electron diffraction (SAED) was performed using the JEM 2100F (JEOL, Japan). X-ray diffraction (XRD) patterns were collected on a Japanese Science Ultima IV (Rigaku Corporation, Japan) diffractometer equipped with a Cu K α radiation source, operated at 40 kV and 40 mA. The data were collected at a scan speed of 5°·min⁻¹ in the 2 θ range of 15–85°.

X-ray photoelectron spectroscopy (XPS) experiments were carried out on a Thermo Scientific ESCALAB Xi+ XPS instrument (Thermo, Massachusetts, USA). Spectra of In 3d, C 1s, and Pd 3d were obtained, which were calibrated with the C 1s peak at 284.8 eV. To avoid the influence of air for the XPS test, the sample was protected by Ar gas first and then was vacuum packaged before transferring to the chamber of the XPS equipment. Hydrogen temperature-programmed reduction (H₂-TPR) was performed on a ChemBET Pulsar (Quantachrome, Florida, USA). Typically, 50 mg of sample was placed in a U-pipe and purged with an argon flow (30 mL·min⁻¹) at 260 °C for 60 min. The temperature was then decreased to 50 °C. Meanwhile, the gas flow was switched to a 10% H₂/Ar mixture (30 mL·min⁻¹) and the temperature was increased from 50 to 400 °C at a rate of 10 °C·min⁻¹. The effluent gas was monitored in real time via a thermal conductivity detector (TCD). CO₂ temperature-programmed desorption (CO₂-TPD-MS) was performed on a lab-made reactor, and the outlet gases were analyzed by mass spectrum (HPR-20 EGA, HIDEN, Warrington, UK). In particular, the catalysts were flushed with He gas flow (30 mL·min⁻¹) at room temperature for 30 min. Next, the catalysts were saturated with 10% CO₂/He (30 mL·min⁻¹) at room temperature for 30 min, followed by purging with He flow (30 mL·min⁻¹) for 30 min. Then, the CO₂-TPD experiment was measured from room temperature to 400 °C with a ramping rate of 10 °C·min⁻¹ under He gas flow (30 mL·min⁻¹). H₂ temperature-programmed desorption (H₂-TPD) was also performed on a ChemBET Pulsar (Quantachrome, FL, USA). The catalysts were flushed with He gas flow (30 mL·min⁻¹) at room temperature for 30 min. Next, the catalysts were saturated with 10% H₂/He (30 mL·min⁻¹) at room temperature for 30 min, followed by purging with He flow (30 mL·min⁻¹) for 30 min. Then, the H₂-TPD experiment was measured from room temperature to 450 °C with a ramping rate of 10 °C·min⁻¹ under He gas flow (30 mL·min⁻¹).

In situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) spectra were collected using a Thermo IS10 FTIR (Massachusetts, USA) spectrometer with a mercury cadmium telluride (MCT) detector cooled with liquid nitrogen. The CO₂ and H₂

treatment on the xPd-InO_x catalyst was investigated at 200 °C. Before the measurement, 30 mg of the sample was pretreated at 380 °C for 30 min under 10% H₂/Ar mixed gas. Then, the gas was changed to Ar for 30 min. After background acquisition, the reaction gas with H₂/CO₂/Ar = 69/23/8 was introduced into the chamber. All DRIFTS results were analyzed by using OPUS software (OMMIC 9.2).

3.4. Catalytic Performance Evaluation

The catalytic performance of CO₂ hydrogenation was evaluated using a vertical fixed-bed reactor. Before the reaction, the catalyst was in situ reduced by H₂ (99.999%) at 380 °C for 120 min. After cooling to room temperature, the feed reactants (H₂/CO₂/Ar = 69/23/8) were introduced at a weight hourly velocity (WHSV) of 3000 mL·gcat^{−1}·h^{−1} under 5 MPa with the reaction temperature ranging from 200 to 300 °C. Effluent analysis was performed by an online gas chromatograph (Agilent 8890, Beijing, China) equipped with a flame-ionized detector (FID) and a thermal conductivity detector (TCD). To prevent CH₃OH condensation, all lines and valves post the reactor were maintained at 170 °C.

4. Conclusions

In this study, the investigation focused on Pd-containing InO_x catalysts for CO₂ hydrogenation, aiming to uncover the structure–function relationships. A comprehensive suite of characterization techniques revealed distinct structural disparities among the catalysts. Lower Pd loadings exhibited Pd-O(H)-In sites, while higher loadings resulted in Pd₂In₃ intermetallic compounds. Catalysts with Pd-O(H)-In sites exhibit heightened activity at lower temperatures, attributed to enhanced CO₂ adsorption and H₂ activation capabilities. Conversely, catalysts featuring Pd₂In₃ showed enhanced performance at elevated temperatures, facilitated by the strengthened H₂ activation. In situ DRIFTS studies revealed a shift in the main reaction pathway, altering key intermediates from *HCOO over In-O bonds to *COOH over Pd-O(H)-In and Pd₂In₃ sites. Moreover, Pd₂In₃ significantly enhanced the conversion capability of *HCO₃[−]. The alteration led to a change in product distribution. These findings contribute to the understanding of InO_x-based catalysts and offer insights into the design of catalysts for CO₂ hydrogenation to CH₃OH.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules29163715/s1>, Figure S1: SEM image and EDS elemental mapping of InO_x; Figure S2: SEM images and EDS elemental mapping of (a) 0.4Pd-InO_x and (b) 1.2Pd-InO_x; Figure S3: STEM-EDX image of InO_x; Figure S4: STEM-EDX image of 0.4Pd-InO_x; Figure S5: STEM-EDX image of 1.2Pd-InO_x; Figure S6: SAED patterns showing polycrystalline diffraction rings acquired of 1.2Pd-InO_x; Figure S7: XPS full spectrum of different samples; Figure S8: CH₃OH selectivity versus temperature. Reaction condition: 5 MPa, CO₂/H₂ = 1/3, 3000 mL·gcat^{−1}·h^{−1}; Table S1: Composition and porous properties of the samples with different Pd contents; Table S2: Comparison of catalytic performance between Pd-InO_x and other representative catalysts; Table S3: The assignment of in-situ DRIFT peaks. references [10,12,13,17,46–50] are cited in the Supplementary Materials.

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