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Recent Advances in Coal-to-Olefins Conversion and Its Catalysts

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Abstract: Olefins serve as a crucial organic chemical feedstock in synthetic chemistry due to their extensive applications. With recent advancements in coal-to-olefins (CTO) technology, coal, a long-standing primary energy resource in China, has demonstrated considerable potential as an alternative raw material. This review aims to provide a systematic overview of CTO technologies, seeking to identify current research gaps and outline promising avenues for future investigation.

1. Introduction

Olefins occupy a paramount position as fundamental feedstocks for a vast array of chemical products, such as polymers, synthetic rubber, synthetic fibers, fine chemicals, and polymeric materials. Olefin production has predominantly relied on petroleum (naphtha) cracking. However, China faces a shortage of petroleum resources, rapidly growing energy demand, high dependence on imported crude oil, and consequently, tight supplies of olefin feedstocks. Simultaneously, petroleum-based olefin production is associated with high energy consumption, substantial CO_2 emissions, and significant generation of wastewater and solid waste, leading to considerable environmental strain. Therefore, developing more environmentally friendly, efficient, and cost-effective olefin production routes is a critical strategic imperative for the future. The coal chemical industry, deeply embedded in China's energy structure, offers a viable pathway. Its development not only optimizes coal resource utilization and bolsters ensure energy security but can also stimulates regional economic growth. While hurdles in resource sustainability, environmental protection, and techno-economic feasibility remain, continuous technological innovation and systemic industrial upgrading are poised to enable a greener, more efficient and sustainable future for coal industry. China's coal chemical industry has entered a critical period of high-quality development, with the coal-to-olefins industry gradually moving toward large-scale, intensive, and low-carbon development. According to the latest industry data, the current capacity of coal-to-olefins in China has exceeded 18 million tonnes per year, accounting for more than 30% of the total olefin production capacity, effectively alleviating the structural shortage of petroleum-based olefins. In the context of the dual-carbon strategy, the research and development of high-efficiency, long-life, and low-emission catalysts has become the core driving force for the technological upgrading of the coal-to-olefins industry. The rational design of catalytic materials not only improves the conversion efficiency and product selectivity of the reaction process but also reduces the energy consumption and carbon emission intensity of the whole industry chain, which is of great significance for the coal chemical industry to achieve carbon peaking and carbon neutrality goals.

2. Industrial routes for coal-to-olefins

The coal-to-olefins (CTO) process mainly comprises three principal stages. Initially, coal is gasified to produce crude synthesis gas (syngas). This crude syngas is subsequently purified to remove impurities and then catalytically converted into methanol (CTM). In the final stage, methanol serves as a key intermediate and is transformed into olefins via methanol-to-olefins (MTO) reaction. This integrated pathway provides an efficient method for converting coal into fundamental chemical feedstocks. The coal-to-olefins (CTO) process mainly comprises three principal stages, as illustrated in Figure 1.

2.1 Coal-to-Methanol (CTM)

Coal gasification is regarded as one of the core technologies for clean coal utilization, This process converts solid coal into synthesis gas (syngas), mainly composed of CO and H_2, under conditions of high temperature, high pressure, and a controlled oxygen atmosphere[1].The subsequent synthesis of methanol from syngas is primarily governed by the following reactions: $CO + 2H_2 \rightarrow CH_3OH$ (main reaction) and $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ (side reaction). The catalyst employed for the main reaction is a fundamental determinant of process viability, with its performance directly dictates the methanol yield, product selectivity, and operational stability of the plant.

$Cu/ZnO/Al_2O_3$ is the most classical and widely used catalyst for methanol synthesis, supporting a global annual production exceeding 110 million tonnes. Over the past decades, researchers have conducted extensive studies on the $Cu/ZnO/Al_2O_3$ catalyst, revealing multifaceted deactivation mechanisms (Table 1) and optimization strategies.

