

# Study on Modification Methods for Supports of Methanol Steam Reforming Catalysts: Mini-Review

Yupeng Xia

University of Shanghai for Science and Technology, Shanghai 200000, China

---

## Abstract

Load-type catalysts are widely used in heterogeneous catalytic reaction systems due to their high active component utilization, tunable structure, and ease of industrial scaling. Among these, methanol catalytic reforming for hydrogen production represents a significant hydrogen energy acquisition pathway. Methanol's abundant sources, convenient storage and transportation, and relatively high energy density make it highly promising for distributed hydrogen production. However, this reaction system features high Gibbs free energy and involves complex multistep processes including dehydrogenation, bond cleavage, and multivalent redox transformations. This complexity inevitably generates various carbon-containing chemical intermediates such as CO, formates, and methoxy groups. These intermediates not only occupy catalytic active sites and reduce reaction rates but may also lead to coking or metal sintering, causing catalyst deactivation and severely limiting overall reaction kinetics and stability. Therefore, there is an urgent need to develop supported catalysts with high activity, high selectivity, and long lifetime to achieve efficient hydrogen production with low byproduct formation. This paper focuses on supported catalysts, systematically reviewing current research progress in catalytic methanol reforming from two perspectives: support regulation and modification of supported active components. It emphasizes the influence of support acidity/basicity, defect/pore structure, metal dispersion, and interfacial interactions on catalytic performance. Finally, it summarizes and outlines future design strategies and development directions.

## Keywords

**Supported Catalyst; Methanol Catalytic Reforming; Product Selectivity; Sintering; Carrier Modification.**

---

## 1. Introduction

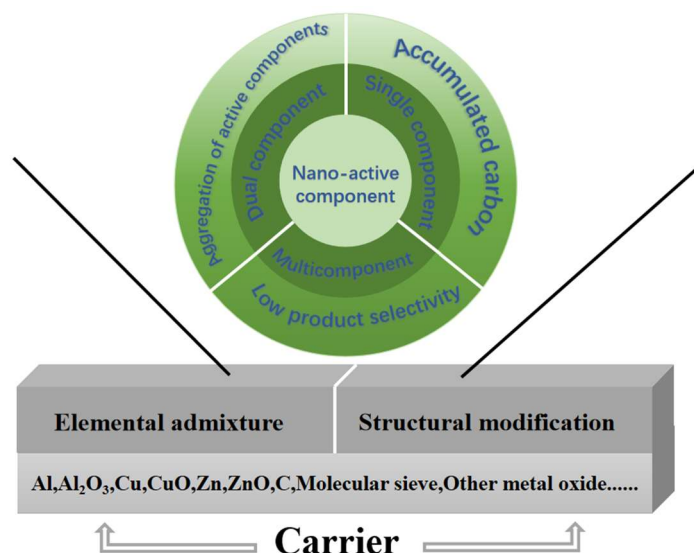
Hydrogen is an important secondary energy carrier for low-carbon society due to its environmental friendliness and zero emissions, and it has been widely applied in transportation, stationary power generation, fuel cells, aerospace, and energy storage systems [1–3]. Among hydrogen production routes such as water electrolysis, ammonia cracking, and hydrocarbon reforming, methanol reforming has attracted sustained attention because methanol features high hydrogen density, convenient storage/transportation, and feasibility for on-demand hydrogen generation [4–6]. In particular, methanol steam reforming (MSR) has been extensively explored from laboratory to pilot scales, showing high efficiency and promising integration potential. As a liquid fuel under ambient conditions, methanol is safer than compressed hydrogen and can be produced from fossil feedstocks, biomass, or CO<sub>2</sub> hydrogenation, enabling sustainable hydrogen supply chains [7–9].

Despite these advantages, MSR remains limited by thermodynamic and kinetic constraints. As an endothermic reaction, MSR requires continuous heat input, and high temperatures and pressures are often necessary to achieve high methanol conversion and hydrogen yield. Under moderate

temperatures, insufficient intrinsic activity may result in low reforming rates and undesired side reactions. According to the Arrhenius relationship ( $\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$ ), decreasing the activation energy is an effective approach to accelerate MSR under milder conditions. Therefore, developing catalysts with high intrinsic activity and optimized adsorption/desorption behavior is critical for efficient hydrogen production.

Supported catalysts are the most widely applied MSR catalysts due to tunable microstructures, controllable dispersion of active sites, and compatibility with continuous-flow reactors [10–13]. Nanosizing active components can increase the fraction of low-coordination atoms, improve atom utilization, and enhance activity/selectivity. Thus, loading nanoscale metals onto supports such as Cu-based oxides, Al<sub>2</sub>O<sub>3</sub>, ZnO, carbon materials, molecular sieves, or porous frameworks has become a common strategy for high-performance MSR catalysis [14–18]. Meanwhile, support engineering enables regulation of porosity, diffusion paths, thermal conductivity, and mechanical strength for practical operation.

However, supported MSR catalysts still face key challenges: (i) nanoparticle agglomeration and sintering under high-temperature steam, leading to loss of active sites [19–22]; (ii) coking and poisoning caused by CO and other carbon-containing intermediates/byproducts, which block sites and pores and often require harsh regeneration [23–26]; and (iii) complex reaction pathways that limit selectivity and conversion, while CO suppression remains essential for fuel-cell-grade hydrogen [27–30]. To overcome these limitations, both supports and active phases must be rationally engineered. Support modification (defects, oxygen vacancies, pore structure, and SMSI) improves dispersion and stability, while active component design (mono-/bi-/multimetallic systems) enables synergistic effects that promote methanol activation and suppress CO poisoning. Overall, MSR performance depends on interfacial synergy, which is summarized in this review (Figure 1).



**Figure 1.** Modification Methods for Methanol Steam Reforming Supported Catalysts and Common Issues.

## 2. Modification of Supported Catalyst Carriers

Research on supported catalysts primarily focuses on selecting which nanoactive components to load and combining them with appropriate modification techniques to leverage the superior catalytic performance of these nanoactive components. However, the role of the support material in the catalytic process is often overlooked. Clearly, treating the support merely as a carrier for the nanoactive component is far from sufficient. Therefore, the rational selection and modification of the support for supported catalysts to achieve synergistic effects with the nanoactive component and

enhance the catalyst's performance is crucial. Common supports for supported catalysts are listed in Table 1.

**Table 1.** Common supported catalysts

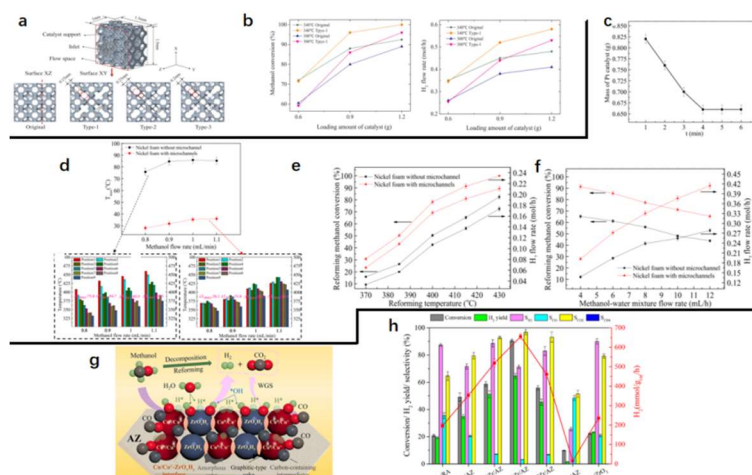
Metal-based carrier	Inorganic non-metallic-based carrier	Single-layer/multi-layer composite carrier
Al/Cu/Zn	CNTs/MWCNT	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>
TiO <sub>2</sub>	DND	SnO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>
ZrO <sub>2</sub>	h-BN	ZnO-Al <sub>2</sub> O <sub>3</sub>
XAl <sub>2</sub> O <sub>4</sub> (X=Cu,Zn,Ni)	SiC	CuO/ZnO/Al <sub>2</sub> O <sub>3</sub>
CuZnAl	Molecular sieves	CeO <sub>2</sub> -CuO,CeO <sub>2</sub> -ZnO,CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> ,CeO <sub>2</sub> -TiO <sub>2</sub>
PdZnAl	Graphene	ZnO/ZrO <sub>2</sub>
REO(RE=La,Pr,Sm,Ce,Y,In)	Graphene/carbon nanotubes	X-TiO <sub>2</sub> (X=La,Sm,Zn,Pt,Pd)
ZnZrOx	Graphene quantum dots	CuO/ZnO
MoC	Carbon nitride	M-Al <sub>2</sub> O <sub>3</sub> (M=Mg,Ni,Co,Zn,Fe)

