Methane steam reforming at low temperature: Effect of light alkanes' presence on coke formation

Sofia D. Angeli, Fotis G. Pilitsis, Angeliki A. Lemonidou*

Department of Chemical Engineering, Aristotle University of Thessaloniki, University Campus, GR-54124 Thessaloniki, Greece

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ABSTRACT

Steam reforming of natural gas for the production of hydrogen at low operation temperature offers significant financial and environmental advantages. However, the presence of higher hydrocarbons as minor components of natural gas can significantly affect the formation of coke and thus the effectiveness of the catalyst. In this study, the effect of the presence of C2–C3 alkanes in the feedstock on the carbon accumulation during low temperature steam reforming of methane is investigated over Ni and Rh catalysts supported on lanthanum doped ceria–zirconia mixed oxide. Both catalysts showed high resistance to coke formation and especially in the case of Rh/La/CeO$_2$–ZrO$_2$, the carbon accumulation detected was low even after 10 h on stream in steam reforming of all mixtures of hydrocarbons tested. The presence of higher alkanes in methane increased the amount of carbon on Ni(10)CeZrLa compared to pure methane as well as the nature of the carbonaceous species. Increase in the C-number of the additive alkane had almost no influence on the total amount of carbon formed (C/H feed ratio = constant) but favored the formation of filamentous carbon.

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1. Introduction

Due to the increase in hydrogen demand and the importance of syngas production, steam reforming of natural gas will play an important role in the future applications related to the hydrogen economy [1]. The conventional process consisted of a reforming reactor operating at temperature over 800 °C followed by a WGS reactor and products separation, results in high operation cost and GHG emissions.
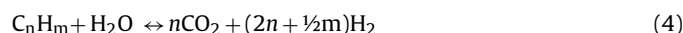
Aiming at the intensification, a process based on low-temperature steam reforming (400–550 °C) is proposed. As renewable and C-free heat source, concentrated solar power (CSP) plant can be used in conjunction with a mixture of molten nitrates as a heat transfer and storage medium. The utilization of CSP plant as an external heat supplier results in the reduction of GHG emissions [2] and the molten salts up to 550 °C with a heat storage device can ensure constant-rate solar heat supply for an energy demanding industrial chemical process like steam reforming [3]. Furthermore, the compact small-scale process proposed, offers flexibility to use as primary fuel, not only natural gas, but biogas or bioethanol as well, according to local availability. Reforming

reactions are carried out in a low-temperature operating reactor, where conversion is enhanced by the use of a hydrogen selective membrane. Thus, high purity H$_2$ stream is produced, and at the same time the shift of the reforming reaction is favored [4,5].

The main advantages of low temperature operation are the decreased energy demands and cost for materials and engineering. Furthermore, compared to the conventional high temperature steam reforming, this low temperature process ensures quick start-up and does not require a CO shift due to favorable equilibrium of WGS reaction.

The key issue for the successful realization of the described process is the development of catalysts which are able to activate methane at low temperature and drive its conversion up to equilibrium values at short contact times [4,6,7] and, in addition, to be resistant to deactivation factors, such as coke formation [8–10].

Steam reforming of natural gas is described by reactions (1)–(3):

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{1}$$

$$C_nH_m + nH_2O \leftrightarrow nCO + (n + \tfrac{1}{2}m)H_2 \tag{2}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{3}$$

$$C_nH_m + H_2O \leftrightarrow nCO_2 + (2n + \tfrac{1}{2}m)H_2 \tag{4}$$

C$_n$H$_m$ represent hydrocarbons higher than methane, such as ethane and propane, which are secondary components of natural gas. The formation of carbon on the catalyst under steam reforming

conditions may take place mostly through cracking of hydrocarbons (Eqs. (5) and (6)) as well as the Boudouard reaction (Eq. (7)).

$$CH_4 \leftrightarrow C + 2H_2 \tag{5}$$

$$C_nH_m \leftrightarrow nC + m/2H_2 \tag{6}$$

$$2CO \leftrightarrow C + CO_2 \tag{7}$$

The presence of higher hydrocarbons can significantly affect the formation of surface carbon species and thus the effectiveness of the catalyst.

Sperle et al. [11] determined the coking tendency for steam reforming of methane in the presence of C2 and C3 hydrocarbons over a Ni/MgAl$_2$O$_4$ catalyst. It was found that coking increased with carbon number and a dramatic increase was noted for olefins. Sidjabat and Trimm [12] also found that coke formation increased with the molecular weight of the feed and that the deactivation rates during SR of ethane and propane over Ni/MgO were higher compared to methane.

It should be noted, however, that catalysts containing CeO$_2$ or CeO$_2$–ZrO$_2$ mixed oxides as supports are preferable for the reforming of methane at low temperature, as stated in a recent review [13]. The participation of ceria-based oxides in the reaction mechanism leads to higher activity of both SR and WGS [14–18] as well as to the gasification of surface carbon species [19–21]. The activity of ceria based catalysts, but also the resistance to coke and deactivation factors have been related to the strong interaction that can be induced between the support and the metal particles [22–24]. The incorporation of Zr into the ceria lattice is well known to increase the oxygen storage capacity and improve the redox properties [25] while, at the same time, efficient steam activation is provided by Zr cations [26]. In addition, La has been reported to improve the oxygen mobility [27] and the carbon tolerance of the catalyst [28,29].

