

A Review on the Performance of Bimetallic Catalysts for Methanol Synthesis via CO₂ Hydrogenation

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Abstract. The greenhouse effect and global warming caused by excessive CO₂ emissions are becoming increasingly serious. To realize the recycling of carbon resources and the sustainable development of energy, CO₂ can be converted into high value-added methanol through catalytic hydrogenation. In view of the problems of low activity, poor selectivity and insufficient stability of traditional monometallic catalysts in the process of methanol synthesis via CO₂ hydrogenation, this paper systematically reviews the research progress of high-efficiency bimetallic catalysts. From three dimensions of electronic effect, synergistic catalysis and interface effect, this paper deeply analyzes the internal mechanism of bimetallic catalysts in improving performance by optimizing the electronic structure of active sites and constructing multifunctional sites. The mainstream preparation methods, catalytic performance and characterization techniques of three major systems including Cu-based, Ni-based and Pd-based catalysts are mainly discussed. Cross-system comparison shows that the long-term stability of catalysts mainly depends on the electronic anchoring effect between components and the ability to form sintering-resistant alloy phases. Finally, aiming at the challenges such as unclear reaction mechanism and weak carbon deposition resistance, the design direction of high-efficiency bimetallic catalytic systems in the future is proposed, which provides a theoretical reference for improving reaction activity and stability, and finally realizing the recycling of carbon resources and industrial application.

Keywords: CO₂ hydrogenation, Methanol, Bimetallic catalysts, Synergistic effect

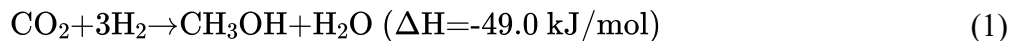
1. Research background

With the acceleration of global industrialization, CO₂ emissions continue to increase, which leads to the intensification of the greenhouse effect and increasingly serious climate change problems. According to the statistics of the International Energy Agency (IEA), global CO₂ emissions exceeded 37 billion tons in 2023, among which industry, transportation and energy production are the main emission sources [1]. Reducing CO₂ emissions and realizing its resource utilization has become an important goal of sustainable development strategies in various countries.

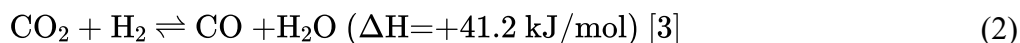
Among many emission reduction and conversion pathways, converting CO₂ into high value-added chemicals or fuels is regarded as one of the key technologies to realize "carbon cycling". Methanol (CH₃OH) is not only an important chemical raw material, but also a clean liquid fuel carrier with high energy density [2]. Methanol synthesis via CO₂ hydrogenation can convert

greenhouse gases into usable energy, which has both environmental and energy benefits and has attracted extensive attention.

The main reaction of methanol synthesis via CO₂ hydrogenation can be expressed as:



Side reaction:



This reaction is exothermic and reversible with volume reduction. Low temperature and high pressure are conducive to the formation of methanol, but also limit the conversion of CO₂ to a certain extent. At the same time, the occurrence of side reactions will also affect the selectivity of methanol. There are multiple reaction pathways for this reaction. Researchers have found through density functional theory (DFT) studies that the formate pathway is one of the main reaction pathways for Cu-based, In-based and other catalysts. In this pathway, CO₂ is first adsorbed and activated at metal sites, and then combines with dissociated H to form formate intermediates, which are gradually hydrogenated to form CH₂O, CH₃O and CH₃OH [4, 5]. In the carboxylate pathway, CO₂ first reacts with H to form COOH, and then reacts to form a series of intermediates such as COHOH, COH and HCOH, and finally is hydrogenated to methanol. The reverse water-gas shift pathway starts with the direct dissociation of CO₂ to form CO and O, and the generated CO is then continuously hydrogenated to form intermediates such as HCO, H₂CO and H₃CO, and finally methanol is generated.

Monometallic catalysts are widely used in CO₂ hydrogenation systems, but often show varying degrees of limitations due to their own properties. The most common catalytic systems in CO₂ hydrogenation reactions are Cu-based, Co-based, In-based catalysts, etc. Cu-based catalysts have high activity and selectivity, but their hydrogenation activity is weak at low temperatures and the catalysts are prone to deactivation at high temperatures, thus giving rise to the idea of introducing hydrogen-philic metals to construct bimetallic catalysts [6]. Co-based catalysts also have high activity, but C-O bonds are easily broken, resulting in low methanol selectivity and easy methane production, so oxygen-philic metals need to be introduced to stabilize C-O bonds [7]. In₂O₃-based catalysts have high methanol selectivity, and the surface lattice oxygen of In₂O₃ can effectively activate CO₂ and H₂. However, they have low CO₂ conversion rate, poor structural stability, and are prone to excessive reduction and deactivation, so a second metal needs to be introduced to stabilize the oxygen vacancy structure [8]. Pd-based catalysts have excellent methanol selectivity in specific alloy structures, but single Pd sites tend to trigger reverse water-gas shift to produce CO, so a second metal needs to be introduced to isolate Pd active sites and block side reaction pathways [9]. Although Ni-based catalysts have efficient hydrogen activation ability, they are prone to excessive hydrogenation to produce methane and are extremely dependent on the interaction with supports, so oxygen-philic components need to be introduced to inhibit methanation [10].

