

Advances in heterogeneous catalysis for hydrogen production *via* steam reforming of biomass-derived alcohols: Catalytic structure-activity relationships from ethanol to glycerol systems

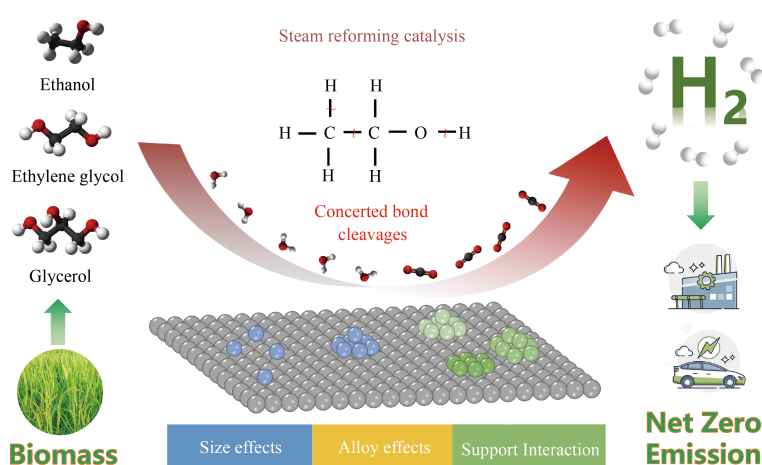
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Abstract: Steam reforming of biomass-derived alcohols (ethanol, ethylene glycol, glycerol, etc.) represents a critical pathway for sustainable hydrogen energy systems. This review systematically examines recent advances in heterogeneous catalysis, elucidating structure-performance correlations between alcohol molecular structures and catalyst requirements. Ethanol is prone to dehydration and methanation side reactions, while ethylene glycol leverages its dihydroxy structure to enhance dehydrogenation and C–C cleavage,

improving H₂ selectivity. In contrast, glycerol suffers from intensified reaction network complexity and carbon-induced deactivation due to its trihydroxy configuration. The unified catalyst design strategy involves precisely modulating metal electronic structures (e.g., alloying/atomic-level dispersion) and support oxygen mobility (e.g., rare-earth modification) to synergistically optimize dehydrogenation and carbon resistance. Ni-based catalysts dominate owing to low cost and high C–C bond activation capability, yet their stability requires synergistic enhancement *via* alloying (Fe, Co, Cu, etc.) or rare-earth modification (Ce, Pr, La, etc.). Noble metal systems (Pt, Rh, Ir, etc.) exhibit low-temperature activity advantages, but are transitioning strategically toward single-atom catalysis and high-entropy-oxide-based multicomponent architectures under cost constraints. Future efforts are suggested to integrate *in situ/operando* characterization with theoretical modeling to uncover dynamic structure-activity relationships, establish elementary reaction databases for data-driven rational catalyst design, and achieve cross-scale catalyst-reactor synergy, thereby providing a scientific foundation for efficient sustainable hydrogen production.

Key words: biomass-derived polyols; steam reforming for hydrogen production; heterogeneous catalysis; structure-activity relationship; coke resistance



Driven by the global imperative of carbon neutrality, hydrogen has emerged as a key clean energy carrier owing to its exceptional gravimetric energy density (142 MJ/kg) and near-zero carbon emissions^[1]. However, hydrogen

production remains overwhelmingly reliant on fossil resources, with steam methane reforming and coal gasification alone accounting for annual CO₂ emissions exceeding 70 million tons, which constitutes a fundamental

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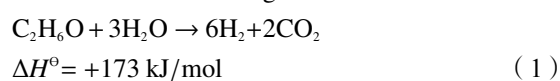
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conflict with carbon neutrality strategies^[2]. This challenge is particularly acute in China, the world's largest hydrogen producer (~33 million tons annually), where approximately 70% of output originates from fossil-derived routes. Transitioning to renewable hydrogen production is therefore critical to meeting China's 2030 carbon peak target. As a consequence, China's Medium- and Long-Term Plan for the Development of the Hydrogen Energy Industry (2021–2035) has explicitly identified hydrogen production from renewable energy sources as a strategic priority for national development^[3].

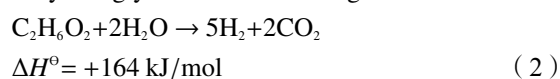
Among renewable feedstocks, biomass-derived small-molecule alcohols (ethanol, ethylene glycol, glycerol, etc.) stand out as highly promising alternatives to fossil-based hydrogen sources due to their renewable origin and intrinsic carbon-neutral lifecycle^[4]. These liquid organic compounds offer both environmental friendliness and economic advantages in storage and transportation—their sulfur-free nature avoids sulfur poisoning risks for platinum electrodes in fuel cells, and they can directly utilize existing fuel infrastructure, thereby reducing application costs. Industrially, ethanol is the most mature bio-alcohol, with global annual production exceeding 100 billion liters *via* fermentation of corn or sugarcane^[5]. Glycerol, a by-product of biodiesel production, is currently in surplus (global annual output exceeding 4 million tons), making its efficient conversion to hydrogen valuable for both resource utilization and cost control^[6]. Meanwhile, ethylene glycol produced *via* catalytic conversion of cellulose has advanced to kiloton-scale pilot demonstration, establishing it as a versatile biomass platform molecule^[7].

Steam reforming of biomass-derived alcohols involves the high-temperature co-conversion of the alcohol and steam, cleaving C–C, C–H and O–H bonds to H₂ and CO₂. In contrast to direct dehydrogenation pathways, steam reforming extracts hydrogen from both the alcohol substrate and water, dramatically boosting theoretical hydrogen yields. Taking ethanol, ethylene glycol, and glycerol as examples, their theoretical hydrogen yields reach 6, 5, and 7 mol H₂ per mole of alcohol reactant, respectively (eqs (1)–(3)). However, the strongly endothermic nature of these reactions typically necessitates operation at 500–800 °C^[7]. Such harsh conditions often lead to severe catalyst deactivation caused by metal sintering and carbon deposition, while also favoring hydrogen-consuming side reactions like methanation and reverse water–gas shift reaction. Therefore, the development of heterogeneous catalysts with high activity, selectivity and anti-coking stability under mild conditions remains the main challenge^[8–12].

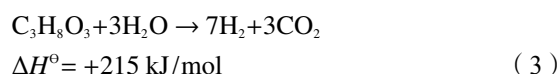
Ethanol steam reforming:



Ethylene glycol steam reforming:



Glycerol steam reforming:



In recent years, research on heterogeneous catalysts for steam reforming of biomass-derived alcohols to hydrogen has achieved remarkable progress, several review papers have systematically elucidated catalytic systems for specific alcohol reactants (e.g., ethanol, glycerol)^[13–17]. However, these reviews seldom provide cross-comparisons of hydrogen-production mechanisms among different biomass alcohols, making it difficult to establish universal structure-performance correlations. Given that the molecular structural features of biomass alcohols (such as hydroxyl number, carbon chain length) profoundly influence their bond-cleavage pathways and carbon deposition behavior, and thus differentially dictate the required catalytic active sites, it is particularly urgent to systematically analyze the reaction networks and catalyst structure-activity relationships for different biomass alcohols in steam reforming. Such analysis would not only offer theoretical anchors for the development of high-performance catalysts but also promote the targeted application of novel concepts in heterogeneous catalyst design (e.g., single-atom catalysis, strong metal-support interactions, etc.) in the field of biomass-based hydrogen production. Therefore, from the perspective of linking reactant structure to catalyst structure-activity relationships, this review focuses on the similarities and differences in the hydrogen-production mechanisms and structure-activity correlations for three representative biomass alcohols (i.e., ethanol, ethylene glycol, and glycerol), aiming to provide multi-scale theoretical support for the precise design of catalysts for steam reforming of biomass alcohols.

1 Reaction networks in steam reforming of biomass-derived alcohols for hydrogen production

1.1 Ethanol steam reforming

The steam reforming of ethanol proceeds through a complex network involving dehydrogenation, C–C bond cleavage, oxidation, dehydration, and the water-gas shift (WGS) reaction (Figure 1). The process is initiated by the dissociative adsorption of ethanol on basic or metallic sites, yielding ethoxy species and adsorbed hydrogen atoms. Subsequent β -dehydrogenation of the ethoxy intermediate yield acetaldehyde, which then undergoes C–C scission to generate CH_x ($x \leq 3$) fragments and CO^[18–20]. CO is further converted to CO₂ *via* the WGS reaction, whereas the CH_x species follow two primary pathways: hydrogenation to

methane or progressive dehydrogenation/polymerization to carbon deposits^[21–23]. At elevated temperatures, surface oxygen species derived from steam dissociation play a crucial role by gasifying coke precursors into CO/CO₂ and promoting the oxidation of ethoxy/acetaldehyde to acetate (or acetic acid) intermediates^[24–26]. Acetate decarboxylation directly affords CO₂ and additional CH_x, bypassing the CO route and thereby enhancing overall hydrogen efficiency^[27].

Surface acid-base properties strongly modulate side reactions. Acidic sites favor dehydration pathways, forming ethylene or diethyl ether, while Lewis acid-base pairs catalyze aldol condensation of acetaldehyde or acetate ketonization to acetone^[28–30]. Both ethylene and acetone can oligomerize and aromatize into polycyclic aromatic hydrocarbons, ultimately evolving into graphitic coke^[31–33]. Although these byproducts are amenable to secondary reforming, their activation barriers are substantially higher than the desired direct pathway, necessitating targeted catalyst design to suppress their formation^[34]. Additional coking contributions arise from methane cracking and the Boudouard reaction (2CO → CO₂ + C)^[35]. Collectively, these considerations highlight that lowering the operating temperature while preserving activity is essential for maximizing H₂ selectivity and minimizing coke formation^[36].

