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Cesium-Promoted Nanostructured Catalysts in Dry Reforming of Methane: A Review

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ABSTRACT

Dry reformation of methane (DRM), which uses two greenhouse gases, CO_2 and CH_4, at the same time, is a sustainable method of producing syngas. DRM is hampered by catalyst deactivation brought on by coking, sintering, and structural instability under extreme operating conditions, despite its potential for the environment and industry. Recent developments demonstrate how well cesium (Cs) works as a promoter in nanostructured catalysts, where its strong basicity, large ionic radius, and electron-donating capacity improve CO_2 activation, suppress coke formation, and stabilize active metal sites. With a focus on their electrical and structural impacts, catalyst–reactant interactions, thermodynamic and kinetic functions, and the impact of various supports, this review synthesizes the state of knowledge about Cs-promoted nanostructured catalysts for DRM. Stability trends, structure-performance correlations, and Cs loading optimization for increased activity and durability are all given special consideration. Complemented by a section on generic, overarching concepts such as combined catalytic- and electrochemical processes, reactor design driven by simulation and integrated reactor concepts including hybrid applications, the authors discuss new strategies to address long-term durability, impurity management, feedstock tolerance and upscaling of power-to-X products. Overall, this investigation provides key new insights into the special promotion role of cesium in preparing nanostructured DRM catalysts for efficient and durable syngas production.

1. INTRODUCTION

Syngas, composed of CO and H2, is an important feedstock for both energy anchemical industries. From the significant decrease in fossil fuels and increased environmental awareness that led to cleaner syngas production processes [1]. One of the sustainable pathways is dry reforming of methane (DRM) where greenhouse gases CO_2 and CH_4 are utilized simultaneously. The reaction ($CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$) generates syngas with H_2/CO equilibrium ratio (~1), appropriate for methanol synthesis and Fischer–Tropsch reaction [2]. As DRM sequesters the toxic waste as valuable product it is a means of carbon capture and utilization and a positive step toward the circular carbon economy [3]. Catalyst deactivation by carbon laydown, particle sintering and structural degradation at the high reaction temperatures (700 900 °C) required for DRM is a major limitation of this process. These issues decrease efficiency and indicate a requirement of more durable catalysts, resistant to coke [4]. With the aid of nanostructured catalysts, these shortcomings can be bypassed by increasing active surface area, metal dispersion and reactant-catalyst interaction [5]. They also result in improved coking resistance and increased the catalyst durability at severe DRM conditions. Promoters, e.g., the alkali metals Li, Na, K, Rb and Cs are typically employed to inhibit coke formation and enhance the basicity of the catalyst for CO_2 activation [6]. Cesium (Cs) is one of them with its high basicity, big ionic radius and electron donation to the metal; it can enhance CO2 activation, promote metal–support interactions and suppress coke generation. Due to these characteristics, Cs is one of the most efficient promoters for both stable and active DRM catalysts [7]. The majority of the reviews have been limited to either general alkali promoters or archetypal Ni-based catalysts, and little emphasis accorded Cs-promoted nanostructured systems. In view of Cs's distinct contributions to CO_2 activation, stabilization and deactivation suppression, a focused review is necessary. The work reported by us fills this knowledge gap by investigating Cs role in nanostructured catalysts for DRM in terms of both catalytic activity, stability and syngas composition under extreme operating conditions as well as coke-resistance. It also describes some remaining challenges as well as future prospects for advancing Cs-promoted DRM catalysts to industrial application.

2. Dry Reforming of Methane (DRM)

Additionally, the dry reformation of methane (DRM), requiring temperatures ranging from 700 to 900 °C, is an extremely endothermic reaction for transforming CH_4 and CO_2 into syngas ($CO + H_2$) ($\Delta H° = +247$ kJ/mol). Besides the desired reaction, also side reactions such as reverse water–gas shift, methane cracking or Boudouard reaction commonly take place. These suppress the hydrogen generation and lead to carbon deposition, which is a predominant reason for catalyst deactivation [2]. DRM is critical to the environment as it's one of the leading carbon capture and use technologies and a cornerstone technology in the circular carbon economy, taking two of the most potent greenhouse gases out altogether. The need for a more rigorous, coke-resistant catalyst is underscored by the fact that its harsh operating conditions and susceptibility to catalyst deactivation remain major roadblocks to industrial implementation [3].

3. Cesium-Promoted Nanostructured Catalysts in DRM

Cs in DRM catalyst Cs is of great interest due to its remarkable influence on catalytic performance. The alkali metal Cs alters the electronic and structural properties of the catalyst and enhances its stability and activity for DRM (Figure 4). 1). For exploring basic effects promoted by Cs, the structural and electrical consequences of Cs, its contribution to catalyst-reactant interactions as well as thermodynamic and kinetic considerations are focused on in this section.