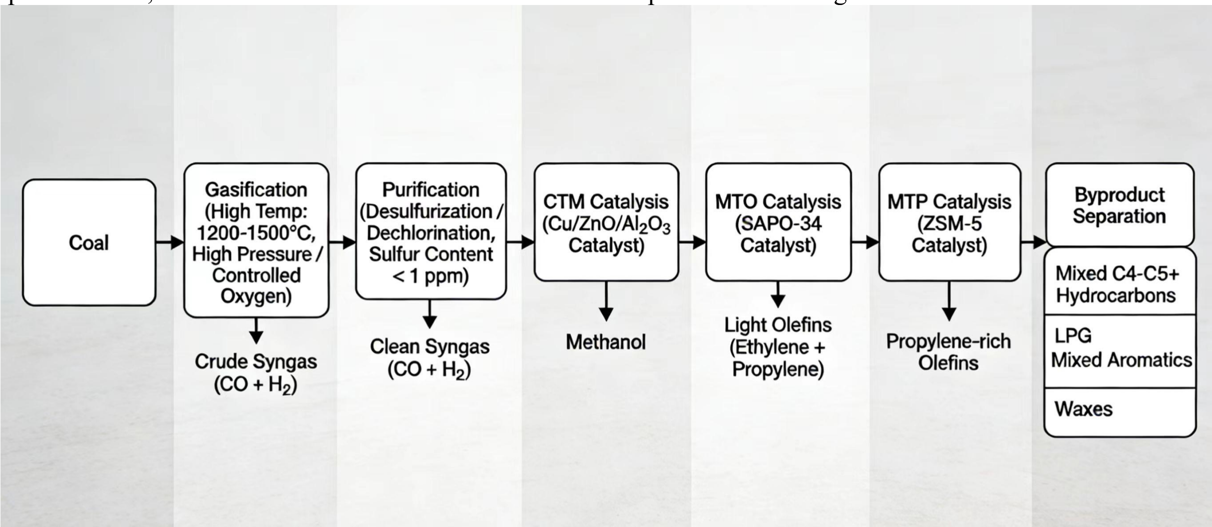

Figure 1. Schematic Flow Diagram of the Coal-to-Olefins (CTO) Process

Table 1. Deactivation Mechanisms of $Cu/ZnO/Al_2O_3$ Catalysts in CTM Process

Deactivation Type	Trigger Factors	Consequences	Mitigation Measures
Thermal Sintering	Operating temperature >260°C	Cu^0 particle growth, irreversible activity loss	addition of sintering inhibitors (e.g., ZrO_2)
Oxidative Deactivation	H_2O/CO_2 in syngas; trace O_2 during regeneration	Cu^0 oxidation to inactive Cu^{2+}	Minimize O_2 ingress; optimize syngas moisture content
Sulfur/Chlorine Poisoning	ppm-level H_2S/HCl in syngas	Formation of inert $CuS/CuCl_x$	ZnO-based desulfurization (syngas S <0.1 ppm)
Water-Induced Agglomeration	High water partial pressure	$Zn(OH)_2$ migration; Al_2O_3 conversion to boehmite	Reduce syngas moisture; modify catalyst with hydrophobic components
Mechanical Attrition	Fluidized-bed/slurry-bed reactors	Loss of catalyst fines (<10 μm) via gas entrainment	Improve catalyst particle strength; install cyclone separators

The rational design of $Cu/ZnO/Al_2O_3$ primarily aims to enhance Cu^0 dispersion, inhibit sintering, and promote CO_2 adsorption and activation. For example, Wang et al. [2] reported that 4 wt% ZrO_2 loading lowers the catalyst reduction temperature and boosts CO_2 conversion by 7.5%. Liu et al[3]. found that adding 2 wt% MnO_2 increases methanol yield by 19% via oxygen vacancy formation. Non-precious metal oxide catalysts (e.g., ZnZrO, $InZrO_x$, $ZnGaO_x$) are also promising, with weak basic sites accelerating CO_2 dissociation and methanol formation, while strong basic sites inhibit reaction via carbonate formation[4].

