Turning a methanation Co catalyst into an In-Co methanol producer

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ABSTRACT The direct hydrogenation of CO₂ to methanol using hydrogen is regarded as a potential technology to reduce greenhouse gas emissions and the dependence on fossil fuels. For this technology to become feasible, highly selective and productive catalysts that can operate under a wide range of reaction conditions near thermodynamic conversion are required. Here we combine a CO-producing In oxide catalyst with a methane-producing Co catalyst to obtain In/Co catalyst for CO₂ reduction to methanol. Density functional (DFT) simulations demonstrate that the charge transfer between Co support and In oxide film leads to enrichment of the surface of indium oxide with O vacancies, which serve as active sites for selective conversion of CO₂ to methanol. Moreover, our simulations suggest that CO₂ reduction on Co-supported In₂O_{3-x} films will

preferentially yield methanol, rather than CO and methane. As a result, the prepared In@Co catalysts produce methanol from CO₂ with high selectivity (>80%) and productivity (0.86 g_{CH₃OH}·g_{catalyst}⁻¹·h⁻¹) at conversion levels close to thermodynamic equilibrium, even at temperatures as high as 300 °C and at moderate pressures (50 bar).

KEYWORDS indium, cobalt, carbon dioxide, methanol, hydrogenation

1. INTRODUCTION

The capture and utilization of carbon dioxide, the primary greenhouse gas, are of vital importance.¹ Hydrogenating CO₂ into valuable feedstocks using green hydrogen offers the possibility of directly sequestering this greenhouse gas into highly demanded utility chemicals. Among the potential products, methanol is a very attractive chemical platform and clean fuel.² Sustainable methanol production requires sources of renewable hydrogen, inexpensively captured carbon dioxide and an efficient and highly selective catalyst.³ Clean routes to produce renewable H₂ by means of solar energy, hydropower, wind power or biomass are reported to be currently feasible⁴, while efficient carbon capture technologies require more advances.³

Since Imperial Chemical Industries developed the first heterogeneous catalyst for methanol synthesis from a mixture of synthesis gas and CO₂ (Cu-ZnO-Al₂O₃), research has focused on investigating this material.³ The ternary Cu-ZnO-Al₂O₃ system, however, is not perfect. The methanol selectivity at moderate pressures is limited due to the competing reverse water gas shift reaction (RWGS); moreover, stability issues arise when pure CO₂ is hydrogenated. To avoid these issues, this reference catalyst is used at temperatures that do not exceed 250 °C and pressures that do not dip lower than 70 bar. Still, under these conditions, a large part of the product stream needs to be recycled to convert the produced CO into MeOH.⁵ This requirement results in high compressor and cooling costs and low per-pass productivity. Catalysts that can maintain good methanol selectivity at higher temperatures and lower pressures will be more cost effective and facilitate potential coupling to higher-temperature processes such as the methanol to olefin (MTO) reactions.

A few alternative catalysts for the transformation of carbon dioxide to methanol have been proposed. Photo- and electrocatalytic systems have advanced significantly over the last decades,