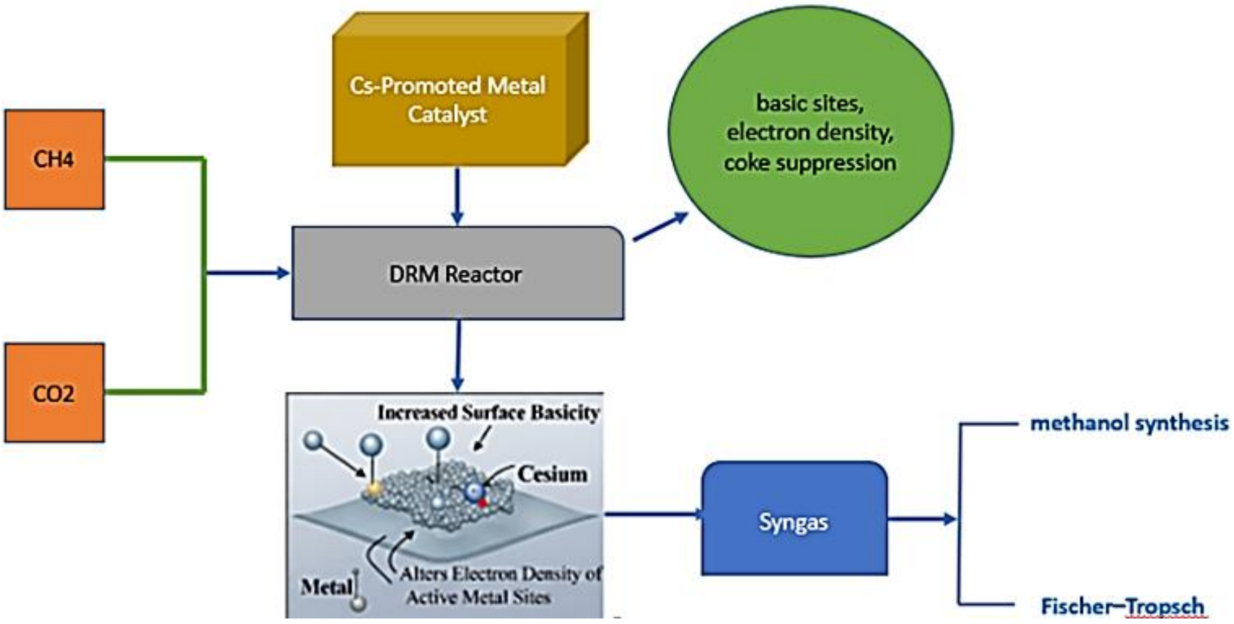

Figure 1. Schematic of Cs-promoted catalysts for dry reforming of methane to syngas

3.1 Electronic and Structural Effects of Cesium

Cesium promotes DRM in the main by altering the electronic properties of the catalyst. Cs donates electrons to metal catalysts, for example nickel (Ni) or platinum (Pt), and thereby changes electron density at the surface of the metal [8]. Having larger ionic radius in comparison to Na and K, Cs is of better electondonating property and hence the more distinct change caused by that of metal electron density. While K is known to promote basicity, Cs tends to enhance the metal–support interactions with improved DRM tolerance [9]. Catalyst activity for promoting methane (CH_4) and carbon dioxide (CO_2) activation is enhanced by electron donation. Cesium is also involved in controlling the transfer of oxygen species along the catalyst surface, which favours a more efficient CO 2 activation [10]. The addition of cesium further enhances the surface basicity of the material, contributing to enhance adsorption and subsequent activation of acidic CO2 molecules and facilitating their insertion into the reforming pathway [11].

3.2 Influence on Catalyst–Reactant Interaction

The presence of Cs leads to a more effective communication with the reactants (methane and CO_2), indicating an increased reaction efficiency. Enhancing the basicity resulting from Cs woodiness and the ability to adsorb CO_2, and then helps in its activation as well as integration into reaction [12]. In addition, Cs's electron donation strengthens the activation of CH4 and facilitates C–H bond cleavage in CH_4 [13]. Another important effect of Cs promotion is its role in reducing coke generation, which is a common issue found in DRM. Cs can improve catalyst durability and long-term stability by stabilizing the surface of the catalyst and altering the deposition process of carbon [14]. Although the adsorption of CO2 is promoted by both K and Rb, stronger binding with CO2 as well as higher polarizability of Cs leads to a better conversion efficiency. The contrary happens in the case of Li or Na as they usually require higher loading to achieve similar performance leading to pore clogging and a lower dispersion of the metal [9]

