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Methane Steam Reforming on Supported Nickel Based Catalysts. Effect of Oxide ZrO₂, La₂O₃ and Nickel Composition

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ABSTRACT

The catalytic properties of Ni (4 and 10 wt%) supported on both La₂O₃ and ZrO₂ were investigated for the methane steam reforming reaction between 475°C and 700°C at atmospheric pressure. The catalysts were prepared by the impregnation method and characterized by several techniques (atomic absorption, BET method, X-ray diffraction and TG-TPO). The catalytic activity of Ni/support systems strongly depends on both of the nature and physico-chemical properties of the support. No deactivation was observed in catalytic systems, whatever the reaction temperature indicating high stability of the catalyst.

Keywords: Methane Steam Reforming; Nickel; Coke; Supported Catalysts

1. Introduction

The valorization of the natural gas via the conversion of methane presents attracting interest because of the abundance of natural gas and its low cost. The methane conversion to synthesis gas (mixture of CO and H₂) can be realized by different processes like the methane steam reforming (MSR) with H₂O [1-4], dry methane reforming with CO₂ [5-6] and methane oxidation with molecular oxygen [7-8]. The most catalysts are usually nickel-based systems because of their thermal stability and low cost [2, 9-11].

One of the major problems of these processes is the catalyst deactivation caused by carbon deposits formed on the surface which is related to high temperatures needed to activate the stable methane molecule. It has been reported in several works that the coke formation on Ni-based catalysts is sensitive to the acido basic character of support, metal-support interactions and metal crystalline structure. Supports with strong Lewis basicity as TiO₂, ZrO₂ [12-14] strong interactions between Ni and support lead to the formation of small Ni crystallites [15], and Ni in a spinel structure as NiAl₂O₄ [16] can minimize carbon deposit. Moreover, the Ni/Al₂O₃ systems with

additives such as alkaline oxides (CaO, MgO) have also shown to be more resistant to coke formation [17-18].

However, some studies have shown that the deactivation of the catalyst is quite sensitive to the nature of carbon formed on the catalyst surface. Thus, the comparative study on two Ni/γ-Al₂O₃ and Ni/SiC systems showed that the carbon as nanofilament formed with Ni/γ-Al₂O₃, is originally the catalyst deactivation by blocking the active sites while the carbon in the nucleation form and growth observed on Ni/SiC favors the conversion of methane. The formation of different structures of carbon from the nickel surface was attributed to the existence of various metal-support interactions which modified the exposed faces of the metal [19].

In MSR reaction over supported Pt based systems, it was observed an enhancement of the catalytic activity that has been attributed to the high amount of carbon deposits around or near the Ni metal particles [20]. It has been underlined that the decomposition of CH₄ may take place on the metal particle, resulting in the formation of carbon and hydrogen and that carbon formed can partially reduce the support near the metal particles. Thus, the increase of carbon deposits around or near the particle metal should favor the methane conversion and the active sites are not encapsulated by carbon deposited.

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The aim of the present work is to report the catalytic behaviour of Ni/ZrO₂ and Ni/La₂O₃ with strong Lewis basicity of support and different loading of Ni (4 and 10 wt%), in the MSR reaction in the temperature range 475˚C - 700˚C. The catalysts have been characterized by BET, atomic absorption, X-ray diffraction (XRD) and TG-TPO techniques.

2. Experimental

2.1. Sample Preparation

ZrO₂ was prepared as described by Boulayt *et al.* [21] from zirconium n-propylate in propane-2-ol (70%). The ZrO₂-based precipitate was filtered off, washed several times, dried overnight at 110˚C and then calcined at 300 ˚C/2h and 500˚C/2h with a rate of 2˚C/min under oxygen flow (1.2 L/h). The supported systems, Ni/MO [MO= La₂O₃ (Merck) and ZrO₂] were prepared by impregnation of the support MO with Ni(NO₃)₂·6H₂O aqueous solution (1 M). The mixture was stirred during 2 h at 80˚C. The samples were dried at 80˚C/12h, and calcined under air flow (1.2 L/h) at 300˚C/2h and 500˚C/2h with a rate of 4˚C/min. The catalysts were then sieved to have a particle diameter less than 0.16 mm.