To overcome the mutual restriction of "activity-selectivity-stability" faced by traditional monometallic catalysts, the construction of bimetallic catalytic systems has become a mainstream means to break through the bottleneck. Bimetallic catalysts improve catalyst activity, reaction stability and selectivity through synergistic effects. Jian-Feng Wu et al. summarized bimetallic catalysts such as Mn-Co and Ni-In, showing that bimetallic catalysts can break only one C=O bond at a suitable temperature to directionally produce methanol. Through deep coupling between components, bimetallic catalysts [11] can not only adjust the geometric structure, but also optimize

the electronic structure, form synergistic active sites, and improve the performance of catalysts in reactions.

2. Mechanism of bimetallic catalysts

Methanol synthesis via CO₂ hydrogenation is an exothermic reaction with a decrease in the number of gas molecules, and low temperature and high pressure are favorable for the forward reaction. An ideal bimetallic catalyst must achieve efficient and selective activation of CO₂ molecules at an appropriate temperature, that is, precisely break one C=O bond and hydrogenate it, while effectively inhibiting excessive hydrogenation or complete cleavage of C-O bonds [7].

The electronic effect is a key feature that sets bimetallic catalysts apart from monometallic catalysts in catalytic reactions. Two metal atoms form a new energy band structure through orbital overlap and hybridization. This change alters the electronic structure of active sites and regulates reaction activation energy and pathway selection [12]. Adding a second metal to the catalyst can change the d-band center of the main catalytic metal. An upward shift of the d-band usually strengthens the interaction between metals and adsorbed substances, while a downward shift leads to the opposite result [13]. In Pt-Ru catalysts, Pt and Ru atoms form strong coupling through d-orbitals. This coupling weakens the adsorption of intermediates like COOH and H, promotes product desorption and improves CO₂ reduction efficiency [14]. Electron transfer between bimetals is a direct sign of the electronic effect. Electrons flow from metals with lower electronegativity to metals with higher electronegativity along the electronegativity gradient. Charges redistribute at interfaces or active sites, and this process affects the overall catalytic performance. In research on Ni-Co catalysts, electrons move from Co atoms to adjacent Ni atoms, creating a charge density gradient at the Ni-Co interface. So, Ni-rich regions are more suitable for stable adsorption of intermediates, while electron-deficient Co interfaces help with substrate polarization and intermediate desorption [15]. In research on Pt-Sn/ γ -Al₂O₃ catalysts, both the addition of Sn and the formation of Pt₃Sn alloy change the electronic structure of Pt. After the electronic structure is adjusted, its d-band center shifts upward accordingly and increases the adsorption energy [16].

Through the coupling between active sites, bimetallic catalyst components show different types of synergistic working modes in reactions. These modes include bifunctional synergy, geometric synergy, electronic hybridization synergy, and spatial decoupling synergy. Bifunctional synergy means one metal activates reactants, and the other activates small molecules like oxygen and hydrogen. In research on Pt-Sn/ γ -Al₂O₃ catalysts, Pt sites can break down H₂ efficiently. SnO_x components first adsorb and polarize C-O bonds through their oxophilic property and acidity, which effectively lowers the energy barrier for breaking C-O bonds [16]. Geometric synergy means two metals form special atomic-scale structures. These structures provide a good reaction environment for the adsorption of reaction intermediates and the formation of transition states. The distance between Co-Ti bimetallic sites is about 2.6 Å. It is close to the ideal distance for OCCHOH, the key intermediate of C-C coupling, so it optimizes the coupling conditions of CO and CHOH [17]. Studies on the Ni-Co system have found that this structure can change the adsorption form of CO₂. After modification, CO₂ stays in an asymmetric adsorption state. This can help gas-phase H radicals take part in the reaction, and lowers the reaction energy barrier of the following hydrogenation steps [15]. Electronic hybridization synergy works through charge transfer and orbital hybridization. The two factors together optimize the electronic structure of active sites and reduce the energy barrier of the rate-determining step in catalytic reactions. Studies on Cu-Ni/Al₂O₃-ZrO₂ catalysts have found that Ni doping causes a Cu-Ni synergistic effect. This effect can promote CO₂ activation, improve H₂ dissociation efficiency, and change the path of catalytic reactions [18]. Spatial decoupling

synergy divides the whole catalytic process into several steps that are separated in space. Each step is efficiently catalyzed by different components or sites of the catalyst respectively.

