Flame Spray Pyrolysis as a Synthesis Platform to Assess Metal Promotion in In$_2$O$_3$-Catalyzed CO$_2$ Hydrogenation

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A plethora of metal promoters have been applied to enhance the performance of In$_2$O$_3$ in CO$_2$ hydrogenation to methanol, a prospective energy carrier. However, the lack of systematic catalyst preparation and evaluation precludes a direct comparison of their speciation and promotional effects, and consequently, the design of an optimal system. Herein, flame spray pyrolysis (FSP) is employed as a standardized synthesis method to introduce nine metal promoters (0.5 wt.%) into In$_2$O$_3$. Methanol productivity generally increased on M-In$_2$O$_3$ with selectivity following Pd > Pt > Rh = Ru = Ir > Ni = Co > Ag = In$_2$O$_3$ > Au. In-depth characterization, kinetic analyses, and theoretical calculations reveal a range of metal-dependent speciation which dictate catalyst architecture and degree of promotion. Atomically-dispersed promoters (Pd, Pt, Rh, Ru, and Ir) grant the highest improvement in performance, particularly Pd and Pt, which markedly promote hydrogen activation while hindering undesired CO formation. In contrast, metals in clustered (Ni and Co) and nanoparticle (Ag and Au) forms display moderate and no promotion, respectively. This study provides an atomic-level understanding of In$_2$O$_3$ promotion based on a unified protocol, and highlights the potential of FSP to engineer complex catalytic systems toward more efficient energy transformations.

1. Introduction

With a global annual demand of 80 million tonnes projected to further grow by 4% annually, methanol (CH$_3$OH) is a key platform chemical and prospective energy carrier envisaged to play a crucial role in global efforts tackling climate change by lowering the carbon footprint.[1–4] To this end, captured carbon dioxide (CO$_2$) and renewable hydrogen (H$_2$) attained from water electrolysis should be used as the feedstock to generate the so-called e-methanol. The thermocatalytic hydrogenation of CO$_2$ using heterogeneous nanostructured catalysts offers an efficient approach to realize this route.[4–6]

Among many catalytic materials studied, indium oxide (In$_2$O$_3$) has emerged as an attractive active catalyst due to its high methanol selectivity and stability.[7] Owing to its anisotropic surface, oxygen vacancies are selectively generated under reaction conditions forming an In$_3$O$_5$ ensemble, which is capable of activating and hydrogenating CO$_2$ to methanol very selectively, while the competitive reverse water-gas shift reaction (RWGS) forming carbon monoxide is energetically hindered.[8] Since hydrogen activation is the most demanding step in the mechanism, a plethora of metal promoters was investigated to alleviate this drawback and boost the catalyst activity.

Palladium nanoparticles incorporated by dry impregnation (0.9 wt.%)[8] were shown to cause substantial selectivity loss due to their RWGS activity, as well as stability issues owing to excessive In$_2$O$_3$ reduction by the spilled hydrogen.[9] Coprecipitation forming low-nuclearity palladium clusters anchored to the oxide surface (0.75 wt.%) curtailed these detrimental impacts, attaining the highest sustained methanol productivity of 0.96 g$_{\text{MeOH}}$ h$^{-1}$ g$_{\text{cat}}^{-1}$ among In$_2$O$_3$-based catalysts.[10] The same synthetic protocol was used to introduce platinum (0.58 wt.%) forming atomically dispersed Pt$^{2+}$ species granting a remarkable selectivity increase.[11] Platinum, rhodium, ruthenium, and silver introduced by deposition-precipitation (1.07, 1.07, 1.00, and 0.33 wt.%, respectively) as highly dispersed species also allowed to reach a very high selectivity but at very low reaction temperatures, where the RWGS reaction is thermodynamically unfavored.[12–15]

A methanol space-time...
yield (STY) of 0.76 gMeOH h\(^{-1}\) g\(_{\text{cat}}\)^{-1} was achieved over iridium-promoted indium oxide produced by wetness impregnation, but applying 10 wt.% Ir.\(^{[16]}\) Despite the high metal content, the promoter formed nanoparticles of only \(\approx 1\) nm, which favored methanol formation through the RWGS route.\(^{[16]}\) Similarly sized nanoparticles of gold (1 wt.%) on indium oxide generated by deposition-precipitation enabled a promotional effect owing to the creation of Au\(^{\delta+}\)-In\(_2\)O\(_{3-x}\) interfacial sites.\(^{[17]}\) Oxygen vacancy formation is also enhanced at similar Ag-In\(_2\)O\(_3\) and Rh-In\(_2\)O\(_3\) interfaces, resulting in increased CO\(_2\) activation on catalysts containing low loadings of silver (0.33 wt.%) and rhodium (0.64 wt.%), respectively.\(^{[15,18]}\) Cobalt nanoparticles decorated by In\(_2\)O\(_3\) were attained by coprecipitation,\(^{[19]}\) with charge transfer between oxide and metal curtailing the methanation properties typical of cobalt and fostering methanol production. A similar result was reported following a MOF-based route,\(^{[20]}\) generating a composite containing indium and cobalt oxides as well as mixed carbides of the two elements. The addition and interaction of nickel with In\(_2\)O\(_3\) has been more widely studied with a larger variety of synthesis methods and metal loadings. An optimal promotional effect was attained at 1 wt.% loading applying dry impregnation, with the formation of two-dimensional In\(_2\)Ni\(_3\) nanostructures supplying activated hydrogen, but not converting CO\(_2\) into methane.\(^{[21]}\) The latter only took place for nickel contents exceeding 15 wt.%, with the formation of some metallic nickel particles exhibiting their intrinsic behavior. Strong interaction of Ni with In\(_2\)O\(_3\) without alloying has concurrently been theorized at higher loadings, for flame-synthesized Ni-In\(_2\)O\(_3\) up to 6 wt.%\(^{[22]}\) as well as a 10 wt.% system prepared by wet chemical reduction.\(^{[22,24]}\) Overall, metal promoters supported on In\(_2\)O\(_3\) as low-nuclearity species appear to improve methanol productivity to a greater extent. Nonetheless, metal promoters were introduced using dissimilar synthesis methods and loadings on differently prepared In\(_2\)O\(_3\) leading to different architectures, and the resulting catalysts were tested under diverse temperature and pressure conditions, making comparison of catalytic data impractical. These scattered approaches preclude a direct and reliable comparison of speciation and promotional effects among metal-promoted In\(_2\)O\(_3\) catalysts, which is critical for the design of an optimal system.

Here, we employ flame spray pyrolysis (FSP) as a unified synthetic protocol to assess In\(_2\)O\(_3\) promotion by palladium, platinum, rhodium, ruthenium, iridium, nickel, cobalt, gold, and silver, on the basis of a metal loading of 0.5 wt.%. Equivalent catalytic evaluation, extensive density functional theory (DFT) simulations, in-depth characterization, and kinetic analyses unveil the metal speciations and their effects on oxygen vacancy formation, hydrogen splitting, as well as activity patterns in CO\(_2\) hydrogenation to methanol and in the competing RWGS. Our study provides an atomic-level rationalization of In\(_2\)O\(_3\) promotion and uncovers common trends and descriptors for different metal dopants based on a standardized synthesis approach, with potential for extrapolation to other catalysts for energy applications.

