Rationally designed indium oxide catalysts for CO₂ hydrogenation to methanol with high activity and selectivity

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Renewable energy-driven methanol synthesis from CO₂ and green hydrogen is a viable and key process in both the “methanol economy” and “liquid sunshine” visions. Recently, In₂O₃-based catalysts have shown great promise in overcoming the disadvantages of traditional Cu-based catalysts. Here, we report a successful case of theory-guided rational design of a much higher performance In₂O₃ nanocatalyst. Density functional theory calculations of CO₂ hydrogenation pathways over stable facets of cubic and hexagonal In₂O₃ predict the hexagonal In₂O₃(104) surface to have far superior catalytic performance. This promotes the synthesis and evaluation of In₂O₃ in pure phases with different morphologies. Confirming our theoretical prediction, a novel hexagonal In₂O₃ nanomaterial with high proportion of the exposed (104) surface exhibits the highest activity and methanol selectivity with high catalytic stability. The synergy between theory and experiment proves highly effective in the rational design and experimental realization of oxide catalysts for industry-relevant reactions.

INTRODUCTION
The rapid increase in global energy demand is driving up carbon dioxide (CO₂) emission. In 2017, global CO₂ emission from energy consumption reached 33 gigatons, twice more than could be taken up by land- and ocean-based CO₂ sinks (1). Therefore, it is urgent to develop effective strategies to slow down the increase and even reduce the level of atmospheric CO₂ concentration by efficient capture and utilization of the CO₂ to be emitted. As methanol is a viable clean alternative fuel to gasoline and diesel and an important feedstock to produce commodity chemicals, the catalytic conversion of CO₂ to methanol using H₂ originated from renewable energy sources is a promising approach to reduce the CO₂ emission and our dependence on fossil fuels by carbon recycling and to store the renewable energy (solar, wind, biomass, and so on) as chemical energy (2–5). In addition, efficient CO₂ hydrogenation to methanol is central to the successful development of the recently proposed “methanol economy” (6) and “liquid sunshine” (1).

Although many types of metal-based catalysts are well known for the CO₂ hydrogenation to methanol reaction, modified copper (Cu) catalysts remained the most efficient and the most extensively investigated (7–13). Different from industrial methanol synthesis from syngas (CO/H₂), one of the main challenges of CO₂ hydrogenation to methanol is the low product selectivity due to the parasitic reverse water–gas shift reaction (RWGS; CO₂ + H₂ → CO + H₂O), for which Cu is among the most active catalysts. The selectivity toward methanol is usually lower than 60% over traditional Cu/ZnO-based catalysts (14–16). Recently, extensive density functional theory (DFT) and experimental studies on CO₂ hydrogenation over the (110) surface of the cubic phase of In₂O₃ suggested that methanol formation over the surface oxygen vacancy site was favorable to the RWGS reaction (17–21). With the In₂O₃ catalyst, methanol selectivity reached nearly 100% at a high space velocity (gas hourly space velocity of >16,000 hour⁻¹) in the temperature range of 200° to 300°C, although the low reactivity led to relatively low single-pass conversions and thus limited space-time yield (STY) of methanol (22). Therefore, the design and development of more efficient In₂O₃-based nanocatalysts are imperative for their industrial adoption in CO₂ hydrogenation to methanol, although it remains a great challenge to vastly improve their catalytic performance.

To rationally design In₂O₃ materials with favorable methanol synthesis performance, it is necessary to fully understand the reaction mechanisms of CO₂ hydrogenation to methanol and the RWGS reaction for CO formation over different surface active sites. Previous studies show that methanol formation follows the formate (HCOO⁻) and methoxy (H₂COO⁻) intermediates (17). In this catalytic mechanism, CO₂ hydrogenation to HCOO⁻ occurs at the oxygen vacancy site, which is thermodynamically and kinetically favorable with the formation of stable HCOO⁻ and H₂COO⁻ species, whereas the formation of H₂COO⁻ on the Cu(111) surface is unfavorable with thermodynamically unstable formaldehyde (H₂CO⁻) species (19, 23). In addition, Ghuman et al. (24) performed experimental and computational studies on the catalytic mechanism of the RWGS reaction on the In₂O₃(111) surface and suggested that the active site consisted of a Lewis base hydroxide adjacent to a Lewis acid indium, in addition to the oxygen vacancy.

Previous experimental and theoretical studies on the In₂O₃ catalysts focused on the stable surfaces of the cubic In₂O₃ (c-In₂O₃) phase, especially its (110) surface. Even for this extensively investigated surface, there remains uncertainty on the detailed catalytic mechanism for CO₂ hydrogenation to methanol and the RWGS reaction. Furthermore, two additional phases are known for In₂O₃,

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the corundum-type hexagonal phase ($h$–In$_2$O$_3$) and the Rh$_2$O$_3$(II)-type orthorhombic phase ($o$–In$_2$O$_3$) (25, 26). Among the three phases, $c$–In$_2$O$_3$ is thermodynamically the most stable, both $c$–In$_2$O$_3$ and $h$–In$_2$O$_3$ can form at ambient conditions, whereas $o$–In$_2$O$_3$ may form at high pressure (>15 GPa) (25, 27–29). Since both $c$–In$_2$O$_3$ and $h$–In$_2$O$_3$ are stable in the temperature range of the CO$_2$ hydrogenation to methanol reaction (200° to 300°C) (30), both may work as catalysts for this reaction. In addition, previous studies show that the thermodynamically most stable surfaces are the (110) and (111) surfaces for $c$–In$_2$O$_3$ (27, 31–34) and the (104) and (012) surfaces for $h$–In$_2$O$_3$ (27, 28, 35–37).