3.3 Thermodynamic and Kinetic Considerations

From a thermodynamics and kinetics point of view, the promotive effects of Cs are tremendous for DRM [15]. As illustrated in (Fig. 2) by decreasing the energy barriers required for C–H bond cleave in methane and CO_2 activation, Cs changes chemical pathways. These compensations lead to a beneficial reaction environment enabling the reforming at lower energies. The reduced energy barrier expedites the reaction rate, it makes DRM process thermodynamically and kinetically more favorable [16]. These key understanding into the promotion of Cs, could also guide designing more active and robust catalysts for syngas production [17].

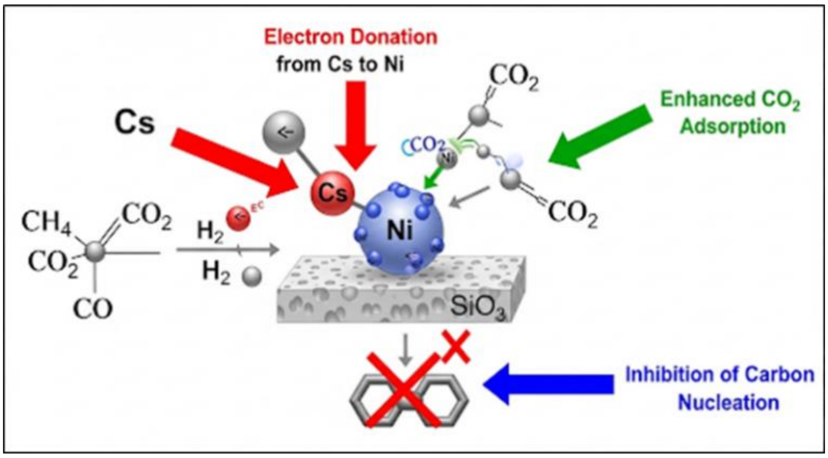

Figure 2. Schematic of the mechanistic pathways of Cs-promoted Ni catalysts in DRM.

4. Nanostructured Catalyst Supports for Cesium Promotion

The right selection of the support for the catalysts is critical to increase the activity and stability of Cs-promoted catalysts in DRM including others. Nano-structured supports with a variety of pore size and surface area have been extensively investigated in order to enhance the loading of Cs and dispersion of metal resulting in overall improvement in catalytic activity (Table 1). This part defines different sorts of support, for which various pros and cons can be listed.

4.1 Conventional Supports

Alumina (Al_2O_3), which has a high surface area and mechanical strength, is commonly used as the support for catalysts. However, such has relatively low thermodynamic stability, which could restrict its application to high-temperature applications like DRM. In addition, reactions with the acidic sites of alumina may sometimes lead to undesirable side reactions [18]. According to Wang et al. [19] performed better in terms of CH_4 and CO_2 conversions as compared to unpromoted Ni/Al_2O_3, yet exhibited significant deactivation due to coke formation. It indicates that Cs could to some extent but not thoroughly lift the limit of alumina. Silica (SiO_2) is another widely used support, largely because of its large surface area and chemical inactivity. Yet, CO_2 adsorption is restrictred due to the lack of basic sites.In contrast to Ni/SiO_2, Cs–Ni/SiO_2 catalysts showed improved CO_2 activation and greater stability, with Cs making up for the lack of intrinsic basicity, as Bagheri et al. [20] showed. Although titanium dioxide (TiO_2) has a low surface area and restricted metal dispersion, it has good heat stability and oxygen transport capabilities [21]. Though activity was still lower than that of Ni/CeO_2-based composites, BaQais et al. [22] discovered that Ni/TiO_2 systems unpromoted Ni/TiO_2 in terms of syngas selectivity outperformed and coke resistance. Zirconia (ZrO_2) is known for its remarkable ability to store oxygen and its remarkable thermal stability. Although phase changes at extended reaction periods decreased surface area and metal dispersion [23], Kim et al. [24] showed that Cs–Ni/ZrO_2 catalysts obtained high conversions and sustained stability at 900 °C. Because of its strong basicity, which improves CO_2 adsorption, magnesium (MgO) is prized [25]. It is harmed by sintering at high temperatures, though. According to Chen et al. [26], Cs–Ni/MgO catalysts demonstrated significant

CO_2 adsorption and superior coke resistance; however, at DRM conditions, MgO crystallite growth reduced long-term stability.

