

Editorial

Catalysts for Production and Conversion of Syngas[†]

Rufino M. Navarro Yerga

Instituto de Catálisis y Petroleoquímica (CSIC), C/Marie Curie 2, Cantoblanco, 28049 Madrid, Spain; r.navarro@icp.csic.es

[†] On behalf of my colleague José Luis García Fierro who sadly passed away last 3 February 2020 and who was co-editor of this special volume until the date of his passing.

Synthesis gas, or syngas for short, is a mixture of CO, CO₂, and H₂. Syngas is a crucial production platform for the production of various products, such as synthetic hydrocarbons and oxygenates fuels [1]. Recent advances in the understanding and development of active phases, supports, promoters, and reactor configurations to control selectivity in syngas production and conversion are the most challenging topics for scientific research in syngas conversion [2]. This Special Issue compiles and provides an overview of the latest advances in catalytic syngas production from various sources (fossil, biomass) and the conversion of syngas into value-added products. Catalytic processes for syngas production have been reviewed, including production from natural gas (partial oxidation and steam reforming) and biomass (thermochemical conversion).

Currently, the main technologies for syngas production are based on steam reforming of natural gas. Direct syngas production from oxy-steam reforming of liquefied natural gas (LNG) can be a promising way to improve efficiency over conventional steam reforming of natural gas, but requires catalysts with high activity and resistance to deactivation by carbon deposits. For example, Mierczynski et al. [3] studied Ni catalysts supported on ZrO₂ modified with CeO₂ and La₂O₃ for oxy-steam reforming of LNG and reported a strong improvement of Ni catalyst stability after CeO₂ addition associated with the uniform distribution of Ni species, which was explained by the increased mobility of oxygen that can oxidize the carbon deposit or methane adsorbed on the nickel metal surface during oxy-steam reforming, thus protecting the catalyst surface against carbon deposits.

Partial oxidation of methane (POM) is also one of the most powerful processes for syngas production, but the noble metal-based catalysts used in the process limit its research and application. In order to increase the atomic utilization of noble metals and solve the stability problem of nanoparticle-based catalysts, Wang et al. [4] have proposed the encapsulation of noble metal nanoparticles as a way to develop catalogs with improved activity and stability in the partial oxidation of methane to syngas. The authors prepared Pt nanoparticles confined in silicalite-1 (S-1) zeolite under hydrothermal conditions and, strikingly, the combination of Pt nanoparticles and zeolite micropores, which limited their agglomeration during the reaction, led to enhanced catalytic activity and stability in POM, which was of great importance in increasing metal utilization and reducing catalyst costs.

Thermochemical conversion of biomass with in situ CO₂ capture is a promising technology for the production of high quality syngas with precise adjustment of the CO/CO₂/H₂ ratio. In order to improve the CO₂ adsorption capacity, Zhao et al. [5] have studied CaO-based catalysts in the thermochemical conversion of biomass with in situ CO₂ capture.

The adsorption competition mechanism of gas molecules (H₂, H₂O, CO, CH₄, and H₂) on CaO-based catalysts was studied using density functional theory (DFT). The results indicated that the adsorption capacity of CO₂ on the surface of CaO-based catalysts surface was strongest at 650 °C. Furthermore, the adsorption competition mechanism of gas molecules was investigated by the DFT method, demonstrating that, in contrast with a CaO surface, a 10 wt % Ni/CaO surface is conducive for in situ CO₂ capture in biomass



Citation: Yerga, R.M.N. Catalysts for Production and Conversion of Syngas. *Catalysts* **2021**, *11*, 752. <https://doi.org/10.3390/catal11060752>

Received: 3 June 2021

Accepted: 8 June 2021

Published: 21 June 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 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/>).

pyrolysis. The above results provide theoretical support for in-depth studies on complex catalytic reactions in biomass pyrolysis with in situ CO₂ capture.

