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THEORETICAL ANALYSIS OF CATALYST DEACTIVATION DUE TO POISONING BY H_2S AND SOLID CARBON DEPOSITION: EFFECT OF ADDITION OF RARE-EARTH (La_2O_3 and CeO_2)[1]

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Abstract

The aim of this research is to identify, by means of a thermodynamic analysis, the beneficial effects of La_2O_3 and CeO_2 addition to catalysts used in biogas reforming. Operating conditions, under which deactivation of Ni catalyst by H_2S poisoning and/or solid carbon deposition can be reduced or prevented, are determined. In this work, the stability of different phases of solid carbon – graphite and multi-walled carbon nanotubes – under biogas stream reforming atmosphere is analyzed. The results from the present study contribute to the development of multifunctional catalysts.

Key words: H_2S; Biogas; Catalyst; Thermodynamic simulation.

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1 INTRODUCTION

Biogas is a highly variable mixture of gases predominantly consisting of methane and carbon dioxide, usually methane-rich in a ratio of approximately 2:1.(1) It can be produced by anaerobic digestion or fermentation of any biodegradable organic matter, including municipal solid waste, seawage sludge, agricultural wastes, animal dung and energy crops.(2) Biogas can be catalytically converted into *syngas* in a reformer. *Syngas* (a mixture of H_2 and CO) can be used as fuel in the anode of Solid Oxide Fuel Cells (SOFCs) to produce electrical and heat energy.(3) Supported nickel-based catalysts are commonly used in hydrocarbon conversion processes due to excellent activity, low cost and wide availability of Ni.(4) The development of Ni-based catalysts is critical to biogas utilization. They have lower durability than more expensive catalysts (Ru and Rh) and deactivate relatively quickly due to carbon deposition and poisoning by H_2S.(5) Desulfurization of biogas is usually required before use. However, even in low concentration (<10ppm), H_2S can cause significant deactivation of Ni catalysts. H_2S poisons Ni surface through chemisorption, with Ni surface coverage, or through formation of a bulk sulfide phase, typically Ni_3S_2. Sulfur prevents reactants from accessing the nickel surface and can hinder various surface reaction processes, such as reactant decomposition and diffusion.(1) Carbon deposition can deactivate nickel catalysts for various reasons, which include poisoning of nickel surface, encapsulation of nickel particles or forming whisker-like filaments. Large amounts of carbon must be avoided.(1,6) Nevertheless, it would be interesting to investigate the possibility of obtaining simultaneously a *syngas* with high H_2 content together with carbonaceous nanostructured materials with high added value.(7)

Doping Ni catalysts with small amounts of other materials is shown to be an effective approach to alleviate carbon deposition and sulfur poisoning.(1,8) CeO_2 is an important material for a variety of catalytic reactions. It contains a high concentration of highly mobile oxygen vacancies, which act as a local sources or sinks for oxygen involved in reactions taking place on its surface. It is reported that the redox property of ceria improves the resistance toward carbon deposition. The gas-solid reactions between the gaseous components in the system and the lattice oxygen (O_x) on ceria surface could prevent the formation of carbon on Ni surface.(9) Besides, rare earth oxides can be used as sorbents for the removal of H_2S from fuel, due to their strong affinity for sulfur.(10) In this context, the aim of this research is to identify, by means of a thermodynamic analysis, the beneficial effects of La_2O_3 and CeO_2 addition to catalysts used in biogas reforming. Operating conditions under which deactivation of Ni catalyst by H_2S poisoning and/or solid carbon deposition can be reduced or prevented are determined. In addition, this work aims to describe equilibrium composition for reforming systems, including different phases for describing carbon deposits, that is, the stability of graphite and multi-walled carbon nanotubes is analyzed.

