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Strong Electronic Oxide–Support Interaction over In_2O_3/ZrO_2 for Highly Selective CO₂ Hydrogenation to Methanol

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 In_2O_3/m - ZrO_2 is much higher than that of In_2O_3/t - ZrO_2 (t-: tetragonal), which is due to the high dispersion of the In-O-In structure over m- ZrO_2 as determined by *in situ* Raman spectra. The electron transfer from m- ZrO_2 to In_2O_3 is confirmed by XPS and DFT calculations and improves the electron density of In_2O_3 , which promotes H_2 dissociation and hydrogenation of formate intermediates to methanol. The concept of the electronic interaction between an oxide and a support provides guidelines to develop hydrogenation catalysts.

INTRODUCTION

CO₂ hydrogenation is an approach to produce clean fuels and valuable chemicals from a gas mixture of CO₂ and H₂, which can reduce the use of fossil fuels and control greenhouse gas emissions. In particular, the methanol synthesis by CO₂ hydrogenation is attractive because of its potential as a highenergy-density fuel.¹ Oxide-supported metal catalysts (Cu/ $ZnO/Al_2O_3^2$ and Pd/ZnO³) and oxide catalysts ($In_2O_3^2$) Ga_2O_3 ⁵ ZnCr₂O₄⁶ and ZnO-ZrO₂⁷) have been widely applied in methanol synthesis and extensively studied for decades. Generally, oxide catalysts are expected to be superior to metal catalysts due to their higher selectivity to methanol, durability, and stability, especially in a wide temperature range (300-600 °C). However, the activation of H₂ is difficult, and CO₂ conversion is low for oxide catalysts.⁸ The major challenge of improving CO2 conversion for oxide catalysts lies in understanding the correlation between the complex oxide structure and methanol synthesis activity.

methanol selectivity up to 84.6% with a CO₂ conversion of 12.1%. Moreover, at a wide range of temperatures, the methanol yield of

Improved catalytic performance for oxide-based catalysts can be achieved by the efforts of (i) promoters and (ii) proper supports.^{9–11} Recently, more attention has been focused on tuning the local environment of an active oxide.¹² For supported metal nanoparticle (NP) catalysts, the metal– support interaction plays an important role and has been investigated in numerous processes, for example, the electronic modulation effect,¹³ excellent metal dispersion,¹⁴ and the encapsulation process.¹⁵ For exothermic chemical reactions, hot electrons are generated via the surface electron excitation and turn into low-energy electrons within the length scale of the electron mean free path (electron transfer), which can change the charge state of the surface adsorbate, activate reaction intermediates, and mediate the activity or selectivity of heterogeneous catalysts involving both ionic and covalent pathways.¹⁶ However, little is known about this electronic interaction between an oxide catalyst and oxide support.

Metal cations of the oxide catalyst can bind strongly to an oxide support at the interface, forming binary oxide nanostructures.¹⁷ When investigating the oxide–oxide interfaces at the atomic scale, the metal–O–metal bonding is a crucial structural unit.¹⁸ In heterogeneous catalysis, different metal–O–metal bonding can provide different chemical environments, such as different valence, defect, and coordination statuses for these active centers, leading to unique catalytic properties.^{19,20} Therefore, finding two adaptive oxide compounds with catalytically active metal–O–metal bonding is a potentially effective solution to enhance the catalytic performance of oxide–oxide systems.

Received: July 4, 2020



A supported indium oxide (In_2O_3) catalyst is a promising model system for methanol synthesis to investigate the surface structure. Perez-Ramirez et al. claimed that supported In2O3 with abundant oxygen vacancies (V_0) shows higher indium-specific activity.^{4,21} V_0 on In₂O₃ can be modulated and increased by CO treatment and interaction with a latticemismatching zirconia carrier, which regulates the CO₂ adsorption and is proposed as an active site for this reaction. Muller and co-workers proposed In_2O_{3-x} is the active phase, while the formation of In⁰ leads to catalyst deactivation.¹ Nonetheless, the interface of binary oxides and the electronic effect of a support during CO₂ hydrogenation are still unclear at the molecular level. Up to now, the application of this catalyst is still in the bottleneck, due to the lack of knowledge on both hydrogenation reaction mechanisms and the fundamental understanding of the relationship between oxide structure and catalytic activity.

In this work, In_2O_3 supported on zirconium oxide (ZrO₂) with different crystalline phases (both m-: monoclinic and t-: tetragonal phases) was prepared by Li doping into ZrO₂. The results show that the methanol selectivity and yield are strongly related to the ZrO₂ crystalline phase. The binary oxide, In₂O₃ supported on an m-ZrO₂ catalyst, exhibited maximized methanol selectivity at high CO₂ single-pass conversion, which achieved a dramatic enhancement in methanol yield in comparison with In2O3/t-ZrO2. Herein, the experimental observation shows the electron transfer from m-ZrO₂ to In_2O_3 due to the oxide-support interaction. The In_2O_3 structure and key intermediates during CO₂ hydrogenation were identified. In addition, the kinetic experiments confirmed that the electron transfer between In_2O_3 and m-ZrO₂ could promote the hydrogenation process and account for the excellent performance in methanol synthesis.