Currently, the optimization potential for $Cu/ZnO/Al_2O_3$ is approaching theoretical limits, shifting research focus to electrocatalytic CO_2-to-methanol routes. However, technical bottlenecks persist: low methanol selectivity, difficult product separation from aqueous solutions, and over-hydrogenation to light paraffins (LP) during methanol to light olefins (MeOH→LO) conversion, limiting LO/LP ratio improvement[5]. In addition to ZrO_2 and MnO_2 doping, the modification of $Cu/ZnO/Al_2O_3$ catalysts with rare earth oxides (e.g., La_2O_3, CeO_2) has also achieved good results in recent studies. La_2O_3 can form a stable interface with Cu species, inhibit the sintering of Cu particles at high temperatures, and improve the thermal stability of the catalyst; CeO_2 with oxygen storage capacity can promote the adsorption and activation of CO_2 molecules, further increasing the methanol selectivity of the catalyst. The composite modification of multiple metal oxides has become a new research trend, which can combine the advantages of different modifiers and realize the synergistic improvement of catalyst activity, selectivity and stability.

2.2 Methanol-to-olefins Technology (MTO)

In a broad sense, the MTO process is a catalytic route for converting methanol into light olefins, primarily ethylene and propylene. It is broadly categorized into two technological pathways: methanol-to-olefins (MTO), which yields a mixture of ethylene and propylene, and methanol-to-propylene (MTP), which is selective toward propylene. At present, MTO serve as the core hub for the convergence of “coal-to-oil” and “green hydrogen + CO_2” technical routes, and it also stands as the fastest-growing technology for the supply of non-petroleum-based olefins worldwide.[6] Catalysts for MTO are primarily zeolites, with SAPO-34 and ZSM-5 as the most widely used (Table 2). SAPO-34 (8-membered ring, pore diameter

0.38–0.50 nm) exhibits 83–89% ethylene-propylene selectivity via size restriction of C4+ species ZSM-5 (ten-membered ring, pore diameter ≈0.55 nm) favors propylene/butenes but is more prone to coking The MTP process proceeds via methanol dehydration to dimethyl ether (DME), followed by selective propylene formation over ZSM-5.At present, the modified SAPO-34 and ZSM-5 catalysts have been successfully applied in industrial MTO units in China, such as the 1.8 million tonnes per year coal-to-olefins project in Inner Mongolia and the 2 million tonnes per year project in Shaanxi. The industrial application results show that the hierarchical porous modified SAPO-34 catalyst can extend the single-cycle operation time of the reactor from 48 h to 72 h, and the ethylene-propylene selectivity is maintained at more than 88%, which significantly reduces the regeneration frequency of the catalyst and the operating cost of the unit. The ZSM-5 catalyst modified by P/Mg doping has been applied in the methanol-to-propylene (MTP) process, with the propylene selectivity reaching more than 75% and the catalyst service life exceeding 2 years, realizing the long-term stable operation of the industrial device.

Table 2. Performance Comparison of SAPO-34 and ZSM-5 Catalysts in MTO Process

Catalyst Property	SAPO-34	ZSM-5
Pore Structure	Pore size <0.50 nm, ellipsoidal cages	pore size ≈0.55 nm, straight/curved channels
Olefin Selectivity	Ethylene + Propylene: 83–89%	Propylene + Butenes: 75–80%
Coking Tendency	Moderate	High (due to larger pore size)
Regeneration Stability	Framework Al susceptible to hydrolytic dealumination	Better hydrothermal stability than SAPO-34
Modification Strategies	Mesopore introduction; ion exchange	P/Mg doping; UiO-66 shell coating

Both catalysts face critical bottlenecks: microporous structure restricting mass transfer (accelerating coking), challenging acid-base site optimization, and irreversible framework degradation during regeneration. To address these, integrated modification strategies have been proposed:

- Hierarchical porosity engineering: Liquid-phase etching with citric acid/NH_4F introduces mesopores, reducing diffusion limitations.
- Acidity adjustment: 0.3–0.8 wt% K^+ ion exchange moderates strong acid sites, enhancing ethylene selectivity by 4–5 percentage points[7].
- Hydrothermal stability enhancement: Synergistic P/Mg doping forms $MgAl_2O_4$ anchoring sites, retaining 92% crystallinity after 800°C hydrothermal treatment[8].
- Coking inhibition: Coating 20–30 nm SAPO-34 nanosheets with UiO-66 shell decreases coking rate by 35% and diolefin selectivity to 82–90%[9].

