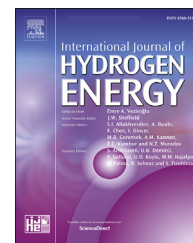




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An in depth investigation of deactivation through carbon formation during the biogas dry reforming reaction for Ni supported on modified with CeO₂ and La₂O₃ zirconia catalysts

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ABSTRACT

The dry reforming of biogas on a Ni catalyst supported on three commercially available materials (ZrO₂, La₂O₃–ZrO₂ and CeO₂–ZrO₂), has been investigated, paying particular attention to carbon deposition. The DRM efficiency of the catalysts was studied in the temperature range of 500–800 °C at three distinct space velocities, and their time-on-stream stability at four temperatures (550, 650, 750 and 800 °C) was determined for 10 or 50 h operation. The morphological, textural and other physicochemical characteristics of fresh and spent catalysts together with the amount and type of carbon deposited were examined by a number of techniques including BET–BJH method, CO₂ and NH₃-TPD, XPS, SEM, TEM, STEM-HAADF, Raman spectroscopy, and TGA/DTG. The impact of the La₂O₃ and CeO₂ modifiers on the DRM performance and time-on-stream stability of the Ni/ZrO₂ catalyst was found to be very beneficial: up to 20 and 30% enhancement in CH₄ and CO₂ conversions respectively, accompanied with a CO-enriched syngas product, while the 50 h time-on-stream catalytic performance deterioration of ~30–35% on Ni/ZrO₂ was limited to less than ~15–20% on the La₂O₃ and CeO₂ modified samples. Their influence on the amount and type of carbon formed was substantial: it was revealed that faster oxidation of the

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deposited carbon at elevated temperatures occurs on the modified catalysts. Correlations between the La₂O₃ and CeO₂-induced modifications on the surface characteristics and physicochemical properties of the catalyst with their concomitant support-mediated effects on the overall DRM performance and carbon deposition were revealed.

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Introduction

The Dry Reforming of Methane (DRM) uses biogas for the production of syngas, which is suitable for the synthesis of oxygenated chemicals and hydrocarbons by means of Fisher – Tropsch process. As the main components of biogas are CH₄ and CO₂, the process can help mitigate the effects of climate change. DRM (Eq. (1)) is a highly endothermic reaction ($\Delta H^{\circ}_{298} = +247$ kJ/mol), which is influenced by the simultaneous occurrence of the Reverse Water Gas Shift reaction (RWGS, Eq. (2)) [1–4]. A number of carbon forming reactions may also occur, such as methane decomposition (Eq. (3)) and carbon monoxide disproportionation (or Boudouard reaction, Eq. (4)). Moreover, part of the as-formed surface carbon can form CO or CO₂ via the carbon gasification (Eq. (5)) or the carbon oxidation reactions (Eqs. (6) and (7)). Another reaction to be considered is the CO methanation reaction (Eq. (8)) [5–8].

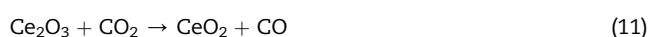
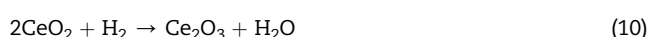


Although noble metals (Rh, Ru, Pd, Ir and Pt) have been successfully tested in the DRM, their high cost inhibits their use in industrial applications [9–12]. Thus, research is being directed towards Ni based catalysts as it is known that if it is highly dispersed on to the support that Ni can offer exceptional activity, [13–17]. The major drawback of nickel-based systems is that they suffer from deactivation due to carbon formation [17–19] and metal particles sintering due to a lack of adequate thermal stability [20,21]. Apart from the loss of active metallic sites, sintering further aggravates carbon deposition, as large metal aggregates induce the formation of coke [22,23]. Nickel particles are often reported to be encapsulated by carbon within filaments (or whiskers), formed during the reaction, which leads to a loss of activity. It has also been reported that Ni particles may be pushed on to the filament top and remain active during the reaction. However, extensive whisker

formation can expand the catalyst bed and plug the reactor, lead to a blockage of the porosity of the catalytic particles and make it difficult to regenerate the catalytic system, as the contact between metal and support is lost [24,25].

As is well understood, catalytic activity depends on the nature of the support, active phase precursor, synthesis method and pre-treatment [26–28]. Thus, researchers have tested a variety of different metal oxides (e.g., Al₂O₃, SiO₂, La₂O₃, CeO₂, ZrO₂) as supports for Ni based catalysts [26–29], and have used transition metals (e.g., Fe, Co, W, Sn) [30,31], noble metals (e.g., Ag, Pt, Pd) [32,33], lanthanide metals (e.g., La, Ce, Pr) [20,25,26] or alkaline earth metals (e.g., Sr, Ca, Ba) [34,35] as modifiers in the supports, in an effort to induce support-mediated promotional effects on the catalytic system.

An approach which appears promising is the utilization of metal oxides that possess high oxygen storage capacity (OSC), as it has been reported that such oxides can enhance nickel dispersion and participate in surface carbon oxidation reactions [36,37]. CeO₂ has currently become a ubiquitous constituent in many catalytic systems due to its ability to act as an oxygen buffer, storing/releasing oxygen via the Ce³⁺/Ce⁴⁺ redox couple (Eq. (9)) [38]. In particular, in the DRM process, CeO₂ can also release water as it may react with H₂ (Eq. (10)) and the reduced Ce³⁺ can be re-oxidized by CO₂ (Eq. (11)). Moreover, CeO₂ can also remove in-situ the carbon deposited on to the catalyst surface via Eq. (12), and thus affect the DRM reaction process in several ways [39,40].



As ceria is known to be thermally unstable, and since the DRM is more effective at high temperatures, such properties (Eqs. (9)–(12)) are best utilized by incorporation of CeO₂ in a thermally stable support. Zirconia is thermally stable and has the additional advantage of forming non-stoichiometric fluoride Ce_xZr_{1-x}O₂ solid solutions possessing high oxygen ion lability [41,42], and low acidity [43,44].

On the other hand, when lanthana is used in the support of DRM catalysts, CO₂ is activated by La₂O₃ through the formation of La₂O₂CO₃, which can eliminate the deposited carbon at the Ni–La₂O₃ interface by means of coke oxidation [25,45].

In a previous preliminary work [46], we reported on the DRM catalytic efficiency of Ni dispersed on three commercially available catalytic supports (ZrO₂, La₂O₃–ZrO₂ and

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