In this work, we first performed extensive DFT calculations to establish the catalytic mechanisms of the In$_2$O$_3$ catalyst during CO$_2$ hydrogenation to methanol and to CO by identifying the preferred pathways and rate-determining steps (RDSs). We then evaluated the performance of the stable surfaces of $c$–In$_2$O$_3$ and $h$–In$_2$O$_3$ as mentioned above based on the theoretical data to search for a superior catalyst. Our calculations predict the $h$–In$_2$O$_3$(104) surface to have the best catalytic performance in terms of reactivity and selectivity. On the basis of our computational studies, we synthesized nanoparticles in pure $c$–In$_2$O$_3$ and $h$–In$_2$O$_3$ phases of different morphologies and evaluated their performance for CO$_2$ hydrogenation to methanol. The results show that the catalytic performance depends on the shape of In$_2$O$_3$ nanoparticles due to their different phases and exposed facets. Furthermore, $h$–In$_2$O$_3$ nanocrystals with a high proportion of the exposed [104] surface exhibited the best performance with high catalytic stability during CO$_2$ hydrogenation, confirming our DFT prediction. Methanol selectivity reached 92.4% with a single-pass CO$_2$ conversion of more than 17% under the reaction conditions of 300°C, 5.0 MPa, 9000 ml g$_{cat}^{-1}$ hour$^{-1}$, and H$_2$/CO$_2$ = 6. Thus, our work serves as an exemplary case toward using computational methods to design new and more efficient catalysts.

**RESULTS AND DISCUSSIONS**

We first performed extensive DFT calculations to determine the most favorable reaction pathways and the corresponding RDS for the formations of CH$_3$OH and CO from CO$_2$ hydrogenation on the $c$–In$_2$O$_3$(110) surface with an oxygen vacancy. Although several groups including ourselves have previously investigated CO$_2$ hydrogenation pathways on this surface, there remain debates in the formation mechanisms of these two major products.

As shown in fig. S1A, model of the perfect $c$–In$_2$O$_3$(110) surface is similar to that used in our previous study. According to the calculated formation energies of the different surface oxygen vacancies, we chose the oxygen vacancy at the O$_{4a}$ site with the highest formation energy as the active site for CO$_2$ hydrogenation, in expectation that higher oxygen affinity of the O$_{4a}$ site would lead to stronger CO$_2$ adsorption and reactivity. Thus, model of the defective $c$–In$_2$O$_3$(110) surface shown in Fig. 1A also resembles that used in our previous work. An important finding in this work is our identification of the distinct roles of two different CO$_2$ adsorption configurations at the O$_{4a}$ site, the linear and bent structures denoted as In–CO$_2^*$ and bt–CO$_2^*$, as shown in Fig. 1B. In addition, because of the presence of some surface O sites, CO$_2$ can also chemisorb at the O site to form the carb–CO$_2^*$ structure, as shown in Fig. S2A. Calculated adsorption energies of these three configurations are −0.09, −0.42, and −0.85 eV, respectively. In In–CO$_2^*$, CO$_2$ physisorbs above the O$_{4a}$ site, whereas in bt–CO$_2^*$, it chemisorbs at the O$_{4a}$ site by forming the In–C and In–O bonds. In carb–CO$_2^*$, CO$_2$ reacts with the remaining surface O site to form a carbonate species. Despite the thermodynamic stability of carb–CO$_2^*$, our further calculations suggest it to be a spectator species.

Calculations of the reaction pathways reveal that the In–CO$_2^*$ and bt–CO$_2^*$ structures are relevant to CO$_2$ hydrogenation pathways to different products, as shown in Fig. 1C by the black lines starting from In–CO$_2^*$ for CH$_3$OH formation and the red lines starting from bt–CO$_2^*$ for CO formation on the defective $c$–In$_2$O$_3$(110) surface. In the former pathway, CO$_2$ in In–CO$_2^*$ is first hydrogenated by a hydride adsorbed at the In$_3$ site to yield mono–HCOO* via transition state T3 (E$_{TS} = 0.24$ eV). After facile conversion of mono–HCOO* to bi–HCOO* by a simple rotation, it is further hydrogenated by another hydride located at the In$_3$ site to yield the H$_2$COO* structure via TS2 with a very high energy barrier of 1.54 eV. H$_2$COO* dissociates to fill the oxygen vacancy site giving the H$_2$CO* intermediate via TS3 (E$_2 = 0.69$ eV). H$_2$CO* is again hydrogenated by a hydride situated at the In$_3$ site with the assistance of a proton adsorbed at the O$_4$ site to produce the methoxy H$_3$CO* intermediate.
via TS4 ($E_a = 0.11$ eV). H$_3$CO* is further protonated by the proton located at the O$_3$ site to generate the H$_3$COH* structure via TS5 ($E_a = 0.02$ eV). Desorption of the physisorbed CH$_3$OH molecule in H$_3$COH* results in the perfect c–In$_2$O$_3$(110) surface, and the oxygen vacancy site regenerates by its reaction with H$_2$. Thus, from the calculated energy barriers, the RDS for CH$_3$OH formation is hydrogenation of bi–HCOO* to H$_2$COO* with an energy barrier of 1.54 eV. Consistent with our previous calculations, the formate (bi–HCOO*) and methoxy (H$_3$CO*) species are thermodynamically the most stable surface intermediates in the CO$_2$ hydrogenation to CH$_3$OH pathway.

In sharp contrast, the chemisorbed CO$_2$ molecule in the bt–CO$_2$* structure is first protonated by a proton adsorbed at the nearby O$_3$ site to yield the COOH* structure via TS1b with a high energy barrier of 1.26 eV. COOH* then dissociates to fill the oxygen vacancy by the hydroxyl OH* intermediate and to also give the CO* intermediate via TS2b ($E_a = 0.71$ eV). Desorption of the physisorbed CO molecule results in the protonated c–In$_2$O$_3$(110) surface, and the oxygen vacancy site also regenerates by its reaction with H$_2$. Thus, the RDS for CO formation is protonation of bt–CO$_2$* to COOH* with an energy barrier of 1.26 eV. As the energy barrier of the RDS for CH$_3$OH formation is higher than that for CO formation, CH$_3$OH selectivity should be lower than CO selectivity when catalyzed by the O$_3$ site on the defective c–In$_2$O$_3$(110) surface. Furthermore, compared to ln–CO$_2$*, stronger CO$_2$ adsorption in bt–CO$_2$* should result in a higher sticking coefficient for the CO formation pathway, which further favors CO formation over CH$_3$OH formation.

