

Editorial

# New Catalysts and Reactors for the Synthesis or Conversion of Methanol

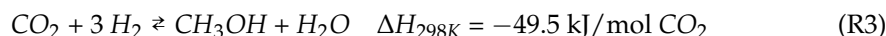
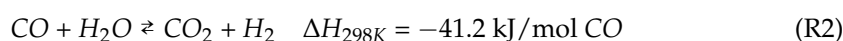
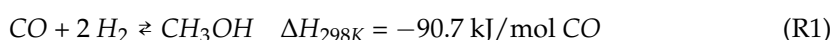
Jaime Soler 

Catalysis and Reactor Engineering Group (CREG), Aragon Institute of Engineering Research (I3A), Universidad de Zaragoza, c/Mariano Esquillor s/n, 50018 Zaragoza, Spain; jsoler@unizar.es

Energy storage is a critical issue in the development of an economy based on the use of renewable energy. A suitable method for storing large amounts of energy for long periods of time is to transform electrical energy from renewable sources into fuels, which leads to so-called “e-fuels”. Several processes are currently used to produce e-fuels, mostly on a laboratory or pilot plant scale, although several demonstration projects with capacities of several MW are already under development. These technologies, also a part of the so-called “Power to Liquids” technologies, have been widely studied in Europe, with more than 200 projects planned, in development, or finished [1]. Power-to-fuels would have the following advantages:

- High energy density;
- Applicable for existing technologies;
- Suited for heavy-duty applications;
- Quick deployment since no infrastructural adaptations are required.

Among liquid e-fuels, methanol is considered one of the most promising technologies [2,3]. It is a versatile matter used both for industrial purposes and for various day-to-day life activities, and as it exhibits high effectiveness as an energy carrier, renewable methanol has been proposed by the Nobel Prize Winner G. Olah as a way to close the CO<sub>2</sub> loop [4]. Methanol can be environmentally synthesized from any feedstock, and its reforming reaction does not alter net CO<sub>2</sub> emissions to the atmosphere. Industrial production of methanol from syngas (R1) occurs at temperatures around 220–300 °C and pressures of 50–100 bar, generally occurring in the presence of copper or nickel–alumina-based catalysts. Along the path of methanol synthesis, the reactions that take place are the hydrogenation of carbon monoxide (R1), water–gas shift (R2), and the hydrogenation of carbon dioxide [5]:



Methanol formation is exothermic, and therefore, the thermodynamic equilibrium is favored at low temperatures, while kinetics is favored by high temperature. Although reaction (R1) and reaction (R3) both give methanol as a major product, it was confirmed through reagents with isotopes that, under industrial conditions, the first reaction is more favorable, and when reactions are enabled without carbon monoxide as a starting material, methanol is entirely formed through reaction (R1) without passing through the third reaction [6]. In addition, the difference between the number of moles of starting materials and products requires operation at high pressure to obtain a high yield to methanol. Methyl alcohol is exclusively achieved through the direct hydrogenation of carbon dioxide (reaction 1) [7]. CO<sub>2</sub> hydrogenation competes with reverse water-gas shift (reaction 2), which drops the selectivity to methanol. Reverse water–gas shift is endothermic, and thus, its equilibrium is favored at high temperatures. Although methanol is currently obtained



**Citation:** Soler, J. New Catalysts and Reactors for the Synthesis or Conversion of Methanol. *Catalysts* **2024**, *14*, 640. <https://doi.org/10.3390/catal14090640>

Received: 19 July 2024

Accepted: 19 September 2024

Published: 20 September 2024



**Copyright:** © 2024 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

from fossil fuels (via synthesis gas), in a future decarbonized economy, it could be obtained via the reaction of hydrogen (coming from water hydrolysis) and carbon dioxide (from carbon capture processes).

On the other hand, methanol is a raw material for the chemical industry. In recent years, alternative processes have been developed to substitute crude oil by methanol. The new route of methanol transformation into light olefins (mainly ethylene and propylene) is known as the Methanol-to-Olefins (or MTO) process [8–11]. The MTO process is usually carried out over zeolite-based catalysts, such as ZSM-5 or SAPO-34, which, because of their shape selectivity, are able to produce a well-defined range of hydrocarbons [12–14].