## 2.1 Structural Modifiers

For supported catalysts, the carrier typically requires a large specific surface area, well-defined pore structure, and strong coordination ability with active components. Through interfacial interactions, the support disperses the active phase and provides abundant accessible catalytic sites [31–33]. In methanol steam reforming (MSR), supports should also exhibit high thermal stability, hydrothermal corrosion resistance, and suitable surface chemistry to regulate adsorption/desorption of reactants and intermediates, since high-temperature steam can accelerate nanoparticle sintering and surface reconstruction. Therefore, catalyst supports are not inert diluents but functional components that strongly influence activity, selectivity, and durability.

Because active components are usually nanoscale, carrier modification is essential to anchor nanoparticles and prevent agglomeration and deactivation during preparation and operation [34]. Nanosized particles have high surface free energy and tend to migrate and coalesce under MSR conditions. Thus, supports are often engineered to provide anchoring sites, confinement effects, or strong metal–support interaction (SMSI), suppressing particle diffusion and maintaining high dispersion. In addition, interfacial charge transfer can tune the electronic structure of loaded metals, optimizing adsorption strength toward key intermediates such as methoxy, formate, and CO and mitigating poisoning. A widely used strategy is structural modification of supports to introduce intrinsic defects, hierarchical porosity, or surface functional groups. These structural features determine surface area, pore volume, defect density, and surface energy, which govern catalytic behavior. Constructing mesoporous structures and utilizing pore defects to confine or anchor nano-active components is an effective approach to improve stability [35–37]. Hierarchical micro-/meso-/macroporous supports can balance dispersion and mass transport: micropores provide confinement and high surface area, mesopores improve diffusion, and macropores reduce pressure drop, facilitating continuous-flow MSR. Defect sites such as vacancies and unsaturated coordination atoms further enhance precursor binding, promoting nucleation and suppressing particle growth. Liu et al. [36] modified copper into a porous foam support and loaded Cu/Zn/Al/Zr particles via impregnation (Figure 2). Compared with non-porous foam Cu, the porous structure enhanced axial/radial mass transport and improved heat transfer, enabling stable loading above 0.9 g/g and delivering high methanol conversion and hydrogen flux. Zheng et al. [38] employed multi-channel porous foam Ni to anchor Pt nanoparticles, forming Pt/Ni catalysts with improved adhesion and

thermal management. This structure reduced the maximum operating temperature by 33.8 °C and the maximum temperature difference by 57.8 °C, suppressing sintering and improving operational stability. Zeolites and molecular sieves are also effective MSR supports due to abundant micro/mesopores and tunable acidity/basicity. Chen et al. [39] loaded Cu–Zr nanoparticles on attapulgite-based zeolite (AZ), where confinement and strong coordination created interfacial active sites that enhanced heat/mass transfer, promoted intermediate decomposition, suppressed CO accumulation and coking, and improved overall catalytic performance[40–42].



**Figure 2.** (a) Schematic diagram of the foam copper support structure [36]. (b) Relationship between foam copper loading and methanol conversion rate and hydrogen yield [36]. (c) Foam nickel adhesion test on Pt particles [38]. (d) Maximum temperature and temperature distribution of foam nickel carriers with and without microchannels [38]. (e) Reforming temperature of foam nickel supported catalysts with and without microchannels [38]. (f) Relationship between steam flow rate and methanol conversion rate and hydrogen yield [38]. (g) Catalytic mechanism of CuZr/AZ catalyst [39]. (h) Methanol conversion rate, hydrogen yield, and selectivity toward CO, CO<sub>2</sub>, and CH<sub>4</sub> for different types of supported catalysts [39].

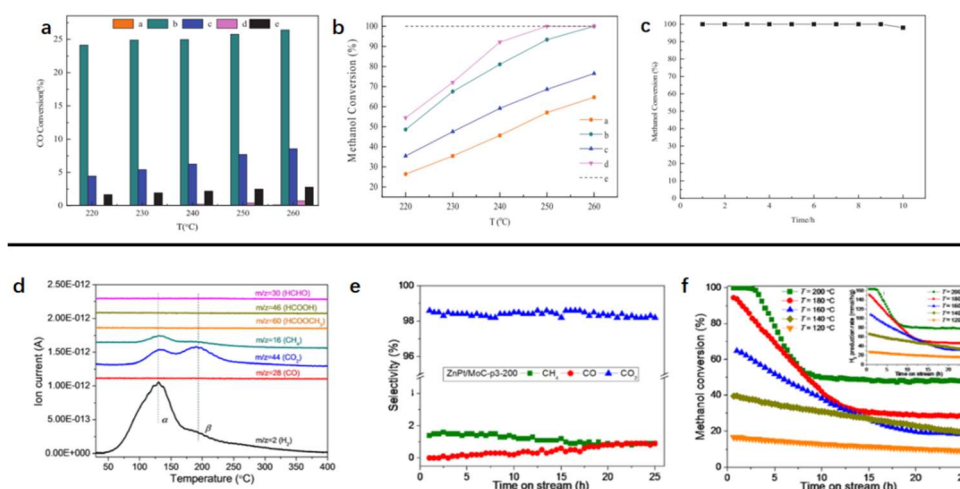
## 2.2 Element Doping

Structural modification of catalyst supports increases porosity and defect density but often weakens mechanical strength, which is critical for methanol steam reforming (MSR) under high temperature and pressure. Thermal cycling, pressure fluctuations, and gas-flow shear can accelerate fatigue and microcrack formation, while high-temperature steam induces hydrothermal corrosion, causing material loss, pore collapse, and phase transformation [43–45]. These effects reduce structural integrity and weaken adhesion between active phases and supports, leading to particle detachment that may clog reactor channels and increase pressure drop. Thus, MSR supports must provide both strong anchoring ability and sufficient mechanical durability.

To balance activity and robustness, chemical composition modification—especially elemental doping—has become effective. Doping can enhance mechanical stability while tuning surface chemistry and electronic structure, inducing lattice distortion, defect formation, and altered acid–base properties to optimize adsorption energies and strengthen metal–support interaction. Conventional doping introduces transition/alkaline-earth or non-metal elements, whereas rare earth doping enhances oxygen vacancies and redox properties. Both improve anchoring and stability under harsh conditions[46].

Zn-based modification has been widely explored due to its favorable MSR behavior, motivating multi-element alloy supports [47]. Yang et al. [48] reported 100% methanol conversion and 98.2% hydrogen yield for Cu on Mg-doped  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/Al, due to improved anchoring and sintering resistance. Qiao et al. [49] showed Zn-doped Al matrices loaded with Cu–Ce achieved optimal Cu dispersion, highest hydrogen yield, and lowest CO content(Figure 3). Overall, elemental doping

improves durability, dispersion control, and MSR performance. Overall, elemental doping improves durability, dispersion control, and MSR performance by regulating both the structural and electronic properties of catalyst supports. Dopants can introduce lattice distortion and defect sites (e.g., vacancies and unsaturated coordination centers), which serve as strong anchoring points to immobilize metal nanoparticles and suppress their migration and sintering under high-temperature steam. Meanwhile, doping can tune surface acidity/basicity and interfacial charge transfer, thereby optimizing adsorption energies of key intermediates such as methoxy, formate, and CO. In addition, multi-element doping may enhance thermal conductivity and corrosion resistance of structured supports, mitigating hydrothermal degradation and maintaining stable metal – support interactions. These synergistic effects collectively increase the density of accessible active sites, reduce deactivation pathways, and enable long-term stable MSR operation.