Although the CH$_3$OH formation pathway predicted by our extensive DFT calculations is in general consistent with the earlier study of Ye and co-workers (17), we note that previous studies have not identified the distinct roles of the different CO$_2$ adsorption structures and especially the different H adsorbates, i.e., hydride adsorbed at the In site and proton adsorbed at the O site, which is crucial for the proper determination of the reaction pathways. Distinction between the two H adsorption structures was obscured in earlier works due to simplified treatment of the oxide surface by ignoring its different nature from the metal surface, in that an H adsorbate at the metal or O site likely carries a negative or positive charge, resulting in its different chemical nature and reactivity.

Conclusions drawn from our mechanistic study of CO$_2$ hydrogenation to CH$_3$OH and CO on the defective c–In$_2$O$_3$(110) surface facilitates the rapid search for the catalytically most effective In$_2$O$_3$ surfaces for CH$_3$OH formation. Thus, we further performed DFT calculations on the other stable c–In$_2$O$_3$ and h–In$_2$O$_3$ surfaces by assuming a similar mechanism, and we also calculated CO$_2$ adsorption energies and energy barriers of the RDS to evaluate the performance of these In$_2$O$_3$ surfaces.

As shown in fig. S1, we predicted the stability of the In$_2$O$_3$ surfaces to follow the order of (111) > (110) for the c–In$_2$O$_3$ phase and (012) > (104) for the h–In$_2$O$_3$ phase. As shown in Fig. 2A, for each surface, we chose the oxygen vacancy site with the highest formation energy as the active site for CO$_2$ hydrogenation. Figure 2B displays the transition state structures for hydrogenation of bi–HCOO* to H$_2$COO*, the RDS for CO$_2$ hydrogenation to CH$_3$OH, whereas Fig. 2C shows those for protonation of bt–CO$_2$* to COOH*, the RDS for CO$_2$ hydrogenation to CO. Structures of the different CO$_2$ adsorption configurations are available in fig. S2.

We compare the calculated energy barriers of the RDS for all four defective In$_2$O$_3$ surfaces in Fig. 2D along with the CO$_2$ adsorption energies at the chosen oxygen vacancy site in ln–CO$_2$* and bt–CO$_2$* to evaluate their performance in catalyzing the CO$_2$ hydrogenation reaction. Our calculations show that the energy barriers of the RDS of CH$_3$OH formation follow the order of c–In$_2$O$_3$(110) (1.54 eV) > h–In$_2$O$_3$(012) (1.27 eV) > h–In$_2$O$_3$(104) (0.88 eV) > c–In$_2$O$_3$(111) (0.64 eV), whereas CO$_2$ adsorption strength in the ln–CO$_2$* structure follows the order of h–In$_2$O$_3$(104) (−0.14 eV) > c–In$_2$O$_3$(110) (−0.09 eV) > c–In$_2$O$_3$(111) (−0.05 eV) ≈ h–In$_2$O$_3$(012) (−0.05 eV), so the defective c–In$_2$O$_3$(111) and h–In$_2$O$_3$(104) surfaces are the most favorable for CO$_2$ hydrogenation to CH$_3$OH in terms of the catalytic activity. On the other hand, the energy barriers for the RDS of CO formation follow the order of c–In$_2$O$_3$(111) (1.39 eV) > h–In$_2$O$_3$(104) (1.29 eV) > c–In$_2$O$_3$(110) (1.26 eV) > h–In$_2$O$_3$(012) (0.69 eV), whereas
CO₂ adsorption strength in bt–CO₂* follows the order of c–In₂O₃(110) (−0.42 eV) > h–In₂O₃(012) (0.18 eV) > c–In₂O₃(111) (0.28 eV) > h–In₂O₃(104) (0.69 eV), so the defective c–In₂O₃(110) and h–In₂O₃(012) surfaces favor CO formation, whereas the defective h–In₂O₃(104) and c–In₂O₃(111) surfaces highly disfavor CO formation. We note that CO₂ adsorption strength in the carb–CO₂* structure follows the order of h–In₂O₃(012) (−0.98 eV) > h–In₂O₃(104) (−0.94 eV) > c–In₂O₃(110) (−0.85 eV) > c–In₂O₃(111) (−0.67 eV), although we predict that this structure is a spectator species (fig. S2).

Previous computational studies examined only the flat c–In₂O₃(110) and c–In₂O₃(111) surfaces for CO₂ hydrogenation, and we further examined the possible role of the stepped surfaces. As shown in fig. S3A, the c–In₂O₃(110) step surface is actually slightly more stable than its flat surface (fig. S1A), whereas the other stepped surfaces (fig. S3, B to D) are notably less stable than their corresponding flat surfaces (fig. S1). Nevertheless, we further predicted the energy barriers of the RDS and CO₂ adsorption energies on all these step surfaces (fig. S3E) and compared to the corresponding flat surfaces. For the c–In₂O₃(110) step surface, the energy barriers of CH₃OH and CO formations are lower by 0.41 and 0.27 eV, respectively, whereas CO₂ adsorption energies are slightly less negative by 0.05 eV. Thus, although the c–In₂O₃(110) step surface is catalytically more active, it also favors CO formation over CH₃OH formation. For the other step surfaces, the energy barriers significantly increase by 0.2 to 0.8 eV except for CH₃OH formation on the c–In₂O₃(110) step and h–In₂O₃(012) step surfaces, where they remain essentially the same. Overall, consideration of these step surfaces does not change our above conclusions, not to ignore the fact that only the c–In₂O₃(110) step surface is sufficiently stable. As illustrated in Fig. 3, we further rationalize that the threefold oxygen vacancy site on the c–In₂O₃(111) and h–In₂O₃(104) surfaces favors the linear CO₂ physisorption structure and the HCOO pathway, leading to high CH₃OH selectivity, whereas the twofold oxygen vacancy site on the c–In₂O₃(110) and h–In₂O₃(012) surfaces facilitates the bent CO₂ chemisorption structure and COOH pathway, resulting in high CO selectivity. As the h–In₂O₃(104) surface is thermodynamically less stable than the h–In₂O₃(012) surface and the h–In₂O₃ phase is less stable than the c–In₂O₃ phase, the highly selective In₂O₃ catalyst for CO₂ hydrogenation to CH₃OH preferentially exposing the h–In₂O₃(104) surface must be prepared by controlled synthesis due to its thermal instability. In contrast, a stable In₂O₃ catalyst mainly exposing the c–In₂O₃(111) surface may result in suboptimal selectivity for this reaction. To test the validity of our theoretical prediction, we prepared a series of In₂O₃ catalysts with different crystal phases, exposed facets, and studied their catalytic performance in CO₂ hydrogenation to methanol. In particular, we strived to obtain and test In₂O₃ catalysts in the hexagonal phase mainly exposing the h–In₂O₃(104) surface.