In a bimetallic catalyst system, the support not only plays a supporting role, but its physicochemical properties and strong interaction with metals play a decisive role in catalytic performance. The support provides physical dispersion and imposes structural constraints. Studies on the t-Sn/ γ -Al₂O₃ system have shown that the pore structure of mesoporous γ -Al₂O₃ not only provides loading sites, but its acidic surface can also stabilize small-sized metal particles [16]. The support directly participates in the catalytic process through its own acidity, basicity and redox properties. For example, acidic supports such as γ -Al₂O₃ and ZSM-5 can enhance the overall acidity of the catalyst system and promote acid-catalyzed steps such as dehydration and etherification [19]; reducible oxides such as TiO₂ and ZrO₂ can stabilize partially reduced metal species and promote the hydrogen spillover effect through strong metal-support interactions, contributing to the formation of highly dispersed Ni-Re alloy nanoparticles [19]. Metal clusters optimize the electronic structure of carbon shells through interfacial charge transfer. The interface between the support and metals is the core region for charge transfer, mass exchange and energy transfer, which directly affects catalytic performance. Support design can precisely regulate the specific functions of catalysts, such as constructing three-dimensionally ordered macroporous structures to improve mass transfer [20], adjusting the pore size and window size of MOFs to achieve molecular sieving [21], or controlling the loading mode of metals on the support through synthesis methods to achieve tight and stable interfacial contact [17].

3. Preparation, activity evaluation and characterization of bimetallic catalyst systems

To address the shortcomings of monometallic catalysts in CO₂ hydrogenation reactions, the development and design of various high-performance bimetallic catalysts have become a research hotspot in recent years. The main catalysts usually take metals such as Cu, Ni and Pd as active centers, and construct efficient and stable reaction centers by introducing a second metal with regulatory functions (such as Zn, In, Ga, Co, Sn, Pt, etc.) and matching with suitable oxide or mesoporous supports.

3.1. Cu-based bimetallic catalysts

Cu-based bimetallic catalysts are the mainstream system for methanol synthesis via CO₂ hydrogenation. A variety of synthesis methods are applied in the preparation of Cu-based bimetallic catalysts. The most common one is the coprecipitation method. This method obtains a uniform mixture by co-precipitating metal precursors under alkaline conditions, and is commonly used to prepare catalysts with uniform structures, such as CeO₂-ZrO₂-supported Cu-Ga [22] and Cu-Zn-Ce [23] systems. The impregnation method is flexible in operation and convenient for loading metals on prefabricated supports [24-26]. The hydrothermal/solvothermal method is often used to synthesize precursors with specific morphologies or structures, achieving component mixing at the atomic and molecular scales [27, 28]. The chemical reduction method is suitable for supported metal nanoparticles or alloys, such as using NaBH₄ as a reducing agent in the preparation of Cu-Ni/In₂O₃ catalysts [29]. The spray pyrolysis method is used for the efficient synthesis of catalysts with special structures, such as preparing porous hollow-structured Cu-In bimetallic catalysts [30].

In various bimetallic catalytic systems, regulating species dispersion and interface structure by introducing a second metal is a key approach to improving the performance of methanol synthesis via CO₂ hydrogenation. The CeO₂-ZrO₂-supported Cu-Ga catalyst achieved a CO₂ conversion rate of

15% and a methanol selectivity of 78% at 300 °C, and XRD characterization confirmed that Ga exists in a highly dispersed or amorphous state (Fig. 1) [22]. The Cu-Zn-MOF catalyst reached a methanol yield of 71.35 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ at 550 °C, and SEM showed that highly dispersed Zn effectively inhibited the sintering of Cu particles [24]. In the pathway-dependent Cu-Zn/ $\gamma\text{-Al}_2\text{O}_3$ catalyst, the CO_2 conversion rate reached 19.6%, and STEM-EDX revealed uniform distribution of Cu elements [31]. The Cu-Ni/ In_2O_3 catalyst achieved a methanol space-time yield of 0.46 g MeOH $\text{gcat}^{-1}\text{h}^{-1}$ at 275 °C. Quasi-in-situ XPS confirmed that the introduction of Ni inhibited Cu-In alloying and provided an appropriate oxygen vacancy concentration, maintaining undecayed stability in a 24-hour test (Fig. 4) [29]. The porous hollow-structured Cu-In catalyst achieved a methanol selectivity of 86.0% at 290 °C, effectively alleviating performance attenuation caused by RWGS. The $\text{CoO}-(\text{Cu}^0/\text{Cu}^+)-\text{In}_2\text{O}_3$ catalyst [28] realized a CO_2 conversion rate of 17.43% and a methanol selectivity of 83.30% at 290 °C. Characterization indicated that the strong interfacial synergistic effect between Cu and Co reconstructed the reaction pathway [30]. In noble metal bimetallic systems, catalysts exhibit excellent low-temperature activity. The Pd-Cu/ SiO_2 catalyst made the CO hydrogenation pathway superior to the COH pathway prone to carbon deposition through the alloy effect (as shown in Fig. 5), improving catalytic stability [26]. The MOF-derived Au-Cu/ ZnO-BTC catalyst also achieved a methanol space-time yield of 359.0 $\text{g}\cdot\text{kgcat}^{-1}\cdot\text{h}^{-1}$ at 250 °C (Fig. 3) [27].