4.2 Mixed Oxides and Composite Supports

Mixed oxides and composite supports amalgamate the benefits of multiple materials, frequently resulting in synergistic effects that enhance performance in catalytic reactions [27]. These supports are tailored to enhance thermal stability and metal dispersion, therefore being particularly beneficial for Cs-promoted catalysts in DRM. These supports are very useful for Cs-promoted catalysts in DRM, because of enhancing metal dispersion and thermal stability of the system [28]. For example, by comparison with Cs–Ni/Al_2O_3 catalysts, it can be seen that the conversions of CH_4 and CO_2 were stronger while less coke was formed in the presence of Cs–Ni/CeO_2–Al_2O_3 catalysts (Tan et al [29]). They attributed the enhancement to the enhanced redox and oxygen storage capacity of CeO2 and its roles in continuously removing carbon during DRM. According to Zhang et al. [30],Cs–Ni/MgO–Al 2 O 3 exhibited high stability for 100 h on stream. MgO improved CO_2 adsorption, and Al_2O_3 had large surface area to achieve the Ni-Si syngas catalyst with an equitable H_2/CO ratio in addition to low coke formation. In another study, Li et al. [31] found that the synergies between ZrO2's high-temperature structural stability and CeO2's oxygen mobility allowed Cs-promoted Ni/ZrO_2–CeO_2 systems to show excellent resistance towards carbon DEPOSITIOnS TanG et al. Taken together, those results confirm that the synergistic effects preferentially enhanced by mixed oxide and composite supports, i.e., CeO_2–Al_2O_3,MgO–Al 2 O 3, and ZrO_2–CeO_2, are available. In the harsh reaction environment of DRM, such synergy strengthens CO_2 activation, suppresses coke deposition and enhances catalyst stability.

4.3 Zeolitic and Mesoporous Supports

ZSM-5 is also a widely-used zeolitic support known for its well-defined microporous structure. It also offers better control on pore size, which benefits selective catalysis. Despite this, its low surface area may limit the dispersion of metal particles even after modification with Cs for higher activity [32]. As compared to the unpromoted Ni/ZSM-5, Zhao et al. [33] that Cs–Ni/ZSM-5 catalysts showed higher CH_4 and CO_2 conversions and better coke resistance. This was due to Cs-promoted basicity enhancing CO_2 adsorption and inhibiting carbon deposition. SBA-15, which comprises of hexagonal arrangement channels can be regarded as one of the best mesoporous silica types in stabilizing promoters and dispersing nanoparticles. SBA-15 is a type of mesoporous silica material with ordered pore structure, which is suitable as the matrix for supporting metal nanoparticles. It leads to better control of pore size and easy anchoring of Cs, therein enhancing the catalyst's ability to activate CO_2 thereby leading to higher DRM efficiency [34]. According to Park et al. [35], DRMs are continuously active on Cs–Ni/SBA-15 catalysts for 120 h and the syngas selectivity and CO_2 activation were enhanced with good utilisation of support mesoporosity for a homogeneous Cs anchor. Another type of mesoporous silica MCM-41 having uniform pore sizes offers good dispersion and high surface area. MCM-41 is a type of mesoporous silica support exhibiting relatively uniform pores size. It provides metal dispersion and surface area, which makes it suitable for Cs promotion in DRM. The introduction of mesoporous structure enables the utilization of Cs to be improved and enhances the stability of catalyst for reaction after extended periods [36]. Liu et al prepared Ni/graphene under 850 °C DRM condition, and they exhibited RAND by using an electrochemical work. [37] found that Coke formation was controlled and the conversions were high for Cs–Ni/MCM-41 catalysts. The mesoporous structure could enhance the catalyst stability and permit progressive Cs distribution in contrast to conventional supports. In generally, promotion of Cs is enhanced for the large surface area structure controlled zeolitic and mesoporous (ZSM-5, SBA-15 MnCM-41) supports. Outstanding CO_2 activation, syngas formation and tolerance against deactivation at high-temperature DRM are consequences of their effective metal and promoter dispersion.

4.4 Perovskite and Layered Double Hydroxide (LDH) Supports

Perovskites form a family of compounds with a unique crystal structure that makes them highly stable in terms of both thermal stability and redox properties. These supports improve DRM by being able to adsorb a wide variety of metal ions, and thus also improving metal dispersion and reaction efficiency. The activation of perovskite in situ provides that the high catalytic activity is maintained permanently [38]. Gao et al. [39] reported that perovskite-type Cs–$LaNiO_3$ derived catalysts presented remarkable CO_2 and CH_4 conversions, as well as excellent resistance to coke formation. They attributed this enhanced activity to the oxygen mobility of the perovskite lattice and firm metal–support contact, enabling carbon oxidation in DRMs process. Similarly, Huang et al. [40] found that Cs-doped Lan FeO_3 perovskites showed balanced H_2/CO ratios as well as improved stability, which highlights the role of Cs in controlling surface basicity and structural properties in a high-temperature environment. Another interesting supports series is the Layered Double Hydroxide (LDH) supports characterized by a self-regeneration ability, high dispersing properties and tunable composition [41], [42].