2 METHODOLOGY

Thermodynamic equilibrium calculations using the Gibbs energy minimization approach were carried out using both the commercial software FactSage 6.3 and the Solver function contained in the Microsoft Excel spreadsheet package, as described in Silva e Müller.(11)

For the study of the effect of CeO_2 on reformate composition, carbon deposition

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(section 3.1) and prevention of H_2S poisoning of Ni catalyst (section 3.2), FactSage 6.3 program was employed. The selected databases were SGPS and FactPS, which include thermodynamic data for compounds only. The species considered for describing the ideal gas phase were: H_2, H_2O, H_2S, CO, CO_2, CH_4, O_2, S_2, COS, CS, CS_2, SO_2, SO_3, S_2O. The solid phase graphite was considered in the compounds data set to predict carbon deposition over the catalyst. The solid phases selected to describe the Ce-O-S system were the following: $CeO_{1.72}$, $CeO_{1.83}$, CeO_2, Ce_2O_2S, $Ce_2(SO_4)_3$, CeS, Ce_3S_4, Ce_2S_3, Ce_2O_3. The solid phases selected to describe the Ni-S-O system were the following: Ni, Ni_3S_2, Ni_3S_4, Ni_6S_5, NiS, NiS_2, $NiSO_4$, NiO.

The effect of La_2O_3 on the prevention of H_2S poisoning of Ni catalyst (section 3.2) and the stability of different phases of solid carbon (section 3.3) were studied using the Solver function contained in the Microsoft Excel spreadsheet package. Thermodynamic data for describing Gibbs energy of species in gas phase and solid graphite were obtained from Knacke, Kubashewski and Hesselmann.(12) Thermodynamic data of $La_2O_2CO_3$ and La_2O_2S were taken from Shirsat et al.(13) and Kay, Wilson and Jalan,(10) respectively. The Gibbs energy of multi-walled carbon nanotubes (MWCNTs) is considered to be a function of graphite Gibbs energy, as shown in Díaz Alvarado and Gracia.(14)

With respect to sulfur poisoning mechanism for Ni-based catalysts used in reformers or in anodes of SOFCs (typically Ni-YSZ cermet anodes), it would be interesting to pause here and discuss it briefly based on the experimental results reported for fuel conversion in reformers and electrochemical measurements in SOFCs. For an inlet mixture of CH_4/CO_2 containing only few ppms of H_2S, it has been reported that CH_4 conversion decreases dramatically for Ni-based catalysts in the presence of H_2S. According to Ashrafi et al.,(15) the poisoning of the nickel catalyst may occur even when the concentration of hydrogen sulfide ought not to cause the formation of a bulk nickel sulfide. Therefore, hydrogen sulfide may be assumed to be retained by a chemisorption process. The loss of activity of Ni-based catalysts through sulfur compounds could be due to strong sulfur chemisorption on the nickel surface, which prevents the further adsorption of reactant molecules. In a Ni-YSZ cermet anode, sulfur poisoning is characterized by a rapid initial drop in power output upon exposure to sulfur-containing fuels.(16) For describing sulfur chemisorption, Rostrup-Nielsen et al.(17) used a Temkin-like isotherm:

$$\frac{pH_2S}{pH_2} = \exp\left(\frac{\Delta H_0^0(1-\alpha\theta)}{RT} - \frac{\Delta S_0^0}{R}\right) \qquad (1)$$

Based on Equation 1, the equilibrium surface coverage (θ) will be calculated, in the present work, as Equation 2.

$$\theta = \frac{\ln\left(\frac{pH_2S}{pH_2}\right) + \frac{\Delta H_0^0}{RT} + \frac{\Delta S^0}{R}}{\frac{\alpha \Delta H_0^0}{RT}} \qquad (2)$$

With a ΔH_0^0 of 289 kJ mol^{-1}, a ΔS^0 of −19 J mol^{-1} K^{-1}, and a α of 0.69.

After each equilibrium calculation carried out using the Gibbs energy minimization approach, the obtained pH_2S/pH_2 ratio is replaced in Equation 2, and the surface coverage value can be known. Operating conditions under which θ value can be diminished are determined in the present research. The lower the Ni surface coverage, the lower the catalyst poisoning.

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3 RESULTS AND DISCUSSION

3.1 Effect of CeO_2 Addition on Reformate Species and Carbon Deposition

Figure 1 shows the equilibrium data for direct partial oxidation of methane to synthesis gas by CeO_2. From Figure 1e, it is possible to see that *syngas* with a H_2/CO ratio of 2:1 can be directly obtained by the gas-solid reaction between methane and CeO_2. Interestingly, this fact has been experimentally verified in Otsuka et al.(18) *Syngas* can be produced from CH_4 in absence of O_2, H_2O or CO_2. That is, CeO_2 acts as an oxidant for the oxidation of CH_4. When there is no CeO_2 in the system, the only species present at equilibrium are H_2 and C(s), due to CH_4 decomposition.