**Figure 3.** (a) CO molar content in reforming gas at different reaction temperatures [49] and (b) Methanol conversion rate (A: Cu-Ce/Mg-Al; B: Cu-Ce/Ni-Al; C: Cu-Ce/Co-Al; D: Cu-Ce/Zn-Al; E: equil) [49]. (c) Stability of Cu-Ce/Zn-Al catalyst in methanol steam reforming reaction [49]. (d)CH<sub>3</sub>OH–TPSR test of ZnPt/MoC-p3–200 catalyst [47] and (e) Product selectivity test (flow hydrogen reduction treatment temperature 200°C) [47]. (f) Stability test results of the ZnPt/MoC-p3–200 catalyst at different reaction temperatures [47].

In supported catalysts, rare earth elements are often introduced on supports or doped into support lattices, creating interfacial active sites that promote methanol activation, water dissociation, and oxidation/removal of CO-like intermediates [50–52]. Mosayebi et al. [53] doped Ce into Al<sub>2</sub>O<sub>3</sub> to prepare Ni-x/Ce-Al<sub>2</sub>O<sub>3</sub> catalysts (x = Fe, Cu, Zn), enhancing thermal stability and reducing coking while improving conversion and hydrogen yield. Pan et al. [54] incorporated Ce into ZnAl<sub>2</sub>O<sub>4</sub>, where 5 wt% Ce increased TOF by 54.7%, suppressed Cu sintering, strengthened metal–support interaction, and achieved 100.0% methanol conversion with 98.9% hydrogen selectivity. Khani et al. [51] modified TiO<sub>2</sub> with La, Sm, and Ce for Cu/x-TiO<sub>2</sub> photothermal MSR, improving conversion and lowering CO selectivity; Sm minimized catalyst loss and coke formation. Pu et al. [55] doped Sc into Cu/ZnO (Sc<sup>3+</sup> in ZnO lattice), improving Cu dispersion, activity, and thermal stability. Overall, rare earth modification effectively tunes support structure and metal–support interactions for durable MSR catalysts.

### 3. Loaded Nanoactive Components

Supported catalysts utilize the interface coordination between the supported active components and the support to provide the necessary active sites for the reaction process. Currently, the active components of supported catalysts are transitioning from monocomponent to bimetallic and ternary systems. This shift aims to create diverse interfacial interactions and synergistic effects that

collectively enhance catalytic reactions, thereby improving both catalytic activity and catalyst lifespan. Common active components used in supported catalysts are listed in Table 2.

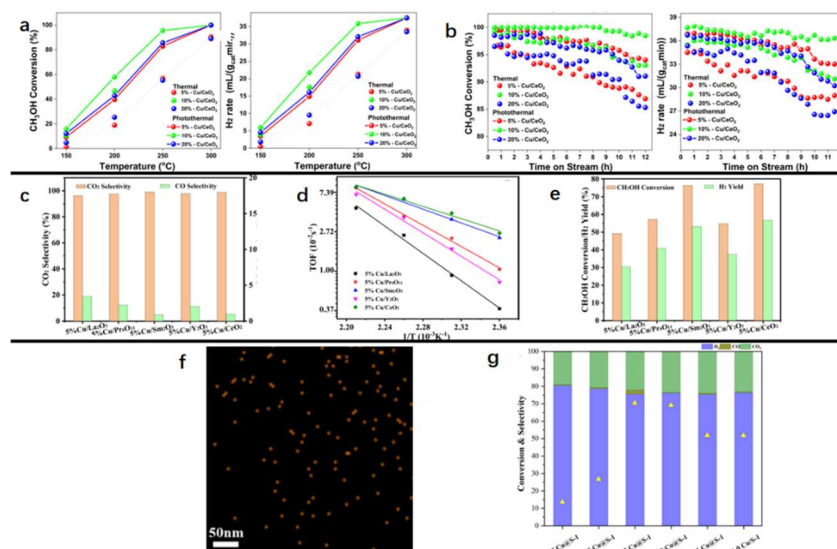
**Table 2.** Common Modification Types for Support Particles in Supported Catalysts

Unary Loading	Binary Loading	Ternary Loading
Cu/Al/Zn	CuX(X=Zn/Pd/Ni/Ce/Zr/Mg/Fe/Au)	CuZnAl
Fe/Co/Ni	PdZn	CuFeCr
Pd/Pt/Ru/Rh/Ag/Au	PtZn	CuFeMg
Ce	NiZn	CuFeAl
Mg	ZnZr	CuCrAl
Gd/Sc/Pr/Sm/La/In/Y	PtNi	CeCuZn

### 3.1 Unitary Metal Nanoparticle-loaded

Single-component supported catalysts are widely used in methanol steam reforming (MSR) due to their simple composition and clear catalytic mechanism. They can be divided into precious-metal catalysts (Pt, Pd) and transition-metal catalysts (Cu, Ni). Precious metals show high activity and stability but are expensive, while transition metals are cost-effective yet often suffer from sintering, redox instability, and poisoning, making stability improvement crucial. Among transition metals, Cu is the most representative active component because it promotes methanol dehydrogenation and intermediate conversion. However, Cu catalysts exhibit poor thermal stability and readily sinter under high-temperature steam and thermal cycling, leading to activity loss [56–59]. Therefore, dispersing Cu nanoparticles on stable supports is widely adopted to stabilize Cu, enhance interfacial sites, and suppress CO formation, especially in photothermal MSR. Khanchi et al. [60] stabilized nano-Cu on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (Si/Al = 0.01), achieving 87.2% H<sub>2</sub> yield at 300 °C. And Liu et al. [61] identified CeO<sub>2</sub> as the optimal rare-earth oxide support at 5% Cu loading. Sanches et al. [62] showed Cu/ZnO and Cu/ZnO/ZrO<sub>2</sub> catalysts were active at 250 °C, benefiting from improved dispersion and intermediate oxidation. Zhao et al. [63] reported 95.5% methanol conversion and 36 mL/(g<sub>cat</sub>·min) H<sub>2</sub> yield for Cu/CeO<sub>2</sub> (10% Cu) at 250 °C. Hong et al. [64] further achieved 72% conversion and 0.2% CO selectivity at 300 °C using Cu confined in MFI zeolite (Figure 4). Overall, rational support selection and dispersion control enable stable Cu-based MSR catalysts with high conversion, high H<sub>2</sub> yield, and low CO selectivity under mild conditions.

In addition to Cu, researchers also favor using transition metal particles primarily composed of Ni as the support to address the tendency of Cu-based catalysts to sinter and deactivate. Mierczynski et al. [65] prepared supported catalysts by loading Ni nanoparticles onto Sn oxide (SnO<sub>2</sub>) and Sn-Al binary oxide (SnO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) supports, yielding Ni/SnO<sub>2</sub> and Ni/SnO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts. The Ni-loaded catalysts achieved high Ni dispersion, exhibiting high hydrogen production rates and methanol conversion rates. At 300°C, the Ni/SnO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst (40% Ni loading) achieved 100% methanol conversion. Jin et al. [66] loaded Ni metal nanoparticles onto a ZrO<sub>2</sub> support, achieving high Ni dispersion. Compared to ZrO<sub>2</sub> catalyst and no catalyst, the Ni/ZrO<sub>2</sub> catalyst exhibited higher methanol conversion, hydrogen yield, and CO<sub>2</sub> selectivity, along with lower CO selectivity, demonstrating excellent catalytic activity and anti-poisoning capability. Ding et al. [67] prepared a NiO/NaF supported catalyst by loading NiO nanoparticles onto a NaF support. This catalyst exhibited high particle dispersion and recyclability. The 6% NiO/NaF catalyst demonstrated high hydrogen production performance and methanol conversion (94%), with hydrogen selectivity reaching 100%. It maintained stable operation at 450°C for 30 hours.



