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Study of the decomposition of supported nickel acetylacetonate by thermal techniques

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Abstract

The decomposition of supported nickel acetylacetonate (AcacNi) was studied by using thermal techniques to evaluate the nature of the calcination products. Thermogravimetric techniques used in this work indicated transformations occurring during preparation and calcination steps. Results demonstrated the important influence of support modifications upon the catalyst nature finally obtained.

Keywords: Nickel catalysts; Nickel acetylacetonate; Methane oxidation; Synthesis gas

1. Introduction

Activity and selectivity are well-known properties of supported nickel catalysts in different natural gas reforming reactions (steam reforming, reforming with CO_2, oxyreforming and mixed reforming processes) for the obtention of synthesis gas [1,2]. However, these catalysts suffer severe deactivation problems due to carbon deposition, nickel sintering and phase transformations [3–6]. Therefore, the development of a new stable Ni-catalyst is of great interest for the practical application of these reactions. The support nature, precursor compounds used to generate the active phase, and pre-treatments have an important role in the performance of the resulting catalyst [7–9]. Previous studies have demonstrated that the use of nickel acetylacetonate (AcacNi) and alumina supports enabled a catalyst of good activity and stability, specially concerning the deactivation due to carbon deposition, compared to catalysts prepared with nickel nitrate as precursor compound [10,11].

A large amount of information about a catalytic system can be obtained by using thermogravimetric techniques (working in a non-steady state and with an appropriate temperature program) [12]. From thermal data, it is possible to achieve information regarding the composition and structure of different phases of a given sample. Our principal objective is the study of the decomposition of the nickel precursor compound (AcacNi) during calcination to evaluate the nature of phases formed through support modifications.

Weight changes as a function of the temperature registered through TGA technique are caused by the formation and rupture of chemical bonds at high

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temperatures, by processes that cause volatile compounds or by reaction products that modify the sample weight. The exit flow analysis of the TGA equipment is very useful to get information on the stoichiometric ratio of the thermally decomposed compounds. The coupled analyzer, a mass spectrometer (MS), makes it possible the determination of the effluent gas composition.

2. Experimental

2.1. Catalyst preparation

Four supported Ni catalysts, with 2 wt.% Ni, were prepared using nickel acetylacetonate (AcacNi) (Aldrich). Table 1 summarizes the studied catalytic systems and their corresponding denomination.

The modification of the α-Al_2O_3 support was carried out by impregnation with $Al(NO_3)_3 \cdot 9H_2O$ (Merck), in such a way that one obtains 1 wt.% Al in the solid. The organometallic catalysts were prepared by impregnation of the corresponding supports, previously calcined at 500 °C for 2 h. AcacNi was used dissolved in benzene, with a solution volume of five times the pore volume of the support. The system was left in contact for 72 h at 60 °C, and later on the solid was filtered and washed.

2.2. Apparatus and measurements

The determination of the textural properties of the supports (superficial area and pore volume) was carried out in a N_2 adsorption equipment (Micromeritics Accursorb 2100E) at −196 °C on a 200 mg sample, previously outgased at 200 °C under *vacuum* for 2 h. The acid–base properties of the different supports were determined by the isopropylalcohol (IPA) decomposition reaction, which is an indirect method [13]. This reaction was carried out in a fixed bed reactor, at temperature between 423 and 573 K, atmospheric pressure and a feed of 4.5% IPA in He, with a flow of 40 $cm^3\,min^{-1}$.

Table 1
Nomenclature of the supports and catalysts studied

Support	Catalyst name
α-Al_2O_3 (T-708 Girdler) (α)	Ni^O_α
α-Al_2O_3 (T-708 Girdler) modified with 1 wt.% Al (α + Al)	$Ni^O_{\alpha+Al}$
γ-Al_2O_3 (Cyanamid Ketjen) (γ)	Ni^O_γ
γ-Al_2O_3 (Prepared in the laboratory) (γp)	$Ni^O_{\gamma p}$

The calcination or activation of the solids was carried out in an oxidizing atmosphere, after the impregnation step, and it was continuously monitored by thermogravimetric analysis (Shimadzu TGA-50 equipment), differential scanning calorimetry (DSC) (Shimadzu DSC-50 equipment) and in a parallel analysis by mass spectrometry (Shimadzu GCMS-QP5050A). Ten milligram sample were used for the thermal decomposition of impregnated materials. The samples were treated with a 30 $cm^3\,min^{-1}$ gas feed flow composed of a He/O_2 mixture (4% O_2), with a heating program of 5 $K\,min^{-1}$, from room temperature up to 393 K, remaining at this level for 30 min (drying stage), and then from 393 to 1073 K, with a heating rate of 5 $K\,min^{-1}$ (stage of calcination).