but their performances are still rather low.⁶ A breakthrough in the field was recently achieved by the group of Ozin, with a report of the photothermal CO₂ hydrogenation to methanol using In₂O_{3-x}(OH)_y with 50% selectivity and 0.06 mmol g_{cat}⁻¹ h⁻¹ productivity.⁷ The vast majority of studies on homogeneous systems focuses on indirect transformations, such as hydrogenation of formates, carbonates or urea, disproportionation of formic acid or cascade multi-step catalysis.⁸ Direct homogeneous CO₂ hydrogenation is difficult to achieve, but several catalysts have been reported in recent years.⁹ These systems operate under relatively mild conditions (125-165 °C), but except for some prominent cases,^{10,11} most catalysts are based on noble metals and/or expensive phosphine ligands.¹²⁻¹⁵ As for heterogeneous catalysts, palladium-gallium catalysts were successfully employed by several research groups as a replacement for copper.¹⁶⁻¹⁸ Other metal-supported catalysts and bimetallic systems were also found to be active, such as Au/ZnO (0.42 g_{MeOH} g_{Au}⁻¹ h⁻¹, *ca.* 40% selectivity to MeOH under 5 bar, 240 °C, 15% conversion)¹⁹, Ni-Ga (*ca.* 0.1 g_{MeOH} g_{catalyst}⁻¹ h⁻¹ under 1 bar and 200 °C, selectivity of *ca.* 100%)²⁰, ZnO-ZrO₂ (0.73 g_{MeOH} g_{catalyst}⁻¹ h⁻¹, methanol selectivity of up to 91% with CO₂ single-pass conversion of *ca.* 10% under 50 bar, and 315 °C)²¹, In₂O₃/ZrO₂ (*ca.* 0.3 g_{MeOH} g_{catalyst}⁻¹ h⁻¹ at 50 bar and 300 °C, selectivity of *ca.* 100%, 5% conversion)²², and more recently a In:Pd(2:1)/SiO₂ with methanol productivity of 0.39 g_{MeOH} g_{catalyst}⁻¹ h⁻¹ and 61% selectivity at 300 °C.²³

Interestingly, recent computational studies revealed that one of the factors limiting selective CO₂ reduction to methanol on In₂O_{3-x} catalysts is the scarcity of indispensable hydridic H^{δ-} species, which preferentially hydrogenate C atoms, in contrast to H^{δ+} species which preferentially hydrogenate O²⁻ species.²⁴ Exceeding rate of H-O bond formation compared to H-C bond formation would result in high CO and low methanol selectivity. This finding is in line with recent

computational studies of electrochemical CO₂²⁵ and CO²⁶ reduction on Cu-based catalysts. We hypothesized that the well-known high methanation activity of metallic Co could be due to the efficient generation of such hydridic H^{δ-} species and, hence, the addition of Co to In₂O₃ catalyst would result in higher methanol production rate.

Here we report the preparation, characterization and performance of a novel and highly selective catalyst based on combination of Co and oxidized In, which would individually produce methane and CO, respectively. The synergetic effect of In and Co on the catalyst's activity and selectivity is revealed by mechanistic density functional (DFT) simulations.

2. EXPERIMENTAL METHODS

The starting materials were cobalt acetate (Co(CH₃COO)₂·6H₂O), indium acetate (In(CH₃COO)₃), water, hydrogen peroxide and ammonia hydroxide solution. Both salts were dissolved in water and added dropwise to a stirred aqueous solution of H₂O₂ and NH₄OH. The mixture further underwent hydrothermal treatment at 180 °C for 8 h. The obtained powder, denoted as In@Co, was recovered, washed and subsequently dried at 60 °C. The compositional, textural, and structural properties of the In@Co catalyst were investigated by powder X-ray diffraction, high-resolution transmission electron microscopy, electron energy loss spectroscopy, temperature-programmed reduction with H₂, and X-ray photoelectron spectroscopy. CO₂ hydrogenation was performed over undiluted catalysts using a Flowrence® 16 parallel reactor system. Prior to the reaction, the In@Co catalyst was preheated in N₂ at 300 °C and 1 bar for 1 h. Further details on catalyst preparation, characterization, and tests are given in the Supporting Information.