$$CH_4 \rightarrow C(s) + 2H_2$$

Figures 1a and 1b show that solid carbon can be gasified to CO as CeO_2 is added to the system. The lattice oxygen must be responsible for the formation of CO. Possibly, the reaction that describes this process is:

$$C(s) + CeO_2 \rightarrow CO + CeO_{2-x}$$

Figure 1g shows that CeO_2, under a reducing atmosphere, is reduced to $CeO_{1.71}$. When CeO_2/CH_4 molar ratio is higher, the more oxidized form, $CeO_{1.83}$, prevails in the system. Under these conditions (CeO_2/CH_4 molar ratios >6), H_2 molar production decreases (Figure 1c), while H_2O and CO_2 increase (Figures 1d and 1f).

Figure 2 shows the effect of CeO_2 addition on reformate composition and H_2/CO ratio for an inlet gas composed of CH_4 and CO_2. The behavior is very similar to that seen in Fig. 1 for pure methane. In the case of methane dry reforming, it is possible to see from Figure 2d that, as CeO_2/CH_4 ratio increases, H_2/CO ratio approaches 1.3, which is the value reached during combined CO_2 reforming and partial oxidation (oxy-CO_2 reforming).(19) Thus, it is clearly seen from Figure 2 that oxy-CO_2 reforming can be carried out with the use of CeO_2 along with the catalyst (Ni). The process could be very stable, since, due to redox properties of CeO_2, solid carbon can be gasified.