### 2. Results and Discussion

#### 2.1. Impact of Promoters on Catalytic Performance

FSP (Figure 1) was selected as the method to synthesize the series of metal-promoted In\(_2\)O\(_3\) catalysts due to its superior control over crystal size, morphology, and specific surface area of the synthesized materials.\(^{[22–27]}\) Additionally, FSP permits a more efficient utilization of expensive metal promoters since it often leads to spatially controlled deposition of metal entities on the surface of carriers without promoting bulk incorporation, a classic drawback of coprecipitation methods.\(^{[28]}\) Finally, FSP is an up-scalable technology capable of producing multi-component materials with well-specified composition, high purity, and thermal stability in a single-step approach, without the need of solvent-intensive washing and post-thermal treatments commonly required for other synthesis methods.\(^{[25,29–31]}\)

![Figure 1. Scheme of the FSP method for the preparation of M-In\(_2\)O\(_3\) catalysts.](image)
After screening the effect of varying loadings up to 2 wt.% with Pd and Pt (vide infra), the nominal loading of 0.5 wt.% was chosen to favor the formation of atomically-resolved promoter structures on In$_2$O$_3$ necessary for the purpose of the study. The actual metal loadings of the promoted catalysts as determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Table S1, Supporting Information) closely matched the nominal loadings. X-ray diffraction (XRD) profiles (Figure S1, Supporting Information) show that In$_2$O$_3$ is present in all fresh catalysts as a crystalline phase, while reflections corresponding to the pure metals are absent indicating the lack of nanoparticles larger than 4 nm. The chosen flame and flow parameters result in consistent In$_2$O$_3$ average crystallite sizes ($d_{\text{in}_{\text{O}_3}}$) of 25–29 nm for all freshly promoted catalysts (Table S2, Supporting Information), except for Ni-In$_2$O$_3$ with moderately larger particles (34 nm). Surface areas of the promoted catalysts were also lower than that of In$_2$O$_3$ prepared by the same method, in line with previous evidence for catalysts attained by different routes.[10,21]

CO$_2$ hydrogenation to methanol was conducted at 553 K and 5 MPa over pristine and metal-promoted In$_2$O$_3$. The catalytic data (Figure 2 and Figure S2, Supporting Information) indicate that, except for Au- and Ag-doped systems, all other catalysts exceeded the overall CO$_2$ conversion ($X_{\text{CO}_2}$) and methanol space-time yield (STY, colored bars) during CO$_2$ hydrogenation over undoped In$_2$O$_3$ and M-In$_2$O$_3$ catalysts (0.5 wt.% of metal) prepared by FSP. The methanol STY is assessed at WHSV = 24000 cm$^{-3}$ h$^{-1}$ g$_{\text{cat}}$$^{-1}$, while $S_{\text{MeOH}}$ at constant CO$_2$ conversion (∼3%) and variable WHSV. Averaged values measured over 24 h on stream are presented with their corresponding error bars. Reaction conditions: $T = 553$ K, $P = 5$ MPa, and $H_2$/$\text{CO}_2 = 4$.

Figure 2. Methanol space-time yield (STY, colored bars) and selectivity ($S_{\text{MeOH}}$, beige bars) during CO$_2$ hydrogenation over undoped In$_2$O$_3$ and M-In$_2$O$_3$ catalysts (0.5 wt.% of metal) prepared by FSP. The methanol STY is assessed at WHSV = 24000 cm$^{-3}$ h$^{-1}$ g$_{\text{cat}}$$^{-1}$, while $S_{\text{MeOH}}$ at constant CO$_2$ conversion (∼3%) and variable WHSV. Averaged values measured over 24 h on stream are presented with their corresponding error bars. Reaction conditions: $T = 553$ K, $P = 5$ MPa, and $H_2$/$\text{CO}_2 = 4$.

impregnation,[10,16,21] deposition-precipitation methods,[15,14] as well as FSP,[22] which also corroborates the superior performance of Pd and Pt. However, the performance of Au-In$_2$O$_3$ was markedly lower than that of a previous study,[17] hinting a limitation and fundamental difference of FSP compared with the deposition-precipitation method.

Since Ni- and Pd-In$_2$O$_3$ catalysts prepared by dry impregnation and coprecipitation, respectively, were reported to experience distinct deactivation levels during hydrogenation of hybrid CO$_2$-CO feeds,[14] the sensitivity of all systems to co-fed CO was also investigated using a feed with CO$_2$/CO ratio = 4 at otherwise the same $T$, $P$, $H_2$/$\text{CO}_2$, and WHSV conditions (Figure S3, Supporting Information). Ir-, Ru-, Rh-, Pt-, and Pd-In$_2$O$_3$ catalysts still show superior performance. However, except for Co-In$_2$O$_3$, methanol productivity is generally inferior for all catalysts in the hybrid CO$_2$-CO feed in comparison to CO$_2$ hydrogenation, most likely due to inhibition of active sites by CO. Specifically for Ni-In$_2$O$_3$, the formation of volatile Ni-carbonyl compounds promoting the sintering into metal nanoparticles is known to contribute to its irreversible deactivation.[12] Similar to undoped In$_2$O$_3$, the presence of CO does not induce a detrimental effect on methanol production over the Co-In$_2$O$_3$ catalyst, whose catalytic activity could be attributed to undoped In$_2$O$_3$ active sites.

For unpromoted In$_2$O$_3$ and Au-, Ag-, Co-, and Ni-promoted In$_2$O$_3$, sintering occurs upon exposure to the reaction mixture and slightly increases during 24 h on stream, as evidenced by the corresponding increase in $d_{\text{in}_{\text{O}_3}}$, as determined by XRD (Table S2, Supporting Information). This trend is also reflected in the marked decrease of Brunauer-Emmett-Teller (BET) surface area ($S_{\text{BET}}$) upon use for all catalysts, with the exceptions of Ir- and, notably, Ru-doped solids, which stand out as the most robust. In general, both $S_{\text{BET}}$ and $d_{\text{in}_{\text{O}_3}}$ further decrease and increase, respectively, upon exposure of catalysts to the hybrid CO$_2$-CO feeds (Table S2), which likely explains their diminished performance in such conditions. Overall, the methanol STY remained unaltered from 2 to at least 24 h on stream for all catalysts except for Au-In$_2$O$_3$, and therefore reflects stable performance. 2 h was thus considered as the time needed for catalyst activation under in situ conditions. Overall, the similar
In$_2$O$_3$ crystallite sizes and the lack of large differences in the BET surface area of activated catalysts show that bulk porous properties would not be a significant confounding factor.

2.2. Promoter Speciation

The speciation of the metal promoters was elucidated by a battery of experimental and theoretical characterization techniques. The promoters were expected to be adsorbed on the In$_2$O$_3$ surface, to be incorporated into the In$_2$O$_3$ lattice, or to segregate into nanoparticles. Characterization was performed on the activated (2 h under reaction conditions) and used (24 h) catalysts. High-resolution electron transmission microscopy (HRTEM, Figure 3a and Figures S4 and S5, Supporting Information) confirmed that highly crystalline In$_2$O$_3$ particles are present in both undoped and promoted catalysts, as indicated by XRD (Figure S1, Supporting Information).