1.2 Steam reforming of polyols

Similar to ethanol, the steam reforming of ethylene glycol and glycerol also involve reactions such as dehydrogenation, dehydration, decarbonylation, and water-gas shift. However, due to differences in molecular structure, the polyols exhibit two distinct characteristics^[37–39]. First, every carbon atom in ethylene glycol and glycerol molecules is bonded to a hydroxyl

group, with no methyl groups present. This structural feature causes the C–C bond cleavage to take precedence over the cleavage of C–O bonds with higher bond energy, thereby facilitating the conversion of carbon atoms into CO_x and significantly reducing the likelihood of CH_x intermediates forming methane or carbon deposits (Figure 2)^[40]. Second, the polyhydroxy structure leads to a more complex reaction network: molecules exhibit enhanced interaction with catalysts *via* multi-coordination adsorption, while also expanding into more reaction pathways^[41]. For example, both ethylene glycol and glycerol can undergo intramolecular/intermolecular dehydration to form cyclic compounds, requiring catalysts with more precisely regulated acid-base sites^[42]. Meanwhile, ethylene glycol reforming yields intermediates such as hydroxyacetaldehyde and glyoxal, whereas glycerol reforming produces glyceraldehyde, dihydroxyacetone, or acrolein. These reactive monomers are prone to polymerize into long-chain molecules that are difficult to desorb, making it more crucial than in ethanol reforming for catalysts to enhance the C–C bond cleavage capability to suppress carbon deposition and deactivation^[43–44].

Specifically, ethylene glycol preferentially undergoes C–O bond activation to sequentially form hydroxyacetaldehyde and glyoxal. Glyoxal undergoes hydration and ring-opening to produce formic acid, which decomposes to CO₂ and H₂. This pathway bypasses the formation of CH_x species resulting from C–C cleavage, significantly reducing the possibility of methane generation^[45]. However, ethylene glycol also exhibits a competing acid-catalyzed pathway: intramolecular dehydration to ethylene oxide, followed by ring-opening polymerization that can evolve into oxygenated polyaromatic coke^[46]. For glycerol, the vicinal triol motif enables cascading transformations.

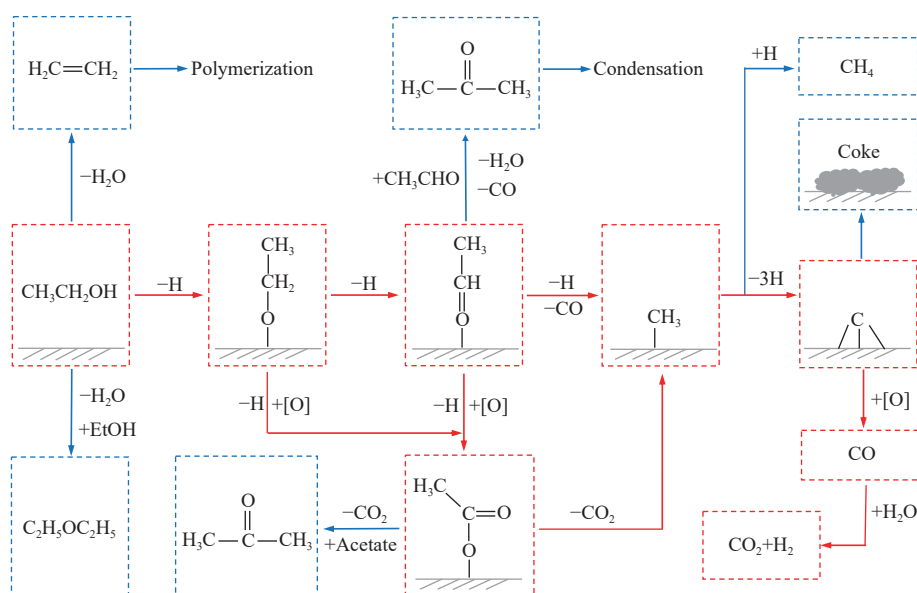


Fig. 1 Reaction pathways for ethanol steam reforming and plausible side reactions of the reactants and products (Main pathways: red; Side pathways: blue; [O] = lattice oxygen species on catalytic surfaces)

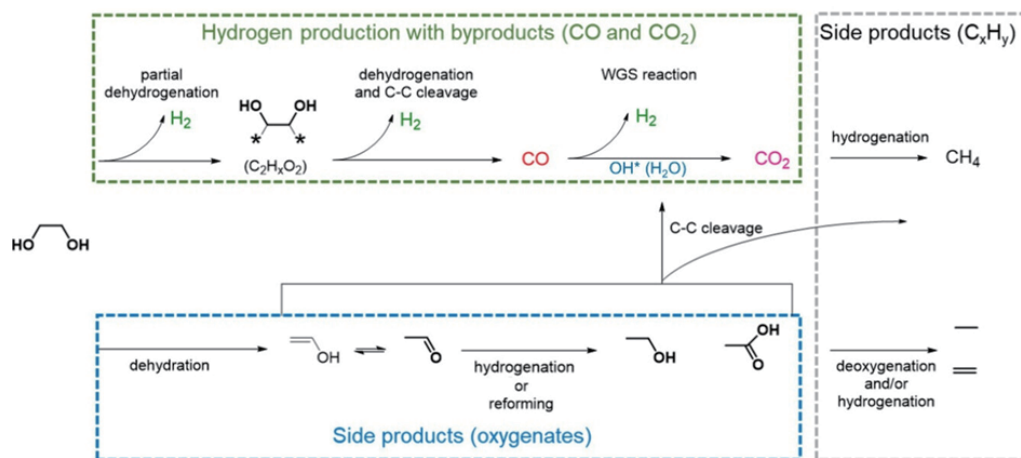


Fig. 2 Reaction pathways for ethylene glycol steam reforming and plausible side reactions of the reactants and products^[40] (with permission from ACS Publications)

Dehydrogenation of the primary alcohol forms glyceraldehyde, whose β -hydroxyl group is prone to rapid dehydration to acrolein. This conjugated enal serves as a potent precursor for benzene-ring construction *via* Diels-Alder cycloaddition, accelerating graphitic coke deposition and catalyst deactivation^[47–49]. Compared with ethanol, ethylene glycol requires a lower operating temperature because it lacks CH₃ groups that need activation. Although glycerol similarly contains no CH₃ groups, its complex vicinal *tri*-hydroxy structure leads to strong adsorption on the catalyst surface and a pronounced tendency toward carbon deposition, thus demanding higher temperatures to activate the reactants^[50].

2 Catalyst systems for steam reforming of biomass-derived alcohols to hydrogen

2.1 Role of metal centers

Metal centers serve as the key active sites in the steam reforming of biomass-derived alcohols to hydrogen, governing the activation of C–C, C–H and O–H bonds^[51–53]. Commonly employed metals include noble metals (Rh, Ru, Pt, Pd, Ir) and non-noble metals (Ni, Co, Cu), whose distinct electronic structures significantly influence the reaction pathway, hydrogen selectivity, and stability^[54–56]. Although noble metals exhibit excellent carbon deposition resistance and low-temperature activity, their high-cost limits industrial scalability. Among non-noble metals, Ni and Co possess strong C–C bond cleavage ability but face challenges of carbon-induced deactivation and metal sintering^[56]. Currently, Ni- and Co-based catalysts dominate research on ethanol reforming for hydrogen production, while Pt-based and other noble-metal systems remain predominant in glycerol reforming^[55–56].

Regarding the performance comparison of noble-metal catalytic centers, Liguras et al.^[57] systematically investigated hydrogen production over Al₂O₃-supported noble-metal catalysts in ethanol steam reforming within the

temperature range of 600–850 °C. Their study revealed the activity order as Rh >> Pt > Pd > Ru, while the hydrogen selectivity followed the order Rh >> Pt > Ru $\approx$ Pd^[57]. Optimization of the reaction system by Markevich et al.^[58] showed that Rh/Al₂O₃ achieved up to 92% hydrogen yield without carbon deposition at 650 °C with a water/ethanol molar ratio of 2.1. Ir-based catalysts have also been demonstrated to exhibit high ethanol conversion activity coupled with methane-reforming capability^[59]. At 650 °C, Ir/CeO₂ achieved 75% hydrogen purity and maintained stable operation for 300 h^[60].

As for the characteristic differences among non-noble metals, Ni generally exhibits higher reforming activity than Co, but its strong hydrogenation tendency leads to high methane selectivity. For instance, in ethylene glycol steam reforming under complete conversion at 500 °C, the CH₄ selectivity over Co/MgAl₂O₄ (8%) was significantly lower than that over Ni/MgAl₂O₄ (24%)^[61]. It should be noted that both Ni- and Co-based catalysts are prone to sintering and carbon deposition. Sintering originates from the low Tammann temperature of the metal particles, while carbon deposition is triggered by the strong adsorption and subsequent dehydrogenative polymerization of CH_x species^[62]. To address these challenges, recent studies have focused on optimizing supports and promoters to synergistically enhance both anti-sintering and anti-coking capabilities. Moreover, the stronger oxygen affinity of Co compared to Ni makes it easier to maintain an oxidized state, which favors H₂O activation^[63].

2.2 Role of supports

Metal oxides with high hydrothermal stability (e.g., CeO₂, ZrO₂, TiO₂, Al₂O₃, MgO) are widely employed as supports in the steam reforming of biomass-derived alcohols. These supports not only disperse and stabilize the active metals but also modulate reaction pathways and carbon deposition behavior through their own acid-base or redox properties^[64]. Taking acid-base effects as an example:

acidic supports such as Al_2O_3 tend to promote ethanol dehydration to ethylene and diethyl ether, eventually leading to carbon deposition and deactivation; whereas basic supports such as MgO preferentially drive the dehydrogenation pathway to form acetaldehyde and acetone^[65]. A similar trend is observed in glycerol conversion: Al_2O_3 induces dehydration to hydroxyacetone, followed by hydrogenation to 1,2-propanediol, while MgO can suppress hydrocarbon formation and enhances hydrogen selectivity due to its basicity^[63,66]. Further investigation into the role of basic sites reveals that they facilitate H_2O dissociation to generate surface OH^* species, which can effectively remove carbon precursors and accelerate the kinetics of the water-gas shift reaction^[67]. Comparative experiments by Batista et al.^[68] on $\text{Co}/\text{Al}_2\text{O}_3$ and Co/MgO catalysts directly demonstrated the critical influence of support acidity/basicity on hydrogen selectivity and catalyst stability in ethanol steam reforming, in which the former exhibited significantly higher carbon deposition.