3. Economic and environmental trade-offs of CTO VS. alternative routes

Under China's "dual-carbon" constraints, CTO's competitiveness depends on balancing economic feasibility and environmental sustainability. Table 3 compares CTO with mainstream alternative olefin production routes (ethane cracking, bio-based routes) in terms of key metrics.

Table 3. Comparison of Olefin Production Routes Under Dual-Carbon Constraints

Metric	Coal-to-Olefins (CTO)	Ethane Cracking (Petroleum-Based)	Bio-Based Routes (Lignocellulosic Biomass)
Feedstock Availability (China)	Abundant	Scarce	Moderate
Production Cost (USD/tonne Olefin)	700–900	650–850 (volatile with crude oil prices)	1200–1500 (high current cost, declining with scale)
CO_2 Emissions (t CO_2/t Olefin)	4.5–6.0	2.0–2.5	0.5–1.0 (carbon-neutral potential)
Energy Consumption (GJ/t Olefin)	45–55	25–30	30–40 (renewable energy integration possible)
Waste Generation	Wastewater (0.8–1.2 m³/t), solid waste	Wastewater (0.3–0.5 m³/t), NO_x emissions	Minimal (biomass residue recyclable as fertilizer)

3.1 Economic Trade-Offs

CTO's core economic advantage lies in abundant and low-cost coal feedstock, making it resilient to crude oil price fluctuations. However, high upfront investment (≈2–3 billion USD for a 1 million tonne/year plant) and water/energy intensity (requiring ≈10,000 m³ water/t olefin) limit profitability in water-scarce regions. Ethane cracking, while cheaper at low crude oil prices, faces supply risks due to China's 70%+ crude oil import dependence. Bio-based routes are currently cost-prohibitive but offer long-term potential with policy support and technological scaling[10].

3.2 Environmental Trade-Offs

CTO's major environmental challenge is high CO_2 emissions, conflicting with dual-carbon goals. However, carbon capture, utilization, and storage (CCUS) integration can reduce emissions by 60–80% (to 1.5–2.0 tonne CO_2/t olefin) at an additional cost of 100–150 USD/t olefin Ethane cracking has lower emissions but remains fossil-dependent, while bio-based routes are nearly carbon-neutral but constrained by feedstock supply and land use.

3.3 Critical Discussion

In terms of industrial policy, the state has issued a series of supportive policies for the low-carbon development of the coal chemical industry, such as the inclusion of coal-to-olefins projects coupled with CCUS technology in the national low-carbon demonstration projects, and the provision of financial subsidies and tax ince.CTO remains strategically important for China's energy security, but its sustainability hinges on CCUS deployment and byproduct valorization. Ethane cracking will dominate in the short term due to cost advantages, while bio-based routes are likely to grow gradually with policy incentives. Future CTO development must prioritize emission reduction (e.g., green hydrogen substitution in syngas production) and cost optimization to compete under dual-carbon constraints.

4. Conclusion

CTO has emerged as a strategic industry in China, leveraging the nation's abundant coal resources to counterbalance its relative scarcity of oil After decades of accelerated technological iteration and industrial upgrading, CTO has matured into a robust pillar of olefin supply, operating in parallel with conventional petroleum-derived routes. The catalytic process is crucial to CTO. Zeolites, employed as catalysts in both CTM and MTO processes, possess topological framework and acidity characteristics that critically determine catalytic performance, reaction pathways, and product selectivity. Although SAPO-34-and ZSM-5-based catalysts have been widely applied in commercial MTO processes, enhancing their catalytic properties remains a critical pursuit. Future research should focus on the following aspect:

1. Synthesizing high-quality nanoscale/mesoporous zeolites to accelerate intra-zeolitic diffusion;
2. Integrating functional components with zeolites for direct coal-to-olefins conversion;
3. Process intensification (microchannel slurry-bed reactors, microwave-assisted regeneration) to shorten cycle times and increase productivity;
4. CCUS integration and green hydrogen substitution to reduce CO_2 emissions;
5. Advanced byproduct upgrading to improve economic and environmental sustainability.