EXPERIMENTAL SECTION

Catalyst Preparation. The monoclinic and tetragonal ZrO₂ were synthesized by a coprecipitation method. First, the hydroxides were precipitated by a dissolving solution of ZrOCl₂·xH₂O (Acros Organics, 99.5%) and LiNO₃ (Acros Organics, 99.5%) (molar ratio of Li/Zr = 5:95) in a mixture of deionized water and ethanol (Sigma-Aldrich, 99.8%), followed by the addition of NH₄OH (Sigma-Aldrich, 25 wt % in H_2O) until the pH reached 9. The resulting solids were dried at 60 $^\circ C$ for 12 h prior to calcination in static air at 350 $^\circ C$ (5 °C·min⁻¹) for 3 h. Other Li-doping ZrO₂ catalysts were prepared by the same procedure with a molar ratio of Li/Zr = 0.100, 20:80, and 40:60, respectively. In₂O₃ was supported on ZrO₂ and Li-ZrO₂, nominally 8 wt % In by isovolumic impregnation. For the isovolumic impregnation, In(NO₃)₃:xH₂O was first dissolved in deionized water. The solution was subsequently added drop by drop to the support, and the resulting slurry was stirred ultrasonically treated for 2 h. Finally, the impregnated extrudates were dried and calcined at 350 °C $(5 \text{ °C} \cdot \text{min}^{-1})$ for 3 h to get the In₂O₃/ZrO₂ and In₂O₃/Li-ZrO₂ samples.

Catalytic Evaluation. The catalytic activity was measured in a fixed-bed reactor of a length of 400 mm and a diameter of 8 mm, made of stainless steel. The bed consisted of 0.2 g of the catalyst (20–40 mesh size distribution) and 2 g of quartz particles placed between two layers of silica wool. First, the pressure of the reactor was increased to 3.0 MPa with N₂ flow, and the temperature was increased to 350 °C. Then, the catalyst was reduced and activated in a stream of diluted hydrogen (10 vol % H_2/N_2) at 350 °C for 1 h. Prior to each experiment, the reactor was cooled down to a specific reaction temperature (200–350 °C). The catalytic activity in the methanol synthesis was tested under the following conditions: gas hourly space velocity (GHSV) of the reactants flow = 12 000 h⁻¹, $H_2/CO_2 = 3$, N_2 flow rate = 10 mL/min. At the outlet of the reactor, the gases were

decompressed to atmospheric pressure, and the reaction products were analyzed with an online gas chromatograph (GC, Agilent 7890A) equipped with two detectors. CH_3OCH_3 , CH_4 , and CH_3OH were determined by a flame ionization detector with an HP-FFAP column using H_2 as a carrier gas. A thermal conductivity detector with columns of MS-SA and Hayesep Q using He as a carrier gas for other gaseous products (including H_2 , CO_2 , N_2 , and CO) was used. The carbon balance was found to be >95% in all the tests. CO_2 conversion, C-containing product selectivity, and the yield of products were calculated as follows

$$X_{\rm CO2}(\%) = \frac{F_{\rm CO2,in} - F_{\rm CO2,out}}{F_{\rm CO2,in}} * 100$$
(1)

$$S_N(\%) = \frac{\%N}{\sum((\%N))} *100$$
 (2)

$$yield_{N}(\%) = X_{CO2} * S_{N}(\%) * 100$$
(3)

Where N represents the carbon-containing species in the products, including CO, CH_3OCH_3 , CH_4 , and CH_3OH . The results were obtained when the reaction had reached a steady state.

Catalyst Characterization. Powder X-ray diffraction (XRD) of different samples was recorded before and after reaction. XRD patterns were performed with 2θ values between 20 and 90° using a Bruker-D8 diffractometer employing graphite filtered Cu K α radiation ($\lambda = 1.54056$ Å). The experiment was operated at 40 kV and 40 mA and employed a Vantec detector. Catalysts were characterized after being filled in the glassy sample cell. The diameter of ZrO₂ nanoparticles was calculated by the Sherrer equation. In the equation, k stands for the Sherrer constant, λ is the wavelength of an X-ray, B is the full width at half-maximum (fwhm) of the diffraction peak, and θ is the angle of diffraction.

$$D = \frac{k\lambda}{B\cos\theta} \tag{4}$$

The fraction of m-ZrO₂ in the ZrO₂ support (I_{m-Zr}/I_{Zr}) was calculated based on the intensity of the characteristic diffraction peaks of t-ZrO₂(101) $(I_{t-Zr}$ ca. 30.0°) and m-ZrO₂(111) $(I_{m-Zr}$ ca. 31.5°). The equation was listed as follows

$$I_{m-Zr}/I_{Zr} = \frac{I_{m-Zr}}{I_{m-Zr} + I_{t-Zr}}$$
(5)