Feng et al. [43] demonstrated that due to the strong anchoring of Cs species and well-dispersed metal, Cs–Ni/Mg–Al LDH catalysts could suppress coke formation, and achieved stability for a long time compared with conventional oxide-support. Related work Zhang et al. [44] Cs–Ni/Co–Al LDHs also exhibited strong syngas selectivity and increased CO_2 adsorption capacity due to the layered structure and basic sites of the Cp–LDH introduced by LDH, as well as its promoter Cs.

Selection of the type of catalyst carrier to promote Cs in DRM is important for activity control. Conventional supports, such as alumina and silica, have good dispersion and stability properties but may be lacking in the interactions with CO_2. Mixed oxides and composite supports provide the synergy effects, while zeolitic and mesoporous ones allow to control with high accuracy pore size and metal distribution. On the whole, perovskites and LDHs display excellent stability, in-situ activation ability and self-regeneration capacity, making them highly attractive candidates for advanced DRM catalysis. Table 1 lists the principle support materials used in Cs-promoted DRM catalysts and describes their surface areas, thermal stability, strength of Cs interactions, and performance ranges achievable. Zeolites are known to be selective, but also tend to deactivate via coking. On the other hand, MgO and perovskite supports have a more firmly bound Cs with also higher coking resistance. ZrO2 and Al2 O3 offer moderate stability with varying coking resistance and catalytic activity, whereas LDHs show superior metal dispersion.

Table 1: Supports for Cs-Promoted catalysts in DRM

Support Type	**Example Studies**	**Surface Area (m^2/g)**	**Thermal Stability**	**Interaction with Cs**	**Typical DRM Performance Outcomes**	**Ref.**
Al_2O_3 (Alumina)	Cs–Ni/Al_2O_3 with improved CO_2 adsorption and moderate coke suppression	100–250	Moderate (~500–700 °C)	Moderate	Moderate CH_4 conversion; improved stability with Cs; coke still possible	[45]
ZrO_2 (Zirconia)	Cs–Ni/ZrO_2 improved stability and suppressed coke	50–100	Very High (~800–1000 °C)	Moderate	High stability, moderate catalytic activity, and coke resistance were improved.	[46].
MgO (Magnesia)	Cs–Ni/MgO achieved high CO_2 adsorption and enhanced coke resistance	50–150	High (~700–900 °C)	Strong	High CH_4 and CO_2 conversions; strong basicity; suppressed coking	[47]
Zeolites (ZSM-5, BEA)	Cs–Ni/ZSM-5 gave higher conversions, but coke remained an issue	200–800	Moderate (~400–600 °C)	Weak	High selectivity; Cs improved stability, but coke-prone	[48].
Perovskites ($LaNiO_3$, $LaFeO_3$, etc.)	Cs–$LaNiO_3$ with high conversions & coke resistance; Cs–$LaFeO_3$ with stable H_2/CO ratios	20–100	Very High (~800–1000 °C)	Strong	Excellent coke resistance; high stability; tunable basicity	[49].
LDHs (Layered Double Hydroxides)	Cs–Ni/Mg–Al LDH with long-term stability; Cs–Ni/Co–Al LDH with high CO_2 adsorption	100–300	Moderate (~500–700 °C)	Moderate	Excellent dispersion; strong Cs anchoring; high stability	[50]
MCM-41) (Mesoporous silica)	Cs–Ni/MCM-41 suppressed coke and maintained conversions at 850 °C	800–1000	High(~700–900 °C)	Strong	Uniform Cs distribution; extended durability; coke suppression	[51]

5. Performance Trends of Cesium-Promoted Catalysts in DRM

It has been reported that the introduction of cesium into dry reforming of methane (DRM) catalysts can remarkably improve the catalytic behavior. The performance trends associated with Cs-modified systems in terms of activity, stability, selectivity and deactivation resistance are presented in this section. The enhancement is highly sensitive to cesium loading, degree of metal–support interaction, and synergetic effects between Cs, active metal and support. One difficulty encountered in DRM is coke formation that gradually poisons the catalyst. Introducing Cesium to the system solves this problem, by stabilizing the metal–support interface, suppressing carbon nucleation and encouraging carbon desorption 52.

