

# Mitigating Climate Change through Catalytic Conversions of CO<sub>2</sub>: A review

Safi Naseer Ahmad<sup>1,2\*</sup> and Kamran Azharulhaq<sup>1\*</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Nangarhar University, Nangarhar, Afghanistan

<sup>2</sup>Department of Reaction Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin, China

\*Corresponding author: [naseerahmad\\_safi@tju.edu.cn](mailto:naseerahmad_safi@tju.edu.cn) or [izharulhaqnu@gmail.com](mailto:izharulhaqnu@gmail.com)

## ABSTRACT

In the pursuit of a carbon-neutral economy, CO<sub>2</sub> catalytic hydrogenation to methanol emerges as a pivotal technology for mitigating CO<sub>2</sub> and addressing the manufacturing needs of future fuels, chemicals, and materials. The development of this technology not only offers solutions to environmental challenges, such as the greenhouse effect, but also facilitates the effective utilization of CO<sub>2</sub> resources. The aims of this review is reveal intuitions into the structural and surface properties of heterogeneous catalysts, emphasizing the interface between metal and support. The exploration of these factors delves into their functions in reaction mechanisms, influencing catalytic activity, selectivity, and stability in CO<sub>2</sub> hydrogenation to methanol.

**Keywords:** Environmental mitigation, carbon natural economy, heterogeneous catalysts, methanol production

## INTRODUCTION

Global warming and air pollution are acknowledged as primary threats to sustainable human development. These issues stem predominantly from anthropogenic activities involving the combustion of fossil resources, leading to the release of substantial amounts of carbon dioxide, carbon monoxide, nitrogen oxides, and soot into the atmosphere (Aresta et al., 2013). The CO<sub>2</sub> catalytic conversion to high-value chemicals is considered as an ideal solution to meantime address both the environmental and chemicals issues (Mikkelsen et al., 2010). Among various approaches, CO<sub>2</sub> hydrogenation emerges as a promising means to regenerate combusted hydrocarbons (Bai et al., 2021).

Hydrogen (H<sub>2</sub>) serves as an effective reagent for facilitating CO<sub>2</sub> conversion, obtainable through water electrolysis powered by renewable energy sources such as hydro, wind, solar, and geothermal (Gao et al., 2020; Jadhav et al., 2014). However, Methanol is a significant C1 chemistry compound among potential CO<sub>2</sub> hydrogenation products, with a demand exceeding 110 Mt/year (Figure 1a) in various applications. Methanol assist as a crucial chemical intermediate and molecular platform, facilitating the synthesis of key products like acetic acid, formaldehyde, and gasoline (MTG) (Ali et al., 2015). Due to its high octane grade, it can also be an excellent replacement or additive for fuel and retrofit diesel engines (Jadhav et al., 2014). Thus, the production of methanol from CO<sub>2</sub> is beneficial from an environmental and economic perspective (Ye et al., 2019). A catalyst is typically required to convert CO<sub>2</sub> into methanol due to the high stability of CO<sub>2</sub>. Metal and/or metal oxide-based catalysts, such as Cu (Marcos et al., 2022), Zn (Deerattrakul et al., 2019), Cr (Kirilin et al., 2017), and Pd, are commonly used to facilitate the redox reaction. Additionally, various materials as promoters or supports have been reported (Snider et al., 2019).

This study aims to explore the mechanistic aspects of CO<sub>2</sub> hydrogenation to methanol, with a specific emphasis on metal-based heterogeneous catalysts. These catalysts present numerous advantages, including enhanced stability, ease of recycling, and the potential for lower manufacturing costs, all of which are crucial for industrial applications.