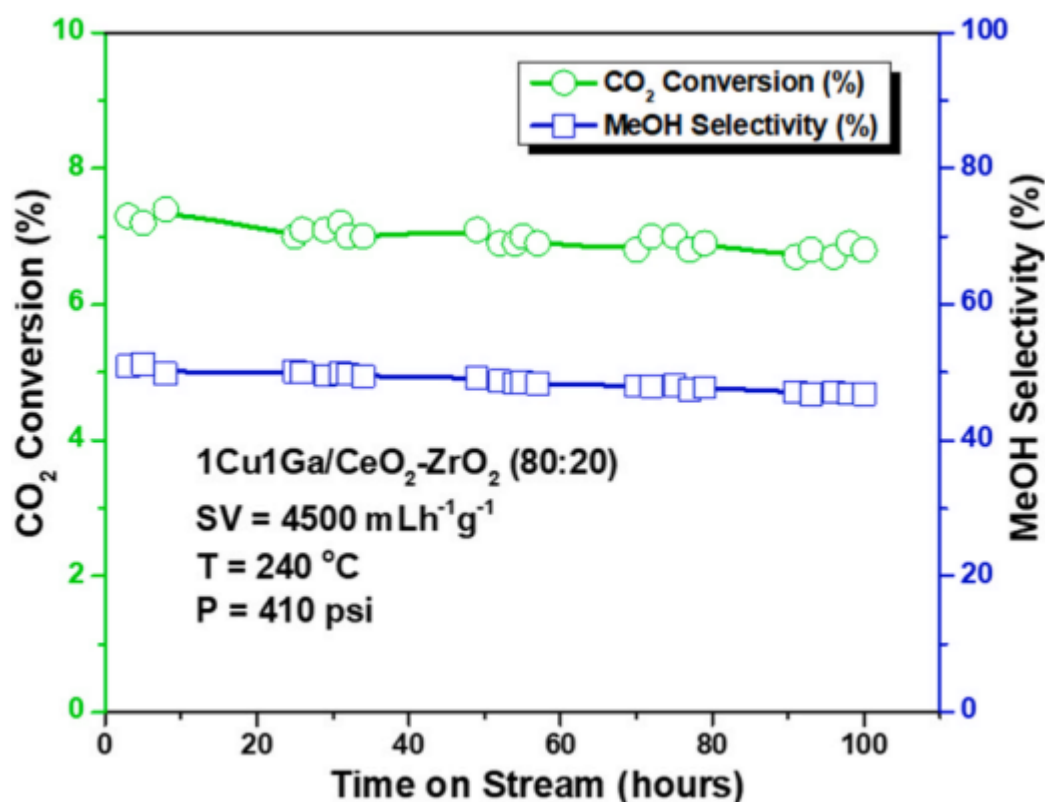


Figure 1. Effect of highly dispersed/amorphous Ga species on the stability of Cu-Ga/ $\text{CeO}_2\text{-ZrO}_2$ catalysts [22]

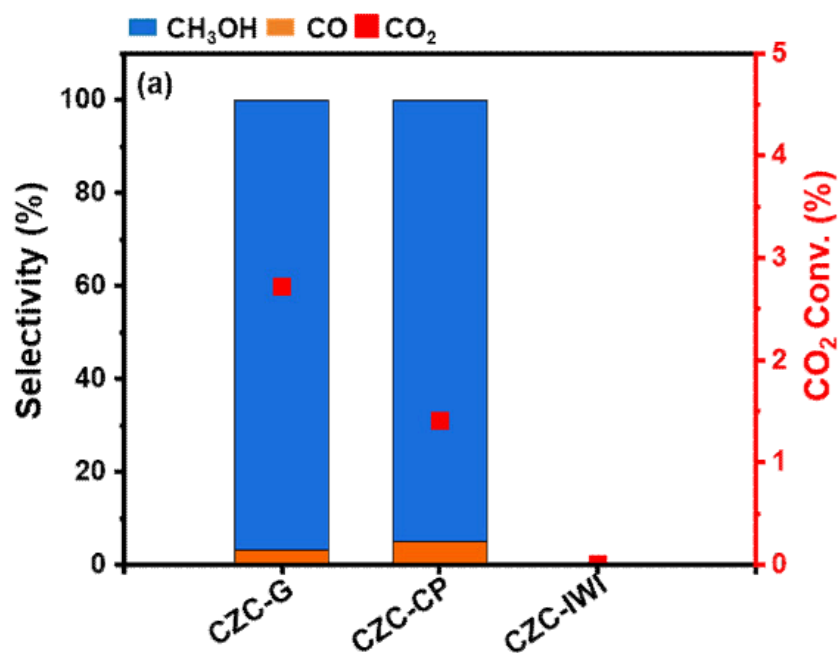


Figure 2. Performance of Cu-Zn-Ce (abbreviated as CZC) catalysts prepared by different methods for methanol synthesis via CO₂ hydrogenation [23]