A H2/CO syngas ratio, methane conversion and CO2 conversion are parameters employed for determining the effectiveness of Cs-promoted catalysts [54]. The H2/CO ratio is often close to unity (≈1:1) at the optimal loading, and for further synthesis steps this fact would be rather advantageous [55]. Most studies indicate that the decomposition of CO_3 2− is enhanced by the addition of Cs, leading to higher uptake and conversion [56]. However, the correct loading amount is required to obtain this effect, too high of Cs may block active sites and promote deactivation, whereas too low of Cs may inhibit CO_2 activation and methane conversion. The claimed optimum cesium levels are up to about 1-10 wt.-% of the catalyst composition [57, 58].

Cesium behaves differently with the active metal as well. In Ni-based systems, Cs enhances CC adsorption, and inhibits coke deposition [59]. Cobalt catalysts possess enhanced high temperature stability and lower sintering when promoted by Cs [60]. Noble metals, such as Ru and Rh, exhibit a better product selectivity than Pt based systems with a greater CO_2 activation capacity and higher syngas production [61]. The properties of the supporting materials highly affect cesium anchoring, active metal dispersion and stability. Typical supports are alumina (Al_2O_3), ceria (CeO_2) and zirconia, all of which have structural stability together with usefully high surface areas. Mesoporous silica or ceria based materials can be used to provide an even better environment for incorporating Cs, and consequently an improved catalytic activity. [62],[63],[64].

The activity of cesium is often more effective at the lower loadings than other alkali promoters. K or Na typically require relatively high levels such that they may block active sites, whereas Cs is often very effective at 3 to 7 weight percent. Activity and durability is compensated by cesium's greater basicity, its ability to stay uniformly dispersed even under mild loading conditions. [65].

Table 2: Stability and performance of Cs-promoted catalysts in DRM**.**

Catalyst Composition	Cs Loading (%)	Temperature (°C)	CH_4 Conversion (%)	CO_2 Conversion (%)	H_2/CO Ratio	Stability Test Duration (hr)	Ref.
Ni/Al_2O_3 with Cs	5	800	85	83	1.05	100	[66]
Ni/CeO_2 with Cs	7	850	88	86	1.1	150	[67]
Ni/ZrO_2 with Cs	10	900	90	87	1.15	120	[56]
Ni-SBA-15 with Cs	5	750	82	80	1.0	80	[68]
Pt/ZSM-5 with Cs	3	700	78	75	1.2	200	[69]
$LaNiO_3$ with Cs	8	850	87	85	1.1	140	[70]
Ni-MgO with Cs	6	800	88	83	1.1.5	160	[63]
Pt-CeO_2 with Cs	4	800	84	82	1.1	180	[71]
Ni/CuO with Cs	5	900	83	81	1.05	120	[72]
Ni/La_2O_3 with Cs	7	850	89	88	1.2	150	[73]

6. Structure–Performance Relationship

The relationship between the structural aspects of Cs-promoted catalysts and their DRM performance is one of important research interests because it presents information on the atomic- or molecular-level changes that improve catalytic activity. The structure–performance relationship of the catalysts is analyzed, including morphological and textural effects, electronic structure and basicity as well as thermochemical stability, and correlation models are developed between preparation parameters and catalytic performance.

6.1 Morphological and Textural Effects

Especially in DRM, the shape and texture of Cs-promoted catalysts are indispensable for their catalytic performance. In order to improve the efficiency of catalysts, it is essential to understand how Cs impact on the synthesis process of catalyst such as surface area, pore size and particle distribution. Due to more active sites for reactants absorption and activation, increasing dispersal of metal particles as well as Cs on the catalyst surface results in high catalytic activity. [74]. The homogeneous distribution of Cs on the active metal surface improves the exposure with reactants and consequently positive contribution for its increased catalytic activity [75]. The surface area plays an important role in catalytic activity, higher is the surface area of the catalyst, more active sites are available for reactant adsorption and interaction leading to greater catalytic performance [76]. In addition, Cs also can alter the porosity of the catalyst by which this affects diffusing of the reactants and products through out the catalyst [77]. The pore shape and the distribution of pore size in the catalysts are quite important also because they likewise effect how easily the reactants will access the catalytically active sites and penetrate within them [78]. In DRM, dumbbell-shaped nanostructured catalysts (that have pore size of 2-50 nm) are commonly preferred because of their better compromise between a high surface area and an efficient diffusion of reactants. cs can alter the porosity and pore size distribution of support materials. The addition of Cs offers well-developed mesopores for more efficient reactant diffusion and to increase the catalytic activity in general [79]. It is clear that spatial distribution of cesium and active metal particles is also very important for catalytic activity. Wide distribution of metal particles can be used to play off their interaction with the reagents, which leads to a consideration of an increase in overall rates. Compared to the former with particle agglomeration, the catalysts of uniform dispersion have higher CH_4 conversion and better stability [80]. In addition, the mesoporous feature of Cs-promoted catalysts offers better accessibility to active sites and lessened diffusion resistances for enhancing catalytic performance [81].

