

Review

Recent Advances in Catalyst Design and Process Intensification for Ethanol Steam Reforming

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Abstract

Producing hydrogen from ethanol steam reforming (ESR) is a carbon-neutral and environment-friendly method, which has been expected to reduce the excessive emission of environmental pollution and over-exploitation of fossil resources. Currently, great advances have been made on heterogeneous catalysts, but an in-depth and more comprehensive understanding to further promote this reaction process is still required. Herein, the thermodynamic and kinetic analyses of ESR are firstly highlighted. Then, various reaction pathways of ESR are discussed in detail, respectively combined with experimental studies and density functional theory calculations. On this basis, the key factors affecting the catalytic performance over non-noble and noble metal catalysts are summarized, such as alloying, optimization of the preparation methods, promoter addition and support modification. In addition, the process intensification technologies, including catalytic membrane reactors, adsorption-enhanced reforming and microchannel reactors, are analyzed regarding breaking the thermodynamic limitations and improving the heat and mass transfer efficiency. Finally, the challenges and potential strategies of ESR in the research of dynamic reaction mechanisms, regulation of catalyst stability and integration of intensification technologies are summarized.

Keywords: ethanol steam reforming; hydrogen production; catalyst design; process intensification



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1. Introduction

Hydrogen has attracted widespread attention as a promising clean secondary energy carrier, owing to its high mass energy density (40 kW·h/kg) and calorific value (1.4×10^8 J/kg). Nevertheless, hydrogen exhibits a low volumetric energy density of only 3.0 Wh/L under ambient temperature and pressure, which poses great challenges to its storage and transportation [1]. The key to the large-scale application of hydrogen lies in the development of safe and efficient production methods [2]. In particular, alcohol steam reforming has been considered as an attractive method because the liquid alcohols have safe and convenient storage and transportation processes under ambient conditions [3]. Among the various alcohols, ethanol has been developed as the best candidate due to its high theoretical hydrogen storage capacity (~6.1 wt.%), non-toxicity, storage and transport in liquid form. Moreover, ethanol is predominantly available as a bio-based product, derivable from starch-rich feedstocks including sugarcane [4] and corn [5], as well as from lignocellulosic biomass [6] (e.g., agricultural and forestry residues) [7]. Therefore, ethanol

steam reforming (ESR) emerges as a promising pathway to facilitate renewable energy generation and enable the efficient utilization of biogenic carbon resources.

Generally, the ethanol steam reforming (ESR) process primarily involves the breakage of O-H, C-H, and C-C, showing a high and similar dissociation energy of (463 kJ/mol) (413 kJ/mol), and (347 kJ/mol), respectively. This results in high activation energy barriers and complex parallel and sequential reaction pathways, including dehydration, dehydrogenation, cracking, and water–gas shift reactions [8,9]. Thermodynamically, ESR is a strongly endothermic process accompanied by a net increase in the number of gaseous molecules, making it favorable under high temperatures (>400 °C) and low pressures [10]. These severe reaction conditions often may induce sintering of the active metal phases and carbon deposition on catalysts, resulting in poor catalytic performances [11]. Therefore, the rational design of supported metal catalysts (active components such as Ni [12], Co [13], and Rh [14]; supports such as CeO₂ [15] and Al₂O₃ [16]) is crucial for improving the catalytic performance of ESR.

Recent years have witnessed significant progress in ESR, particularly in the design of efficient heterogeneous catalysts, the application of in situ characterization techniques, and the use of theoretical calculations to probe reaction intermediates and optimize reactor configurations. Furthermore, a number of review articles have documented advances in ESR, though most have centered on facets of the field, such as reaction mechanistic studies [17], catalyst preparation [18,19], or the optimization of reaction conditions [20]. Nevertheless, identifying the key factors that govern catalytic performance remains challenging due to the complex interplay of multiple variables. In order to improve the process of ESR, it is necessary to provide an in-depth and more comprehensive understanding, from the reaction mechanisms to the effective preparation catalysts and their systematic investigations.

Herein, we first summarize the reaction mechanism of ESR through thermodynamic and kinetic analyses. The effects of modification strategies including alloying, synthesis optimization, promoter addition and support design on improving the activity of non-noble and noble metal catalysts are highlighted. Subsequently, recent advances in process intensification technologies such as catalytic membrane reactors, sorption-enhanced reforming, and microchannel reactors are further summarized. Finally, we put forward the current crucial challenges and potential strategies for the future design and characterization of efficient and stable catalytic systems, so as to further encourage future investigation for this promising field.

2. Reaction Characteristics of Ethanol Steam Reforming

2.1. Thermodynamics Analysis

Ethanol steam reforming is typically represented as: ethanol (C₂H₅OH) reacts with steam (H₂O) to form hydrogen (H₂) and carbon dioxide (CO₂). The ESR reaction is a highly endothermic process with an increasing number of molecules, so it is more favorable in a higher temperature (400–700 °C) and lower pressure. The severe reaction conditions are prone to causing a series of side reactions, including ethanol dehydration, decomposition, and dehydrogenation, followed by the formation various by-products such as CO, CH₄, acetaldehyde (CH₃CHO), acetone (CH₃OCH₃), and ethylene (C₂H₄). Additionally, the exothermic side reactions, e.g., the water–gas shift and Boudouard reactions, become dominant at lower temperatures, leading to a reduction in hydrogen selectivity and yield. Thus, ESR is usually regarded as a complex reaction system, involving the numerous parallel and sequential reactions in Table 1 [21,22].

The ethanol steam reforming (ESR) reaction system involves multiple chemical equilibria, making thermodynamic analysis essential for evaluating reaction limits and optimizing operating conditions. The Gibbs free energy minimization method, implemented via the

HSC Chemistry 6 (version 6.00) software [23], is employed to assess the thermodynamic equilibrium behavior. This approach directly calculates the equilibrium composition under specified conditions without presupposing any reaction pathways. The effects of the temperature (300–900 °C), steam-to-ethanol (S/E) molar ratio (1–6), and pressure (1–20 bar) on the hydrogen selectivity and product distribution are systematically investigated.

Table 1. Main and side reactions and reaction for hydrogen production via ethanol steam reforming.

No.	Reaction Name	Reaction	ΔH_r , 298 K KJ·mol ^{−1}
1	Ethanol Steam Reforming	$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2$	+174
2	Ethanol Partial Reforming	$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2$	+256
3	Ethanol Dehydration	$C_2H_5OH \rightarrow C_2H_4 + H_2O$	+45
4	Ethylene Steam Reforming	$C_2H_4 + 4H_2O \rightarrow 2CO_2 + 6H_2$	+127.7
5	Ethanol Decomposition	$C_2H_5OH \rightarrow CO + CH_4 + H_2$	+49
6	Ethanol Dehydrogenation	$C_2H_5OH \rightarrow CH_3CHO + H_2$	+111.5
7	Acetaldehyde Condensation	$2CH_3CHO \rightarrow CH_3COCH_3 + CO + H_2$	+4.1
8	Methane Steam Reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	+206
9	Water–Gas Shift Reaction	$CO + H_2O \rightarrow CO_2 + H_2$	−41
10	CO Methanation	$CO + 3H_2 \rightarrow CH_4 + H_2O$	−206
11	Boudouard Reaction	$2CO \rightarrow CO_2 + C$	−172.5
12	Methane Decomposition	$CH_4 \rightarrow C + 2H_2$	+74.6
13	Ethylene Polymerization	$nC_2H_4 \rightarrow C_{2n} + 2nH_2$	/

As illustrated in Figure 1a, the ESR reaction becomes increasingly favorable as the temperature rises. Above 350 °C, the ESR dominates, while the methanation reaction is suppressed, resulting in a product composition primarily consisting of H₂, CO, and CO₂. Moreover, the mole fraction of hydrogen in the outcome increases with the temperature elevating, as in Figure 1b. Meanwhile, the thermodynamic equilibrium content of by-product CH₄ decreases, probably due to suppression by the high temperature. According to Figure 1c, increasing the S/E ratio promotes H₂ selectivity, because it favors the water–gas shift reaction toward the product side. In addition, the higher pressure inhibits the H₂ selectivity, affected by the increasing mole number reaction (Figure 1d). A high temperature, low pressure, and moderate S/E ratio are favorable for the main ESR reaction. Therefore, when comparing the performance of different catalysts, the differences in reaction conditions should be comprehensively considered.

2.2. Reaction Pathway

To provide critical guidance for the rational design of efficient catalysts, various possible reaction paths are summarized and proposed in Figure 2 (pathway A), based on recent theoretical and experimental advances for ESR. Among these ways, the activation of ethanol on the catalyst surface usually serves as the key step, which primarily is divided into parallel dehydrogenation and dehydration paths.

2.2.1. Dehydrogenation Pathway

The dehydrogenation pathway refers to the preferential dehydrogenation of ethanol to ethoxide (CH₃CH₂O*) in Figure 2 (pathway B). Then, ethoxide is successively converted into the acetaldehyde (CH₃CHO*), acetyl (CH₃CO*), ketene (CH₂CO*), ketylenyl (CHCO*), acetate (CH₃COO*), methyl (CH₃*), and other intermediate species. Meanwhile, H₂O, as another reactant, dissociates into active OH* species, which is used to react with the C1 intermediates above to form CO₂. CO, via the water–gas shift (WGS) reaction, is

further converted into CO_2 and H_2 . This pathway is usually subdivided into the stepwise dehydrogenation and acetate pathways [24].

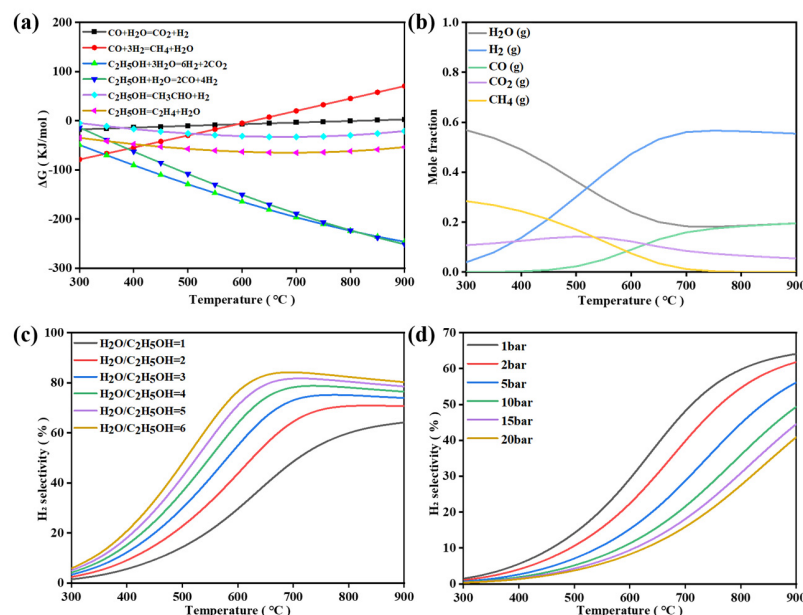


Figure 1. (a) Gibbs free energy as a function of reaction temperature. (b) Gaseous products as a function of temperature at atmospheric pressure and a S/E ratio of one. (c) Hydrogen selectivity as a function of temperature at different S/E ratios with atmospheric pressure. (d) Hydrogen selectivity as a function of temperature at different pressures, with a S/E ratio of one.

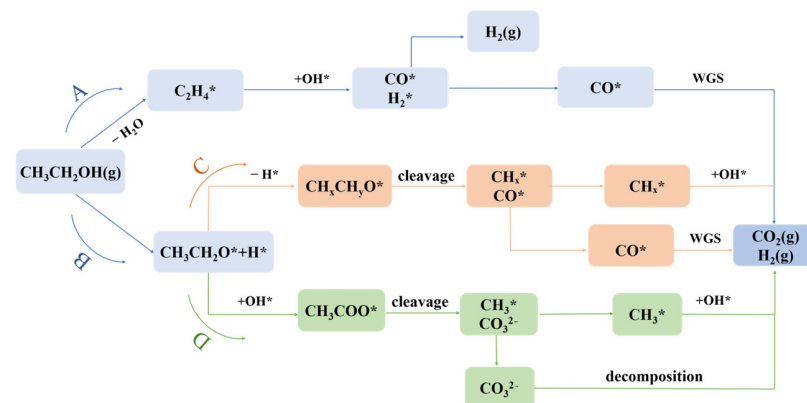


Figure 2. Various reaction pathways of ESR. A, dehydration pathway; B, dehydrogenation pathway; C, stepwise dehydrogenation pathway; D, acetate pathway. "*" denotes surface-adsorbed species.