Catalytic transformations of syngas, with an emphasis on the selective production of low molecular weight alcohols and acids (methanol, acetic acid), dimethyl ether (DME), aromatics, and hydrocarbons (C₅+ as liquid fuels) were also discussed in this Special Issue. The use of syngas in microbial electrosynthesis using homoacetogenic cultures has been considered as an interesting alternative to produce acetate as the primary final product of homoacetogenesis under mild conditions. The primary challenge in this process is the limitations in the gas–liquid mass transfer of syngas, especially for hydrogen, in the mixed-culture homoacetogenic reactor, which is a bottleneck limiting the efficiency in syngas transformation. In this regard, the paper by Sivalingam et al. [6] provides a series of experiments to test the integration of syngas in a microbial electrosynthesis reactor by studying the effect of syngas pressure on the efficiency of product synthesis. The authors demonstrated significantly higher product synthesis efficiency associated with increasing hydrogen solubility and consumption rate with increasing syngas pressure. This result opens an avenue for integrating synthesis gas with microbial synthesis processes as a sustainable way to produce organic chemicals.

Methanation of syngas and CO₂ could transform renewable energy into viable energy for transportation and high density. The methanation reaction has been extensively studied using different types of metals and supports. Among them, Ni-based catalysts are the most widely used due to their high activity and CH₄ selectivity; however, it is difficult to achieve high conversion at low temperature on Ni catalysts due to the high activation energy required. For example, Chen et al. [7] investigated the methanation performance of mono- and bimetallic Ni- and Ru-based catalysts and showed that the low-temperature methanation performance can be higher for Ni-Ru bimetallic catalysts relative to their monometallic counterparts.

Syngas conversion is a promising route to obtain high-value chemicals from non-petroleum resources due to the wide variety of syngas sources. Considerable efforts have been made in the conversion of syngas into a number of hydrocarbons such as olefins, paraffins, and aromatics. Recently, bifunctional catalysts combining metal oxides with zeolites have been developed and high selectivity to light olefins and aromatics has been achieved. Among them, ZrO₂-based oxides and HZSM-5 bifunctional catalysts have shown good selectivity and stability in converting syngas into aromatics. In the work of Wang et al. [8], it was shown that the crystalline phases of ZrO₂ in ZrO₂/HZSM-5 bifunctional catalysts have important effects on C–O activation and C–C coupling during conversion of syngas into aromatics.

The ZrO₂ in monoclinic phase (m-ZrO₂) exhibits higher CO conversion with a higher selectivity to C₂+ hydrocarbons. The surface of m-ZrO₂ contains more hydroxyl groups that react with CO to produce formate species, and these are crucial for C–O activation.

NMR results revealed that there are more acid and basic sites in m-ZrO₂, which exhibits higher activity for C–C coupling. Both CO conversion, as well as selectivity of aromatic hydrocarbons can be improved after the combination of ZrO₂ with HZSM-5, and m-ZrO₂/HZSM-5-mix showed superior activity for the selective conversion of syngas to aromatics with less CH₄.

Fischer–Tropsch synthesis is an important process for producing fuels from a non-petroleum synthesis gas. The primary products of hydrogenation of C₁ oxides are olefins; some paraffins can also be produced directly, but are also obtained by secondary hydrogenation of olefins. The olefin/paraffin (o/p) ratio observed for a given chain length depends on the process conditions as well as on the catalyst formulation. In this scenario, the manuscript by Rytter et al. [9] studies the light hydrocarbon olefin/paraffin ratio (o/p ratio) as a powerful tool to analyze and understand the low-temperature Fischer–Tropsch synthesis of cobalt and the nature of the catalyst investigated. The relationship between propene and propane during Fischer–Tropsch synthesis was analyzed based on both literature reports and experiments for five Co catalysts with variations in pore size and Co

loading. It was possible to rationalize all data based on secondary hydrogenation of olefins. There is often a positive correlation between C_3 o/p and selectivity towards longer chains. However, further development of the mechanism and kinetics, as well as surface science, is needed. More data is needed for a multitude of catalyst formulations to make the o/p ratio an effective tool in catalyst design.

Methanol is one of the most important chemicals used in various industries and is produced from syngas mixtures over the well-known Cu/ZnO/Al₂O₃ catalysts. The Cu/ZnO/Al₂O₃ catalysts are affected by the Na⁺ ions used in the preparation of the hydroxycarbonate precursors by coprecipitation. Guil-Lopez et al. [10] studied in detail the influence of residual sodium nitrate present in hydroxycarbonate precursors on the formation and configuration of the final active sites of Cu/ZnO/Al₂O₃ catalysts. The results of this work demonstrated for the first time the mechanism of deactivation of residual sodium nitrate. Sodium nitrate was found to facilitate the decomposition of hydroxycarbonate precursors, leading to segregation and crystallization of CuO and ZnO with loss of mesostructured area, it affects their further evolution after reduction, producing large Cu particles in poor contact with ZnO_x, resulting in active sites with poor intrinsic activity.