We synthesized bulk In₂O₃ (sphere) by the conventional precipitation method. We also prepared three additional crystalline In₂O₃ nanoparticles (plate, lamellar, and rod) using the same hydrothermal method only with different ratios of water and ethanol for the solvents (table S1). X-ray diffraction (XRD), scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HRTEM) data in Fig. 4 and fig. S4 show that both spherical and plate-shaped nanoparticles consists of a highly crystalline c–In₂O₃ structure with a = b = c = 10.118 Å [Joint Committee on Powder Diffraction Standards (JCPDS) 06-0416]. In contrast, for lamellar and rod forms of In₂O₃ (Fig. 4, A and B), the same analyses indicate that the crystal phase is h–In₂O₃ with a = b = 5.487 Å and c = 14.510 Å (JCPDS 22-0336) and no other phases are present (Fig. 4, C and D). TEM and HRTEM pictures showed spherical c–In₂O₃ nanoparticles (c–In₂O₃–S) of around 8 nm (Fig. 4C1), which form aggregates. Lattice fringes identified at multiple locations, yielded d-spacings of 0.292 and 0.178 nm, corresponding to the (222) and (440) planes of c–In₂O₃, respectively (Fig. 4C), which are multiples of the (111) and (110) planes. In addition, aberration-corrected scanning transmission electron microscopy (ac-STEM) studies on c–In₂O₃–S clearly show the [110] surface adjoining the [111] surface (Fig. 4C3). For other samples, the selected area electron diffraction (SAED) patterns (Fig. 4, D2 to F2, and fig. S4D2) demonstrate the single-crystalline structure of the c–In₂O₃ nanoplates (denoted as c–In₂O₃–P) and h–In₂O₃ nanolamellar (denoted as h–In₂O₃–L) and nanorod (denoted as h–In₂O₃–R) without the presence of twins or stacking faults. As shown in SEM and TEM images (Fig. 4 and fig. S4), the average thickness of c–In₂O₃–P is greater than that of h–In₂O₃–L (~36 nm versus ~20 nm), while the length of c–In₂O₃–P is smaller than the diameter of h–In₂O₃–L (~200 nm versus ~280 nm). According to the sixfold rotational symmetry observed in the SAED pattern of c–In₂O₃–P (Fig. 4D2 and fig. S4D2), the zone axis should be [111]. In addition, as observed from the HRTEM images, the main exposed planes of c–In₂O₃–P are [111], which are the only planes normalized by the set of (440) planes with a lattice spacing of 0.178 nm and the set of (211) planes with a lattice spacing of 0.413 nm, and both the interfacial angles are 60° (Fig. 4D and fig. S4, D and F). The preferential exposure of the [111] facet in the c–In₂O₃ nanocatalysts is consistent with our DFT prediction that this facet is considerably more stable than the other facets (fig. S1), although the c–In₂O₃–S nanocatalyst also exposes [110] facet. For h–In₂O₃, we predict the (012) facet to be slightly more stable than the (104) facet (fig. S1). As shown in Fig. 4A, the

Fig. 3. Schematic illustration of the most favorable CO₂ hydrogenation pathways on different c–In₂O₃ and h–In₂O₃ surfaces.

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(012)/(024) XRD peak intensities of $h$–In$_2$O$_3$-L are much higher than those of $h$–In$_2$O$_3$-R, and nearly no (012) peak can be observed for $h$–In$_2$O$_3$-R, while the rod structure exhibits a relatively higher (104) XRD peak intensity, which is the strongest peak of XRD patterns of $h$–In$_2$O$_3$-R. The HRTEM image of $h$–In$_2$O$_3$-L viewed along the [421] direction shows the (012) and (1T2) planes with a lattice spacing of 0.397 nm and an angle of 87.2° (Fig. 4E). On the basis of these results and the corresponding SAED image, we identified the flat plane...
of the h–In₂O₃-L as [012]. Although the shape of nanolamellar is irregular, the surface area of flat planes is obviously larger than that of side faces, and thus, we can conclude that the major exposed planes of h–In₂O₃-L are [012] (fig. S4G). Representative SEM and TEM images of h–In₂O₃-R shown in Fig. 4F1 and fig. S4 revealed that the nanorods with the diameter within 10 to 50 nm aggregated to form cactus-like morphology. On the basis of the HRTEM images and the SAED patterns of h–In₂O₃-R, we observed that the flat planes (perpendicular to the observation direction) of nanorods are [104]. Combining with the XRD results, we can also speculate that the [104] facets are exposed on the two sides of the nanorod from the analysis of more than 10 randomly chosen particles (Fig. 4F and fig. S4E). Therefore, the h–In₂O₃-R nanorods are mainly rounded by [104] planes (fig. S4H). We further simulated the three-dimensional morphology of h–In₂O₃-R by assuming preferentially exposed [104] surfaces, and the simulated morphology (fig. S4I) is consistent with the experimentally derived one. Consequently, h–In₂O₃-L contains a higher proportion of the exposed [012] facets than h–In₂O₃-R, whereas h–In₂O₃-R has a higher fraction of the exposed [104] facets than h–In₂O₃-L. We can synthesize c–In₂O₃ and h–In₂O₃ nanoparticles with different morphologies and dominant exposed planes by the simple preparation method in the absence of any long chain capping ligands, the commonly used agents in the synthesis process to control the nanocrystals’ morphology, which can exclude the additional effects of residual impurities on the catalytic performance. Tuning the ratio of the solvents and hydrothermal time may change the regularity and aspect ratio of the nanorod, which may further increase the proportion of the exposed [104] facets.