The GC/MS equipment had a capillary column of 30 m × 0.25 mm, with SPB-5TM (Supelco) as stationary phase, operated in an isothermal mode at 303 K.

The temperature-programmed reduction (TPR) tests were carried out in a conventional dynamic equipment, with a ratio H_2/N_2 in the feed flow of 1/9, and a heating rate of 10 $K\,min^{-1}$ from room temperature up to 1273 K.

3. Results and discussion

The final properties of a catalyst depend on the nature of the precursor-support interaction generated during the preparation step. In this case, the acid–base properties of the support play an important role. For this reason, a characterization of textural properties and superficial acidity of different studied supports was carried out (Table 2).

The isopropylalcohol reaction (IPA) was used for the characterization of the superficial acidity. The selectivity towards different reaction products changes if the superficial acid–base properties are modified. Thus, a higher selectivity towards propene and di-isopropylether (SP + D) evidences the existence of a relatively higher concentration of acid sites [11]. Supports based on γ-Al_2O_3 present a higher contribution of acid sites than supports based on α-Al_2O_3. This fact may influence the interaction

Table 2
Textural and acid–base properties of the supports employed

Support	BET surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	IPA conversion (%)[a]	SP + D (%)[b]
α	5.1	0.22	12	80
α + Al	5.5	0.20	30	83
γp	216	0.50	60	92
γ	185	0.54	100	100

[a] Test conditions: 523 K, atmospheric pressure, feed composition 4.5% IPA in He, feed flow 40 $cm^3 min^{-1}$.

[b] SP + D = selectivity to propene and diisopropylether, measured at a conversion of IPA of 40%.

degree of the nickel precursor compound and the support during the preparation step. The modification of the α-Al_2O_3 support with an aluminum oxide layer (α + Al) causes a certain increase in the total acidity measured by a higher activity and selectivity towards di-isopropylether and propene (SP + D).

The evolution of pure AcacNi by TGA and DSC was determined to obtain decomposition patterns during the calcination step. The derivative of the weight change from TGA tests (DrTGA/mg min^{-1}) is represented in Fig. 1 for better visualization of weight changes. Results obtained by DSC show that all decomposition reactions are exothermic transformations, except for the water loss occurring in the drying step ($T < 393$ K), which is naturally an endothermic process. During the drying step (up to 393 K), the sample presented a mass loss of the order of 10.4% (P_w), due to water loss. In the calcination step, three main peaks are observed: a minor one, P_1, at 477 K (that represents a mass loss of 18.7%), a bigger one, P_2, at 600 K with a shoulder, P_3, at 633 K (together represent 51.8% of mass loss). The theoretical total mass loss would represent 71% if AcacNi decomposes forming NiO. Results of this test gave a mass loss determined during the calcination step of 70.5% measured as ($P_1 + P_2 + P_3$); this result demonstrates that the decomposition product of AcacNi is NiO.

Fig. 2 shows TGA diagrams corresponding to the calcination step (>393 K) for all studied catalysts. The decomposition pattern is strongly influenced by the support nature. The Ni^O_α catalyst presents a TGA diagram (Fig. 2a) quite similar to that of non-supported AcacNi. Differences that can be pointed out are a shift of all peaks to higher temperatures (approximately 30 K) and a slightly bigger contribution of P_1 peak. This P_1 peak appears at 516 K, representing a mass loss of 33%, and the second peak, P_2, appears at 603 K with a shoulder, P_3, at 683 K, representing a mass loss ($P_2 + P_3$) of 67%.