Stepwise Dehydrogenation Pathway

The stepwise dehydrogenation pathway involves the sequential removal of hydrogen atoms from ethanol to form a series of oxygen-containing intermediates $\text{CH}_x\text{CH}_y\text{O}^*$, following by C-C bond cleavage and subsequent oxidation to form CO_2 , as shown in Figure 2 (pathway C). Previous studies found $\text{CH}_3\text{CH}_2\text{O}^*$ on the catalyst surface by means of operando DRIFTS experiments, attributed to ethanol dissociation in the first step of ESR [25,26]. Grzybek et al. [27] reported that the energy barrier for acetaldehyde desorption (1.27 eV) is higher than that for C-H cleavage (0.79 eV) on $\text{KCo}/\alpha\text{-Al}_2\text{O}_3$ by density functional theory (DFT) calculations (Figure 3a), and the adsorbed acetaldehyde is dehydrogenated to acetyl (CH_3CO^*). Wu et al. [28] showed by DFT that C-C cleavage occurs on CH_2CO^* over Rh(111) terraces, but directly on CH_3CO^* over Rh(211) steps (Figure 3b). Ma et al. [29] found that continuous dehydrogenation of ethoxy to $\text{CH}_x\text{CH}_y\text{O}^*$ intermediates is the rate-determining step.

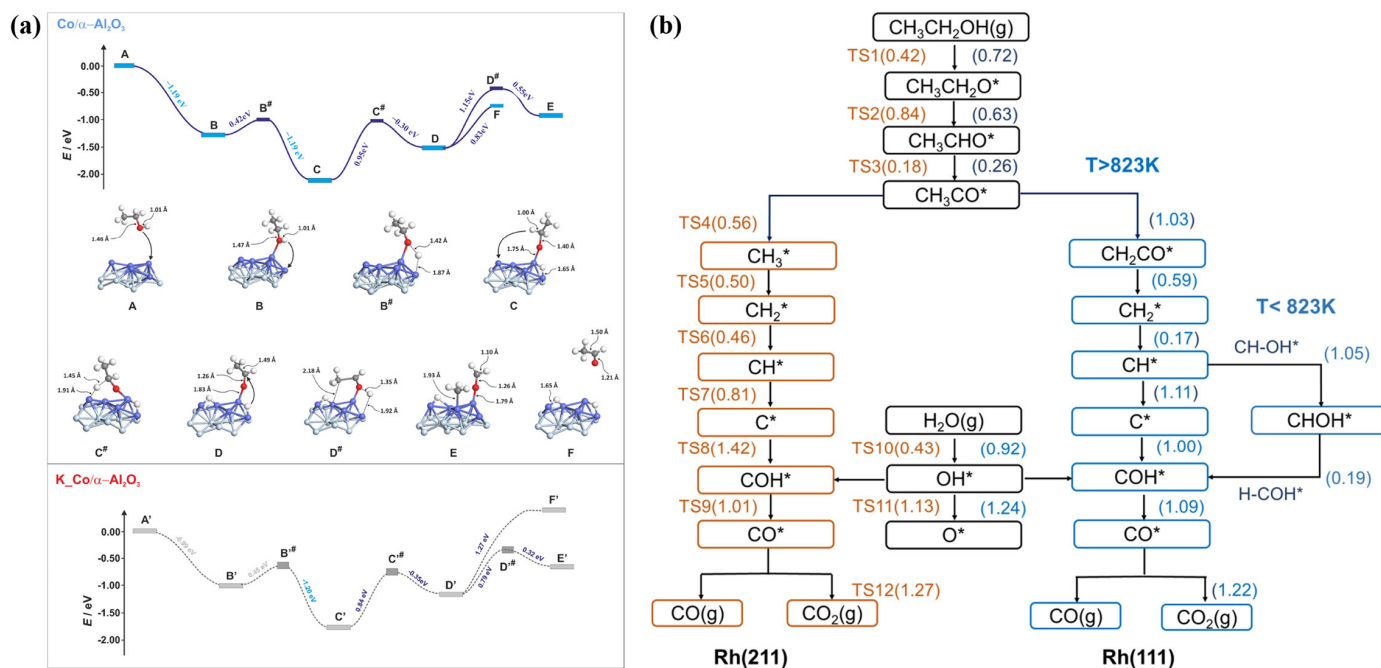


Figure 3. (a) Comparison of the energy profiles and geometries of key intermediates for ethanol steam reforming on bare versus potassium-doped Co/α-Al₂O₃ catalysts [27]. (b) Main reaction pathways and energy barriers for ethanol steam reforming to CO and CO₂ on Rh(211) and Rh(111) surfaces over the temperature range of 450–800 °C [28]. “*” denotes surface-adsorbed species; “#” indicates a transition state.

Acetate Pathway

As for the acetate pathway in Figure 2 (pathway D), ethoxy intermediates are further oxidized by surface oxygen species to form acetate (CH₃COO*). Acetate decomposes into CH₃* and surface carbonate species. Then, CH₃* reacts with OH* from water dissociation to form CO₂ and H₂, and the carbonate species subsequently decomposes into CO₂. This decarboxylation pathway is common on CeO₂-based catalysts (e.g., Ni/CeMgAl and Ni-CeO₂/MgAl₂O₄) [30]. Ogo et al. [31] found that CH₃CH₂O* is oxidized by surface oxygen to acetate using H/D exchange and in situ infrared spectroscopy experiments. Xu et al. [25] identified characteristic bands of CH₃CH₂O* species at ~1050 and 1110 cm^{−1} and CH₃COO* species at ~1430 and 1560 cm^{−1} via in situ DRIFTS (Figure 4), confirming the reaction sequence of CH₃CH₂O* converting to CH₃COO*, carbonate, OH* and CH₃* intermediates.

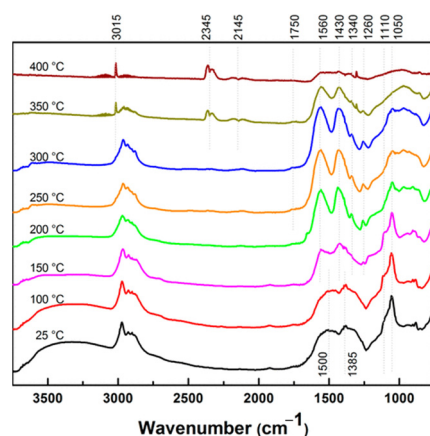


Figure 4. DRIFTS spectra for Ni/CeO₂ at elevating temperatures in a pure EtOH vapor environment [25].

2.2.2. Dehydration Pathway

In the dehydration pathway, $\text{CH}_3\text{CH}_2\text{OH}$ dehydrates to C_2H_4 , which, as a key intermediate, may react with water to produce CO_2 and H_2 , or directly dehydrogenate to form coke. The ethylene was detected by gas chromatography (GC) studied by Iglesias-Vázquez et al. [32] and Choong et al. [33], indicating the ethanol dehydration pathway. Valecillos et al. [34] conducted ethylene and water co-feeding experiments with online micro-GC analysis at 500 and 600 °C (Figure 5), using a steam/ethylene ratio of three. The products included H_2 , CO , and CO_2 , with a distribution similar to ethanol steam reforming. In contrast, a pure ethylene feed without water only produced H_2 and carbon. This means that ethylene undergoes steam reforming in the presence of water, and CO is further converted to CO_2 and H_2 via the water–gas shift reaction.

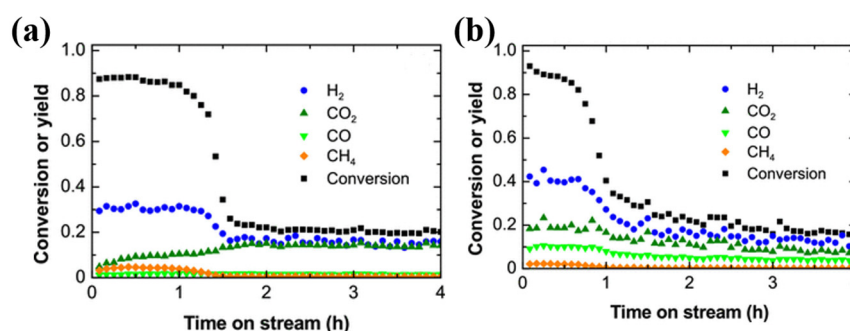


Figure 5. Evolution with time on stream of the ethylene conversion and product yields for ethylene steam reforming at (a) 500 and (b) 600 °C. Reaction conditions: equivalent space time, 0.025 h; ethylene partial pressure, 0.05 bar; steam/ethylene/ N_2 molar ratio, 3:1:16 [34].

3. Catalysts for Ethanol Steam Reforming

Metals with unpaired outer d-electrons can interact with the C–C, O–H, and C–H bonds and some oxygen-containing intermediates, which may promote ethanol activation. Thus, supported metal catalysts are usually used for hydrogen production by ESR, which are generally divided into non-noble metal (e.g., Ni, Co, and Cu) and noble metal (e.g., Rh, Ru, and Pt)-based catalysts.

3.1. Ni-Based Catalysts

Nickel-based catalysts have attracted extensive attention due to their abundant reserves, low cost, and excellent C–C and C–H bond cleavage performance in ESR. However, Ni-based catalysts are easily sintered at high temperatures and promote the polymerization of intermediates such as C_2H_4 , leading to severe carbon deposition and catalyst deactivation. In recent years, researchers have adopted many strategies, including alloying, preparation optimization, support modification, and promoter addition, to improve Ni dispersion, tailor the surface electronic structure, and strengthen the metal–support interaction, thus significantly enhancing the activity, selectivity, and stability of Ni catalysts.

3.1.1. Incorporating Other Metals

Single Ni active sites usually show a high catalytic activity followed by some side reactions such as deep hydrogenation (methanation) and deep dehydrogenation (carbon deposition). To inhibit side reactions, reduce carbon deposition and improve stability, other metals (e.g., Cu, Co, Fe, etc.) are usually introduced to adjust the geometric structure and electronic properties of single Ni by means of forming bimetallic or multi-metallic Ni-based catalysts.

Co, as a common alloying component, is usually used to form NiCo alloy to modulate Ni properties. Aker et al. [35] reported that Ni–Co/ Al_2O_3 with a Ni/Co molar ratio of 2:1

achieves complete ethanol conversion and high H_2 selectivity (95.14%) at 600 °C, surpassing the ethanol conversion and H_2 selectivity of the monometallic Ni/ $MgAl_2O_4$ catalyst. This is because the CoNi alloy showed a higher metal dispersion and smaller metal particle size compared with the single Ni catalyst. In addition, the distinctive metal–oxide interfaces may be formed on a Co and Ni bimetallic catalyst, which could promote the conversion of reaction intermediates. Shi et al. [36] found that Co could be oxidized to CoO and form a Ni–CoO interface, in which the Ni^0 promoted the dissociation of C–C bonds and the interfacial CoO promoted the activation of H_2O to OH^* (surface-adsorbed hydroxyl species). Similarly, Fe shows dual roles of electronic modulation and carbon deposition inhibition in Ni-based catalysts. Wu et al. [37] prepared a series of NiFe/ $MgAl_2O_4$ catalysts, where Ni–Fe alloys of 7–9 nm formed. In situ DRIFTS, CO-TPD, and XPS analyses revealed the dual role of Fe species (Figure 6): Ni–Fe alloys weakened CO adsorption via electron transfer, suppressing methanation; meanwhile, the oxidation capacity of $\gamma\text{-Fe}_2O_3$ species promoted the transformation of ethoxy to acetate groups and the elimination of carbon deposits. At 400 °C, the H_2 yield increased from 2.7 mol H_2 /mol EtOH over the monometallic Ni catalyst to 4.6 mol H_2 /mol EtOH on the optimal NiFe bimetallic catalyst. In a 30 h stability test, the NiFe/ $MgAl_2O_4$ catalyst maintained high activity without obvious deactivation, whereas the unmodified Ni/ $MgAl_2O_4$ catalyst deactivated rapidly after 15 h due to severe carbon deposition covering the active sites.