We conducted the CO₂ hydrogenation to methanol reaction over various In₂O₃ under the standard reaction conditions of 300°C, a total pressure of 5.0 MPa, 9000 ml g⁻¹ h⁻¹, and H₂/CO₂/N₂ = 73/24/3. Compared to c–In₂O₃-S, c–In₂O₃-P mainly exposing the {111} surface exhibits higher methanol selectivity and lower CO₂ conversion (Fig. 5A). This is consistent with our DFT prediction that compared with c–In₂O₃(110), c–In₂O₃(111) is favorable for methanol formation but has much weaker CO₂ adsorption strength in the b–CO₂²⁻ structure resulting in lower RWGS activity, so CO₂ adsorption strength is another important factor in determining the catalytic activity besides the energy barrier of the RDS. For h–In₂O₃ catalysts, h–In₂O₃-R has simultaneously better activity and methanol selectivity in comparison to h–In₂O₃-L. In addition, we obtained a maximum methanol selectivity of 85.4% over h–In₂O₃-R predominantly exposing [104] surfaces. As shown in table S2, the CO₂ conversion over h–In₂O₃-R is nearly twice higher than other bulk In₂O₃ and even higher than that over ZrO₂ support-promoted In₂O₃ catalyst under the similar reaction conditions. From our DFT calculations, the defective h–In₂O₃(104) surface exhibits superior performance for both CO₂ adsorption and CO₂ hydrogenation to methanol with the lowest RWGS activity, which is consistent with our experimental results. Therefore, the crystal phase and exposed surfaces of In₂O₃ catalysts do play important roles in determining the catalytic performance for CO₂ hydrogenation to methanol.

As shown in Fig. 5B, when the reaction temperature increases from 240°C to 360°C, methanol selectivity decreases significantly from 95.9 to 17.8% over the c–In₂O₃-S catalyst, although CO₂ conversion increases markedly. We observed similar trend of catalytic performance for h–In₂O₃-R. Nevertheless, methanol selectivity decreases only moderately from 97.9 to 73.4% when the temperature increases from 240°C to 360°C, while the CO₂ conversion increases sharply from 3.2 to 15.4%. The increase of reaction temperature favors the RWGS reaction, since it is an endothermic reaction. Our DFT calculations suggest that the defective h–In₂O₃(104) surface highly disfavors CO formation. Therefore, compared with the RWGS reaction, the methanol synthesis reaction over h–In₂O₃-R is more favorable even at the very high temperature of 360°C. The STY of methanol over c–In₂O₃-S reaches the maximum at 320°C, whereas the STY of methanol over h–In₂O₃-R increases linearly with the reaction temperature mainly due to the moderate decrease of methanol selectivity (Fig. 5C). At 360°C, the STY of methanol reached 10.9 mmol g⁻¹ cat⁻¹ hour⁻¹ over h–In₂O₃-R, twice higher than that over c–In₂O₃-S. The relative performance of these two catalysts agrees with our DFT predictions, further offering experimental evidence to support the strong promotional effect of the h–In₂O₃(104) facet on methanol synthesis from CO₂ hydrogenation. Moreover, we found higher space velocity and H₂/CO₂ ratio to favor methanol formation. Both the selectivity and STY of methanol increase significantly with increasing space velocity or H₂/CO₂ ratio (fig. S5A and Fig. 5D). The STY of methanol reached above 10.4 mmol g⁻¹ cat⁻¹ hour⁻¹ at weight hourly space velocity of >20,000 ml g⁻¹ hour⁻¹, outperforming the other In₂O₃ (38), In₂O₃/ZrO₂ (22), supported Cu (11), and noble metal (39) catalysts that are already excellent for CO₂ hydrogenation to methanol (table S2). In addition, when increasing the ratio of H₂/CO₂ to 6:1, the STY of methanol reached 9.0 mmol g⁻¹ cat⁻¹ hour⁻¹ over h–In₂O₃-R with methanol selectivity of 92.4% and CO₂ conversion of 17.6% at 300°C.

The h–In₂O₃-R catalyst displayed a good stability in a 136-hour test. Figure 5E shows that methanol selectivity increased markedly (from 71 to 85%), while CO₂ conversion decreased slightly (from 9.3 to 7.5%) during the initial 44 hours of test. Nevertheless, there was no further deterioration in the CO₂ conversion rate, and methanol selectivity maintained at 85 to 89% after 44 hours. It is very interesting that the STY of methanol kept at 6.2 mmol g⁻¹ cat⁻¹ hour⁻¹ for 136 hours on stream. As shown in fig. S6A, XRD analysis of the used catalysts showed that the average particle size of spent h–In₂O₃-R after 44 hours increased substantially from about 7 to 24 nm, whereas the In₂O₃ crystal size largely remained after the initial period (28 nm after 136 hours on stream). The formation of water vapor is inevitable for CO₂ hydrogenation to methanol, which will dissociate and fill the oxygen vacancies and decrease the catalytic activity. However, H₂O inhibition only moderately reduces the CO₂ conversion and STY of methanol over h–In₂O₃-R by 20% and 18%, respectively, when the amount of cofeeding water increases from 0 to 3.2 mol percent, and we observed a similar trend over c–In₂O₃-S (fig. S5). Further increasing the amount of cofeeding water, a much bigger drop in CO₂ conversion and STY of methanol occurred over c–In₂O₃-S than over h–In₂O₃-R, which is likely due to the lower H₂O adsorption strength on defective h–In₂O₃(104) surfaces and higher thermal stability of h–In₂O₃-R nanoparticles (fig. S5C).