## CATALYSTS of CO<sub>2</sub> CONVERSION to METHANOL

### *Transitional metal-based catalysts*

The predominant catalyst for methanol synthesis is metal-based, such as copper-based catalysts, typically prepared through co-precipitation from its salt using basic precipitation agents (bicarbonates, hydroxides or carbonates) in an aqueous medium. Subsequent processes, including aging, calcination, and reduction, may be employed (Niu et al., 2022). Previous studies indicate that both CO<sub>2</sub> and CO can undergo hydrogenation to form methanol. On the Cu<sup>0</sup> surface, CO<sub>2</sub> acts as the predominant carbon source, while on the Cu<sup>+</sup> surface CO as the

dominant source of carbon (Liu et al., 2017). Moreover, the hydrogenation rate of  $\text{CO}_2$  is more rapid than that of CO (Lee et al., 1993). Furthermore, Cu assists as the active sites for  $\text{H}_2$  dissociation, while the supports potentially catering more active sites, thereby facilitating  $\text{CO}_2$  activation (Arena et al., 2008). In addition, ceria-zirconia solid solution could improve the dispersion of Cu particles on the Cu/Ce-Zr surface, and generating  $\text{Cu}^+-\text{O}-\text{M}$  (M= Ce, Zr),  $\text{Ce}^{3+}-\text{Vo}-\text{Zr}^{4+}$ , (Vo= oxygen vacancy) thus led to enhanced the methanol formation (Safi et al., 2022; Wang et al., 2021). However (Kattel et al., 2017), conducted an investigation of the active site of the Cu-Zn catalyst. The findings indicate methanol formation through formate intermediates ( $\text{HCOO}^-$ ) on both catalysts. Additionally, Zn or ZnO present in ZnCu and ZnO/Cu catalysts stabilize the  $^*\text{HCOOH}$  intermediate via Zn-O interactions, while boosting the activation of  $^*\text{HCOO}$  during hydrogenation (Graciani et al., 2014). Moreover, through density functional theory (DFT) calculation, the reaction mechanism was studied on a commercial Cu-based catalyst. Cu/CeO<sub>2</sub> presents the potential for effective  $\text{CO}_2$  hydrogenation to produce methanol. The active site for methanol synthesis from  $\text{CO}_2$  has been recognized at the Cu-CeO<sub>2</sub> interface, involving a CO intermediate in a contrasting CeO<sub>2</sub>/Cu (111) model catalyst (C. Grabow & Mavrikakis, 2011).

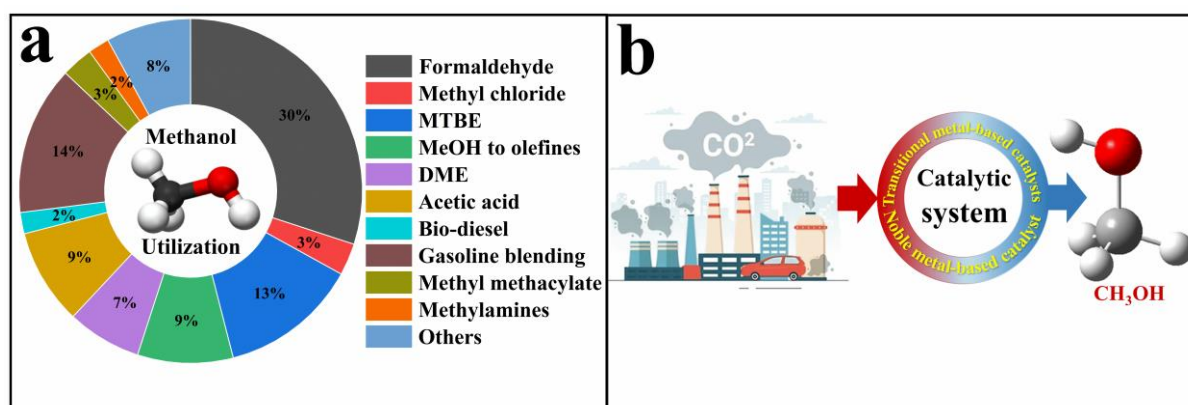


Fig. 1. (a) Methanol utilization by industries, (b) diverse catalysts employed in  $\text{CO}_2$ -to-methanol synthesis.

