

# Carbon-Based Catalysts for Selective Hydrogenation of Carbon Oxides (Methanation)

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**Abstract**—This review describes a process for methanation (selective hydrogenation) of carbon oxides with an emphasis on its importance for environmentally friendly and distributed energy generation. The drawbacks of oxide-supported catalysts and the advantages of carbon-based catalysts are assessed in terms of green chemistry principles. Catalysts based on carbon nanotubes, carbon nanofibers, and biomass derivatives are further discussed. Major research approaches are outlined for the implementation of carbon-based catalysts in selective hydrogenation of carbon oxides. This discussion suggests that the most promising catalysts for methanation are those based on biomass-derived carbon materials.

**Keywords:** carbon materials, methanation, activated carbon, carbon nanotubes, carbon nanofibers, hydrothermal synthesis

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## INTRODUCTION

Today's realities call for environmental friendliness. This suggests an urgent need for the principles of green chemistry to be implemented as an integral part of scientific and technological progress. Despite the growing worldwide importance of renewable energy sources (RES), recent years have seen a huge spike in the global emissions of carbon dioxide (CO<sub>2</sub>) reaching 36.57 billion metric tons [1]. Plainly, carbon capture efforts to date have been insufficient. Finding innovative approaches to RES generation could become a key to reducing greenhouse gas emissions. These approaches will not only reduce the concentrations of CO<sub>2</sub> and carbon monoxide (CO) in the atmosphere but also convert the byproduct to an important link in the energy chain. The potential of plant and animal biomass for the production of CO<sub>2</sub>-neutral fuels has previously been discussed [2, 3].

Although the prevailing approach in the petrochemical industry is to convert CO<sub>2</sub> and CO to a variety of hydrocarbons starting with C<sub>2</sub>, it is worth emphasizing the importance of methanation for achieving the decarbonization goals. Catalytic hydrogenation of CO<sub>2</sub>

and CO into methane (CH<sub>4</sub>) has attracted much interest among researchers throughout the world because this product can further be used both for the storage of chemical energy and for direct injection into existing gas pipelines. Therefore, methane production from carbon oxides is perfectly suited for transition to distributed energy generation and zero-emission production.

However, the transition to zero-emission production in itself would be insufficient to have a significant impact on the global environmental situation. The pursuit of environmental excellence requires a far more comprehensive approach that would combine an appropriate choice of chemical process with the development of an optimum method for its implementation. Accordingly, green chemistry principles must apply both to the process itself and to the production of an environmentally friendly catalyst.

Ni-based catalysts [4–6], including those promoted by Co [7, 8] and Fe [9], have been most extensively used in industrial methanation due to their relatively low price and high activity. Ru-based and Rh-based catalysts have also been fairly common due to their high CO methanation

activity [10]. Oxide supports, which are typically used in these catalysts [11], have major disadvantages: rapid sintering of metal nanoparticles due to the lack of internal metal–oxide interaction; and the formation of mixed oxides, thus disturbing the homogeneity of the catalytic system [1]. Therefore, researchers have increasingly tended to eliminate the use of oxide supports in the hydrogenation of carbon oxides. In particular, the methanation of carbon monoxide over composite catalysts based on nickel and polyvinyl alcohol has been studied [12]. This catalytic hydrogenation achieved CO conversion of 29% and a methane yield of 28 g/m<sup>3</sup> CO.

It is also worth noting that oxide-supported catalysts are inferior to their carbon-based counterparts in terms of environmental impacts. Indeed, the high temperatures and various toxic solvents (e.g., benzene, toluene, and diethyl ether) necessarily used to synthesize oxide-supported catalysts make their production far from green-chemistry-principles “friendly”. On the other hand, the ability of carbon as a precursor to take on different forms, from graphite powder to complex ordered structures, offers new prospects for catalytic design. Thus, the development of effective carbon-based catalysts for methanation would simultaneously achieve a number of pressing goals: transitioning to distributed energy resources; reducing the E-factor; and eliminating the undesirable metal–support interaction.

One classical carbon-based catalyst—metal particles supported on activated carbon (AC)—has been extensively studied since the 1980s. However, this research was historically focused on hydrocarbon oligomerization rather than methanation. For example, Chen et al. [13] demonstrate the high performance of carbon-based iron–cobalt and potassium–iron–cobalt carbonyl cluster catalysts in CO hydrogenation into olefins. Liu et al. [14] note that the intricate porous structure of AC-based catalysts with large amounts of micropores facilitates good dispersion of metals, resulting in high catalytic activity. Highly structured carbonaceous materials such as nanotubes, nanofibers, and carbonized biomass, known for their unique properties, have shown promising catalytic performance in petrochemical reactions [15–18].

