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MOF- and COF-Based Nanocatalysts for Selective CO_2 Hydrogenation to Methanol under Mild Conditions: Recent Advances (2023–2025) and Industrial Prospects in Iran

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ABSTRACT

Carbon dioxide hydrogenation to methanol using green hydrogen is a promising carbon capture and utilization (CCU) route for achieving carbon neutrality. This review focuses on the latest advances (2023–2025) in metal-organic framework (MOF) and covalent organic framework (COF)-based nanocatalysts for selective CO_2-to-methanol conversion under mild conditions (T < 150 °C, P < 20 bar). Single-atom Cu anchored on amino-functionalized UiO-66, defect-engineered TpPa-1 COFs with Cu-N_4 sites, and hierarchical MOF–COF hybrids have achieved methanol yields exceeding 85% and space-time yields up to 2.8 g g_cat^{-1} h^{-1} by enhancing CO_2 adsorption, H_2 activation, and water tolerance. Key challenges such as hydrothermal instability and water poisoning are addressed through defect engineering, hydrophobic functionalization, and sorption-enhanced reactors. Iran, with over 12 Mt yr^{-1} methanol capacity and abundant CO_2 emissions from Assaluyeh and Mahshahr complexes, is uniquely positioned to lead green methanol production. Integration of solar-driven hydrogen (LCOH ≈ \$1.5–2 kg^{-1} in southern Iran) with existing methanol plants could yield 2–5 Mt yr^{-1} green methanol by 2030 at a levelized cost of \$300–450 t^{-1}. Pilot-scale implementation of UiO-66–TpPa-1 catalysts and policy incentives for 20% CCU blending are recommended to accelerate commercialization. These breakthroughs, combined with Iran's abundant CO_2 point sources and solar potential, pave the way for cost-competitive green methanol production and significant decarbonization of the petrochemical sector by 2030.

Keywords: **CO_2 hydrogenation, Methanol, MOF, COF, Single-atom catalyst, Green hydrogen, Iran, Mild conditions**

1. *INTRODUCTION*

The escalating concentration of atmospheric CO_2 driven by anthropogenic emissions represents one of the most pressing global challenges of the 21st century. Global energy-related CO_2 emissions reached a record 37.8 Gt in 2024 and are projected to surpassification exceed 40 Gt by 2030 without immediate and decisive mitigation actions [1]. In this context, carbon capture and utilization (CCU) has emerged as a powerful dual-purpose strategy that simultaneously reduces net emissions and converts CO_2 into value-added chemicals and fuels [2,3]. Among various CCU pathways, the hydrogenation of CO_2 to methanol using green hydrogen stands out as one of the most promising routes toward carbon-neutral fuel and chemical production [4,5]. Methanol is a versatile C1 platform chemical and an emerging clean energy carrier. By 2025, global methanol production capacity has approached 120 million metric tons per year, with Iran ranking as the world's second-largest producer (over 12 Mt yr^{-1}) after China, primarily through large-scale plants such as Zagros, Fanavaran, Kaveh, and Marjan [6]. However, conventional methanol synthesis from syngas remains heavily dependent on fossil resources. In contrast, direct CO_2 hydrogenation to "green methanol" offers a genuinely carbon-neutral alternative when coupled with renewable hydrogen and captured CO_2 from point sources such as Assaluyeh and Mahshahr petrochemical complexes [7,8]. The main technological bottleneck for industrial-scale CO_2-to-methanol processes lies in developing highly active and selective catalysts capable of operating under mild conditions (T < 150 °C, P < 20 bar) [9]. Commercial Cu/ZnO/Al_2O_3 catalysts, while robust at 230–300 °C and 50–100 bar, exhibit low CO_2 conversion (<20 %) and poor methanol selectivity under milder conditions due to thermodynamic constraints and water-induced deactivation [10]. In recent years, metal–organic frameworks (MOFs) and covalent organic frameworks (COFs) have attracted tremendous attention

as next-generation catalyst supports thanks to their ultra-high surface areas (>3000 $m^2 g^{-1}$), precisely tunable pore environments, and ability to stabilize single-atom active sites [11–13]. Between 2023 and 2025, remarkable breakthroughs have been reported: single-atom Cu anchored on amino-functionalized UiO-66 [14], defect-engineered TpPa-1 COFs with Cu-N_4 sites [15], and hierarchical MOF@COF hybrids [16] have achieved methanol selectivity and yields exceeding 85 % together with space-time yields up to 2.8 g $g_cat^{-1} h^{-1}$ under mild conditions. This review critically examines the most significant advances in MOF- and COF-based nanocatalysts for selective CO_2 hydrogenation to methanol reported between 2023 and 2025, highlights strategies to overcome key challenges (hydrothermal instability, water poisoning, and green H_2 supply), and evaluates the unique industrial prospects for rapid deployment of this technology in Iran, leveraging its abundant point-source CO_2, world-class methanol infrastructure, and exceptional solar potential in the south.

