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Indium Oxide-based Catalysts for Solar Fuels Production

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The need to pursue renewable, carbon neutral forms of energy has led to a far reaching-research effort to generate and store solar energy. It has been shown that indium oxide-based materials have the potential to catalyze the reduction of carbon dioxide to carbon monoxide or even continue reduction to methanol. Recent advances and current challenges in further developing indium oxide catalysis as a means of producing a sustainable liquid fuel supply will be addressed. This project will give an overview of the research in indium oxide catalysts for solar fuels generation and the immediate relevance of recent work within the Bussell Research Group in WWU's Chemistry Department.

Contents

1. Introduction

Anthropogenic carbon dioxide (CO_2) emissions since the beginning of the industrial revolution

has quickly elevated the atmospheric level of CO_2 to an average annual concentration of 409.8 ppm in

2019.[1] Furthermore, the increase in atmospheric concentration from human sources only reflects half of

anthropogenic emissions. Though large quantities of CO_2 is sequestered in biomass, this amount is

nearly negated by land-use change such as deforestation.[2,3] An even greater portion of anthropogenic

CO_2 emissions have been absorbed into the ocean,[2,3] contributing to its acidification. The observable

impact of fossil fuel use and industry, together with increasing demand for energy, elevate the need for

a carbon-neutral energy economy.

Despite concerted regulatory and industrial efforts to move toward such an energy economy,

challenges arise in implementing renewable sources of energy into the energy grid. Peak wind and solar

energy production times do not align with times of peak demand for power, and so a means of storing

the energy for peak demand is required. Batteries are expensive, require metals such as lithium or

cobalt, which are environmentally costly to mine and ultimately have a finite number of charge cycles.

Additionally, in weight sensitive applications such as aviation, batteries cannot store energy with the

same density as liquid fuel. A renewable source of gas or liquid fuel is therefore highly desirable.

Research in indium oxide-based catalysis could potentially address the demand for renewable and

carbon-neutral energy sources.[4,5]

Indium oxide-based catalysts are especially promising due to their ability to absorb across the

spectrum of available solar irradiance. Many photocatalysts, such as titania, are limited by their ability to

absorb only a narrow band of solar irradiance in the ultra-violet (UV) region. They therefore only utilize a

fraction of the available solar energy (Fig. 1). Indium-oxide based catalysts can be modified to broaden

their absorption from the UV and across the entire visible spectrum to capture more available energy.
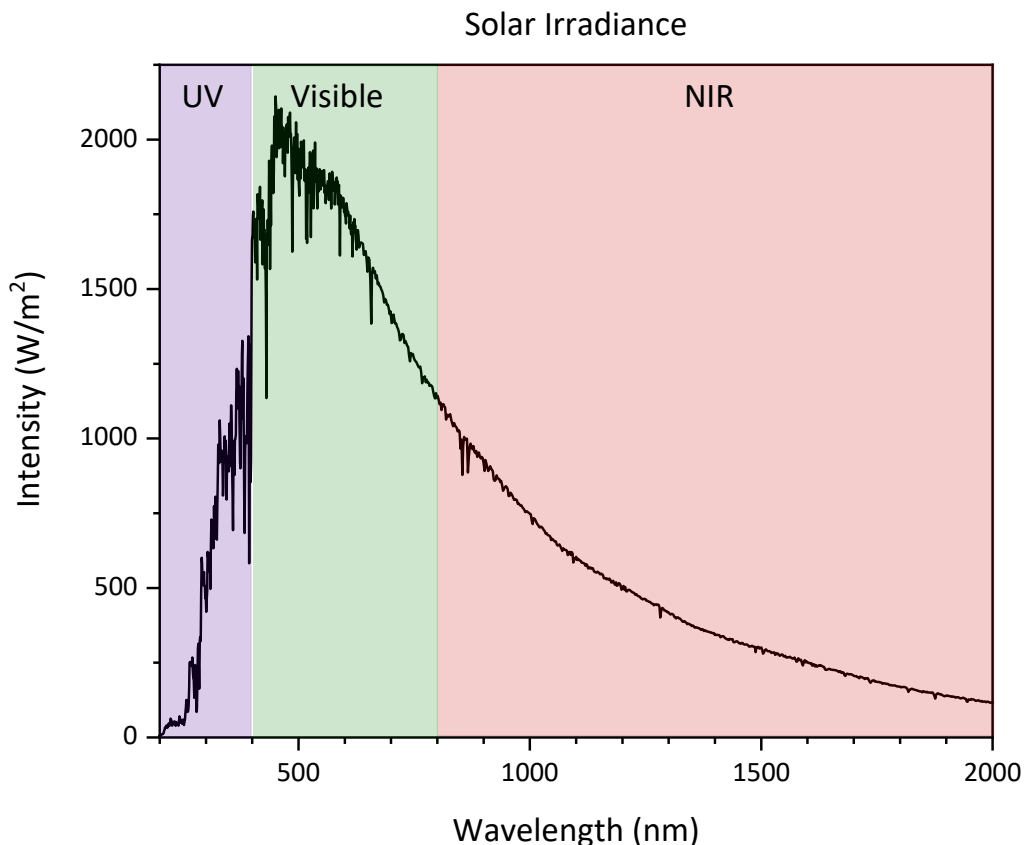
Solar Irradiance