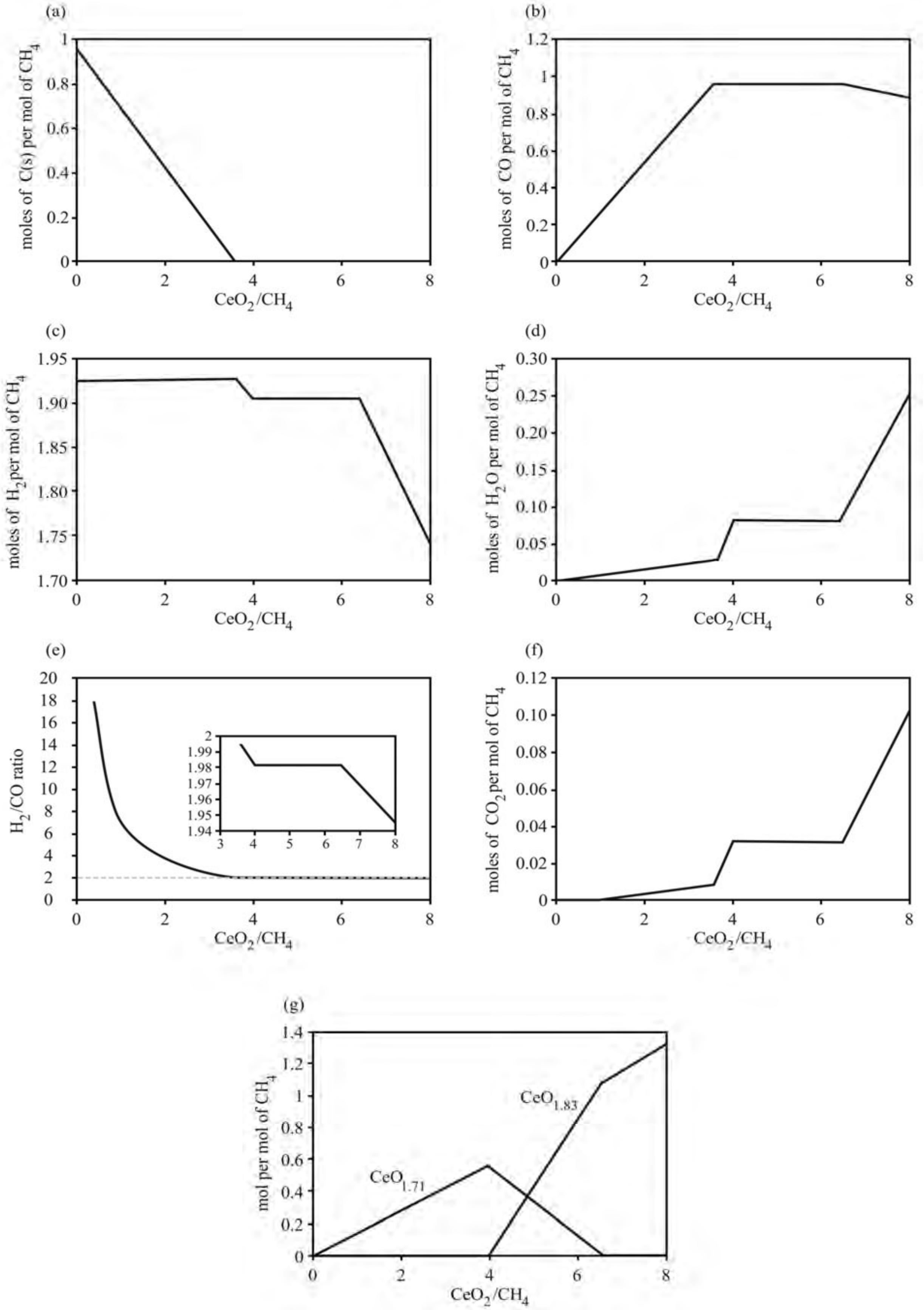

Figure 1. Effect of CeO_2/CH_4 ratio on the production (mol per mol of CH_4) of (a) solid carbon (b) CO (c) H_2 (d) H_2O, (f) CO_2, (g) $CeO_{1.71}$ and $CeO_{1.83}$, and (e) H_2/CO ratio. Feedstock: pure methane, T=1.173K.