2.2. Characterization

Solid composition was determined by atomic absorption with a spectrometer type Perkin-Elmer 1100B. The specific surface area was determined by the BET method using nitrogen gas as absorbate on a surface analyzer (Coultronics 2100E) after pre-treatment of samples under vacuum at 200˚C for 1 h (5˚C/min) to have a clean surface.

X-ray diffraction powder patterns were recorded with a $\theta/2\theta$ diffractometer (CGF) using Mo Kα radiation (λ = 0.70930 Å). The apparent sizes of nickel oxide and metal nickel particles were calculated from the Scherrer formula, L = 0.9λ/βcosθ, where β is the width of the most intense peak at half-height and θ the corresponding diffraction angle [22].

2.3. Activity Measurements

The MSR reaction carried out in a quartz fixed bed tubular reactor (L = 65 cm, ϕ = 1 cm) under atmospheric pressure in the temperature range (450˚C - 700˚C), with on-line TCD chromatograph analysis (Hewlett-Packard 5730) using carbosieve B column, 100 - 200 mesh, of 2 m length and hydrogen as vector gas. A thermocouple was installed within the reactor, in contact with catalyst bed. Calcined Ni/MO sample (100 mg) was activated *in situ* overnight at 500˚C under hydrogen flow (1.2 L/h). The gas feed consisted of methane and water in a ratio H₂O/CH₄ = 3.3. CH₄ (10%)/Ar was introduced to the reaction zone by flowing through a water saturator maintained at 65˚C with a flow rate of 1.2 L/h. Before each analysis, the reactants and products pass through a water-trap at 0˚C to remove water. The conversion of CH₄ and product selectivities is calculated using following formulas:

$$\text{Conversion}_{\text{CH}_4}\left(\%\right) = \frac{n_{\text{CH}_4}^{in} - n_{\text{CH}_4}^{out}}{n_{\text{CH}_4}^{in}} \times 100$$

$$\text{Selectivity}_{\text{CO}}\left(\%\right) = \frac{n_{\text{CO}}^{out}}{n_{\text{CH}_4}^{in} - n_{\text{CH4}}^{out}} \times 100$$

$$\text{Selectivity}_{\text{CO}_2}\left(\%\right) = \frac{n_{\text{CO}_2}^{out}}{n_{\text{CH}_4}^{in} - n_{\text{CH}_4}^{out}} \times 100$$

$$\%C = \left(n_{\text{CH}_4}^{in} - \left(n_{\text{CH}_4}^{out} + n_{\text{CO}}^{out} + n_{\text{CO}_2}^{out}\right)\right) \times 100$$

n˚: number of moles.

2.4. Coke Oxidation

In order to determine the carbon amount, the oxidation of coked catalyst was performed using MTB 10 - 8 Setaram Microbalance with relative and absolute sensitivities of 4.10 - 8 and 4.10 - 7 g respectively. The microbalance is linked to a computer via a Cobra interface. 30 mg of coked sample was pretreated at 50˚C under vacuum (10 - 3 Pa) until stabilization of the weight. Molecular oxygen was introduced at a pressure of 200 mbar. The oxidation temperature rose to 550˚C (5˚C/min) and the sample was maintained at this temperature during 6 h.

3. Results and Discussion

3.1. Catalytic Systems Characterization

The physical characteristics of the solids are summarised in **Table 1** and XRD patterns of 4% Ni/La₂O₃ in **Figure 1**. The atomic absorption analysis shows that the composition of different systems is very close to the theoretical one.