**Figure 4.** (a) Methanol conversion and hydrogen yield of Cu/CeO<sub>2</sub> catalysts at different Cu loadings under thermal and photothermal conditions [63], and (b) Stability testing [63]. (c) CO<sub>2</sub> and CO selectivity testing of 5% Cu/REO catalyst [61], (d) Catalyst TOF value test [61] and (e) Methanol conversion rate and hydrogen yield test [61]. (f) EDX spectrum of Cu element on S-1 support [64]. (g) Methanol conversion rate and H<sub>2</sub>, CO<sub>2</sub>, CO selectivity tests for catalysts with different Cu loadings [64].

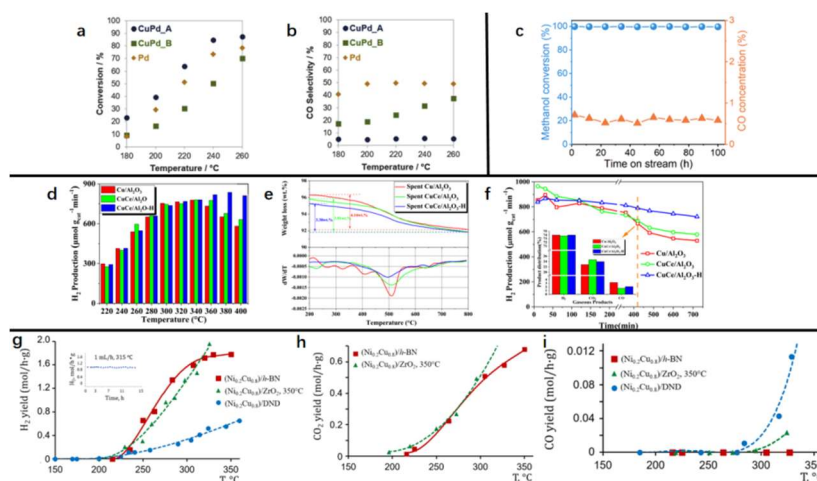
Transition-metal particles such as Cu and Ni often show inadequate stability under harsh methanol steam reforming (MSR) conditions, suffering from weak anchoring ability, agglomeration, limited adsorption capacity, and poor metal–support binding. Therefore, noble metals (Pt, Pd, Ru, Rh) have been increasingly adopted due to their unfilled d-orbitals that enhance reactant adsorption and catalytic activity [68–72]. Chen et al. [73] developed a single-site Ru<sub>1</sub>/CeO<sub>2</sub> catalyst, achieving a hydrogen production rate of 9360 mol H<sub>2</sub>/mol Ru/h and 99.5% CO<sub>2</sub> selectivity. Xie et al. [5] loaded Ru nanoparticles on rod-shaped CeO<sub>2</sub>, improving dispersion and delivering higher H<sub>2</sub> yield with lower CO selectivity. Cai et al. [74] anchored Pd, Pt, Ru, and Rh on MoC, where 0.5Pd/MoC exhibited the best activity and stability compared with other noble metals and industrial CuZnAl. Noble metal/TiO<sub>2</sub> photothermal catalysts are also effective: Bingham et al. [75] reported H<sub>2</sub> rates of Pt > Pd > Au > Ag, with Pt/TiO<sub>2</sub> showing ~100% photocatalytic efficiency, while Abdullah et al. [76] achieved highly dispersed Pd/TiO<sub>2</sub> (0.6 wt%) with excellent hydrogen production.

### 3.2 Bimetallic Nanoparticle Loading

Dual-component loading has been widely adopted to achieve high catalytic activity in methanol steam reforming (MSR) while maintaining strong resistance to poisoning, thermal stability, and high selectivity. Compared with single-metal catalysts, bimetallic systems provide complementary functions and “1+1>2” synergy, improving intrinsic activity, enhancing CO<sub>2</sub>/H<sub>2</sub> selectivity, and extending lifetime under harsh reforming conditions. Since MSR catalysts commonly deactivate through nanoparticle sintering, strong adsorption of CO-like intermediates, and carbon deposition, bimetallic design helps by tuning active-site electronic structure, regulating intermediate adsorption energies, and strengthening interfacial stabilization.

Representative examples include CuPd/ZrO<sub>2</sub>, where Pd improves dispersion, mitigates Cu sintering, and reduces CO accumulation [77]. Ni<sub>0.2</sub>Cu<sub>0.8</sub>/h-BN operates at 220–320 °C with high CO<sub>2</sub> selectivity and no detectable CO, demonstrating stable performance (315 °C, 15 h) [78]. CuCe nanoalloys on porous Al<sub>2</sub>O<sub>3</sub> show enhanced thermal stability and coking resistance through stronger interfacial stabilization [79]. PdZn/Al<sub>2</sub>O<sub>3</sub> prepared by ball milling achieves high conversion, low CO selectivity, and stability over 100 h with only 2% Pd, due to weakened CO adsorption and improved poisoning resistance [80](Figure 5). Overall, rational alloy composition, particle size control, and support

coupling are critical for durable MSR catalysts. Synergy in bimetallic catalysts mainly arises from: (i) ligand effects, where one metal alters the electron density and d-band center of the other, optimizing adsorption strength (especially CO binding); (ii) ensemble effects, where alloying changes surface atomic arrangements to suppress undesired pathways and create favorable active ensembles; (iii) bifunctional mechanisms, in which different metals promote distinct steps such as methanol dehydrogenation and water activation/oxidative intermediate removal; and (iv) interfacial effects, where boundary sites with unique coordination improve activity and anti-sintering stability, enabling efficient low-temperature operation.

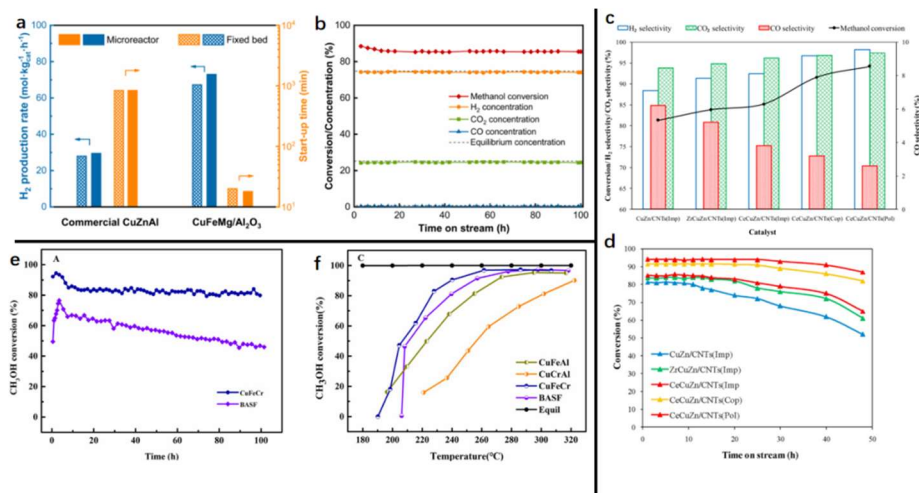


**Figure 5.** (a) Methanol conversion rates of CuPd/ZrO<sub>2</sub> and Pd/ZrO<sub>2</sub> catalysts [77] and (b) CO selectivity tests [77]. (c) Stability test of 2% PdZn/Al<sub>2</sub>O<sub>3</sub> catalyst over 100 hours: methanol conversion rate and CO selectivity [80]. (d) Hydrogen yield tests for CuCe/Al<sub>2</sub>O<sub>3</sub> and Cu/Al<sub>2</sub>O<sub>3</sub> catalysts [79], (e) TG-DTG tests [79], and (f) Stability tests (at 400°C for 720 min) [79]. (g) Temperature dependence of H<sub>2</sub> [78], (h) CO<sub>2</sub> [78], and (i) CO yield in methanol steam reforming on different supports [78] (DND: detonation-synthesized nanodiamond).