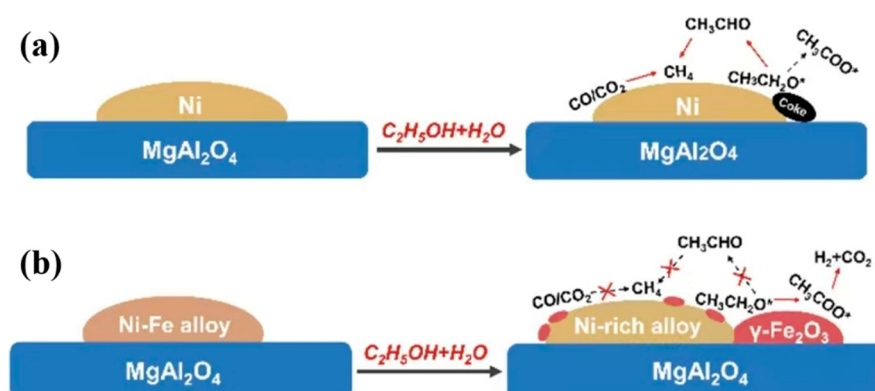


Figure 6. Reaction mechanism of Ni10/ $MgAl_2O_4$ and Ni10Fe10/ $MgAl_2O_4$ catalysts. (a) Proposed reaction pathway in ESR over a Ni10/ $MgAl_2O_4$ catalyst. (b) Proposed reaction pathway in ESR over a Ni10Fe10/ $MgAl_2O_4$ catalyst [37].

Apart from non-precious metals, precious metals also are used to form alloys and stabilize Ni nanoparticles. Meng et al. [38] prepared a series of RhNi/ TiO_2 catalysts via topological transformation of RhNiTi layered double hydroxides. The unique (Rh– $Ni^{\delta-}$ – O_v – Ti^{3+}) multifunctional interface may be formed by means of the strong bimetal–support interaction (Figure 7a). This interface could stabilize RhNi nanoparticles through a reversible TiO_2 overlayer, preventing active-site loss and sintering. At 400 °C, ethanol conversion reached 99.7% with stable activity over 300 h (Figure 7b,c), which is much higher than that of Ni/ TiO_2 (49.5%) and Rh/Ni (39.3%) catalysts after 40 h.

Recently, Ni-based multi-metal catalysts display the well abilities of cracking, oxidation, trapping, and reconstruction through the multi-metal synergistic effect. Liao et al. [39] prepared a nanorod-shaped quinary metal oxide $NiCoMnCeCaO_x$ via the coprecipitation method. The ethanol conversion of the optimal $NiCoMnCeCaO_x$ catalyst reached up to 99.92% and the hydrogen production rate was 120.5 $\mu\text{mol/s}$, which is 27.2% higher than that of unmodified NiCo/ CeO_2 , at 600 °C, an ethanol/water molar ratio of 1:3 and a space velocity of 44.79 h^{-1} . This is because the Mn and Ce may improve the lattice oxygen

mobility, enhancing CH_x and CO oxidation and reducing carbon deposition. Meanwhile, the basic sites generated from Ca could promote in situ adsorption of CO_2 .

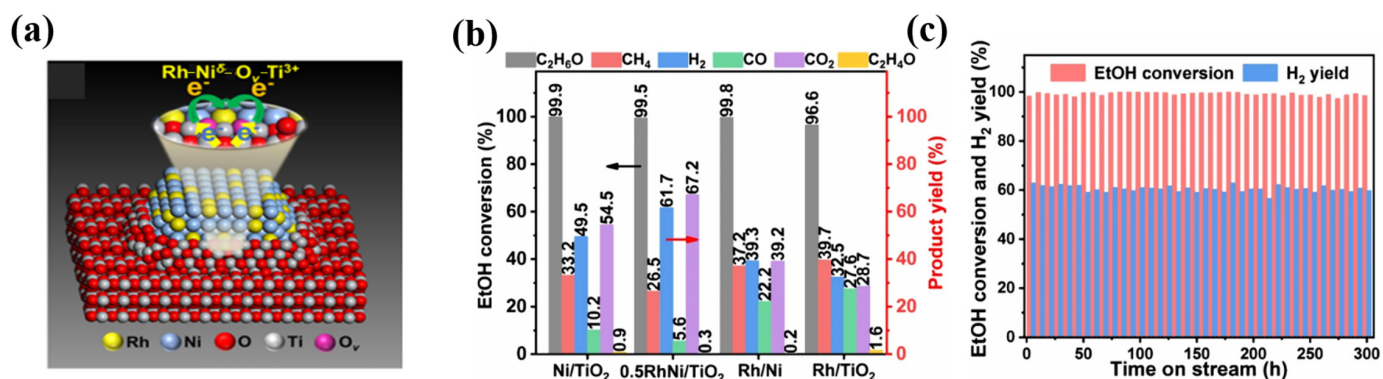


Figure 7. (a). Schematic diagram of the 0.5RhNi/TiO₂ catalyst. (b). Ethanol conversion, product yield (c). Time on stream (TOS) test of the 0.5RhNi/TiO₂ catalyst at 400 °C [38].

3.1.2. Optimizing Catalyst Preparation Methods

The catalyst preparation methods are usually regarded as the key factors regulating the structure and properties of active sites, including the impregnation, coprecipitation, hydrothermal and sol-gel methods, and so on. Alipour et al. [40] compared the ESR reaction performance of Ni/Al₂O₃ catalysts prepared by the mechanochemical, impregnation, and coprecipitation methods, respectively. Among them, the ethanol conversion achieved 92% and hydrogen yield was up to 86% with the impregnation method due to the higher specific surface area and Ni dispersion. Sosa et al. [41] studied the catalytic performance of Ni/CeO₂ catalysts prepared by magnetron sputtering deposition (SP) and incipient wetness impregnation (IWI) for the ESR reaction. The Ni/CeO₂-SP catalyst exhibited a higher ethanol conversion of 90% and H₂ yield of 8.1 L·h⁻¹·gcat⁻¹ at 500 °C, as seen in Figure 8, relative to the Ni/CeO₂-SP catalyst (60% and 5.8 L·h⁻¹·gcat⁻¹). This is because the former showed the highly dispersed Ni and abundant oxygen vacancies for the formation of weakly encapsulated graphitic carbon, while the latter may tend to form amorphous carbon and cover active sites.

Optimizing preparation methods can regulate the size distribution of Ni particles, and alter the morphology and migration behavior of carbon deposits. Bao et al. [42] prepared a series of Ni/SiC_xO_y catalysts with a “multi-size distribution” feature using inverse microemulsion and precipitation methods. The Ni/SiC_xO_y maintained good ethanol conversion (95%) and H₂ selectivity (69.2%) after 20 h, superior to the H₂ selectivity (56% after 20 h) of Ni/MgO at 500 °C and a steam/ethanol ratio of 8:1. The small Ni particle size may promote the formation of loose carbon nanowires instead of amorphous carbon, and accelerate carbon mass transfer to avoid coverage of active sites. Villagran-Olivares et al. [43] prepared a Ni/MgAl₂O₄-CeO₂ catalyst using an EDTA-assisted impregnation method. The introduction of EDTA reduced the NiO particle size and promoted the strong Ni-CeO₂ interaction, increasing the surface Ce³⁺ concentration and interfacial oxygen mobility. The carbon-containing intermediates may be efficiently oxidized to decrease the coking rate from 30.6 to 1.4 mgC/(gcat·h).

The structure of active phases can be modulated by different preparation methods. Chen et al. [44] reported that the Ni/Al₂O₃ catalyst prepared by the one-pot (OS) method achieved nearly complete ethanol conversion (99%), while the one synthesized by impregnation (IMP) only reached 74% and decreased to 58% after 55 h, at 500 °C and a S/E molar ratio of six. This was mainly attributed to the more active Ni⁰ species based on the highly dispersed NiO in Ni/Al₂O₃-OS. In contrast, the Ni/Al₂O₃-IMP catalyst displayed

a large amount of unreducible NiAl_2O_4 spinel and fewer active Ni^0 sites. Additionally, a suitable preparation method can regulate the electronic properties of Ni, such as the ratio of both Ni^0 and Ni^{2+} species. Ni^0 nanoparticles were responsible for C-C bond cleavage, whereas electron-deficient Ni^{2+} sites enriched in the support strengthened C-H activation and suppressed methanation. Tian et al. [45] synthesized a series of $\text{Ni}/\text{Ni}_x\text{Mg}_{1-x}\text{O}$ catalysts with unbalanced $\text{Ni}^0/\text{Ni}^{2+}$ ratios via a non-equilibrium two-step calcination method at the same total Ni loading (20 wt%). When applying in the ESR at 400 °C with a S/E of six, the pure solid solution without Ni^0 (15NiMg ss) showed only 20% ethanol conversion and 10% acetaldehyde formation, as in Figure 9a. In contrast, 10ss-5NiO with suitable Ni^0 (88.6% surface Ni^{2+}) achieved nearly complete ethanol conversion, with a H_2 yield of $11.5 \text{ L} \cdot \text{h}^{-1} \cdot \text{gcat}^{-1}$ and stable operation for 30 h due to the synergistic effect of balanced Ni^0 and Ni^{2+} , as seen in Figure 9b.

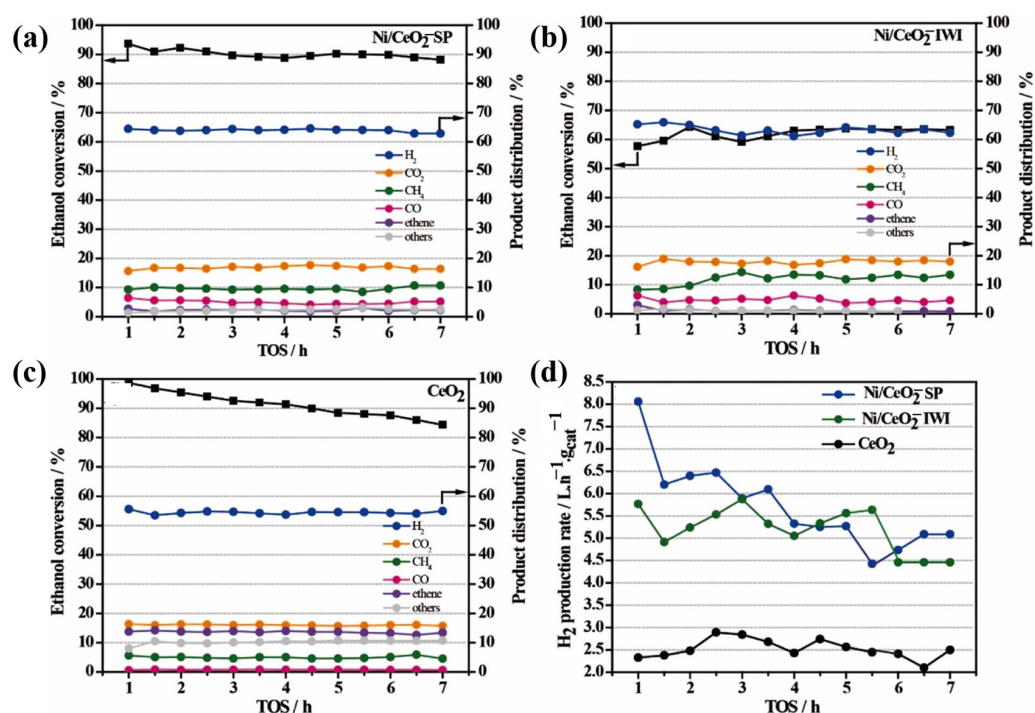


Figure 8. Ethanol conversion and product distribution for (a) Ni/CeO₂-SP and (b) Ni/CeO₂-IWI catalysts and (c) pure CeO₂. (d) H₂ production rate. Reaction conditions: 500 °C, S/E = 6, W/F = 0.2 gcat h/gEtOH [41].