Dimethyl ether is a versatile feedstock and an interesting alternative fuel that can be produced by direct catalytic transformation of synthesis gas. Therefore, the direct synthesis of dimethyl ether (DME) from syngas is another important topic developed in this special volume. The work of Jeong et al. [11] investigated Al₂O₃/Cu/ZnO catalysts with 60–80% Al wt. for the direct hydrogenation of CO₂ to dimethyl ether.

Al-rich Al₂O₃/Cu/ZnO catalysts retained acid sites responsible for the methanol dehydration to DME. Due to this bifunctional character, the catalysts could yield DME as the major product. Furthermore, Al-rich Al₂O₃/Cu/ZnO catalysts were coupled with ferrierite zeolite in a dual-bed system that was demonstrated to produce selectively DME (CO-free selectivity >90%). Consequently, the suggested process scheme would be an important contribution to the commercial production of DME from CO₂. The performance of bifunctional hybrid catalysts based on phosphotungstic acid supported on TiO₂ combined with Cu-ZnO (Al) catalysts was investigated in the work of Millán et al. [12]. It was found that physical hybridization of the supported heteropolyacids with Cu-ZnO (Al) results in a decrease of the copper surface area of the Cu-ZnO (Al) catalysts and the disappearance of the strong acid sites of the heteropolyacids. The catalytic performance of CZA-xHPW/Ti hybrid catalysts for the direct synthesis of DME from syngas depends on their HPW loading. Only hybrids with HPW loadings higher than 1.7 monolayers are effective for the direct synthesis of DME, with the hybrid with 2.7 monolayers reaching the highest selectivity for DME (53.0%). These hybrids exhibit three-dimensional HPW structures in which pseudo-liquid behavior could occur enhancing methanol access to acid sites. The sample loaded with 2.7 heteropolyacid monolayers had higher activity than the reference hybrid representative of the most widely applied catalysts based on the combination of Cu-ZnO (Al) with HZSM-5. The development of bifunctional/hybrid catalysts for the direct synthesis of DME from CO₂ is challenging because their metal and acid functions required for methanol synthesis and dehydration, respectively, must be combined in a correct ratio with controlled interaction.

In this context, the excellent review by Mota et al. [13] contains a brief survey of recent advances in the direct synthesis of DME from CO₂, with special attention to the design and strategy followed for the development of active and selective heterogeneous catalysts for direct synthesis. To achieve this objective, the review looked at the following areas regarding the development of bifunctional/hybrid catalysts for the direct synthesis of DME from CO₂: (i) a comprehensive overview of the challenges in thermodynamics and kinetics of direct CO₂ to DME hydrogenation; (ii) the analysis of the latest developments in metal and acid functions required for methanol synthesis from CO₂ and methanol dehydration; (iii) review of recent strategies for the construction of bifunctional/hybrid catalysts with emphasis on their controlled contact and interaction between metal and acid

functions; (iv) status of catalyst development for the direct synthesis of DME from CO₂; and (v) analysis of future prospects for making this technology a competitive process.

In summary, the articles published in this Special Issue represent well the advances and trends in the important field of catalytic syngas production from various sources (fossil, biomass) and catalytic conversion of syngas into value-added products. I would like to thank the authors for their valuable contributions, the editorial office of *Catalysts* for their kind support, and also the reviewers for improving the quality of the articles with their comments. I hope that this Special Issue will inspire students and researchers to further increase knowledge and development in this exciting world of catalytic syngas production and conversion.