2. Overview of Methods for Converting CO_2 to Methanol

Several approaches exist for CO_2-to-methanol conversion, including thermal, photocatalytic, electrocatalytic, and biological routes [4,17]. Heterogeneous catalytic hydrogenation remains the most industrially viable method due to its scalability and compatibility with existing infrastructure [5,18].

2.1 Classical Thermal Processes

Conventional $Cu/ZnO/Al_2O_3$ catalysts operate at 230–300 °C and 50–100 bar, achieving 15–25% CO_2 conversion and >90% methanol selectivity [10]. However, high energy demand, low single-pass conversion, and rapid deactivation by water limit their suitability for green methanol production [10,19].

2.2Photocatalytic and Electrocatalytic Routes

Photocatalytic systems using TiO_2, g-C_3N_4, or MOF/COF hybrids operate at ambient conditions but suffer from low quantum efficiency and poor scalability [20,21]. Electrocatalytic CO_2 reduction has reached Faradaic efficiencies up to 77% for methanol, yet high overpotentials and short catalyst lifetime (<100 h) hinder commercial application [22,23].

2.3 Catalytic Hydrogenation The Preferred Industrial Route

Direct hydrogenation using advanced catalysts is currently the most realistic path for large-scale green methanol production, especially when integrated with renewable H_2 and captured CO_2 [5,18,24].

3. Next-Generation Nanocatalysts

Introduction to Metal-Organic Frameworks (MOFs) and Covalent Organic Frameworks (COFs) MOFs are crystalline porous materials constructed from metal nodes and organic linkers, offering surface areas up to 7000 $m^2 g^{-1}$ [11,25]. COFs are fully organic counterparts linked by strong covalent bonds, exhibiting superior chemical and hydrothermal stability [12,26]. Advantages of MOF/COF over Traditional Catalysts Ultra-high surface area, tunable pore chemistry, and precise single-atom dispersion enable unprecedented CO_2 adsorption capacity and suppress the reverse water-gas shift (RWGS) reaction [11–13,27]. Loading of Active Metals on MOF/COF Supports Cu, Zn, Pd, and Ni are commonly introduced via impregnation, encapsulation, or atomic layer deposition. Single-atom Cu-N_4 sites and Cu–Zr interfaces are particularly effective for methanol synthesis [14,28,29].

4.Advances in 2023–2025

UiO-66-NH_2-Supported Cu Catalysts Single-atom Cu on amino-functionalized UiO-66 achieved 85% methanol selectivity and STY of 1.2 g $g_cat^{-1} h^{-1}$ at 130 °C and 10 bar [14]. Defect-engineered Hf-UiO-66 further enhanced performance via stronger CO_2 activation [9]. Defect-Engineered COFs with Single-Atom Sites Defect-rich TpPa-1 bearing isolated Cu-N_4 sites delivered 88% selectivity and STY of 2.1 g $g_cat^{-1} h^{-1}$

at 130 °C and 8 bar [15]. Porphyrin-based TpBD-COFs with embedded Ni single atoms exhibited excellent water tolerance [30]. Hierarchical MOF@COF Hybrids Core-shell UiO-66@TpPa-1 and Zr-MOF@TpBD structures combine high CO_2 uptake of MOFs with the stability and hydrophobicity of COFs, reaching 90% selectivity and STY up to 2.8 g g_cat^{-1} h^{-1} at 135 °C and 7 bar [16,31].

5.Challenges and Solutions

Hydrothermal Stability MOF hydrolysis is mitigated by COF protective shells or siloxane bridging [9,16]. Resulting catalysts retain activity for >500 h [32] Water Poisoning Hydrophobic functionalization and in-situ water removal via sorption-enhanced reactors maintain >85% activity in the presence of produced water [19,30]. Green Hydrogen Supply in Iran Southern Iran offers solar irradiation >2500 kWh m^{-2} yr^{-1}, enabling green H_2 at \$1.5–2 kg^{-1} via PEM electrolysis coupled with desalination [33–35].

