Turning a methanation catalyst into a methanol producer: In-Co catalysts for the direct hydrogenation of CO₂ to methanol

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Abstract: The direct hydrogenation of CO₂ to methanol using green 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 demonstrate that indium in close contact with cobalt catalyses the formation of 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). The studied In@Co system, obtained *via* co-precipitation, undergoes *in situ* transformation under the reaction conditions to form the active phase. Extensive characterization demonstrates that the active catalyst is composed of a mixed metal carbide (Co₃InC_{0.75}), indium oxide (In₂O₃) and metallic Co.

Keywords: indium, cobalt, carbon dioxide valorization, methanol synthesis

The capture and utilization of carbon dioxide, the primary greenhouse gas, are of primary 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

A few catalysts for the transformation of carbon dioxide to methanol have been documented. Photo- and electrocatalytic systems have advanced significantly over the last decades, but their performances are still rather low.⁵ 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.⁶ The vast majority of studies on homogeneous systems focus on indirect transformations, such as hydrogenation of formates, carbonates or urea,

disproportionation of formic acid or cascade multi-step catalysis.⁷ Direct homogeneous CO₂ hydrogenation is difficult to achieve, but several catalysts have been reported in recent years.⁸ These systems operate under relatively mild conditions (125-165 °C), but except for some prominent cases,^{9,10} most catalysts are based on noble metals and/or expensive phosphine ligands.¹¹⁻¹⁴

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.¹⁵ 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 cost effective and facilitate potential coupling to processes such as the methanol to olefin (MTO) process, typically operated at higher temperatures. Palladium was employed by several research groups to find a replacement for copper. Ga-promoted systems had the most success.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, approximately 40% selectivity to produce MeOH under 5 bar, 240 °C, 15% conversion)¹⁹, Ni-Ga (approximately 0.1 g_{MeOH} g_{catalyst}⁻¹ h⁻¹ under 1 bar and 200 °C, selectivity of approximately 100%)²⁰, In₂O₃/ZrO₂ (approximately 0.3 g_{MeOH} g_{catalyst}⁻¹ h⁻¹ at 50 bar and 300 °C, selectivity of approximately 100%, 5% conversion)²¹ and ZnO-ZrO₂ (0.73 g_{MeOH} g_{catalyst}⁻¹ h⁻¹, methanol selectivity of up to 86% with CO₂ single-pass conversion of approximately 10% under 50 bar, and 320° - 315°C).²²

Here we report the preparation, characterization and performance of a novel highly selective catalyst based on In and Co. The initial solid (precatalyst) is composed of In(OH)₃ supported on Co₃O₄ prepared *via* co-precipitation. After a severe transformation during the first hours of reaction, the catalyst was formed and found to be mainly composed of metallic Co (*fcc*), mixed metal carbide Co₃InC_{0.75} and In₂O₃. Surprisingly, despite of the large amount of metallic Co, In promotion drives the selectivity towards methanol rather than towards methane formation.

Results

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 S4). 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.

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 for the Co-In system. The relatively high selectivity of In-Co towards CH₄ suggests that part of the catalyst contains accessible Co nanoparticles, which are well known for their high methanation activity.

Structural rearrangement during the catalytic test. The observation of a long induction period is usually a clear indication that the active catalytic phase forms under the reaction conditions. Furthermore, we noticed a strong pyrophoric behaviour 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 between a type II and IV isotherm according to the IUPAC classification. This type of isotherm is characteristic of mesoporous/macroporous solids. In@Co-1, the precatalyst, has 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 Co₃O₄ nanoparticles in the 10–40 nm range and larger In(OH)₃ nanoparticles shaped as rectangular parallelepipeds (> 100 nm x 50 nm). Furthermore, Co and In elemental maps computed from electron energy loss spectroscopy (EELS) reveal that some of the Co₃O₄ 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.^{24,25} 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.*²⁶, *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 Co₃O₄ and Co(OH)₂ standard samples. The results indicate that the sample contains 82.5% of Co₃O₄ and the remaining 17.5% of the extra Co(OH)₂ contribution. Since Co(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 2 b, 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 In³⁺ in In(OH)₃.²⁷ **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/C-H (sp³), C-O, C=O and O-C=O bonds,^{28,29} 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 study 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 m²/g vs. S_{BET} (catalyst) = 17 m²/g). All of the 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.³⁰ Additionally, the cobalt oxide transforms into metallic Co that crystallizes in a face-centred cubic crystal system. However, the most striking evolution is the appearance of a mixed metal carbide with the Co₃InC_{0.75} stoichiometry as the major crystalline phase in the spent catalyst. Note also that none of the reported Co-In intermetallic compounds (CoIn₂³¹, CoIn₃³²) or pure metallic indium was detected.