Finally, I would like to pay a special tribute to Professor José Luis García Fierro [14], who was co-editor of this special volume and who sadly passed away during the preparation of this volume. It was a real pleasure to collaborate with José Luis during the last 25 years and to prepare this special volume with him. Farewell, good friend.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Kasipandi, S.; Bae, J.W. Recent Advances in Direct Synthesis of Value-Added Aromatic Chemicals from Syngas by Cascade Reactions over Bifunctional Catalysts. *Adv. Mater.* **2019**, *31*, 1803390. [[CrossRef](#)] [[PubMed](#)]
2. Bao, J.; Yang, G.; Yoneyama, Y.; Tsubaki, N. Significant advances in C1 catalysis: Highly efficient catalysts and catalytic reactions. *ACS Catal.* **2019**, *9*, 3026–3053. [[CrossRef](#)]
3. Mierczynski, P.; Stepinska, N.; Mosinska, M.; Chalupka, K.; Albinska, J.; Maniukiewicz, W.; Rogowski, J.; Nowosileska, M.; Szykowska, M.I. Hydrogen production via the Oxy-Steam Reforming of LNG or methane on Ni Catalysts. *Catalysts* **2020**, *10*, 346. [[CrossRef](#)]
4. Wang, J.; Ma, L.; Ding, C.; Xue, Y.; Zhang, Y.; Gao, Z. In Situ Encapsulated Pt Nanoparticles Dispersed in Low Temperature Oxygen for Partial Oxidation of Methane to Syngas. *Catalysts* **2019**, *9*, 720. [[CrossRef](#)]
5. Zhao, B.; Wang, J.; Zhu, D.; Song, G.; Yang, H.; Chen, L.; Sun, L.; Yang, S.; Guan, H.; Xie, X. Adsorption Characteristics of Gas Molecules (H₂O, CO₂, CH₄ and H₂) on Cao-Based Catalysts during Biomass Thermal Conversion with In Situ CO₂ Capture. *Catalysts* **2019**, *9*, 757. [[CrossRef](#)]
6. Sivalingam, V.; Ahmadi, V.; Bbafemi, O.; Dinamarca, C. Integrating Syngas Fermentation into a Single-Cell Microbial Electrosynthesis (MES) Reactor. *Catalysts* **2021**, *11*, 40. [[CrossRef](#)]
7. Chein, R.-Y.; Wang, C.-C. Experimental Study on CO₂ Methanation over Ni/Al₂O₃, Ru/Al₂O₃ and Ru-Ni/Al₂O₃ Catalysts. *Catalysts* **2020**, *10*, 1112. [[CrossRef](#)]
8. Wang, S.; Fang, Y.; Huang, Z.; Xu, H.; Shen, W. The Effects of the Crystalline Phase of Zirconia on C-O Activation and C-C Coupling in Converting Syngas into Aromatics. *Catalysts* **2020**, *10*, 262. [[CrossRef](#)]
9. Rytter, E.; Yang, J.; Borg, O.; Holment, A. Significance of C3 Olefin to Paraffin Ratio in Cobalt Fischer-Tropsch Synthesis. *Catalysts* **2020**, *10*, 967. [[CrossRef](#)]
10. Guil-López, R.; Mota, N.; Llorente, J.; Millan, E.; Pawelec, B.G.; Fierro, J.L.G.; Navarro, R.M. Unravelling the Structural Modification (Meso-Nano-) of Cu/ZnO-Al₂O₃ Catalysts for Methanol Synthesis by the Residual NaNO₃ in Hydroxycarbonate Precursors. *Catalysts* **2020**, *10*, 1346. [[CrossRef](#)]
11. Jeong, C.; Kim, J.; Kim, J.-H.; Lee, S.; Bae, J.P.; Suh, Y.-W. Direct conversion of CO₂ into Dimethyl Ether over Al₂O₃/Cu/ZnO Catalysts Prepared by Sequential Precipitation. *Catalysts* **2019**, *9*, 524. [[CrossRef](#)]
12. Millán, E.; Mota, N.; Guil-López, R.; Pawelec, B.; Fierro, J.L.G.; Navarro, R.M. Direct Synthesis of Dimethyl Ether from Syngas on Bifunctional Hybrid Catalysts Based on Supported H₃PW₁₂O₄₀ and Cu-ZnO (Al): Effect of Heteropolyacid Loading on Hybrid Structure and Catalytic Activity. *Catalysts* **2020**, *10*, 1071. [[CrossRef](#)]
13. Mota, N.; Ordoñez, E.M.; Pawelec, B.; Fierro, J.L.G.; Navarro, R.M. Direct Synthesis of Dimethyl Ether from CO₂: Recent Advances in Bifunctional/Hybrid Catalytic Systems. *Catalysts* **2021**, *11*, 411. [[CrossRef](#)]
14. Navarro, R.M. Remembering Professor Jose Luis García Fierro (1948–2020). *Catalysts* **2020**, *10*, 357. [[CrossRef](#)]