![Figure 3](image_url)

**Figure 3.** a) HRTEM micrographs of In$_2$O$_3$ and b–j) HAADF-STEM micrographs with EDX maps of M-In$_2$O$_3$ after activation in CO$_2$ hydrogenation for 2 h. Scale bars are equivalent to 10 nm unless otherwise indicated. Indium and metal promoter M are colored in blue and red in EDX maps, respectively. Activation conditions: $T = 553$ K, $P = 5$ MPa, $H_2/CO_2 = 4$, and WHSV = 24000 cm$^3$ h$^{-1}$ g$_{cat}^{-1}$. 

Adv. Energy Mater. 2022, 12, 2103707
For Au- and Ag-In₂O₃, some metal nanoparticles with variable sizes were clearly visible in the HRTEM images (Figures S4 and S5, Supporting Information). In addition, Au, Ag, and Co nanoparticles and smaller clusters are also evidenced by high-angle annular dark-field scanning transmission electron microscopy coupled to energy-dispersive X-ray spectroscopy (HAADF-STEM-EDX, Figure 3b–d). Interestingly, no metal nanoparticles were detected for any of the other promoters (Figure 3e–i), which are highly dispersed on In₂O₃ as low-nuclearity species, with Ir, Ru, Rh, Pt, and Pd likely less clustered than Co and Ni. These findings are well in line with previous studies in which nanoparticles were only observed at metal loadings well above the 0.5 wt.% chosen to attain an atomic dispersion.[12,16,21] Additionally, temperature-programmed reduction with hydrogen (H₂-TPR, Figure S6, Supporting Information) revealed no distinguishable signals indicative of the reduction of promoters to pure metallic nanoparticles, not even for Au- and Ag-In₂O₃, suggesting that all catalysts feature strong metal-support interactions.

Most of the promoters are fully reduced to metallic species under reaction conditions, except for Co- and Rh-In₂O₃, as indicated by X-ray absorption near-edge structure spectra (XANES, Figure S7, Supporting Information). While the spectra of these two catalysts resemble that of cationic Co²⁺ and Rh⁺⁺ in CoO and Rh₂O₃, respectively, the white-line intensity and position are not identical to those of the corresponding reference oxides. This suggests that these promoters are indeed in an oxidic state, but strongly interacting with In₂O₃. Changes in the electronic structure of metallic Au, Ni, Ir, Ru, and Pt, with respect to the corresponding metal foils, upon interaction with In₂O₃, are also observed, hinting the presence of M–In bonds. Analysis of the extended X-ray absorption fine structure (EXAFS, Figure 4a and Table S3, Supporting Information) in fact revealed mainly M–In bonds in the first coordination shell of Ir, Ru, and Pt with coordination numbers of ≈3–5. This confirms high dispersion of these metals and (considering a strong correlation between the Debye-Waller factors with the number of neighbors) is in line with the theoretical models of atomic dispersed dopants, In₁MO₃, in Figure 4b. The coordination number of the Au–In shell is higher, indicating clustering of Au, in agreement with microscopy findings (Figure 3a). The presence of M–M along with M–In bonds cannot be completely excluded, due to similar scattering factors of indium and metals such as palladium, rhodium, and silver. Nonetheless, based on the low metal loading, high dispersion of Pd and Rh, and, more importantly, the harsh catalyst synthesis and CO₂ hydrogenation conditions, these elements are likely to also form small intermetallic clusters with indium, as suggested in previous studies.[10] Since no oxygen shell is present for Au- and Ag-In₂O₃, these metals are very unlikely to be incorporated into the oxide bulk structure, and therefore, they form a mixture of nanoparticles and low-nuclearity species, as supported by XANES and microscopy findings. In contrast, M–O and M–O–In bonds are clearly present in Co- and Rh-promoted systems, indicating that In₂O₃ contains a significant population of cobalt and rhodium species incorporated into its lattice structure, at least near the surface. Furthermore, cobalt forms surface CoOₓ clusters and nanoparticles in line with microscopy and XANES. On the other hand, similarly to other promoters (i.e., palladium, iridium, platinum, and ruthenium), rhodium also forms surface Min₃ ensembles. Besides, nickel may alloy with indium into extended structures, as previously reported.[31] It is worth noting that a weak signal at the oxygen shell is evidenced for Pd-In₂O₃ catalysts, suggesting the formation of M–O bonds, while such signals are absent for Ir-, Ru-, and Pt-In₂O₃. Still, only a few palladium atoms are expected to be bound to oxygen upon reaction conditions, mostly incorporated to surface lattice sites as In₂MO₃ (Figure 4b). X-ray photoelectron spectroscopy (XPS) confirmed that all metal promoters are present at the surface (In₁MO₃ in Figure 4b), although cobalt is most likely incorporated into bulk In₂O₃ (Co@In₂O₃, bulk in Figure 4b), as suggested by the particularly low intensity of the Co 2p signal for Co-In₂O₃ (Figure S8, Supporting Information) and computed Bader charges and XPS signals (Figure S19, Supporting Information). In contrast to XANES, most promoters appear partially or fully oxidized according to XPS. Such contrasting results are likely owing to samples being shortly exposed to air before XPS measurements. For Au-In₂O₃, metallic Au is detected but its binding energy is shifted to lower values, indicating a strong metal–oxide interaction between Au nanoparticles and In₂O₃ at interfacial sites, as previously reported for Au-In₂O₃ systems. This observation is further corroborated by XANES findings (Figure S7, Supporting Information), in which a more intense white line peak is evidenced for Au-In₂O₃ compared to the metallic gold foil reference. In addition, microscopy images and EDX maps (Figure 3 and Figure S5, Supporting Information) clearly show the presence of Au nanoparticles supported on In₂O₃.