Today researchers are only in the early stages of the transition from oxide supports to carbonaceous materials. The present review covers the currently available data—limited as they are—on methanation over this catalyst type. The paper focuses on the application of catalysts based on carbon nanotubes (CNTs), carbon nanofibers

(CNFs), and biomass in methanation; particular attention is paid to the unique properties of carbon-based catalysts. The review further discusses the current developments, challenges, and potential applications of carbon-based methanation catalysts.

## CNT-BASED CATALYSTS

CNTs are hollow cylindrical graphene structures. In turn, graphene is a structure consisting of regular hexagons with carbon atoms at their vertices. In recent years, a substantial amount of research has been focused on CNT-based catalysts for Fischer–Tropsch synthesis [19–21]. CNTs safely meet the requirements for Fischer–Tropsch catalysts, namely: well-developed surface area, high metal dispersion, as well as adequate mechanical resistance, activity, stability, and selectivity. Moreover, CNTs are common carbonaceous structures that have been best explored exactly for catalytic methanation of CO<sub>2</sub> [1]. CNTs are of interest for catalytic production of hydrocarbons due to their chemical inertness and mechanical stability and because their surface properties can be modified by artificially generated defects. CNT-supported catalysts have shown activity many times higher than oxide-supported catalysts [22, 23]. Wang et al. [24] synthesized a catalyst from nickel nanoparticles grown on nitrogen-doped CNTs (Ni/N–CNT). At 360°C this catalyst exhibited promising results in methanation, specifically CO<sub>2</sub> conversion of 80% and methane selectivity of 99%. Gonçalves et al. [11] confirmed the importance of N-doping by a comparative assessment of the catalytic performance of N-doped (Ni/CNT–N) and pristine (Ni/CNT) CNT-based samples in methanation. The comparison demonstrated that Ni/CNT–N achieved a higher CO<sub>2</sub> conversion (81.2%) with CH<sub>4</sub> selectivity of 99.2% at a lower temperature (400°C), and showing excellent stability of 48 hours.

In fact, CNTs are the first and only structured carbonaceous nanomaterial manufactured on an industrial scale. Indeed, CNTs have been extensively used in electrochemical devices and in composites [25, 26] due to their inertness, stability, and doping capabilities. Nonetheless, a number of limitations have to date hindered the full implementation of CNTs in the catalytic industry: high price, poor homogeneity, low bulk density, and propensity for degradation in aggressive environments at high temperatures [27]. One promising solution to the above challenges is oxidative functionalization of CNTs, a technique that immobilizes

carboxyl and hydroxyl groups and generates surface defects. As a result, the defects prevent particles from migrating at high temperatures, and oxygenated groups fix metal ions during impregnation due to electrostatic interaction. Moreover, this functionalization enhances the bulk density of CNTs [28]. Li et al. [29] report on CO<sub>2</sub> methanation over Mn-promoted Ni nanoparticles supported on oxygen-functionalized CNTs. The CNTs were pretreated by boiling in concentrated nitric acid at 140°C for 14 h. The resultant catalyst exhibited high methane selectivity (nearly 100%), CO<sub>2</sub> conversion of 71.6%, and sintering resistance over more than 140 hours. In addition, the growing production of CNTs has led to a steady decline in their prices [15].

### CNF-BASED CATALYSTS

Carbon nanofibers (CNFs) consist of interwoven graphite fibers characterized by high chemical inertness, purity, and mechanical strength, properties that make them a very promising precursor for the synthesis of methanation catalysts. When compared to CNTs, CNFs have cost-benefit advantages due to simpler and less costly synthesis, a higher yield, and resulting purity [30]. Besides, CNFs are also distinguished by well-developed surface areas, and high thermal conductivity [16]. Jiménez et al. [31] investigated the catalytic performance of CNF-supported Ru catalysts for the methanation of CO, CO<sub>2</sub>, and their mixtures. In the solo-methanation of CO or CO<sub>2</sub>, the CO conversion reached 100% with high selectivity at 340°C. In contrast, the co-methanation of CO/CO<sub>2</sub> mixtures exhibited poor catalytic performance for all the investigated catalysts (the conversion never reached above 53%), because they promote the undesired reverse water-gas shift reaction (RWGSR). However, adding 30% water vapor to the feedstock inhibited the RWGSR, thus enhancing CO hydrogenation. Hu et al. [32] employed co-electrospinning to develop a catalyst based on Ni nanoparticles encapsulated in highly mesoporous nanofibers with oxygen vacancies. This catalyst exhibited good catalytic performance with CO<sub>2</sub> conversion of 50.6% and 82.3% at low temperatures of 250 and 300°C, respectively, and excellent stability of 60 h at a high temperature of 400°C.