Figure 1. Extraterrestrial solar irradiance.[6]

2. Catalytic Goals

Current research is focused on developing indium oxide-based catalysts which could use thermal or solar energy to reduce CO_2. There are two main divergent schemes in indium oxide catalyzed reduction of CO_2. Following the reverse water gas shift (RWGS) reaction, CO_2 is reduced to carbon monoxide (CO). Alternately, CO_2 can be further reduced and hydrogenated to produce methanol.

1) $CO_{2(g)} + H_{2(g)} \longrightarrow CO_{(g)} + H_2O_{(g)}$ $\Delta H = -49.2$ kJ/mol

2) $CO_{2(g)} + 3H_{2(g)} \longrightarrow CH_3OH_{(g)} + H_2O_{(g)}$ $\Delta H = 42.1$ kJ/mol

Figure 2. RWGS scheme (1) and CO_2 to methanol scheme (2), both at 5 MPa, 423-723 K.[7]

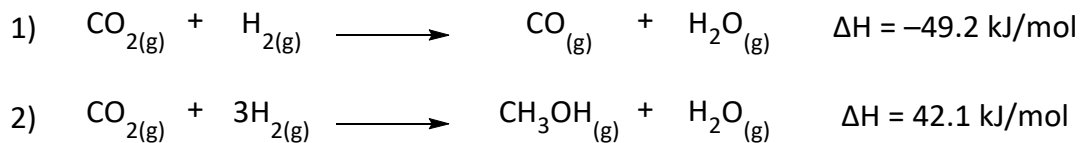**2a. Reverse Water Gas Shift**

Using hydrogen (H_2), CO_2 can be reduced to CO. Because long term storage of CO poses safety concerns due to its high toxicity, this can then be directly burned for energy or used as a feedstock for C_1-based feeds (CH_4, CH_3OH, or $HCOOH$) such as Fischer-Tropsch production of fuel range hydrocarbons. Further, carbon monoxide and other C_1 feedstocks have broad industrial importance beyond energy production and may be used to produce olefin polymer feedstocks.

2b. Methanol Production

Greater H_2/CO_2 ratios, higher pressures and temperatures are necessary to favor continued reduction of CO_2 to methanol. Though the net conversion from reactants to products is estimated to be exergonic,[7] the higher pressures and temperatures required may result in a higher energy input to produce methanol than CO from CO_2. Methanol production may occur as a continuation of the hydrogenation of carbon monoxide produced through the RWGS pathway or through a separate formate pathway.[8]

