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To cite this article: S Y Liew *et al* 2022 *J. Phys.: Conf. Ser.* **2259** 012020

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A short review on the promotional effects of ceria-based catalyst for dry reforming methane

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Abstract. Dry reforming of methane (DRM) appears as a promising process for the industrial production of syngas in comparison to other conventional reforming technologies. However, DRM process suffers from catalyst deactivation induced by carbonaceous species which reduces the catalyst lifespan. Currently, catalytic designs in DRM have trended towards the incorporation rare-earth metals. As such, ceria (Ce) based catalyst has recently attracted research interest for its key feature to mitigate catalyst deactivation owing to its complementary redox and oxygen storage properties for the removal of surface carbon deposit. The present short review summarizes on the recent catalytic performance of Ce-based catalyst and impact of ceria redox on the DRM mechanism. The utilization of oxygen vacancies introduced by the Ce redox support enhances the catalytic activity by providing additional bifunctional sites and intermediate species to facilitate the surface reaction rate. This perspective will elucidate the role of oxygen vacancies in Ce supports and fine tune the catalytic performance of DRM for industrial applications.

1. Introduction

Dry reforming methane appears as promising method to produce syngas which is an essential feedstock for the production of synthetic long-chained hydrocarbons via Fischer-Tropsch, petrochemicals and methanol generation [1, 2]. Thermodynamically, DRM is an endothermic reaction involving methane (CH_4) and carbon dioxide (CO_2) reactant gases which occurs at elevated temperatures. Due to this pre-requisite reaction condition, DRM suffers from several drawbacks including carbon deposition due to concurring competing side reactions such as methane decomposition, Boudouard reaction, reverse carbon gasification and also lower H_2/CO values due to occurrence of reverse water gas shift reaction (RWGS) corresponding to the equations as shown [3]:

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad \Delta H^\circ_{298k} = 245 \text{ kJ/mol} \qquad (1)$$

$$CH_4 \rightleftharpoons 2H_2 + C \qquad \Delta H^\circ_{298k} = 75 \text{ kJ/mol} \qquad (2)$$

$$2CO \rightleftharpoons CO_2 + C \qquad \Delta H^\circ_{298k} = -171 \text{ kJ/mol} \qquad (3)$$

$$CO + H_2 \rightleftharpoons C + H_2O \qquad \Delta H^\circ_{298k} = -131 \text{ kJ/mol} \qquad (4)$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad \Delta H^\circ_{298k} = 41 \text{ kJ/mol} \qquad (5)$$

The employment of noble metals to catalyze the DRM reaction has been widely accepted due to their excellent resilience towards carbon formation and catalyst stability. However, the high cost of these noble metals has restrained their extensive use in industrial fields. Meanwhile, non-noble catalysts such as Ni, Cu, Co and Fe have extensively been focused as a practical substitute owing to their high availability, low cost and more importantly, they exhibit a comparable catalytic activity in comparison to noble metals. Though, non-noble metals are susceptible to metal sintering and coke deposition under dry reforming conditions which can deteriorate the catalyst performance and lead to reactor blockage [4, 5]. For these reasons, the introduction of rare-earth metals into catalyst support has been explored in the recent years to address these drawbacks.

Cerium oxide (CeO_2) or Ce-based supports have been extensively investigated on DRM and displayed promising results in suppressing the deposition of carbonaceous species [6]. In addition, it was found Ce-based catalyst could also enhance the metal-support interaction (MSI) which can greatly enhance the performance of DRM reaction [7]. Despite its advantages, an in-depth review elucidating on the DRM performance over Ce-based catalyst are still considerably insufficient in literature as of current. On the basis of this background, it would be of interest to understand the catalytic behaviour of ceria on the DRM performance and insights on the promotional effect of ceria on the elementary steps of DRM. Hence, in this paper the emphasis has been put on findings from recent studies on the catalytic performance of Ce-based catalyst. Moreover, the impact of physiochemical properties of the Ce-based catalyst and its promotional effect of Ce^{4+}/Ce^{3+} redox cycle on the DRM mechanism was also discussed.