3. COMPUTATIONAL METHODS

Periodic spin-polarized density functional theory calculations with the PBE exchange-correlation functional were performed using the Vienna Ab initio Simulation Package (VASP).²⁷⁻³⁰ The projector augmented wave (PAW) pseudopotentials were implemented to describe core electrons.^{31,32} Plane wave basis sets had a kinetic energy cut-off of 500 eV. The first-order Methfessel-Paxton smearing of 0.1 eV and $3 \times 3 \times 1$ Monkhorst-Pack k-point grid were employed.^{33,34} Calculations were performed until the forces on each atom were within 0.015 eV/Å. Displacements of 0.03 Å were used to obtain vibrational frequencies. Free energies were obtained using the ideal gas approximation at $T = 300^\circ\text{C}$ and $P = 50$ bar, considering only the harmonic vibrational contribution for adsorbed species. Pure $\text{In}_2\text{O}_3(111)$ slabs were five-layers thick while $\text{In}_2\text{O}_3\text{-Co}$ slabs contained one O-In-O trilayer of $\text{In}_2\text{O}_3(111)$ on top of four layers of fcc-Co(111). The vacuum spacing in both slabs was 16 Å. Gibbs oxygen vacancy formation energies were calculated as $G_{\text{vac}} = G[\text{In}_x\text{O}_{y-1}] + G[\text{H}_2\text{O}] - G[\text{In}_x\text{O}_y] - G[\text{H}_2]$, where $G[\text{H}_2\text{O}]$ and $G[\text{H}_2]$ are the Gibbs energies of gas phase water and hydrogen molecules and $G[\text{In}_x\text{O}_{y-1}]$ and $G[\text{In}_x\text{O}_y]$ are the electronic energies of the vacancy-containing pristine or Co-supported indium oxide films, where the last value is also corrected by the free energy contributions from the vibrations of the oxygen atom to be pulled out. The key calculated structures are displayed at the end of the Supporting Information, where their atomic coordinates are listed as well.

4. RESULTS AND DISCUSSION

Multiple preparation methods were investigated for the synthesis of In@Co solids, namely, precipitation, incipient wet impregnation and ball milling (Table S1, *cf.* Supplementary Information (SI)). All prepared solids showed similar trends in terms of methanol selectivity

during carbon dioxide hydrogenation. However, among all the synthesized catalysts, those prepared by reverse co-precipitation provided the highest methanol productivity and the lowest CH₄ selectivity (*cf.* Table S2). For that reason, this study focuses on the latter preparation method. A series of catalysts was prepared with different indium contents (see SI). The precatalyst containing 20 wt% of indium was found to display the best performance and is denoted as In@Co-1.

4.1. Catalytic performance. The In@Co-1 solid was tested for CO₂ hydrogenation for 270 h at 300 °C and 50 bar (Figure S1). The results show an initial induction period of 30 h followed by a stable performance reaching a CO₂ conversion of 19%. The prevalent product is methanol ($S_{\text{MeOH}} = 69\%$), with a limited formation of carbon monoxide ($S_{\text{CO}} = 23\%$) and methane ($S_{\text{CH}_4} = 8\%$) as byproducts (Figure S2). Under the same experimental conditions, the commercial Cu-ZnO-Al₂O₃ catalyst has no induction period but displays a much lower selectivity to methanol ($S_{\text{MeOH}} = 25\%$). A comparison of the methanol productivity at the steady state – 0.45 vs. 0.27 g_{MeOH} g_{catalyst}⁻¹ h⁻¹ for In@Co-1 and Cu-ZnO-Al₂O₃, respectively – highlights an important improvement in the catalytic performance. From these results, it is clear that the activity of the Cu system in the undesired RWGS reaction is much higher than that of the Co-In system. The relatively high selectivity of In-Co towards CH₄ suggests that part of the catalyst contains Co nanoparticles with accessible surface, which are well known for their high methanation activity.

4.2. Structural rearrangement under reaction conditions. The observation of a long induction period is usually a clear indication that the active catalytic phase forms under reaction conditions. Furthermore, we noticed a strong pyrophoric behavior of the final In@Co-1 catalyst. Hence, the structural characterization of the spent catalyst was conducted with appropriate

precautions to avoid any air exposure (details in the SI). In the following section, the structural rearrangements subsequent to CO₂ hydrogenation are presented in detail.

The reverse co-precipitation with a metal solution including both In(CH₃CO₂)₃ and Co(CH₃CO₂)₂ salts and an ammonia solution as a precipitation agent, followed by hydrothermal treatment, initially produces a mixture of dzhaliindite (In(OH)₃) and cobalt (II, III) oxide (Co₃O₄) as nanoparticles. This result is easily identified in Figure 1 by considering the ensemble of d-spacings observed by powder X-ray diffraction (PXRD). The precipitation is nearly quantitative, with a synthesis yield of 61% based on indium and 59% based on cobalt.