3. Mechanistic Insights from Computation

The most likely mechanism for the formation of methanol from CO_2 was found to be adsorption of one of the oxygen atoms of CO_2 into an oxygen vacancy on the In_2O_3 surface, and the successive additions of three hydrogens to the carbon to produce an intermediate resembling formate, bound to the surface by the oxygen bonded to an indium atom.[9] The final step is the addition of hydrogen to the oxygen forming methanol which desorbs from the In_2O_3 surface.[9] Oxygen vacancies of In_2O_3 are recognized as the active sites of the catalyst. They are formed by reduction of stoichiometric In_2O_3 and are replenished by oxygen from CO_2.[10] The formation of oxygen vacancies may be altered by the addition of catalytic promoters which have better adsorption properties and better promote catalyst reduction.[8]

Computational analyses of indium oxide have analyzed cubic (c-In_2O_3) and hexagonal (h-In_2O_3) crystal phases of indium oxide. While it has been proposed that the production of methanol is more energetically favorable over h-In_2O_3,[11,12] c-In_2O_3 is experimentally observed to have a higher normalized methanol yield than h-In_2O_3 until 593 K.[11] Above 593 K, h-In_2O_3 has better methanol yields; however, c-In_2O_3 has better RWGS activity for CO production.[13] H-In_2O_3 is less stable than c-In_2O_3, and h-In_2O_3 was observed to convert to the c-In_2O_3 above 450 °C under reaction conditions.[13] Ultimately, the application of computational studies with phase-pure, crystalline In_2O_3 is complicated with a loss of crystallinity in the recent shift of focus to intentionally sub-stoichiometric In_2O_{3-x}, which provides higher yields than any previously analyzed indium-oxide based catalyst.[4]

4. Catalyst Design

Understanding the function of the indium oxide-based catalysts allows refinement of their design. The indium oxide can be modified directly by the control of oxygen vacancies, and several other factors more routinely considered in the optimization of heterogeneous catalysts such as the addition of promoters and use of supports are also relevant. Modifications to the catalyst must be considered wholistically, as any single change can have a complex set of effects.

4a. Optimizing Light Absorption

Incident light capture is of high importance for a solar-energy catalyst and increasing the ability of the catalyst to absorb light and use it to drive chemical reactions is critical to the feasibility of indium oxide catalysts. Photocatalysts, which often use only small portions of the available solar energy to perform specific, quantized electron excitations to promote chemical reactivity are limited to utilization of only small bands of the available light. Recent work on reduction of indium oxide to sub-stoichiometric In_2O_{3-x} turns the indium oxide from yellow to black and promotes far greater absorption of available light.[4] This absorption allows the In_2O_{3-x} to function using photoexcitation by UV-range

photons and broad spectrum warming of the catalysts by lower energy photons. This broader spectrum

activity is referred to as photothermal catalysis.[5]

4b. Promoters

Promoters are generally metals which improve the activity of a catalyst by favoring adsorption

of the substrates or desorption of the desired product. Either or both effects may also contribute to

reduced coking of the catalyst on-stream. Promoters may be added over the primary phase of the

catalyst or during the synthesis of the active phase. The latter method usually has improved and more

stable activity due to sintering resistance.[7,14]

Palladium is by far the most common promoter tested in indium-oxide based catalysts.

Palladium-promoted indium oxide was modelled by DFT as 4 atom palladium clusters on the indium

oxide surface.[8] The interface between the palladium clusters and the indium oxide was found to be

more active than indium oxide alone for CO_2 adsorption and hydrogenation.[8] The success of small

palladium clusters is emphasized in later studies which find larger palladium clusters promote sintering

of In_2O_3 particles.[7,15] Interestingly, the increase in yield of palladium-promotion of In_2O_3 supported on

SBA-15 decrease from 533 K, until the behavior of promoted catalysts is indistinguishable from the un-

promoted In_2O_3 on SBA-15 at 633 K.[16]

The critical effect of promoter particle size is also observed in gold promoted In_2O_3. If the gold

particles are sufficiently small, Rui et al. describes a partial positive charge in the gold particles which

forms due to the withdrawal of electrons by the In_2O_3.[17] The charge transfer has the effect of improving

the adsorption behavior of the gold and improving its effect as a promoter. The methanol yield was

found to be better than that of copper/zinc-oxide/alumina catalysts currently in use for methanol

production.[17]

Other noble metals such as platinum and rhodium have recently been used as promoters for indium-oxide based catalysts.[14,18] The rhodium-promoted In_2O_3 was found to significantly improve the methanol yield similarly to the effects of gold-promotion.