Fig. 2b shows the $Ni^O_{\alpha+Al}$ sample behavior. This sample also presents three decomposition peaks (P_1 at 502 K, P_2 at 606 K and P_3 at 683 K). In this case, peaks appear at temperatures similar to those of Ni^O_α catalyst,

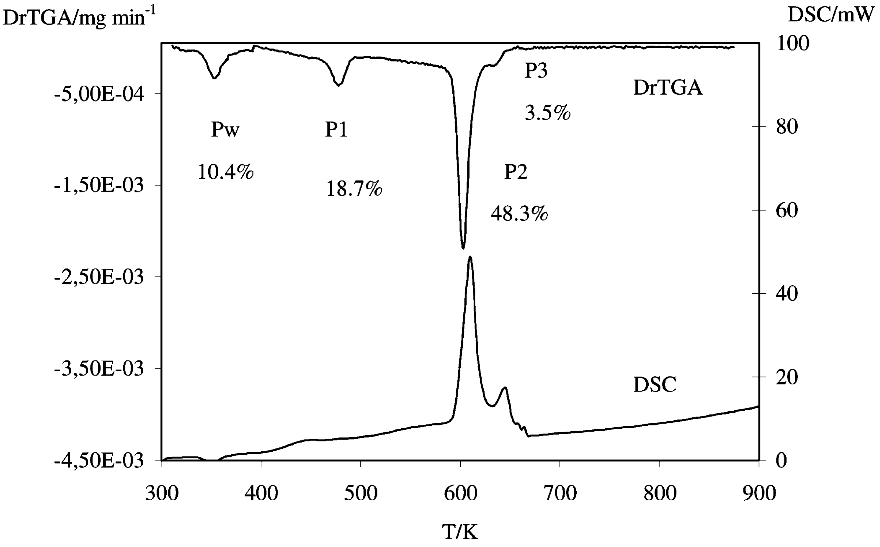

Fig. 1. TGA–DSC curves for the decomposition of bulk AcacNi.

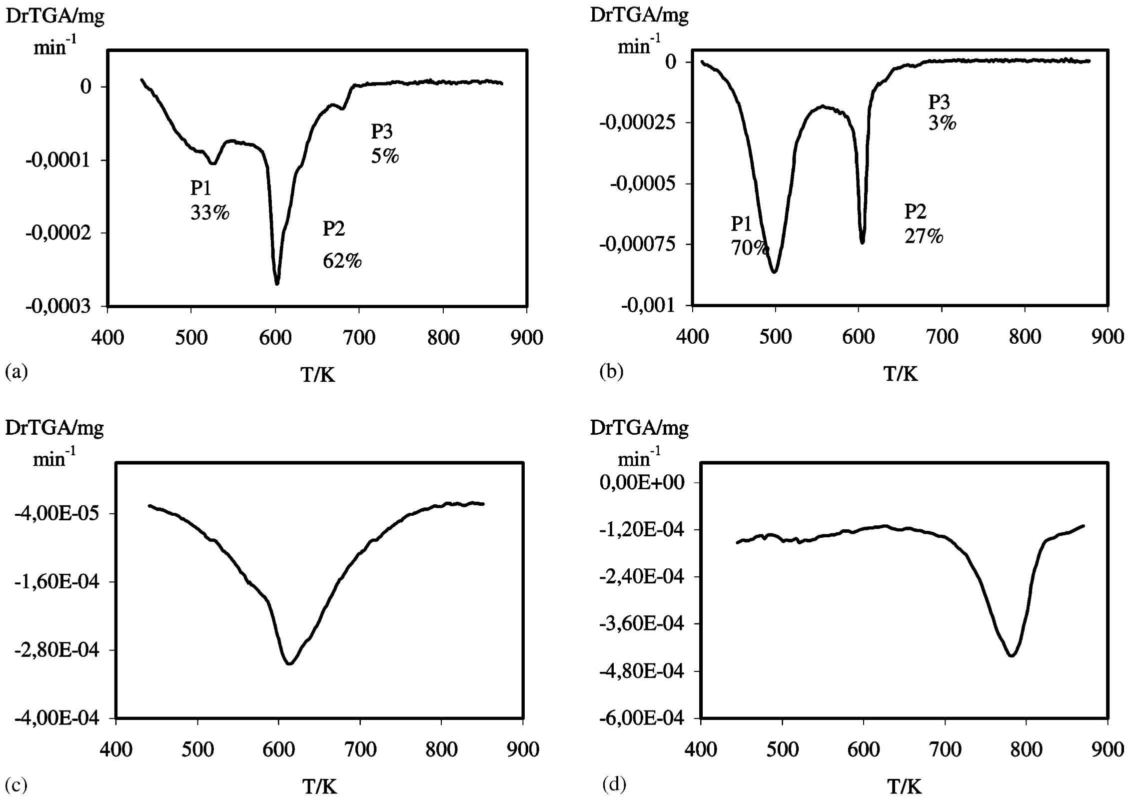

Fig. 2. TGA curve for the decomposition of catalyst: (a) Ni^O_α, (b) $Ni^O_{\alpha+Al}$, (c) $Ni^O_{\gamma p}$, and (d) Ni^O_γ.