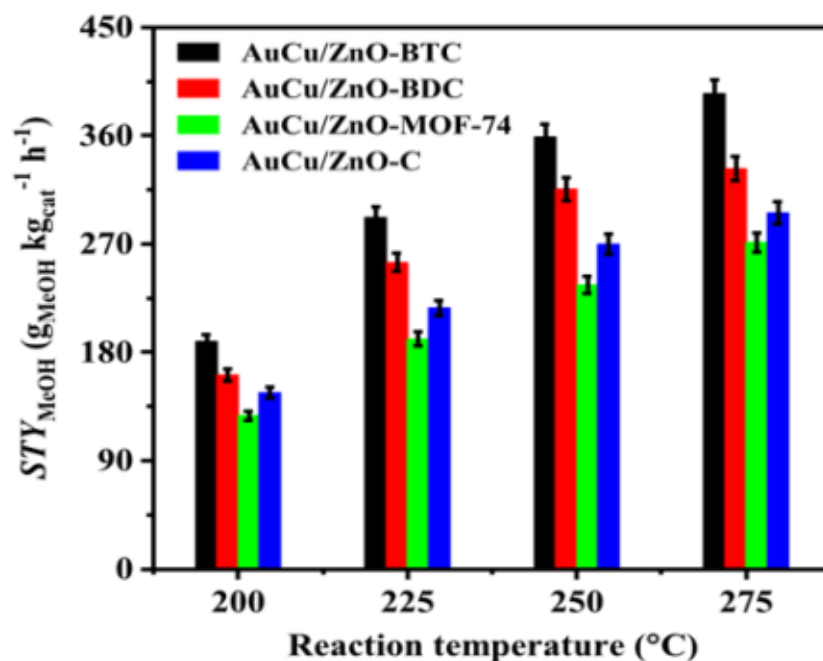


Figure 3. Effect of different MOF-derived supports on the methanol space-time yield of Au-Cu/ZnO catalysts [27]

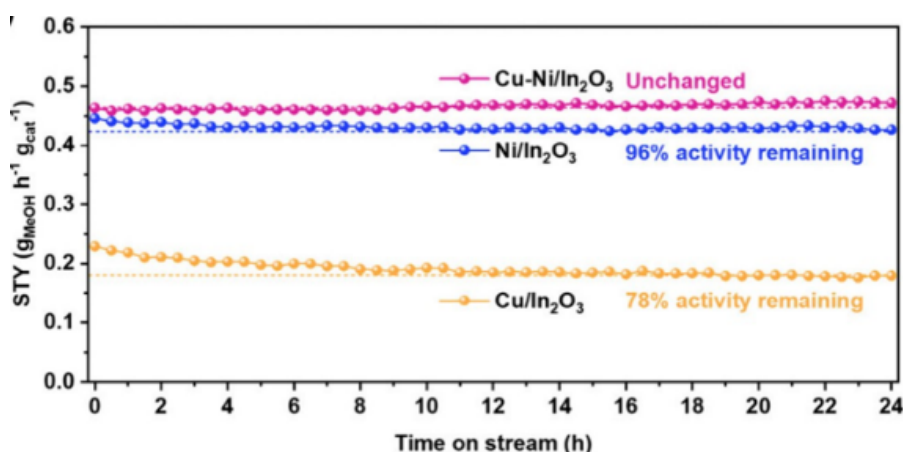


Figure 4. Comparison of methanol space-time conversion and long-term stability between Cu-Ni/In₂O₃ catalysts and monometallic catalysts [29]

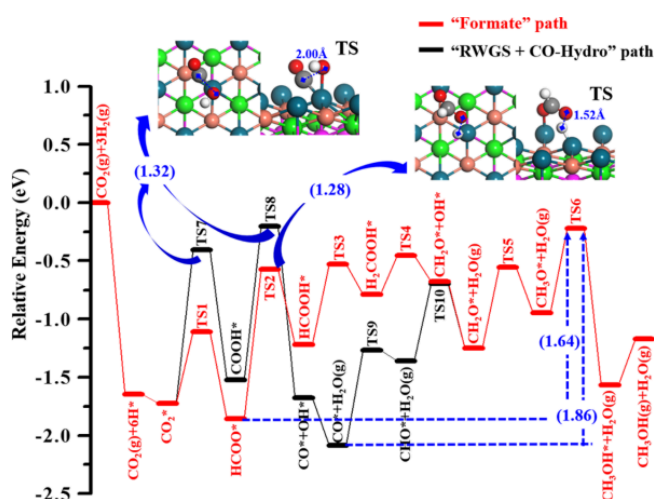


Figure 5. Energy barrier comparison between the formate pathway and the RWGS+CO hydrogenation pathway over Pd-Cu/SiO₂ catalysts [26]

Table 1. Performance comparison of Cu-based bimetallic catalysts for methanol synthesis via CO₂ hydrogenation

catalyst	TR(°C)	H ₂ /CO ₂ ratio	PR(MPa)	Space velocity ^a	Conv.(%)	Sel.(%)	STY ^b
Cu ₁ Ga ₁ /CZ(80:20) [22]	240	3:1	2.83	(W)4500	7.2	50	/
Cu _{0.5} Zn _{0.35} -MOR [24]	550	/	/	(W)36000	/	/	2.285
Cu-Ni/In ₂ O ₃ [29]	275	76:19	4.1	(W)21000	12.7	66.6	460
Pd-Cu(0.25)/SiO ₂ [26]	523	3:1	5	(G)30000	2.8	18.5	0.05
Pd-Cu(0.5)/SiO ₂ [26]	523	3:1	5	(G)30000	1.6	26.9	0.043
Pd-Cu(0.5)/SiO ₂ [26]	523	3:1	5	(G)12000	2.4	24	0.023
Au-Cu/ZnO-BTC [27]	250	3:1	3	/	6.2	68	359
Au ₁ -Cu ₄ /In ₂ O ₃ [27]	250	4:1	5	(G)21000	/	/	260
Cu:In(1:2) [30]	290	3:1	3	(W)15000	11.5	86	/

a(W) = WHSV = mass flow rate/catalyst mass, mL g_{cat}⁻¹ h⁻¹, (G) = GHSV = volume flow rate/bed volume, h⁻¹, a(W) = WHSV = mass flow rate/catalyst mass, mL g_{cat}⁻¹ h⁻¹, (G) = GHSV = volume flow rate/bed volume, h⁻¹, b STY (gMeOH kg_{cat}⁻¹ h⁻¹)