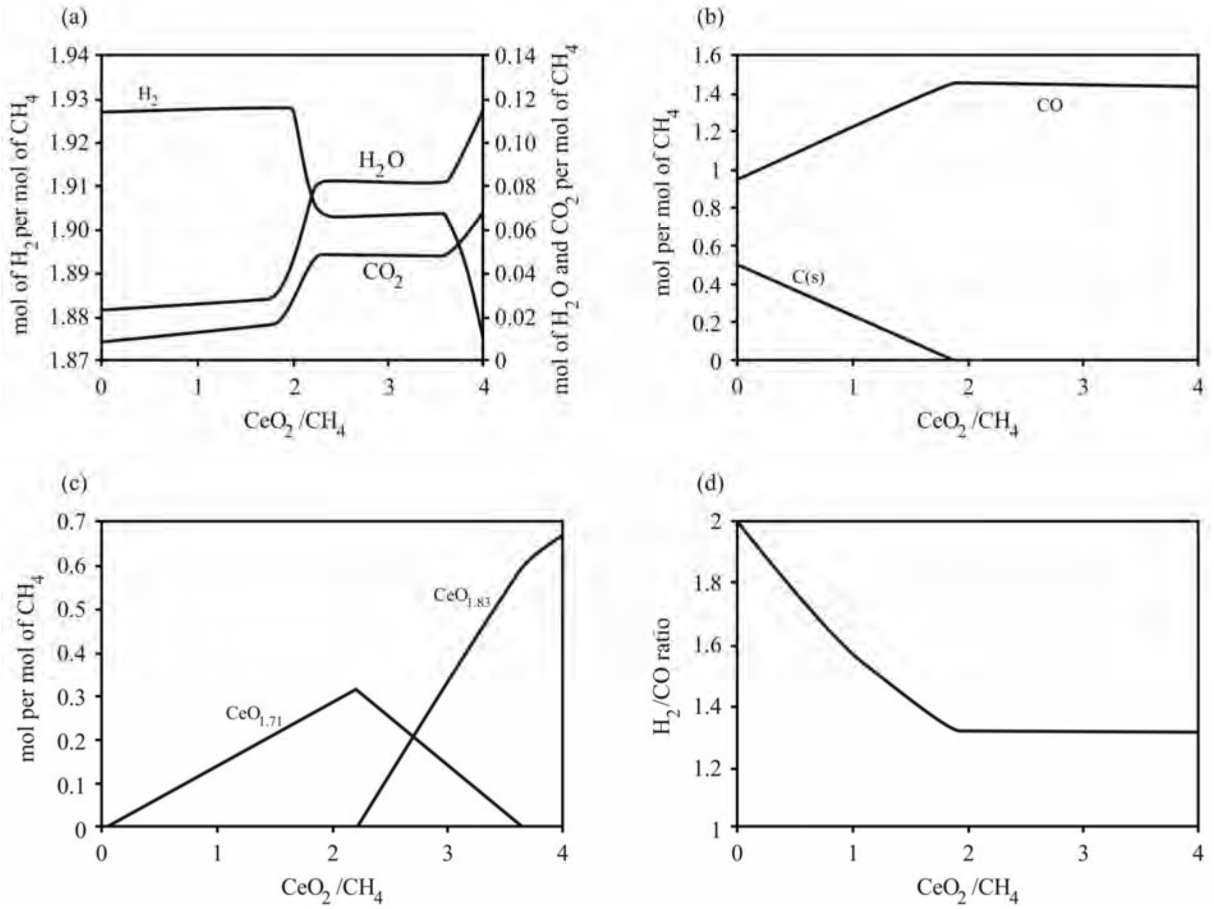

Figure 2. Effect of CeO_2/CH_4 ratio on the production (mol per mol of CH_4) of (a) H_2, H_2O, CO_2 (b) solid carbon and CO (c) $CeO_{1.71}$ and $CeO_{1.83}$ and (d) H_2/CO ratio. Feedstock: CH_4/CO_2 molar ratio=2:1, T=1.173K.

3.2 Effect of CeO_2 and La_2O_3 Addition on Prevention of Ni Poisoning by H_2S During Biogas Reforming

Figure 3 shows the effect of CeO_2 addition on surface coverage (θ) of Ni catalyst. For inlet mixtures richer in CH_4 (CH_4/CO_2 molar ratio of 2:1 (Figures 3a and 3b), one can see that at T>1.173K, CeO_2 addition results in lower θ values. At these temperatures, the solid phase Ce_2O_2S can be formed, lowering the partial pressure of H_2S. It should be noted from Figure 3b that Ce_2O_2S can only be present at equilibrium when the reduced form of ceria ($CeO_{1.71}$) prevails in the system. As can be seen for inlet mixtures poorer in CH_4 (CH_4/CO_2 molar ratio of 0.5:1 (Figures 3c and 3d), a more oxidized form of ceria ($CeO_{1.83}$) is stable, and, under these conditions, the solid phase Ce_2O_2S is not able to be formed. Thus, for a biogas poorer in CH_4, the addition of CeO_2 is not effective to improve the resistance of Ni catalyst to H_2S poisoning. It is worth pointing out that ceria does not form a stable carbonate above 773K.(20)

Figure 4 shows the effect of La_2O_3 addition on surface coverage (θ) of Ni catalyst. For both inlet gas mixtures (CH_4/CO_2= 2:1 and 0.5:1), the surface coverage value is practically not affected by the addition of La_2O_3 at 873K. At this temperature, La_2O_3 reacts preferentially with CO_2 rather than H_2S, forming mostly lanthanide oxycarbonate ($La_2O_2CO_3$). However, at higher temperatures, $La_2O_2CO_3$ phase becomes unstable, and the formation of La_2O_2S is favored, especially for the biogas composition richer in CH_4. As can be seen from Figure 4a, at 1.273 K, θ is reduced to a value as low as 0.6 (at 1.273 K, θ=0.6 falls in the region of 'clean Ni surface' of the diagram from Wang and Liu(21) which means that, for such a value of surface coverage, Ni catalyst would not be deactivated by H_2S).

It is interesting to compare the performances of the different sorbents (CeO_2 and La_2O_3). From Figure 3a, one can see that the best value for θ that can be achieved with CeO_2 is 0.75 at 1.273 K. The same value for θ could be achieved with La_2O_3 sorbent at a lower temperature – 1.073 K (Figure 4a). These results indicate that La_2O_3 can be a better choice than CeO_2.

Figure 5 compares Ni surface coverage values when biogas (CH_4/CO_2 molar ratio of 2:1) or H_2 is used as fuel in the reformer. As can be observed, the catalyst poisoning tends to be more severe in the case of biogas over the whole temperature range. These theoretical findings are in agreement with experimental observations reported by Xu et al.(22)

