Nature of Ni–Al developed phases during thermal activation in relation to the preparation techniques. Part I: calcination

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Abstract

In this work, the thermal activation of different catalytic systems based on Ni (bulk and supported) was analyzed. These solids are used to obtain synthesis gas from reforming of methane. The evolution of these systems during calcination in air atmosphere was studied by using differential thermal analysis, thermogravimetry analysis and X-ray diffraction. Results obtained, allowed the determination of calcination temperatures necessary for decomposition of precursors of active phases (for different preparation methods) as well as definition of a route to obtain supported Ni catalysts via deposition–precipitation with urea. © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

Ni catalysts are extensively used in industrial processes such as for the manufacturing of synthesis gas from methane reforming with steam or carbon dioxide and partial oxidation of methane [1–5].

High operation temperatures in these processes affect notably the stability of catalysts due to acceleration of sintering processes.

The need of using supports thermally inert and stable, e.g. α-Al$_2$O$_3$, does not favour the interaction between Ni precursors and the support, which does not allow the resistance increase of Ni active phase with respect to sintering. For this reason, the use of stability promoters in the Ni active phase, e.g. Al, Mo [6,7], is one of the applied strategies.

Although these catalytic materials are quite well known, few studies are reported in bibliography referring to the nature of phases observed during activation stages. In this work, the evolution of different systems prepared in laboratory is studied during thermal activation stage in air atmosphere (heat treatment) using differential thermal analysis (DTA) and thermogravimetry analysis (TGA), complemented with X-ray diffraction (XRD). Catalytic materials used are bulk and supported. Bulk catalysts are prepared in two ways: physical (calcination) and chemical (precipita-

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tion by alkalinization). Supported catalysts are obtained by impregnation and deposition–precipitation on an α-Al_2O_3 support.

2. Experimental methods

Reactives used in these preparations are: $Ni(NO_3)_2 \cdot 6H_2O$ (Merck, purity 99.925%), $Al(NO_3)_3 \cdot 9H_2O$ (Riedel-de Haën, purity 99.965%) and urea (Mallinckrodt, purity 99.97%). Solids were prepared by precipitation from an homogenous solution of precursors (bulk systems) or by deposition on pre-formed supports (supported systems). For all samples, after a heating treatment at 373 K, a portion of these ones was used to study the programmed thermal activation (DTA–TGA) and the other portions were calcined in dry air atmosphere at different temperatures between 623 and 1173 K (XRD).

2.1. Bulk systems

Physical method: The solids called NiEV and AlEV correspond to the materials obtained by thermal treatment (calcination) of nickel and aluminium nitrates, respectively. NiAlEV catalyst was prepared by mixing nickel and aluminium nitrates at 353 K (in melting state) with an atomic ratio Al/Ni = 0.5. The samples were dried in heater at 373 K, for 1 h.

Chemical method: Aqueous solutions of nickel nitrate (2M), aluminium nitrate (1M) and urea (3M) were prepared. Two solids were obtained by mixing: (i) equal volumes of nickel nitrate and urea solutions (NiCOPU) and (ii) equal volumes of nickel and aluminium nitrate solution and an equivalent volume to that of urea (NiAlCOPU). Each sample was heated up to 363 K to produce urea, hydrolysis and precipitation of a solid phase by alkalinization. The precipitate was filtered and washed with distilled water. The samples were dried in heater at 373 K, for 12 h.

2.2. Supported systems

These solids were prepared on two supports: (i) α-Al_2O_3, called S, was prepared according to the method reported in bibliography [8,9], with a specific surface area of 1.4 $m^2 g^{-1}$ and a pore volume of 0.25 $cm^3 g^{-1}$; (ii) S modified by an Al layer, called S + Al, obtained

by impregnation of S from an aluminium nitrate salt dissolved in its hydration water by melting at 353 K. The modified supports were dried at 373 K and calcinated at 873 K, for 2 h.