however, the first peak, P_1, is noticeably bigger in the case of $Ni^O_{\alpha+Al}$, since it represents 70% of the total mass loss in the calcination step, while for Ni^O_α catalyst, P_1 peak represents a mass loss of 33%.

Results obtained with $Ni^O_{\gamma p}$ and Ni^O_γ catalysts differ from those obtained for Ni^O_α, $Ni^O_{\alpha+Al}$ and AcacNi samples. Fig. 2c presents the TGA diagram corresponding to $Ni^O_{\gamma p}$ catalyst, where a single decomposition peak appears, with a maximum at approximately 613 K. Ni^O_γ catalyst (Fig. 2d) presents its single decomposition peak at approximately 783 K, a temperature noticeably higher than in the other samples.

All decomposition reactions occurring during the calcination step are exothermic transformations observed by DSC. In the case of Ni^O_α and $Ni^O_{\alpha+Al}$ samples, the second peak, P_2, represents a more exothermic process than the first peak, P_1. This behavior could be explained by the fact that in the region corresponding to P_1 peak the contribution of rupture reactions (endothermic) is more important than in the region corresponding to P_2 peak, where the combustion reactions (exothermic) are markedly predominant. The decomposition at high temperatures would indicate a stronger interaction of AcacNi with the support. According to these results, the growing order in the interaction with the support would be $Ni^O_\alpha < Ni^O_{\alpha+Al} < Ni^O_{\gamma p} < Ni^O_\gamma$. The P_1 peak contribution (representing lesser exothermic processes) related to the sum of peaks ($P_2 + P_3$) would indicate the rupture ratio and combustion reactions during the decomposition step. When comparing Ni^O_α and $Ni^O_{\alpha+Al}$ samples, results indicate that with the modified support α + Al, the contribution of rupture reactions is more important than when the α support is used.

In agreement with what has been proposed for characterization results of different supports employed, the acid nature of γ-Al_2O_3 supports generates a stronger interaction with the precursor compound, causing its decomposition at higher temperatures than pure AcacNi or supported on α-Al_2O_3.

Additional GC/MS tests were performed on samples to analyze the composition (both qualitative and quantitative) of gases evolved during their decomposition. Results obtained in these analyses together with those obtained by TGA indicate that there are no organic fragments left on the surface in Ni^O_α and $Ni^O_{\alpha+Al}$ catalysts after reaching 723 K. Results obtained by IR spectroscopy on the calcined samples were similar with the subsequent disappearance of the wide band at $1600\,cm^{-1}$ assigned to organic fragments of AcacNi [14].

For a better comprehension of results obtained by GC/MS, values of relative abundance (%) of main fragments (m/z) are shown in Fig. 3 for each one of the tested materials. With regard to the composition of effluent gases produced during the calcination of pure AcacNi, the main fragment corresponds to CO_2 ($m/z = 44$) in agreement with DSC results that show the high decomposition exothermicity.

If the composition of effluents for Ni^O_α and $Ni^O_{\alpha+Al}$ samples is analyzed, the most significant differences when compared with AcacNi are the major abundance of small fragments ($m/z = 12$) with smaller CO_2 amounts ($m/z = 44$). This is consistent with a higher relative contribution of rupture reactions in the region of P_1 peak. With the interaction increase of AcacNi with the support, it is possible to suppose that a weakening of the molecule internal bonds could be produced causing consequently an increase in the number of ruptures and also a percentage increase of light fragments during decomposition.

When studying the thermal decomposition of $Ni^O_{\gamma p}$ and Ni^O_γ catalysts, the process is different to the AcacNi, Ni^O_α and $Ni^O_{\alpha+Al}$ decomposition. The main fragment is not the one corresponding to CO_2 ($m/z =$ 44) but to a fragment with $m/z = 43$ (Fig. 3) and heaviest fragments do not appear at $m/z = 85$ and 100 but rather up to $m/z = 58$. These results are similar to the previous ones: γ_p and γ supports presented higher relative acidity than the a and $\alpha + Al$ supports, a result that has been correlated with a stronger precursor-support interaction. These facts may be responsible for a shift of the decomposition towards higher temperatures, together with a more important contribution of rupture reactions.