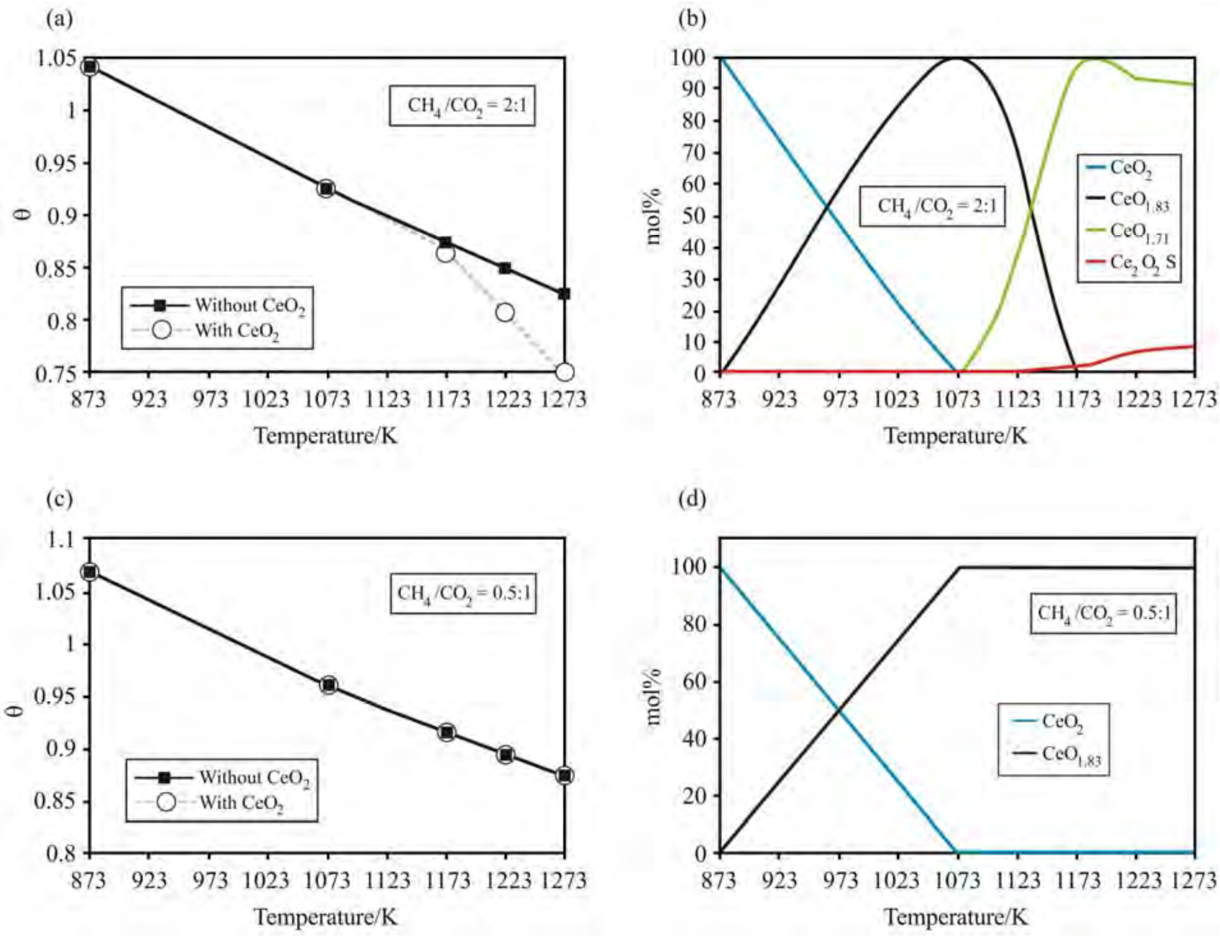

Figure 3. Effect of CeO_2 on θ values (a) and (c). Phase distribution as a function of temperature (b) and (d). (a) and (b) refer to a biogas richer in CH_4 (CH_4/CO_2 molar ratio=2:1), and (c) and (d) to a biogas poorer in CH_4 (CH_4/CO_2 molar ratio=0.5:1). H_2S content=100ppm; Ni/CeO_2 molar ratio=20:1; CeO_2/CH_4 molar ratio:0.01 (for (a) and (b)), 0.04 (for (c) and (d)).