### 3.3 Ternary Metal Nanoparticle-Loaded

While research and development of bimetallic particle-supported catalysts progressed, numerous researchers proposed strategies employing ternary metal particle modifications and conducted in-depth studies [81]. Compared with monometallic and bimetallic systems, ternary catalysts provide an extra compositional degree of freedom, enabling a more balanced optimization of catalytic activity, stability, and selectivity. Methanol steam reforming (MSR) involves multiple elementary steps, including methanol adsorption/dehydrogenation, water activation, intermediate conversion, and CO<sub>2</sub>/H<sub>2</sub> desorption. Therefore, single-metal catalysts are often unable to simultaneously accelerate all key steps and suppress deactivation pathways. Although bimetallic systems improve performance through synergy, challenges such as steam-induced sintering, carbon deposition, and incomplete CO control can remain. As a result, ternary catalysts have become an important direction because the third component can act as a structural stabilizer, electronic modulator, or functional promoter, achieving more comprehensive enhancement. Zhang et al. [82] prepared a CuFeMg/Al<sub>2</sub>O<sub>3</sub> supported catalyst by leveraging metal–oxide interactions, establishing an interaction model between ternary metal particles and the oxide support. Al<sub>2</sub>O<sub>3</sub> offers a robust and thermally stable framework, while Fe and Mg introduction modifies the Cu electronic environment and strengthens anchoring to the support, improving dispersion stability under reforming conditions. Compared with commercial CuZnAl catalysts, CuFeMg/Al<sub>2</sub>O<sub>3</sub> exhibited shorter start-up time and enhanced activity, achieving 85% methanol conversion with higher hydrogen yield. It also showed superior TOF and no CO poisoning during operation, indicating effective regulation of intermediate conversion. Notably, the catalyst maintained stable performance for 100 h and displayed excellent coking resistance (Figure 6). Overall, ternary metal particle modification improves MSR performance by introducing an additional

compositional degree of freedom to simultaneously regulate structure and reaction chemistry. The third element can act as a stabilizer that increases diffusion barriers and suppresses nanoparticle migration/sintering, maintaining high dispersion under steam reforming conditions. It can also tune the electronic structure via ligand effects and interfacial charge transfer, optimizing adsorption energies of key intermediates (methoxy, formate, CO) and weakening CO poisoning. Moreover, ternary systems often generate multifunctional interfacial sites that promote methanol dehydrogenation, water activation, and oxidative removal of carbonaceous species, thereby enhancing CO<sub>2</sub> selectivity and long-term durability.



**Figure 6.** (a) Hydrogen yield versus start-up time for CuFeMg/Al<sub>2</sub>O<sub>3</sub> catalyst and commercial CuZnAl catalyst [82]. (b) Operating time curve for CuFeMg/Al<sub>2</sub>O<sub>3</sub> catalyst in a microreactor at 250 °C [82]. (c) H<sub>2</sub> selectivity, CO<sub>2</sub> selectivity, CO selectivity, and methanol conversion tests for each catalyst group [81]. (d) Stability tests for each catalyst group: methanol conversion [81]. (e) Stability test comparison between CuFeCr/Al<sub>2</sub>O<sub>3</sub> catalyst and commercial catalyst (BASF) [57]. (f) Comparison of methanol conversion rates for each catalyst group [57].

#### 4. Summary and Outlook

This paper briefly analyzes common issues associated with supported catalysts used in methanol steam reforming reactions, providing detailed discussions on two key aspects: support modification and active site modification. While research and development of supported catalysts for methanol steam reforming are increasingly mature, there remains room for advancement:

- (1) The support in supported catalysts not only serves to load active particles but also significantly impacts catalyst lifespan and catalytic activity. However, research on supported catalysts for methanol steam reforming has primarily focused on the catalytic activity, product selectivity, and anti-poisoning capabilities of the loaded nanoparticles. Developing supports with high nanoparticle anchoring capability, good mechanical strength, and strong interactions with loaded particles to fully leverage the synergistic effect between metal particles and supports in catalytic reactions remains a challenge to overcome.
- (2) The modification of loaded particles in supported catalysts is shifting toward diversification and complexity. As the number of components in the loaded nanoparticles increases, the interfacial interactions between metal particles and the support also change, thereby increasing the complexity of material design and theoretical calculations. Clarifying the specific roles and mechanisms of each component in the multimetallic particles for catalytic reactions, the synergistic effects among components, and the interfacial effects between multimetallic particles and the support will provide a solid theoretical foundation for future research and development in the synthesis and preparation of supported catalysts.

(3) Modification strategies for supported catalysts should not be limited to a single approach. Instead, multiple modification methods should be rationally employed to enhance both the support and the loaded particles. For instance, suitable elements can be used to dope carriers with appropriate shapes and structures to support nanoparticles with optimal chemical compositions. However, it is crucial to recognize the potential negative impacts of various modification methods on supported catalysts. For example, selecting a specific element for carrier doping or choosing nanoparticles with incorrect chemical compositions may paradoxically increase the catalyst's selectivity toward CO while diminishing its resistance to poisoning and overall catalytic activity.

## Acknowledgments

Natural Science Foundation.

## References

- [1] Y. Chang, G. Li, S. Ma, X. Zhao, N. Li, X. Zhou, Y. Zhang, Effect of hierarchical pore structure of oxygen carrier on the performance of biomass chemical looping hydrogen generation, *Energy*. 254(2022) 124301.
- [2] F. Zhang, L. Zhu, Y. Wang, L. Sun, Exergy analysis on the process for three reactors chemical looping hydrogen generation, *International Journal of Hydrogen Energy*. 45(46)(2020) 24322-24332.
- [3] Y. Deng, S. Li, L. Appels, R. Dewil, H. Zhang, J. Baeyens, H. Mikulcic, Producing hydrogen by catalytic steam reforming of methanol using non-noble metal catalysts, *Journal of environmental management*. 321(2022) 116019.
- [4] X. Jia, H. Zhang, B. Ren, J. Xie, P. Ge, B. Zhang, Fe–Ni–Ce–Zr-modified CuO–ZnO catalyst for methanol steam reforming, *Journal of the Energy Institute*. 110(2023) 101316.
- [5] L. Xie, B. Hu, R. Shu, Z. Tian, Y. Chen, C. Wang, Effect of oxygen vacancy influenced by CeO<sub>2</sub> morphology on the methanol catalytic reforming for hydrogen production, *International Journal of Hydrogen Energy*. 48(85)(2023) 33119-33129.
- [6] M. Morales, M. Laguna-Bercero, E. Jiménez-Piqué, Hydrogen-Rich Gas Production by Steam Reforming and Oxidative Steam Reforming of Methanol over La(0.6)Sr(0.4)CoO(3- $\delta$ ): Effects of Preparation, Operation Conditions, and Redox Cycles, *ACS applied energy materials*. 6(15)(2023) 7887-7898.
- [7] G.R. Peddiahgari Vasu, K.R. Motakatla Venkata, R.R. Kakarla, K.V.S. Ranganath, T.M. Aminabhavi, Recent advances in sustainable N-heterocyclic carbene-Pd(II)-pyridine (PEPPSI) catalysts: A review, *Environmental research*. 225(2023) 115515.
- [8] X. Xu, Y. Zhang, Y. Chen, C. Liu, W. Wang, J. Wang, H. Huang, J. Feng, Z. Li, Z. Zou, Revealing \*OOH key intermediates and regulating H<sub>2</sub>O<sub>2</sub> photoactivation by surface relaxation of Fenton-like catalysts, *Proceedings of the National Academy of Sciences of the United States of America*. 119(36)(2022) e2205562119.
- [9] D. Dedić, A. Dorniak, U. Rinner, W. Schöfberger, Recent Progress in (Photo-)Electrochemical Conversion of CO<sub>2</sub> With Metal Porphyrinoid-Systems, *Frontiers in chemistry*. 9(2021) 685619.
- [10] G. Hu, J. Wang, D. Liu, X. Zhang, B. Yu, T. Huang, M. Zhu, H. Yu, A Joule-heated carbon nanofiber aerogel-supported catalyst for hydrogen production via methanol steam reforming, *Carbon*. 214(2023) 118311.
- [11] R. Wang, X. Yang, Y. Wang, J. Jia, H. Wu, Mechanism of methanol steam reforming on dual-atom catalysts of PtZn/TiO<sub>2</sub> and PdZn/TiO<sub>2</sub>: Density functional theory studies, *Materials Today Communications*. 35(2023) 106125.
- [12] H. Zhou, X. Sun, W. Guo, T. Bao, Y. Zhang, C. Guo, H. Xiao, H. Qin, P. Gao, Preparation of a Durable CuO/ZnO/CeO<sub>2</sub>/ZrO<sub>2</sub> Catalyst on an SiC Support by an Inverse Microemulsion/Precipitation Method for Methanol Steam Reforming, *ChemistrySelect*. 8(28)(2023) e202301088.
- [13] J. Yu, Z. Jiang, T. Huang, C. Tang, BN/Cu/CNT nanoparticles as an efficient tri-functional electrocatalyst for ORR and OER, *International Journal of Hydrogen Energy*. 48(53)(2023) 20368-20377.
- [14] F. Bossola, T. Roongcharoen, M. Coduri, C. Evangelisti, F. Somodi, L. Sementa, A. Fortunelli, V. Dal Santo, Discovering indium as hydrogen production booster for a Cu/SiO<sub>2</sub> catalyst in steam reforming of methanol, *Applied Catalysis B: Environmental*. 297(2021) 120398.