Figure 1. Powder XRD patterns of the In@Co-1 solid before and after reaction acquired in transmission with flame-sealed capillaries and using Mo K α radiation as the X-ray source. The assignment of the main reflections is labelled as follows: * Co₃O₄, ♥ In(OH)₃, ♣ Co₃InC_{0.75}, ♦ Co(*fcc*), • In₂O₃.

The nitrogen adsorption–desorption isotherm of the In@Co-1 precatalyst (Figure S3a) is characteristic of a mesoporous/macroporous solid (type II-IV) and indicates a low specific surface area of 30 m² g⁻¹. Imaging by annular dark field scanning transmission electron microscopy (ADF-

STEM) was used to investigate the morphological properties of the In@Co-1 catalyst before reaction. The micrograph presented in Figure S4 shows a typical example of agglomerates containing round Co_3O_4 nanoparticles in the 10–40 nm range and larger $\text{In}(\text{OH})_3$ nanoparticles shaped as rectangular parallelepipeds ($> 100 \text{ nm} \times 50 \text{ nm}$). Co and In elemental maps computed from electron energy loss spectroscopy (EELS) reveal that some of the Co_3O_4 aggregates are sometimes filled or trapped within an amorphous indium hydroxide phase (Figure S4, c and d).

The high-resolution X-ray photoelectron spectroscopy (XPS) image of the Co 2p core level of the sample before reaction is shown in Figure 2a (top). The spectrum consists of two main broad peaks at 779.8 eV and 794.9 eV corresponding to $2p_{3/2}$, $2p_{1/2}$ spin orbit lines, respectively. The spectrum also contains satellite structures at the high binding energy side of the $2p_{3/2}$ and $2p_{1/2}$ main peaks, which indicates the existence of cobalt in oxide form.^{35,36} To identify the oxidation state of cobalt, peak fitting of Co $2p_{3/2}$ was conducted. The approach used for the peak fitting is similar to that used by Biesinger *et al.*³⁷, i.e., fitting of a broad main peak combined with the satellite structure. A Shirley background was applied across the Co $2p_{3/2}$ peak of the spectrum. The Co $2p_{3/2}$ from the sample before reaction in Figure 2 is well fitted using a combination of the parameters derived from both Co_3O_4 and $\text{Co}(\text{OH})_2$ standard samples. The results indicate that the sample contains 82.5% of Co_3O_4 and the remaining 17.5% of the extra $\text{Co}(\text{OH})_2$ contribution. Since $\text{Co}(\text{OH})_2$ was not detected by XRD, we propose that this could be related to the presence of an amorphous Co hydroxide. The high-resolution XPS spectrum of the In 3d core level (Figure 2b, top) consists of two main broad peaks at 445.0 eV and 452.6 eV corresponding to $3d_{5/2}$, $3d_{3/2}$ spin orbit lines, respectively. The In $3d_{5/2}$ peak was fitted using a single component located at 445.0 eV attributed to In^{3+} in $\text{In}(\text{OH})_3$.³⁸ Figure 2c (top) shows the high-resolution XPS spectrum of the C 1s core level of the sample. The C 1s core level from the sample before reaction was fitted using

four components located at 285.0 eV, 286.4 eV, 288.3 eV and 289.5 eV corresponding to the C-C-H (sp^3), C-O, C=O and O-C=O bonds,^{39,40} respectively. These contributions indicate that acetate anions remain adsorbed on the surface of the In@Co solid despite extensive washing.

Figure 2. High-resolution X-ray photoelectron spectroscopy of the In@Co-1 solid before and after reaction with core levels a) Co(2p), b) In(3d), and c) C(1s). The open symbols are the experimental data, while the full lines are the components used for the decomposition of the spectra.