The electronic structure of In_2O_3/ZrO_2 was studied by *quasi-in-situ* X-ray photoelectron spectroscopy (XPS). The binding energies were calibrated using the C 1s peak at 284.6 eV as a reference. Specifically, the catalysts were pretreated in a reaction cell directly connected to the spectrometer chamber, which allows sample transfer without exposure to air. The CO₂ hydrogenation reaction was performed under the following conditions: CO_2/H_2 mixture (ratio = 1:3, flow rate is 40 mL/min) for 0.5 h at 280 °C.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to record the vibrational spectra of species adsorbed on the surface of catalysts under CO₂ hydrogenation. In situ DRIFTS experiments were performed on a Thermo Scientific Nicolet IS50 spectrometer, equipped with a Harrick Scientific DRIFT cell and a mercury-cadmium-telluride (MCT) detector cooled by liquid N₂. About 100 mg of sample was packed in the in situ chamber. All the samples were pretreated at 350 $^\circ$ C in 10% H₂/Ar flow (30 mL/min) for 1 h and cooled to the desired temperature to obtain the background spectrum, and the spectra of samples for each measurement were then collected by subtracting the background spectrum. The absorbance was normalized to the mass of the catalysts. Generally, the in situ reactions were carried out under 0.8 MPa, 280 °C, 40 mL/min of $CO_2 + H_2(D_2)$, and $CO_2/H_2(D_2) = 1:3$. The spectra were recorded by collecting 64 scans at a resolution of 8 cm⁻¹. The outlet of the DRIFT cell was connected to an online mass spectrometer (MS), so the gas component in the effluent can be monitored and recorded by the MS. Typically, the mass/charge ratio

(m/z) values are 33 for CH₃OD, 34 for CH₂DOD, 35 for CD₂HOD, and 36 for CD₃OD in hydrogen isotope analysis.

DFT Method. The plane-wave-based Vienna Ab initio Simulation package (VASP) was applied to perform our density functional theory calculations.²² The electron exchange and correlation effects were described by the generalized gradient approximation (GGA) in the form of the PBE + U functional.²³ A plane-wave basis set with a cutoff energy of 400 eV was applied in all slab calculations, with a force convergence criterium of 0.02 eV/Å. After convergence tests, k-point grids of $(2 \times 2 \times 1)$ for m-ZrO₂(111) and $(3 \times 3 \times 1)$ for t-ZrO₂(101), respectively, were used to sample the calculation space. For the In–Zr binary model, we used the same k-point sets for m- and t-ZrO₂(111) as above. A 15 Å vacuum space is sufficiently applied in all models to avoid periodic interaction along the Z-directions. In addition, the transition states were located by the climbing-image nudged elastic band method.²⁴

Modeling of In₂O₃. The interaction between atomic cores and electrons was described by the projector augmented wave (PAW) method.²⁵ The perfect In₂O₃(111) surface was modeled with a (1 × 1) supercell, built from the optimized In₂O₃ bulk with lattice parameters a = b = c = 10.34 Å, which is in good agreement with the previous experimental results.²⁶ And the surface of In₂O₃(111) comprise 24 In atoms and 16 O atoms. To eliminate the periodic interaction in the *Z*-direction, a sufficient 15 Å vacuum space was applied. In all calculations, the bottom two layers were frozen at their equilibrium bulk positions, whereas the top two layers together with the adsorbates could relax.

Modeling of ZrO₂. The bulk structures of monoclinic and tetragonal zirconia (m-ZrO₂ and t-ZrO₂) have been well optimized in our calculation, with lattice parameters a = 5.19 Å, b = 5.25 Å, c = 5.29 Å for m-ZrO₂ and a = b = 3.64 Å and c = 5.27 Å for t-ZrO₂, consistent with the experiments.²⁷ According to the experiment part, we chose m-ZrO₂(111) and t-ZrO₂(101) for further calculation, both with a (2 × 2) unit cell and a 15 Å vacuum space. After convergence tests, k-point grids of (2 × 2 × 1) for m-ZrO₂(111) and (3 × 3 × 1) for t-ZrO₂(101), respectively, were used to sample the calculation space. Similar to In₂O₃(111), we fixed the bottom two layers and relaxed the top two layers of the ZrO₂ slabs with adsorbates in all the calculation.

Modeling of In–Zr Binary Structures. To elucidate the electronic interactions between a large In_2O_3 particle and its support ZrO_2 , we created ZrO_2 -supported In_2O_3 nanostripe models (32 In atoms) to estimate the charge transfer between ZrO_2 and In_2O_3 . The same method has been applied in $ZnO-ZrO_2$.¹⁰

RESULTS AND DISCUSSION

Synthesis and Morphology. ZrO_2 was chosen as supports for In_2O_3 nanoparticles, due to its inactivity for CO_2 hydrogenation and adjustable crystalline structure by changing the Li-doping amount (*x*Li-ZrO₂, *x* represents molar percentage of Li, metal base). In this work, Li-doped ZrO_2 was prepared by ammonia coprecipitation. N_2 sorption isotherms exhibit similar surface areas for both ZrO_2 and Li-doped ZrO_2 (Table S1). In_2O_3 was supported on ZrO_2 by an impregnation method. Inductively coupled plasma (ICP) analyses show that the indium content was ~8 wt % for the samples (Table S2). Moreover, the Zr/ In on the surface of the catalysts is about 2:1 as obtained from XPS (Table S2), suggesting the distribution of In species is mainly concentrated on the surfaces of catalysts.

High-resolution transmission electron microscopy (HRTEM) images show In_2O_3 mostly localized on the surface of ZrO_2 (Figure 1). Most of the In_2O_3 nanoparticles in the various samples have comparable average diameters, with distributions in the range of 8–15 nm (Figures 1A,B and S1A,B). Element distribution analysis shows that the In species is dispersed evenly on ZrO_2 and $SLi-ZrO_2$ (Figure 1C,D).