### Noble metal-based catalysts

However (Ou et al., 2020), studied an unsupported catalyst consisting of Pd-based nanoparticles and exhibited a significant increase in methanol selectivity. Meanwhile, the production of methanol without supports or promoters through pure Pd sites remains a challenging task (Iwasa et al., 2004). Therefore, various oxides, such as ZnO (Zabitskiy et al., 2021), CeO<sub>2</sub> (Choi et al., 2017), and Ga<sub>2</sub>O<sub>3</sub> (García-Trenco et al., 2017), have been utilized as supports for Pd-based catalysts. (Fujitani et al., 1995), pioneered the study of Pd/Ga<sub>2</sub>O<sub>3</sub> catalysts for methanol synthesis through  $\text{CO}_2$  hydrogenation, and employed a co-precipitation method for catalyst preparation. Their findings revealed a Pd/Ga<sub>2</sub>O<sub>3</sub> catalyst with a conversion rate 20-times better than that of a Cu/ZnO catalyst. (García-Trenco et al., 2017), prepared colloidal Pd<sub>2</sub>Ga-based catalysts through a simple modification method, adjusting the Ga<sub>2</sub>O<sub>3</sub> phase by varying the molar Pd:Ga ratio from the precursors. Additionally, an increase in Ga<sub>2</sub>O<sub>3</sub> content led to a significant enhancement in intrinsic activity. These findings suggest a bifunctional active site, with both the Pd<sub>2</sub>Ga and Ga<sub>2</sub>O<sub>3</sub> phases playing a role in the synthesis of methanol. This finding exceeds Pd performance on diverse metal oxide supports like SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub> and ZnO. The varying activity among these oxides relates to their capacity for stabilizing the Pd<sup>n+</sup> (0 < n < 2) species (Chen et al., 2012). Furthermore (Sun et al., 2020), assessed a Pt single-atom catalyst, enhancing its activity by efficiently incorporating Pt into In<sub>2</sub>O<sub>3</sub> through co-precipitation. In  $\text{CO}_2$  hydrogenation, positively charged Pt species, along with reduced and sintered forms, actively facilitate the creation of oxygen vacancies crucial for  $\text{CO}_2$  activation. Additionally, Pt<sup>n+</sup> species promote the heterolytic dissociation of  $\text{H}_2$  and methanol formation. Additionally, while metal species at the atomic scale exhibit remarkable activity, their state may change to larger species during  $\text{CO}_2$  hydrogenation due to reduction or sintering processes. Hence, generating a stable noble catalyst, particularly a single-atom noble metal catalyst, poses a challenge. Accordingly, the exploration of suitable synthesis strategies and/or enhanced reaction conditions is imperative.

## CONCLUSION

The global interest in carbon dioxide capture and utilization is increasing within both academic and industrial communities. The technological process of methanol synthesis through CO<sub>2</sub> hydrogenation has the potential to address environmental issues, generate new forms of clean energy, and produce high-value-added chemicals. Catalysts play a crucial role in the conversion of CO<sub>2</sub> and utilization; therefore, variation in catalyst design and preparation is of utmost importance. However, in recent studies, researchers have conducted numerous experiments concentrating on the mechanistic aspects of the reaction. This information is crucial for advancing the development of the next generation of catalysts. Heretofore, the potential mechanisms have been suggested: formates and Trans COOH\* pathways. (Figure 1b) shown the diverse catalysts employed in CO<sub>2</sub>-to-methanol synthesis. Furthermore, integrating experimental work with DFT computations is crucial for exploring structure-function relationships and accelerating the discovery of catalytic mechanisms. Nevertheless, various factors impact catalytic behavior, making precise classification challenging. The physicochemical properties of metals and support materials, such as state, cluster size, phase, composition, morphology, and alkalinity, significantly influence their catalytic activity.

**ACKNOWLEDGMENT:** The authors would like to express their gratitude to the [Faculty of Science Nangahar University] and the [School of Chemical Engineering and Technology of Tianjin University], for their invaluable guidance and support throughout the development of this paper.