Experimental characterization shows that FSP in general maximizes the dispersion of the metal promoter atoms on the In₂O₃ surface, making their presence as single sites or as low-nuclearity clusters more feasible as compared to incorporation of the atoms into the lattice. Therefore, DFT was employed to explore the presence of promoters as adatoms at the 26 non-equivalent adsorption sites on the In₂O₃(111) surface. They correspond to top, bridge, and three-fold positions, as shown in Figure S13, Supporting Information. This surface is corrugated and features a pocket and a protrusion, being the latest active site for CO₂ hydrogenation upon vacancy formation. Interestingly, the most favored adsorption site for all metal promoters is the bridge position (In₁M₂O₃ in Figure 4b) between two oxygen atoms in the protrusion (Table S7, Supporting Information). In turn, adsorption at this position is more favorable than incorporation into lattice sites for all metals, except Ru (Figure 4c and Figure S15, Supporting Information). Au does not easily incorporate nor deposit, which fosters the formation of nanoparticles (Mₓ, in Figure 4b). The large Au nanoparticles were modeled as an Au(111) surface whereas the smallest possible Auₙ cluster capable of blocking an In₂O₃ active site was modeled as an Auₙₓₙ ensemble, whose formation is strongly exothermic (~0.98 eV, Figure S20, Supporting Information). Under the CO₂ hydrogenation conditions, H₂ dissociates heterolytically on a surface M–O pair forming hydride (MH) and hydroxy (OH) groups on the In₁M₂O₃ ensemble, followed by concomitant water formation and desorption leading to the In₁M₂O₃ moiety (Figures S22 and S23, Supporting Information). Then, the diffusion of the metal from the bridge to the oxygen vacancy position is feasible, forming the InₐMO₃ ensemble. This structure is in line with the metallic character.
adopted by the metal promoters in the XANES spectra (Figure S7, Supporting Information) and $M$–In signals showed in the EXAFS spectra (Figure 4a) for the activated catalysts, and in particular for Pd, Pt, Ru, and Ir. Additionally, we explored the possibility that the metal promoters could be incorporated into the In$_2$O$_3$ lattice, either at bulk or surface positions ($M$@In$_2$O$_3$,bulk and In$_2$M@O$_5$ in Figure 4b), as shown in Section S2.1, Figures S14–S18, and Table S8, Supporting Information. However, this speciation would only be likely for Co and Rh (Figure 4d and Figure S16, Supporting Information) and such sites would not be relevant for catalysis. Finally, Pd and Rh can form In$_2$M$_2$O$_6$ clusters, with a catalytic activity akin to that of In$_3$M@O$_4$ (Figure 4e, Section S2.2, and Table S9, Supporting Information).[10]

To summarize, the metal speciation derived from experimental characterization and DFT modeling show that under CO$_2$ hydrogenation conditions, the most active promoters (Pd, Pt, Rh, Ru, and Ir) are deposited on the In$_2$O$_3$ surface predominantly as In$_3$M@O$_4$. This ensemble cannot be discarded for Co, Ni, Ag, and Au. Co is mostly present in an oxidic state, either as single atoms incorporated into the bulk In$_2$O$_3$ sites (Co@In$_2$O$_3$,bulk) or as CoO$_2$ clusters and nanoparticles. Additionally, Ni can alloy with the support,[21] and Ag and Au can form metallic nanoparticles. As metals are generally favored

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**Figure 4.** a) EXAFS with model fit for $M$–In$_2$O$_3$ catalysts after activation in CO$_2$ hydrogenation for 2 h (K-edge for Ag, Co, Ni, Ru, Rh, and Pd whereas L$_3$-edge for Au, Ir, and Pt). b) Models employed in DFT simulations to rationalize different metal promoters speciation and promotional effects. Oxygen, indium, and metal promoter atoms are shown in red, green, and blue, respectively. Shaded red atoms represent oxygen atoms where the vacancy formation is considered. Potential energies relationship between c) dopant incorporated into its most favored In$_2$O$_3$ lattice site versus dopant deposited as adatom at a bridge site ($E_{M@In_{2}O_{3,bulk}}$ and $E_{M@In_{2}O_{3,bridge}}$, respectively); and d) surface versus bulk incorporated species ($E_{M@In_{2}O_{3, bulk}}$ and $E_{M@In_{2}O_{3, bridge}}$, respectively). Dashed and dotted black lines indicate the relative stability of most stable speciation and the constant offset energy required to incorporate at surface and bulk sites, respectively. e) Energy required to form In$_2$M$_2$O$_4$($E_{In_{2}MO_{4}}$) metal promoter dimers versus the sum of their precursors potential energies ($E_{In_{2}MO_{4}} + E_{In_{2}MO_{3}}$). Activation conditions: $T = 553$ K, $P = 5$ MPa, H$_2$/CO$_2 = 4$, and WHSV = 24000 cm$^3$ h$^{-1}$ g$^{-1}$. 

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to be deposited on the In$_2$O$_3$ surface rather than incorporated into the In$_x$O$_y$ lattice by substituting an In atom, the In$_x$MO$_3$ and M@In$_x$O$_y$ bulk models are not considered. As such, the models that are relevant in further mechanistic evaluations are the single site In$_3$MO$_5$ (all metals) and the M(111) surface (Ag and Au nanoparticles).

### 2.3. Effect of Promoters on Vacancy Formation

To investigate the impact of the promoters on the formation of oxygen vacancies, H$_2$-TPR experiments were conducted for all fresh samples (Figure S6, Supporting Information). Generally, all catalysts show three features in the low-temperature range (273–700 K), which are associated with hydrogen consumption to form surface oxygen vacancies. There is no significant increase in the peak intensities except for Ni-In$_2$O$_3$, which is capable of stripping many surface oxygen atoms based on a previous study.$^{[21]}$ XPS was also measured to gather additional information about oxygen vacancies on the activated catalysts by fitting the XPS O 1$s$ spectra (Figure S9a, Supporting Information) with the signals signifying oxygen atoms next to a defect (O$_{\text{defect}}$) indirectly (vide infra) assigned to oxygen vacancies (Table S3, Supporting Information).$^{[7,32,34]}$ The O$_{\text{defect}}$ proportion remains virtually unchanged upon activation for all metal-promoted systems compared to In$_2$O$_3$ (14–19% and 17%, respectively), with the notable exception of Pd-In$_2$O$_3$ (34%). This is in line with previous results on this system prepared by coprecipitation.$^{[10]}$ DFT models also show that additional oxygen vacancy formation is favored for Pd-In$_2$O$_3$ systems (Table S11, Supporting Information), both for models with the Pd atom deposited at surface bridge and a position previously occupied by an oxygen atom (In$_3$MO$_5$O$_6$ and In$_3$MO$_3$) as well as incorporated into the surface In$_2$O$_3$ lattice (In$_2$MO$_4$). However, it must be noted that quantification of oxygen vacancies using such XPS analyses is not foolproof as surface adventitious hydroxyl signals are measured in lieu of actual vacancies that heal upon exposure to air, and contributions from OH groups to the O 1$s$ signal in the O$_{\text{defect}}$ region have been computation-ally suggested to be difficult to separate.$^{[35,36]}$ Hence, further complementary in situ or operando studies (e.g., EPR) would be required to attain a more accurate quantitative assessment of the density of oxygen vacancies. No detrimental over-reduction of In$_2$O$_3$ up to metallic indium occurs under reaction conditions, as evidenced by the InMNN Auger spectra showing that indium species are always in the 3+ state (Figure S9b, Supporting Information), supporting the XRD results. Alloy formation between reduced In$_2$O$_3$ and metal promoters is therefore not likely. However, at different synthetic or reaction conditions where the metal promoters and In$_2$O$_3$ could be reduced, alloy formation cannot be completely discarded as predicted by DFT (Table S12, Supporting Information).