2. Catalytic performance of Ce-based catalyst

The role of Ce-based catalyst has been applied extensively towards DRM reaction owing to its superb redox properties and oxygen storage capacity (OSC) accommodating a high density of oxygen vacancies to form under-stochiometric CeO_2 at fairly reducing surrounding, hence leading to remarkable enhancement in catalytic performance and stability [8]. According to literature [9], the oxygen vacancies present in the ceria reportedly play as reactive sites for the Mars-van-Krevelen mechanism towards oxidation reaction where the surface oxygen of ceria initially reacts with reactant and leaving an oxygen vacancy, which can be subsequently refilled by oxygen from oxidizing agents. table 1 summarizes the catalytic performance of recent reported Ce-based catalyst for DRM process.

Liu et al. [10] investigated the MSI effects of 0.5%Ru/CeO_2 catalyst on surface carbon. They found that reduction on the catalyst gives rise to Ru-O-Ce interactions detected by *in-situ* ambient pressure (AP)-X-ray photoelectron spectroscopy (XPS) and Ru K-edge extended X-ray adsorption fine structure (EXAFS) at temperature as low as 300-400°C. They believe this interaction contributed to the generation of O adatoms and CO from CO_2 as a result of oxygen ion spillover from the lattice oxygen to metal sites. They then traced the removal of surface carbon by ceria under DRM conditions using *in-situ* AP-XPS. They observed through the removal of lattice oxygen, Ce^{3+} continued to generate from 25 to 300 °C producing labile oxygens. At 400 °C reoxidation of the catalyst begins to occur in the presence of CO_2 which is simultaneously accompanied by the drastic reduction of surface carbon. This was confirmed by the generated peak of CO gas at 350 °C as detected by residual gas analysis (RGA) mass spectrometer results which verified the role of MSI on Ce^{3+}/Ce^{4+} redox cycle to facilitates the removal of surface carbon on the catalyst.

Meanwhile, Yentekakis et al. [11] compared the propensity of carbon removal between Ce-based catalyst and alumina-based catalyst namely 1%Rh/Al_2O_3, 0.8%Rh/Al_2O_3-$Ce_{0.5}Zr_{0.5}O_{2-\delta}$ and 0.8%Rh/$Ce_{0.5}Zr_{0.5}O_{2-\delta}$. They reported the latter catalyst (0.8%Rh/$Ce_{0.5}Zr_{0.5}O_{2-\delta}$) was able to suppress the formation of carbidic carbon by 3-folds in comparison to γ-Al_2O_3 support as captured by temperature-programmed oxidation (TPO) and XPS measurements. Their TPO results showed the nature of the carbon species formed propagated from pyrolytic carbon to reactive carbide and amorphous carbonaceous species due to the inhibition of carbon filament formation, nucleation and growth by Ce-based support catalyst. This was in agreement with Marinho et al. [12] who also obtained carbon mostly in the form of amorphous carbon and traces of multi-walled carbon nanotube (MWCNT) with Ni/CeO_2-Al_2O_3 catalyst with a carbon formation rate of 2 mg$_{carbon}$/g$_{cat}$·h. They ascribed the decrease in carbon content corresponded to the amount of OSC present in the catalyst support with carbon content decreasing in the order Rh/$Ce_{0.5}Zr_{0.5}O_{2-\delta}$ (557 μmol O_2/g)>Rh/Al_2O_3-$Ce_{0.5}Zr_{0.5}O_{2-\delta}$ (101 μmol