The Brunauer-Emmett-Teller (BET) surface area of c–In₂O₃-S nanoparticles is up to 112 m² g⁻¹, and the other samples exhibit relatively lower specific surface areas (table S3). As thermal treatment can lead to the oxygen vacancy of In₂O₃, we further pretreated the samples in argon (Ar) at 300°C for 1 hour before the CO₂ hydrogenation reaction. The electron paramagnetic resonance (EPR) spectroscopy revealed a symmetrical signal at g = 2.004 over all fresh In₂O₃ samples, which corresponds to the oxygen vacancies, indicating that the vacancies were already present after the calcination (fig. S6B). After Ar thermal treatment, the increase in the intensity of the
EPR signal suggests the greater density of oxygen vacancies. In addition, the BET surface area of $c$--In$_2$O$_3$--S dropped sharply from 112 to 90 m$^2$ g$^{-1}$, while we observed only a slight decrease for other In$_2$O$_3$ samples due to the higher thermal stability (table S3). Compared with $c$--In$_2$O$_3$--P and $h$--In$_2$O$_3$--L, $c$--In$_2$O$_3$--S and $h$--In$_2$O$_3$--R have much higher concentration of surface oxygen defects (O defect, ~30% versus ~25%) estimated by measuring the number of O atoms next to the defects in O 1-s spectra by in situ near-ambient pressure x-ray photoelectron spectroscopy (NAP-XPS) at 300°C (Fig. 6A). This result is consistent with the higher activity obtained over the $c$--In$_2$O$_3$--S and $h$--In$_2$O$_3$--R samples for CO$_2$ hydrogenation (Fig. 5A and fig. SSD).

We further characterized the pretreated In$_2$O$_3$ oxides using CO$_2$--temperature-programmed desorption (TPD). We observed two types of absorption peaks for all samples (Fig. 6B). The low temperature $\alpha$ peak (100° to 200°C) corresponds to physisorbed CO$_2$, and the high temperature $\beta$ peak (350° to 450°C) corresponds to the chemisorbed CO$_2$ due to its reaction with thermally induced oxygen vacancy sites (22). Compared with $c$--In$_2$O$_3$ samples, the CO$_2$ desorption temperature of the $\beta$ peak for $h$--In$_2$O$_3$ is higher, indicating that CO$_2$ chemisorption around the oxygen vacancy site of $h$--In$_2$O$_3$ is stronger than those of $c$--In$_2$O$_3$ surfaces, which is in line with our DFT results. Signals of the $\beta$ peak for the $h$--In$_2$O$_3$ samples are more intense than those for $c$--In$_2$O$_3$, hinting at a greater...
number of thermal-induced oxygen vacancies. Moreover, we studied the reducibility of In$_2$O$_3$ by temperature-programmed reduction in hydrogen (H$_2$-TPR). Presence of the reduction peak in hydrogen before the onset of bulk reduction indicates that oxygen vacancies on both c-In$_2$O$_3$ and h-In$_2$O$_3$ catalyst surfaces could also form upon exposure to the reducing agents (fig. S6C). The h-In$_2$O$_3$ materials show much higher H$_2$ consumption in the low temperature region, suggesting that hexagonal In$_2$O$_3$ has more H$_2$-induced oxygen vacancies. Although H$_2$ reduction is favorable for the formation of oxygen vacancies, the BET surface area decreased significantly after the treatment of fresh In$_2$O$_3$ in pure H$_2$ at 300°C for 1 hour (table S3). We found that both c-In$_2$O$_3$-S and h-In$_2$O$_3$-R catalysts pretreated in Ar yielded higher STY of methanol than those activated in H$_2$ (fig. S5E), which may be due to the substantial drop in the surface area. Therefore, we activated the catalysts in Ar at 300°C before the CO$_2$ hydrogenation reaction.

We carried out operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to further understand the mechanism of CO$_2$ activation and hydrogenation over partially reduced c-In$_2$O$_3$ and h-In$_2$O$_3$ samples. As shown in fig. S7A, we observed several infrared (IR) peaks at 900 to 1100 cm$^{-1}$ after the adsorption of CO$_2$ on the In$_2$O$_3$ sample activated in Ar at 300°C, which was due to the interaction of CO$_2$ with the oxygen vacancies, as predicted by our DFT calculations (fig. S2). The adsorbed CO$_2$ species over h-In$_2$O$_3$-R were relatively stable and could not be removed completely by Ar treatment even at 350°C, whereas nearly no bands between 900 and 1100 cm$^{-1}$ were present over other In$_2$O$_3$ samples at 300°C (fig. S7A). For CO$_2$ adsorption at the oxygen vacancies of h-In$_2$O$_3$-R, which is consistent with our CO$_2$-TPD and DFT results. The introduction of H$_2$ generates both formate (HCOO*) and methoxy (CH$_3$O*) species over c-In$_2$O$_3$-S and h-In$_2$O$_3$-R even at the relatively low temperature of 240°C (Fig. 6, C and D). In addition, peak intensities of these species change slightly as the temperature increases from 240° to 300°C. These observations confirm the predicted reaction mechanism for the CO$_2$ hydrogenation to methanol reaction on the In$_2$O$_3$ catalyst.