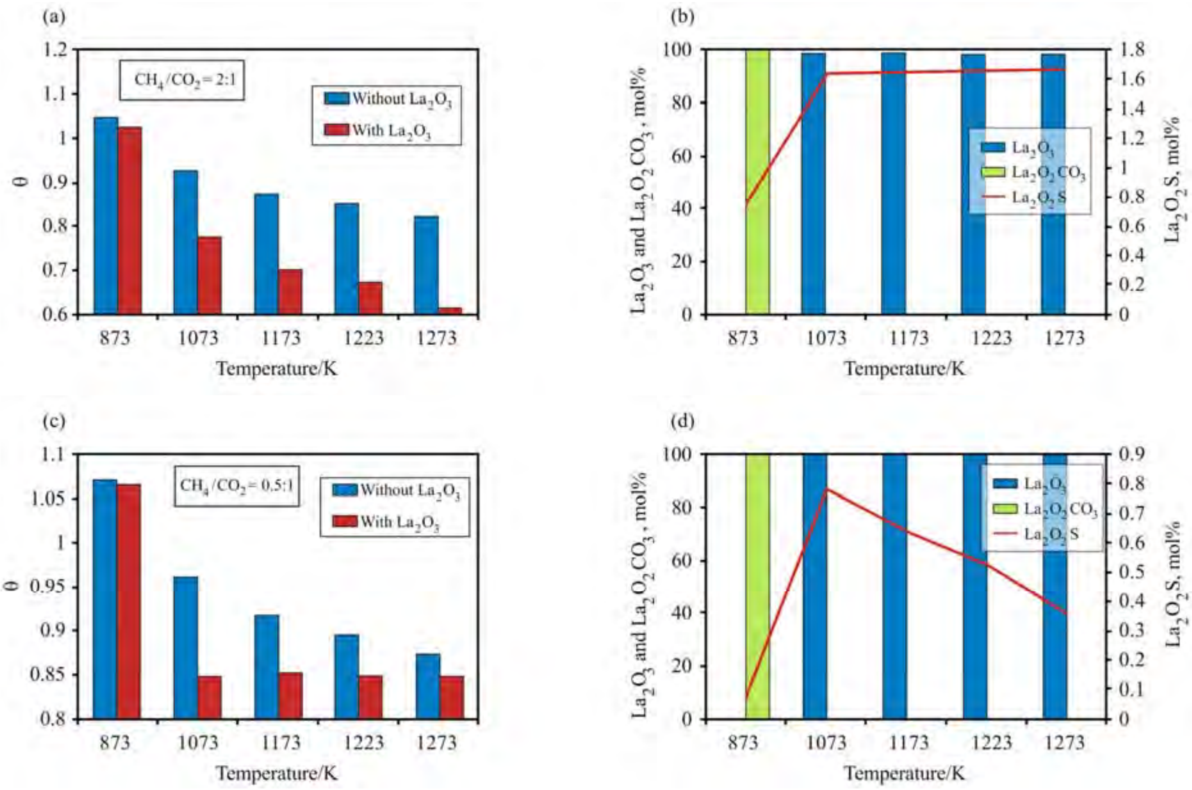

Figure 4. Effect of La_2O_3 on θ values (a) and (c). Phase distribution as a function of temperature (b) and (d). (a) and (b) refer to a biogas richer in CH_4 (CH_4/CO_2 molar ratio=2:1), and (c) and (d) to a biogas poorer in CH_4 (CH_4/CO_2 molar ratio=0.5:1). H_2S content=100ppm; Ni/La_2O_3 molar ratio=20:1; La_2O_3/CH_4 molar ratio:0.01 (for (a) and (b)), 0.04 (for (c) and (d)).

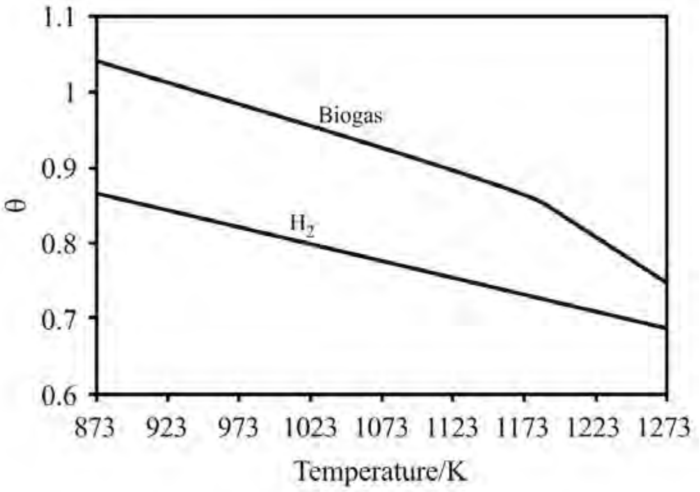

Figure 5. Surface coverage values (θ) as a function of temperature for different reformer feedstock (biogas or H_2). Biogas (CH_4/CO_2=2:1). H_2S content =100ppm; Ni/CeO_2 molar ratio=20:1; CeO_2/CH_4 molar ratio = 0.01 . CeO_2/H_2 molar ratio =0.006.