Redox-type supports, represented by CeO_2 , rely on their high lattice-oxygen mobility to continuously supply active oxygen species during the reaction, assisting in bond cleavage and carbon removal. Notably, their crystal-plane effects are significant: in the cubic fluorite structure, the oxygen migration capability of the (110) and (100) facets are much higher than that of the (111) facet^[69]. This characteristic has been fully verified in Ni/CeO_2 systems. When Ni is supported on CeO_2 nanorods dominated by (110)/(100) facets, its anti-coking performance is markedly better than that on CeO_2 polycrystalline particles dominated by the (111) facet^[70]. A similar facet-dependent behavior was also observed by Kourtelesis et al.^[71] in Pt/CeO_2 systems. Combining infrared spectroscopy, temperature-programmed surface reactions and theoretical calculations, Vecchietti et al.^[72] revealed that ethanol tends to undergo dehydration on the $\text{CeO}_2(111)$ surface, whereas C–C bond cleavage is preferred on the (100) surface. This difference originates from the adsorption configuration and stability of the β -hydrogen elimination intermediates from ethoxy species on different crystal facets (Figure 3). Support particle size also plays a decisive role: reducing CeO_2 from 120 to 3.5 nm markedly enhances reducibility, generating abundant Ce^{3+} that suppresses surface acidity and blocks dehydration routes^[73].

Recent studies have further extended the regulation to composite oxide supports. For example, $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid solutions are widely used in steam reforming and water-gas shift reactions due to their excellent oxygen storage capacity^[74]. Kim et al.^[75] systematically investigated the effect of the Ce/Zr ratio on the catalytic performance of $\text{Ni}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ and found that increasing the Ce content enhances both surface and bulk oxygen vacancy concentrations. Surface oxygen vacancies dominate low-temperature oxygen migration, while bulk oxygen vacancies play a non-negligible role in replenishing lattice oxygen at elevated temperatures. Vecchietti et al.^[76], in their study of Ni -based catalysts supported on CeGaO_x composite oxides,

revealed that Ga^{3+} at the Ce-O-Ga interface enhances lattice oxygen mobility by weakening the Ce-O bond energy, promoting the cleavage and conversion of ethoxy groups *via* acetate intermediates. Simultaneously, Ga-H species drive the low-temperature decomposition of acetates into CO_2 and CH_4 , markedly increasing the H_2/CO_2 ratio and suppressing carbon deposition. Beyond direct participation in the reactions, the interaction between the support and metal sites is also a key factor, which will be discussed in detail in Section 3.3.

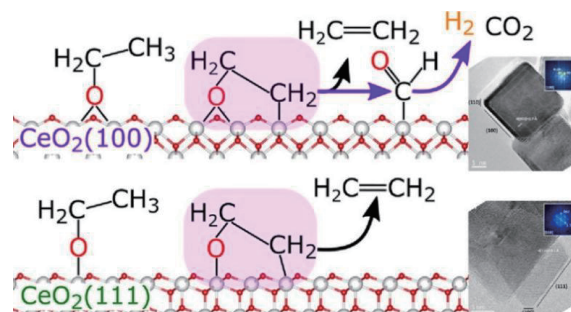


Fig. 3 Reaction pathways of ethanol conversion on $\text{CeO}_2(111)$ and $\text{CeO}_2(100)$ surfaces^[72]
(with permission from ACS Publications)

2.3 Role of promoters

The introduction of functional promoters can synergistically optimize the performance of both metal centers and supports. Alkaline promoters (e.g., K^+ , Na^+) significantly influence the reaction pathway by tuning the surface acidity/basicity of the support. Grzybek et al.^[77] found that introducing K^+ into Co catalysts supported on USY zeolite reduced ethylene selectivity from 65%–70% to 45%–55%, while simultaneously increasing hydrogen selectivity and suppressing carbon deposition. Wang et al.^[78] demonstrated that doping K^+ into Ni -based catalysts formed a Ni-O-K interfacial structure, which promoted C–C bond cleavage of acetaldehyde and enhanced water activation. In ethylene glycol reforming, Na^+ modification was found to block the acidic sites of $\text{Pt}/\gamma\text{-Mo}_2\text{N}$ catalysts, inhibiting C–O cleavage side reactions and accelerating the water-gas shift reaction^[40]. This resulted in a high hydrogen production rate of 270.8 mmol/(g·h) at 250 °C and 10 bar, with a CO_2 selectivity of 89% (CO only 1%). Additionally, CaO as a CO_2 adsorbent was used to reduce CO_2 concentration in the product stream in both ethanol and glycerol reforming systems, shifting the steam-reforming equilibrium forward and improving H_2 purity^[79–80].

Rare-earth promoters (e.g., La , Pr , Ce) enhance the performance of reforming catalysts through a dual mechanism: they can modulate acid-base sites while simultaneously introducing active lattice oxygen for carbon removal. Pizzolitto et al.^[81] showed that the addition of La significantly reduced support acidity of Ni-ZrO_2 catalysts, improving both hydrogen production efficiency and

stability. Xiao et al.^[82] introduced Pr to CeO₂ (Ce_{1-x}Pr_xO_{2-δ}), which increased oxygen vacancy concentration and lattice-oxygen mobility. By optimizing the doping level ($x \approx 0.2$), they accelerated H₂O activation and directed ethoxy species toward acetate conversion, effectively suppressed the ethylene/acetaldehyde pathway and subsequent methanation. The catalyst operated 50 h under harsh conditions (600 °C, water/ethanol = 4) without deactivation, and its carbon deposition rate was two orders lower than that of conventional Ni-based catalysts. Notably, beyond serving as a support, CeO₂ can also act as an efficient promoter. For example, Go et al. reported that adding a small amount of Ce (< 2%) to Ni-Fe/Al₂O₃ significantly improved glycerol-reforming conversion and hydrogen selectivity while reducing carbon deposition^[83].

2.4 Substrate-specific catalytic demands

The ultimate goal of biomass-derived alcohols steam reforming is to fully cleave C–C, C–H and O–H bonds, convert carbon atoms in the alcohol molecules into CO₂, and maximize the extraction of hydrogen atoms from both the alcohol and water to produce H₂. As described above, structural differences among the reactants directly lead to significant variations in the required catalytic functionalities. As a monohydric primary alcohol, ethanol readily undergoes methanation and dehydration side reactions due to the preferential activation of its C–O bonds. Consequently, its conversion need metal centers with stronger C–C and C–H bond activation capabilities, also required alkaline supports or basic promoters to suppress surface acid sites and block the dehydration pathway. In contrast, the vicinal di-hydroxy structure of ethylene glycol enhances the tendency for C–C cleavage *via* bidentate coordination, reducing the demand for metal-mediated bond-breaking. Moreover, the absence of methyl groups in the molecule suppresses methanation. However, this same structure also facilitates intermolecular dehydration, leading to ring-forming and condensation reactions that generate high-molecular-weight products. These products adsorb strongly on the catalyst surface, significantly increasing the risk of carbon deposition. For the structurally more complex glycerol, carbon deposition effects are further intensified, necessitating precise control over support acidity to inhibit condensation reactions. Notably, water plays a dual role in the reaction, serving both as a reactant in the water-gas shift reaction and as a cooperative agent in activating and removing carbon deposits. Thus, systems with a pronounced tendency for coking (e.g., glycerol reforming) have an especially urgent need for enhanced water activation capability. Based on these differences, the metal-support-promoter ternary components must be synergistically optimized according to the structural features of each alcohol molecule. The next section will focus on strategies for tuning the structure and performance of metal centers, systematically discussing recent advances in establishing

structure-activity relationships for catalysts used in hydrogen production *via* steam reforming of biomass-derived alcohols.

3 Structure-activity relationships in catalysts for steam reforming of biomass-derived alcohols to hydrogen

3.1 Metal particle size effects

Steam reforming of biomass-derived alcohols is a typical structure-sensitive reaction, where the metal particle size profoundly influences catalytic performance. However, reported trends vary significantly across catalyst systems and reaction conditions. In ethanol steam reforming, Noronha et al. observed that the intrinsic activity (turnover frequency, TOF) of Co atoms on carbon nanofiber-supported catalysts continuously increased as the Co particle size decreased from 16 to 2 nm^[84]. Similarly, Parlett et al.^[85] found that within the 2–4 nm range, the TOF of Ni confined in three-dimensional ordered mesoporous KIT-6 increased with decreasing Ni particle size. In contrast, Greluk et al.^[86] reported an opposite trend for Co/CeO₂ and Ni/CeO₂ catalysts, where TOF increased with increasing particle size (from 7 to 22 nm). Zhang et al.^[87] also confirmed using Ni@SiO₂ core-shell catalysts that TOF rose steadily as the Ni size increased from 6 to 30 nm, then plateaued between 30–40 nm. This discrepancy may stem from changes in the rate-determining step, which could be either ethanol dehydrogenation or C–C bond cleavage of its derived intermediates^[88–89]. Notably, the influence of metal particle size on carbon deposition shows more consistent trends across systems: smaller particles significantly suppress carbon formation. For example, Srisiriwat et al.^[90] demonstrated that reducing the Ni particle size from 16.5 to 8.2 nm decreased the coking rate by nearly an order of magnitude, and Valecillos et al.^[91] further validated the anti-coking advantage of small Ni particles (1.8–3.6 nm), which maintained long-term stability.

Extending to steam reforming of polyols such as glycerol, the particle-size effect exhibits more complex regulation. Sadanandam et al.^[92], in a study of Ni/ γ -Al₂O₃ catalysts, found that catalytic performance followed a volcano-type dependence on Ni particle size. At 8.5 nm, the low Ni loading exposed Lewis acid sites on the support, promoting glycerol dehydration and polymerization, which led to carbon deposition and deactivation. When the Ni size increased to 13.1 nm, the weakened metal-support interaction induced sintering and coking. Only at an optimized size of ~10 nm did the catalyst achieve a hydrogen yield of 67.5% at 650 °C with lowest carbon deposition. This trend is echoed in Co-based catalyst systems: Moogi et al.^[93] observed that a Co/MgO catalyst with small Co particles (~7 nm) achieved a hydrogen yield of 74.6%, whereas larger particles (~15 nm) led to increased coking and reduced hydrogen production.