The crystallite size was calculated from X-ray line broadening of NiO and that of Ni peaks (2θ = 19.5˚ and 20˚ respectively) using the Scherrer equation. The results show that the support influence significantly the average size of Ni particles with ca. 12 nm and ca. 22 nm for Ni/La₂O₃ and Ni/ZrO₂ respectively, while for the NiO particles, the value is ca. 36 nm for both carriers. The formation of small Ni particles observed in presence ofLa₂O₃ can be associated to the stronger interactions between Ni, NiO and La₂O₃, more basic than ZrO₂, as observed in the case of Ni/MgO catalyst [23]. It is noted that the particle size of NiO and Ni appear to be independent of the deposited amount of active phase.

The specific surface areas of 4wt% and 10wt% Ni/ ZrO₂ are similar with 86 and 88 m²/g, slightly lower than

Table 1. Characteristics of Ni/support systems.

Samples	S_{BET} (m²/g)	Ni exp (wt%)	Ni theo (wt%)	XRD results			
				d^a(nm) NiO	d^a(nm) Ni	before reaction	after reaction
La₂O₃	1					La₂O₃, La(OH)₃	
4Ni/La₂O₃	15	4	4	36.4	11.7	NiO, Ni(OH)₂, La(OH)₃	Ni˚, Ni(OH)₂·0.75H₂O, La(OH)₃, C
10Ni/La₂O₃	8	10.3	10	35.2	11.7	NiO, La(OH)₃	Ni˚, La(OH)₃, C
ZrO₂	93					ZrO₂	
4Ni/ZrO₂	86	4.3	4	35.8	21.5	NiO, ZrO₂	Ni˚, ZrO₂
10Ni/ZrO₂	88	9.98	10	35.3	21.6	NiO, ZrO₂	Ni˚, ZrO₂
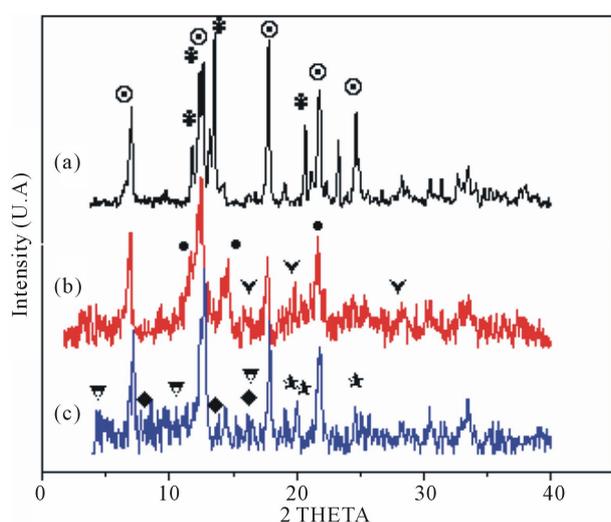
Figure 1. XRD patterns of support (a) La₂O₃ and catalysts 4(%) Ni/La₂O₃ (b) before and (c) after reaction ⊙: La(OH)₃; *: La₂O₃; ⌄: Nio; ●: Ni(OH)₂; ▽: Ni(OH)₂ 0.75H₂O; ✭: Ni˚,◆Camorphe.

that of the ZrO₂ support (93 m²/g). La₂O₃ support has a very low surface area (1 m²/g) that increases to 8 and 15 m²/g after impregnation of 10 and 4 wt% Ni respectively. This increase may be due to the presence of both La(OH)₃ and Ni(OH)₂ phases examined by XRD analysis. Contrarily to Ni/ZrO₂ system, in presence of La₂O₃, the specific surface area decreases from 15 to 8 m²/g with increasing of Ni percentage from 4 wt% to 10 wt%. This decrease could be explained by the formation of agglomerates on the support surface.

After calcination at 500˚C, the XRD pattern of 4 wt% Ni/La₂O₃ (**Figure 1**) shows peaks assigned to Ni(OH)₂, La(OH)₃ and NiO and no peak corresponding to La₂O₃ is observed. It is well known that La₂O₃ is highly hygroscopic at room temperature.