3.3 Stability of Different Phases of Solid Carbon – Graphite and Multi-Walled Carbon Nanotubes

Figure 6 shows that it is possible to produce *syngas* with high H_2 content along with carbon nanotubes at temperatures higher than 773K. Graphite is stable only at lower temperatures (573-673K). Consistently, thermodynamic analysis of steam reforming of ethanol shows that graphite is stable below 673K and nanotubes above 673K.(14) Besides, it has been experimentally demonstrated that catalytic decomposition of biogas can be carried out with a Ni/Al_2O_3 catalyst obtaining simultaneously a *syngas* with high H_2 content together with carbonaceous nanostructured materials with high added value.(7)

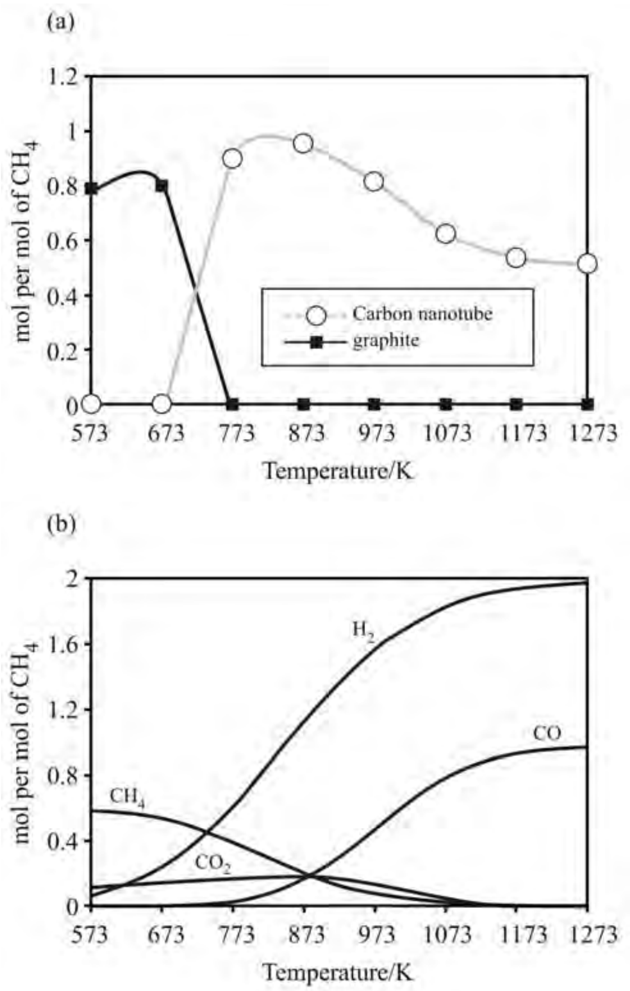

Figure 6. Phase distribution for solid carbon (a) and reformate composition (b) as a function of temperature. Feedstock biogas (CH_4/CO_2 molar ratio=2:1).

4 CONCLUSION

The present work was aimed at identifying, by means of a thermodynamic analysis, the beneficial effects of La_2O_3 and CeO_2 addition to catalysts used in biogas reforming. The stability of different phases of solid carbon was also analyzed. The following conclusions can be drawn from the present study:

- *Syngas* can be directly obtained by the gas-solid reaction between methane and CeO_2, in absence of O_2, H_2O or CO_2. Due to redox properties of CeO_2, solid carbon can be gasified, which can result in a very stable process. Thus, in order to avoid catalyst deactivation due to carbon deposition during methane/biogas reforming, the use of CeO_2 as dopant or catalyst support is recommendable;
- La_2O_3 and CeO_2 dopants are effective in diminishing H_2S poisoning of Ni catalysts. The beneficial effect is more pronounced at higher temperatures and for biogas composition richer in CH_4. La_2O_3 is possibly a better choice than CeO_2;

- *Syngas* with high H_2 content can be produced together with carbon nanotubes at temperatures higher than 773K. Graphite is stable only at lower temperatures (573-673K).

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