- [15] O.O. Fasanya, A.Y. Atta, M.T.Z. Myint, J. Dutta, B.Y. Jibril, Effects of synthesis methods on performance of CuZn/MCM-41 catalysts in methanol steam reforming, *International Journal of Hydrogen Energy*. 46(5)(2021) 3539-3553.
- [16] K. Nomoto, H. Miura, T. Shishido, Inhibitory effect of trace impurities on methanol reforming by Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst: Steam reforming and autothermal reforming of model bio-methanol, *Applied Catalysis B: Environmental*. 325(2023) 122374.
- [17] Y. Wang, H. Liu, D. Mei, S. Yu, Direct ink writing of 3D SiC scaffold as catalyst support for thermally autonomous methanol steam reforming microreactor, *Renewable Energy*. 187(2022) 923-932.
- [18] C. Guo, H. Xiao, W. Guo, T. Bao, J. Xie, H. Qin, P. Gao, Direct synthesis of CuO–ZnO–CeO<sub>2</sub> catalyst on Al<sub>2</sub>O<sub>3</sub>/cordierite monolith for methanol steam reforming, *Ceramics International*. 49(5)(2023) 8212-8222.
- [19] Z. Zhai, J. Chu, L. Sun, X. Zhao, D. Huang, X. Yang, C. Zhuang, C. Min, Y. Wang, Ultrahigh Metal Content Carbon-Based Catalyst for Efficient Hydrogenation of Furfural: The Regulatory Effect of Glycerol, *ACS applied materials & interfaces*. 14(39)(2022) 44439-44449.
- [20] G. Zhang, J. Zhao, T. Yang, Q. Zhang, L. Zhang, In-situ self-assembled Cu<sub>2</sub>O/ZnO core-shell catalysts synergistically enhance the durability of methanol steam reforming, *Applied Catalysis A: General*. 616(2021) 118072.
- [21] K. Ploner, P. Delir Kheyrollahi Nezhad, M. Watschinger, L. Schlicker, M.F. Bekheet, A. Gurlo, A. Gili, A. Doran, S. Schwarz, M. Stöger-Pollach Steering the methanol steam reforming performance of Cu/ZrO<sub>2</sub> catalysts by modification of the Cu-ZrO<sub>2</sub> interface dimensions resulting from Cu loading variation, *Applied Catalysis A: General*. 623(2021) 118279.
- [22] P. Yan, P. Tian, C. Cai, S. Zhou, X. Yu, S. Zhao, S.-T. Tu, C. Deng, Y. Sun, Antioxidative and stable PdZn/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst coatings concerning methanol steam reforming for fuel cell-powered vehicles, *Applied Energy*. 268(2020) 115043.
- [23] Q. Shen, Z. Cai, X. Zhang, G. Chen, G. Yang, S. Li, Novel spinel oxide catalysts CuFe<sub>x</sub>Al<sub>2-x</sub>O<sub>4</sub> with high H<sub>2</sub> selectivity with low CO generation in methanol steam reforming, *Journal of Alloys and Compounds*. 951(2023) 169878.
- [24] Z. Sun, S. Yu, S. Toan, R. Abiev, M. Fan, Z. Sun, Enabling Low-Temperature Methanol Activation via Lattice Oxygen Induced Cu–O–Cr Catalysis, *ACS Catalysis*. 13(20)(2023) 13704-13716.
- [25] A.M. Seyedi, M. Haghighi, A. Sokhansanj, Coprecipitation dispersion of Cu-Zn-Zr mixed oxides nanocatalyst over Si and Al-Based supports applied in selective and stable hydrogen production from Methanol: Experimental study and rate of reaction engineering via intelligent optimization of CFD method, *Energy Conversion and Management*. 295(2023) 117613.
- [26] A.H. Mohammed Abbas, K.K. Cheralathan, E. Porpatham, S.K. Arumugam, Hydrogen generation using methanol steam reforming – catalysts, reactors, and thermo-chemical recuperation, *Renewable and Sustainable Energy Reviews*. 191(2024) 114147.
- [27] L. Li, J. Chen, C. Zeng, Q. Liu, H. Hu, Q. Huang, X. Chen, Preparation of CuZnZrAl catalysts by coprecipitation-ammonia method for methanol steam reforming and the effect of promoters Y and Ce, *Molecular Catalysis*. 537(2023) 112887.
- [28] L. Wang, Q. Li, X. Liu, C. Li, Z. Zhao, S. Diao, D. Cao, D. Xiang, C. Wu, K. Liu, Improved CO-PROX selectivity of CuO/CeO<sub>2</sub> catalysts by decorating with lanthanum via surface Cu<sup>2+</sup> redox site, *Applied Surface Science*. (2023) 159087.
- [29] Q. Shen, Z. Cai, G. Chen, X. Zhang, S. Li, G. Yang, Optimization of the sol gel synthesis process parameters by orthogonal experiment of novel spinel oxide catalyst CuFe<sub>1.2</sub>Al<sub>0.8</sub>O<sub>4</sub> with improved performance for methanol steam reforming, *Journal of Sol-Gel Science and Technology*. 107(2)(2023) 490-502.
- [30] J. Wang, Y. Zhang, S. Peng, S. Yu, J. Ran, K.J. Chua, M. Li, S. Yunlin, S. Liu, Thermal analysis of a micro tubular reactor for methanol steam reforming by optimizing the multilayer arrangement of catalyst bed for the catalytic combustion of methanol, *International Journal of Hydrogen Energy*. 48(73)(2023) 28315-28332.
- [31] W. Peng, Z. Kuai, J. Peng, W. Guo, H. Li, C. Peng, S. Chen, MXene-based gold nanoparticle catalyst with high activity and stability for 4-nitrophenol reduction, *Journal of Solid State Chemistry*. 325(2023) 124166.