After CO₂ hydrogenation, large changes in the phase composition and morphological properties are observed, although the textural properties remain comparable (S_{BET} (precatalyst) = 30 m²g⁻¹ vs. S_{BET} (catalyst) = 17 m²g⁻¹). Most indium hydroxide converts into indium oxide (In₂O₃) by dehydration (Figure 1). The thermal decomposition likely occurs during preheating under N₂ at 300 °C because this transformation is known to occur at approximately 220 °C.⁴¹ Additionally, the cobalt oxide transforms into metallic Co that crystallizes in a face-centred cubic crystal system. Finally, a mixed metal carbide with the Co₃InC_{0.75} stoichiometry is observed in the spent catalyst.

Note also that none of the reported Co-In intermetallic compounds (CoIn_2 ⁴², CoIn_3 ⁴³) or pure metallic indium was detected.

The transformations of each phase in the precatalyst were also characterized after CO_2 hydrogenation using ADF-STEM imaging and EELS (Figure 3). The large and rectangular $\text{In}(\text{OH})_3$ nanoparticles are converted into much smaller In_2O_3 crystallites (Figure S5 a,b and purple color in Figure 3b). The Co_3O_4 nanoparticles are transformed into metallic Co nanoparticles (Figure S5 c, d and green color in Figure 3b). Interestingly, there is also a new component in the spent catalyst that is often observed but cannot be detected by XRD. This is illustrated in Figure 3 using ADF imaging at high magnification (Figure 4a), where some metallic Co nanoparticles are decorated with a lighter material. Quantitative analysis of the EELS data (details in the SI) indicates that the presence of the lighter material is due to the formation of an oxidized indium-cobalt layer with a range of thicknesses between 1 and 4 nm (Figure 4b). This surface layer includes an irregular amount of oxygen through the sample and still contains much more cobalt than indium atoms (minimum Co/In ratio measured ≈ 2.5).

Figure 3. Low magnification ADF-STEM imaging and elemental mapping of the In@Co-1 catalyst after the reaction: (a) dark field imaging, b) colour mix built with elemental maps computed from EELS data: Co (green), In (blue) and O (red).

Figure 4. ADF-STEM imaging and elemental mapping of metallic Co nanoparticles covered by an indium layer after the reaction: (a) dark field imaging, b) color mix built with quantitative elemental maps computed from EELS data: Co (green), In (blue) and O (red). The inset shows a line profile of the Co, O and In atomic composition from the surface to the bulk (carbon edge taken into account during quantitative analysis).

Surface characterization by XPS suggests that the surface state is also heavily modified after the reaction. The elemental composition (Figure S7) evolves with a decrease in the oxygen content from 49.9 at.% to 20.5 at.% and a simultaneous increase in the carbon content from 13.2 at.% to 24.6 at.%. Overall, this result means that the In@Co solids rearranged during CO₂ hydrogenation to present more indium on their surface, which is also in accordance with the TEM results (*vide supra*). Figure 2a shows the high-resolution XPS spectrum of the Co 2p core level of the sample after the reaction. The Co 2p_{3/2} is well fitted using a combination of the parameters derived from metallic cobalt and mixed cobalt oxides from standard samples. The dominant Co 2p_{3/2} is located at 778.2 eV and corresponds to metallic cobalt and/or cobalt carbides, whereas the broad peak centered at approximately ~ 781.1 eV corresponds to cobalt mixed oxides.^{37,44,45} The In@Co

catalyst still contains 7.1 % oxidized cobalt atoms after the reaction. The In 3d_{5/2} peak was fitted using two components located at 443.7 eV and 444.7 eV attributed to indium in a metallic state or within the Co₃InC_{0.75} carbide (55.7 at.%)⁴⁶ and to indium in In₂O₃ (44.3 at.%).^{46,47}