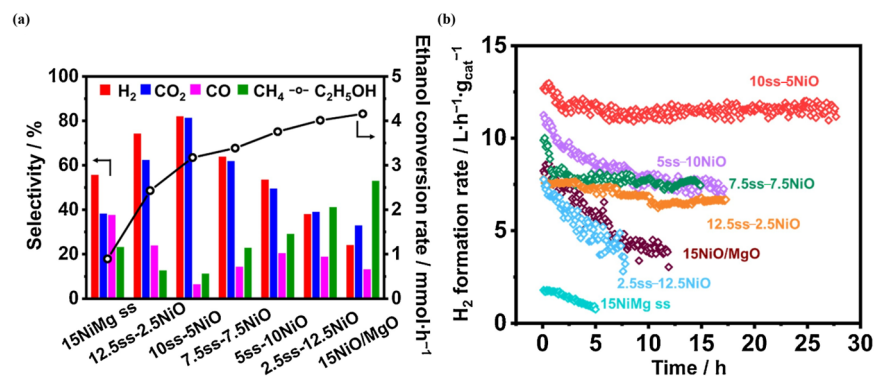


Figure 9. (a) Initial product distribution and ethanol conversion rate over different Ni/Ni_xMg_{1-x}O. (b) Stability test of Ni/Ni_xMg_{1-x}O [45].

3.1.3. Introducing Promoters

The promoters may modify the active site structure and influence the reaction performance, mainly including the rare-earth elements such as La and Pr, as well as alkali and alkaline-earth metals including K and Mg. Rare-earth metal promoters are commonly used to adjust the redox properties and stabilize nickel species in CeO₂-supported Ni-based catalysts. Xiao et al. [46] prepared a La-doped Ni-CeLa_{0.2} catalyst, achieving a high ethanol conversion of 100% and a low coking rate of 0.48 mgC/(g_{cat}·h) at 600 °C; the unmodified Ni-CeO₂ showed a stability of 70.1% with a coking rate of 2.60 mgC/(g_{cat}·h). DFT calculations indicated that La doping reduced the formation energy of oxygen vacancies on the CeO₂ surface to −0.96 eV (Figure 10a). The formation of oxygen vacancies significantly promoted water molecule dissociation (energy barrier of −0.25 eV) (Figure 10b), which in turn promoted the gasification of surface carbon species.

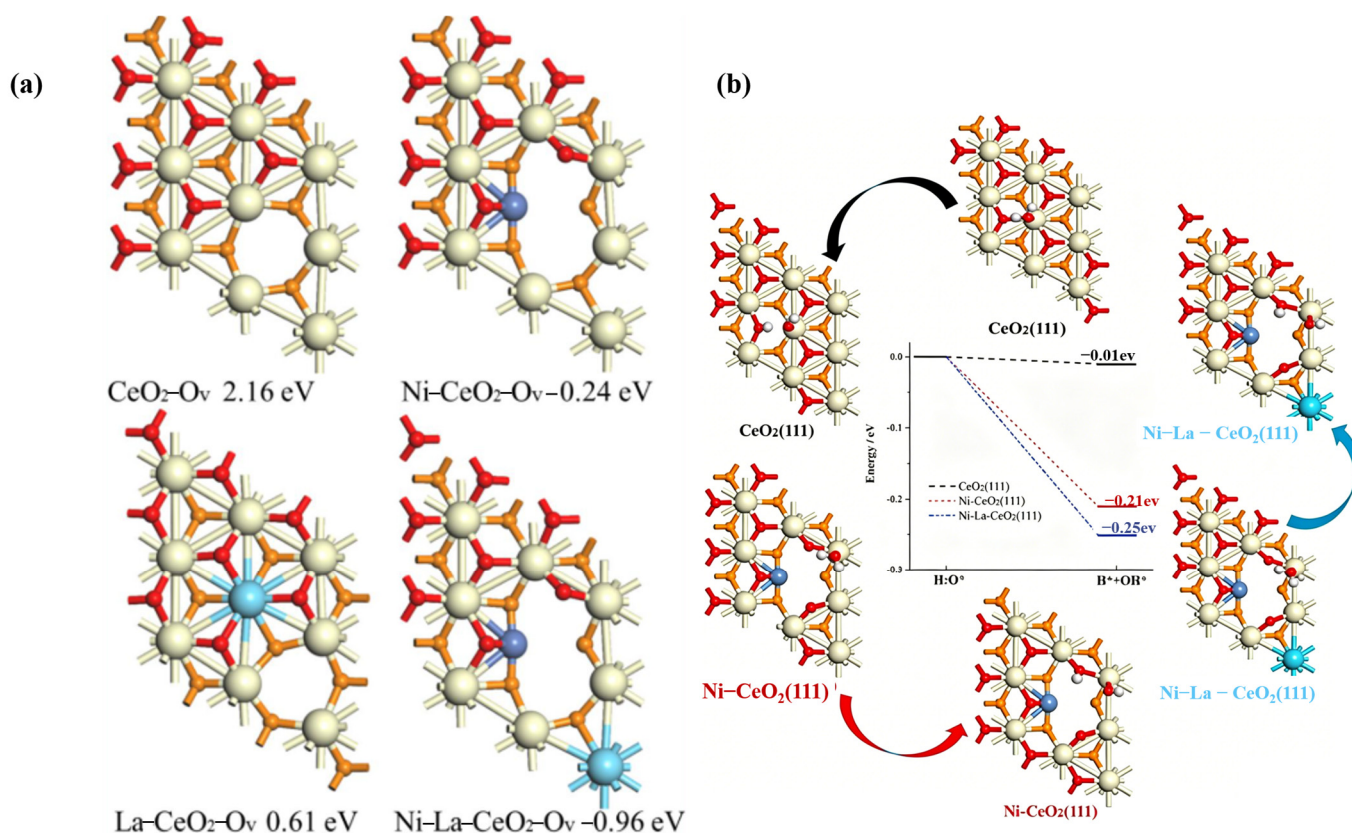


Figure 10. (a) Top view of various structures with oxygen vacancies and corresponding formation energies: CeO₂-vac, La-CeO₂-vac, Ni-CeO₂-vac and Ni-La-CeO₂-vac. (b) The relative dissociation energies of H₂O (ΔE) on CeO₂ (111), Ni-CeO₂ (111) and Ni-La co-doped CeO₂ (111) surfaces. The light yellow, light blue, red/orange, and dark blue spheres, respectively, represent Ce atoms, La atoms, surface/subsurface O atoms, and Ni atoms [46].

Pr can also decrease the oxygen vacancy formation energy of CeO₂ supports via co-doping, and facilitate the generation and migration of active oxygen species, so as to improve the anti-coking ability and long-term stability of catalysts. Xiao et al. [47] found that an appropriate amount of Pr doping (10Ni-CePr_{0.20}), and as revealed by DFT calculations, co-doping of Ni and Pr, lowered the oxygen vacancy formation energy on the CeO₂ (111) surface to −1.39 eV (Figure 11a), far below that of pure CeO₂ (2.14 eV) (Figure 11b). This promoted the generation and migration of active oxygen species, enabling the catalyst to operate stably for over 120 h with an extremely low coking rate of 0.00056 mgC/(g_{cat}·h).

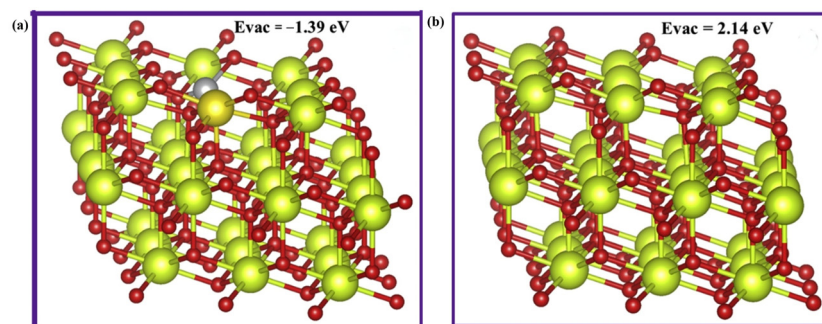


Figure 11. Various structures with oxygen vacancies and corresponding formation energies. (a) Ni-Pr-CeO₂-vac and (b) CeO₂-vac. The light yellow, deep yellow, red, and gray spheres, respectively, represent Ce atoms, Pr atoms, O atoms, and Ni atoms [47].

Alkali metal promoters such as K, Ca and Mg neutralize acidic sites on the support surface and may suppress the dehydration reaction pathway, and thereby hinder the formation of carbon deposition precursors. Shi et al. [48] reported the MgAl₂O₄ spinel formed by a Mg promoter could make the acidity of the support decrease from 297 to 119 $\mu\text{mol/g}$ and inhibit ethanol dehydration to ethylene in Process B of Figure 12. Meanwhile, Mg could promote the increase of Ni crystallinity, which suppresses carbon dissolution and diffusion, and prevents Ni₃C formation in Process C of Figure 12. The main carbon species is filamentous carbon (Process A, Figure 12), which barely covers active sites. The coking rate decreases from 15.1 to 3.7 mgC/(gcat·h), indicating good anti-coking stability. Mg also promotes steam reforming of the by-product methane and enhances hydrogen selectivity. Niazi et al. [49] revealed that H₂ selectivity could reach 74% and CH₄ selectivity was as low as 1% at 600 °C on 13Ni-4Mg/CeO₂ (Ni-Mg) catalysts. This is because the surface basicity (CO₂ uptake: 35 $\mu\text{mol/g}$) measured by CO₂-TPD may be a help for the methane steam reforming. The alkali metal K is also used to tune the electronic properties by constructing unique active interfaces. Wang et al. [50] found that the unique Ni-O-K interface formed on a K-modified Ni-K/KL catalyst achieved 97.5% ethanol conversion and 76.3% hydrogen yield. However, the unmodified Ni/KL catalyst deactivated rapidly after 2 h. This might be attributed to the interface-promoted water molecule activation and accelerated reactions such as the water–gas shift.

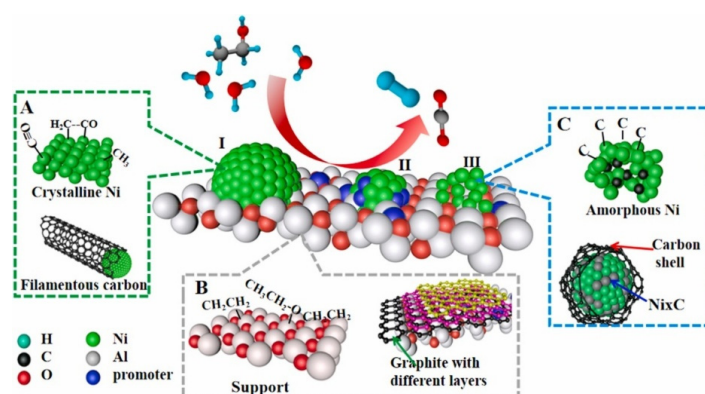


Figure 12. Schematic representation of the carbon deposition progress over a Ni/M-Al₂O₃ surface [48].

3.1.4. Modifying Supports

The different supports exhibit various structures and properties, such as the acid–base sites, oxygen vacancy sites and so on, which may promote the catalytic performance of ESR. Seriyala et al. [51,52] found the oxygen vacancy concentration increased from 20% to 35% by means of the doping of La or Zr into CeO₂. This leads to a significantly improved

catalytic activity, achieving 100% ethanol conversion and decreasing carbon deposition from 20 wt% to 2.4 wt%. Baig et al. [53] found the coking rate in the ESR reaction decreased from 20 to 2 mgC/(gcat·h), when introducing La_2O_3 into $\text{CeO}_2\text{-ZrO}_2$. This was because the $\text{La}_2\text{O}_2\text{CO}_3$ intermediates, formed by the adsorption and activation of CO_2 on La_2O_3 , could react with the deposited carbon species ($\text{La}_2\text{O}_2\text{CO}_3 + \text{C} = \text{La}_2\text{O}_3 + 2\text{CO}$). Liu et al. [54] found that the Ni-Mg/HCa catalyst, with a high specific surface area and strong basic sites, effectively inhibited ethanol dehydration and C-C bond cleavage, so as to obtain a high ethanol conversion of 100% and H_2 yield of 86% at 650 °C.