The catalytic activity and selectivity of Cu-based bimetallic catalysts for methanol synthesis via CO₂ hydrogenation are not only affected by reaction conditions such as reaction temperature and space velocity, but also depend on the synergistic effect between bimetallic components, catalyst interface structure, metal dispersion and support properties. The current research focus in this field mainly lies in the inhibition of side reactions and the improvement of the long-term structural stability of catalysts.

3.2. Ni-based bimetallic catalysts

Given Ni's inherent strong C–C bond cleavage and methanation capabilities, the synthesis strategy for Ni-based bimetallic catalysts is critically important. The most widely employed methods are the incipient wetness impregnation method and the impregnation method. In Ni-based bimetallic catalytic systems, rational regulation of the catalyst microstructure and introduction of external field assistance can flexibly optimize CO₂ conversion and methanol selectivity. In traditional thermal catalytic hydrogenation systems, the Ni₅Sn₁/MC catalyst exhibited outstanding performance under reaction conditions of 175 °C and a CO₂:H₂ ratio of 1:7, achieving a CO₂ conversion of 39.9% and a methanol selectivity of 87.9% (as shown in Fig. 6) [32]. The Ni–Cu catalyst, under atmospheric pressure and 240 °C, reached a methanol space–time yield of 665.7 μmol·g⁻¹·h⁻¹, with CO₂ conversion and methanol selectivity of 1.2% and 16.8%, respectively. The synergistic effect between Ni nanoparticles and Cu single atoms optimized the adsorption and activation capabilities of active sites toward reactant molecules [33]. In non-thermal catalytic pathways such as plasma catalysis, bimetallic components can significantly lower the reaction temperature window. For instance, the 7Ni3Co/Al₂O₃ catalyst achieved a CO₂ conversion of 24% and a methanol selectivity of 46% under mild conditions of 35 °C. Relevant characterizations revealed that the formation of the Ni–Co alloy promoted electron transfer between components and regulated the electronic structure of active sites, thereby meeting the reaction requirements for activating CO₂ molecules under mild conditions such as room temperature and atmospheric pressure (as shown in Fig. 7) [15].

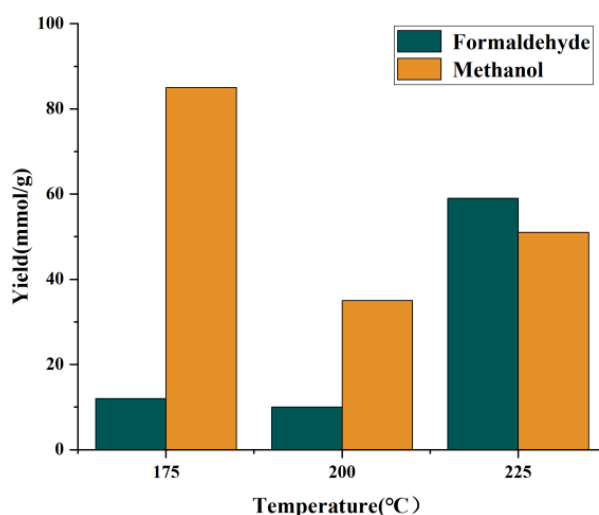


Figure 6. Methanol yield variation of the Ni₅Sn₁/MC catalyst at different temperatures [32]

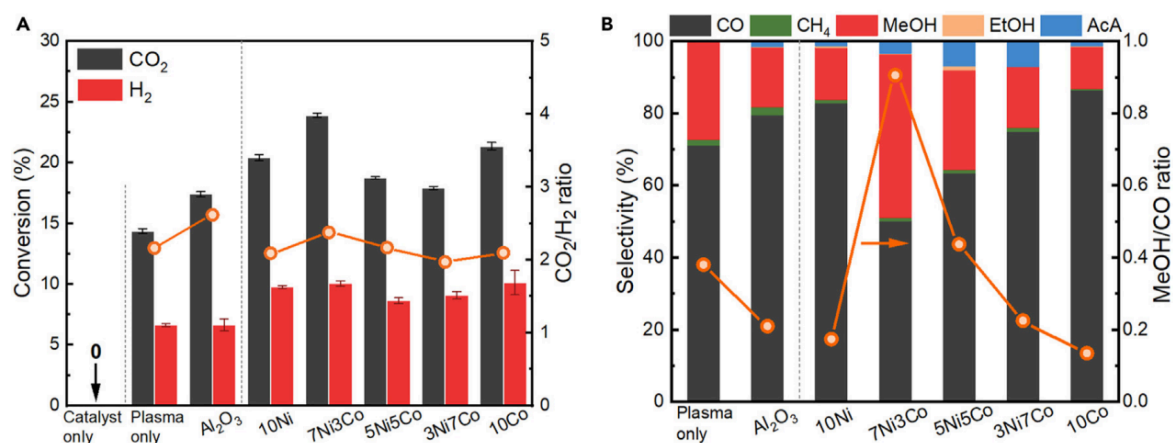


Figure 7. CO₂ conversion of the Ni–Co catalyst [15]