After MSR reaction, the presence of Ni˚ metallic species and that of support are visible in the patterns of Ni/ZrO₂ (**Table 1**), whereas in the case of Ni/ La₂O₃, in addition to the presence of Ni˚ metallic species, there

appear peaks attributed to carbon, Ni(OH)₂ and La(OH)₃. The absence of peaks corresponding to carbon in presence of Ni/ZrO₂ catalyst could be due to an amorphous form of carbon.

3.2. Methane Steam Reforming Reaction

The catalytic performances of supported Ni systems in the MSR reaction were examined in the temperature range (475˚C - 700˚C), after reduction pretreatment under hydrogen flow at 500˚C (1.2 L/h) for 12 h [24]. The MSR reaction over the catalysts leads to the formation of CO, CO₂, H₂ and carbon and the results are reported in **Figures 2**, **3** and **Tables 2**, **3**.

3.2.1. Effect of Calcination Temperature

For the preparation of 4%Ni/ZrO₂ sample, two calcinations temperatures (500˚C and 700˚C) [25] were used to examine their effect on the catalytic performance. **Figure 2** shows methane conversion and CO selectivity as a function of reaction temperature. After reduction pretreatment (H2/500˚C/overnight), 4%Ni/ZrO₂ system leads to similar evolution of the methane conversion with reaction temperature for calcinations temperatures 500˚C and 700˚C. When the catalyst is calcined at 500˚C, the CO formation is favoured at low reaction temperatures (<650˚C) and from 650˚C; the CO selectivity is the same for both calcinations temperatures. This result shows that the used calcination temperature, during the catalyst preparation, does not have a significant effect on the conversion whereas CO formation is favored when the calcination temperature is 500˚C. So, the calcination temperature was fixed at 500˚C for all studied systems.

3.2.2. Steady-State Performance

The catalytic activity of 4%wt Ni/support in the MSR reaction was examined in the temperature range (475˚C - 700˚C) after *in situ* pre-treatment of the catalyst under hydrogen flow at 500˚C overnight (**Figure 3**).

Similar evolutions of the methane conversion as a

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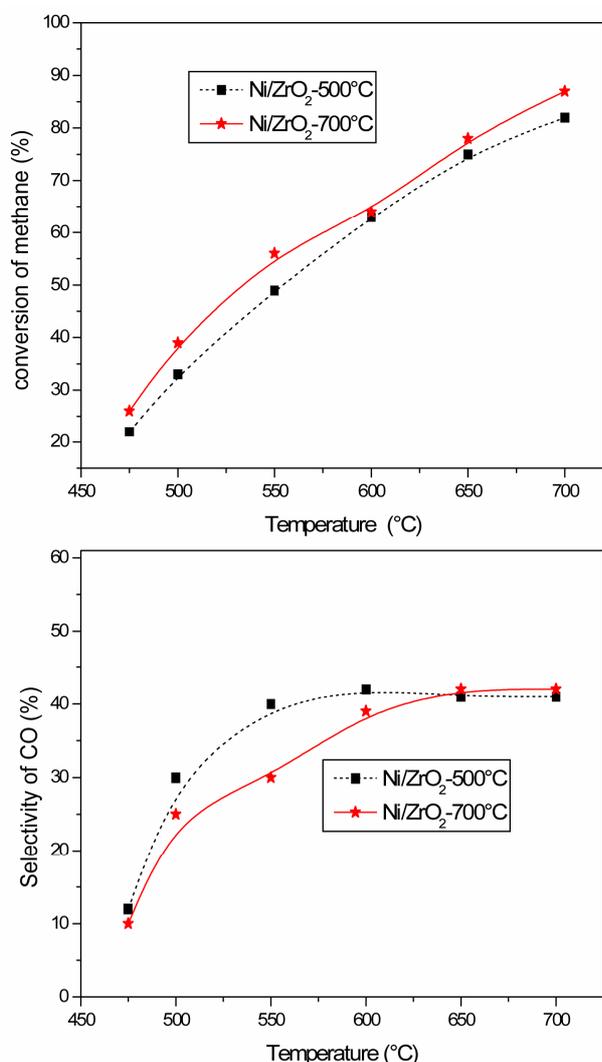
Figure 2. Methane conversion and CO selectivity for 4%Ni/ZrO₂ calcined at 500°C and at 700°C at different reaction temperatures, m = 0.1 g, Tred = 500°C/H₂/over-night, d = 1.2 L·h⁻¹, H₂O/CH₄ = 3.3.