Zr



Figure 1. HRTEM images of In_2O_3/ZrO_2 (A) and $In_2O_3/5Li-ZrO_2$ (B). Aberration corrected scanning TEM-high-angle annular dark-field images and element distribution of In_2O_3/ZrO_2 (C) and $In_2O_3/SLi-ZrO_2$ (D).

Zr

ln

ln

Adjustment of ZrO_2 Crystalline Structure via Li Doping. To figure out the effect of doping on the structure of catalysts, a series of spectroscopic techniques were carried out. XRD patterns in Figure S2A demonstrate that the pure ZrO_2 is in tetragonal phase (30.0°, t- $ZrO_2(101)$). When a small amount of lithium is added ($5Li-ZrO_2$), the crystal form of ZrO_2 is changed completely to monoclinic phase (28.1°, m- $ZrO_2(-111)$ and 31.5°, m- $ZrO_2(111)$). However, higher Li content (20 to 40%) for Li- ZrO_2 tends to transform the ZrO_2 crystalline structure from monoclinic back to the tetragonal phase.²⁸

In situ Raman spectroscopy with different laser sources was used to detect the structure of the In₂O₃/Li-ZrO₂ catalyst in different depths due to light absorption and light scattering.²⁵ Generally, the phase in the bulk of catalysts (the depth is >50 nm) is sensitively detected by Raman spectroscopy with laser sources at 532 nm.³⁰ In Figure 2A, the appearance of Raman peaks at 187, 334, and 380 cm⁻¹ indicates that the bulk of $In_2O_3/5Li-ZrO_2$ is monoclinic ZrO_2 .³¹ The additional peak at 269 cm⁻¹ became obvious for In₂O₃/ZrO₂ and In₂O₃/40Li- ZrO_2 , which is characteristic of the tetragonal ZrO_2 phase.³² Both of these results are very consistent with the abovediscussed XRD analysis. Actually, the average Zr-O distance in m-ZrO₂ is 2.159 Å, whereas Zr-O distance in t-ZrO₂ is 2.226 Å.³³ During the doping process, the atomic arrangement changes significantly, and this results in different Zr-O distances and the t-m phase transition.

On the other hand, the phase near the skin layer (about 10 nm) is detected by ultraviolet Raman spectroscopy with a 325 nm excitation laser.³⁰ Strong E_g vibrational modes of tetragonal ZrO₂ phases at 269 cm⁻¹ were observed over In₂O₃/ZrO₂. As for In₂O₃/SLi–ZrO₂, only monoclinic ZrO₂ (A_g, 187 cm⁻¹) was detected. These results above demonstrate the existence of the monoclinic phase through the particle, i.e., from the



Figure 2. (A) *In situ* Raman spectra of catalysts with a 532 nm laser. (B) *In situ* Raman spectra of catalysts with a 325 nm laser. Raman shift from 250 to 400 cm⁻¹ in Figure 2B for In_2O_3/ZrO_2 (C), $In_2O_3/SLi-ZrO_2$ (D), and $In_2O_3/40Li-ZrO_2$ (E).

particle core to the skin layer of $In_2O_3/SLi-ZrO_2$. In contrast, the bulk of In_2O_3/ZrO_2 and $In_2O_3/40Li-ZrO_2$ is primarily in the tetragonal phase, whereas the surface is in the coexistence of tetragonal and monoclinic phases. It is worth noting that the tetragonal ZrO_2 phase dominated in the skin layer of $In_2O_3/$ ZrO_2 . As shown in Figure 2B, the peaks at 305 and 502 cm⁻¹ are assigned to $\delta(InO_6)$ and $\nu(InO_6)$ of InO_6 structure units,³⁴ whereas the peak at 345 cm⁻¹ is assigned to the stretching vibrations of the In–O–In structures highly dispersed on the surface of ZrO_2 .³⁵ A higher proportion of the In–O–In structure ($\nu_s(In–O–In)$)/ $\delta(InO_6)$ was found on the $In_2O_3/$ $SLi–ZrO_2$, suggesting a stronger interaction between In_2O_3 and m-ZrO₂ (Figure 2C–E and Table S2).

The phase transition of ZrO_2 caused by Li doping is also supported by the ultraviolet-visible (UV-vis) absorption spectra and the Tauc plots. The supports show different absorption edges at around 250 nm (Figure S1C), which is associated with the indirect band gap energy (E_g) of Li-doped ZrO_2 . According to the Tauc plots, the estimated E_g of SLi- ZrO_2 is up to 4.96 eV, which is higher than that of ZrO_2 (4.78 eV) and $40Li-ZrO_2$ (4.86 eV) (Figure S1D and Table S3), suggesting that Li doping adjusted the crystalline form and band structure of ZrO_2 .