- [32] Q. Xu, T. Sun, P. Zhang, Z. Gao, T. Zheng, L. Xu, Different loading of Ni<sub>2</sub>P nanoparticles supported on Co-N-doped ordered macro-/mesoporous carbon for hydrogen evolution reaction, *Journal of Solid State Chemistry*. 309(2022) 122941.
- [33] E. Koohsaryan, M. Anbia, K.T. Heydar, Mo-modified hierarchical FAU zeolite: A catalyst-adsorbent for oxidative desulfurization of fuel oil, *Journal of Solid State Chemistry*. 312(2022) 123218.
- [34] J. Ding, C. Xu, G. Fan, T. Naren, Y. Wang, Y. Liu, X. Gu, L. Wu, S. Zeng, Engineering CeO<sub>2</sub> configurations to regulate the CuO dispersion and switch pathways of preferential CO oxidation, *Applied Catalysis B: Environmental*. 331(2023) 122686.
- [35] A.h. Abaidi, B. Madani, Intensification of hydrogen production from methanol steam reforming by catalyst segmentation and metallic foam insert, *International Journal of Hydrogen Energy*. 46(75)(2021) 37583-37598.
- [36] Y. Liu, W. Zhou, Y. Lin, L. Chen, X. Chu, T. Zheng, S. Wan, J. Lin, Novel copper foam with ordered hole arrays as catalyst support for methanol steam reforming microreactor, *Applied Energy*. 246(2019) 24-37.
- [37] C. Ha, Z. Wang, C. Wang, J. Qin, Z. Zhou, S. Wang, Z. Liu, B. Li, High-performance catalyst of methanol steam reformer based on Cu foam with nanofiber architectures, *International Journal of Hydrogen Energy*. (2022)
- [38] T. Zheng, W. Zhou, Y. Yang, Y. Zhong, H. You, X. Li, X. Chu, K.S. Hui, W. Ding, Novel Nickel Foam with Multiple Microchannels as Combustion Reaction Support for the Self-Heating Methanol Steam Reforming Microreactor, *Energy & Fuels*. 35(3)(2020) 2815-2825.
- [39] M. Chen, G. Sun, Y. Wang, D. Liang, C. Li, J. Wang, Q. Liu, Steam reforming of methanol for hydrogen production over attapulgite-based zeolite-supported Cu-Zr catalyst, *Fuel*. 314(2022) 122733.
- [40] D.H. Kim, J.H. Kim, Y.S. Jang, J.C. Kim, Hydrogen production by oxidative steam reforming of methanol over anodic aluminum oxide-supported Cu-Zn catalyst, *International Journal of Hydrogen Energy*. 44(20)(2019) 9873-9882.
- [41] Q. Wang, G. Zhang, J. Zhao, L. Zhang, Q. Zhang, Robust Mesh-type structured CuFeMg/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/Al catalyst for methanol steam reforming in microreactors, *International Journal of Hydrogen Energy*. 47(60)(2022) 25256-25265.
- [42] J.H. Kim, Y.S. Jang, J.C. Kim, D.H. Kim, Anodic aluminum oxide supported Cu-Zn catalyst for oxidative steam reforming of methanol, *Korean Journal of Chemical Engineering*. 36(3)(2019) 368-376.
- [43] Y. Hu, C. Han, W. Li, Q. Hu, H. Wu, Z. Luo, Experimental evaluation of methanol steam reforming reactor heated by catalyst combustion for kW-class SOFC, *International Journal of Hydrogen Energy*. 48(12)(2023) 4649-4664.
- [44] H.-Y. Lian, X.-S. Li, J.-L. Liu, A.-M. Zhu, Methanol steam reforming by heat-insulated warm plasma catalysis for efficient hydrogen production, *Catalysis Today*. 337(2019) 76-82.
- [45] W.-W. Yang, X. Ma, X.-Y. Tang, P.-Y. Dou, Y.-J. Yang, Y.-L. He, Review on developments of catalytic system for methanol steam reforming from the perspective of energy-mass conversion, *Fuel*. 345(2023) 128234.
- [46] S. Bepari, M. Khan, X. Li, N. Mohammad, D. Kuila, Effect of Ce and Zn on Cu-Based Mesoporous Carbon Catalyst for Methanol Steam Reforming, *Topics in Catalysis*. 66(5-8)(2023) 375-392.
- [47] F. Cai, J.J. Ibrahim, Y. Fu, W. Kong, S. Li, J. Zhang, Y. Sun, Methanol Steam Reforming over ZnPt/MoC Catalysts: Effects of Hydrogen Treatment, *Industrial & Engineering Chemistry Research*. 59(42)(2020) 18756-18770.
- [48] T. Yang, G. Zhang, Q. Zhang, B. Liu, L. Zhang, Magnesium Modified Mesh-TYPE Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/Al Catalysts: Low Acid Density Catalysts for Methanol Steam Reforming, *Catalysis Letters*. 150(10)(2020) 2978-2990.
- [49] W. Qiao, S. Yang, L. Zhang, Y. Tian, H. Wang, C. Zhang, Z. Gao, Performance of Cu-Ce/M-Al (M = Mg, Ni, Co, Zn) hydrotalcite derived catalysts for hydrogen production from methanol steam reforming, *International Journal of Energy Research*. 45(9)(2021) 12773-12783.
- [50] X. Chen, Z. Feng, D. Zhao, Q. Yang, C. Li, Efficient methanol steam reforming over ZnCeZrO<sub>x</sub>: the unique role of cerium, *Catalysis Science & Technology*. 12(23)(2022) 7048-7056.