**CONFLICT of INTEREST:** All authors express no conflict of interest in any part of the research.

**FUNDING:** This research received no external funding.

**AUTHORS CONTRIBUTIONS:** Safi Naseer Ahmad: writing-original draft, visualization, review and editing.

**Kamran Azharulhaq:** writing-original draft, review and editing, visualization.

---

## REFERENCES

- Ali, K. A., Abdullah, A. Z., & Mohamed, A. R. (2015). Recent development in catalytic technologies for methanol synthesis from renewable sources: A critical review. *Renewable and Sustainable Energy Reviews*, 44, 508–518. <https://doi.org/10.1016/J.RSER.2015.01.010>
- Arena, F., Italiano, G., Barbera, K., Bordiga, S., Bonura, G., Spadaro, L., & Frusteri, F. (2008). Solid-state interactions, adsorption sites and functionality of Cu-ZnO/ZrO<sub>2</sub> catalysts in the CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH. *Applied Catalysis A: General*, 350(1), 16–23. <https://doi.org/10.1016/j.apcata.2008.07.028>
- Aresta, M., Dibenedetto, A., & Angelini, A. (2013). Catalysis for the Valorization of Exhaust Carbon: from CO<sub>2</sub> to Chemicals, Materials, and Fuels. *Technological Use of CO<sub>2</sub>*. *Chemical Reviews*, 114(3), 1709–1742. <https://doi.org/10.1021/cr4002758>
- Bai, S. T., De Smet, G., Liao, Y., Sun, R., Zhou, C., Beller, M., Maes, B. U. W., & Sels, B. F. (2021). Homogeneous and heterogeneous catalysts for hydrogenation of CO<sub>2</sub> to methanol under mild conditions. *Chemical Society Reviews*, 50(7), 4259–4298. <https://doi.org/10.1039/d0cs01331e>
- C. Grabow, L., & Mavrikakis, M. (2011). Mechanism of Methanol Synthesis on Cu through CO<sub>2</sub> and CO Hydrogenation. *ACS Catalysis*, 1(4), 365–384. <https://doi.org/10.1021/cs200055d>
- Chen, S., Yao, Y., Lan, L., Cao, Y., Yan, C., Gong, M., & Chen, Y. (2012). Effect of zirconium precursor on performance of Pd/Ce<sub>0.45</sub>Zr<sub>0.45</sub>La<sub>0.1</sub>O<sub>1.95</sub> three-way catalyst. *Cuihua Xuebao/Chinese Journal of Catalysis*, 33(11), 1762–1771. [https://doi.org/10.1016/s1872-2067\(11\)60445-2](https://doi.org/10.1016/s1872-2067(11)60445-2)
- Choi, E. J., Lee, Y. H., Lee, D. W., Moon, D. J., & Lee, K. Y. (2017). Hydrogenation of CO<sub>2</sub> to methanol over Pd-Cu/CeO<sub>2</sub> catalysts. *Molecular Catalysis*, 434(2017), 146–153. <https://doi.org/10.1016/j.mcat.2017.02.005>
- Deerattrakul, V., Yigit, N., Rupprechter, G., & Kongkachuichay, P. (2019). The roles of nitrogen species on graphene aerogel supported Cu-Zn as efficient catalysts for CO<sub>2</sub> hydrogenation to methanol. *Applied Catalysis A: General*, 580(January), 46–52. <https://doi.org/10.1016/j.apcata.2019.04.030>
- Fujitani, T., Saito, M., Kanai, Y., Watanabe, T., Nakamura, J., & Uchijima, T. (1995). Development of an active Ga<sub>2</sub>O<sub>3</sub> supported palladium catalyst for the synthesis of methanol from carbon dioxide and hydrogen. *Applied Catalysis A, General*, 125(2), 0–3. [https://doi.org/10.1016/0926-860X\(95\)00049-6](https://doi.org/10.1016/0926-860X(95)00049-6)
- Gao, P., Zhang, L., Li, S., Zhou, Z., & Sun, Y. (2020). Novel Heterogeneous Catalysts for CO<sub>2</sub> Hydrogenation to Liquid Fuels. *ACS Central Science*, 6(10), 1657–1670. <https://doi.org/10.1021/acscentsci.0c00976>
- García-Trenco, A., R. White, E., Regoutz, A., J. Payne, D., S. P. Shaffer, M., & K. Williams, C. (2017). Pd<sub>2</sub>Ga-