The emergence of single-atom catalysis offers a new strategy to understand size limitations. By constructing precise atomic-scale interfaces, it effectively inhibits high-temperature sintering and carbon deposition. Zhao et al.^[94] established Rh–O–Ce single-atom sites in Rh–Ce/Al₂O₃, which significantly promoted water activation and the water-gas shift reaction, simultaneously enhancing hydrogen production efficiency and anti-coking performance. Peng et al.^[95] utilized an α -MoC support to construct Pt/Ir single-atom interfaces. By avoiding the excessive C–C cleavage and methanation side reactions typically driven by metal clusters, they achieved the cooperative conversion of ethanol and water into hydrogen and high-value-added acetic acid. This system delivered a hydrogen production rate of 331.3 mmol/(g·h) at 270 °C with 84.5% acetic acid selectivity (near-zero CO₂/CH₄ formation), demonstrating the precise control over reaction pathways enabled by atomic-level engineering. Recently, Li et al.^[96] developed a Ni system featuring coexisting single atoms and nanoclusters on a Mo₂TiAlC₂ composite support. Compared to pure single-atom and pure cluster systems, the hydrogen selectivity increased by 43.7% and 29.3%, respectively (at 550 °C), and the catalyst remained stable during a 120 h continuous reaction. Mechanistic studies further revealed that Ni single atoms dominated ethanol adsorption and activation, while adjacent nanoclusters lowered the dehydrogenation energy barrier. The two components formed cooperative active sites *via* a Ni–Mo

alloying interface, synergistically boosting catalytic performance (Figure 4)^[97]. This work highlights the significant advantage of multi-scale structural synergy in biomass-alcohol steam reforming and establishes a theoretical foundation for the design of next-generation catalysts.

3.2 Bimetallic/alloy effects

Bimetallic/alloying strategies, leveraging synergistic effects, can significantly enhance the performance of biomass-derived alcohol steam reforming. Among these, Ni-based bimetallic system was a major research focus due to the excellent C–C/C–H bond cleavage capability of the Ni component^[97]. Nichele et al.^[97], by precisely tuning the Cu/Ni ratio in Ni–Cu/ZrO₂ catalysts, revealed that Cu not only enhances the reducibility of the catalyst but also stabilizes Ni active sites through electronic interactions. Liu et al.^[98] further confirmed in Ni–Cu/Al₂O₃ systems that the introduction of 5% Cu significantly improves the reducibility of NiO. When extending the studies to Ni–Co systems, Rodríguez-Gómez et al.^[99] observed that the Co₂C phase formed in high-Co-content Ni–Co/SBA-15 catalysts effectively suppresses the over-cleavage of acetaldehyde. Meanwhile, Braga et al.^[100] found that the alloy sites exposed in Ni–Co/MgAl₂O₄ catalysts efficiently promote C–C bond cleavage at 450–550 °C.

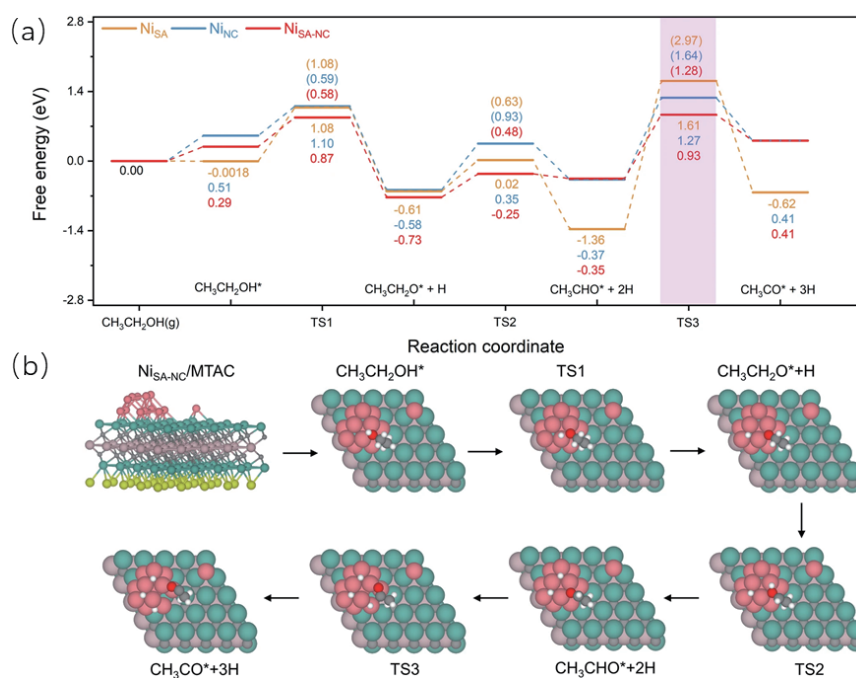


Fig. 4 Synergy between Ni single sites (Ni_{SA}) and Ni nanoclusters in catalyzing ethanol dehydrogenation: (a) DFT-calculated energy profiles for ethanol dehydrogenation on Ni_{SA}/Mo₂TiAlC₂(004) (orange), Ni_{NC}/Mo₂TiAlC₂(004) (blue) and Ni_{SA-NC}/Mo₂TiAlC₂(004) (red); (b) Corresponding geometric configurations of key intermediates on Ni_{SA-NC}/Mo₂TiAlC₂(004)^[97] (with permission from Springer Nature)

The introduction of metals such as Fe, W and Mo further expands the functional dimensions. Wu et al.^[101] demonstrated that in Ni-Fe/MgAl₂O₄ catalysts, electron transfer from Fe to Ni weakens CO adsorption strength, while the presence of the γ -Fe₂O₃ phase under reaction conditions drives the oxidation of ethoxy species to acetates, opening a new efficient pathway for C–C cleavage (Figure 5). Similarly, Ni-W/Mo bimetallic systems induce active oxygen generation *via* Ni–O–W(Mo) bridging bonds, synergistically optimizing the kinetics of the water-gas shift reaction and anti-coking ability^[89].

The synergistic effects between noble metals (e.g., Pt, Rh, Ru, Pd, Ir) and Ni offer distinct advantages in low-temperature activity and anti-coking performance. Palma et al.^[102] found that introducing Pt into Ni-based catalysts promotes CO/CH_x reforming reactions, significantly enhancing hydrogen yield while suppressing methane formation. Chagas et al.^[103] demonstrated that the Pd-Ni interface efficiently activates the methyl group of acetate intermediates, thereby blocking carbon deposition pathways at the source. Similarly, Campos et al.^[104] reported that incorporating a small amount of Rh into Ni-based catalysts effectively modulates the migration rate of active surface oxygen, accelerating CH_x conversion and reducing carbon deposition. Notably, Sierra et al.^[105] observed that in a Ni-Rh/La-Ce-Al₂O₃ catalyst containing 1% Rh, carbon accumulation was reduced by 560-fold compared to the unmodified catalyst, and the catalyst fully regained its activity after regeneration in air. When extending the studies to glycerol reforming, Reynoso-Estévez et al.^[106] showed that electron transfer between metals in Pt-Co/Al₂O₃ catalysts significantly improves CO₂ selectivity, while Silva et al.^[107] found that Rh-Co/SiO₂ catalysts promote deep cracking of glycerol by enhancing water activation, effectively suppressing olefin by-product formation.

Novel structural designs of bimetallic catalysts provide new opportunities for hydrogen production from biomass-derived alcohol steam reforming. Recently, Choong et al.^[108] constructed a multi-center synergistic interface in an

Ir-Fe bimetallic system, achieving a balance between catalytic activity and stability: Fe $\rightarrow$ Ir electron transfer strengthens the Ir–O bond and water activation capability, while the Fe²⁺/Fe³⁺ redox cycle establishes a reversible storage-release mechanism for active oxygen, ensuring timely and continuous removal of surface carbon species. Dai et al.^[109] employed a mesoporous SiO₂ (*m*SiO₂) encapsulation strategy to construct a pitaya-like (dragon-fruit-like) Pt-Cu@*m*SiO₂ catalyst. Within the confined mesoporous environment, the catalyst utilizes bimetallic electronic effects to synergistically optimize reactant adsorption configurations and product distribution, effectively suppressing CO formation and maintaining long-term stable operation in low-temperature reforming. Xue et al.^[110] further fabricated a more complex core-shell NiRh@NiO@*m*SiO₂ catalyst, revealing that the alloyed NiRh core and NiO shell cooperatively promote the ethoxy dehydrogenation pathway, while the *m*SiO₂ meso-structure ensures efficient mass transfer of water molecules and products, thereby significantly inhibiting metal sintering and enhancing anti-coking ability.

3.3 Metal-support interactions

Strong Metal-Support Interaction (SMSI), as a key strategy for regulating the performance of biomass-alcohol steam reforming, enhances metal-support functional synergy by reducing metal particle size and increasing interface proportion. Li et al.^[111] introduced CeO₂ into mesoporous SBA-15 zeolite and utilized SMSI to precisely control the dispersion of Ni particles. The constructed uniform Ni–O–Ce interface enabled the catalyst to achieve > 95% ethanol conversion and excellent anti-coking performance in ethanol steam reforming at 600 °C. Greluk et al.^[86,112] further promoted the dispersion of metal particles and enhanced the SMSI effect by adding citric acid during the synthesis of Ni/CeO₂ and Co/CeO₂ catalysts, obtaining high H₂ yield and strong water-gas shift capability under mild conditions at 420 °C.

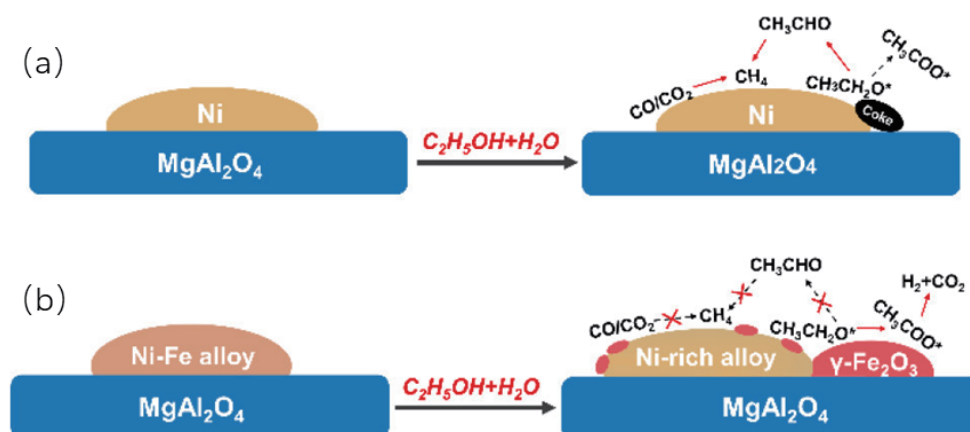


Fig. 5 Role of Fe species in Ni-based catalysts for ethanol steam reforming: (a) Proposed reaction pathway on Ni/MgAl₂O₄ catalyst; (b) Proposed reaction pathway on Ni-Fe/MgAl₂O₄ catalyst^[101] (with permission from ACS Publications)

Besides particle-size control, SMSI also influences metal valence states through charge transfer. Tian et al.^[113] developed a non-equilibrium synthesis method to precisely regulate the $\text{Ni}^0/\text{Ni}^{2+}$ ratio in $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ catalysts. Using *in situ* spectroscopy, they revealed a synergistic mechanism between Ni^0 and Ni^{2+} active sites, in which Ni^0 nanoparticles cleave the $\alpha\text{-C-H}$ bond of ethanol, while adjacent Ni^{2+} sites promote methyl dehydrogenation. This synergy effectively improves hydrogen production efficiency, achieving a hydrogen generation rate of 513.4 mmol/(g·h) at 400 °C with methane selectivity < 5%.