To better compete with the cost of current methanol production catalysts, transition metal promotion is being actively researched.[7,19] While nickel-promoted indium-oxides have not yet matched the yields of palladium-promoted indium oxides, nickel-promoted catalysts still have better methanol yields than most indium-oxide based catalysts.[19] Nickel-promoted In_2O_3, like palladium-promoted In_2O_3, is prone to deactivation by CO.[7] Unlike, palladium however, the deactivation is more complete, matching the activity of unpromoted In_2O_3, and no lost activity is recovered in the absence of CO.[7]

4c. Indium-Gallium Oxides

Though not directly considered as a Fischer-Tropsch catalyst, there is active research in integrating the CO_2 to methanol activity of indium oxide-based catalysts into lower-olefin production schemes. Fischer-Tropsch catalysts for hydrocarbon production from CO and H_2 have optimal yields at higher temperature ranges than those of indium oxide-based CO_2 to CO catalysts. While lower temperatures are more feasible for photothermal catalysis, increasing the optimal yield temperature of CO_2 to CO conversion could enable the design of a bifunctional CO_2 to CO to hydrocarbon catalyst. A higher optimal yield temperature of CO_2 to CO conversion was achieved by synthesizing a mixed indium-gallium oxide ($In_{2-x}Ga_xO_3$).[20] This finding is potentially convergent with the substitution of gallium into indium-oxide to shift the band-gap and allow tunability of the light absorption.

Alternately, an indium-zirconium oxide was used to catalyze CO_2 to C_2-C_4 olefin production, where the indium-zirconium oxide was found to be a more stable catalyst than indium oxide alone.[21] This result is especially interesting when compared with the use of zirconia as a support in the work of Araújo et al. where monoclinic zirconia had higher yields and better CO tolerance than In_2O_3 alone.[7]

4d. Supported Indium Oxides

Supporting the active phase of a catalyst has long been used to increase active surface area using a less costly material such as silica. Though at times considered inert, supports in indium oxide-based catalysis allows more efficient use of indium and can increase the functionality of the indium oxide over bulk indium-oxide.

Inert supports such as alumina (Al_2O_3) and SBA-15 are not expected to directly influence the behavior of the In_2O_3 active phase, and they only contribute by spreading out the active phase. If the support fails to increase the surface area of the active phase, no improvement is observed. This is the case in Araújo et al. for 5wt% In_2O_3/Al_2O_3, which was observed to have the same or worse activity when compared to that of bulk In_2O_3 when normalized for mass of In_2O_3.[7]

Other types of supports, such as monoclinic zirconia (m-ZrO_2) are observed to greatly increase the activity of indium oxide.[7] 5wt% In_2O_3/ m-ZrO_2 has 25% better activity than bulk phase In_2O_3 while not suffering from CO-induced deactivation.[7] Unexpectedly, triclinic ZrO_2 shows almost no improvement over bulk indium oxide when normalized for mass of In_2O_3.[7] Zeolites which are themselves active catalysts can be incorporated into indium oxide-based catalysts as supports for the design of bifunctional catalysts. These bifunctional catalysts can be designed for more complex reactions as was attempted with SAPO-34 for CO_2 to methanol to olefin production.[21]

5. Process Design

Though reduction from stoichiometric indium oxides is found to be catalytically beneficial, over-reduction has been observed, reducing the activity of the catalyst. Carbon monoxide has also been observed to reduce indium oxide-based catalysts under catalytically relevant conditions. The pure CO_2 feeds most often studied are not a perfect analog of industrial applications, where the feed is likely to be contaminated by CO.[7] Reduction of several indium oxide-based catalysts was observed with CO-TPR as CO_2 was evolved from bulk phase indium oxide as low as 370 K.[7] The effects of different supports

likely bring this CO-induced reduction temperature even lower as the oxidation state of indium in the two most effective catalysts in the study of CO_2-CO mixed feeds was observed to change over the 44-hour and 24-hour cycles. The reduction state of the indium oxide is by no means fixed over the course of catalysis, and considerations must be made to maintain an optimal reduction state.