Figure 3. Methane conversion vs. reaction time, for catalysts 4% Ni/La₂O₃ and 4% Ni/ZrO₂ at different temperatures, m = 0.1 g, Tred = 500°C/H₂/overnight, d = 1.2 L·h⁻¹, H₂O/CH₄ = 3.3.

function of time-on-stream were obtained at different temperatures for 4%wt Ni/ZrO₂ catalyst. Steady-state was reached at the beginning of reaction for all temperatures indicating a good stability of this system. Unlike to 4%wt Ni/ZrO₂, the catalytic activity of 4%wt Ni/La₂O₃ decreased with the reaction time and became stable in less than 3 h for reaction temperatures below 700°C. The methane conversion increases from ca. 20 to ca. 85% in presence of 4%wt Ni/ZrO₂ and from ca. 5 to ca. 90% for 4%wt Ni/La₂O₃ with increasing of reaction temperature from 500°C to 700°C, reflecting the endothermic nature of MSR reaction. It is important to note that the catalytic conversion remained unchanged up to 7 h on stream indicating the complete absence of deactivation under the reaction conditions. It is well known that this type of reaction leads to a large amount of carbon on the catalyst surface inducing deactivation [19,24-26].

These results show the promotional effect of both La₂O₃ and ZrO₂ supports on the stability of active sites namely Ni metal. This is probably due to strong metal-support interactions related to the basicity of the support, responsible of the high activity and stability of the catalyst for the H₂O reforming of CH₄.

3.2.3. Effect of Reaction Temperature

The methane conversion and product distribution on the MSR reaction over different Ni/support systems in the temperature range 475°C - 700°C with a H₂O/CH₄ molar ratio of 3.3 are shown in **Tables 2** and **3**. The testing results show that catalytic performances of Ni/ZrO₂ are very sensitive to Ni content. In the 500°C - 700°C temperature range, 4%wt Ni/ZrO₂ is more active than 10%wt Ni/ZrO₂ with conversions of 22% - 82% against 22% -

Table 2. Catalytic activities of Ni/ZrO$_2$ catalyst.

Catalysts	Temperature (˚C)	Methane conversion (%)	Selectivity CO (%)	Selectivity CO$_2$ (%)	% C	H$_2 \cdot 10^{-3}$ (mol/g h)
4%Ni/ZrO$_2$	475	22	12	42	46	-
	500	33	30	23	47	17.0
	550	49	46	6	48	17.2
	600	62	42	traces	58	17.4
	650	75	41	0	59	17.5
	700	82	41	0	59	17.5
10%Ni/ZrO$_2$	475	traces	-	traces	-	
	500	22	29	30	41	25.0
	550	33	35	6	59	39.6
	600	48	36	3	61	61.4
	650	67	38	0 traces	62	67.9
	700	72	40	0	60	76.0

Table 3. Catalytic activities of Ni/La$_2$O$_3$ catalyst.