4.3. Unravelling the active catalytic phase. With the composition of the In@Co-1 catalyst in hand, catalytic tests were performed with individual components and their physical mixtures (Table S2). Cobalt oxide, once converted to metallic Co under the reaction conditions, predictably converted carbon dioxide to methane with 100% selectivity. Pure In₂O₃ showed a negligible conversion of approximately 1% with carbon monoxide as the only product. A 97% pure Co₃InCoC_{0.75} phase was obtained from metal organic framework-mediated synthesis *via* pyrolysis of a Co-In MOF (see the SI). The resultant Co₃InC_{0.75} carbide, alone or mixed with In₂O₃ in different proportions, did not produce any methanol, but did produce CO. The systematic elimination of the former candidates suggests that the oxidized indium-cobalt layer around metallic cobalt is the active phase for the selective formation of methanol.

Figure 5 shows the catalytic behavior of catalysts that were prepared by the same method of varying the indium and cobalt contents. The best performance is achieved on In@Co-1 with an In/Co ratio of 0.38. Decreasing the indium content in the solid leads to a higher yield of undesired methane; in this case, the surface of metallic cobalt is less perturbed by the presence of indium and thus can eventually achieve the complete hydrogenation of carbon dioxide. In contrast, with a high indium content, the selectivity towards methane drops to 1%, together with a drastic decrease in the conversion rate (19 % *vs.* 11 %).

Figure 5. Catalytic activity of a) In@Co-1 and b) In@Co-2 catalysts with different indium to cobalt ratios. 300°C, 50 bar, 80% H₂ 20% CO₂ feed, 50 mg of catalyst, GHSV = 19200 h⁻¹.

To challenge the assignment of the active phase to In oxide films on Co support, we investigated pristine and Co-supported In₂O₃ catalysts using DFT simulations. Previous studies revealed that CO₂ conversion to methanol on In₂O₃-based catalysts required the presence of O vacancies on the surface.^{24,48} In line with previous reports,⁴⁸ our simulations showed that one O vacancy will form per unit cell of pristine In₂O₃ surface with G_{vac} of -0.82 eV at the reaction conditions, while there is no thermodynamic driving force for the generation of a second oxygen vacancy, with G_{vac} of 0.01 eV. When we computationally screened sequential formation of O vacancies on all surface sites on Co-supported indium oxide films, we found that at least three oxygen vacancies may be generated on such films (Figure 6) significantly increasing the number of active sites for CO₂ reduction. The higher propensity of Co-supported films to form O vacancies is in line with the decrease of the average Bader charge on surface In atoms from +1.8 to +1.5 due to the charge transfer between the oxide film and the metal support. The partial reduction of In-ions in the vicinity of electron reservoir provided by metallic Co support weakens electrostatic interaction

between In atoms and lattice O atoms and enables the generation of more oxygen vacancies.

Figure 6. Top view of the In_2O_3 film on Co surface and the most exothermic Gibbs free energies (in eV) for sequential formation of the three surface O vacancies by H_2 oxidation under the experimental conditions.

Since Co catalysts were observed to reduce CO_2 to methane and pristine In_2O_3 catalysts were observed to produce CO, we simulated the feasibility of both processes on Co-supported In_2O_3 films compared to the methanol production. When CO is formed upon CO_2 reduction on pristine or Co-supported indium oxide catalysts, the C atom remains bound to two O atoms, one pointing away from the surface and another within the oxide lattice (Figure 7). On pristine In_2O_3 such adsorbate has comparable probabilities of desorbing either as CO or extracting an O atom from the surface and desorbing as CO_2 due to similar exothermicity of both outcomes, compare the energy of $\text{CO}^{(\text{g})} + \text{H}_2\text{O}^{(\text{g})}$ versus that of $\text{CO}_2^{(\text{g})} + \text{H}_2\text{O}^{(\text{g})} + \text{vacancy}$, black/gray lines in Figure 7. Thus, pristine In_2O_3 surface is calculated to convert some amount of CO_2 to CO similarly to the experimental results. In turn, on similar Co-supported In_2O_3 films such adsorbate is much more likely to desorb as CO_2 rather than CO, due to the significantly higher exothermicity of the former process, compare the energy of $\text{CO}^{(\text{g})} + \text{H}_2\text{O}^{(\text{g})}$ versus that of $\text{CO}_2^{(\text{g})} + \text{H}_2\text{O}^{(\text{g})} + \text{vacancy}$, red/orange lines in Figure 7. The effect of Co support on the relative energies of possible final states reflects its effect on the O vacancy formation energies, which are lowered by the metal-oxide charge

transfer. The calculated reaction energy profiles are consistent with the suppressed CO production observed experimentally on In@Co catalysts during CO₂ reduction.