6.2 Electronic Structure and Basicity

In the case of DRM, the electronic structure/basicty of catalysts play key roles governing its reactivity and activity. Cs is reported to be able to modulate the surface basicity of the support and electronic properties of metal catalysts [82]. This modification significantly enhances the activation of such reactants as methane and carbon dioxide, thereby improving conversion and syngas selectivity. Cs don ate electrons to the metal catalyst (e.g., Ni Pt) increasing electron density at metal interface. This electron transfer serves to increase the metalls abilityto activate methane and CO2. Cesium increases the electronegativity of the metal for better interaction between metals and reactants as important step for efficient digital rights management of dry repair reactions.. XPS can demonstrate Cs effect on catalyst surface chemistry. For instance, Cs has influence on the adsorption of CO 2, which plays a key role in the activation of CO 2 by catalyst for DRM [83]. Cs promotes generation of more basic sites on the catalyst surface. Cs-modified catalysts have better CO_2 adsorption and stronger interaction with the adsorbed CO_2, leading to a higher surface basicity. The core sites are crucial for the activation of CO2 and represent a key aspect for controlling the digital rights in DRM [84]. The Cs-promoted catalysts usually show several peaks of desorption at different temperatures representing the weak and strong basic sites. The enhanced number of basic sites improves the capability of the catalyst in adsorption and activation of CO_2, resulting to an increase on methane conversion with a syngas selectivity. The introduction of Cs significantly promotes CO_2 adsorption and activation, which is a key to optimizing DRM performance. Cs promotes the adsorption of CO_2 on the catalyst surface, and subsequently increase the utilization of CO_2 in syngas production [85]. Cs-modified catalysts often show an enhanced formate production from CO2, indicating a superior CO2 activation. This is directly linked to the increase in basic character and electron density of CS, which favour CO_2 and CH_4 decomposition into more reactive species. For example, Cs could suppress the formation of coke related species on the catalyst surface, where no C–H and C–C stretching vibrations associated with carbon deposition can be observed [86]. Coke-resistance performance of Cs-modified catalysts is improved owing to stabilization of metal-support interface and promotion of the surface removal of carbon species [87]. Altogether, Cs significantly changes the electrical landscape and basicity of the catalyst leading to an enhancement in CH_4 conversion, CO_2 activation and syngas formation.

Cs exhibits the best-promoted surface basicity among alkali metals, accompanied by a larger desorption of CO 2. The one with broader range of CO2 activation and thus more likely suitable for DRM process is Cs, which gives both strong and weak sites, while K and Na tend to give weaker basic site [88].

6.3 Thermochemical Stability

The thermochemical stability is one of the important factors that significantly dictates the long-term performance of DRM catalysts. The stability of a catalyst at reaction conditions, including its ability to withstand high temperatures and cycling in redox, is the critical factor for the long-term use of it within industry. Cs affects this step, as evidenced by the changes in reduction peaks, indicating that it can modify reducibility of metal species. The reduction temperature is often lowered with Cs-modification, which leads to an easier reduction and formation of very active catalyst. Cs acts as a stabilizing agent for the active metal particles, which prevents their sintering, an issue commonly observed in DRM operations [89]. A catalyst with high reduction activity generally possesses relatively good thermal stability, and can survive the harsh temperature during DRM without significant deactivation. Overall, catalysts promoted with Cs presented reduced temperature for carbon deposit oxidation which may facilitate coke removal and prevent catalyst deactivation [90]. Meanwhile, Cs as promoter can lower carbon deposit and keep the stability of metal-support interface. The coke yield for Cs-modified catalysts lowers than that for untreated catalyst, and also the modified catalyst promotes the oxidation of coke at a lower temperature. This leads in DRM processes to an improved catalyst lifetime and stability. As Cs-modified catalysts retard the stable coke formation and promote oxidation of carbon species, they show higher stability for continuous DRM operation [91]. The redox activity of a catalyst refers to its ability to go through repeated reduction and oxidation cycles, while remaining highly active. In DRM reactions, catalysts suffer from the C/R cycle and redox stability is therefore an important factor in long-term performance. For both these cases, Cs stabilizes not only active sites of the metals but also supports interaction, and eventually reinforces a more facile redox cycle. This stabilizing effect enables the catalyst to resist sintering and deactivation which can occur during cycling redox process [92]. The enhanced redox property shows that Cs-modified catalysts are capable of sustaining its activity for a long time. Higher redox stability of Cs-promoted catalysts minimizes the requirement for catalyst regeneration resulting in their long term economic attractiveness. [93]. Their capacity to suppress coke generation further improves the thermochemical stability of Cs-modified catalysts. Cs also modifies the metal-support interface, thereby suppressing carbon nucleation and coke formation. This stability effect ensures the catalyst integrity during DRM operation with high temperature. The presence of Cs allows for excellent dispersion of the metal and also prevents close packing of the particles, which in fact increases susceptibility to carbon deposit. Therefore, Cs-modified catalysts have been found with enhanced performance stability and coke resistance. [94]. Cs promotes the regeneration ability of the catalyst after carbon deposition. Catalysts modified with Cs form less coke, and the oxidation of carbon deposits is facilitated compared to the unmodified catalyst leading to an improved regeneration efficiency.