Reduction profiles were also determined by TPR for all calcined catalysts (Fig. 4). As it is well documented in numerous studies carried out on the nickel reduction

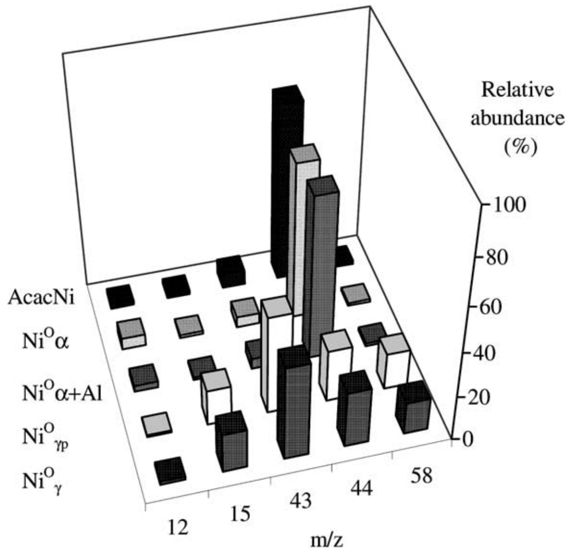

Fig. 3. Decomposition fragments detected by GC/MS analysis, obtained during the calcination of bulk AcacNi and Ni catalysts.

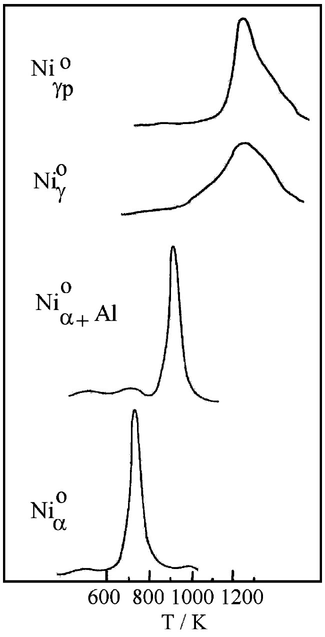

Fig. 4. TPR profiles for Ni studied catalysts.

supported on alumina, three reduction peaks can be found: the first, in the region of 600–700 K assigned to the presence of bulk NiO or a nickel oxide having a weak interaction with the support; the second, in the region between 700 and 1000 K, corresponding to nickel species and aluminum mixed oxides in strong interaction with the support; and the last, in the region of 1000–1300 K assigned to the existence of $NiAl_2O_4$ species, a crystalline spinel characterized by a strong interaction of the nickel with the support [15,16].

Fig. 4 shows the effect of the support nature upon TPR profiles. When comparing the catalyst supported on $\alpha+Al$ with the catalyst supported on α, the peak of maximum H_2 consumption is shifted towards higher temperatures in the first catalyst. In the case of Ni^O_α catalyst, reduction temperatures do not differ appreciably from what is generally assigned to nickel with relatively weak interaction with the support. On the other hand, for $Ni^O_{\alpha+Al}$ catalyst, mixed oxides could be present in the region at which the reduction occurs, probably precursors of the $NiAl_2O_4$ spinel. $Ni^O_{\gamma p}$ and Ni^O_γ catalytic systems present reduction temperatures above 1150 K. These reduction temperatures evidence the formation of the $NiAl_2O_4$ spinel.

The sequence of reduction temperatures measured by TPR, $Ni^O_\alpha < Ni^O_{\alpha+Al} < Ni^O_{\gamma p} < Ni^O_\gamma$ goes in the same direction than that of the interaction degree determined by TGA and GC/MS, and indicates that the metal-support interaction degree achieved during the preparation step is maintained after the activation step of catalytic systems.

Results obtained when the four catalytic systems were submitted to the partial oxidation of methane reaction are presented in Table 3. Marked differences among different catalysts are observed with respect to their activity and catalytic stability. Catalysts based on γ-Al_2O_3 supports presented a low activity level when compared with catalysts based on α-Al_2O_3. Taking into account that the active phase under the operating conditions of the oxyreforming reaction is the reduced Ni [8], low activity levels observed for $Ni^O_{\gamma p}$ and Ni^O_γ could be assigned to the low reducibility of nickel species in these catalysts.