Figure 7. Gibbs energy profile for the reduction of CO₂ to carbon monoxide on (black) pristine and (red) Co-supported indium oxide surfaces with an O vacancy (two O vacancies when CO₂ is formed as a product) constructed in line with Ref.²⁴. Insets show the atomic structures of key interfaces where In atoms are displayed as yellow spheres, C – black, H – white, O atoms composing CO₂ – purple, O atoms composing In₂O₃ – red.

Another key elementary step in CO₂ reduction is CH₃O hydrogenation. According to Ref. 23, methanol could be formed through the interaction of CH₃O with H^{δ+} adsorbed on lattice O with insignificant barrier. At the same time, methane production requires the formation of another C-H bond, which was shown to proceed via H^{δ-} species adsorbed on In sites.²³ Such species form via heterolytic H₂ activation in the presence of O vacancies (Figure S8). Our calculations reveal that H^{δ-} species on In sites are by >1 eV less thermodynamically stable on Co-supported In₂O₃ catalysts compared to H^{δ+} species on O sites in the vicinity of adsorbed methoxy species (Figure 8). The higher stability of H^{δ+} species can explain catalyst selectivity towards methanol production.

Figure 8. Binding energies of $H^{\delta+}$ atoms to surface O atoms (black values) and of $H^{\delta-}$ to In atoms in the vicinity of CH_3O species (blue values) on Co-supported In_2O_3 films.

4.4 Optimization of the catalyst formulation. Despite its promising performances, the first In@Co-1 catalyst had significant amounts of In_2O_3 and Co_3O_4 phases that, according to the above DFT calculations, do not contribute to the selective formation of methanol. Inspired by these insights, we omitted the hydrothermal treatment used for the previous preparation of In@Co-1 samples in order to avoid segregation of the $In(OH)_3$ and Co_3O_4 phases. Hence, a second series of catalysts with varying In/Co ratios was prepared and denoted as In@Co-2.

The In@Co-2 precatalyst is composed of an intricate mixture of Co and In atoms with some crystalline and amorphous components, as observed by ADF-STEM/EELS (Figure S6). The crystalline part was characterized by PXRD as a mixture of CoO and In_2O_3 nanoparticles (Figure S10). In addition, the nitrogen adsorption–desorption isotherms of materials synthesized without hydrothermal treatment are type IV, which is typical of a mesoporous solid (Figure S3 b). The specific surface area markedly increased to a range of $80\text{--}200\text{ m}^2\text{ g}^{-1}$ compared to the initial $30\text{ m}^2\text{ g}^{-1}$ of the In@Co-1 precatalyst. The crystalline phases after catalyst activation were also found to be a mixture of $Co_3InC_{0.75}$, In_2O_3 and Co (*fcc*) phases similar to the In@Co-1 catalyst (Figure S10).

Figure 9. Methanol selectivity, yield and productivity over an In@Co-2 catalyst at different temperatures and feed flows. Reaction conditions (unless otherwise stated in the figure itself) are 300°C, 50 bar, 80% H₂ 20% CO₂ feed, 50 mg of catalyst, 56.1 wt% In in the precatalyst.