- [51] Y. Khani, P. Tahay, F. Bahadoran, N. Safari, S. Soltanali, A. Alavi, Synergic effect of heat and light on the catalytic reforming of methanol over Cu/x-TiO<sub>2</sub>(x=La, Zn, Sm, Ce) nanocatalysts, *Applied Catalysis A: General*. 594(2020) 117456.
- [52] X. Liu, J. Ma, C. Lu, J. Xu, X. Xu, X. Fang, X. Wang, Probing crystalline phase effect of rare earth metal oxides (REO) on Cu/REO (RE=Gd, Eu, Sm) catalysts for methanol steam reforming (MSR) to produce H<sub>2</sub>, *Journal of Rare Earths*. 41(6)(2023) 820-829.
- [53] A. Mosayebi, M.H. Eghbal Ahmadi, M. Hamidzirezefi, Combined steam and dry reforming of methanol over Ni-M/Ce-Al<sub>2</sub>O<sub>3</sub> (M=Fe, Cu, and Zn) catalysts to syngas formation, *International Journal of Hydrogen Energy*. 48(85)(2023) 33098-33110.
- [54] J. Pan, J. Zheng, H. Kang, X. Gao, W. Chu, Promoting Effect of Ce Doping on the CuZn/ZnAl<sub>2</sub>O<sub>4</sub> Catalysts for Methanol Decomposition to Hydrogen and Carbon Monoxide, *Catalysis Letters*. 152(4)(2021) 1109-1118.
- [55] Y.-C. Pu, S.-R. Li, S. Yan, X. Huang, D. Wang, Y.-Y. Ye, Y.-Q. Liu, An improved Cu/ZnO catalyst promoted by Sc<sub>2</sub>O<sub>3</sub> for hydrogen production from methanol reforming, *Fuel*. 241(2019) 607-615.
- [56] F. Bai, T. Zhang, W. Qiao, L. Zhang, H. Ma, H. Sun, H. Guo, S. Ma, T. Ren, Z. He, A composite having a porous substrate and polyhedral Cu-Fe oxide nanoparticles showing high catalytic activity during the steam reforming of methanol at low temperatures, *Journal of Alloys and Compounds*. 885(2021) 106854.
- [57] P. Li, S. Wang, S. Wang, Unravelling the synergistic promotion effect of simultaneous doping Fe and Cr into Cu-based spinel oxide on methanol steam reforming, *International Journal of Hydrogen Energy*. 48(49)(2023) 18731-18743.
- [58] C. Mateos-Pedrero, C. Azenha, P.T. D.A, J.M. Sousa, A. Mendes, The influence of the support composition on the physicochemical and catalytic properties of Cu catalysts supported on Zirconia-Alumina for methanol steam reforming, *Applied Catalysis B: Environmental*. 277(2020) 119243.
- [59] Y.-X. Wang, H.-L. Zhang, P. An, H.-S. Wu, J.-F. Jia, Effect of Potassium on Methanol Steam Reforming on the Cu(111) and Cu(110) Surfaces: A DFT Study, *The Journal of Physical Chemistry C*. 125(38)(2021) 20905-20918.
- [60] M. Khanchi, S.M.A. Mousavian, S. Soltanali, Methanol steam reforming over Cu supported on SiO<sub>2</sub>, amorphous SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub> catalysts: Influence of support nature, *International Journal of Energy Research*. 46(3)(2021) 3057-3071.
- [61] X. Liu, J. Ma, L. Mao, J. Xu, X. Xu, X. Fang, X. Wang, Cu/REO (RE = La, Pr, Sm, Y, Ce) catalysts for methanol steam reforming: Understanding the interaction between Cu and individual REO supports, *Fuel*. 357(2024) 130080.
- [62] S.G. Sanches, J.H. Flores, M.I.P. da Silva, Cu/ZnO and Cu/ZnO/ZrO<sub>2</sub> catalysts used for methanol steam reforming, *Molecular Catalysis*. 454(2018) 55-62.
- [63] L. Zhao, M. Tang, F. Wang, X. Qiu, Efficient Cu/CeO<sub>2</sub> composites for hydrogen production from photothermal methanol steam reforming: The utility of synergism of photo and thermal catalysis, *Fuel*. 331(2023) 125748.
- [64] Y. Hong, Y. Zheng, N. Yan, X. Liu, P. Guo and Z. Liu, Cu nanoparticles confined in siliceous MFI zeolite for methanol steam reforming, *Catalysis Science & Technology*. 13(20)(2023) 6068-6074.
- [65] P. Mierczynski, A. Mierczynska, R. Ciesielski, W. Maniukiewicz, J. Rogowski, T.P. Maniecki, S. Dubkov, A. Sysa, D. Gromov, M.I. Szyrkowska Modern Ni and Pd-Ni Catalysts Supported on Sn-Al Binary Oxide for Oxy-Steam Reforming of Methanol, *Energy Technology*. 6(9)(2018) 1687-1699.
- [66] Q. Jin, S. Chen, X. Meng, R. Zhou, M. Xu, M. Yang, H. Xu, X. Fan, H. Chen, Methanol steam reforming for hydrogen production over Ni/ZrO<sub>2</sub> catalyst: Comparison of thermal and non-thermal plasma catalysis, *Catalysis Today*. 425(2024) 114360.
- [67] Y. Ding, T. Zhang, Z. Ge, P. Li, Y. Shen, High-efficiency steam reforming of methanol on the surface of a recyclable NiO/NaF catalyst for hydrogen production, *Composites Part B: Engineering*. 243(2022) 110113.
- [68] G. Modragón-Galicia, M. Toledo Toledo, F. Morales-Anzures, P. Salinas-Hernández, A. Gutiérrez-Martínez, M.E.F. García, F. Tzompantzi, A. Barrera, J. Reyna-Alvarado, O.A. López-Galán Catalytic Aspects of Pt/Pd Supported on ZnO Rods for Hydrogen Production in Methanol Steam Reforming, *Topics in Catalysis*. 65(13-16)(2022) 1556-1569.

- [69] R. Pérez-Hernández, Reactivity of Pt/Ni supported on CeO<sub>2</sub>-nanorods on methanol steam reforming for H<sub>2</sub> production: Steady state and DRIFTS studies, *International Journal of Hydrogen Energy*. 46(51)(2021) 25954-25964.
- [70] L. Thoni, N. Metzkwow, A. Eychmüller, Influence of drying technique on Pt/In<sub>2</sub>O<sub>3</sub> aerogels for methanol steam reforming, *Journal of Sol-Gel Science and Technology*. 107(2)(2022) 218-226.
- [71] H. Wang, L. Wang, D. Lin, X. Feng, X. Chu, L. Li, F.-S. Xiao, Titanosilicate zeolite supported Pt nanoparticles with electronic metal-support interactions for efficient methanol steam reforming, *Catalysis Today*. 382(2021) 42-47.
- [72] G.J. Kim, M.S. Kim, J.-Y. Byun, S.C. Hong, Effects of Ru addition to Pd/Al<sub>2</sub>O<sub>3</sub> catalysts on methanol steam reforming reaction: A mechanistic study, *Applied Catalysis A: General*. 572(2019) 115-123.
- [73] L. Chen, Z. Qi, X. Peng, J.L. Chen, C.W. Pao, X. Zhang, C. Dun, M. Young, D. Prendergast, J.J. Urban Insights into the Mechanism of Methanol Steam Reforming Tandem Reaction over CeO(2) Supported Single-Site Catalysts, *J Am Chem Soc*. 143(31)(2021) 12074-12081.
- [74] F. Cai, Y. Guo, J.J. Ibrahim, J. Zhang, Y. Sun, A highly active and stable Pd/MoC catalyst for hydrogen production from methanol decomposition, *Applied Catalysis B: Environmental*. 299(2021)
- [75] M. Bingham, A. Mills, Photonic efficiency and selectivity study of M (M=Pt, Pd, Au and Ag)/TiO<sub>2</sub> photocatalysts for methanol reforming in the gas phase, *Journal of Photochemistry and Photobiology A: Chemistry*. 389(2020) 112257.
- [76] N. Abdullah, H. Bahruji, S.M. Rogers, P.P. Wells, C.R.A. Catlow and M. Bowker, Pd local structure and size correlations to the activity of Pd/TiO<sub>2</sub> for photocatalytic reforming of methanol, *Physical Chemistry Chemical Physics*. 21(29)(2019) 16154-16160.
- [77] C. Azenha, T. Lagarteira, C. Mateos-Pedrero and A. Mendes, Production of hydrogen from methanol steam reforming using CuPd/ZrO<sub>2</sub> catalysts – Influence of the catalytic surface on methanol conversion and CO selectivity, *International Journal of Hydrogen Energy*. 46(33)(2021) 17490-17499.
- [78] A.M. Kovalskii, A.T. Matveev, Z.I. Popov, I.N. Volkov, E.V. Sukhanova, A.A. Lytkina, A.B. Yaroslavtsev, A.S. Konopatsky, D.V. Leybo, A.V. Bondarev, (Ni,Cu)/hexagonal BN nanohybrids – New efficient catalysts for methanol steam reforming and carbon monoxide oxidation, *Chemical Engineering Journal*. 395(2020) 125109.
- [79] C. Wang, J. Weng, M. Liao, Q. Luo, X. Luo, Z. Tian, R. Shu, Y. Chen, Y. Du, Configuration of coupling methanol steam reforming over Cu-based catalyst in a synthetic palladium membrane for one-step high purity hydrogen production, *Journal of the Energy Institute*. 108(2023) 101245.
- [80] X. Yao, S. Yuan, C. Li, L. Wang, X. Yu, P. Tian, S.-t. Tu, ZnO-supported palladium catalysts via ball milling as an effective heterogeneous catalyst for methanol steam reforming, *Fuel*. 358(2024) 130133.
- [81] H. Shahsavar, M. Taghizadeh, A.D. Kiadchi, Effects of catalyst preparation route and promoters (Ce and Zr) on catalytic activity of CuZn/CNTs catalysts for hydrogen production from methanol steam reforming, *International Journal of Hydrogen Energy*. 46(13)(2021) 8906-8921.
- [82] G. Zhang, J. Zhao, Q. Wang, T. Yang, Q. Zhang, L. Zhang, Fast start-up structured CuFeMg/Al<sub>2</sub>O<sub>3</sub> catalyst applied in microreactor for efficient hydrogen production in methanol steam reforming, *Chemical Engineering Journal*. 426(2021) 130644.