By addressing these areas, CTO can continue to play a vital role in China's olefin supply chain while aligning with dual-carbon goals.

References

1. YANG S, YANG Q, LI H, et al. *An Integrated Framework for Modeling, Synthesis, Analysis, and Optimization of Coal Gasification-Based Energy and Chemical Processes[J]. Industrial & Engineering Chemistry Research, 2012, 51(48): 15763-15777.*
2. Wang, P.; Zhang, H.; Wang, S.; Li, J. *Controlling H2 Adsorption of Cu/ZnO/Al2O3/MgO with Enhancing the Performance of CO2 Hydrogenation to Methanol at Low Temperature. J. Alloys Compd.* ***2023****, 966, 171577. https://doi.org/10.1016/j.jallcom.2023.171577.*
3. Liu, Y.; Cui, L.; Liu, C.; Huang, L.; Cao, F. *Enhanced CO2 Hydrogenation to Methanol over Cu-ZnO-Al2O3 Catalyst Modified with Zirconium: Experimental and Theoretical Insights. Chem. Eng. J.* ***2025****, 511, 162221. https://doi.org/10.1016/j.cej.2025.162221.*
4. Chernyak, S. A.; Corda, M.; Marinova, M.; Safonova, O. V.; Kondratenko, V. A.; Kondratenko, E. V.; Kolyagin, Y. G.; Cheng, K.; Ordomsky, V. V.; Khodakov, A. Y. *Decisive Influence of SAPO-34 Zeolite on Light Olefin Selectivity in Methanol-Meditated CO_2 Hydrogenation over Metal Oxide-Zeolite Catalysts. ACS Catal.* **2023**, *13* (22), 14627–14638. https://doi.org/10.1021/acscatal.3c03759.
5. Yang, M.; Fan, D.; Wei, Y.; Tian, P.; Liu, Z. Recent Progress in Methanol-to-Olefins (MTO) Catalysts. *Adv. Mater.* **2019**, *31* (50), 1902181. https://doi.org/10.1002/adma.201902181.
6. AL-SHAFEI E, SHAKOR Z. *Non-linear kinetic model of coke deactivation in methanol-to-gasoline conversion: Effects of nano and micro ZSM-5 crystals[J]. Journal of Analytical and Applied Pyrolysis, 2024, 183: 106830.*
7. Zhang, K.; Tang, Q.; Liu, L.; Dong, J. *Engineering Acid Site Distribution in Hierarchical ZSM-5 Microspheres toward High-Efficiency Benzene-Butene Alkylation Catalysis. Chem. Eng. Sci.* ***2025****, 318, 122190. https://doi.org/10.1016/j.ces.2025.122190.*
8. Moradiyan, E.; Halladj, R.; Askari, S. *Beneficial Use of Ultrasound in Rapid-Synthesis of SAPO34/ZSM-5 Nanocomposite and Its Catalytic Performances on MTO Reaction. Ind. Eng. Chem. Res.* ***2018****, 57 (6), 1871–1882. https://doi.org/10.1021/acs.iecr.7b03772.*
9. Zhang, L.; Liu, H.; Yue, Y.; Olsbye, U.; Bao, X. *Design and in Situ Synthesis of Hierarchical SAPO-34@kaolin Composites as Catalysts for Methanol to Olefins. Catal. Sci. Technol.* ***2019****, 9*

(22), 6438–6451. https://doi.org/10.1039/C9CY01663E.

10. Xie, J.; Li, X.; Yang, B.; Ma, H. *Life Cycle Carbon Footprint and Cost Assessment of Modern Coal Chemical Industry Coupled with Carbon Capture Utilization and Storage Technology. Fuel* ***2025****, 401, 135788. https://doi.org/10.1016/j.fuel.2025.135788.*