The spatial confinement effect on the support also plays a key role in inhibiting the sintering of catalytic active metal sites and carbon deposition. Murthy et al. [55] prepared similar Ni-based catalysts for the ESR reaction using the siliceous mesocellular foam (MCF-S) and SiO_2 as support, respectively. The H_2 selectivity of the MCF-S-supported Ni catalyst increased from 47.2% to 68%, compared with conventional Ni/ SiO_2 . This was because the spatial confinement effect formed by the protective pore channels inhibited sintering and carbon coverage of active sites. Xue et al. [56] synthesized a NiRh@NiO@mSiO_2 catalyst with an alloy-core, oxide-shell, porous-encapsulated structure, and the controlled catalyst NiRh-SiO_2 without a mesoporous shell, shown in Figure 13. At 550 °C, the conversion loss (17 h) of NiRh@NiO@m-SiO_2 was 10.9%, which is much lower than that of 57.8 (1 h) on the NiRh-SiO_2 catalyst. The mesoporous SiO_2 layer suppressed sintering and leaching of the metal sites via the confinement effect, and promoted the effective in-diffusion of water and out-diffusion of carbonaceous products, verified by the results of EXAFS, TEM-EDS mapping, depth profile XPS, N_2 physisorption, H_2 -TPR, and XRD. Similarly, An et al. [57] found a core-shell $\text{SiO}_2\text{@NiCuMgAl}$ catalyst displayed complete ethanol conversion at 500 °C and remained stable for 21 h, shown in Table 2, superior to the unmodified NiAl catalyst deactivated within 6 h. This was attributed to the highly dispersed active sites and enhanced structural stability. Table 2 summarizes the performance of some Ni-based catalysts in ESR from recent reports mentioned above.

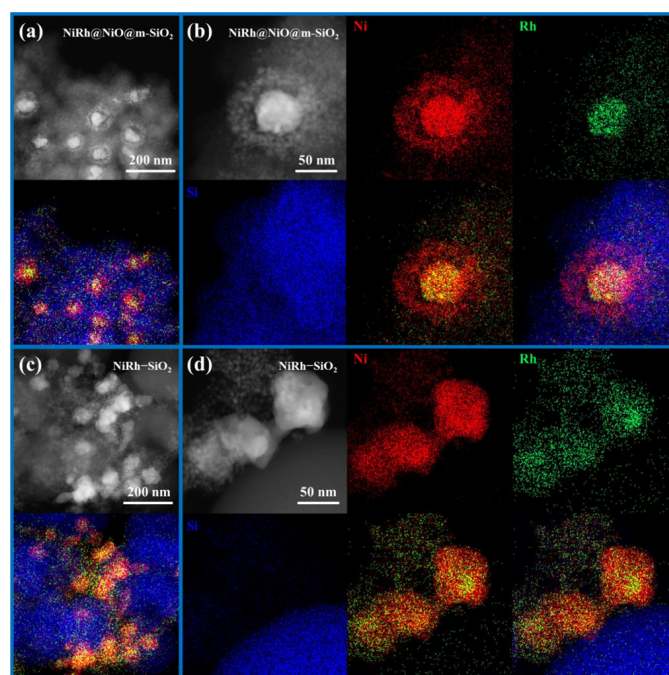


Figure 13. TEM dark field images and EDS mapping profiles of reduced (a,b) NiRh@NiO@m-SiO_2 and (c,d) NiRh-SiO_2 catalysts [56].

Table 2. ESR reaction performance of some reported Ni-based catalysts at atmospheric pressure.

Catalyst	T °C	GHSV mL·gcat ^{−1} ·h ^{−1}	Ratio S/E	Con. %	Sel. H ₂ %	Ref.
2Ni-Co/Al ₂ O ₃	600	57,120	24	100	95.14	[35]
9Ni1Co/CeMgAl	450	10,000	6	~100	~70	[36]
Ni10Fe10/MgAl ₂ O ₄	400	59,146	8	~100	~70	[37]
0.5RhNi/TiO ₂	400	16,700	6	99.7	61.7	[38]
NiCoMnCeCaO _x	600	30,100	3	99.92		[39]
12.5Ni/Al ₂ O ₃	600	24,000	3	92	86	[40]
Ni/CeO ₂ -SP	500	30,000	6	90	65	[41]
Ni/SiC _x O _y	500		8	100	74	[42]
NiEDTA(0.5)/MgAl ₂ O ₄ -CeO ₂	650	292,000	4.85	~90	~65	[43]
NiEDTA(1)/MgAl ₂ O ₄ -CeO ₂	650	292,000	4.85	~100	~95	[43]
Ni/Al ₂ O ₃ -OS	400	35,960	8	100		[44]
Ni/Al ₂ O ₃ -IMP	400	35,960	8	74		[44]
5ss-10NiO	400	33,940	6		~55	[45]
Ni-CeLa _{0.20}	600	55,920	4	~95		[46]
Ni-CeTb _{0.20}	600	55,920	4	~100		[46]
Ni-CeZr _{0.20}	600	55,920	4	~95		[46]
10Ni-CePr _{0.20}	600	44,240	4	100		[47]
Ni/Mg-Al ₂ O ₃	500	60,000	6	~100	~60	[48]
13Ni/CeO ₂	600	20,000	6	~89	71	[49]
13Ni-4Cu/CeO ₂	600	20,000	6	100	73	[49]
13Ni-4Mg/CeO ₂	600	20,000	6	96	74	[49]
13Ni-4Mo/CeO ₂	600	20,000	6	91	73	[49]
Ni-K/KL	600	19.96 h ^{−1}	6	97.5	76.3	[50]
Ni _{0.56} Sn _{0.57} (5)/Ce _{0.67} La _{0.33} O ₂	400	7697 h ^{−1}	12	100	60	[51]
NS5/CZ12	400	12,720	12	100	69	[52]
7.5Ni-7.5La/Ce-Zr	600	2.48h ^{−1}	4.5	97	65	[53]
15Ni-HCa	650	32,900	6	100	85	[54]
10 wt% Ni/MCF-S	700	17,160	4	100	68	[55]
NiRh@NiO@m-SiO ₂	550	21 h ^{−1}	4	100		[56]
NiCuMgAl	350	49,100	3	99.43	61	[57]
SiO ₂ @NiCuMgAl	600	49,100	3	100	75	[57]

3.2. Co-Based Catalysts

Co-based catalysts are also used for ESR reaction, because they can effectively activate C-C and C-H bonds, promote the water-gas shift reaction. And, with the presence of appropriate carriers or additives, Co catalysts may inhibit carbon deposition and maintain hydrogen selectivity. However, Co-based catalysts show a relatively poor catalytic activity at low temperature limits large-scale industrial application. Optimizing preparation methods, adding alkali or rare-earth promoters, and using redox supports such as CeO₂ could improve their low-temperature activity and balance activity and stability.

3.2.1. Regulating Catalyst Synthesis Methods

Co species tend to agglomerate and migrate when using traditional preparation methods. Optimizing preparation methods can effectively regulate the structure of active phases, enhance the metal-support interaction, and inhibit Co migration. Grzybek et al. [58] compared Co/ α -Al₂O₃ catalysts prepared by incipient wetness impregnation (IWI), hydrothermal (HT), and sonochemical (SC) methods. The highly dispersed mixed phases of Co₃O₄ and CoAl₂O₄, formed by SC method, via ultrasonic cavitation, displayed an enhanced metal-support interaction and suppressed Co migration. At 500 °C, the SC-derived catalyst achieved the highest Co mass activity (CTY = 4.1 molEtOH·gCo^{−1}·h^{−1}), 3.7 times that of the

IWI catalyst and 2.6 times that of the HT catalyst (Figure 14), with ethylene formation almost completely suppressed. Appropriate preparation methods can simultaneously form porous carbon supports and metal nanoparticles, simplifying synthesis and improving energy efficiency. Efimov et al. [59] synthesized a Co-Ru alloy catalyst supported on carbonized polyacrylonitrile (IR-PAN-Co-Ru) via a one-step infrared radiation heating method. As the carbonized polyacrylonitrile support formed a graphitic carbon shell which protected the metal nanoparticles, under infrared heating, the catalyst operated continuously for 17 h without deactivation, with a hydrogen yield of 5.6 mol/mol EtOH. Its performance was significantly higher than that of the Co/carbon nanotube catalyst (2.5 mol H₂·mol EtOH^{−1}). The impregnation order also influences the catalytic performance via the impregnation method. Escalante et al. [60] found that in the Co-CeO₂/MgAl₂O₄ system, the catalyst prepared by co-impregnation showed higher Co dispersion (68.5%) than that by sequential impregnation (33.8%). At 650 °C, the co-impregnated catalyst exhibited 5.3 mol H₂/mol EtOH H₂ yield, while the sequential impregnated sample gave only 1.6 mol H₂/mol EtOH.

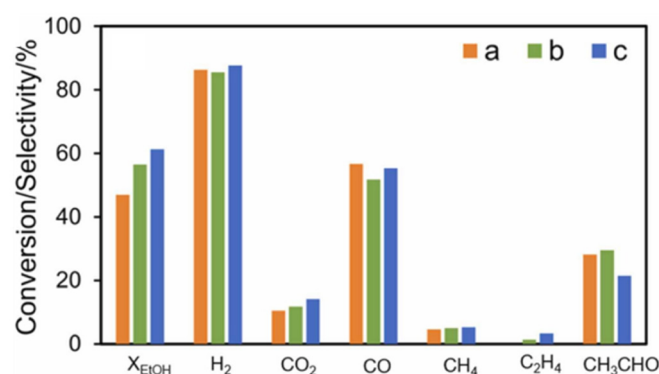


Figure 14. The effect of the cobalt phase deposition method on the ethanol conversion and selectivity to ESR products (500 °C, EtOH:H₂O = 1:4, 21 h) for: a—Co(IWI) | Al₂O₃-S3, b—Co(HT) | Al₂O₃-S3, and c—Co(SC) | Al₂O₃-S3 [58].

3.2.2. Adding Promoters

The promoters may affect active centers, so as to reduce the energy barrier of key reactions and inhibit carbon deposition through electronic effects, thereby improving the performance of catalysts. Grzybek et al. [61] found that the electron-enriched Co^{δ−} formed by electron transfer from K to Co could adjust the oxidation state of Co in the K-CoZn | α-Al₂O₃ catalyst. It reduced the energy barrier for C-C bond cleavage, suppressed acetaldehyde desorption and promoted deep reforming to produce H₂ and CO₂. Grzybek et al. [62] found that K-modified K-Co/b-Al₂O₃ achieved 100% ethanol conversion, compared with approximately 80% for unmodified Co/b-Al₂O₃.

The rare-earth Ce may accelerate carbon deposition gasification by promoting oxygen migration on the CeO₂ surface. Greluk et al. [63] found that the Co-Ce interaction and surface oxygen migration could be enhanced by a low Ce loading, promoting carbon gasification in the Co-0.1Ce/CeO₂ catalyst. This catalyst remained stable for 21 h at 500 °C, whereas Co/CeO₂ suffered rapid deactivation at the initial stage due to blocked active sites by carbon deposition. Ranjekar et al. [64] reported that CeO₂ promoted initial ethanol dehydrogenation and eliminated coke precursors, while a Cu-Co alloy facilitated C-C bond cleavage and the WGS reaction (Figure 15). At 673 K, the catalyst exhibited 97.4% ethanol conversion, 92 mol% hydrogen selectivity and stable operation for 120 h.