Catalysts	Temperature (˚C)	Methane conversion (%)	Selectivity CO (%)	Selectivity CO$_2$ (%)	% C	H$_2 \cdot 10^{-3}$ (mol/g h)
4% Ni/La$_2$O$_3$	475	-	-	-	-	-
	500	traces	-	-	-	-
	550	20	50	35	15	26.1
	600	50	52	6	42	56.6
	650	79	35	2	63	67.4
	700	88	31	traces	69	80.2
10% Ni/La$_2$O$_3$	475					
	500	traces	traces	-	-	-
	550	26	20	39	-	-
	600	51	34	26	22	36.2
	650	79	50	2	63	38.2
	700	88	52	traces	68	40.4

72% and more selective toward CO with 30% - 46% against 29% - 40%. It is also noted that 10%wt Ni/ZrO$_2$ shows no activity at 475˚C contrary to 4%wt Ni/ZrO$_2$ that displays a conversion of 22%. On the other hand, over 4%wt Ni/ZrO$_2$ catalyst, the amount of hydrogen did not change markedly with temperature (17.0 - 17.5 mmol/g·h), while on 10%wt Ni/ZrO$_2$, the hydrogen quantity increases substantially from 25.0 to 76.0 mmol/g·h.

CO$_2$ is reaction product at low temperature with 42% of selectivity over 4 wt% Ni/ZrO$_2$ at 475˚C and 30% in the case of 10 wt% Ni/ZrO$_2$ at 500˚C. These values de-

crease with increasing temperature until they reach zero value above 600˚C. On the contrary, the carbon is the major product at 550˚C with selectivity varying between 48% - 59% for 4%Ni/ZrO$_2$ and from 500˚C with selectivity varying between 41% - 62% for 10%Ni/ZrO$_2$. These results show that the increase of carbon deposits favored the methane conversion. Moreover, the selectivities toward CO and H$_2$ have practically not changed during reaction beyond 550˚C.

The comparison of the results of **Tables 2** and **3** shows that the nature of support has an effect on catalytic per-

formance of Ni based catalyst, particularly on the product distribution. In contrast to Ni/ZrO_2 system, the amount of Ni supported on La_2O_3 has no effect on the activity of solid. Similar evolution conversions from 20% - 26% to 88% with increasing the reaction temperature from 550˚C to 700˚C, were observed for 4 wt% Ni/La_2O_3 and 10 wt% Ni/La_2O_3 while the effect of Ni content on the product distribution is more pronounced. Thus on 4 wt% Ni/La_2O_3, high CO selectivities were obtained at low reaction temperature (550˚C and 600˚C), 50 and 52% against 20% and 34% respectively for 10 wt% Ni/La_2O_3. The formation of hydrogen favored on 4 wt% Ni/La_2O_3 with a amount varying between 26.1 - 80.2 against 0.0 - 40. 4 mmol/g·h for 10 wt% Ni/La_2O_3. It is noteworthy that 4 wt% Ni/La_2O_3 is more selective than Ni/ZrO_2 catalyst.

The carbon is the major product beyond 650˚C with selectivities of 63% - 69% for Ni/La_2O_3 catalysts while the CO_2 product is observed only in trace amounts (2% of selectivity) in the presence of 10 wt% Ni/La_2O_3 at 550˚C. These results show also that the increase of carbon deposits favored the methane conversion as in the case of Ni/ZrO_2.

The enhancement of the activity (**Tables 2** and **3**) and the stability (**Figure 2**) of both Ni/ZrO_2 and Ni/La_2O_3 on the MSR reaction can be attributed to the high amount carbon deposits around or near the Ni metal particles. These results are in agreement with those obtained by other authors on Pt/Al_2O_3, Pt/ZrO_2 and $Pt/Ce-ZrO_2$ systems [7-8,27-28]. It has been reported in these works that the decomposition of CH_4 takes place on the metal particle, resulting in the formation of carbon and hydrogen and that carbon formed can partially reduce the support near the metal particles. Thus, the increase of carbon deposits near the metal particles favors the methane conversion and the active sites (Ni metal) were not encapsulated by carbon deposited.