6. Summary and Outlook

Active research in the field of indium oxide-based catalysts is progressing towards viable methods of producing C_1 feedstocks. Availability of these industrially relevant compounds will be instrumental in the transition away from a reliance on petroleum for energy and consumer goods. Indium oxide-based catalysts may find early applications in CO_2 emission reduction by converting CO_2 from carbon industrial capture technologies into valuable compounds, and therefore providing economic incentive to further develop carbon capture.

Further development of indium oxide-based catalysts to improve activity their economic and energetic feasibility. The simpler synthesis and greater stability of c-In_2O_3 suggest that it will be more relevant than h-In_2O_3 for scalable applications. The cubic phase is further favored by greater RWGS activity at lower temperatures which are more achievable for solar-powered reactions. Maintaining a balanced surface reduction of the indium oxide to create oxygen vacancies will be essential to optimizing catalyst performance. This reduction can be performed with H_2 or CO as a pre-treatment and then maintained under feed conditions. The use of promoter metals not only facilitates the creation of oxygen vacancies but also improves the overall adsorption behavior of the catalyst for CO_2 reduction. Eventual wide-scale adoption of these catalysts would likely require independence from costly and rare noble metals. Transition metal promoters such as nickel-phosphides may provide added stability on-stream over nickel promoted catalysts without the cost of metals such as palladium.

The rate of development of indium oxide-based catalysts has increased over the last decade and will likely continue towards their eventual application in CO_2 utilization. Contingent upon the availability

of a renewable source of H_2, indium oxide-based catalysts are positioned to have an important role in

the realization of a carbon-neutral energy economy.

References

1. Arndt, D. S., J. Blunden, and Dunn, R. J. H. Abstract and Introduction [in "State of the Climate in 2019"]. *Bulletin of the American Meteorological Society* 2020, *101* (8), Siii–S8 https://doi.org/10.1175/2020BAMSStateoftheClimate_Intro.1.

2. Le Quéré, C.; Andrew, R. M.; Friedlingstein, P.; Sitch, S.; Pongratz, J.; Manning, A. C.; Korsbakken, J. I.; Peters, G. P.; Canadell, J. G.; Jackson, R. B.; Boden, T. A.; Tans, P. P.; Andrews, O. D.; Arora, V. K.; Bakker, D. C. E.; Barbero, L.; Becker, M.; Betts, R. A.; Bopp, L.; Chevallier, F.; Chini, L. P.; Ciais, P.; Cosca, C. E.; Cross, J.; Currie, K.; Gasser, T.; Harris, I.; Hauck, J.; Haverd, V.; Houghton, R. A.; Hunt, C. W.; Hurtt, G.; Ilyina, T.; Jain, A. K.; Kato, E.; Kautz, M.; Keeling, R. F.; Klein Goldewijk, K.; Körtzinger, A.; Landschützer, P.; Lefèvre, N.; Lenton, A.; Lienert, S.; Lima, I.; Lombardozzi, D.; Metzl, N.; Millero, F.; Monteiro, P. M. S.; Munro, D. R.; Nabel, J. E. M. S.; Nakaoka, S.; Nojiri, Y.; Padin, X. A.; Peregon, A.; Pfeil, B.; Pierrot, D.; Poulter, B.; Rehder, G.; Reimer, J.; Rödenbeck, C.; Schwinger, J.; Séférian, R.; Skjelvan, I.; Stocker, B. D.; Tian, H.; Tilbrook, B.; Tubiello, F. N.; van der Laan-Luijkx, I. T.; van der Werf, G. R.; van Heuven, S.; Viovy, N.; Vuichard, N.; Walker, A. P.; Watson, A. J.; Wiltshire, A. J.; Zaehle, S.; Zhu, D. Global Carbon Budget 2017. *Earth System Science Data* 2018, *10* (1), 405–448 https://doi.org/10.5194/essd-10-405-2018.