Carbon deposition and metal agglomeration are the primary causes of deactivation for Ni-based catalysts. Monometallic Ni catalysts are prone to rapid deactivation due to carbon deposition and sintering [32, 34]. The introduction of a second metal can effectively enhance carbon deposition resistance and stability. Bimetallic catalysts reduce carbon deposition by regulating surface adsorption. For example, the Ni–Cu bimetallic system [19] can dilute Ni active sites through alloying, regulate intermediate adsorption, and inhibit carbon deposition formation at the source. In cyclic tests, the Ni₅Sn₁/MC catalyst only experienced a 4.5% decrease in conversion after four cycles, with stable structure and no obvious carbon deposition [32]. For the 7Ni3Co/Al₂O₃ catalyst, the carbon deposition amount after reaction was less than 2%, far lower than that of the monometallic Ni catalyst [15].

Ni-based bimetallic catalysts effectively regulate the CO₂ conversion pathway and product selectivity through rational component design. By adjusting the electronic structure of active sites, inhibiting methanation, promoting carbon deposition gasification, and alleviating metal agglomeration, these catalysts significantly enhance carbon deposition resistance and long-term catalytic stability, showing broad application prospects in thermal catalysis, plasma catalysis, and other fields.

3.3. Pd-based bimetallic catalysts

Pd-based bimetallic catalysts are widely considered as catalytic systems with very strong ability to activate hydrogen molecules. They can achieve excellent methanol yields under low temperature and low pressure conditions. By controlling the grain size of metal alloy phases and the formation of specific alloy phases, the inhibitory effect on the RWGS reaction can be effectively adjusted.

Pd catalysts usually achieve satisfactory CO₂ conversion and methanol selectivity under reaction conditions of 200–300 °C and 3–5 MPa. The precious metal Pd has a strong ability to absorb and activate H₂, and its bimetallic systems have various preparation methods. Besides traditional co-impregnation [34, 35], sequential impregnation [36–38] and coprecipitation methods [39], fine control at the solution level is often used: specific Pd alloy sol particles are first prepared and then encapsulated [22]. Another method is the ion-exchange method, in which Pd ions are fixed by the carrier's natural electrostatic steric hindrance and then reduced to grow. The core of these complex techniques is to obtain ultra-small bimetallic nanoparticles or clusters with minimized particle sizes and mutual restriction. In the Pd–In system, carrier acidity plays a main role in alloy regulation. A highly acidic MFI carrier favors the formation of the In–Pd alloy, reaching a CO₂ conversion of

8.2% and a methanol selectivity of 83.6% at 300 °C [36]. In the Pd–Zn system, alloy crystal phases and pore structures show joint improvement effects. The fine alloy particles (4.41 nm) and mesoporous structure in the Pd–Zn/Fe₂O₄ catalyst jointly promote reactant mass transfer, realizing a methanol space–time yield of 593 g·kgcat^{−1}·h^{−1} [40]. As shown in Fig. 8, the Pd–Zn/ZnO–TiO₂ catalyst follows the formate pathway. It undergoes continuous hydrogenation and dehydration through PdZn alloy active sites (green), effectively avoiding RWGS or COH pathways that tend to produce carbon. This precise control of the reaction pathway, combined with a surface oxygen vacancy content as high as 71.8% (blue), leads to an outstanding space–time yield of 1267.1 mmol·kgcat^{−1}·h^{−1} [41]. Building specific active interfaces or coexisting alloy phases can greatly reshape reaction pathways. The Pd–Ga system uses the constructed metal–oxide interface and formate pathway, raising intrinsic activity to over 200 times that of monometallic Pd [39, 43]. The Pd–Cu/SiO₂ catalyst provides abundant weakly adsorbed hydrogen species through the coexistence of Pd–Cu and Pd–Cu₃ dual alloy phases. It doubles the methanol formation rate and shows good performance in a 100-hour stability test [34].