- Based Colloids as Highly Active Catalysts for the Hydrogenation of CO<sub>2</sub> to Methanol. *ACS Catalysis*, 7(2), 1186–1196. <https://doi.org/10.1021/acscatal.6b02928>
- Graciani, J., Mudiyansele, K., Xu, F., Baber, A. E., Evans, J., Senanayake, S. D., Stacchiola, D. J., Liu, P., Hrbek, J., Fernández Sanz, J., & Rodriguez, J. A. (2014). Highly active copper-ceria and copper-ceria-titania catalysts for methanol synthesis from CO<sub>2</sub>. *Science*, 345(6196), 546–550. <https://doi.org/10.1126/science.1253057>
- Iwasa, N., Suzuki, H., MasaoTerashita, Arai, M., & Takezawa, N. (2004). Methanol synthesis from CO<sub>2</sub> under atmospheric pressure over supported Pd catalysts. *Catalysis Letters*, 96(1–2), 75–78. <https://doi.org/10.1023/B:CATL.0000029533.41604.13>
- Jadhav, S. G., Vaidya, P. D., Bhanage, B. M., & Joshi, J. B. (2014). Catalytic carbon dioxide hydrogenation to methanol: A review of recent studies. *Chemical Engineering Research and Design*, 92(11), 2557–2567. <https://doi.org/10.1016/J.CHERD.2014.03.005>
- Kattel, S., Liu, P., & G. Chen, J. (2017). Tuning Selectivity of CO<sub>2</sub> Hydrogenation Reactions at the Metal/Oxide Interface. *Journal of the American Chemical Society*, 139(29), 9739–9754. <https://doi.org/10.1021/jacs.7b05362>
- Kirilin, A. V., Dewilde, J. F., Santos, V., Chojecki, A., Scieranka, K., & Malek, A. (2017). Conversion of Synthesis Gas to Light Olefins: Impact of Hydrogenation Activity of Methanol Synthesis Catalyst on the Hybrid Process Selectivity over Cr-Zn and Cu-Zn with SAPO-34. *Industrial and Engineering Chemistry Research*, 56(45), 13392–13401. <https://doi.org/10.1021/acs.iecr.7b02401>
- Lee, J. S., Lee, K. H., Lee, S. Y., & Kim, Y. G. (1993). A Comparative Study of Methanol Synthesis from CO<sub>2</sub>/H<sub>2</sub> and CO/H<sub>2</sub> over a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> Catalyst. *Journal of Catalysis*, 144(2), 414–424. <https://doi.org/10.1006/JCAT.1993.1342>
- Liu, Y. M., Liu, J. T., Liu, S. Z., Li, J., Gao, Z. H., Zuo, Z. J., & Huang, W. (2017). Reaction mechanisms of methanol synthesis from CO/CO<sub>2</sub> hydrogenation on Cu<sub>2</sub>O(111): Comparison with Cu(111). *Journal of CO<sub>2</sub> Utilization*, 20(January), 59–65. <https://doi.org/10.1016/j.jcou.2017.05.005>
- Marcos, F. C. F., Cavalcanti, F. M., Petrolini, D. D., Lin, L., Betancourt, L. E., Senanayake, S. D., Rodriguez, J. A., Assaf, J. M., Giudici, R., & Assaf, E. M. (2022). Effect of operating parameters on H<sub>2</sub>/CO<sub>2</sub> conversion to methanol over Cu-Zn oxide supported on ZrO<sub>2</sub> polymorph catalysts: Characterization and kinetics. *Chemical Engineering Journal*, 427, 130947. <https://doi.org/10.1016/J.CEJ.2021.130947>