Catalytic Performance for CO₂ Hydrogenation. The catalytic performance for CO₂ hydrogenation was tested at 200–350 °C and 3.0 MPa (Figure 3). As shown in Figure 3B, the selectivity toward CH₃OH decreased along with the increasing of the reaction temperature. Therefore, a volcano type of yield has been observed (Figure 3C). More importantly, a significant improvement on the CH₃OH yield of $In_2O_3/SLi-ZrO_2$ than that of In_2O_3/ZrO_2 and $In_2O_3/40Li-ZrO_2$ was observed at a wide range of temperatures from 220 to 350 °C (Figure 3C). At 280 °C, the reaction temperature with the highest CH₃OH yield, $In_2O_3/SLi-ZrO_2$ produced CH₃OH with 84.6% selectivity at 12.1% of CO₂ conversion (Figure S3A), which is much higher than that obtained over In_2O_3/ZrO_2 (61.6% of CH₃OH selectivity at 6.0% conversion). As Li was further added into ZrO_2 support



Figure 3. (A) CO₂ conversion and (B) product distribution for CO₂ hydrogenation over different catalysts. Methanol selectivity: solid bar, CO selectivity: shaded bar. (C) Methanol yield for CO₂ hydrogenation over different catalysts at various temperatures. (D) The proportion of In–O–In structure and methanol selectivity for CO₂ hydrogenation over In₂O₃/ZrO₂ and In₂O₃/Li–ZrO₂ catalysts as a function of I_{m-Zr}/I_{Zr} at 280 °C. Reaction conditions: P = 3.0 MPa, CO₂/H₂ = 1:3, and GHSV = 12 000 h⁻¹.

(20–40%), both CH₃OH selectivity and CO₂ conversion decreased.

The XRD characterization after reaction shows that t-ZrO₂ still dominates in used In_2O_3/ZrO_2 , and m-ZrO₂ dominates in used $In_2O_3/5Li-ZrO_2$ (Figure S2B). The fraction of m-ZrO₂ in the ZrO₂ support was obtained by normalizing the diffraction peak intensity of m-ZrO₂ and t-ZrO₂ $(I_{m-Zr}/I_{Zr'})$ eq 5 in Experimental Section). It is interesting to note that the CH₃OH selectivity exhibits a positive correlation with I_{m-7r}/I_{Zr} (Figure 3D). Thus, we propose the m- ZrO_2 support plays an important role in promoting methanol production. In addition, In₂O₃/ZrO₂ and In₂O₃/5Li-ZrO₂ show different apparent activation energies (E_a) of methanol, suggesting that there are different active sites over In2O3/m-ZrO2 and In2O3/t-ZrO2 (Table S4 and Figure S3B,C). Based on the ultraviolet Raman spectrum in Figure 2B, the proportion of the In-O-In structure bonded to m-ZrO2 is correlated with the methanol selectivity. That is, the In-O-In structure shows higher reactivity. Therefore, the In-O-In structure could potentially be the major active site for methanol synthesis (Figure 3D).

To eliminate the influence of Li serving as an electronic additive, an $In_2O_3 + SLi/ZrO_2$ catalyst was prepared via coimpregnation of In and a Li precursor, which exhibited lower CO_2 conversion (7.2%) and methanol selectivity (66.3%) than $In_2O_3/SLi-ZrO_2$ (Figure S3D,E). Therefore, the promotion in catalytic performance for $In_2O_3/SLi-ZrO_2$ should be attributed to the existence of the monoclinic phase caused by SLi doping into ZrO_2 as opposed to the Li additive.

Electronic Interaction between In_2O_3 and m-ZrO₂. To find out the origin of the high methanol yield for $In_2O_3/5Li$ – ZrO_2 , quasi-in-situ XPS was carried out to characterize the surface structure of the catalyst during CO₂ hydrogenation. As shown in Figure S4A, In_2O_3/ZrO_2 and $In_2O_3/Li-ZrO_2$ catalysts showed peaks at ~444.5–445.0 eV, corresponding to In_2O_3 .³⁶ After the reaction, $In_2O_3/5Li-ZrO_2$ showed a lower binding energy of In $3d_{5/2}$ (444.4 eV) as opposed to



Figure 4. (A) Methanol yield and binding energy (BE) shift of In $3d_{5/2}$ (yellow) and Zr $3d_{5/2}$ (purple) among catalysts in the initial stage of the reaction as a function of I_{m-Zr}/I_{Zr} . The BE of In $3d_{5/2}$ and Zr $3d_{5/2}$ over In_2O_3/ZrO_2 was chosen as the reference. (B) ESR spectra of used catalysts. (C) DFT simulation of charge transfer in the In_2O_3 stripe/m-ZrO₂ and In_2O_3 stripe/t-ZrO₂ catalyst models. In: light brown, Zr: mint green, O atoms in ZrO₂: red, and O atoms in In_4O_6 : blue. The black numbers in the image are the total number of valence electrons on In atoms. (D) The binding energy of In $3d_{5/2}$ plotted as a function of time on stream for In_2O_3/ZrO_2 and $In_2O_3/Li-ZrO_2$ catalysts. (E) The V_O concentration plotted as a function of time on stream for In_2O_3/ZrO_2 and $In_2O_3/Li-ZrO_2$ catalysts. (E) The v_O concentration plotted as a function of V_O concentration for In_2O_3/ZrO_2 and $In_2O_3/Li-ZrO_2$ catalysts.

other samples (Figure S4A). On the contrary, the binding energy of Zr $3d_{5/2}$ in $In_2O_3/5Li-ZrO_2$ (182.0 eV) is higher than that in In_2O_3/ZrO_2 (181.7 eV) (Figure S4B).³⁷ This phenomenon indicates In_2O_3 supported on $5Li-ZrO_2$ has a higher electron density than that in In_2O_3/ZrO_2 (Figure S4A– C and Table S5). Also, there was no binding energy shift of Zr $3d_{5/2}$ observed for pure ZrO_2 and $Li-ZrO_2$ support after the same treatment (Figure S4C), revealing that the addition of Li has no influence on the electron density of Zr.