Impregnation method: The impregnation solutions were Ni nitrate (Ni/S) and Ni and Al nitrates with an Al/Ni ratio equal to 0.5 (NiAl/S), in both cases dissolved in their hydration water by melting at 353 K. The supports were inmersed in these solutions for 0.5 h. When impregnation stage finished, the solids were dried for 1 h in heater at 373 K.

Deposition–precipitation method: Aqueous solutions of Ni nitrate (2M) and urea (3M) were mixed in a volumetric ratio equal to 1. Supports were immersed in solution for 0.25 h. Then, it was heated up to 363 K to produce urea hydrolysis generating adequate conditions to generate Ni deposition–precipitation on S (NiDP/S) and S + Al (NiDP/S + Al) supports following the methodology similar to the one reported in bibliography about silica [10]. These conditions were maintained for 1 h, then the solids were dried in heater for 1 h at 373 K.

Thermal activation by DTA and TGA were carried out in a Netzsch STA 409 equipment, Model 414/2. Solids were placed in alumina sample crucibles using α-Al_2O_3 as reference. Tests were performed in dry air flow of 30 $cm^3 min^{-1}$ at atmospheric pressure. The temperature was increased from 373 to 1173 K with a heating rate of 10 K min^{-1}. XRD analyses were made in a Philips PW 1140/00 equipment using $CuK\alpha$ radiation ($\lambda = 0.155$ nm) and Ni filter (40 KW and 20 mA).

Ni content was determined by atomic absorption technique.

3. Results and discussion

The Ni content for different catalysts analysed is shown in Table 1.

3.1. Bulk systems

Figs. 1 and 2 show DTA–TGA diagrams obtained for NiEV and AlEV samples during thermal activation in air atmosphere between 373 and 1173 K.

In the NiEV solid (Fig. 1) three endothermic peaks are observed at 413, 480 and 579 K assigned to the

Table 1
Ni content (%) for the bulk and supported systems

Bulk systems			Supported systems		
NiEV	NiAlCOPU	Ni/S	NiAl/S	NiDP/S	NiDP/S+Al
58.6	50.1	8.4	6.2	1.2	2.6

removal of hydration water and decomposition of nitrate groups of nickel nitrate, respectively. The change of relative weight of the initial mass (Δw) determined in TGA diagram for temperatures below 520 K is 58.1%, which is compatible with the loss of six water molecules and to one of the nitrate groups of $Ni(NO_3)_2 \cdot 6H_2O$. The Δw value measured between

Fig. 1. DTA–TGA diagrams for NiEV samples. Initial mass = 71 mg.

520 and 873 K is 17.7% corresponding to removal of the second nitrate group to form NiO as final product.

In the AlEV solid (Fig. 2) an endothermic peak is observed with important intensity at 434 K together with two peaks of low intensity at 497 and 885 K. The Δw value is 64.4% for temperatures below 473 K corresponding to removal of one third of hydration water and to the three nitrate groups of starting $Al(NO_3)_3 \cdot 9H_2O$. Between 473 and 900 K, small endothermic transformations are produced assigned to different alumina transitions; the calculated value for Δw is 18% corresponding to removal of remaining water molecules from aluminium nitrate.

DTA–TGA diagrams for NiAlEV are shown in Fig. 3. The Al/Ni atomic ratio selected is 0.5; this value corresponds to the maximum catalytic activity achieved for this type of solids in the methane steam reforming process [11]. Three endothermic transformations are observed at 440, 456 and 590 K. Taking into account the individual behaviour observed in each one of the nitrates (NiEV and AlEV) and the Δw value of 58% determined below 520 K, transformations
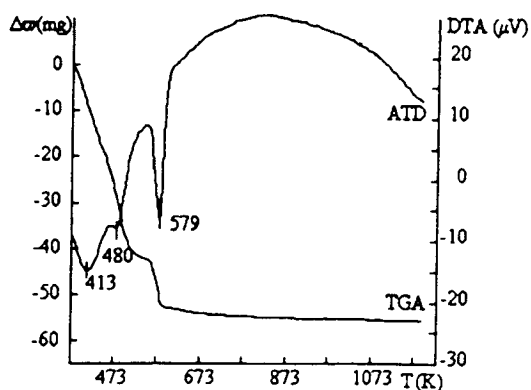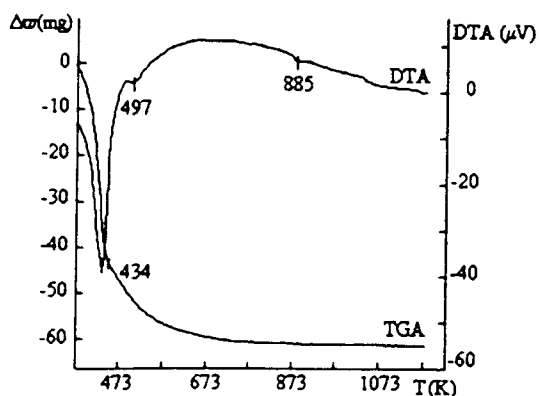