As our DFT calculations showed the HCOO* and CH$_3$O* species to be the key intermediates during CO$_2$ hydrogenation over In$_2$O$_3$ catalysts, we also investigated the interaction between these species and the catalyst surface by in situ DRIFTS of formic acid and methanol adsorption. With the direct introduction of the formic acid vapor, the IR intensities for $\nu_{as}$ (OCO) and $\nu_{s}$ (OCO) of HCOO* are much higher over c-In$_2$O$_3$-S than those over h-In$_2$O$_3$-R (fig. S7B). This trend remained under reaction conditions as shown in Fig. 6 (C and D). In addition, we observed the notable IR peaks for CH$_3$O* upon the adsorption of methanol over c-In$_2$O$_3$-S and h-In$_2$O$_3$-R samples (fig. S7C). Previous studies found that the dehydrogenation of CH$_3$O* to HCOO* could occur over Cu/ZrO$_2$ at room temperature.
(40). In our case, the dehydrogenation of CH$_3$O* to HCOO* obviously occurred over c–In$_2$O$_3$-S at 30°C, but the peaks attributed to HCOO* were much weaker over h–In$_2$O$_3$-R, indicating the stronger stability of CH$_3$O* as opposed to HCOO* over the defective h–In$_2$O$_3$(104) surface (fig. S7C). Therefore, the defective h–In$_2$O$_3$(104) surface can substantially stabilize the key intermediates involved in methanol formation, which gives the higher methanol selectivity in catalytic CO$_2$ hydrogenation compared with cubic In$_2$O$_3$.

Our combined computational and experimental studies have demonstrated the structure sensitivity of the In$_2$O$_3$ catalyst during CO$_2$ hydrogenation in terms of both the phase and the exposed facet. In addition to the development of a promising high-performance In$_2$O$_3$ material for CO$_2$ hydrogenation to methanol, the present work also opens new avenues toward computer-aided rational design of efficient oxide catalysts for processes beyond methanol synthesis.

**MATERIALS AND METHODS**

**DFT calculations**

Periodic DFT calculations were carried out with the Vienna Ab Initio Simulation Package using the Perdew–Burke–Ernzerhof exchange–correlation functional and the projector–augmented wave potentials. The semicore 4d electrons of In were treated as valence electrons, with an energy cutoff of 400 eV and a Gaussian smearing potential. The semicore 4d electrons of In were treated as valence electrons, with an energy cutoff of 400 eV and a Gaussian smearing potential. The convergences for the electronic energy of the supercell and the force on all unconstrained atoms are $10^{-4}$ eV and 0.03 eV Å$^{-1}$, respectively.

We first optimized the primitive unit cells (PUC) of c–In$_2$O$_3$ and h–In$_2$O$_3$. The optimized h–In$_2$O$_3$ PUC have lattice parameters of $a = b = 5.55$ Å and $c = 14.18$ Å, consistent with the experimental data (a = b = 5.44 Å and c = 14.18 Å) (27). The c–In$_2$O$_3$(111) surface model is a (1 × 1) slab consisting of 48 O atoms and 32 In atoms distributed in two O–In–O trilayers optimized using a Γ-centered (3 × 3 × 1) Monkhorst-Pack k-point mesh. The supercell has a dimension of 14.44 Å by 14.44 Å by 15.04 Å. The model of the c–In$_2$O$_3$(110) surface is a (1 × 1 × 2) slab also with 48 O atoms and 32 In atoms but distributed in four atomic layers optimized using a Γ-centered (4 × 3 × 1) Monkhorst-Pack k-point mesh. The supercell has a dimension of 10.21 Å by 14.44 Å by 15.99 Å. The h–In$_2$O$_3$(102) surface model is a (2 × 2) slab consisting of 48 O atoms and 32 In atoms distributed in four atomic layers optimized using a Γ-centered (2 × 2 × 1) Monkhorst-Pack k-point mesh. The supercell has a dimension of 11.04 Å by 11.68 Å by 16.39 Å. The h–In$_2$O$_3$(104) surface model is a (1 × 1) slab consisting of 48 O atoms and 32 In atoms distributed in four atomic layers optimized using a Γ-centered (3 × 2 × 1) Monkhorst-Pack k-point mesh. The supercell has a dimension of 8.04 Å by 11.09 Å by 21.62 Å. The vacuum layer thickness is 10 Å between adjacent slabs.

An oxygen vacancy on the defective In$_2$O$_3$ surface forms upon removing one oxygen atom from the perfect In$_2$O$_3$ surface. The formation energy of an oxygen vacancy is the reaction energy of the thermal desorption of molecular oxygen (In$_2$O$_3$P → In$_2$O$_3$D + 1/2O$_2$), where In$_2$O$_3$P and In$_2$O$_3$D denote the perfect and defective surfaces. The adsorption energy of an adsorbate A on a slab surface S was defined as $E_{ads}(A) = E_{A/S} - (E_A + E_S)$, where $E_{A/S}$, $E_A$, and $E_S$ are total energies of the In$_2$O$_3$ slab with the adsorbate, the clean In$_2$O$_3$ slab, and the adsorbate as a free molecule, respectively. Transition states were obtained using the climbing image nudged elastic band method and were confirmed by further frequency calculations showing one and only one imaginary frequency. All structures were built and visualized using Materials Visualizer from Materials Studio.

**Catalyst preparation**

The spherical In$_2$O$_3$ was prepared by a precipitation method at 25°C. Typically, 16.26 g of In(NO$_3$)$_3$·4.5H$_2$O was dissolved in a mixture of 48 ml of deionized water and 140 ml of ethanol and a mixture of 36 ml of NH$_4$OH (25 weight % in H$_2$O), and 108 ml of ethanol was used as the precipitant. The product was aged at 80°C for 10 min and then filtered and washed with deionized water until the pH is 7. The filter cakes were dried overnight at 60°C and calcined in air at 300°C for 5 hours to get the oxides named as the c–In$_2$O$_3$-S. The c–In$_2$O$_3$-P, h–In$_2$O$_3$-L, and h–In$_2$O$_3$-R samples were prepared by the hydrothermal method. First, In(NO$_3$)$_3$·4.5H$_2$O was dissolved in a mixture of deionized water or ethanol, followed by addition of urea solution (urea dissolving into deionized water or ethanol) under vigorous stirring, and the mixture was stirred for 2 hours at room temperature. Then, the aqueous solution was transferred into a Teflon-lined autoclave and crystallized at 120°C for 17 hours. After centrifuging and washing by deionized water, the resulting product was dried overnight at 60°C and then calcined in air at 300°C for 5 hours to get the oxides. Changing the molar ratio of the deionized water and ethanol resulted in synthesizing In$_2$O$_3$ with different crystal phases and morphology structures. Synthesis parameters and corresponding nominations are listed in table S1.