3. Global Carbon Project 2017. Supplemental data of Global Carbon Budget 2017 (Version 1.0) [Data set]. Global Carbon Project https://doi.org/10.18160/gcp-2017.

4. Wang, L.; Dong, Y.; Yan, T.; Hu, Z.; Jelle, A. A.; Meira, D. M.; Duchesne, P. N.; Loh, J. Y. Y.; Qiu, C.; Storey, E. E.; Xu, Y.; Sun, W.; Ghoussoub, M.; Kherani, N. P.; Helmy, A. S.; Ozin, G. A. Black Indium Oxide a Photothermal CO_2 Hydrogenation Catalyst. *Nature Communications* **2020**, *11* (1), 2432-2437 https://doi.org/10.1038/s41467-020-16336-z.

5. Ghoussoub, M.; Xia, M.; Duchesne, P. N.; Segal, D.; Ozin, G. Principles of Photothermal Gas-Phase Heterogeneous CO_2 Catalysis. *Energy Environ. Sci.* **2019**, *12* (4), 1122–1142 https://doi.org/10.1039/C8EE02790K.

6. 2000 ASTM Standard Extraterrestrial Spectrum Reference E-490-00 https://www.nrel.gov/grid/solar-resource/spectra-astm-e490.html.

7. Araújo, T. P.; Shah, A.; Mondelli, C.; Stewart, J. A.; Curulla Ferré, D.; Pérez-Ramírez, J. Impact of Hybrid CO_2-CO Feeds on Methanol Synthesis over In_2O_3-Based Catalysts. *Applied Catalysis B: Environmental* **2021**, 285, 119878. https://doi.org/10.1016/j.apcatb.2021.119878.

8. Ye, J.; Liu, C.; Mei, D.; Ge, Q. Methanol Synthesis from CO_2 Hydrogenation over a Pd_4/In_2O_3 Model Catalyst: A Combined DFT and Kinetic Study. *Journal of Catalysis* **2014**, *317*, 44–53 https://doi.org/10.1016/j.jcat.2014.06.002.

9. Ye, J.; Liu, C.; Ge, Q. DFT Study of CO_2 Adsorption and Hydrogenation on the In_2O_3 Surface. *J. Phys. Chem. C* **2012**, 116 (14), 7817–7825 https://doi.org/10.1021/jp3004773.

10. Ye, J.; Liu, C.; Mei, D.; Ge, Q. Active Oxygen Vacancy Site for Methanol Synthesis from CO_2 Hydrogenation on In_2O_3(110): A DFT Study. *ACS Catal.,* **2013**, *3* (6), 1296–1306

https://doi.org/10.1021/cs400132a.

11. Dang, S.; Qin, B.; Yang, Y.; Wang, H.; Cai, J.; Han, Y.; Li, S.; Gao, P.; Sun, Y. Rationally Designed Indium Oxide Catalysts for CO_2 Hydrogenation to Methanol with High Activity and Selectivity. *Science Advances* **2020**, *6* (25), 1-11. https://doi.org/10.1126/sciadv.aaz2060.

12. Qin, B.; Li, S. First Principles Investigation of Dissociative Adsorption of H_2 during CO_2 Hydrogenation over Cubic and Hexagonal In_2O_3 Catalysts. *Phys. Chem. Chem. Phys.* **2020**, *22* (6), 3390–3399. https://doi.org/10.1039/C9CP05867B.

13. Wang, J.; Liu, C.-Y.; Senftle, T. P.; Zhu, J.; Zhang, G.; Guo, X.; Song, C. Variation in the In_2O_3 Crystal Phase Alters Catalytic Performance toward the Reverse Water Gas Shift Reaction. *ACS Catal.* **2020**, *10* (5), 3264–3273 https://doi.org/10.1021/acscatal.9b04239.