The MTG (Methanol to Gasoline) process allows us to transform methanol into hydrocarbons within the range of gasoline boiling points [15]. The conversion of methanol to hydrocarbons can be carried out with a wide variety of acid catalysts. Some studies report the use of non-zeolitic catalysts for the MTG reaction [16–18]. However, those based on zeolite have offered the best performance. Among them, the HZSM-5 zeolite stands out from the rest [19].

Additional uses for methanol are currently under study [20], so the Special Issue entitled “New Catalysts and Reactors for the Synthesis or Conversion of Methanol” allows readers to gain a complete view of the state of the art for methanol applications based on new catalysts or reactors.

In contribution 1, a review of the utilization of methanol to produce dimethyl carbonate (DMC) is presented. DMC is widely used as an intermediate and solvent in the organic chemical industry. In recent years, compared with the traditional DMC production methods (phosgene method, transesterification method), the methanol oxidation carbonylation method, the gas-phase methyl nitrite method, and the direct synthesis of CO<sub>2</sub> and methanol have made significant progress in the synthesis process and catalyst development.

In contribution 2, the authors use a colloidal synthesis technique to produce MoP nanoparticles (4 nm average particle size) which they deposit on metal oxide supports for a systematic study on interface effects on CO<sub>2</sub> hydrogenation. The results reveal MoP/ZrO<sub>2</sub> as an exceptionally active and selective catalyst for methanol synthesis.

The preparation, characterization, and testing of different catalysts through the modification of the traditional catalyst CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> are shown in contribution 3. The authors compare them in terms of their conversion of and selectivity to methanol at low pressure.

Different catalysts based on HZSM-5 zeolite for the reaction of Methanol to Gasoline (MTG) are prepared, characterized, and tested in the contribution 4. The three catalysts obtained were active in the reaction and did not suffer severe textural deterioration after use (decrease of approximately 10% in their specific areas).

Contribution 5 studies the advantages of the Powder Bed Fusion by Electron Beam (PBF-EB) additive manufacturing process with the kinetically controlled catalytic activation of Raney-type Cu to induce highly active and selective methanol synthesis. The catalysts thus obtained were evaluated for the hydrogenation of CO.

In contribution 6, the changes that occur in the hybrid photocatalyst during the reaction of hydrogen production from aqueous methanol under UV light are studied. The authors investigate the structure, composition, particle morphology, and surface area of the photocatalyst before and after the photocatalytic reaction, as well as analyzing the composition of the reaction solution during the photocatalytic process.

An experimental and simulation-based investigation is carried out for the selective oxidation of green methanol to the oxygenates dimethoxymethane and methyl formate in contribution 7. It includes an initial catalyst screening, the derivation of a reaction kinetic model, and a feasibility study of a fixed-bed and membrane reactor with oxygen distribution.

Finally, in contribution 8, the authors compare different kinetic models for methanol synthesis under similar conditions with a better-performing model for CO<sub>2</sub> hydrogenation to methanol (CH<sub>3</sub>OH) with CO in the feed.

I would like to express gratitude to MDPI Editorial and the *Catalysts* journal for the opportunity to serve as a Guest Editor, contributing to the current state of the art in

environmental catalysis for water remediation, as well as to the Assistant Editor, Ms. Bella Zhang, who worked diligently alongside me to publish this Special Issue. In addition, I would like to thank all the authors who shared their research and the referees for their invaluable contributions.

**Acknowledgments:** Ministerio de Ciencia, Innovación y Universidades (Project PID2022-139819OB-I00) is gratefully acknowledged.