### NOVEL BIOMASS-BASED CATALYSTS

Recently researchers in petroleum chemistry have become particularly interested in catalysts consisting of metal nanoparticles supported on biomass derivatives

(e.g., biochar and microcellulose). This is because various potential effects of particle size on the catalytic activity and selectivity have been demonstrated [33]. In particular, metal nanoparticles are able to enhance the activity of advanced heterogeneous catalysts (the currently dominant catalyst type). The main advantage of nanoparticles is their ability to enhance the surface area of active catalytic sites, thus facilitating interaction between reactants and these sites. At the same time, the use of these catalysts is limited by the extreme exothermicity of the reactions, a property typical of most petrochemical processes, including methanation. Failure to take additional thermal stability measures may lead to agglomeration and sintering of particles, resulting in low product selectivity.

A number of approaches have been offered to enhance the long-term stability of carbon-supported metal catalysts, such as providing a strong metal-support interaction [34] and encapsulating metal particles in the support [35]. Encapsulated nanoparticles are a novel type of carbonaceous nanomaterials. These nanoparticles have a typical core-shell (metal-carbon) structure and possess unique magnetic and electrical properties combined with high thermal and chemical stability. These catalysts can be synthesized by time-consuming and difficult-to-control methods such as high-temperature annealing, arc discharge, or chemical vapor deposition. The main weakness of these synthesis methods is unpredictable product yield. A recent publication has described hydrothermal synthesis of a biomass-derived feedstock for this catalyst type, a method attractive from both the cost-benefit and environmental viewpoints [36]. This method provides for the installation of a batch reactor to ensure the high temperatures required for carbonization and simultaneously retain all the evolved vapors to increase the reaction pressure. Autogenous high pressure extends the heating time without volumetric shrinkage, thereby enhancing the biomass conversion efficiency. For example, Yan et al. [37] developed a hydrothermal carbonization method for the synthesis of carbon-encapsulated iron nanoparticles, with wood being used as a carbon source. These nanoparticles exhibited excellent catalytic performance in Fischer-Tropsch synthesis. In the reactions with biomass-derived syngas at 290°C, this catalyst achieved CO conversion of 89.5% and hydrocarbon selectivity of 65%.

Unfortunately, to date the performance of this catalyst type in methanation has been underexplored. Further research is needed to elaborate methods for synthesizing

catalysts suitable for methanation, and in particular to investigate the effects of their preparation conditions and evaluate the selectivity and activity of specific metals in the hydrogenation of carbon oxides.

### CONCLUSIONS

This review outlines promising approaches for future research on carbon-based catalysts for methanation. First, efforts must be made to choose an appropriate catalyst support structure, and particularly its mesopore and micropore sizes, to ensure that metal nanoparticles are retained in these pores and uniformly dispersed over the entire surface of the catalyst. Second, further research should be focused on improving existing methods for loading metal particles on the carbon support to ensure better control over the particle size, dispersion, and catalytic performance. In addition to conventional synthesis techniques such as impregnation, coprecipitation, and sol–gel, new methods need to be developed for incorporating metal particles into carbon-based supports to produce uniformly dispersed crystalline nanoparticles. The authors of this review believe that, from the viewpoint of green chemistry, the most promising catalysts for methanation are those based on biomass-derived carbon materials.

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### CONFLICT OF INTEREST

The authors declare no conflict of interest requiring disclosure in this article.