- Mikkelsen, M., Jørgensen, M., & Krebs, F. C. (2010). The teraton challenge. A review of fixation and transformation of carbon dioxide. *Energy and Environmental Science*, 3(1), 43–81. <https://doi.org/10.1039/b912904a>
- Niu, J., Liu, H., Jin, Y., Fan, B., Qi, W., & Ran, J. (2022). Comprehensive review of Cu-based CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH: Insights from experimental work and theoretical analysis. *International Journal of Hydrogen Energy*, 47(15), 9183–9200. <https://doi.org/10.1016/j.ijhydene.2022.01.021>
- Ou, Z., Ran, J., Niu, J., Qin, C., He, W., & Yang, L. (2020). A density functional theory study of CO<sub>2</sub> hydrogenation to methanol over Pd/TiO<sub>2</sub> catalyst: The role of interfacial site. *International Journal of Hydrogen Energy*, 45(11), 6328–6340. <https://doi.org/10.1016/J.IJHYDENE.2019.12.099>
- Safi, N. A., Li, Y., Yu, B., Liu, P., Wang, J., Ge, H., & Zhang, K. (2022). The dependence of high catalytic performance on the tunable oxygen vacancy in the CZ<sub>x</sub>S/Zn-HZSM-5 bifunctional catalyst for alkylation of benzene and syngas. *Applied Organometallic Chemistry*, 36(7). <https://doi.org/10.1002/aoc.6744>
- Snider, J. L., Streibel, V., A. Hubert, M., S. Choksi, T., Valle, E., Chester Upham, D., Schumann, J., S. Duyar, M., Gallo, A., Abild-Pedersen, F., & F. Jaramillo, T. (2019). Revealing the Synergy between Oxide and Alloy Phases on the Performance of Bimetallic In–Pd Catalysts for CO<sub>2</sub> Hydrogenation to Methanol. *ACS Catalysis*, 9(4), 3399–3412. <https://doi.org/10.1021/acscatal.8b04848>
- Sun, K., Rui, N., Zhang, Z., Sun, Z., Ge, Q., & Liu, C. J. (2020). A highly active Pt/In<sub>2</sub>O<sub>3</sub> catalyst for CO<sub>2</sub> hydrogenation to methanol with enhanced stability. *Green Chemistry*, 22(15), 5059–5066. <https://doi.org/10.1039/d0gc01597k>
- Wang, H., Zhang, G., Fan, G., Yang, L., & Li, F. (2021). Fabrication of Zr–Ce Oxide Solid Solution Surrounded Cu-Based Catalyst Assisted by a Microliquid Film Reactor for Efficient CO<sub>2</sub> Hydrogenation to Produce Methanol. *Industrial & Engineering Chemistry Research*, 60(45), 16188–16200. <https://doi.org/10.1021/acs.iecr.1c03117>
- Ye, R., Ding, J., Gong, W., Argyle, M. D., Zhong, Q., Wang, Y., Russell, C. K., Xu, Z., Russell, A. G., Li, Q., Fan, M., & Yao, Y. (2019). CO<sub>2</sub> hydrogenation to high-value products via heterogeneous catalysis. *Nature Communications*. <https://doi.org/10.1038/s41467-019-13638-9>
- Zabilskiy, M., Sushkevich, V. L., Newton, M. A., Krumeich, F., Nachtegaal, M., & van Bokhoven, J. A. (2021). Mechanistic Study of Carbon Dioxide Hydrogenation over Pd/ZnO-Based Catalysts: The Role of Palladium–Zinc Alloy in Selective Methanol Synthesis. *Angewandte Chemie - International Edition*, 60(31), 17053–17059. <https://doi.org/10.1002/anie.202103087>