**Catalyst characterization**

Powder XRD was analyzed in the 20 range 5° to 90° using a Rigaku Ultima 4 x-ray diffractometer with Cu Ka radiation, operating at 40 kV and 40 mA and in the step mode (0.0167°). Raman spectroscopy was performed using the Thermo Scientific DXR Raman microscope comprising a source with He-Ne laser of 532 nm. The textual properties such as surface area (BET) were derived from N$_2$ adsorption-desorption measurements by using a TriStar II 3020 instrument at −196°C, following the evacuation of samples in vacuum at 200°C for 10 hours. EPR measurements of the free radicals were recorded by using 5,5-dimethyl-1-pyrroline N-oxide as a probe at a Bruker Ems-plus instrument (Bruker A300). The morphology of the samples was observed by a SUPPRATM 55 SEM with an accelerating voltage of 2.0 keV. The nanostructure of catalysts was investigated by an ac-STEM instrument (JEM-ARM300F) at 300 kV and a FEI Tecnai G2 F20 S-Twin HRTEM, which was operated at 200 kV. CO$_2$-TPD experiments were carried out with an Omnistar GSD320 mass spectrometer. First, the catalyst (100 mg) was treated at 300°C for 60 min in a flow of pure Ar (60 ml min$^{-1}$) and then cooled down to 50°C. After that, the catalyst was saturated in flowing CO$_2$ for 1 hour with 30 ml min$^{-1}$, followed by flushing in Ar for 3 hours to remove any physisorbed molecules. The CO$_2$-TPD measurement was carried out at 50° to 750°C with heating rate of 10°C min$^{-1}$ under continuous flow of Ar at 40 ml min$^{-1}$. The H$_2$-TPR was carried out on a Micromeritics Chemisorb 2920 with a thermal conductivity detector. Typically, the catalyst sample (54 mg) was placed in a quartz reactor and pretreated in flowing Ar of 60 ml min$^{-1}$ at 150°C for 1 hour, followed by cooling down to 50°C. Then, the temperature was raised to 700°C at a rate of 5°C min$^{-1}$ with 5% H$_2$/Ar mixture gas (30 ml min$^{-1}$). In situ NAP-XPS was carried out on a SPECS Surface Nano Analysis GmbH equipped...
with two chambers, including an analysis chamber and a quick ample load-lock chamber. The analysis chamber is composed of a PHOIBOS NAP hemispherical electron energy analyzer, a micro-focus monochromatized Al Kα x-ray source with a beam size of 300 μm, a SPECS IQE-11A ion gun, and an IR laser heater. The samples were treated in Ar at 573 K for 1 hour, and then the spectra were collected in the analysis chamber. The in situ DRIFTS measurements were recorded on a Nicolet 6700 instrument equipped with a liquid N2-cooled mercury-cadmium-telluride detector including a cell having a cylindrical cavity (5 mm in diameter and 5 mm in vertical length) for the sample placement. About 20 mg of catalyst powder was placed in the cell and pretreated at 300°C for 1 hour under continuous flow of Ar with 30 ml min⁻¹ and then cooled to 50°C. The background spectrum was collected during the cooling process. After that, the catalyst was saturated in flowing CO2 of 20 ml min⁻¹ for 1 hour and followed by flushing in Ar for 20 min to remove any physically sorbed molecules. Then, the temperature was increased from 50° to 350°C with the Ar (20 ml min⁻¹) for 1 hour and then cooled down to 30°C. Then, the vapor of methanol or formic acid was introduced by Ar bubbling through the corresponding high pure liquid reagents for 8 min and then changed to introduce pure Ar.

Catalytic evaluation

The catalytic performance was carried out in a continuous-flow, high-pressure, fixed-bed reactor (d_int = 12 mm). In2O3 oxide (1.0 g) (40 to 60 mesh) with quartz sand mixing in equal volume was placed in a stainless-steel tube reactor. Before reaction, the sample was pretreated at 300°C for 1 hour in pure Ar (150 ml min⁻¹), and then reactant gas mixture with a H2/CO2/N2 ratio of 73/24/3 was introduced into the reactor under a pressure of 5.0 MPa. The effluents were analyzed online with a Shimadzu GC-2010C gas chromatograph equipped with thermal conductivity and flame ionization detectors. The CO2 conversion was calculated by an internal normalization method. The catalytic performance after 44 hours of reaction was typically used for discussion. The CO2 conversion denoted as X(CO2), CH3OH selectivity denoted as S(CH3OH) and STY of methanol denoted as STY(CO2) were calculated according to the following equations

\[
X(CO_2) = \frac{CO_2_{\text{inlet}} - CO_2_{\text{outlet}}}{CO_2_{\text{inlet}}} \times 100\%
\]

\[
S(CH_3OH) = \frac{CH_3OH_{\text{outlet}}}{CO_2_{\text{inlet}}} \times 100\%
\]

\[
STY(CH_3OH) = \frac{\text{GHSV} \times 0.24 \times X(CO_2) S(CH_3OH)}{1000 \times 22.4 \times 1000} \times 1000
\]

\[
= \frac{\text{GHSV} \times 0.24 \times X(CO_2) S(CH_3OH)}{22.4 \times 10000}
\]

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/content/full/6/25/eaaz2060/DC1

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