### REFERENCES

- Mohanty, A., Viet, C.D., Roger, A.C., Adam, A., Mertz, D., Baaziz, W., and Janowska, I., *Appl. Catal. B*, 2021, vol. 298, p. 120589. <https://doi.org/10.1016/J.APCATB.2021.120589>
- Kulikova, M.V., Krylova, A.Yu., Zhagfarov, F.G., and Krysanova, K.O., *Chem. Technol. Fuels Oils*, 2022, vol. 630, no. 2, pp. 46–50. <https://doi.org/10.32935/0023-1169-2022-630-2-46-50>
- Kulikova, M.V., Krylova, A.Yu., Zhagfarov, F.G., Krysanova, K.O., and Lapidus, A.L., *Chem. Technol. Fuels Oils*, 2022, vol. 629, no. 1, pp. 50–56. <https://doi.org/10.32935/0023-1169-2022-629-1-50-56>
- Kristiani, A. and Takeishi, K., *Catal. Commun.*, 2022, vol. 165, p. 106435. <https://doi.org/10.1016/J.CATCOM.2022.106435>
- Zhang, W., Liu, Y., Dong, Y., Hao, Y., Chen, L., Li, J., Zeng, S., and Wang, H., *Appl. Surf. Sci. North-Holland*, 2022, vol. 598, p. 153802. <https://doi.org/10.1016/J.APSUSC.2022.153802>
- Zhang, Y., Chen, Y., and Liu, Q., *Int. J. Hydrogen Energy*, 2021, vol. 46, no. 63, pp. 32003–32016. <https://doi.org/10.1016/J.IJHYDENE.2021.06.209>
- Summa, P., Świrk, K., Wang, Y., Samojeden, B., Rønning, M., Hu, C., Motak, M., and da Costa, P., *Appl. Mater. Today*, 2021, vol. 25, p. 101211. <https://doi.org/10.1016/J.APMT.2021.101211>
- Liu, Q., Bian, B., Fan, J., and Yang, J., *Int. J. Hydrogen Energy*, 2018, vol. 43, no. 10, pp. 4893–4901. <https://doi.org/10.1016/J.IJHYDENE.2018.01.132>
- Li, Y.T., Zhou, L., Cui, W.G., Li, Z.F., Li, W., and Hu, T.L., *J. CO<sub>2</sub> Util.*, 2022, vol. 62, p. 102093. <https://doi.org/10.1016/j.jcou.2022.102093>
- Gómez, L., Martínez, I., Navarro, M.V., García, T., and Murillo, R., *Chem. Eng. J.*, 2022, vol. 440, p. 135842. <https://doi.org/10.1016/j.cej.2022.135842>
- Gonçalves, L.P.L., Meledina, M., Meledin, A., Petrovykh, D.Y., Sousa, J.P.S., Soares, O.S.G.P., Kolen'ko, Y.V., and Pereira, M.F.R., *Carbon*, 2022, vol. 195, pp. 35–43. <https://doi.org/10.1016/j.carbon.2022.03.059>
- Popandopulo, M.V., Ivantsov, M.I., Kulikova, M.V., and Zhagfarov, F.G., *Chem. Technol. Fuels Oils*, 2022, vol. 629, no. 1, pp. 29–33. <https://doi.org/10.32935/0023-1169-2022-629-1-29-33>
- Chen, A.A., Kaminsky, M., Geoffroy, G.L., and Vannice, M.A., *J. Phys. Chem. Am. Chem. Soc.*, 1986, vol. 90, no. 20, pp. 4810–4819. <https://doi.org/10.1021/j100411a020>