**Conflicts of Interest:** The author declares no conflicts of interest.

#### List of Contributions:

1. Kaiser, D.; Beckmann, L.; Walter, J.; Bertau, M. Conversion of Green Methanol to Methyl Formate. *Catalysts* **2021**, *11*, 869. <https://doi.org/10.3390/catal11070869>.
2. Duyar, M.S.; Gallo, A.; Regli, S.K.; Snider, J.L.; Singh, J.A.; Valle, E.; McEnaney, J.; Bent, S.F.; Rønning, M.; Jaramillo, T.F. Understanding Selectivity in CO<sub>2</sub> Hydrogenation to Methanol for MoP Nanoparticle Catalysts Using In Situ Techniques. *Catalysts* **2021**, *11*, 143. <https://doi.org/10.3390/catal11010143>.
3. Trifan, B.; Lasobras, J.; Soler, J.; Herguido, J.; Menéndez, M. Modifications in the Composition of CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> Catalyst for the Synthesis of Methanol by CO<sub>2</sub> Hydrogenation. *Catalysts* **2021**, *11*, 774. <https://doi.org/10.3390/catal11070774>.
4. Sanz-Martínez, A.; Lasobras, J.; Soler, J.; Herguido, J.; Menéndez, M. Methanol to Gasoline (MTG): Preparation, Characterization and Testing of HZSM-5 Zeolite-Based Catalysts to Be Used in a Fluidized Bed Reactor. *Catalysts* **2022**, *12*, 134. <https://doi.org/10.3390/catal12020134>.
5. Poller, M.J.; Torsten, C.; Wolf, T.; Körne, C.; Wasserscheid, P.; Albert, J. 3D-Printed Raney-Cu POCS as Promising New Catalysts for Methanol Synthesis. *Catalysts* **2022**, *12*, 1288. <https://doi.org/10.3390/catal12101288>.
6. Rodionov, I.A.; Gruzdeva, E.O.; Mazur, A.S.; Kurnosenko, S.A.; Silyukov, O.I.; Zvereva, I.A. Photocatalytic Hydrogen Generation from Aqueous Methanol Solution over n-Butylamine-Intercalated Layered Titanate H<sub>2</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>: Activity and Stability of the Hybrid Photocatalyst. *Catalysts* **2022**, *12*, 1556. <https://doi.org/10.3390/catal12121556>.
7. Walter, J.P.; Wolff, T.; Hamel, C. Selective Methanol Oxidation to Green Oxygenates—Catalyst Screening, Reaction Kinetics and Performance in Fixed-Bed and Membrane Reactors. *Catalysts* **2023**, *13*, 787. <https://doi.org/10.3390/catal13050787>.
8. Mbatha, S.; Thomas, S.; Parkhomenko, K.; Roger A.C.; Louis, B.; Cui, X.; Everson, R.; Langmi, H.; Musyoka, N.; Ren, J. Development of an Improved Kinetic Model for CO<sub>2</sub> Hydrogenation to Methanol. *Catalysts* **2023**, *13*, 1349. <https://doi.org/10.3390/catal13101349>.