The oxygen vacancy content and basicity of metal-oxide supports play a regulatory role in SMSI. Kim et al.^[75,114] confirmed that by adjusting the Ce/Zr ratio in $\text{Ni}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts, Ce-enriched structures increase oxygen vacancy concentration, thereby strengthening SMSI and synergistically promoting ethanol dehydrogenation, steam reforming, and water-gas shift reactions. Recently, Sosa et al.^[115] employed magnetron-sputtering technology to enhance the oxygen vacancy concentration at the Ni-CeO_2 interface, significantly improving ethanol dehydrogenation and water activation efficiency. The synergy between basic supports and SMSI is equally crucial. Braga et al.^[100,116] combined the basic sites of the support with SMSI in $\text{Ni-Co}/\text{MgAl}_2\text{O}_4$ catalysts, effectively suppressing ethylene by-products and enhancing hydrogen selectivity in ethanol steam reforming, enabling long-term stable operation. Similarly, Alizadeh et al.^[117] demonstrated in glycerol steam reforming that the coexistence of the $\text{Ni-Fe}_x\text{O}_y$ phase formed *via* SMSI and the basic sites of MgO in $\text{Ni-Fe}/\text{MgAl}_2\text{O}_4$ catalysts synergistically strengthens the water-gas shift reaction and inhibits carbon deposition.

It is particularly important to emphasize that the strength of SMSI must be precisely controlled to optimize hydrogen production from biomass-alcohol steam reforming. When Zhu et al.^[118] studied the influence of TiO_2 crystal phases on Ni/TiO_2 catalysts, they found that anatase TiO_2 , due to

excessively strong SMSI with metallic Ni, caused over 90% of the Ni surface covered by TiO_x overlayers, severely hindering the exposure of active Ni^0 and Ni-TiO_2 sites. In contrast, rutile TiO_2 formed a moderate SMSI with Ni, preserving sufficient Ni^0 sites while exposing highly active Ni-TiO_2 interfaces. This promoted C–C bond cleavage *via* the acetate pathway and suppressed methane formation, while the interfacial confinement effect significantly inhibited sintering and carbon deposition (coking rate only 0.9 mg/(g·h)). This catalyst achieved a hydrogen production rate of 657.13 mmol/(g·h) at 500 °C and operated stably for 420 h.

Strong Bimetal-Support Interaction (SBMSI), by integrating metal-metal synergy with metal-support coupling effects, opens new avenues for enhancing the performance of biomass-alcohol steam reforming. Meng et al.^[119] constructed a RhNi/TiO_2 catalyst with well-defined interfacial structure from a RhNiTi layered double hydroxide precursor. *In situ* spectroscopic characterization revealed that its multifunctional interfacial active sites ($\text{Rh-Ni}^{\delta-}\text{-O}_v\text{-Ti}^{3+}$) utilize multi-electron transfer to drive efficient activation and reforming conversion of CO and CH_x intermediates (Figure 6)^[119]. In ethanol steam reforming, this catalyst achieved a hydrogen yield of 61.7% and a hydrogen production rate of 544.64 mmol/(g·h) at 400 °C, with no significant deactivation during 300 h of operation. Similarly, Smal et al.^[120] discovered in a $\text{Ni-Ru}/\text{Mn}_x\text{Cr}_{3-x}\text{O}_4$ ($x = 0.3\text{--}2.7$) system that the SBMSI effect drives the segregation and reconstruction of Ni and Ru from the subsurface of the support into highly dispersed alloy nanoparticles under ethanol steam reforming conditions. By adjusting the Mn/Cr ratio in the support to form a MnCr_2O_4 spinel phase, the optimized SMSI strength, lattice oxygen mobility, and NiRu alloy structure synergistically enhanced the efficiency of ethanol C–C bond cleavage and enabled rapid *in situ* oxidation removal of surface carbon species.

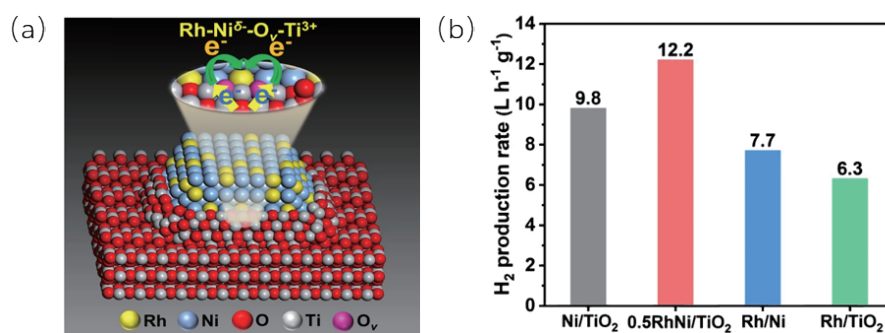


Fig. 6 SBMSI effect in ethanol steam reforming: (a) Schematic illustration of multifunctional interfacial active sites in RhNi/TiO_2 catalyst; (b) H_2 production rate comparison between RhNi/TiO_2 and reference catalysts (400 °C, 0.15 g catalyst, $\text{H}_2\text{O}/\text{EtOH} = 1.5$)^[119] (with permission from Springer Nature)

The utilization of compositionally homogeneous multi-component composite oxides or high-entropy oxides (HEOs) as precursors for bimetallic catalysts has emerged

as a prominent research trend in recent years, further expanding the tunable dimensions of SBMSI. Liao et al.^[121] synthesized nanorod-like NiCoMnCeCaO_x penta-

component composite oxides. During the initial stage of ethanol steam reforming, NiCo alloys were exsolved from the lattice under the introduction of oxygen vacancies and ethanol. The NiCo alloys were responsible for C–C bond cleavage and dehydrogenation, while Mn and Ce provided active lattice oxygen, and Ca enhanced water activation capability and CO₂ capture through basic sites. The synergistic interplay among these multiple components achieved a hydrogen production rate of 433.8 mmol/(g·h) at 600 °C. Liao et al.^[122] employed a perovskite-type La₂CaNiCoMnO_x high-entropy oxide as a catalyst precursor. They observed that during glycerol steam reforming, it undergoes *in situ* self-reconstruction to form a highly stable “semi-embedded” NiCo/HEO catalytic interface. A sustained oxygen-vacancy migration network involving Mn, Ca and La enabled a dynamic equilibrium between water activation and carbon removal. This SBMSI effect allowed the catalyst to achieve 88% H₂ selectivity and operate stably for 20 h at a high temperature of 800 °C.

4 Conclusions and outlook

Steam reforming of biomass-derived alcohols (ethanol, ethylene glycol and glycerol) for hydrogen production demonstrates broad prospects in renewable hydrogen energy generation. A distinct contrast exists in the molecular structures and reaction pathways of these three alcohols: ethanol is prone to dehydration and constrained by side reactions such as acetone formation and methanation; ethylene glycol leverages its dual hydroxyl groups to synergistically enhance dehydrogenation and C–C bond cleavage, thereby improving hydrogen selectivity; the tri-hydroxyl structure of glycerol, however, leads to reaction network complexity and an increased tendency for carbon deposition. A core principle emerges: an increase in the number of hydroxyl groups strengthens molecule-surface interactions. While this intensifies the divergence of reaction pathways, it simultaneously opens new opportunities for constructing controllable interfaces and multifunctional active sites.

Catalyst design must address universal requirements—efficiently synergizing dehydrogenation, C–C cleavage, and the water-gas shift reaction, while simultaneously blocking carbon deposition precursors like ethylene or enols. It must also respond precisely to system-specific differences: ethanol-based systems should focus on tuning metal-support interfaces to suppress ethylene/acetone/methane pathways; ethylene glycol systems require a dynamic balance between oxygen mobility and water activation capability; glycerol systems demand a stronger emphasis on anti-coking performance and high-temperature stability. Ni-based catalysts dominate due to their cost-effectiveness and strong C–C bond activation capability. However, strategies such as alloying (with Fe, Co, Cu, etc.) or incorporating rare-earth supports/promoters (Ce, Pr, La, etc.) are essential to

construct synergistic interfaces that overcome the bottlenecks of carbon deposition and sintering. Although noble metals (Pt, Rh, Ir, etc.) exhibit superior low-temperature activity and stability, alternative strategies are evolving towards single-atom catalysis and multicomponent catalytic systems driven by strong bimetallic-support interaction (SBMSI).

Looking ahead, the field of heterogeneous catalysis for steam reforming of biomass-derived alcohols still faces three key challenges:

(1) Deep understanding of reaction mechanisms and structure-performance relationships. By integrating *in situ/operando* characterization with theoretical simulations, it is essential to elucidate the differential mechanisms by which different alcohol molecular structures (e.g., hydroxyl number, topological configuration) induce dynamic reconstruction of active sites in multi-component catalyst systems. This will enable the establishment of quantitative mapping models linking alcohol structural parameters (e.g., hydroxyl density) to interfacial electronic states and reaction pathways, providing a mechanistic anchor for the differentiated design of catalysts tailored to specific biomass-alcohol steam reforming systems.

(2) Data-driven rational design of catalysts. There is a need to construct open database platforms encompassing fundamental reaction energy barriers, adsorption energies, and interfacial state densities. These platforms should incorporate descriptors for alcohol molecular structure features and integrate machine learning with high-throughput screening technologies. This will pave the way for accurate prediction of macroscopic performance from electronic structures. Priority should be given to developing anti-coking/anti-sintering catalysts based on inexpensive metals and rare-earth oxides, thereby expanding the versatility of biomass-derived alcohol steam reforming catalysts and overcoming the stability-cost trade-off dilemma.