It was underlined that the catalyst deactivation is also sensitive to the nature of the support. Thus, the comparative study performed on two $Ni/\gamma-Al_2O_3$ and Ni/SiC systems showed that the carbon as nanofilament was originally the catalyst deactivation by blocking the active sites while the carbon in the nucleation and growth form favored the conversion of methane. The formation of different structures of carbon from the nickel surface was attributed to the existence of different metal-support interactions which modified the exposed faces of the metal [19].

3.2.4. Determination of Coke Deposited

Temperature-programmed oxidation (TPO) coupled to-thermogravimetric analysis (TG) was carried out on the Ni/support catalysts after 7 h of SRM reaction at 700˚C (**Figure 4**). The TG curves of 4% Ni/ZrO_2 and 4% Ni/La_2O_3 (figure not shown) catalysts are similar with

weight losses divided into two major events between 340˚C and 500˚C and between 350˚C and 550˚C respectively attributed to CO_2 release, coming probably from two different forms of carbon. It has been reported that graphitic carbon was ignited at a higher temperature of around 500˚C and reactive carbonaceous deposit or adsorbed carbon monoxide on the surface was ignited at a lower temperature below 400˚C [29]. The results also revealed the formation of a higher amount of carbon on 4% Ni/ZrO_2 catalyst compared to the 4% Ni/La_2O_3 catalyst (35 wt% of CO_2 against 10 wt%).

TPO-TG analysis shows a different behavior between 10 wt% Ni/support and 4 wt% Ni/support. Thus, with Ni content of 10 wt%, gradual weight losses of ca. 20 wt% from 350˚C to 550˚C for Ni/ZrO_2 and of 65 wt% from 360˚C to 500˚C for Ni/La_2O_3 were observed.

These results indicate that the carbon formation depends on Ni loading and support nature. La_2O_3 support favored the carbon deposited when Ni content is high contrarily to ZrO_2 support.

4. Conclusion

The obtained results showed that supported Ni (4 and 10 wt%) on ZrO_2 and La_2O_3 support exhibited high catalytic activity (72% - 88% of methane conversion) at 700˚C and high stability for the steam reforming methane reaction to synthesis gas. The large amount of carbon depos-

(a)

(b)
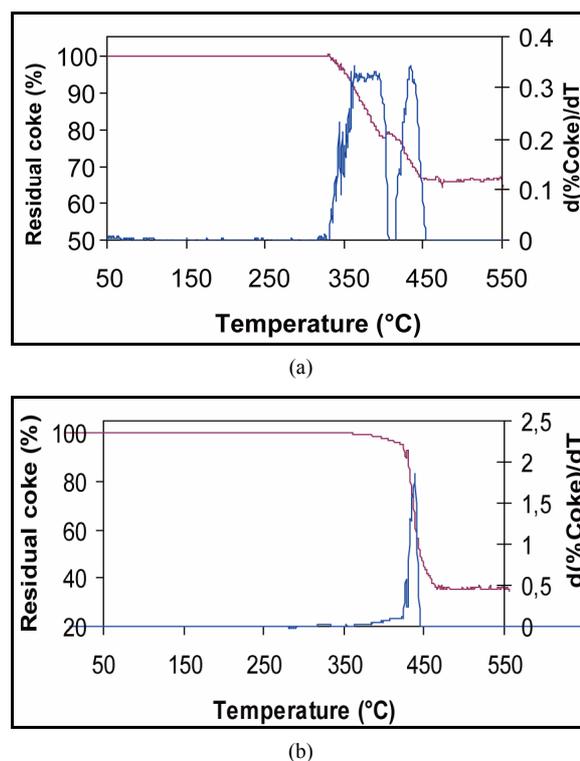
Figure 4. Residual coke (%) and the DTG during the TPO of: (a)—4% Ni/ZrO_2 , (b)—10% Ni/La_2O_3.

ited on the catalyst surface does not affect the activity of the Ni/ZrO_2 and Ni/ La_2O_3 systems, probably due to a form of carbon that is not detrimental to catalyst activity. On the other hand, the catalysts seem to develop a self-stabilization process during the reaction.

5. Acknowledgements

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