O_2/g)>Rh/Al_2O_3 (0 μmol O_2/g). They also evaluated the effects of Ce-based and alumina-based catalyst on the Rh oxidation states via *in-situ* XPS. It showed 0.8%Rh/$Ce_{0.5}Zr_{0.5}O_{2-\delta}$ after DRM conditions fully converted RhO to Rh° metallic, whereas 0.8%Rh/Al_2O_3-$Ce_{0.5}Zr_{0.5}O_{2-\delta}$ and 1%Rh/Al_2O_3 consisted of 72% and 55% Rh° metallic content, respectively, with remaining traces of Rh^{3+} and Rh carbide (alumina-based catalyst has two-times more Rh carbide than alumina-ceria-based catalyst). This suggests the CeO_2 enhances the reducibility of the metallic Rh and simultaneously eliminates of Rh carbide accumulation sites to improve catalytic performance and minimize the deposition of coke on the catalyst itself. Therefore, the OSC led to lower apparent activation energy of both CH_4 and CO_2 reactant gasses with the effect being more significant with reactant CO_2. Rh/$Ce_{0.5}Zr_{0.5}O_{2-\delta}$ showed an increase of 2.5% and 3.7% in CH_4 and CO_2 conversion in comparison to Rh/Al_2O_3-$Ce_{0.5}Zr_{0.5}O_{2-\delta}$, respectively.

Similarly, Marinho et al. [12] also observed the effects of OSC on the removal of carbon on Ni-CeO_2-Al_2O_3 and Ni/CeO_2-Al_2O_3 catalysts surface. They found that the embedment of Ni into the CeO_2-Al_2O_3 support resulted to 45% more surface area than the incipient wetness impregnated Ni loaded on CeO_2-Al_2O_3 support denoted as Ni/CeO_2-Al_2O_3. Using *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), the authors intrinsically observed that the incorporation of ceria increases the reservoir of surface oxygen in terms of hydroxyl groups derived from alumina and carbonate intermediate species. They proposed these intermediate groups act as indicators of surface oxygen species. Interestingly, they identified the carbon removal is directly enhanced by the availability of surface oxygen for carbon oxidation rather than OSC. Ni-CeO_2-Al_2O_3 with an OSC of 309 μmol CO_2/g did not form any carbon after DRM reaction TOS of 72 h and showed high catalytic stability in comparison to Ni/CeO_2-Al_2O_3 (323 μmol CO_2/g) which experienced reactor blockage within 24 h of reaction run. Despite the former catalyst having slightly lesser OSC, a distinguished high intensity peak at 2053 cm^{-1} assigned to linear CO stretching bond absorbed on metallic Ni in the absence of CO_2 reflects the greater concentration of the surface oxygen from the lattice oxygen to readily react with carbon for the removal of coke. This peak is evidently almost non-existent in Ni/CeO_2-Al_2O_3 catalyst which also displayed lower concentrations of hydroxyl and carbonate species in comparison to Ni-CeO_2-Al_2O_3 catalyst under DRM conditions implying a lower amount of surface oxygen available for carbon removal. They implicated that higher oxygen vacancies may have facilitated the bulk diffusion of oxygen resulting to higher surface exchange activity. Though, the trade-off for Ni-CeO_2-Al_2O_3 catalytic stability is the lower CH_4 and CO_2 conversion which was 16% and 8.5% lower than Ni/CeO_2-Al_2O_3, respectively. This was also observed in Safavinia et al. [13] work which managed to reduced the coking rate by 64% with their catalyst Ni:CeO_2-ZrO_2 however, at the cost of 11.8% and 16.4% reduction in CH_4 and CO_2 conversion correspondingly than their reference catalyst. They attributed the location of Ni were at the subsurface which lowered its catalytic activity despite yielding low coking rate. Thus, the catalyst stability significantly relies on the balance between the rate of regeneration of surface oxygen species for carbon removal and the rate of methane decomposition aside from the reservoir of OSC within the catalyst.