(3) Cross-scale integration of catalytic materials and reaction engineering. Given the differing demands of various biomass-derived alcohol steam reforming systems on catalytic functions such as C–C/C–H bond activation and anti-coking performance, it is crucial to promote the deep matching of microchannel reactors, membrane reactors, and photo-/electro-assisted systems with catalyst structures. By enhancing mass/heat transfer and thermal management, an integrated design of “alcohol structure–catalyst–reactor” can be achieved, ensuring the transferability of performance from laboratory to industrial scale-up.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] EUROSTAT. Hydrogen—Reporting Instructions (Annual

- Data)[R]. Luxembourg: European Commission, 2023: 7.
- [2] International Energy Agency (IEA). Global Hydrogen Review 2023—Executive Summary[R]. Paris: IEA, 2023.
- [3] National Development and Reform Commission, National Energy Administration, Medium- and Long-Term Plan for the Development of Hydrogen Energy Industry (2021–2035)[R]. Beijing: NDRC, 2022.
- [4] AZIZAN M T, AQSHA A, AMEEN M, et al. Catalytic reforming of oxygenated hydrocarbons for the hydrogen production: An outlook[J]. *Biomass Convers Biorefin*, 2023, 13(10): 8441–8464.
- [5] U S DOE Alternative Fuels Data Center, Renewable Fuels Association. Global Ethanol Production by Country or Region (2007–2022)[R]. Washington, DC: AFDC, 2023.
- [6] CIRIMINNA R, DELLAPINA C, ROSSI M, et al. Understanding the glycerol market[J]. *Eur J Lipid Sci Technol*, 2014, 116(10): 1432–1439.
- [7] WANG A, ZHANG T. One-pot conversion of cellulose to ethylene glycol with multifunctional tungsten-based catalysts[J]. *Acc Chem Res*, 2013, 46(7): 1377–1386.
- [8] MATTOS L V, JACOBS G, DAVIS B H, et al. Production of hydrogen from ethanol: Review of reaction mechanism and catalyst deactivation[J]. *Chem Rev*, 2012, 112(7): 4094–4123.
- [9] HOU T F, ZHANG S Y, CHEN Y D, et al. Hydrogen production from ethanol reforming: Catalysts and reaction mechanism[J]. *Renew Sustain Energy Rev*, 2015, 44: 132–148.
- [10] VAIDYA P D, RODRIGUES A E. Insights into steam reforming of ethanol to produce hydrogen[J]. *Chem Eng Technol*, 2006, 29(12): 1369–1376.
- [11] WU K, SU S, WANG X, et al. Characteristics of the sustained release of Cu-Al spinel pretreated by different methods for hydrogen production from methanol steam reforming[J]. *J Fuel Chem Technol*, 2025, 53(7): 1050–1060.
- [12] FENG X, ZHAO Y, ZHAO Y, et al. A mini review on recent progress of steam reforming of ethanol[J]. *RSC Adv*, 2023, 13(34): 23991–24002.
- [13] MENG H, ZHANG J, YANG Y, et al. Recent status in catalyst modification strategies for hydrogen production from ethanol steam reforming[J]. *ChemCatChem*, 2023, 15(17): e202300733.
- [14] ZHANG X S, HUA W D, LIN Y, et al. Unraveling Ni particle size effects in ethanol steam reforming over Ni/CeO₂ catalysts[J]. *Carbon Hydrogen*, 2025, 27(4): 473–482.
- [15] LIAO W M, LIU S Y, XIE H, et al. Mechanistic insights into facet-dependent interfacial chemistry governing ethanol steam reforming on Ni/CeO₂[J]. *ACS Catal*, 2026, 16(5): 4653–4665.
- [16] GUJAR J P, VERMA A, MODHERA B. Optimizing glycerol conversion to hydrogen: A critical review of catalytic reforming processes and catalyst design strategies[J]. *Int J Hydrogen Energy*, 2025, 109: 823–850.
- [17] BAÚTI S, FEYH J V T, ANTUNES F C, ET al. Medium- and high-entropy catalysts for hydrogen production from strategic renewable fuel reforming: A review[J]. *J Energy Chem*, 2025, 111: 513–544.
- [18] SHENG P Y, YEE A, BOWMAKER G A, et al. H₂ production from ethanol over Rh–Pt/CeO₂ catalysts: The role of Rh for the efficient dissociation of the carbon–carbon bond[J]. *J Catal*, 2002, 208(2): 393–403.
- [19] FRENI S, CAVALLARO S. Hydrogen production from ethanol steam reforming over Ni/MgO catalysts[J]. *Catal Today*, 2004, 83(1/4): 3–15.
- [20] KONSOLAKIS M. The role of supports on the activity and selectivity of Rh catalysts in the steam reforming of ethanol[J]. *Appl Catal B: Environ*, 2016, 198: 479–491.
- [21] VAIDYA P D, RODRIGUES A E. Insights into steam reforming of ethanol to produce hydrogen for fuel cells[J]. *Chem Eng J*, 2006, 117(1): 39–49.
- [22] FRUSTERI F, SPADARO L. Ethanol steam reforming on Ni/Al₂O₃ catalysts: On the role of the support and Ni loading[J]. *Appl Catal A: Gen*, 2004, 270(1): 1–9.
- [23] LLORCA J, HOMS N, SALES J, et al. Low-pressure ethanol steam reforming on CeO₂–ZrO₂–Rh catalysts[J]. *J Catal*, 2004, 227(2): 556–560.
- [24] IDRIS H. Ethanol reactions over the surfaces of noble metal/cerium oxide catalysts[J]. *Platin Met Rev*, 2004, 48(3): 105–115.
- [25] CHEN L, LUO M F. The ethanol steam reforming over MgO-supported metal catalysts[J]. *J Catal*, 2008, 257(1): 172–180.
- [26] DA SILVA A M, DE SOUZA K R, JACOBS G, et al. Steam and CO₂ reforming of ethanol over Rh/CeO₂ catalyst[J]. *Appl Catal B Environ*, 2011, 102(1-2): 94–109.
- [27] MARTINELLI M, WATSON C D, JACOBS G. Sodium doping of Pt/m-ZrO₂ promotes C–C scission and decarboxylation during ethanol steam reforming[J]. *Int J Hydrogen Energy*, 2020, 45(36): 18490–18501.
- [28] SHARMA Y C, KUMAR S. Biohydrogen economy: A review on production processes, techno-economic analysis, life-cycle assessment and challenges[J]. *Renewable Sustainable Energy Rev*, 2017, 74: 89–103.
- [29] PODOBIŃSKI J, ZIMOWSKA M, ŚLIWA M, et al. IR studies of ethoxy groups on CeO₂[J]. *Molecules*, 2023, 28(3): 1251.
- [30] VIKÁR A, SOLT H E, NOVODARSZKI G, et al. A study of the mechanism of triglyceride hydrodeoxygenation over alumina-supported and phosphatized-alumina-supported Pd catalysts[J]. *J Catal*, 2021, 404: 67–79.
- [31] WANG J, ZHAO H, HALLER G, et al. Recent advances in the selective catalytic reduction of NO with NH₃ on Cu-chabazite catalysts[J]. *ACS Catal*, 2020, 10(3): 1369–1383.
- [32] ALONSO D M, WETTSTEIN S G, DUMESIC J A. Bimetallic catalysts for upgrading biomass to fuels and chemicals[J]. *Chem Soc Rev*, 2012, 41(24): 8075–8098.
- [33] LU Y, YUE C, LI Y, et al. Atomically dispersed Ni on Mo₂C embedded in N, P co-doped carbon derived from polyoxometalate supramolecule for high-efficiency hydrogen evolution electrocatalysis[J]. *Appl Catal B: Environ*, 2021, 296: 120336.