To compare the ease of forming surface oxygen vacancies on undoped In$_2$O$_3$ and M-In$_2$O$_3$, such mechanisms were computed for the thermodynamically favored clean In$_2$O$_3$(111) surface (Figure S21, Supporting Information) and for In$_3$MO$_5$ surface models (Figures S22 and S23, Supporting Information). For undoped In$_2$O$_3$, vacancy formation eventually leads to the active In$_3$O$_5$ ensemble for CO$_2$ hydrogenation as described earlier. The mechanism begins with either homolytic or heterolytic dissociation of H$_2$, to form two surface *OH species ($\Delta E_{\text{OH}} = -2.60$ eV, $E_h = 1.08$ eV) or an InH*OH pair ($\Delta E_{\text{InH-OH}} = 0.64$ eV, $E_h = 0.36$ eV). The high stability of the hydroxyl groups suggests that the surface can be highly hydroxylated under reaction conditions, in line with a previous report$^{[36]}$ and our XPS data (Table S3, Supporting Information). The vacancy formation proceeds then with water formation and desorption, being the heterolytic path going through InH*OH the most favored (Figure S21 and Table S13, Supporting Information). For the doped systems, the formation of a second oxygen vacancy on the already reduced In$_3$MO$_5$ configuration leads to the In$_3$MO$_4$ active ensemble. This process starts with the homolytic dissociation of H$_2$ on the metal dopant, followed by the formation of MH and adjacent *OH groups, then combining into a water molecule that finally desorbs (Figures S22 and S23, Supporting Information). Exceptionally, an additional third vacancy can be formed, and such a process is most exothermic for Pd-In$_2$O$_3$ (Table S11, Supporting Information) in agreement with its XPS-determined O$_{\text{defect}}$ proportion (Table S3, Supporting Information). The mechanism of CO$_2$ hydrogenation would not be affected by the presence of the third vacancy, as only two are needed to accommodate the metal and the adsorbed CO$_2$. In contrast to the undoped In$_2$O$_3$ system, the homolytic H$_2$ dissociation is barrierless for all M-In$_2$O$_3$ catalysts except for Ag and Au promoters ($E_h = 2.15$ and 1.73 eV, respectively). These two metals lead to an alternative mechanism, where H$_2$ is heterolytically dissociated on an M–O pair leading to *OH and MH groups ($E_h = 0.39$ and 0.30 eV for Au and Ag, respectively). Hydrogen splitting is then followed by water formation and desorption (Figure S22, Supporting Information). In addition, the most demanding elementary step to generate the active ensemble, both for clean and doped systems (In$_2$O$_3$ and M$_x$O$_y$, respectively), is water formation from MH + *OH ($E_h$ between 0.88 and 1.21 eV, except for Pt, $E_h = 0.58$ eV, Figure S5 and Table S13, Supporting Information). The water desorption step was found to be in a narrow range between 0.66 and 0.81 eV, easily surmountable under CO$_2$ hydrogenation conditions.

### 2.4. Kinetic and Mechanistic Insights

Kinetic analyses were conducted to experimentally assess the mechanistic origin of promotional effects. Previous theoretical studies on M-In$_2$O$_3$ showed that CO can act as an intermediate in the CO$_2$ hydrogenation to methanol, a process that is preferred when small clusters typically containing 4 metal atoms are formed around the active site.$^{[14,16,24]}$ However, this mechanism requires at least 3 exposed metal atoms, as observed in a previous Pd-In$_2$O$_3$ study.$^{[10]}$ Such a mechanism should not apply to M-In$_2$O$_3$ catalysts synthesized by FSP, as a general decrease in methanol productivity was observed for CO-CO$_2$ feeds (Figure S3, Supporting Information). Moreover, experimental and DFT characterization carried out in this work point to single-metal sites (In$_3$MO$_5$) as the dominant speciation of the most active M-In$_2$O$_3$ systems (Pd, Pt, Rh, Ru, Ir). It may also be present for the remaining metals, but less likely Au and Co. Therefore, only the alternative path having formate (HCO$_2$*) as
In the methanol path, two hydrides are transferred to the C of CO₂ leading to CH₂O* and then CH₃OH*, which is protonated to CH₃OH. The C–OH bond then breaks and the OH is desorbed as water upon a proton transfer to obtain formaldehyde (CH₂O*). Finally, a proton and a hydride are transferred to CH₂O* to form CH₃OH*, which desorbs. In contrast, the RWGS competing path starts when CO₂ is protonated to form a carboxylate (–COOH) which is protonated and dehydrated to produce CO.

The apparent activation energies for methanol synthesis and the RWGS reaction (Figure 6a), derived from catalytic tests conducted at variable temperature (Figure S10, Supporting Information), show some general trends with selectivity patterns. For instance, activation barriers for methanol synthesis are generally lower than for the RWGS reaction for all promoted systems in comparison to undoped In₂O₃, with Au-In₂O₃ being an exception. For the latter, the smaller activation energy for the RWGS reaction rationalizes its lower selectivity to methanol compared to undoped In₂O₃ and the other M-In₂O₃ systems. It is noteworthy that some systems, including In₂O₃, show slightly lower activation barriers for RWGS than for methanol formation, even though these systems are more selective to methanol. Besides, there is no correlation between the apparent activation energies and the observed reaction rates (Figure S12, Supporting Information), suggesting that there is an important contribution of other phenomena which do not depend exponentially on 1/T (i.e., gas diffusion, on-surface diffusion, adsorption, etc.) to drive selectivity. In principle, the higher degree of hydroxylations/defects on these systems (Table S3, Supporting Information) could also play a role as more surface oxygen atoms bound to protons could reduce the entropic penalty to form CO, or in the final step to form methanol. The excess of hydroxyl groups can also interconvert to hydrides favoring C–H hydrogenations.

Since promotion of In₂O₃ is often related to the ability of metal dopants to facilitate hydrogen activation, apparent reaction orders with respect to this reactant were determined from experiments at variable partial pressures of H₂ in the feed (Figure 6b and Figure S11, Supporting Information). For methanol synthesis, the reaction order decreased for all metal-promoted systems compared to In₂O₃ except for Au-In₂O₃. Pd- and Pt-In₂O₃ reach the lowest values (≈0.9 instead of 1.3 for undoped In₂O₃), suggesting a higher availability of hydrides (MH) and therefore a promotion of all C–H hydrogenation reactions for these systems. For the RWGS reaction, the reaction orders significantly increased for Au-In₂O₃, while remaining at their lowest for all other systems, indicating that split H₂ is predominantly involved in the CO pathway on Au as opposed to the other promoted systems. Given the limited insights, these trends from kinetic analysis were supplemented by DFT-derived mechanistic elucidations in order to better account for the structure-selectivity patterns of each individual promoter.

Energy profiles for methanol and CO formation for undoped In₂O₃ and the nine metal-promoted In₂O₃ systems are presented in Figures S24–S26, Supporting Information. The In₃MO₄ ensemble was selected as the most representative for the promotion considering all experimental characterization and previous theoretical simulations, to explore the reactivity toward CO₂ hydrogenation. Significant differences between the profiles for clean In₂O₃ and M-In₂O₃ were not found. Thus, the CO₂ to methanol reaction mechanism does not have a significant contribution.