Safavinia et al. [13] have identified core-shell structures are capable of increasing both DRM catalytic activity and reducing the coking rate. In order to harness the benefits of this structure, some studies have also integrated ceria into core-shell catalyst to add adverse enhancement effects on the catalyst stability and performance for low temperature DRM. Kawi and co-authors [14, 15] have worked on Ce-based core-shell catalyst by employing ceria as the shell due to its redox properties and OSC attributes for coke removal. Li et al. [14] synthesized nickel phyllosilicate (Ni-phyllosilicate)@CeO_2 core-shell hollow catalyst whereby Ni-phyllosilicate was formed on SiO_2 hollow core before being coated by a layer of thin CeO_2 shell. They found that that the incorporation of CeO_2 shell reduced the carbon deposited from 73.3 wt% to 10 wt% with Ni@CeO_2. This led to a consistent catalytic performance of 72.8% and 79.1% CH_4 and CO_2 conversion, respectively for TOS of 85 h at 700 °C. The effects of metal sintering was suppressed through the phyllosilicate process of Ni on SiO_2 and ceria shell which only resulted to a 1.2 nm increase in Ni particle. Similarly, Das et al. [15] designed a sandwiched core-shell structured Ni-SiO_2@CeO_2 found that the addition of CeO_2 shell suppressed the agglomeration of Ni with an average particle size of 3-5 nm when compared with Ni-SiO_2 spent catalyst (6-8 nm) as detected using XRD and high resolution (HR)-transmission electron microscopy (TEM). As a result, this led to a 1.5-fold increment in CH_4 consumption by Ni-SiO_2@CeO_2 in comparison to Ni-SiO_2 and

subdued the surface carbon accumulation that led to reactor blockage in the absence of the ceria encapsulation shell, though the conversions for the reactant gasses were not reported by the authors. They further evaluated the reaction on the catalyst surface using *in-situ* DRIFTS and found in the presence of ceria shell, wavelength 2040 cm^{-1} correlated to C-O on Ni metal site found in Ni-SiO$_2$ subsides concomitantly with the increase of carbonate groups on CeO$_2$ in the Ni-SiO$_2$@CeO$_2$ catalyst. They postulated that this implies the additional bifunctional sites arise from ceria encapsulation in comparison to the monofunctional Ni-SiO$_2$ core which may have increased the catalytic performance, coinciding with Mars van Krevelen mechanism.

Table 1. List of catalytic performance for recently employed Ce-based catalysts in DRM reaction

Catalyst	GHSV	T (°C)	Conversion (%)		H$_2$/CO ratio	Ref.
			CH$_4$	CO$_2$		
0.5%Ru/CeO$_2$	180	700	39.3	48.1	0.82	[10]
0.8%Rh/80%Al$_2$O$_3$-20%Ce$_{0.5}$Zr$_{0.5}$O$_{2-\delta}$	120	750	50.9	64.6	0.84	[11]
0.8%Rh/Ce$_{0.5}$Zr$_{0.5}$O$_{2-\delta}$	120	750	53.4	68.3	0.85	[11]
10%Ni/CeO$_2$-Al$_2$O$_3$	n.d	800	81.8	93.6	0.93	[12]
10%Ni-CeO$_2$-Al$_2$O$_3$	n.d	800	65.8	85.1	0.87	[12]
Ni@CeO$_2$	36	700	72.8	79.1	0.85	[14]
Ni-SiO$_2$@CeO$_2$	200	600	-	-	0.50	[15]

## 3. Promotional effect of Ce-based catalyst on DRM mechanism

Dry reforming of methane is widely known for its complex multiple parallel reactions to yield syngas. Commonly, noble metal-based catalyst would undergo a competitive chemisorption between CH$_4$ and CO$_2$ gas reactants on its metal sites [12, 15]. CH$_4$ molecule will undergo decomposition on the metal sites to produce CH$_x$ species and H adatoms prior to the formation of H$_2$ gas and surface carbon on the metal site. CO$_2$ would also be scission on the metal site and react with the surface carbon to yield CO gas. The monofunctional sites limit the efficacy of syngas production as well as lead to severe catalyst poisoning [12, 15].