- [34] DALENA F, GIGLIO E, MARINO A, et al. Steam reforming of bioethanol using metallic catalysts on zeolitic supports[J]. Catalysts, 2022, 12(6): 617.
- [35] FRENI S, CAVALLARO S, MONDELLO N, et al. Hydrogen production by steam reforming of ethanol on Ni–Ru supported catalysts[J]. Int J Hydrogen Energy, 2001, 26(10): 1103–1109.
- [36] ROSHA P, ALI FM, IBRAHIM H, et al. Recent advances in hydrogen production through catalytic steam reforming of ethanol: Advances in catalytic design[J]. Can J Chem Eng, 2023, 101(10): 5498–5518.
- [37] ADHIKARI S, FERNANDO S D, HARYANTO A. Hydrogen production from glycerol: An update[J]. Energy Convers Manage, 2009, 50(10): 2600–2604.
- [38] BAGNATO G, IULIANELLI A, SANNA A, et al. Glycerol production and transformation: A critical review with particular emphasis on glycerol reforming reaction for producing hydrogen in conventional and membrane reactors[J]. Membranes, 2017, 7(2): 17.
- [39] CARRERO A, CALLES J A, GARCÍA-MORENO L, et al. Production of renewable hydrogen from glycerol steam reforming over bimetallic Ni-(Cu, Co, Cr) catalysts supported on SBA-15 silica[J]. Catalysts, 2017, 7(2): 55.
- [40] LIANG X, GAO Z R, PENG X J, et al. Efficient hydrogen production from ethylene glycol steam reforming catalyzed by Na-promoted Pt/ γ -Mo₂N[J]. J Am Chem Soc, 2025, 147(45): 33395–33402.
- [41] DOU B, SONG Y, WANG C, et al. Hydrogen production from glycerol steam reforming over Ni/CeO₂ catalysts. Appl Catal B: Environ, 2014, 147: 597–606.
- [42] SUGIYAMA S, FUKUNAGA S, ITO K, et al. Catalysts for vapor-phase dehydration of ethylene glycol and their application to pyruvic acid synthesis[J]. J Catal, 1991, 129: 12–18.
- [43] CHELLAPPA A S, FISCHER C M, THOMSON W J. Production of hydrogen from methane and glycerol by steam reforming over Ni/CeO₂ catalysts[J]. Appl Catal B: Environ, 2002, 39(2): 145–160.
- [44] GRELUK M, GAC W, ROTKO M, et al. Steam reforming of glycerol over Ni/Al₂O₃ catalysts: Effect of support modification with La, Ce, and Mg[J]. Int J Hydrogen Energy, 2021, 46(45): 24535–24549.
- [45] LI X, CHEN K, ZHAO Y, et al. Steam reforming of ethanol over Ni/CeO₂ catalysts: Effects of the Ni loading[J]. J Catal, 2018, 367: 180–192.
- [46] LI S, LI M, ZHANG C, et al. Steam reforming of ethanol over Ni/ZrO₂ catalysts: Effects of the preparation method[J]. Appl Catal A: Gen, 2020, 595: 117506.
- [47] MARQUEVICH M, CZERNIK E, CHORNET E, et al. Hydrogen from biomass: Steam reforming of model compounds of fast pyrolysis oil[J]. Ind Eng Chem Res, 2000, 39(3): 543–549.
- [48] VIZCAÍNO A J, CARRERO A, CALLES J A. Hydrogen production by ethanol steam reforming over Cu–Ni supported catalysts[J]. Int J Hydrogen Energy, 2007, 32(10/11): 1450–1461.
- [49] DONG X, ZHANG Q, WANG J, et al. Steam reforming of ethanol over Ni/CeO₂–ZrO₂ catalysts: Effects of the Ni loading[J]. J Catal, 2021, 398: 28–41.
- [50] SONG J H, YOO S, YOO J, et al. Hydrogen production by steam reforming of ethanol over Ni/Al₂O₃–La₂O₃ xerogel catalysts[J]. Mol Catal, 2017, 434: 123–133.
- [51] BEPARI S, KUILA D. Steam reforming of methanol, ethanol and glycerol over nickel-based catalysts: A review[J]. Int J Hydrogen Energy, 2020, 45(36): 18090–18113.
- [52] XU W, LIU Z, JOHNSTON-PECK A C, et al. Steam reforming of ethanol on Ni/CeO₂: Reaction pathway and Ni–CeO₂ interaction[J]. ACS Catal, 2013, 3(5): 975–984.
- [53] LIU Z, DUCHOŇ T, WANG H, et al. AP-XPS/IRRAS study of ethanol steam reforming over Ni–CeO₂ model and powder catalysts[J]. Phys Chem Chem Phys, 2016, 18(24): 16621–16628.
- [54] QIAO W, ZHANG L, ZHANG K, et al. Low temperature synthesis of Cu_{1-x}Al_{2.5} spinel solid solution as sustained release catalyst for methanol to hydrogen[J]. Int J Hydrogen Energy, 2022, 47(75): 32133–32144.
- [55] KONSOLAKIS M, IOAKIMIDIS Z, KRAIA T, et al. Hydrogen production by ethanol steam reforming (ESR) over CeO₂-supported transition-metal (Fe, Co, Ni, Cu) catalysts: Insight into the structure–activity relationship[J]. Catalysts, 2016, 6(3): 39.
- [56] FENG X, ZHAO Y, WANG H, et al. A mini-review on recent progress of steam reforming of ethanol[J]. RSC Adv, 2023, 13(35): 24695–24717.
- [57] LIGURAS D K, KONDARIDES D I, VERYKIOS X E. Production of hydrogen for fuel cells by steam reforming of ethanol over supported noble metal catalysts[J]. Appl Catal B: Environ, 2003, 43(4): 345–354.
- [58] MARQUEVICH M, CZERNIK S, CHORNET E, et al. Hydrogen from biomass: Steam reforming of model compounds of fast-pyrolysis oil[J]. Energy Fuels, 1999, 13(6): 1160–1166.
- [59] PALMA V, CASTALDO F, CIAMBELLI P, et al. On the activity of bimetallic catalysts for ethanol steam reforming[J]. Int J Hydrogen Energy, 2014, 39(31): 18005–18017.
- [60] ZHANG B, CAI W, LI Y, et al. Hydrogen production by steam reforming of ethanol over an Ir/CeO₂ catalyst: Reaction mechanism and stability of the catalyst[J]. Int J Hydrogen Energy, 2008, 33(16): 4377–4386.
- [61] JIAO J, MURAKAMI K, ITAMI K. Catalytic methods for aromatic C–H amination: An ideal strategy for nitrogen-based functional molecules[J]. ACS Catal, 2016, 6(2): 610–633.
- [62] SANTAMARIA L, LOPEZ G, ARREGI A, et al. Progress on catalyst development for the steam reforming of biomass and waste plastics pyrolysis volatiles: A review[J]. Energy Fuels, 2021, 35(21): 17051–17084.
- [63] WANG Z, LI Y, ZHANG B, et al. A review of waste-to-hydrogen conversion technologies for solid waste management: Opportunities and challenges[J]. Renewable Sustainable Energy Rev, 2023, 175: 113184.
- [64] LI S, GONG J. Ethanol steam reforming over Ni/MO_x (M = Ce, La, Zr and Mg) catalysts supported on carbon

- nanotubes in an electric field[J]. J Power Sources, 2012, 216: 281–290.
- [65] ADHIKARI S, FERNANDO S, HARYANTO A. A comparative thermodynamic and experimental analysis on hydrogen production by steam reforming of glycerin[J]. Energy Fuels, 2007, 21(4): 2306–2310.
- [66] BOBADILLA L F, PENKOVA A, ROMERO-SARRIA F, et al. Influence of the acid–base properties over NiSn/MgO–Al₂O₃ catalysts in the hydrogen production from glycerol steam reforming[J]. Int J Hydrogen Energy, 2014, 39: 5704–5712.
- [67] ZHANG X, LIU S, XUE F, et al. Ni catalysts supported on defective-fluorite La–Ce oxides for ethanol steam reforming: Structure–stability correlations and carbon evolution[J]. Mol Catal, 2026, 600: 116091.
- [68] BATISTA M S, SANTOS R K S, ASSAF E M, et al. Characterization of the activity and stability of supported cobalt catalysts for the steam reforming of ethanol[J]. J Power Sources, 2003, 124(1): 99–103.
- [69] LAWRENCE N J, BREWER J R, WANG L, et al. Facet-dependent surface chemistry and oxygen vacancy formation on ceria nanocrystals[J]. ACS Appl Nano Mater, 2021, 4(7): 7421–7430.
- [70] ARAIZA D G, GÓMEZ-CORTÉS A, DÍAZ G. Effect of ceria morphology on the carbon deposition during steam reforming of ethanol over Ni/CeO₂ catalysts[J]. Catal Today, 2020, 349: 235–243.
- [71] KOURTELESIS M, MARNELLOS G E, KONSOLAKIS M. The effects of support morphology on the performance of Pt/CeO₂ catalysts for the low-temperature steam reforming of ethanol[J]. Appl Catal B: Environ, 2021, 284: 119757.
- [72] VECCHIETTI J, COMETTO F P, BONIVARDI A, et al. Shape-controlled pathways in ethanol steam reforming over ceria: A combined experimental and theoretical study[J]. ACS Catal, 2022, 12(17): 10482–10496.
- [73] SOYKAL I I, SOHN H, BENNETT J, et al. Reduction characteristics of ceria under ethanol steam reforming conditions[J]. ACS Catal, 2014, 4(2): 585–592.
- [74] TROVARELLI A, FORNASIERO P. Catalysis by Ceria and Related Materials (2nd ed.) [M]. London: Imperial College Press, 2013.
- [75] KIM S Y, WANG M, NGUYEN-PHU H, et al. Investigating the influence of Ni–Ce_xZr_{1–x}O₂ interaction on oxygen vacancy and catalytic behavior of Ni/Ce_xZr_{1–x}O₂ catalysts for ethanol steam reforming[J]. J Catal, 2022, 416: 240–252.
- [76] VECCHIETTI J, BONIVARDI A, LAPLACETTE G, et al. Ga-modified ceria (CeGaO_x) as support of Ni for ethanol steam reforming: Interfacial Ce–O–Ga sites promote oxygen mobility and acetate pathway[J]. Appl Catal B: Environ, 2020, 277: 119103.
- [77] GRZYBEK G, GORA-MAREK K, TARACH K, et al. Tuning the properties of the cobalt–zeolite nanocomposite catalyst by potassium: Switching between dehydration and dehydrogenation of ethanol[J]. J Catal, 2022, 407: 364–380.
- [78] WANG Y, SUN X, LIANG D, et al. Ethanol steam reforming for hydrogen production over alkali metals modified kaolin-supported Ni catalysts[J]. Int J Hydrogen Energy, 2025, 129: 113–129.
- [79] SUN Z, CHEN S, LIU T, et al. Tailoring lattice oxygen for sorption-enhanced steam reforming of ethanol[J]. Appl Catal B: Environ, 2022, 316: 121642.
- [80] GU Z, ZHOU J, AN X, et al. A dual-biomimetic photocatalytic fuel cell for efficient electricity generation from degradation of refractory organic pollutants[J]. Appl Catal B: Environ, 2021, 298: 120501.
- [81] PIZZOLITTO C, MENEGAZZO F, GHEDINI E, et al. Ethanol steam reforming on lanthanum Ni–ZrO₂ catalysts[J]. ACS Sustainable Chem Eng, 2020, 8(28): 10756–10766.
- [82] XIAO Z, LI G, HOU F, et al. Engineering oxygen vacancies and nickel dispersion on CeO₂ by Pr doping for highly stable ethanol steam reforming[J]. Appl Catal B: Environ, 2019, 258: 117940.
- [83] GO G S, LEE H J, MOON D J, et al. Glycerol steam reforming over Ni–Fe/Al₂O₃ for hydrogen production[J]. Res Chem Intermed, 2016, 42(2): 289–304.
- [84] DA SILVA A L M, DEN BREEJEN J P, MATTOS L V, et al. Cobalt particle size effects on catalytic performance for ethanol steam reforming—smaller is better[J]. J Catal, 2014, 318: 67–74.
- [85] PARLETT C M A, AYDIN M, DURNDELL L J, et al. Ethanol steam reforming on Ni/KIT-6 catalysts: Influence of mesostructure on metal particle size and catalytic performance[J]. ACS Catal, 2016, 6(12): 7878–7892.
- [86] GRELUK M, GAC W, ROTKO M, et al. Co/CeO₂ and Ni/CeO₂ catalysts for ethanol steam reforming: Effect of the cobalt/nickel dispersion on catalysts properties[J]. J Catal, 2021, 393: 159–178.
- [87] ZHANG L, JACKSON S D. Structure sensitivity of ethanol steam reforming over Rh catalysts[J]. ACS Catal, 2014, 4(2): 448–456.
- [88] FERMOSSO J, HE L, CHEN D. Production of high-purity hydrogen by sorption-enhanced steam reforming of crude glycerol[J]. React Chem Eng, 2018, 3(6): 883–897.
- [89] WU Z, YANG F. Structure sensitivity of ethanol steam reforming over the Rh catalyst: Reaction kinetics and deactivation mechanisms[J]. Appl Surf Sci, 2023, 614: 156116.
- [90] SRISIRIWAT N, THERDTHIANWONG S, THERDTHIANWONG A. Oxidative steam reforming of ethanol over Ni/Al₂O₃ catalysts promoted by CeO₂, ZrO₂ and both CeO₂–ZrO₂[J]. Int J Hydrogen Energy, 2009, 34(5): 2224–2234.
- [91] VALECILLOS J, BILBAO J, GAYUBO A G, et al. Insights into the reaction routes for H₂ formation in the ethanol steam reforming on a catalyst derived from NiAl₂O₄ spinel[J]. Energy Fuels, 2021, 35(21): 17197–17211.
- [92] SADANANDAM G, LALITHA K, KUMARI V D, et al. A study to initiate development of sustainable Ni/γ-Al₂O₃ catalyst for hydrogen production from steam reforming of biomass-derived glycerol[J]. RSC Adv, 2014, 4(61): 32429–32438.
- [93] MOOGI S, NAKKA L, POTHARAJU S S P, et al. Copper-