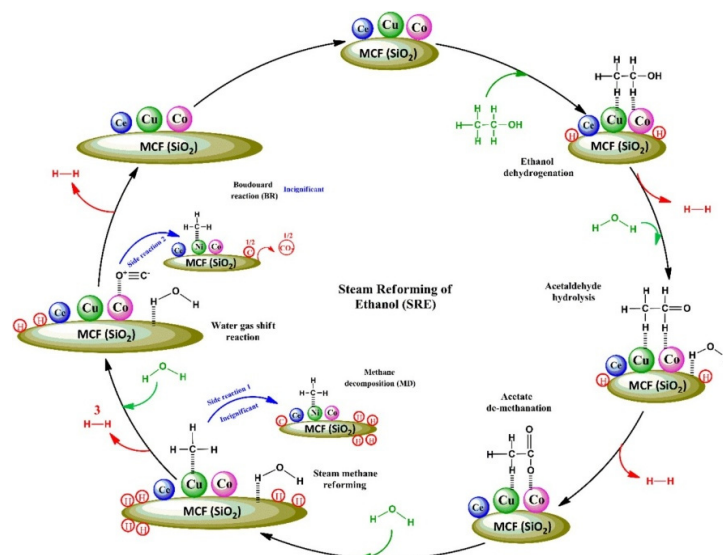


Figure 15. Prospective reaction mechanism of ESR [64].

3.2.3. Optimizing Supports

The Co-based catalysts also need suitable supports to modulate the active phase structure for the enhanced catalytic performance of ESR. Grzybek et al. [65] prepared a series of Co/ZSM-5 catalysts with different Si/Al ratios (32, 750, ∞) via incipient wetness impregnation. As the Al content decreased, the density of Brønsted acid sites significantly reduced, demonstrated by the FT-IR pyridine adsorption, XPS and H_2 -TPR characterizations. The ethylene selectivity dropped from 50% to 0%, when the acid density decreased from 445 $\mu\text{mol/g}$ at Si/Al = 32 to 0 $\mu\text{mol/g}$ at Si/Al = ∞ . Zeolite supports can regulate the particle size and dispersion of active metals. Da Costa-Serra et al. [66] found a smaller Co particle size and higher dispersion on the Co/ITQ-6 catalyst using layered zeolite ITQ-6 as support, due to strong metal–support interaction, which displayed good ethanol conversion of 90.5% and H_2 selectivity of 41.3% (5 h) at $\text{H}_2\text{O}/\text{EtOH} = 13$, GHSV = 4700 h^{-1} , 400 $^\circ\text{C}$ and atmospheric pressure.

CeO_2 -based supports show a good oxygen storage and release capacity, and tunable structural properties (porosity, crystal facets, etc.), which may affect catalyst performance in ethanol steam reforming. Lupa et al. [67] synthesized porous microspherical CeO_2 via hard templating and prepared a Co/ CeO_2 -XAD catalyst, with commercial nano- CeO_2 as a reference (Co/ CeO_2 -COM). At 420 $^\circ\text{C}$, Co/ CeO_2 -XAD showed an initial ethanol conversion near 100%, retained 54% after 21 h, and achieved 72% H_2 selectivity, while Co/ CeO_2 -COM exhibited only 58%, 27% and 63%, respectively. This stemmed from the smaller size of the metal crystallites, a well-developed internal surface and highly defective particles of support reported by comprehensive studies. Tuning the exposed crystal planes of CeO_2 enables modulation of the electronic valence state of active metals. Li et al. [68] reported the chemical states of Co sites could be tuned by the preferred exposure of CeO_2 facets (Figure 16a) in Co/ CeO_2 catalysts revealed by XRD and TEM (Figure 16b,c). The Co/ CeO_2 -(M) with a (111) facet maintained Co in a low oxidation state, enhancing C–C bond cleavage and suppressing condensation. This results in a high ethanol conversion of 100%, H_2 selectivity of 97%, and stable operation for 42 h. In contrast, the Co/ CeO_2 -(U) catalyst with a (100) plane induced high Co oxidation states, promoting chain growth and coking, and displayed a low ethanol conversion (87.2%) and H_2 selectivity (65.8%), which declined to 60.5% after 12 h (Figure 16d).

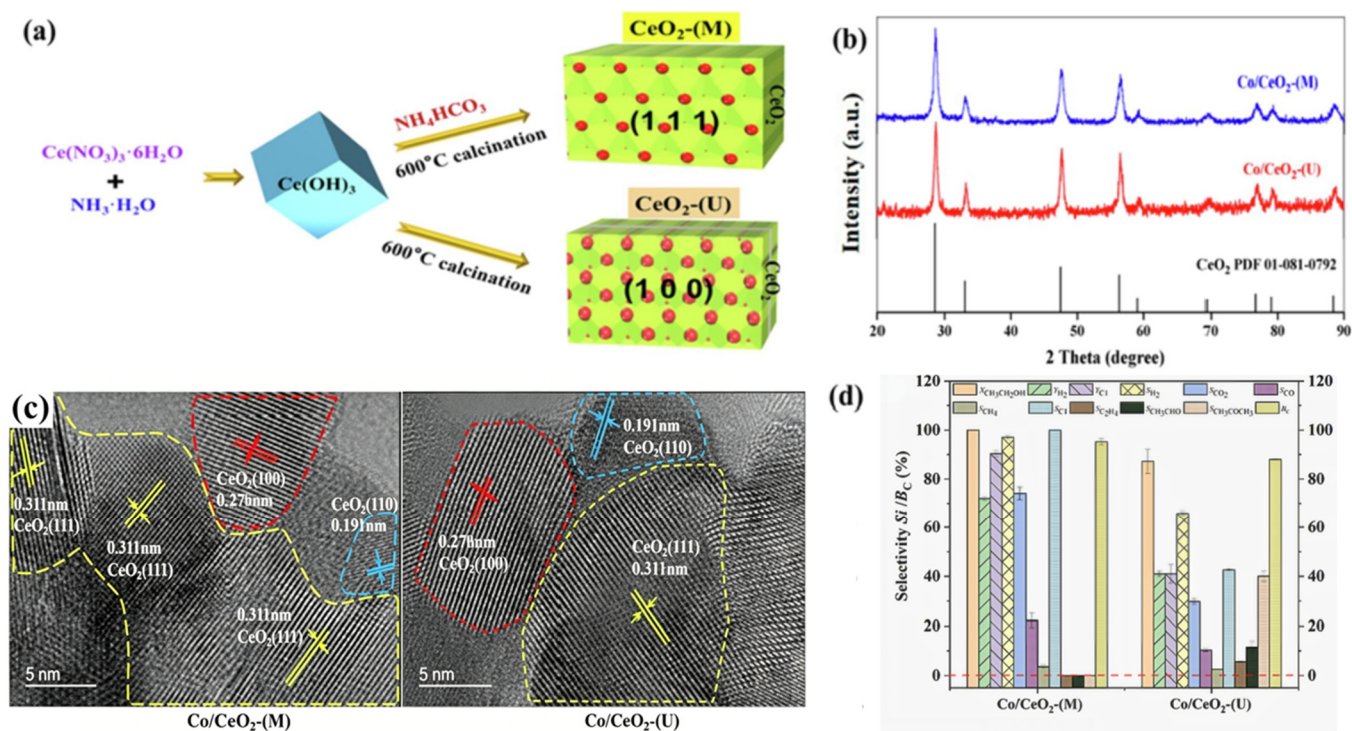


Figure 16. (a) The synthetic procedure of $\text{CeO}_2\text{-(M)}$ and $\text{CeO}_2\text{-(U)}$. (b) XRD patterns, (c) HRTEM. (d) Calculated energetic profiles for acetaldehyde conversion steps in the catalytic ESR reaction over Co (100) and CoO (100) slab models. The lowest red line indicates the carbon balance value, reflecting the degree of carbon deposition on the catalyst [68].

Introducing heteroatoms into the oxide lattice to form solid solutions can induce stronger charge transfer, regulating the valence state and reducibility. Li et al. [69] doped CeO_2 with La^{3+} to form a solid solution on the $\text{Co}/\text{La}_x\text{Ce}_{1-x}\text{O}_{2-y}$ catalyst. The ethanol conversion and H_2 selectivity reached up to nearly 100% and 94.3%, which is higher than that of Co/CeO_2 (73.3% and 65.8%). La^{3+} doping generated surface peroxide anions (O_p) that donated electrons to cobalt, lowering its valence, thus enhancing C-C bond cleavage. Similarly, Fornero et al. [70] found the Ga-incorporated CeO_2 catalyst, $\text{Co}/\text{Ce}_{90}\text{Ga}_{10}\text{O}_x$, was more efficient for ESR, and the production of acetaldehyde, acetone and oxygenated by-products (Figure 17), than Co/CeO_2 . This is because the surface area increased from 58 to 108 m^2/g and formed highly active Ce-O-Ga interfaces. Li et al. [71] synthesized a $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ solid solution from Si_3N_4 and Al_2O_3 and prepared a $\text{Co}/\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ catalyst. It exhibited 97% ethanol conversion, much higher than $\text{Co}/\text{Si}_3\text{N}_4$ (74%) and $\text{Co}/\text{Al}_2\text{O}_3$ (81%). The electronic effects of this support transferred electrons to cobalt species, lowering its valence state and increasing the Co^0 content, thereby enhancing its C-C bond cleavage capability. Table 3 summarizes the performance of other non-noble catalysts in ESR from recent reports mentioned above.

Table 3. ESR performance of some reported other non-noble catalysts at atmospheric pressure.

Catalyst	T °C	GHSV $\text{mL} \cdot \text{gcat}^{-1} \cdot \text{h}^{-1}$	Ratio S/E	Con. %	Sel. H_2 %	Ref.
$\text{Co(IWI)} \mid \text{Al}_2\text{O}_3\text{-S3}$	500		4	~47	50	[58]
$\text{Co(HT)} \mid \text{Al}_2\text{O}_3\text{-S3}$	500		4	~56	55	[58]
$\text{Co(SC)} \mid \text{Al}_2\text{O}_3\text{-S3}$	500		4	~61	60	[58]
IR-PAN-Co-Ru	550	1341	3	98.7	94.8	[59]

Table 3. Cont.

Catalyst	T °C	GHSV mL·gcat ^{−1} ·h ^{−1}	Ratio S/E	Con. %	Sel. H ₂ %	Ref.
IR-PAN-Co	550	1341	3	82.7	55.61	[59]
IR-PAN-Ru	550	1341	3	54.7	47.50	[59]
4CoCe/S	650		4.9	~87		[60]
8CoCe/S	650		4.9	~100		[60]
K-Co _{2.6} Zn _{0.4} O ₄	540		4	~100	94	[61]
Co/b-Al ₂ O ₃ -I	500	60,000	4	~90	88	[62]
1%K-Co/b-Al ₂ O ₃ -I	500	60,000	4	~100	92	[62]
Co/b-Al ₂ O ₃ -SC	500	60,000	4	100	88	[62]
Co-0.1Ce/CeO ₂	540	60,000	4	100	86	[63]
5%Ce-10%Cu-10%Co/MCF	400	2700	6	95	92	[64]
Co Z(∞)-S	500	52h ^{−1}	12	100	95	[65]
Co/ITQ-6	500	4700h ^{−1}	13	90.5	41.3	[66]
Co/CeO ₂ -XAD	420	60,000	12	100	73	[67]
Co/CeO ₂ -COM	420	60,000	12	58	68	[67]
Co/CeO ₂ -(M)	500	34,500	6	100	97	[68]
Co/CeO ₂ -(U)	500	34,500	6	87.2	65.8	[68]
Co/La _{0.25} Ce _{0.75} O _{1.88}	500	44,400	6	100	94.3	[69]
1.0 wt% Co/CeO ₂	500	867	6	100	35	[70]
1.0 wt% Co/Ce ₉₀ Ga ₁₀ O _x	500	867	6	100	50	[70]
Co/Al ₂ O ₃	500	44,400	6	81	83	[71]
Co/Si ₃ N ₄	500	44,400	6	74	86	[71]
Co/Si ₄ Al ₂ O ₂ N ₆	500	44,400	6	97	92	[71]

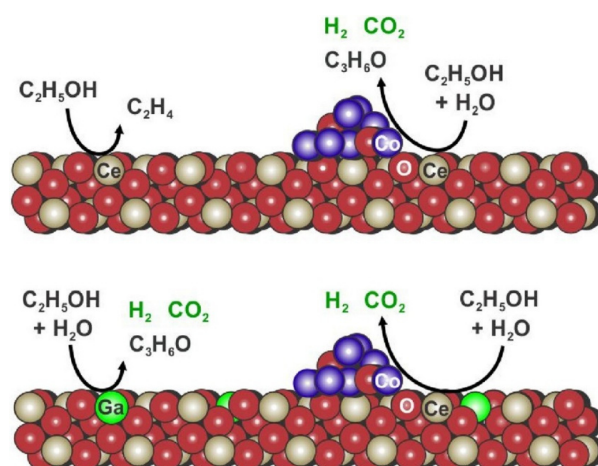


Figure 17. Schematic representation of ethanol conversion on different sites of Co/CeO₂ (top) and Co/Ce₉₀Ga₁₀O_x (bottom) catalysts under ESR conditions [70].