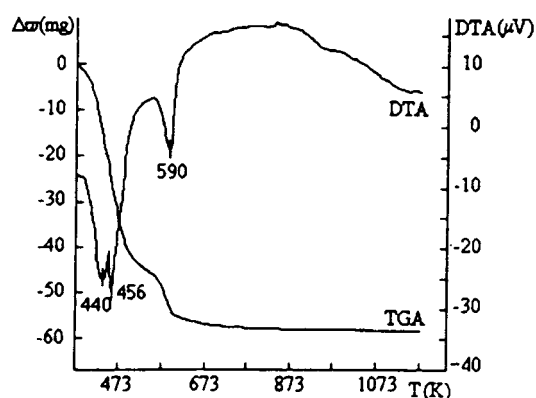Fig. 2. DTA–TGA diagrams for AlEV samples. Initial mass = 73 mg.

Fig. 3. DTA–TGA diagrams for NiAlEV samples. Initial mass = 72 mg.

observed at 440 and 456 K are assigned to: (i) whole removal of total hydration water of nickel nitrate and partial of aluminium nitrate; (ii) removal of nitrate groups of aluminium nitrate and one of the nitrate groups of nickel nitrate. The weight change determined between 520 and 873 K ($\Delta w = 17\%$) is compatible with remaining water removal from aluminium nitrate and the other nitrate group removal from nickel nitrate. The endothermic transformation observed at 590 K is in agreement with the removal of this nitrate group, but it is shifted respect to the one of NiEV. All these results show that the thermal activation of the mixture of nickel and aluminium nitrates (in presence of air and at temperature 873 K as minimum) lead to mixed nickel and aluminium oxides with complete removal of nitrate groups and of the hydration water of precursors. The theoretical balance of mass for this transformation, as is represented in scheme (1), implies a solid mass decrease of 74% with respect to the initially treated and this value is in agreement with the one experimentally calculated (75%).

$$Ni(NO_3)_2.6H_2O + 0.5Al(NO_3)_3.9H_2O$$
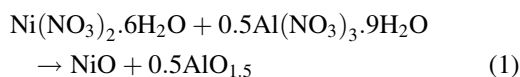$$\rightarrow NiO + 0.5AlO_{1.5} \qquad (1)$$