- promoted Co/MgO: A stable and efficient catalyst for glycerol steam reforming[J]. Catalysts, 2021, 11(12): 1455.
- [94] ZHAO L, WANG Q, HE H, et al. Single-atom Rh on high-index CeO₂ facet for highly enhanced catalytic CO oxidation[J]. Catal Sci Technol, 2025, 15(13): 3613–3623.
- [95] PENG M, GE Y, GAO R, et al. Thermal catalytic reforming for hydrogen production with zero CO₂ emissions[J]. Science, 2025, 387(6708): eadt0682.
- [96] LI D, ZENG L, LI X, et al. Concerted catalysis of single atom and nanocluster enhances bio-ethanol reforming for hydrogen production[J]. Nat Commun, 2025, 16: 3935.
- [97] NICHELE V, SIGNORETTO M, MENEGAZZO F, et al. Ni-modified CeO₂ and ZrO₂ catalysts for low-temperature ESR[J]. Mol Catal, 2014, 392: 63–73.
- [98] LIU Q, LI C, WU H, et al. Hydrogen production by ethanol reforming on supported Ni–Cu catalysts[J]. ACS Omega, 2022, 7(7): 6038–6050.
- [99] RODRÍGUEZ-GÓMEZ A, CABALLERO A, Bimetallic Ni–Co/SBA-15 catalysts for reforming of ethanol: How cobalt modifies the nickel metal phase and product distribution[J]. Mol Catal, 2018, 449: 122–130.
- [100] BRAGA A H, DE OLIVEIRA D C, TASCHIN A R, et al. Steam reforming of ethanol using Ni–Co catalysts supported on MgAl₂O₄: Structural study and catalytic properties at different temperatures[J]. ACS Catal, 2021, 11(4): 2047–2061.
- [101] WU Y, PEI C, TIAN H, et al. Role of Fe species of Ni-based catalysts for efficient low-temperature ethanol steam reforming[J]. JACS Au, 2021, 1(10): 1758–1767.
- [102] PALMA V, CASTALDO F, CIAMBELLI P, et al. CeO₂-supported Pt/Ni catalyst for the renewable and clean H₂ production via ethanol steam reforming[J]. Appl Catal B: Environ, 2014, 145: 73–84.
- [103] CHAGAS C A, MANFRO R L, TONIOLO F S. Production of hydrogen by steam reforming of ethanol over Pd-promoted Ni/SiO₂ catalyst[J]. Catal Lett, 2020, 150: 3424–3436.
- [104] CAMPOS C H, OSORIO-VARGAS P, et al. Improved hydrogen production by glycerol aqueous-phase reforming using NiRh bimetallic catalysts supported on La–Ce–Al mixed oxides[J]. Sustainable Energy Technol Assess, 2019, 35: 81–91.
- [105] SIERRA S P, et al. Bimetallic Ni–Co catalysts supported on a nanosilica matrix for ESR: Influence of the ionic liquid template IL/Si molar ratio on the catalytic performance[J]. RSC Adv, 2023, 13(50): 40165–40188.
- [106] REYNOSO-ESTÉVEZ A J, SÁNCHEZ-ARRIAGA M C, IRIONDO A. Aqueous-phase reforming of glycerol over Pt–Co catalyst: Effect of process variables[J]. J Environ Chem Eng, 2022, 10(2): 107402.
- [107] SILVA J M, RIBEIRO L S, ORFÃO J J M, et al. Low-temperature glycerol steam reforming over a Rh-based catalyst combined with oxidative regeneration[J]. Int J Hydrogen Energy, 2019, 44(5): 2461–2473.
- [108] CHOONG C K S, DU Y, POH C K, et al. Structural understanding of IrFe catalyst for renewable hydrogen production from ethanol steam reforming[J]. Appl Catal B: Environ, 2024, 345: 123630.
- [109] DAI R, ZHENG Z, YAN W, et al. Dragon fruit-like Pt–Cu@mSiO₂ nanocomposite as an efficient catalyst for low-temperature ethanol steam reforming[J]. Chem Eng J, 2020, 379: 122299.
- [110] XUE Q, LI Z, YAN B, et al. Mesoporous silica encapsulated core–shell NiRh@NiO nanocatalyst for performance-enhanced ethanol steam reforming[J]. J Catal, 2024, 434: 115536.
- [111] LI D, ZENG X, WANG X, et al. Ceria-promoted Ni/SBA-15 catalysts for ethanol steam reforming with enhanced activity and resistance to deactivation[J]. Appl Catal B: Environ, 2015, 176–177: 532–541.
- [112] GRELUK M, ROTKO M, TURCZYNIAK-SURDACKA S. Enhanced catalytic performance of La₂O₃ promoted Co/CeO₂ and Ni/CeO₂ catalysts for effective hydrogen production by ethanol steam reforming[J]. Renew Energy, 2020, 155: 378–395.
- [113] TIAN H, PEI C, WU Y, et al. Tunable metal–oxide interaction with balanced Ni⁰/Ni²⁺ sites of Ni₁Mg_{1–x}O for ethanol steam reforming[J]. Appl Catal B: Environ, 2021, 293: 120178.
- [114] EBIAD M A, ABD EL-HAFIZ D R, ELSALAMONY R A, et al. Ni supported high surface area CeO₂–ZrO₂ catalysts for hydrogen production from ethanol steam reforming[J]. RSC Adv, 2012, 2(21): 8145–8156.
- [115] SOSA L F, SULLER GARCIA M A, SILVA A C A, et al. Highly efficient low metal content Ni/CeO₂ catalysts prepared by magnetron sputtering deposition for ethanol steam reforming reaction[J]. Appl Catal B: Environ, 2025, 365: 124940.
- [116] MIZUNO S C M, BRAGA A H, HORI C E, et al. Steam reforming of acetic acid over MgAl₂O₄-supported Co and Ni catalysts: Effect of the composition of Ni/Co and reactants on reaction pathways[J]. Catal Today, 2017, 296: 144–153.
- [117] ALIZADEH SAHRAEI O, DESGAGNÉS A, LARACHI F, et al. Hydrogen production from glycerol steam reforming over Ni-promoted Fe/Mg-bearing metallurgical wastes: performances and deactivation[J]. Appl Catal B: Environ, 2017, 219: 183–193.
- [118] ZHU S, HE S, LU J, et al. Regulating and stabilizing strong metal–support interactions on Ni/TiO₂ by crystal phase for ultra-stable ethanol reforming[J]. Adv Energy Mater, 2024, 14(47): 2402295.
- [119] MENG H, YANG Y, SHEN T, et al. A strong bimetal–support interaction in ethanol steam reforming[J]. Nat Commun, 2023, 14: 3189.
- [120] SMAL E A, SIMONOV M N, MEZENTSEVA N V, et al. Spinel-type Mn_xCr_{3–x}O₄-based catalysts for ethanol steam reforming[J]. Appl Catal B: Environ, 2021, 283: 119656.
- [121] LIAO M, QIN C, XU L, et al. Quinary metal oxide NiCoMnCeCaO_x nanorod as a multifunctional catalyst towards hydrogen production from ethanol steam reforming: Synergistic effect of polymetallic component[J]. Chem Eng J, 2024, 497: 154646.
- [122] LIAO M, WANG C, CHEN Y, et al. Self-reconstruction mechanism of high-entropy oxide in glycerol steam reforming: The key to H₂-rich syngas production[J]. ACS Catal, 2025, 15(6): 4845–4857.

生物质醇蒸汽重整制氢多相催化研究进展: 从乙醇到甘油体系的催化构效关系

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摘 要: 生物质衍生醇(乙醇、乙二醇、甘油等)蒸汽重整制氢是可再生氢能体系的关键路径。本工作综述了该领域多相催化研究进展, 阐明不同生物质醇分子结构对反应路径与催化剂需求的构效关联: 乙醇易受脱水及甲烷化等副反应制约; 乙二醇借助双羟基结构强化脱氢与 C-C 断裂, 提升氢选择性; 甘油则因三羟基结构加剧路径复杂化与积炭失活倾向。催化设计共性策略在于, 通过精准调控金属电子结构(如合金化/原子级分散)与载体氧迁移性(如稀土改性), 协同优化脱氢与抗积炭性能。Ni 基催化剂以低成本与高 C-C 键活化能力占据核心地位, 其稳定性需借 Fe、Co、Cu 等合金化或 Ce、Pr、La 稀土改性协同提升; 贵金属体系(Pt、Rh、Ir 等)虽具低温活性优势, 受成本制约正向单原子催化及高熵氧化物基多元催化体系拓展。未来需融合原位/工况表征与理论模拟揭示动态构效关系, 构建基元反应数据库并驱动数据导向的理性设计, 实现催化剂-反应器跨尺度协同, 为可再生氢能高效转化提供科学支撑。

关键词: 生物质醇; 蒸汽重整制氢; 多相催化; 构效关系; 抗积炭

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