When applied in CO₂ hydrogenation, a similar effect of indium loading on the catalytic performance was observed (Figure 59). However, in this case, due to the better initial dispersion of In, a broader range for the optimum molar ratio of In/Co was found. At the same time, both higher productivities and selectivities were observed. A catalytic run with the In@Co-2 catalyst (In/Co = 1) was performed for 170 h under the same chosen standard conditions of 300 °C and 50 bar (Figure 8). The results show the same induction period of 30 h followed by a stable performance, reaching a CO₂ conversion of 16%. The selectivity of methanol reached 75%, with a limited formation of carbon monoxide ($S_{CO} = 21\%$) and methane ($S_{CH_4} = 4\%$). Increasing the gas hourly space velocity (GHSV) from 14400 h⁻¹ to 22200 h⁻¹, the selectivity towards methanol reached 79% with a decrease in the selectivity towards methane from 4 to 2% at a methanol

productivity of $0.76 \text{ g}_{\text{MeOH}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$. Further increasing the GHSV to 27500 h^{-1} leads to a record methanol productivity of $0.86 \text{ g}_{\text{MeOH}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ at a constant selectivity to methanol of 80%. Decreasing the temperature to $285 \text{ }^{\circ}\text{C}$ results in selectivities to methanol on the order of 85% with a negligible formation of undesired methane.

The ratio of four between hydrogen to carbon dioxide was chosen for the standard testing conditions. Considering hydrogen's value, we lowered the ratio, keeping the total flow unchanged (Figure S11). Decreasing hydrogen partial pressure predictably led to a decrease in conversion – ca. 10 and 8% for the ratios 3 and 2, respectively. However, the methanol selectivity did not drop to any considerable degree, affording a methanol productivity of $0.57 \text{ g}_{\text{MeOH}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ with $\text{H}_2/\text{CO}_2=2$.

Figure 10. Comparison of the In@Co-2 system to the conventional Cu-based catalyst from Alfa Aesar. Reaction conditions: 50 bar, 80% H_2 20% CO_2 feed, 50 mg of In@Co-2 catalyst, 56.1 wt% In in the precatalyst.

To extend the comparison between In@Co-2 and $\text{Cu-ZnO-Al}_2\text{O}_3$, for experiments performed under exactly the same conditions, the MeOH yield at 50 bar is plotted for temperatures ranging from $250 \text{ }^{\circ}\text{C}$ to $350 \text{ }^{\circ}\text{C}$ against thermodynamic equilibrium conversion (Figure 10). From this

figure, it is clear that the In@Co-2 system can maintain high methanol selectivities over a wider range of temperatures than the commercial Cu-ZnO-Al₂O₃, allowing a much higher productivity per pass. Even when compared with more recent developments (ZnO-ZrO₂,²¹ and In-Pd,²³ *vide supra*), both in terms of yield per pass and productivity, the reported In@Co catalyst in this study establishes itself as a new state-of-the-art catalyst.

5. CONCLUSIONS By combining two catalysts that individually produce methane and CO, we obtained In@Co catalysts for CO₂ reduction to methanol and established a new state-of-the-art catalyst with >80% selectivity and 0.86 g_{CH₃OH}·g_{catalyst}⁻¹·h⁻¹ productivity for this important reaction. The obtained catalysts showed stable operation at higher temperatures (300 °C), lower pressures (50 bar) and even under conditions close to thermodynamic control. DFT simulations show that charge transfer between the oxide film and Co support boosts the activity of In₂O_{3-x} films by increasing the amount of surface O vacancies, which are known to be the active sites in CO₂ reduction. At the same time, our simulations suggest that Co-supported In₂O_{3-x} films are unlikely to produce methane and, unlike pristine indium oxide, have decreased ability to release CO, which is consistent with their higher selectivity towards methanol during CO₂ reduction. Our results demonstrate that synthesis of methanol directly from CO₂ is feasible and that there is still room for improvement in catalyst development, both in terms of productivity and selectivity.

ASSOCIATED CONTENT

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Supporting Information. Catalyst preparation, carbon dioxide hydrogenation to methanol experiment, catalyst characterization by the means of BET, STEM, XPS, PXRD, CHN analysis, ICP-OES, XANES, DFT details.

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