As discussed in the previous section, ceria plays a crucial role in the enhancement of catalytic performance owing to its remarkable OSC and redox properties in association with the formation of oxygen vacancies. Figure 1 illustrates the proposed promotional effect of ceria on the DRM process in terms of mechanism associated with the ceria redox properties. The CeO$_2$ exists as a cubic fluorite with a face-centered cubic crystal structure consisting of an electronic configuration of 4f^{1}5d^{1}6s^2 [16]. In an ideal CeO$_2$ crystal stoichiometric, each O^{2-} ion is coordinated by four Ce^{4+} ions [17]. However, under reducing conditions (i.e. H$_2$-rich atmosphere) oxygen is released from the CeO$_2$ lattice cell which subsequently resulted to the formation of labile oxygen vacancy and generation of Ce^{3+}. This allows CeO$_2$ to undergo two oxidation states namely Ce^{3+} (Ce$_2$O$_3$) and Ce^{4+} (CeO$_2$) which uniquely belongs to lanthanoids or rare-earth metals. This redox property grants CeO$_2$ high labile oxygen mobility which enables it to participate in the DRM gaseous reaction through a redox cycle between Ce^{4+}/Ce^{3+} under the Mars van Krevelen mechanism [11]. This mechanism facilitates conversion of surface carbon (C) by lattice oxygen (O_l) in equation (6) to produce carbon monoxide (CO) for carbon oxidation in equation (7). Simultaneously, the adsorption and scission of CO$_2$ into CO and O_a adatoms would replenished the surface oxygen vacancies, V_o as shown in equation (8) [6, 11].

$$O_l \rightleftharpoons O_a + V_o \qquad (6)$$

$$C + O_a \rightleftharpoons CO(g) + V_o \qquad (7)$$

$$CO_2(g) + V_o \rightleftharpoons CO(g) + O_a \qquad (8)$$

Evidently, oxygen vacancies existing in ceria plays an indispensable role in both oxygen storage capacity for mobile oxygen ions and also facilitating the reactivity of the catalyst surface to cleave CO$_2$ [18]. These oxygen vacancies also create additional sites to mitigate the competitive chemisorption between CH$_4$ and CO$_2$ reactants on the metal sites allowing the Ce-based catalyst to exhibit a

bifunctional site mechanism and enhance the catalytic performance and catalyst stability [15]. Additionally, the labile oxygen associated with O^{2-} mobility and OSC supplying the reservoir of spillover oxygen from Ce^{3+} oxygen vacancies can stabilize the metallic phase of the hosting metal site and prevent it from undergoing reoxidation [11]. Under DRM conditions, carbonate groups are clearly present during the reaction. Although Das et al. [15] mentioned that the carbonate remains mainly inactive during the reaction, however Liu et al. [10] points out carbonates can aid in the formation of CO under H-activation conditions via RWGS as shown in equation (9):