Table 3: Correlation between catalyst performance and catalyst characteristics.

Key Findings	Observed Performance Correlation	Ref.
Crystalline phases identified, phase purity	Improved catalyst stability, higher activity in reactions	[95]
Surface area: X m²/g, pore size: X nm	Higher surface area correlated with increased catalytic activity	[96]
Elemental composition, oxidation states of metal sites	Enhanced catalytic performance linked to specific oxidation states of metal sites	[97]
Acidic/basic site density and distribution	More active sites led to improved reactivity and product selectivity	[98]
Particle size: X nm, morphology	Smaller particle size and optimal morphology improved reaction efficiency	[99]

7. Challenges and Future Perspectives

7.1 Challenges

The gradual deactivation resulting from the natural degradation of the support is one of the major challenges in catalytic DRM. H_2S poisoning of active sites and catalyst deactivation represent one of the main hindrances toward commercial application, as this contaminant is found in many real feedstocks such as sour natural gas or associated petroleum gas (APG). Reliable performance is indeed dependent upon maintaining the thermal stability and structural integrity of both the catalyst and its support during high-temperature (700–900 °C) operation and subsequent redox cycling. Further challenges are encountered during scale-up, as catalysts that perform well in easily controlled lab facilities often do not meet the grade when transitioning into commercial reactors, where maintaining a uniform product and cost-effective processing continue to be important concerns.

7.2 Future Directions

ML analysis of extensive data sets can predict the optimal catalyst composition and preparation conditions. There is therefore an opportunity to greatly reduce trial-and-error in catalyst design by speeding up the search for optimal, highly active catalytic materials. Hybrid catalytic–plasma DRM is also a promising direction. The ability to reduce reaction temperatures at the catalytic surfaces, when these are combined with a cold plasma, results in reduced energy consumption and enhanced conversion of reactants. Especially at lower operating temperatures, PA activation yields marked advantages in selectivity and reaction efficiency, rendering it attractive for industrial applications. However, as the importance of CO 2 mitigation has intensified, it becomes more critical to optimize catalysts for syngas production from CO 2 -rich feedstocks. These catalysts will have potential in the conversion of CO2 to robust fuels and chemicals, presents a more sustainable means for producing resources of energy and chemicals in accordance with carbon utilization policy worldwide.

8. CONCLUSIONS

Cs is one of the most effective alkali promotor which can be employed in preparation of nano-structured catalysts for dry methane reforming. Due to its high basicity and electron donor ability to promoting CO_2 adsorption, enhancing methane activation, and inhibiting coke generation, it enhances catalyst stability and syngas selectivity. The synergistic effect of cesium, active metal and specifically designed supports such as perovskites, mesoporous silica and layered double hydroxides often leads to a significant enhancement in conversion efficiencies, controlled H_2/CO ratios and durability. Despite all these advantages, there are still important challenges for DRM: maintaining stability at the high TEMPs required by DRM, avoiding deactivation of catalyst with sulfur-containing feeds and ensuring reproducibility from lab to industry conditions. Future work will also involve the development of hybrid plasma–catalytic DRM processes for energy saving, optimization of Cs loading strategy and rational design of catalysts on both experimental measurement and data-driven computational method. Overall, Cs-promoted nanostructured catalysts show great potential for sustainable and cyclic DRM utilizing for green house gases elimination with economic benefit as well, contributing to the worldwide carbon utilizations and clean syngas production.

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