Figure 4A shows the correlation between the binding energy of used catalysts (reference: used In₂O₃/ZrO₂) and methanol yield as a function of I_{m-Zr}/I_{Zr} . The binding energy of In became lower, and the binding energy of Zr shifted to a higher value with I_{m-Zr}/I_{Zr} increased, suggesting that stronger electron transfer from m-ZrO2 to In2O3 leads to more electrons accumulated on the In atom of In_2O_3/m -ZrO₂ than that of In2O3/t-ZrO2.38 XRD results show that after In2O3 was supported onto different ZrO2, both the diffraction peaks of $t-ZrO_2$ and $m-ZrO_2$ are shifted to a higher position (Figure S5), meaning that a fraction of In is incorporated into the ZrO_2 matrix by the form of In-O-Zr bonds.³⁹ The In-O-In structure may be bonded to m-ZrO₂ via In-O-Zr bonds, which changed the coordination of indium and enhanced the electron transfer. As a result, the binding energy shift became more obvious. Moreover, the methanol yield increased with the strengthening of this electronic interaction (Figure 4A), indicating electron-rich In₂O₃ favors the methanol formation.

Ambient pressure XPS (AP-XPS) experiments were also carried out to eliminate possible error caused by measurement under vacuum for *quasi-in-situ* XPS. Similarly, In_2O_3 on m-ZrO₂ shows a lower BE of In, i.e., higher electron density than In_2O_3 on t-ZrO₂ by AP-XPS (Figure S6A). It is worth noting that the pressure of AP-XPS is 0.4 mbar, which is much smaller

than the real reaction pressure. The low pressure may also influence intermediate coverage and cause a different catalyst surface from the actual situation. In contrast, the reaction for *quasi-in-situ* XPS can be pressurized to higher pressure (0.1 MPa). Nevertheless, the combination of *quasi-in-situ* and AP-XPS characterization suggests strong electron transfer electron transfer from m-ZrO₂ to In_2O_3 and the influence on the reaction performance. As shown in Figure S6B–D, the catalysts after a long-term reaction displayed similar trends of binding energy shifts.

Additionally, we applied Bader charge analysis based on density functional theory (DFT) calculations to support the electron transfer between the two oxides (Figure S7). The model of In doped into ZrO_2 show that In in m-ZrO₂ can enrich more electrons (0.04 e⁻) than In in t-ZrO₂ (Figure S8). Figure 4C shows that the In₂O₃ stripe model tends to accept more electrons, ~0.86 e⁻, on m-ZrO₂ than that on t-ZrO₂, indicating In₂O₃ supported on m-ZrO₂ should have greater electron enrichment, which is in agreement with the XPS results.

The types of electron transfer in In_2O_3/ZrO_2 were characterized by electron spin resonance (ESR). The ESR in Figure S4D suggests that the trapped electrons are absent on pure ZrO₂ supports, as no obvious peaks and troughs were observed. After the loading of In_2O_3 , the electron spin count at g = 1.98-2.00 showed an obvious change for all samples (Figure 4B). Thus, the trapped electrons were generated over In_2O_3 or at the In-O-Zr interface, as opposed to over ZrO₂. Figure 4B reveals two intense signals for $In_2O_3/5Li$ -ZrO₂ at g = 2.00 and g = 1.98, whereas only the former signal is detected for In_2O_3/ZrO_2 and $In_2O_3/40Li$ -ZrO₂. The signal at g = 2.00 has commonly been assigned to the delocalized electrons that result from the abstraction of O atoms, probably oxygen

vacancies,⁴⁰ and the signal at g = 1.98 represents unpaired electrons,^{41,42} which may migrate from the conduction band of m-ZrO₂ to In₂O₃. It is therefore evident that the electronic property of the In sites is modified by the neighboring monoclinic Zr sites, when electrons are preferentially deposited over In sites from m-ZrO₂.

In the reducing reaction atmosphere, oxygen vacancies could inevitably be formed on the In_2O_3 surface (Figure S9A-C). It is widely discovered that the V_0 delocalization effect can reduce the binding energy of the corresponding oxide.⁴³ However, in this study, the binding energy of In 3d_{5/2} on all samples continued to decrease (Figure 4D) while the V_0 concentration decreased (Figure 4E and Table S5) during the reaction. This indicates that the electron transfer effect on In electron density at the interface between m-ZrO₂ and In₂O₃ is stronger than the V_0 delocalization effect over the In₂O₃ surface. It is also found that the V_O concentration on the catalyst is not positively correlated with the methanol selectivity (Figure 4F). In other words, the electron transfer at the interface between m-ZrO₂ and In₂O₃ plays a more significant role in the decrease of the binding energy of In sites and promoting methanol synthesis than V_{Ω} .

Above all, the experimental evidence by XPS and ESR, combined with theoretical calculations, proved the existence of electron transfer from m-ZrO₂ to In₂O₃ for In₂O₃/5Li–ZrO₂, which plays crucial roles in promoting catalytic CO₂ to methanol.