Figure 5. a) Schematic of water formation through heterolytic H₂ splitting and subsequent formation of the In₂O₃ and In₃MO₄ active ensembles, for clean and doped In₂O₃(111), respectively. Oxygen, indium, metal promoter, and hydrogen atoms are shown in red, green, blue, and white, respectively, in the initial (top), transition (middle), and final (bottom) states. b) Activation energy (Eₐ) of forming a water molecule, the most demanding elementary step in the formation of the In₂O₃ or In₃MO₄ active ensemble for all systems except Pt-In₂O₃. The bar for Au is shown in gray as there is no evidence that the In₃AuO₄ ensemble exists in detectable quantities.

the key intermediate is responsible for CO₂ hydrogenation to methanol. This mechanism requires that the active sites already contain an oxygen vacancy (In₂O₃ and In₃MO₄ for clean and doped systems, respectively) to accommodate the CO₂ molecule. It begins with the adsorption of CO₂ and H₂ on these ensembles, and then diverges into the methanol and CO paths.
in the promotional effect exhibited by $M$-In$_2$O$_3$ systems. Besides, the lack of correlation between the apparent activation energies and the STY reveals that an entropic process is controlling the net rate (Figure S12, Supporting Information), which could be the availability of either vacancies or $M$H species at the active site. In addition, in order to explore the activity of Ag and Au nanoparticles, energy profiles were computed on Ag(111) and Au(111) surfaces (Figure S27, Supporting Information). The CO$_2$ conversion to methanol follows a different mechanism on bulk metals, where CO$_2$ adsorbs and is then protonated and dehydrated to form CO. Then, CO either desorbs or follows two parallel paths that after concomitant hydrogen transfers lead to methanol. Au and Ag metal surfaces strongly hinder the CO$_2$ adsorption and favored desorption rather than hydrogenation of CO, which explains the lack of activity and selectivity of Au- and Ag-In$_2$O$_3$ towards methanol formation, as they contain mostly metal nanoparticles. In addition, inactive Au$_n$ ensembles containing as few as 3 Au atoms (Figure S20, Supporting Information) can form on the In$_3$AuO$_x$ ensemble and block additional In$_2$O$_3$ active sites, thus lowering the activity and selectivity to methanol.

To provide a comprehensive rationalization of the promoters’ speciation in $M$-In$_2$O$_3$ catalysts under CO$_2$ hydrogenation conditions and its impact on methanol selectivity and productivity, we correlated the methanol STY over $M$-In$_2$O$_3$ for each promoter with the standard formation enthalpy ($\Delta^\circ_{f} H^\circ$) of its oxide $MO_x$ (Figure 7 and Figure S28, Supporting Information). As a general rule, the most active promoters are those more metallic with a less exothermic $\Delta^\circ_{f} H^\circ$, as they promote homolytic hydrogen splitting. Yet, if the promoter has a poor affinity to oxygen, it will not form oxidic precursors and therefore will rather nucleate into metallic nanoclusters and nanoparticles under FSP synthesis conditions (i.e., Ag and Au). In contrast, if these metals were stabilized as adatoms on In$_2$O$_3$ surface [In$_3$MO$_x$], they will be highly active.[17,39] In cases where the promoter has a high affinity to oxygen, such as Co, it will tend to incorporate to the bulk or to form bulk metal oxides.

The key findings attained by performance assessment, characterization, and DFT simulations are graphically summarized in Figure 8. Overall, the promotional effect in $M$-In$_2$O$_3$ systems. Besides, the lack of correlation between the apparent activation energies and the STY reveals that an entropic process is controlling the net rate (Figure S12, Supporting Information), which could be the availability of either vacancies or $M$H species at the active site. In addition, in order to explore the activity of Ag and Au nanoparticles, energy profiles were computed on Ag(111) and Au(111) surfaces (Figure S27, Supporting Information). The CO$_2$ conversion to methanol follows a different mechanism on bulk metals, where CO$_2$ adsorbs and is then protonated and dehydrated to form CO. Then, CO either desorbs or follows two parallel paths that after concomitant hydrogen transfers lead to methanol. Au and Ag metal surfaces strongly hinder the CO$_2$ adsorption and favored desorption rather than hydrogenation of CO, which explains the lack of activity and selectivity of Au- and Ag-In$_2$O$_3$ towards methanol formation, as they contain mostly metal nanoparticles. In addition, inactive Au$_n$ ensembles containing as few as 3 Au atoms (Figure S20, Supporting Information) can form on the In$_3$AuO$_x$ ensemble and block additional In$_2$O$_3$ active sites, thus lowering the activity and selectivity to methanol.

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The key findings attained by performance assessment, characterization, and DFT simulations are graphically summarized in Figure 8. Overall, the promotional effect in $M$-In$_2$O$_3$
is crucially related to the speciation of the metal promoters. It can be traced back to the ability of $\text{In}_3\text{M}$ and $\text{In}_2\text{M}_2$ sites to lower the homolytic $\text{H}_2$ splitting barrier increase the availability of $\text{H}$. These sites are more widespread on Ir-, Ru-, Rh-, Pt-, and Pd-$\text{In}_2\text{O}_3$, especially the latter two comprising highly dispersed promoters, than on Co- and Ni-$\text{In}_2\text{O}_3$ where the density of single metal atom sites is inferior to other promoter architectures, and on Ag- and Au-$\text{In}_2\text{O}_3$ where these sites are too sparse to significantly activate any reactants. In addition, the formation of small Au$_n$ nanoclusters containing as few as three atoms would block the active site. Lastly, undoped $\text{In}_2\text{O}_3$ sites could also be assumed to significantly contribute to the catalytic activity of the Co-$\text{In}_2\text{O}_3$ system, since its performance is only marginally improved in comparison to the undoped oxide phase. Still, the interplay between promoter and active phase is more complex for this catalyst, owing to cobalt exhibiting varied speciation (i.e., nanoparticles, clusters, single atoms). Hence, unlike other promoters, its role as a dopant is still indeed not fully understood and deserves to be tackled in future studies.

In a broader context, the best promoter balances the affinity to oxygen and hydrogen. Metals that are too oxophilic (such as Co) overly incorporate into the $\text{In}_2\text{O}_3$ lattice whereas metals that are too noble (such as Au) do not disperse efficiently. If they are well dispersed, those with higher affinity to hydrogen will become better catalysts, which emphasizes that metals such as Au and Ni would benefit from further studies tackling the optimization of the FSP protocol to improve their dispersion into low-nuclearity species.

3. Conclusions

Through a comparative study using FSP as a standardized synthesis platform, we have successfully obtained a detailed analysis on the speciation and promotional effects of nine

![Figure 7. Relationship between methanol STY during CO$_2$ hydrogenation over M-$\text{In}_2\text{O}_3$ catalysts versus the experimental standard enthalpy of formation of the most stable metal oxide MO$_x$ for each metal promoter ($\Delta H_{MO}^{\circ}$) normalized by the number of metal atoms in the stoichiometric unit.$^{[56-58]}$ The equivalent plot normalized by the number of oxygen atoms is shown in Figure S28, Supporting Information. The gray regression line considers all metals marked by filled circles. Ag$_2$O and Au$_2$O$_3$ are less stable when compared with their pure metals and thus sinter, and lie beyond the activity cliff.$^{[59]}$ Data for CoO and PtO are also plotted to show that this measure is rather independent of the oxide chosen. The STY obtained over undoped $\text{In}_2\text{O}_3$ is marked for comparison.]