3.3. Noble Metal Catalysts

Noble metal catalysts (Rh, Pt, Pd, Ru, Ir, etc.) show potential in ethanol steam reforming due to their good activity, while the excessive price limits large-scale industrial application. Current research focuses on optimizing metal–support interaction, designing special structures and adding promoters to improve catalytic performance, while reducing noble metal loading and enhancing atomic efficiency to balance performance and cost.

The various noble metals display different structures and properties, and corresponding metal–support interactions, which may influence the dispersion state, electronic properties, and catalytic reaction performance. Silva et al. [72] prepared a series of M/CeO₂ catalysts (M = Au, Pd, Pt, Rh, Ru) via urea-assisted deposition for the ESR reaction. Among them, Rh/CeO₂ achieved 100% ethanol conversion (Figure 18a) and 37.8% H₂

yield (Figure 18b). This is attributed to the strong interaction between Rh and CeO₂, which facilitated the formation and migration of oxygen vacancies, and enhanced the C-C bond cleavage. Bampos et al. [73] found the Ru/Al₂O₃ catalyst exhibited nearly 100% conversion of a butanol–ethanol mixture at 700 °C, H₂ selectivity above 95%, and stable performance without deactivation for 45 h. In contrast, Pt/Al₂O₃ suffered from rapid coke formation due to the generation of C₃H_x and C₂H₄ by-products, resulting in a decline of H₂ selectivity from 96% to 82% within 12 h and poor stability. This can be attributed to the higher C-C bond cleavage activity of Ru than Pt.

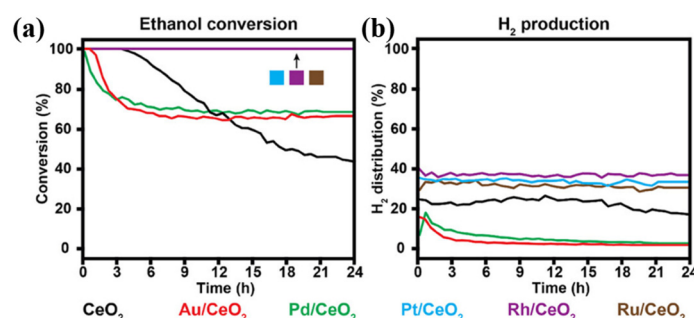


Figure 18. (a) Ethanol conversion and (b) H₂ production for CeO₂ and M/CeO₂ catalysts [72].

Introducing a second component Ce, and controlling its content to construct specific active sites, also plays a key role in improving the catalytic performance. Lin et al. [74] prepared a series of Rh-Ce/Al₂O₃ catalysts with different Ce content from 1 to 10 wt% for the ESR reaction. When introducing 5 wt.% Ce, the Rh-O-Ce sites formed by the CeO₂ nanoparticles trapped single-atom Rh. This structure enhanced water activation, promoted OH species formation, and accelerated acetate conversion and the water–gas shift reaction. This leads to a high H₂ production rate of 22.4 mmol·g^{−1}·min^{−1}, which is higher than that of Ce-free Rh/Al₂O₃ (15.9 mmol·g^{−1}·min^{−1}) at 450 °C. Studies by Martinelli et al. [75] and Rajabi et al. [76] demonstrated that introducing promoters like Na or Cs into Pt/ZrO₂ increased catalyst surface basicity, altering the reaction pathway from ethanol decarbonylation (producing CO) to decarboxylation (producing CO₂), reducing CO selectivity from 34.0% to undetectable levels.

Incorporating Ru into the perovskite lattice and in situ exsolution of highly dispersed Ru nanoparticles may inhibit the sintering of active metals. Tamara S. et al. [77] synthesized Ru solid-solution-doped LaCr_{1-x}Ru_xO₃ via the Pechini method. The unique solid-solution-derived active sites could not only afford abundant active centers but also suppress metal sintering and coke formation significantly via the strong metal–support interaction. The ethanol conversion in the ESR reaction over this catalyst achieved 100% within 85 h. In contrast, the conventional Ru/LaCrO₃ catalyst deactivated rapidly at the initial reaction stage. Lee et al. [78] prepared the Pd_{0.01}Zn_{0.29}Mg_{0.7}Al₂O₄ catalyst encapsulating Zn and trace Pd into the MgAl₂O₄ spinel framework. At 450 °C with S/E = 3, this catalyst maintained 100% ethanol conversion and 80% H₂ yield after a 30 h reaction, with coke deposition only one-third of that over unmodified MgAl₂O₄. The stable spinel structure inhibits sintering of the embedded Zn and Pd, thereby extending the catalyst durability. Dai et al. [79] found the hollow zeolite-confined Pt@HBZ catalyst can confine active metals and suppress sintering. At 350 °C, this catalyst achieved 100% ethanol conversion, and H₂ selectivity increased from 55% over conventional Pt-beta to 68%.

Introducing a second metal to form bimetallic alloys can generate a functional synergistic effect by constructing bimetallic interfaces. Choong et al. [80] constructed an Ir-Fe_xO_y bifunctional interface by introducing Fe into Ir/Al₂O₃. The Ir sites facilitate C-C bond cleavage, while Fe_xO_y promotes the water–gas shift (WGS) reaction. At 400 °C, this Ir-

Fe_xO_y catalyst exhibited a H_2 yield of 4.1 mol H_2 /mol EtOH, much higher than 0.6 mol H_2 /mol EtOH over the monometallic Ir catalyst, with CO_2 selectivity increased from 0% to 52.7%. Similar to the IrFe alloy, the PtCu alloy can also promote the reaction through the bimetallic synergy effect. Dai et al. [81] found the Pt-Cu@mSiO₂ catalyst displays a good ethanol conversion, H_2 selectivity and stability (150 h), relative to the Pt@mSiO₂ reference catalyst (30 h) at 400 °C. The synergistic promotion originates from Pt facilitating C-C bond cleavage and the WGS reaction, while Cu accelerates ethanol dehydrogenation. In addition, the support morphology may influence Pt dispersion. Kourtelesis et al. [82] prepared Pt/CeO₂ catalysts using CeO₂ with three distinct morphologies: nanocubes (CeO₂-NC), nanorods (CeO₂-NR), and flower-like structures (CeO₂-FL). Among them, the Pt/CeO₂-NR exhibited the highest Pt dispersion and surface Pt⁰ fraction, with no obvious decline in ethanol conversion within 28 h. Table 4 summarizes the performance of some noble metal catalysts in ESR from recent reports mentioned above.

Table 4. ESR performance of some reported noble metal catalysts at atmospheric pressure.

Catalyst	T °C	GHSV mL·gcat ^{−1} ·h ^{−1}	Ratio S/E	Con. %	Sel. H ₂ %	Ref.
Au/CeO ₂	550	33,120	3	65	3.1	[72]
Pd/CeO ₂	550	33,120	3	68	4.8	[72]
Pt/CeO ₂	550	33,120	3	100	34.6	[72]
Rh/CeO ₂	550	33,120	3	100	37.8	[72]
Ru/CeO ₂	550	33,120	3	100	31.2	[72]
Ru/Al ₂ O ₃	700	13,500	12	100	~95	[73]
Ru/MgO-Al ₂ O ₃	700	13,500	12	100	~97	[73]
Pt/Al ₂ O ₃	700	13,500	12	100	~82	[73]
Rh/Al ₂ O ₃	450	450,000	8	98	39.6	[74]
Rh-Ce ₅ /Al ₂ O ₃	450	45,000	8	100	55.8	[74]
2%Pt/ZrO ₂	300	381,000	9	63.5	43	[75]
1.8%Na-2%Pt/ZrO ₂	300	381,000	9	51.3	60	[75]
2.9% Cs-2% Pt/ZrO ₂	300	190,560	8.77	73	88	[76]
LaCr _{0.90} Ru _{0.10} O ₃	600	72,000	3	100	~65	[77]
LaCr _{0.80} Ru _{0.20} O ₃	600	72,000	3	100	~70	[77]
Pd _{0.01} Zn _{0.29} Mg _{0.7} Al ₂ O ₄	450	6000	3	100	~90	[78]
Pt@HBZ	350	7020	4	100	68	[79]
Ir/Al ₂ O ₃	400	88,000	9.6	62		[80]
IrFe/Al ₂ O ₃	400	88,000	9.6	100		[80]
Pt-Cu@mSiO ₂	400	8900	4	99.99	70.88	[81]
Pt/CeO ₂ -NC	300	39,720	3	80	30	[82]
Pt/CeO ₂ -NR	300	39,720	3	70	28	[82]
Pt/CeO ₂ -FL	300	39,720	3	65	25	[82]

4. Process Intensification Technologies

4.1. Separation Intensification Technologies

Separation intensification technologies drive the reaction equilibrium forward by in situ coupling of the reaction and separation to selectively remove products. The main technologies include catalytic membrane reactors (CMRs) for hydrogen separation via H_2 -selective membranes, and sorption-enhanced ethanol steam reforming (SESR), where CO_2 capture by solid sorbents indirectly promotes hydrogen production.

4.1.1. Catalytic Membrane Reactor

The catalytic membrane reactor (CMR), as a low cost and high efficiency hydrogen purification technology, is usually formed by conventional reactors coupled with palladium-

based (Pd-based) membranes. Generally, a higher H_2 yield could be achieved compared to traditional reactors. Chen et al. [83] reported a high ethanol conversion of 93% on a Pd-based membrane reactor at a Reynolds number of 500, compared with only 91% conversion in conventional reactors under identical conditions. The difference was mainly attributed to the H_2 removal through the Pd membrane, making the reaction equilibrium system shift towards higher product yields. Lu et al. [84] conducted ESR reactions over metallic nickel hollow fiber membranes (NiHFM) without additional catalyst loading, as the Ni membrane possesses catalytic activity. At 800 °C and ambient pressure with a S/E molar ratio of three, the H_2 yield was increased from 53.97% in the fixed-bed reactor to 59.95% in the metallic NiHFM reactor.

Membrane materials have an impact on reactor performance. Jia et al. [85] prepared a $Pd_{75}Cu_{25}$ alloy membrane on a porous ceramic support via electroless plating. At 873 K and 1.3 MPa, the membrane exhibited 98% H_2 purity over 240 h of continuous operation. In contrast, a pure Pd membrane showed that H_2 purity gradually declined from 96.7% to 91.2%. The authors attributed this improvement to Cu incorporation, which mitigated the hydrogen-induced expansion and defect propagation. The performance of the reactor may be affected by the membrane structure. Ereemeev et al. [86] used a dense Ni-Cu alloy–neodymium tungstate nanocomposite asymmetric supported membrane combined with a metal honeycomb catalyst for the ESR reaction. Compared with the fixed-bed membrane reactor, the asymmetric supported membrane exhibited a higher hydrogen permeation flux of approximately $3.5 \text{ Nml } H_2 \text{ cm}^{-2} \text{ min}^{-1}$ at 900 °C, while that of the fixed-bed configuration was only $1.31 \text{ Nml } H_2 \text{ cm}^{-2} \text{ min}^{-1}$. Meanwhile, the hydrogen yield increased from about 28% to approximately 38%, and the hydrogen recovery rate increased from around 35% to roughly 48%. Chen et al. [87] used a Pd-based membrane in a cross-flow membrane tube reactor for ESR. Under the conditions of an inlet temperature of 600 °C, a S/E molar ratio of three, and a reaction pressure of 6 atm, the hydrogen recovery rate reached 97.78%. Compared with the traditional reactor, the hydrogen yield was significantly increased by 22.26%, while only 0.34 times the amount of catalyst was used (Figure 19).