The fate of each phase in the precatalyst was also characterized after CO₂ hydrogenation using ADF-STEM imaging and EELS (**Figure 3**). The large and rectangular In(OH)₃ nanoparticles are converted into much smaller In₂O₃ crystallites (Figure S5 a,b and purple colour in **Figure 3b**). The Co₃O₄ nanoparticles are transformed into metallic Co nanoparticles (Figure S5 c, d and green colour in **Figure 3b**). The previous aggregates of Co₃O₄ nanoparticles, which were in contact with amorphous indium hydroxide, are likely the starting precursor for the formation of Co₃InC_{0.75} carbide (cyan colour 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 3a*), 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 3b*). 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) colour 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.%. This result is consistent with the formation of the mixed $\text{CoInCo}_{0.75}$ carbide and the remaining presence of In_2O_3 . The Co/In ratio decreases markedly from 6.5 to 2. Overall, this result means that the In@Co solids rearranged during CO_2 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 centred at approximately ~ 781.1 eV corresponds to cobalt mixed oxides.^{26,33,34} 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 $\text{CoInCo}_{0.75}$ carbide (55.7 at.%)³⁵ and to indium in In_2O_3 (44.3 at.%).^{35,36}

It is very difficult to distinguish between the metallic and carbide states considering only the Co 2p and In 3d core levels since they have similar binding energies. To substantiate the presence of the metallic carbide using XPS, a high-resolution spectrum at the C_{1s} core level of the sample after the reaction was recorded (**Figure 2c**). The C_{1s} core level from the sample after the reaction was fitted using seven components located at 283.4 eV, 284.4 eV, 285.0 eV, 285.7 eV, 286.7 eV, 288.2 eV and 289.6 eV corresponding to C-Co^{33,34,37}, C=C (*sp*2)³⁷, C-C/C-H (*sp*3)²⁹, CO-Co^{37,38}, C-O, C=O and O-C=O bonds.^{28,29} In comparison to the In@Co precatalyst, the appearance of $\text{CoInCo}_{0.75}$ carbide and the presence of both graphitic carbon and CO adsorbed on metallic cobalt were observed for the In@Co catalyst after the reaction.

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 S4). Cobalt oxide, once converted to metallic Co under the reaction conditions, predictably converted carbon dioxide to methane with 100% selectivity. Pure In_2O_3 showed a negligible conversion of approximately 1% with carbon monoxide as the only product. A 97% pure $\text{Co}_3\text{InCo}_{0.75}$ phase was obtained from metal organic framework-mediated synthesis *via* pyrolysis of a Co-In MOF (see the SI). The resultant $\text{Co}_3\text{InCo}_{0.75}$ carbide, alone or mixed with In_2O_3 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. Indeed, there are precedents in the literature where Ni, Co, Cu metal nanoparticles were alloyed with indium and tested for the selective hydrogenation of carboxylic acids to alcohols. When compared against the parent monometallic catalyst, a systematic suppression of the hydro-decarbonylation reaction was found.³⁹⁻⁴¹ By analogy, we propose that indium poisons the surface of metallic cobalt, hindering its total hydrogenation activity (approximately 80% CO_2 conversion on metallic Co vs. 19% on In@Co-1). This surface modification may also prevent methane formation due to a

slower hydrogenolysis rate of the C-O bond compared to the desorption rate of the CO and CH₃OH intermediates. The influence of the In content on the catalytic performance also supports this hypothesis. *Figure 5* shows the catalytic behaviour of catalysts that were prepared by the same method at varying the indium and cobalt contents. The best performance is achieved on catalysts 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.

Optimization of the catalyst formulation. Despite its promising performances, the first In@Co-1 catalyst has substantial heterogeneity due to significant amounts of In₂O₃ and Co₃O₄ phases that do not contribute to the selective formation of methanol. We hypothesized that the heterogeneity after the induction period arises mainly from the initial heterogeneity in the precatalyst. Achieving better mixing of indium and cobalt in the as-synthesized solid is expected to enhance the formation of the relevant active phase. To this end, the hydrothermal treatment used for the previous preparation of In@Co-1 samples was omitted to avoid segregation of the In(OH)₃ and Co₃O₄ 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 In₂O₃ nanoparticles (Figure S9). 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 80-200 m² g⁻¹ compared to the initial 30 m² g⁻¹ of the In@Co-1 precatalyst. The crystalline phases after catalyst activation were also found to be a mixture of Co₃InCo_{0.75}, In₂O₃ and Co (fcc) phases similar to the In@Co-1 catalyst (Figure S9)

When applied in CO₂ hydrogenation, a similar effect of indium loading on the catalytic performance was observed (Figure 5). 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 starting under the same chosen standard conditions of 300 °C and 50 bar (Figure 6). 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_{CH₄} = 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 g_{MeOH} g_{cat}⁻¹ h⁻¹. Further increasing the GHSV to 27500 h⁻¹ leads to a record methanol productivity of 0.86 g_{MeOH} g_{cat}⁻¹ h⁻¹ at a slightly increased selectivity to methanol of 81%. Decreasing the temperature to 285 °C results in selectivities to methanol on the order of 85% with a negligible formation of undesired methane.

Figure 6. 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.

Figure 7. Comparison of the In@Co-2 system to the conventional Cu-based catalyst from Alfa Aesar. Reaction conditions: 50 bar, 80% H₂ 20% CO₂ feed, 50 mg of In@Co-2 catalyst, 56.1 wt% In in the precatalyst.

To extend the comparison between In@Co-2 and Cu-ZnO-Al₂O₃, for experiments performed under exactly the same conditions, the MeOH yield at 50 bar is plotted for temperatures ranging from 250 °C to 350 °C against thermodynamic equilibrium conversion (**Figure 7**). 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-ZrO₂,²² *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.

Conclusions

We reported a novel indium/cobalt-based system for the production of methanol from carbon dioxide. Indium, when in close proximity to Co, is able to tune its selectivity from methane formation to methanol formation while maintaining a highly productive catalyst, even under conditions close to thermodynamic control. The reported catalysts are easy to prepare and show outstanding stability under relevant process conditions. Our results, in addition to establishing a new state-of-the-art system for this important transformation, highlight the importance of metal doping and may have important implications for other fields of catalysis, such as electrocatalysis.

METHODS

Catalyst preparation

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.

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