![Figure 8. Summary of promoter speciation and their associated structural-mechanistic features dictating performance of M-$\text{In}_2\text{O}_3$ catalysts.]

metal-promoted indium oxide (M-In$_2$O$_3$, M = Au, Ag, Co, Ni, Ir, Ru, Rh, Pt, and Pd) catalysts in CO$_2$ hydrogenation to methanol. These systematically synthesized materials were fully assessed by an integrated catalytic evaluation, in-depth characterization, kinetic analyses, and DFT. This holistic approach enabled the identification of three main catalyst families, for which performance is strongly governed by the promoters’ specification. The first encompasses systems containing atomically-dispersed and well-stabilized, mostly through M–In bonds, Pd, Pt, Rh, Ru, and Ir species on the In$_2$O$_3$ surface, which reached a methanol selectivity of up to 95%. The second covers Co- and Ni-In$_2$O$_3$, with a less boosted methanol selectivity (≈75%) owing to promoters forming large oxidic and indium alloy-containing clusters, respectively, and in the case of Co, to its partial incorporation into the bulk of In$_2$O$_3$. The third family includes Au and Ag, which sinter into nanoparticles, resulting in inferior or similar methanol selectivity (56 and 67%) to undoped In$_2$O$_3$, respectively. DFT simulations further elucidated that methanol formation is greatly enhanced over systems containing a high concentration of isolated promoter atoms, particularly Pd and Pt, owing to the creation of In$_3$M and In$_3$M$_2$ ensembles, which strongly facilitate homolytic H$_2$ splitting and increase the availability of hydrides, which in turn participate in C–H hydrogenations. As expected, the surface population of the active sites diminishes upon clustering or bulk incorporation of metal promoters such as Ni, Ag, and Co, thereby translating into inferior methanol productivity. Specifically, the formation of larger Au nanoparticles blocks the active ensembles for CO$_2$ hydrogenation and explains the low activity of this Au-In$_2$O$_3$. Overall, this study marks a new step toward the atomic-level understanding of In$_2$O$_3$ promotion by relevant metal promoters, revealing that the degree of promotion is metal speciation-dependent and likely dictated by the density and stability of space resolved In$_3$M and In$_3$M$_2$ ensembles. This offers key guidelines for the design of an optimal system to propel green methanol production. Going beyond CO$_2$ hydrogenation, our strategy to engineer promotion using a universal and scalable preparation method such as FSP holds great potential for tailoring new or existing catalytic systems applicable in diverse energy conversions.

4. Experimental Section

**Catalyst Preparation:** M-In$_2$O$_3$ (M = Au, Ag, Co, Ni, Ir, Ru, Rh, Pt, and Pd) catalysts with a nominal metal promoter content of 0.5 wt.% were prepared by FSP. Briefly, a precursor solution of dissolved indium and promoter complexes (see Table S1, Supporting Information, for a full list) in the desired ratio was pumped through a 0.4 mm nozzle at a flow rate of 5 L min$^{-1}$ and dispersed into a fine spray by flowing oxygen at 1.5 bar at a flow rate of 5 L min$^{-1}$. The spray was ignited by a supporting flame generated using 2.4 L min$^{-1}$ of oxygen and 1.2 L min$^{-1}$ of methane. Such particle-generating flames have been well characterized and reported to generate fresh flame temperatures of 2500–3000 K, with very fast cooling rates (≈10$^8$ K s$^{-1}$). The resulting nanoparticles were collected on a glass fiber filter (GF/A-6) and used in CO$_2$ hydrogenation.

**Catalyst Characterization:** Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed using a Horiba Ultra 2 instrument equipped with a photomultiplier tube detector. Samples were dissolved in hot aqua regia (353 K) for 12 h prior to analysis. Nitrogen sorption at 77 K was carried out using a Micromeritics TriStar II analyzer. Prior to the measurements, samples were degassed under vacuum (10 Pa) at 473 K for 12 h. The total surface area ($S_{BET}$) was determined using the Brunauer–Emmett–Teller method, and the single point pore volume ($V_{pore}$) was determined at p/p$_0$ $\geq$ 0.98. X-ray diffraction (XRD) was conducted using a Rigaku SmartLab diffractometer with a Cu Kα radiation (λ = 0.1541 nm) and operating in the Bragg-Brentano geometry. Data were acquired in the 20–70° 2θ range with an angular step size of 0.025° and a counting time of 1.5 s per step. Temperature-programmed reduction with hydrogen (H$_2$-TPR) was conducted at ambient pressure using a Micromeritics AutoChem HP II coupled to a Pfeiffer OMNISTar mass spectrometer. Samples were loaded into a quartz tube, dried at 423 K in Ar (PanGas, purity 5.0) for 1 h (10 K min$^{-1}$) and cooled down to 223 K (20 K min$^{-1}$) using liquid nitrogen. The temperature-programmed reduction was then carried out using 5 vol.% H$_2$ in Ar (Messner) and increasing the temperature to 1023 K (5 K min$^{-1}$), which was held for 30 min. High-resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were collected using a Talos F200X instrument at an acceleration potential of 200 kV and an aberration-corrected JEM-ARM300F microscope (GrandARM, JEOL) operated at 300 kV in Z contrast mode. Energy-dispersive X-ray (EDX) spectroscopy and elemental maps were measured using the Talos instrument equipped with four silicon drift detectors (SDD). XPS was conducted using a Physical Electronics (PHI) Quantum 2000 XPS featuring monochromatic Al Kα radiation, generated from an electron beam operated at 15 kV and 32.3 W, and a hemispherical capacitor electron-energy analyzer, equipped with a channel plate and a position-sensitive detector. Analyses were conducted at 2 $\times$ 10$^{-7}$ Pa, with an electron take-off angle of 45°, operating the analyzer in the constant pass energy mode. X-ray absorption spectroscopy (XAS) was measured at the SuperXAS beamline at the Swiss Light Source. The incident beam was provided by a Si(111) (for XAS $< 10$ keV), Rh-(10–20 keV), or Pt-coated (≥20 keV) mirror, at 2.5–2.9 mrad and focused by a toroidal Rh (below 20 keV) or Pt-coated (above 20 keV) mirror. The energy was selected by a Si(111) (for Co K, Ni K, Ir L$_2$, Pt L$_2$, Au L$_3$, Rh K, Pd K) and a Si(111)-Ru K and Ag K edges) channel-cut monochromator and calibrated using the corresponding metallic foil of each promoter, which was measured simultaneously with the specimen of interest at suitable absorption edges (Table S4, Supporting Information). The incident X-ray beam was focused on a 0.25 $\times$ 1 mm$^2$ spot. Activated samples were transferred from the reactor to a quartz capillary and sealed under inert atmosphere. Reference oxides for each promoter were measured in transmission mode as a pellet diluted with cellulose. Three 15-cm long ionization chambers filled with nitrogen (below 15 keV) at 2 bar or 50% N$_2$ in Ar at 2 bar (above 15 keV) were used to monitor the incident beam intensity. Transmission through the sample, and the reference metallic foils. For Rh K, Ru K, Pd K, and Ag K edges XAS, quick fluorescence detection mode with a PIPS diode detector (1 Hz monochromator oscillation, 5–10 min data acquisition) was used. For Co K, Ni K, Ir L$_2$, Pt L$_2$, Au L$_3$, XAS of catalysts, an SDD detector and a step-by-step acquisition mode (30–90 min data acquisition) were applied. The spectra were calibrated and averaged with the in-house developed ProXAS software and further analyzed using the Demeter software package. k$^2$-Weighted EXAFS spectra were fitted in the optimal k- and R-windows for each metal. Amplitude reduction factors (S$_0^2$) were determined by fitting of the EXAFS spectrum of pure metal foils (Table S4, Supporting Information). The scattering paths for the fitting were produced using known crystallographic structures and models attained by DFT of metallic, oxidic, and alloy phases of each promoter and indium, as indicated in Table S5, Supporting Information.