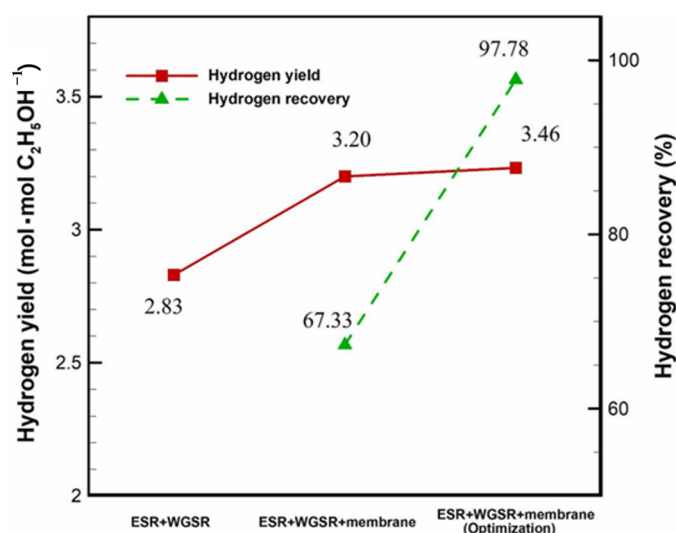


Figure 19. The hydrogen yield and hydrogen recovery under three different reactors. (S/E = 3, T_{in} = 600 °C, P_r = 6 atm) [87].

4.1.2. Sorption-Enhanced Ethanol Steam Reforming

Sorption-enhanced ethanol steam reforming (SE-ESR) employs solid sorbents such as CaO or modified hydrotalcites for in situ CO_2 capture, shifting the reaction equilibrium

toward hydrogen production and thus improving the hydrogen yield. Quan et al. [88] found that the hydrogen yield reached a maximum of 64.4 mmol/g using a 10% Fe/SiC catalyst coupled with 0.3 g CaO, 2.88 times that without a catalyst. In situ CO_2 capture by CaO shifted the reaction equilibrium, and CaCO_3 could be regenerated to CaO at lower temperatures under a H_2 atmosphere, with the regenerated CaO maintaining a high CO_2 adsorption capacity (Figure 20).



Figure 20. Reforming and hydrogenation–reduction reaction flow [88].

Traditional CaO sorbents are prone to sintering at high temperatures, leading to micropore collapse and a sharp decrease in surface area. Wang et al. [89] prepared a series of Ni-CaO-CaZrO₃ catalysts using CaZrO₃ as a structural promoter, which effectively inhibited the sintering of CaO. Among them, Ni10-Ca90Zr10 exhibited excellent stability in 10 cyclic tests (Figure 21). Similarly, Oliveira et al. [90] introduced MgO and Al₂O₃ into CaO to prepare Ni-CaO-CaZrO₃, which was uniformly dispersed among CaO particles as a spacer to stabilize Ni species and mitigate CaO sintering. This reduced the deactivation coefficient (k_d) by a factor of 3–4 compared to the undoped sample, significantly enhancing cyclic stability.

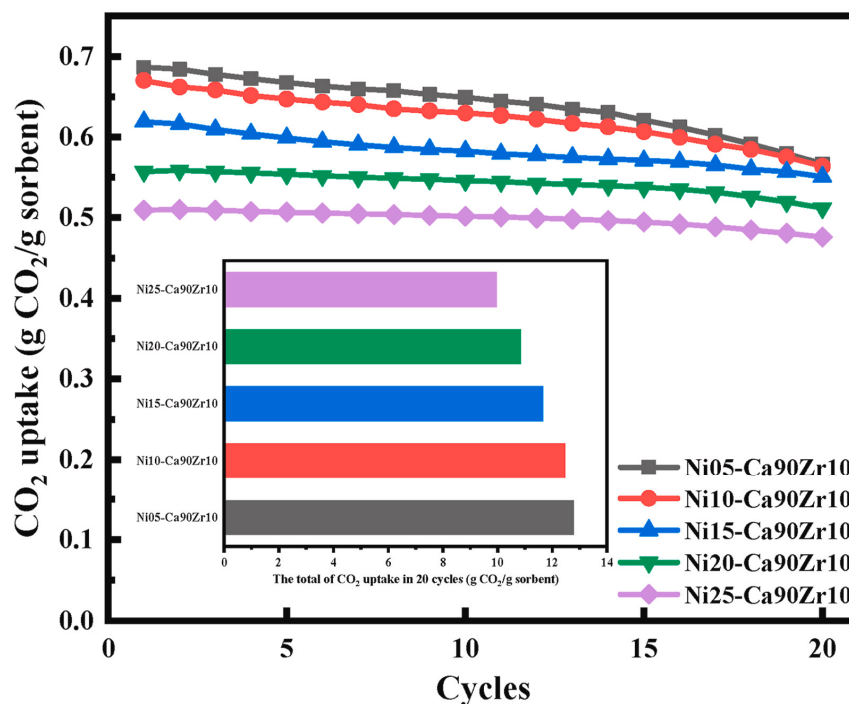


Figure 21. CO_2 sorption performance of calcined bi-functional materials with different Ni loadings [89].

Modifying hydrotalcite-based sorbents with alkali metals can tune surface basicity and enhance adsorption performance. Avendaño et al. [91] modified Mg/Al hydrotalcite sorbents using K_2CO_3 as a precursor. The hydrogen purity increased to 95% within 5 min, while the outlet CO_2 concentration was nearly zero. In contrast, the unmodified control group achieved only about 80% hydrogen purity. Constructing porous structures using templating methods is an effective physical strategy to mitigate sintering. Xu et al. [92] prepared porous spherical CaO sorbents (CaOS-C5) using a cellulose template. BET results showed a fresh surface area of $23.5\text{ m}^2/\text{g}$, much higher than the $11.9\text{ m}^2/\text{g}$ for template-free CaOS. After 100 cycles, the CO_2 uptake remained 0.166 g/g , far exceeding the 0.085 g/g for natural limestone. When coupled with Ni/ Al_2O_3 , the SE-ESR system increased H_2 purity from 75% in conventional SRE to over 90%.

4.2. Microchannel Reactor

Microchannel reactors feature microscale channels (typically inner diameter $< 1\text{ mm}$) with a high specific surface area ($1000\text{--}5000\text{ m}^2\cdot\text{m}^{-3}$) and fast transport rates, enabling millisecond mixing, precise temperature control to eliminate hot spots, and safe scale-up via numbering-up.

Rahman et al. [93] fabricated a catalytic hollow fiber microreactor (CHFMR) by depositing a 10 wt.% Ni/MgO-CeO₂ catalyst on the inner surface of asymmetric Yttria-stabilized Zirconia (YSZ) hollow fibers. SEM images revealed that 80% of the YSZ fiber cross-section consisted of finger-like voids, forming hundreds of tapered microchannels with diameters of $10\text{--}50\text{ }\mu\text{m}$ and lengths of $200\text{ }\mu\text{m}$, increasing the geometric surface area from 0.57 to $1.40\text{ m}^2/\text{g}$. At $510\text{ }^\circ\text{C}$, 18 mg of catalyst produced approximately 8.9 mL/min of hydrogen, comparable to 100 mg of catalyst in a fixed-bed reactor (Figure 22). Cai et al. [94] reported that the microchannel reactor achieved a hydrogen yield of $40\text{ L } H_2\cdot\text{gcat}^{-1}\cdot\text{h}^{-1}$, approximately 33% higher than the $30\text{ L } H_2\cdot\text{gcat}^{-1}\cdot\text{h}^{-1}$ obtained in packed-bed systems at $400\text{ }^\circ\text{C}$.

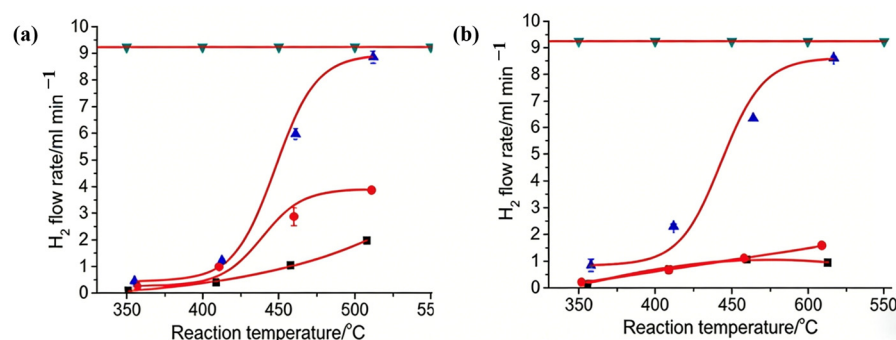


Figure 22. Production rate as a function of reaction temperatures from the ESR reaction performed in (a) the CHFMR. (■) Two units, (●) 4 units and (▲) 8 units of CHFMRs which contain 5 mg, 12 mg and 18 mg of the 10 wt.%Ni/MgO-CeO₂ catalyst, respectively. (b) The fixed reactor with a different amount of the 10 wt.%Ni/MgO-CeO₂ catalyst: (■) 5.7 mg, (●) 13.5 mg and (▲) 100.0 mg. (▼) H_2 flow rate when the selectivity of H_2 reaches 100% [93].

The geometric structure of microchannels also affect the reaction performance. Dehkordi et al. [95] compared three fixed-bed microreactors of identical volume loaded with a commercial Pd/ $\gamma\text{-}Al_2O_3$ catalyst, namely conical (A), cylindrical (B) and inverted conical (C) configurations. At $325\text{ }^\circ\text{C}$, the ethanol conversion in reactor A was 2.5 times that in reactor C. This was attributed to the increasing cross-sectional area of A along the flow direction, which raised catalyst loading and gradually prolonged the contact time from inlet to outlet, favoring conversion at low reactant concentrations in the later reaction stage.

5. Summary and Outlook

This review summarizes the latest research progress of hydrogen production via ESR, including the reaction mechanism, catalyst design and process intensification. Firstly, an in-depth analysis of ESR is conducted from thermodynamic and kinetic perspectives. Combined with experimental studies and DFT calculations, various reaction pathways, including dehydration and dehydrogenation routes, are discussed in detail. Based on supported noble and non-noble metal catalyst systems, the key factors affecting catalytic performance are summarized, including metal alloying, optimization of preparation methods, promoter addition, and support modification. These factors significantly influence the adsorption and activation of reactants, C-C bond cleavage, and the selective formation of CO₂ and CO, thereby determining the catalytic performance in ESR. Meanwhile, this review also explores the roles of process intensification technologies such as catalytic membrane reactors, adsorption-enhanced reforming, and microchannel reactors in breaking thermodynamic limitations and improving heat and mass transfer efficiency. However, there are still numerous challenges and opportunities in comprehensively clarifying the evolution process of active sites, catalyst design, and the scale-up of process intensification technologies due to the complexity of heterogeneous catalysis in the future.

To address these, future research can focus on breakthroughs in the following three aspects: (1) combining in situ/operando characterization with theoretical calculations to deeply reveal the dynamic reaction mechanism and the evolution law of active centers under reaction conditions; (2) achieving precise design of efficient non-noble and noble metal catalysts by means of AI and high-throughput experiments, and breakthroughs in their long-term stability through strategies such as strong metal-support interaction, core-shell structure, and single-atom catalysts; (3) promoting the structural optimization of membrane reactors, microreactors and the material innovation of adsorbents to solve the problems of their compatibility, cyclic stability and scale-up in practical applications.

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