Mechanism Investigation. To further understand the effect of charge transfer between ZrO₂ and In₂O₃ on catalytic performance, the reaction mechanism was investigated. Previous works have proposed that there are mainly two reaction pathways to produce CH₃OH via CO₂ hydrogenation.⁴⁴ One is formed by the *CO intermediate, which is produced from the reverse water-gas shift (RWGS, CO_2 + $H_2 \rightarrow CO + H_2O$ reaction, and *CO is further hydrogenated to CH₂OH; the other pathway is designated as the formate (HCOO*) pathway, where the HCOO* intermediate is formed by *CO₂ hydrogenation and further hydrogenated to the *H₂COOH intermediate, which eventually produces CH2O* and CH3OH after breaking one C-O bond in *H₂COOH. The possible reaction pathway may be associated with different catalyst systems, which show different adsorption properties for reaction intermediates. The identification of the active intermediates is essential to understand the preferred pathways and the role of electron transfer in CO₂ hydrogenation.

The used In_2O_3/ZrO_2 and $In_2O_3/5Li-ZrO_2$ were analyzed by XPS C 1s spectra to identify reaction intermediates (Figure 5A). The peak at approximately 284.6 eV indicated the presence of carbon on both surfaces. Upon reacting at 280 °C, peaks at approximately 288.8 and 286.2 eV were observed for $In_2O_3/5Li-ZrO_2$ but not for In_2O_3/ZrO_2 . These peaks are attributed to the surface formate (HCOO*)/carboxyl (*COOH) species and methoxy (CH₃O*) species respectively, suggesting that abundant COO* or CH₃O* species were formed on $In_2O_3/5Li-ZrO_2$ during CO₂ hydrogenation.^{45,46}

To confirm the reaction route, DRIFTS was carried out under CO_2 flow with pulsed hydrogen, where the hydrogen was insufficient to slow down the transformation and monitor the change of intermediates clearly (Figure 5B). The unsaturated C-H species (2876 cm⁻¹) along with the symmetric and asymmetric OCO stretches (1368 and 1574



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Figure 5. (A) XPS C 1s peaks of In_2O_3/ZrO_2 and $In_2O_3/SLi-ZrO_2$ before and after reaction. (B) *In situ* DRIFT spectra of different catalysts at 280 °C. (C) Absorbance of generated intermediate species over different catalysts after inletting $CO_2 + H_2$ at 280 °C. (D) Absorbance of generated intermediate species over $In_2O_3/SLi-ZrO_2$ after switching from $CO_2 + H_2$ to $CO_2 + D_2$ at 280 °C. (E) Simplified models showing the main reaction mechanism on $In_2O_3/t-ZrO_2$ and $In_2O_3/m-ZrO_2$.

cm⁻¹) confirmed the presence of HCOO* species.^{45,47} As shown in Figures 5C and S10A–C, HCOO* species appeared at the beginning of the reaction owing to the adsorption and hydrogenation of CO₂. With the pulse of H₂ flow, new bands at 2830 and 1025 cm⁻¹ were observed, which are assigned to the stretching vibration of saturated C–H and C–O in CH₃O* species.¹⁰ Noticeably, the stronger IR peak intensity (1025 cm⁻¹) over In₂O₃/5Li–ZrO₂ indicated more CH₃O* species were formed over In₂O₃/5Li–ZrO₂ than other samples, which should account for the high methanol yield. Hence, HCOO* and H₃CO* are key intermediates during CO₂ hydrogenation.

For all the catalysts in Figure 5C, HCOO* species were observed prior to the formation of CH₃O* species. The IR peak intensity of surface HCOO* became stable after a reaction for 30 min, whereas it took more than 60 min for H₃CO* to reach steady state. When CO₂ + H₂ was substituted for CO₂ + D₂ over In₂O₃/5Li–ZrO₂ (Figure S10D), HCOO* and CH₃O* (2876 and 2830 cm⁻¹, respectively) disappeared gradually (Figure 5D). Meanwhile, DCOO* species (2176 cm⁻¹) appeared before the CD₃O* peak (2067 cm⁻¹) arose.⁷ Both the sequences of generated intermediate species in *in situ* DRIFTS and isotope labeling experiments suggest that CH₃O* species come from HCOO* hydrogenation, and the formate route is the preferred pathway on the In₂O₃-based catalyst.

The apparent reaction orders of the reactants were determined by altering the partial pressures of CO_2 and H_2 .⁴⁸ As shown in Figure S11A, the formation rate of methanol increased significantly with the increase of the partial pressure

of H₂, while the methanol formation was suppressed in excess of CO₂. When the partial pressure of H₂ is above the ratio of H₂/CO₂ = 1:1, the orders of H₂ to methanol were calculated at 1.2, 1.6, and 1.4 for In₂O₃/ZrO₂, In₂O₃/SLi–ZrO₂, and In₂O₃/ 40Li–ZrO₂, respectively (Figures S11B and S12A). However, the orders of CO₂ to methanol were about -0.5 for three samples (Figures S11C and S12B). Consequently, the activation and dissociation of H₂ may be the limiting process for methanol synthesis on In₂O₃-based catalysts rather than the activation of CO₂. Furthermore, the reaction order of H₂ to methanol is higher than that to CO (ca. 0.3, Figure S12C), which indicates that the promotion of H₂ activation has a more positive effect on the formation of methanol than CO.

 H_2 -temperature-programmed reduction (H_2 -TPR) and D_2 temperature-programmed surface reaction (D_2 -TPSR) showed that H_2 dissociation and HD formation happened at lower temperatures over $In_2O_3/SLi-ZrO_2$ than In_2O_3/ZrO_2 , In_2O_3 + SLi/ZrO_2 , and $In_2O_3/40Li-ZrO_2$ (Figures S13A,B and 6A).