**Catalyst Evaluation:** The gas-phase hydrogenation of CO$_2$ and hybrid CO$_2$–CO feeds to methanol was performed in a PID EngTech high-pressure continuous-flow setup comprising four parallel fixed-bed reactors, as described elsewhere. Undiluted catalysts (mass, $m_{cat}$ = 0.1 g; particle size = 0.2–0.4 mm) were loaded into each reactor tube (internal diameter 4 mm), held in place by a quartz-wool bed set on a quartz frit,
and purged in flowing He (40 cm³ STP min⁻¹, PanGas, 4.6) for 30 min at ambient pressure. Under the same flow, the pressure was increased to 5.5 MPa for a leak test. The reaction was carried out by feeding a mixture of H₂ (PanGas, 5.0), CO₂ (40 vol.% in H₂, Messer, 4.5), and, in the case of hybrid feeds, also CO (Messer, 5.0), with a molar H₂/CO₂ (CO₂ = CO + CO) ratio of 4 at 533 K, 5 MPa, and a weight hourly space velocity (WHSV) of 24 000 cm³ STP h⁻¹ g⁻¹ cat⁻¹, unless stated otherwise. The selectivity of the catalysts was compared at a constant degree of CO₂ conversion (XCO₂) of 3% by adjusting the WHSV for each system. Kinetic investigations were carried out at doubled WHSV (except for Au-In₂O₃) attained by using a catalyst mass of 0.05 g. To determine activation energies of methanol and CO formation, the reaction was initiated at 473 K and stepwise increased to 573 K in 10-K increments at 5 MPa (mcat = 0.05 g, and H₂/CO₂ = 4 at specified WHSV). Reaction orders with respect to H₂ were acquired by applying a constant flow of CO₂ (8 cm³ STP min⁻¹) and increasing the flow of H₂, while using He to balance the total flow to 44 cm³ STP min⁻¹ (mcat = 0.055 g) at 533 K and 5 MPa.

The effluent streams were analyzed by gas chromatography every 1 h. Response factors (Fᵢ) for each compound i, respective to the internal standard (20 vol.% C₂H₆ in He, Messer, purity 3.5), in the GC analysis were determined by Equation (1):

\[ F_i = \frac{A_i}{A_i^{\text{in}}} \]  

where \( A_i \) is the integrated area determined for the peak of compound i and \( A_i^{\text{in}} \) is the corresponding known molar flow at the reactor inlet. An average of 5 points around the expected analyte concentration was used. The unknown effluent molar flow of compound i was determined using Equation (2):

\[ \dot{n}_i^{\text{out}} = \frac{A_i \times F_i}{A_{CCH₄} \times \dot{n}_{CH₄}^{\text{in}}} \]  

Conversion (Xᵢ), selectivity (Sᵢ), and production rate (rᵢ) were calculated using Equations (3–5):

\[ X_i = \frac{n_i^{\text{in}} - n_i^{\text{out}}}{n_i^{\text{in}}} \]  

\[ S_i = \frac{n_i^{\text{out}} - n_i^{\text{prod}}}{n_{CO₂}^{\text{in}} - n_{CO₂}^{\text{out}}} \]  

\[ r_i = \frac{n_i^{\text{out}}}{\dot{n}_{\text{cat}}} \]  

The methanol STY is the product of \( n_{\text{mol}}^{\text{MeOH}} \) and the molar weight of methanol (32.04 g mol⁻¹). The carbon balance was determined for each experiment according to Equation (6):

\[ \varepsilon_C = \left( 1 - \frac{\dot{n}_{\text{out}}^{\text{CO₂}} + \dot{n}_{\text{out}}^{\text{MeOH}} + \dot{n}_{\text{out}}^{\text{CO₂}}} {\dot{n}_{\text{in}}^{\text{CO₂}}} \right) \]  

and was always within a 5% margin.

**Theoretical Simulations:** DFT studies were carried out employing the Vienna ab initio simulation package (VASP) using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. Core electrons were described by projector augmented-wave (PAW) pseudopotentials and valence electrons were expanded with plane-waves with a kinetic cut-off energy of 500 eV. The Brillouin zone was sampled by a Γ-centered mesh generated through the Monkhorst-Pack method with a reciprocal grid size narrower than 0.021 Å⁻¹. Transition states were obtained with the climbing image nudged elastic band (CI-NEB) method. Spin polarization was included when necessary. In₂O₃ was represented by the cubic bixbyite structure as determined in previous studies from which the In₂O₃(111) termination, the experimentally most stable and abundant (Figure S1, Supporting Information), was built containing five O–In–O trilayers. The two outermost layers were allowed to relax, whereas the three bottommost were fixed to their bulk positions. A vacuum region larger than 12 Å was added between the slabs and the dipole correction was applied along the z axis to account for the asymmetry in the relaxation. Metal promoters were modeled in 26 non-equivalent positions as adatoms and 14 sites where they replaced an In atom in the In₂O₃ lattice (Figures S13 and S14, Supporting Information). Then, their relative stabilities were assessed from their energies as described in the Supporting Information (Data Processing).

The mechanism for vacancy formation and CO₂ reduction to methanol and CO were computed following previous studies.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

T.P.A., J.M.-V., and T.Z. equally contributed to this work. This publication was created as part of NCCR Catalysis, a National Centre of Competence in Research funded by the Swiss National Science Foundation. The Scientific Center for Optical and Electron Microscopy (ScopeM) at the ETH Zurich and the SuperXAS beamline at PSI, are thanked for access to their facilities. The authors are grateful to Prof. Christophe Copéret, Dr. Gina Noh, and Mr. Jan Alfke for assistance with sample preparation for XAS measurements. T.Z. thanks the Agency for Science, Technology, and Research (A*STAR) Singapore for support through a graduate fellowship. The Spanish Ministry of Science and Innovation is acknowledged for financial support (RTI2018-101394-B-I00 and Severo Ochoa Grant MCI/AEI/10.13039/501100010333 CEX2019-000925-S) and the Barcelona Supercomputing Center-MareNostrum (BSC-RES) for providing generous computer resources. Open access funding provided by Eidgenossische Technische Hochschule Zurich.

**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request. All DFT data can be found online in the ioChem-BD repository at https://doi.org/10.19061/iochem-bd-1-219.

**Keywords**

CO₂ hydrogenation, green methanol, indium oxide, metal speciation, promotion.

Received: November 26, 2021
Revised: February 5, 2022
Published online: February 23, 2022

[1] A. González-Garay, M. S. Frei, A. Al-Qtahni, C. Mondelli, G. Guillén-Gosálbez, J. Pérez-Ramírez, Energy Environ. Sci. 2019, 12, 3425.