14. Yan, H.; He, K.; Samek, I. A.; Jing, D.; Nanda, M. G.; Stair, P. C.; Notestein, J. M. Tandem In_2O_3-Pt/Al_2O_3 Catalyst for Coupling of Propane Dehydrogenation to Selective H_2 Combustion. *Science* **2021**, *371* (6535), 1257–1260. https://doi.org/10.1126/science.abd4441.

15. Frei, M. S.; Mondelli, C.; García-Muelas, R.; Kley, K. S.; Puértolas, B.; López, N.; Safonova, O. V.; Stewart, J. A.; Curulla Ferré, D.; Pérez-Ramírez, J. Atomic - Scale Engineering of Indium Oxide Promotion by Palladium for Methanol Production via CO_2 Hydrogenation. *Nature Communications* **2019**, *10* (1), 3377 https://doi.org/10.1038/s41467-019-11349-9.

16. Jiang, H.; Lin, J.; Wu, X.; Wang, W.; Chen, Y.; Zhang, M. Efficient Hydrogenation of CO_2 to Methanol over Pd/In_2O_3/SBA-15 Catalysts. *Journal of CO_2 Utilization* **2020**, *36*, 33–39. https://doi.org/10.1016/j.jcou.2019.10.013.

17. Rui, N.; Zhang, F.; Sun, K.; Liu, Z.; Xu, W.; Stavitski, E.; Senanayake, S. D.; Rodriguez, J. A.; Liu, C.-J. Hydrogenation of CO_2 to Methanol on a $Au^{\delta+}$–In_2O_{3-x} Catalyst. *ACS Catal.* **2020**, *10* (19), 11307–11317. https://doi.org/10.1021/acscatal.0c02120.

18. Wang, J.; Sun, K.; Jia, X.; Liu, C. CO_2 Hydrogenation to Methanol over Rh/In_2O_3 Catalyst. *Catalysis Today* **2021**, *365*, 341–347. https://doi.org/10.1016/j.cattod.2020.05.020.

19. Jia, X.; Sun, K.; Wang, J.; Shen, C.; Liu, C. Selective Hydrogenation of CO_2 to Methanol over Ni/In_2O_3 Catalyst. *Journal of Energy Chemistry* **2020**, *50*, 409–415. https://doi.org/10.1016/j.jechem.2020.03.083.

20. Akkharaphatthawon, N.; Chanlek, N.; Cheng, C. K.; Chareonpanich, M.; Limtrakul, J.; Witoon, T. Tuning Adsorption Properties of $Ga_xIn_{2-x}O_3$ Catalysts for Enhancement of Methanol Synthesis Activity from CO_2 Hydrogenation at High Reaction Temperature. *Applied Surface Science* **2019**, *489*, 278–286 https://doi.org/10.1016/j.apsusc.2019.05.363.

21. Gao, P.; Dang, S.; Li, S.; Bu, X.; Liu, Z.; Qiu, M.; Yang, C.; Wang, H.; Zhong, L.; Han, Y.; Liu, Q.; Wei, W.; Sun, Y. Direct Production of Lower Olefins from CO_2 Conversion via Bifunctional Catalysis. *ACS Catal.* **2018**, *8* (1), 571–578 https://doi.org/10.1021/acscatal.8b02892.

22. Yang, H.; Shi, Q.; Tian, B.; Lu, Q.; Gao, F.; Xie, S.; Fan, J.; Yu, C.; Tu, B.; Zhao, D. One-Step Nanocasting Synthesis of Highly Ordered Single Crystalline Indium Oxide Nanowire Arrays from Mesostructured Frameworks. *J. Am. Chem. Soc.* **2003**, *125* (16), 4724–4733.

23. Yang, H.; Lu, Q.; Gao, F.; Shi, Q.; Yan, Y.; Zhang, F.; Xie, S.; Tu, B.; Zhao, D. One-Step Synthesis of Highly Ordered Mesoporous Silica Monoliths with Metal Oxide Nanocrystals in their Channels. *Adv. Funct. Mater.* **2005**, *15*, 1377-1384. https://doi.org/10.1002/adfm.200500026.