Our recent studies [30,31] in low temperature steam reforming of methane demonstrated that ceria–zirconia support when doped with lanthana can result to the minimization of coking deposition thus improving the stability of the catalyst over time on stream.

However, ceria-based supported catalysts have not been studied to our knowledge, in terms of coke depositions during steam reforming of light hydrocarbon mixtures. Laosiripojana et al. [32] found that ceria doped Ni/Al$_2$O$_3$ showed higher coke resistance in SR of ethane/propane mixture at 900 °C compared to Ni/Al$_2$O$_3$, but no results on coke formation with methane feed are discussed. Wang and Gorte [33] studied the rates of reforming of various single-hydrocarbon feedstocks over Pd and Pt/CeO$_2$ and they found that the rate increases with carbon number in the temperature range of 350–500 °C. Takeguchi et al. [34] compared steam reforming of methane, ethane and ethylene at 800 °C over Ni/YSZ cermets. They also studied the effect of alkaline earth additives on carbon depositions, but only for methane feed.

In this study, the effect of the presence of C2–C3 alkanes in the feedstock on the carbon accumulation during low temperature steam reforming of methane is investigated over Ni and Rh catalysts supported on lanthanum doped ceria–zirconia mixed oxide. The amount of carbon deposited is qualitatively and quantitatively characterized by temperature programmed oxidation.

2. Experimental

2.1. Catalyst preparation

The wet impregnation method was applied for the preparation of catalysts. Ceria and lanthana doped zirconium oxide (78% ZrO$_2$, 17% CeO$_2$ and 5% La$_2$O$_3$) provided by Mel Chemicals (XZO 1768) was used as the support. The pelleted support was crush and sieved to attain particle size in the range of 250–355 μm. Ni(NO$_3$)$_2$·6H$_2$O

(Merck) and RhCl$_3$·xH$_2$O (Pressure Chemical) were used as precursors for nickel (10 wt.%) and Rh (1 wt.%), respectively. The aqueous solution of the metal precursor was mixed with the support particles and stirred for 1 h at 70 °C. The solvent was removed via evaporation under mild vacuum conditions and the sample was dried overnight at 110 °C. Subsequently, the material was calcined in air flow at 800 °C for 5 h. The catalytic material is referred to as M(x)CeZrLa (where M is the active metal and x the metal loading wt.%).

2.2. Catalyst characterization

The surface area of the prepared materials was measured by N$_2$ adsorption at 77 K, using the multipoint BET analysis method with an Autosorb-1 Quantachrome flow apparatus. The samples were dehydrated in vacuum at 250 °C overnight, before surface area measurements. X-ray diffraction (XRD) patterns were obtained using a Siemens D500 diffractometer, with Cu $K\alpha$ radiation, in order to identify the crystalline phases apparent. The crystallite size was calculated using XRD data by the Scherrer equation.

Temperature Programmed Reduction (TPR) experiments were performed in a gas flow system using a U-tube reactor connected online with a quadrupole mass analyzer (Omnistar). The catalyst sample (100 mg) was placed in the reactor and pretreated for 0.5 h at 250 °C followed by cooling at room temperature in He flow. The temperature was then raised from ambient to 800 °C at a rate of 10 °C/min in a 10% H$_2$/He flow (50 mL/min). The mass numbers (m/z) 2 and 18 were used for H$_2$ and H$_2$O monitoring, respectively.

2.3. Catalytic tests and characterization of carbon depositions

The catalytic evaluation experiments were performed at atmospheric pressure in a laboratory unit equipped with a mass flow-controlled system for gases admission, a fixed bed quartz reactor, and an online gas chromatograph. An UFLC pump (Shimadju) was used for the feeding of water to the reactor through a preheated line. The fixed bed reactor was heated electrically by a tubular furnace, with three independently controlled temperature zones. The temperature in the middle of the catalytic bed was measured with a coaxial thermocouple. The hot gases exiting the reactor were cooled to condense the unreacted steam. The gas phase products were analyzed with an online gas chromatograph (Agilent Technologies 7890A) equipped with a TCD. To separate the products, two columns were used; PoraPlotQ for CO$_2$, C$_2$H$_6$ and C$_3$H$_8$ and MS 5A for H$_2$, CO and CH$_4$. In order to investigate the effect of the presence of C$_n$ alkanes (1 < n < 3) in the feedstock on the formation of carbon during steam reforming, two sets of experiments were conducted. The coking tendency was first evaluated by feeding separately undiluted methane, ethane and propane. These tests were conducted at temperatures from 400 to 550 °C, atmospheric pressure and S/C molar ratio of 3. In the case of methane feed, gas hourly space velocity (GHSV) was 70,000 h^{-1} and in the case of ethane and propane, inlet flow of carbon was kept constant, resulting in GHSV of 61,000 and 58,000 h^{-1}, respectively.

The performance of the catalysts is expressed in terms of the composition of the dry effluent stream and is evaluated by comparison with those predicted by thermodynamic equilibrium. The hydrocarbon conversions were calculated from the effluent concentrations as follows:

$$X_{CH_4}, \% = \frac{[CO]_{out} + [CO_2]_{out}}{[CH_4]_{out} + [CO]_{out} + [CO_2]_{out}} \times 100 \tag{8}$$

$$X_{C_nH_m}, \% = \frac{[CH_4]_{out} + [CO]_{out} + [CO_2]_{out}}{n[C_nH_m]_{out} + [CH_4]_{out} + [CO]_{out} + [CO_2]_{out}} \times 100 \tag{9}$$