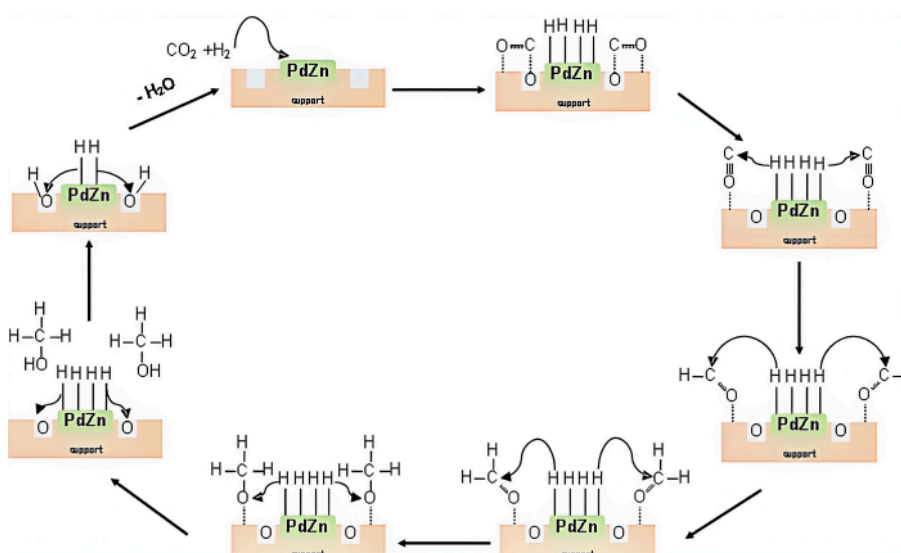


Figure 8. Mechanistic study of CO₂ hydrogenation over the Pd–Zn/ZnO–TiO₂ catalyst [41]

Carbon deposition and side reactions are main factors limiting the stability of Pd-based bimetallic catalysts. The reverse water–gas shift reaction produces a large amount of byproduct CO, which lowers methanol selectivity. To solve this problem, long-term catalysis can be achieved by optimizing the catalyst structure and building stable alloy phases. Building specific alloy structures such as Pd–Zn [42], Pd–Cu [43] and Pd–Ga [34] can effectively separate highly active Pd metal sites, block the RWGS reaction pathway, and at the same time guide the reaction toward the formate intermediate. This not only reduces the formation of byproduct CO but also inhibits carbon deposition on the catalyst surface, improving methanol selectivity and catalyst stability.

Table 2. Performance comparison of Pd-based bimetallic catalysts for methanol synthesis via CO₂ hydrogenation

Catalyst	H ₂ /CO ₂ ratio	TR (°C)	PR (MPa)	Space velocity ^a	Conv. (%)	Sel. (%)	STY ^b
Pd(0.25)-Cu/SiO ₂ [34]	3:1	250	4.1	(G)3600	6.7	30	32.3
Pd(0.25)-Cu/MCM-41 [34]	3:1	250	4.1	(G)3600	6.2	23	20.8
Pd(0.25)-Cu/SBA-15 [34]	3:1	250	4.1	(G)3600	6.5	23	23.1

Table 2. (continued)

Pd(0.25)-Cu/MSU-F [34]	3:1	250	4.1	(G)3600	5.3	18	12.7
4Pd-10In/S-1 [36]	3:1	300	4	(W)21000	8.2	83.6	474
Pd ₁ -Ga ₂₀ [37]	3:1	250	3	(G)7800	/	65	/
Pd-Zn/Fe [40]	3:1	250	4.5	(W)21600	5.78	73.94	330.38
Pd-Zn/Fe [40]	3:1	270	4.5	(W)21600	9.72	61.67	463.34
Pd-Zn/Fe [40]	3:1	290	4.5	(W)21600	13.94	55.02	592.54
Pd-Zn/ZnO-TiO ₂ [41]	4:1	250	2	(W)3600	9.9	46.6	30.4
Pd-Zn/SiC [42]	9:1	250	0.1	/	11	35	/

a(W) = WHSV = mass flow rate/catalyst mass, mL g_{cat}⁻¹ h⁻¹, (G) = GHSV = volume flow rate/bed volume, h⁻¹, b STY (gMeOH kg_{cat}⁻¹ h⁻¹)

4. Challenges and prospects

This paper systematically reviews the research progress of bimetallic catalysts applied in methanol synthesis via CO₂ hydrogenation. Benefiting from the electronic hybridization effect, multi-modal synergistic effect between components, and strong metal-support interaction, bimetallic catalytic systems have significantly broken through the limitations of traditional monometallic catalysts. This paper mainly introduces three core catalytic systems including Cu-based, Ni-based and Pd-based catalysts. The construction of alloy phases and modified interfacial engineering can effectively inhibit the deep methanation and reverse water-gas shift side reactions, and greatly improve the directional selectivity of methanol.

Although bimetallic catalysts show great potential in the field of methanol synthesis via CO₂ hydrogenation, they still face numerous challenges. It is difficult for catalysts to simultaneously achieve high CO₂ conversion, high methanol selectivity and long-term stability under low-temperature and low-pressure conditions. The generation of byproduct CO seriously reduces carbon utilization efficiency. In addition to carbon deposition, catalyst deactivation also involves multiple problems such as sintering and agglomeration of active metal particles and structural damage of supports. At present, the understanding and research on these complex deactivation mechanisms are insufficient, which restricts the rational design of high-efficiency catalysts.

Future research can focus on the following aspects to achieve breakthroughs:

(1) Explore the design strategies of modified bimetallic catalysts with high activity at low temperatures, and investigate the anti-sintering and anti-carbon-deposition deactivation mechanisms under high-temperature conditions.

(2) Develop special supports such as two-dimensional transition metal carbides rich in structural defects and flexible COF/MOF-derived hierarchical networks to strengthen the anti-deactivation synergistic active sites of catalysts.

(3) Fully explore new hydrogenation pathways assisted by photo-thermal synergy, electrocatalysis and non-thermal plasma localization, so as to approach the thermodynamic conversion limit under mild temperature and pressure conditions.

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