Fig. 4 shows diffraction diagrams of NiAlEV materials calcined at 723, 873 and 1073 K. Samples calcined at 723 and 873 K show the NiO phase ($2\theta = 37.2°$, $43.3°$, $62.9°$), but a higher crystallinity is found in the sample calcined at 873 K. When the calcination temperature increases up to 1073 K, peaks of spinel $NiAl_2O_4$ ($2\theta = 45.1°$, $65.5°$) together with the ones of the NiO phase appear. The atomic ratio Al/Ni = 0.5 corresponds to a nickel excess with respect to the stoichiometric amount required for the spinel formation (Al/Ni = 2). Diffractograms obtained in laboratory show an increase in spinel contribution with respect to oxide for samples with higher Al/Ni ratios. These XRD results indicate that it is possible to reach the formation of structures where the aluminium and nickel present a strong interaction (mixed oxides) for solids obtained by physical way from a mixture of nickel and aluminium nitrates. The formation of these phases would explain the shift towards higher temperatures in the third endothermic peak observed in DTA experiments, in the NiAlEV solid with respect to the NiEV solid. A well defined spinel is achieved with this interaction with an adequate thermal treatment (1173 K).
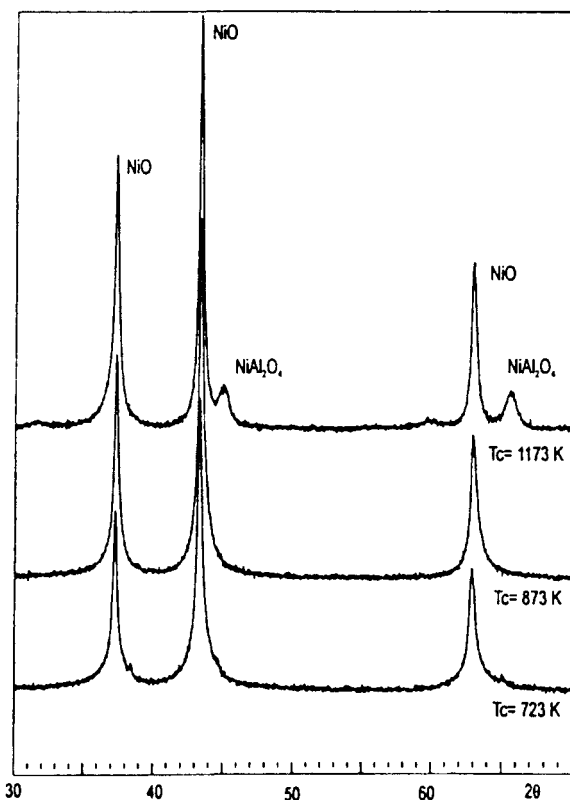

Fig. 4. XRD patterns for the NiAlEV samples calcined at 723, 873 and 1173 K.

Bulk catalysts from aluminium and nickel salt solutions may be obtained by alkalinization of these solutions. The conventional alkalinization is obtained by addition of sodium carbonate, sodium or ammonium hydroxide [12]. In this work, the possibility of alkalinization by urea hydrolysis at 363 K was analysed and this technique may be used in the preparation of supported catalysts.

The experiment performed on the NiCOPU solid (nickel nitrate and urea) evidenced the existence of a global exothermic transformation at 605 K as it is shown in DTA–TGA diagrams of Fig. 5. This peak is produced by the contribution of two thermal effects almost simultaneous: the Ni endothermic transformation at 575 K in its corresponding oxide and exothermic reactions by residual urea oxidation.

Fig. 6 shows DTA–TGA diagrams for NiAlCOPU presenting two thermal effects at 558 K (exothermic) and at 618 K (endothermic). The exothermic band
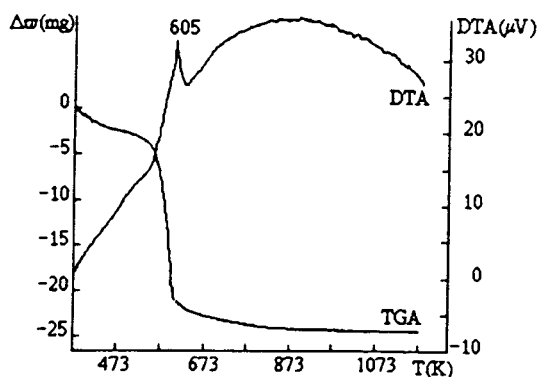
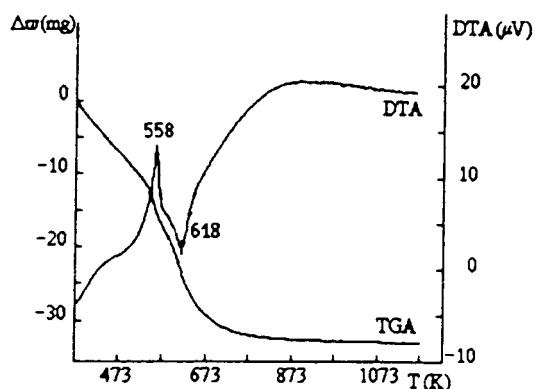Fig. 5. DTA–TGA diagrams for NiCOPU samples. Initial mass = 71 mg.