#### References

1. Wulf, C.; Zapp, P.; Schreiber, A. Review of Power-to-X Demonstration Projects in Europe. *Front. Energy Res.* **2020**, *8*, 191. [[CrossRef](#)]
2. Álvarez, A.; Bansode, A.; Urakawa, A.; Bavykina, A.V.; Wezendonk, T.A.; Makkee, M.; Gascon, J.; Kapteijn, F. Challenges in the Greener Production of Formates/Formic Acid, Methanol, and DME by Heterogeneously Catalyzed CO<sub>2</sub> Hydrogenation Processes. *Chem. Rev.* **2017**, *117*, 9804–9838. [[CrossRef](#)] [[PubMed](#)]
3. Saravanan, A.; Senthil Kumar, P.; Vo Dai-Viet, N.; Jeevanantham, S.; Bhuvaneshwari, V.; Anantha Narayanan, V.; Yaashikaa, P.R.; Swetha, S.; Reshma, B. A comprehensive review on different approaches for CO<sub>2</sub> utilization and conversion pathways. *Chem. Eng. Sci.* **2021**, *236*, 116515. [[CrossRef](#)]
4. Olah, G.A. Beyond Oil and Gas: The Methanol Economy. *Angew. Chem. Int. Ed.* **2005**, *44*, 2636–2639. [[CrossRef](#)] [[PubMed](#)]
5. Maksimov, P.; Laari, A.; Ruuskanen, V.; Koironen, T.; Ahola, J. Methanol synthesis through sorption enhanced carbon dioxide hydrogenation. *Chem. Eng. J.* **2021**, *418*, 129290. [[CrossRef](#)]
6. Riaz, A.; Zahedi, G.; Klemeš, J.J. A review of cleaner production methods for the manufacture of methanol. *J. Clean. Prod.* **2013**, *57*, 19–37. [[CrossRef](#)]
7. Chinchin, G.C.; Spencer, M.S.; Waugh, K.C.; Whan, D.A. Promotion of methanol synthesis and the water-gas shift reactions by adsorbed oxygen on supported copper catalyst. *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **1987**, *83*, 2193–2212. [[CrossRef](#)]
8. Nesterenko, N.; Aguilhon, J.; Bodart, P.; Minoux, D.; Dath, J.P. Methanol to Olefins: An Insight into Reaction Pathways and Products Formation. In *Zeolites and Zeolite-Like Materials*; Sels, B.F., Kustov, L.M., Eds.; Elsevier: Amsterdam, The Netherlands, 2016; pp. 189–263. [[CrossRef](#)]
9. Tian, P.; Wei, Y.; Ye, M.; Liu, Z. Methanol to olefins (MTO): From fundamentals to commercialization. *ACS Catal.* **2015**, *5*, 1922–1938. [[CrossRef](#)]

10. Amghizar, I.; Vandewalle, L.A.; Van Geem, K.M.; Marin, G.B. New Trends in Olefin Production. *Engineering* **2017**, *3*, 171–178. [[CrossRef](#)]
11. Gogate, M.R. Methanol-to-olefins process technology: Current status and future prospects. *Pet. Sci. Technol.* **2019**, *37*, 559–565. [[CrossRef](#)]
12. Ahmadova, R.; Ibrahimov, H.; Babayeva, F.; Rustamov, M.; Kondratenko, E. The perspective of methanol to olefins process over nanostructured zeolite catalysts, mechanism and synthesized methods: A review. *Process Petrochem. Oil Refin.* **2017**, *18*, 171–187.
13. Khadzhev, S.N.; Kolesnichenko, N.V.; Ezhova, N.N. Manufacturing of lower olefins from natural gas through methanol and its derivatives (review). *Pet. Chem.* **2008**, *48*, 325–334. [[CrossRef](#)]
14. Lefevere, J.; Mullens, S.; Meynen, V.; Van Noyen, J. Structured catalysts for methanol-to-olefins conversion: A review. *Chem. Pap.* **2014**, *68*, 1143–1153. [[CrossRef](#)]
15. Zaidi, H.A.; Pant, K.K. Catalytic conversion of methanol to gasoline range hydrocarbons. *Catal. Today* **2004**, *96*, 155–160. [[CrossRef](#)]
16. Kim, L.; Wald, M.M.; Brandenberger, S.G. One-step catalytic synthesis of 2,2,3-trimethylbutane from methanol. *J. Org. Chem.* **1978**, *43*, 3432–3433. [[CrossRef](#)]
17. Hayashi, H.; Moffat, J.B. Conversion of methanol into hydrocarbons over ammonium 12-tungstophosphate. *J. Catal.* **1983**, *83*, 192–204. [[CrossRef](#)]
18. Misono, M. Heterogeneous Catalysis by Heteropoly Compounds of Molybdenum and Tungsten. *Catal. Rev. Sci. Eng.* **1987**, *29*, 269–321. [[CrossRef](#)]
19. Galadima, A.; Muraza, O. From synthesis gas production to methanol synthesis and potential upgrade to gasoline range hydrocarbons: A review. *J. Nat. Gas Sci. Eng.* **2015**, *25*, 303–316. [[CrossRef](#)]
20. Yahyazadeh, A.; Nanda, S.; Dalai, A.K. A Critical Review of the Sustainable Production and Application of Methanol as a Biochemical and Bioenergy Carrier. *Reactions* **2024**, *5*, 1–19. [[CrossRef](#)]

**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.