6.Industrial Outlook in Iran

CO_2 Sources Assaluyeh and Mahshahr complexes emit >40 Mt CO_2 yr^{-1}, capturable at ~\$30 t^{-1} via amine scrubbing [36]. Integration with Existing Plants Retrofitting Zagros, Fanavaran, and Marjan plants with MOF/COF-based reactors can add 2–5 Mt yr^{-1} green methanol capacity by 2030 [6,37]. Economic Feasibility Levelized cost of green methanol is projected at \$300–450 t^{-1} by 2030 with solar H_2 at \$2 kg^{-1} and policy incentives [37,38].

7.Conclusion

Recent breakthroughs in MOF- and COF-based nanocatalysts have made selective CO_2-to-methanol conversion under mild conditions industrially feasible. Iran's unique combination of abundant point-source CO_2, world-class methanol infrastructure, and exceptional solar potential positions it to become a global leader in green methanol production. Immediate pilot-scale demonstration of UiO-66@TpPa-1 catalysts in Assaluyeh, coupled with policy mandates for 20% CCU blending, is strongly recommended.

Despite the remarkable progress achieved between 2023 and 2025, several critical challenges still hinder the large-scale deployment of MOF- and COF-based nanocatalysts for CO_2-to-methanol conversion under mild conditions. The most important obstacles and the state-of-the-art solutions reported in recent literature are summarized in Table 1.

***Table 1.** Major challenges of MOF- and COF-based nanocatalysts for CO_2 hydrogenation to methanol under mild conditions and corresponding recent solutions (2023–2025)*

No.	Challenge	Detailed Problem	Recent Solution (2023–2025)	Performance Achieved	Ref.
1	Hydrothermal instability of MOFs	Zr–O or Cu–O bonds in UiO-66, HKUST-1, and MOF-808 hydrolyze rapidly in the presence of produced water at T > 100 °C	(i) COF protective shell (core–shell UiO-66@TpPa-1 or MOF@COF) (ii) Siloxane or hydrophobic post-synthetic modification (iii) Defect engineering and Na^+/K^+ decoration	>500–1000 h stability at 130–150 °C, <5% activity loss	[9,16,26,31,45]
2	Water poisoning & RWGS promotion	Produced H_2O blocks Lewis acid sites and accelerates Cu sintering and reverse water-gas shift (RWGS)	(i) Hydrophobic functionalization (–CF_3, alkyl chains) (ii) In-situ water removal via sorption-enhanced reactors (13X zeolite or hydrophilic COF layer) (iii) Isolated Cu-N_4 or	Methanol selectivity maintained >85% even at high conversion (>20%)	[15,19,27,30,32]

No.	Challenge	Detailed Problem	Recent Solution (2023–2025)	Performance Achieved	Ref.
			Ni-N_4 sites with high water tolerance		
3	Catalyst deactivation & metal leaching	Single-atom Cu or Ni migration/agglomeration under reductive atmosphere and long-term operation	(i) Strong metal–support interaction via N-anchor or defect trapping (ii) Hierarchical pore design preventing pore blockage	TOF stable for >800 h; Cu particle size <1.2 nm after 500 h	[14,15,27,44]
4	High cost and complex scale-up synthesis	Multi-step synthesis of defect-engineered COFs and core–shell hybrids is time-consuming and expensive	(i) Mechanochemical and one-pot synthesis routes (ii) Use of inexpensive linkers (e.g., TpPa-1 instead of porphyrin-based COFs) (iii) Recyclable templates	Synthesis cost reduced by 40–60%; scalability demonstrated at 50–100 g/batch	[19,27,30]
5	Green H_2 availability & cost in Iran	Current grey H_2 price ~\$1.5 kg^{-1}; green H_2 still >\$4 kg^{-1} in many regions	Solar-rich southern Iran (Bandar Abbas, Chabahar): LCOH projected at \$1.5–2.0 kg^{-1} by 2030 with PEM electrolyzers + desalination	Makes green methanol competitive (<\$450 t^{-1})	[15,33,34,35,38]

These strategies have collectively pushed catalyst lifetime beyond 500–1000 h, methanol selectivity above 85–90%, and space-time yields up to 2.8 g g_cat^{-1} h^{-1} under industrially attractive mild conditions (130–150 °C, 7–20 bar), bringing MOF/COF-based systems very close to pilot- and commercial-scale viability, especially in countries like Iran with abundant CO_2 point sources and solar energy.

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