Fig. 6. DTA–TGA diagrams for NiAlCOPU samples. Initial mass = 71 mg.

Fig. 7. XRD patterns for the NiAlCOPU samples fresh and calcined at 723, 873 and 1173 K.

would correspond to oxidation of urea residues as was explained in the previous case (Fig. 5), while the endothermic one at 618 K, is assigned to the NiO formation stage. XRD diagrams shown in Fig. 7 permit to complete the information and understand the transformations observed. These diffraction diagrams were made on the fresh catalyst (at the end of the washing stage) and on calcined samples at 723, 873 and 1173 K. The XRD diagram obtained for the fresh catalyst is similar to the one observed in a previous work when alkalinization is performed with ammonium by the so called method of controlled pH increase [12]. This fact demonstrates the possibility of using urea to generate nickel and aluminium co-precipitated phases. Diffraction peaks shown by fresh NiAlCOPU ($2\theta = 10.6°$, $20.5°$, $34.9°$, $44.5°$, $61.6°$)

correspond to the presence of structures of double hydroxide type, belong to compounds of the hydro-talcites family, indicative of a strong interaction between Ni and Al. The weight change observed during calcination (Fig. 6) corresponds to a hydro-talcite with stoichiometry $Ni_{0.66}Al_{0.33}(OH)_2(NO_3)_{0.33}$ $\cdot 6H_2O$. Hydrotalcites are precursors of active phases very interesting for steam reforming of methane because they generate Ni and Al phases with higher resistance with respect to sintering; they are also used in other important processes [13,14].

Calcination of NiAlCOPU at 723 K leads to NiO formation; with the increase of calcination temperature a structure rearrangement is produced up to 1173 K where $NiAl_2O_4$ and NiO phases are observed. Comparing the NiAlEV evolution, it is evidenced that the two techniques lead to different precursors during the first preparation stages. However, when they are calcined in air at temperatures of 873 K or higher, the

final phases are similar in both cases. These results are consistent with a model that proposes the co-existence of two phases closely related, one NiO rich and the other of the type of mixed oxide, which at high temperatures is transformed into spinel. The higher slimness of diffraction peaks of NiO in NiAlEV solids in relation to the ones observed for NiAlCOPU indicates a higher dispersion of phases containing nickel in the case of systems obtained by alkalinization.

3.2. Supported systems

Most of commercial catalysts for methane steam reforming are based on supported nickel, although bulk systems have industrial use. The low concentration of active phase present in the supported systems makes it difficult its characterization (for instance by XRD). Consequently, results discussed in previous paragraph for bulk systems are important to understand the nature of phenomena occurring in supported systems.

Supports based on α-Al_2O_3 have a high thermal and structural stability but for this reason they have low surface chemical activity generating low interaction with the nickel precursor, which produces a scarce thermal stability of the active catalytic phase. So, different strategies may be applied as for example the co-impregnation or deposition–precipitation.

Figs. 8 and 9 show DTA–TGA diagrams for Ni/S and NiAl/S systems, respectively. The Ni/S solid presents three endothermic transformations at 405, 470 and 574 K and this behavior may be compared
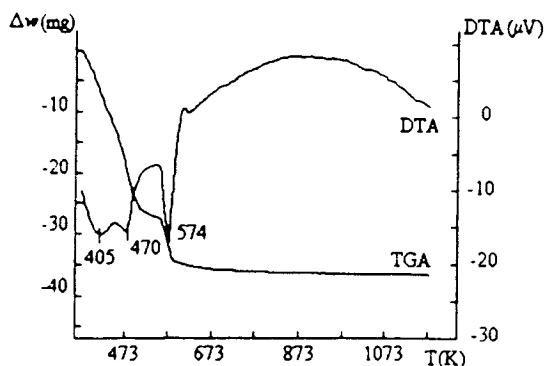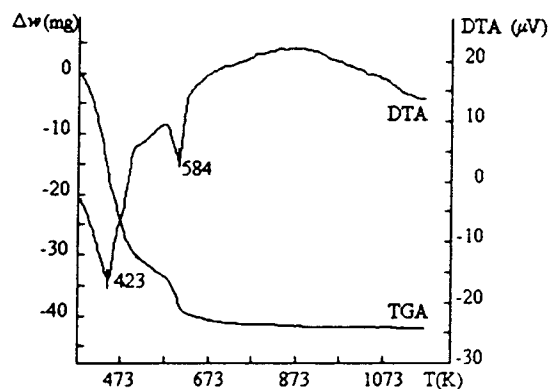
Fig. 9. DTA–TGA diagrams for NiAl/S samples. Initial mass = 197 mg.