14. Liu, J., Chen, Y., Wei, J., Duyar, M.S., Ordonsky, V.Y., and Khodakov, A.Y., *Chem. Soc. Rev.*, 2021, vol. 50, p. 2337.  
<https://doi.org/10.1039/d0cs00905a>
15. de Volder, M.F.L., Tawfick, S.H., Baughman, R.H., and Hart, A.J., *Science*, 2013, vol. 339, no. 6119, pp. 535–539.  
<https://doi.org/10.1126/science.1222453>
16. Gao, X., Liu, G., Wei, Q., Yang, G., Masaki, M., Peng, X., Yang, R., and Tsubaki, N., *Int. J. Hydrogen Energy*, 2017, vol. 42, no. 26, pp. 16547–16556.  
<https://doi.org/10.1016/J.IJHYDENE.2017.05.164>
17. Zacharopoulou, V. and Lemonidou, A.A., *Catalysts*, 2018, vol. 8, p. 2.  
<https://doi.org/10.3390/CATAL8010002>
18. Yan, Q., Street, J., and Yu, F., *Biomass Bioenerg.*, 2015, vol. 83, pp. 85–95.  
<https://doi.org/10.1016/J.BIOMBIOE.2015.09.002>
19. Almkhelfe, H., Li, X., Thapa, P., Hohn, K.L., and Amama, P.B., *J. Catal.*, 2018, vol. 361, pp. 278–289.  
<https://doi.org/10.1016/J.JCAT.2018.02.009>
20. Chernyak, S.A., Ivanov, A.S., Maksimov, S.V., Maslakov, K.I., Isaikina, O.Y., Chernavskii, P.A., Kazantsev, R.V., Eliseev, O.L., and Saviolov, S.S., *J. Catal.*, 2020, vol. 389, pp. 270–284.  
<https://doi.org/10.1016/J.JCAT.2020.06.011>
21. Chew, L.M., Xia, W., Düdder, H., Weide, P., Ruland, H., and Muhler, M., *Catal Today*, 2016, vol. 270, pp. 85–92.  
<https://doi.org/10.1016/J.CATTOD.2015.09.023>
22. Bai, S., Huang, C., Lv, J., and Li, Z., *Catal. Commun.*, 2012, vol. 22, pp. 24–27.  
<https://doi.org/10.1016/J.CATCOM.2012.02.006>
23. Ali S, Zabidi, N.A.M., Al-Marri, M.J., Khader, M.M., *Mater. Today Commun.*, 2017, vol. 10, pp. 67–71.  
<https://doi.org/10.1016/J.MTCOMM.2017.01.004>
24. Wang, W., Duong-Viet, C., Ba, H., Baaziz, W., Tuci, G., Caporali, S., Nguyen-Dinh, L., Ersen, O., Giambastiani, G., and Pham-Huu, C., *ACS Appl. Energy Mater.*, 2019, vol. 2, no. 2, pp. 1111–1120.  
<https://doi.org/10.1021/acsaeem.8b01681>
25. Bohnenberger, T. and Schmid, U., *Thin Solid Films*, 2014, vol. 565, pp. 116–121.  
<https://doi.org/10.1016/J.TSF.2014.05.055>
26. Kaushik, P., Kumar Rastogi, C., Channegowda, M., Patel, A., and Gyanprakash, M., *Mater. Today*, 2023, vol. 74, pp. 324–328.  
<https://doi.org/10.1016/j.matpr.2022.08.258>
27. Chernyak, S., Burtsev, A., Maksimov, S., Kupreenko, S., Maslakov, K., and Saviolov, S., *Appl. Catal. A: General*, 2020, vol. 603, p. 117741.  
<https://doi.org/10.1016/j.apcata.2020.117741>
28. Schulte, H.J., Graf, B., Xia, W., and Muhler, M., *ChemCatChem*, 2012, vol. 4, no. 3, pp. 350–355.  
<https://doi.org/10.1002/CCTC.201100275>
29. Li, J., Zhou, Y., Xiao, X., Wang, W., Wang, N., Qian, W., and Chu, W., *ACS Appl. Mater. Interfaces*, 2018, vol. 10, no. 48, pp. 41224–41236.  
<https://doi.org/10.1021/acsami.8b04220>
30. Popov, M.V. and Bannov, A.G., *Mater. Today*, 2020, vol. 31, pp. 489–491.  
<https://doi.org/10.1016/J.MATPR.2020.05.728>
31. Jiménez, V., Sánchez, P., Panagiotopoulou, P., Valverde, J.L., and Romero, A., *Appl. Catal. A: General*, 2010, vol. 390, nos. 1–2, pp. 35–44.  
<https://doi.org/10.1016/J.APCATA.2010.09.026>
32. Hu, F., Ye, R., Jin, C., Liu, D., Chen, X., Li, C., Lim, K.H., Song, G., Wang, T., Feng, G., Zhang, R., and Kawi, S., *Appl. Catal. B*, 2022, vol. 317, p. 121715.  
<https://doi.org/10.1016/j.apcatb.2022.121715>
33. Torres Galvis, H.M., Bitter, J.H., Khare, C.B., Ruitenbeek, M., Dugulan, A.I., and de Jong, K.P., *Science*, 2012, vol. 335, no. 6070, pp. 835–838.  
<https://doi.org/10.1126/science.1215614>
34. Kwon, K., Jin, S.A., Pak, C., Chang, H., Joo, S.H., Lee, H.I., Kim, J.H., and Kim, J.M., *Catal. Today*, 2011, vol. 164, no. 1, pp. 186–189.  
<https://doi.org/10.1016/J.CATTOD.2010.10.030>
35. Le, T.H., Kim, S.J., Bang, S.H., Lee, S.H., Woo Choi, Y., Kim, P., Kim, Y.H., and Min, J., *Biores. Technol.*, 2012, vol. 104, pp. 795–798.  
<https://doi.org/10.1016/J.BIORTECH.2011.10.064>
36. Kulikova, M.V. and Krylova, A.Yu., *Chem. Sustain. Develop.*, 2022, vol. 30, no. 5, pp. 581–588.  
<https://doi.org/10.15372/KHUR2022417>
37. Yan, Q., Street, J., and Yu, F., *Biomass Bioenerg.*, 2015, vol. 83, pp. 85–95.  
<https://doi.org/10.1016/J.BIOMBIOE.2015.09.002>