$$H_2 + CO_3 \rightarrow CO + H_2O \tag{9}$$
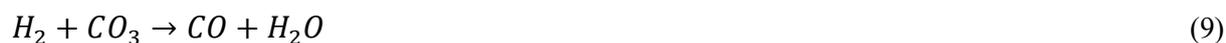
CO₂ adsorbed on the ceria support owing to its basicity properties would form carbonates species which occasionally receives H adatoms cleaved by the metal site to form CO gas and hydroxyl radicals. Subsequently, it will undergo a more stable form with another H adatom to form water.
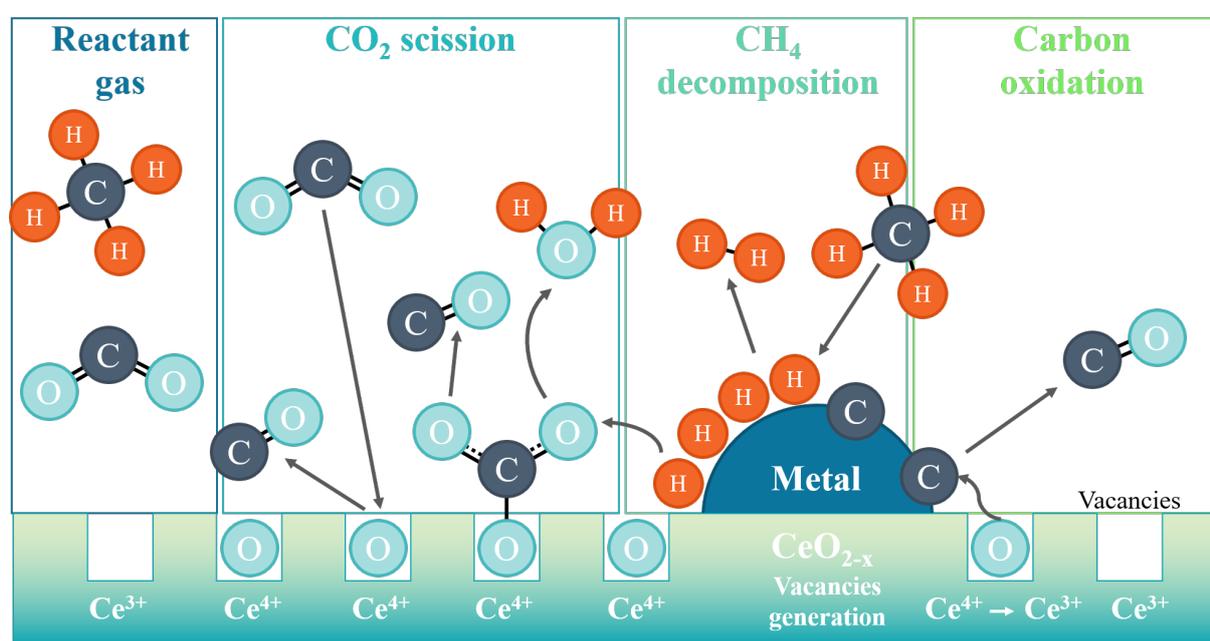

Figure 1. Proposed DRM mechanism through the promotional effect of Ce-based catalyst

4. Conclusion

The DRM process has immense potential for the production of syngas as feedstock for the building block of synthetic fuels for the future energy industry. However, the industrial implementation of DRM is impeded by its severe catalyst poisoning. Hence, the promotion of ceria into the catalyst design has been extensively studied in terms of its catalyst efficacy and stability. Based on literature, the unique redox properties of Ce-based catalysts reportedly not only enhanced the DRM reaction rate by lowering the activation energies but also provided labile oxygen for surface carbon removal on the catalyst surface, thus prolonging the catalyst lifespan. It also improves the metal dispersion and suppresses metal sintering even after exposure at high temperature DRM conditions.

The promotional influence of ceria on DRM is undoubtably as reported on literature. However, Ce-based on DRM mechanism still remains unclear due to its complex reactions. Through the synergistic effect of metal and support interaction, the existence of a bifunctional site mechanism arises through the incorporation of ceria aid in reducing the competitive chemisorption between CH₄ and CO₂ reactants. Moreover, the formation of oxygen vacancies through the Ce^{3+}/Ce^{4+} redox cycle facilitated the CO₂ scission, removal of surface carbon from the metal site as a result of methane decomposition and formation of carbonates as surface oxygen species. Despite numerous in-situ experimental research efforts carried out on Ce-based support to highlight the potential and elucidate the role of Ce-based catalyst in extending the catalyst lifespan for DRM application, fine tuning and material development

on the Ce-support is still required to obtained the desired catalytic activity and retain its performance stability. In addition, the mechanistic pathways can also be validated using DFT calculations to validate the experimental in-situ data obtained and increase its accuracy.

Acknowledgments

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