Figure 6. (A) HD signals of different catalysts in D_2 -TPSR. DRIFT-MS of $CO_2 + H_2$ subsequently switched to $CO_2 + D_2$ at 100 min over In_2O_3/ZrO_2 (B), $In_2O_3/SLi-ZrO_2$ (C), and $In_2O_3/40Li-ZrO_2$ (D). (E) Absorbance of generated intermediate species over In_2O_3/ZrO_2 and $In_2O_3/SLi-ZrO_2$ after HCOOH preadsorption and subsequent H_2 sweeping at 280 °C.

Moreover, $In_2O_3/SLi-ZrO_2$ presented a higher conversion of H_2 to HD in the H_2-D_2 exchange reaction (Figure S13C) than other samples. This conclusion is also supported by the calculation in Figure S14, since H_2 dissociation on In_2O_3/m -ZrO₂ (0.37 eV) shows a lower energy barrier than that on In_2O_3/t -ZrO₂ (0.59 eV). Both tests indicated that electron-rich In_2O_3 of In_2O_3/m -ZrO₂ exhibits higher activity in the H–H bond dissociation and increases the amount of dissociated H species. Since the orders of H_2 are positive, the increased H species can accelerate the rate of methanol formation.

To investigate the effect of this electron transfer on the hydrogenation process of intermediates, the deuteriumcontaining products of isotope labeling experiments were analyzed by mass spectrometry connected with DRIFTS. As shown in Figure 6B–D, the time for CH_2DOD stabilization after switching $CO_2 + H_2$ to $CO_2 + D_2$ reflects the H_2 -dissociation ability of catalysts under reaction conditions, where this process over $In_2O_3/SLi-ZrO_2$ (10 min) was much faster than that over In_2O_3/ZrO_2 (80 min) and $In_2O_3/40Li ZrO_2$ (60 min). Since CH₂DOD was produced via formate reacted with dissociated D, this result affirmed that there is a strong promotion effect on the H₂ activation, facilitating subsequent hydrogenation of intermediates over the electronrich In_2O_3 of $In_2O_3/m-ZrO_2$.

Furthermore, HCOOH was chosen as reactant, which can provide COO* intermediates, to verify the COO* hydrogenation step. Figures 6E and S15A,B show the varying tendency of the preadsorbed COO* with time after H₂ inletting into reaction cell. The IR intensity of adsorbed COO^* (1589 and 1450 cm⁻¹) over In₂O₃/5Li-ZrO₂ dropped rapidly under H₂, accompanied by the formation of CH₃O* species at 1025 cm⁻¹. However, the signal of adsorbed COO* over In₂O₃/ZrO₂ remains barely changed in intensity. Additionally, there was no CH₃O* formed, indicating the COO* species were difficult to be converted to CH₂O* over In_2O_3/ZrO_2 . For the formate pathway, the binding strength of HCOO* should be moderate, and CH₃O* should be destabilized on the surface to allow the production of CH₃OH. Based on the DRIFTS results, the hydrogenation of HCOO* to CH₃O* is easy for In₂O₃/5Li-ZrO₂, but HCOO* is overstabilized on In_2O_3/ZrO_2 , poisoning the surface and thus blocking the formation of CH₃O*. Overall, the electronic interaction over In₂O₃/m-ZrO₂ (In₂O₃/5Li-ZrO₂) leads to a higher methanol yield, which is due to the stronger H₂dissociation activity to convert the formate intermediate to CH_3O^* and thus methanol (Figure 5E).

CONCLUSION

In summary, we describe a strategy to support In_2O_3 over ZrO_2 with different crystallization phases. The best catalytic performance was achieved over In2O3/m-ZrO2, which exhibits high activity and selectivity in the selective CO₂ hydrogenation to methanol. Compared with In2O3/t-ZrO2, the improved catalytic performance is potentially due to the strong interaction between In2O3 and monoclinic ZrO2, where In₂O₃ is dispersed mainly in the form of In-O-Inand electrons were transferred from monoclinic ZrO₂ to In₂O₃, generating the electron-rich In₂O₃. The highly dispersed In-O-In structure is proposed as a major active site to convert CO₂ to methanol. Also, the electron transfer from m-ZrO₂ to In-O-In plays a more significant role in methanol synthesis than V_{0} . It is confirmed experimentally that the production of methanol from CO₂ hydrogenation over an In₂O₃-based catalyst is via formate route. Accordingly, electron-rich In₂O₃ was proven to promote the H₂ dissociation and help HCOO* convert into CH₃O* by hydrogenation. This work extends the application of oxide catalysts in CO₂ hydrogenation to methanol and also reveals the crucial effect of the electronic interaction between the oxide and support in the hydrogenation reaction, which opens an avenue for developing multicomponent oxide catalysts for CO₂ conversion.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c07195.

Further experimental details, catalyst performance data, *quasi-in-situ* XPS, ESR, kinetics of hydrogenation, and *in situ* DRIFTS characterization data (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge the National Key R&D Program of China (2016YFB0600901), the National Natural Science Foundation of China (21525626, 21761132023), and the Program of Introducing Talents of Discipline to Universities (BP0618007)

for financial support. We highly appreciate Dr. Yi Cui, Zhongmiao Gong, and Hao Li (Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences) for the support of AP-XPS.

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