Ni^O_α and $Ni^O_{\alpha+Al}$ catalysts present a good activity level but with marked differences with respect to their catalytic stability. Taking the increase of Ni mean particle size (measured after 24 h of reaction) as a parameter of the catalyst sintering, the $Ni^O_{\alpha+Al}$ catalyst presents a resistance to sintering that it is noticeably higher than in the case of Ni^O_α catalyst. These results confirm what has been observed by TGA and TPR. The existence of nickel species with a higher interaction degree was demonstrated when the $\alpha+Al$ support was used.

Table 3
Catalytic performance in the partial oxidation of methane reaction

Catalyst	Methane conversion[a] X_{CH_4} (%)	Stability coefficient[b] a_{CH_4}	Particle size increment (%)[b]
Ni^O_α	64	0.74	95
$Ni^O_{\alpha+Al}$	82	0.94	21
Ni^O_γ	<5	0	n.d.
$Ni^O_{\gamma p}$	<5	0	n.d.

[a] Test conditions: conventional flow reactor, 773 K, atmospheric pressure, feed composition $N_2/CH_4/O_2$:11/2/1, feed flow: 65 $cm^3\,min^{-1}$, conversion measured at 2 h on stream.

[b] Determined after 24 h on stream. a_{CH_4}: ratio between the rate of consumption of CH_4 after 24 h on stream and the initial rate value. Particle size increment (%): ((mean particle size after 24 h on stream − mean particle size of the fresh catalyst)/mean particle size of the fresh catalyst) × 100, measured by TEM. n.d.: non determined.

4. Conclusions

The interaction among nickel acetylacetonate and different alumina based supports is strongly dependent on the support surface acidity, with the sequence: $\gamma > \gamma p > \alpha + Al > \alpha$. Results of the IPA reaction on the supports, together with those obtained by TGA and CG/MS during the calcination stage of catalysts indicate that the aluminum oxide layer deposited on α-Al_2O_3 by means of an impregnation with aluminum nitrate results in a support having a nature different from the one of transition aluminas here studied.

Following the decomposition of AcacNi by TGA during the calcination step, there is a shift of peaks towards higher temperatures with the increase of the interaction degree between the nickel precursor and the support. The presence of lighter fragments was detected by GC/MS, surely due to a major contribution of rupture reactions. It was demonstrated that above 723 K there are no organic fragments left on the surface, in agreement with previously published IR results.

The metal-support interaction degree observed during preparation of catalysts is maintained after the activation step. TPR results clearly show that the sequence of reduction temperatures is $\mathrm{Ni}^{\mathrm{O}}_{\gamma} > \mathrm{Ni}^{\mathrm{O}}_{\gamma\mathrm{p}} > \mathrm{Ni}^{\mathrm{O}}_{\alpha+\mathrm{Al}} > \mathrm{Ni}^{\mathrm{O}}_{\alpha}$. Reduction temperatures indicate that after calcination steps, nickel interacts with the support and forms mixed oxides in the cases of $\mathrm{Ni}^{\mathrm{O}}_{\gamma}$, $\mathrm{Ni}^{\mathrm{O}}_{\gamma\mathrm{p}}$ and $\mathrm{Ni}^{\mathrm{O}}_{\alpha+\mathrm{Al}}$ supports.

The reaction test employed to determine the catalytic properties of studied materials demonstrates that in $\mathrm{Ni}^{\mathrm{O}}_{\gamma}$ and $\mathrm{Ni}^{\mathrm{O}}_{\gamma\mathrm{p}}$ systems the strong metal-support interaction offers a high resistance of the nickel reduction to a metallic state producing low activity catalysts under the reaction conditions studied. On the other hand, $\mathrm{Ni}^{\mathrm{O}}_{\alpha+\mathrm{Al}}$ and $\mathrm{Ni}^{\mathrm{O}}_{\alpha}$ systems present good activity levels in the oxyreforming reaction. Mixed oxide phases developed in the case of $\mathrm{Ni}^{\mathrm{O}}_{\alpha+\mathrm{Al}}$ with an important metal-support interaction generate a more stable system concerning deactivation by sintering.

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