with one of the NiEV system. These peaks are produced by the removal of hydration water and by nitrate groups of precursor. The NiAl/S solid presents a behaviour similar to the one of NiAlEV sample where the peak observed at higher temperature is again shifted at 584 K. This would indicate the formation of an intermediate phase of the type of mixed oxide between Ni and Al. Δw values calculated from TGA diagram are compatible with complete decomposition of nitrates in their corresponding oxides for calcination temperatures of 873 K or higher. This is an important result for the industrial development of these catalysts.

XRD diagrams of Ni/S and NiAl/S catalysts calcined at 873 K are shown in Fig. 10. Peaks corresponding to α-Al_2O_3 and NiO are observed. NiO peaks appear with lower intensity due to low Ni concentration in the supported systems. For the case of NiAl/S samples, the greatest width of the peak with respect to Ni/S indicates the presence of phases with higher dispersion (smaller particle sizes) surely related to the formation of nickel and aluminium mixed oxides. It was not possible to detect the spinel phase in these compositions.

Catalysts prepared by deposition–precipitation are interesting since results on supports based on α-Al_2O_3 are not reported in bibliography. In this work, and mainly for the case of the modified support by aluminium (S + Al), this technique allowed to fix an acceptable nickel amount (see Table 1). DTA–TGA curves, presented in Fig. 11 are similar with the ones observed for NiAlCOPU (Fig. 6), resulting acceptable

Fig. 8. DTA–TGA diagrams for Ni/S samples. Initial mass = 197 mg.
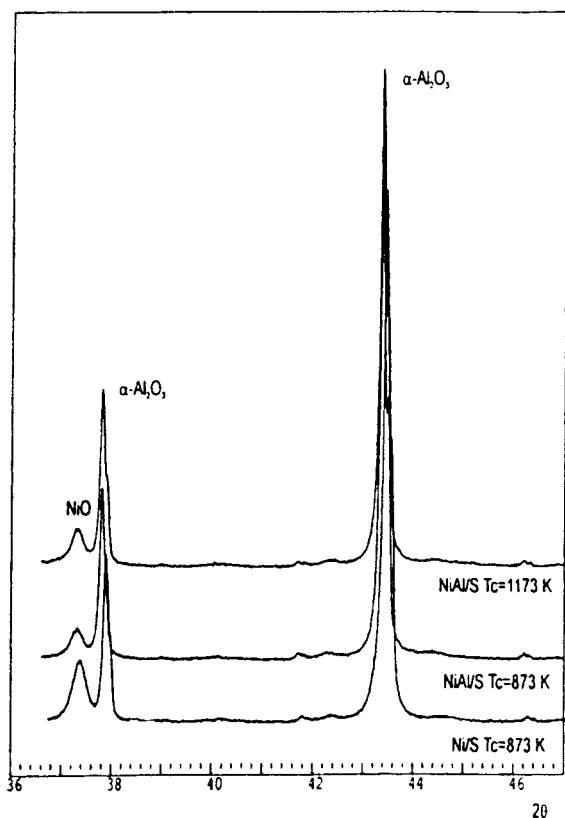
Fig. 10. XRD patterns for the Ni/S and NiAl/S samples.
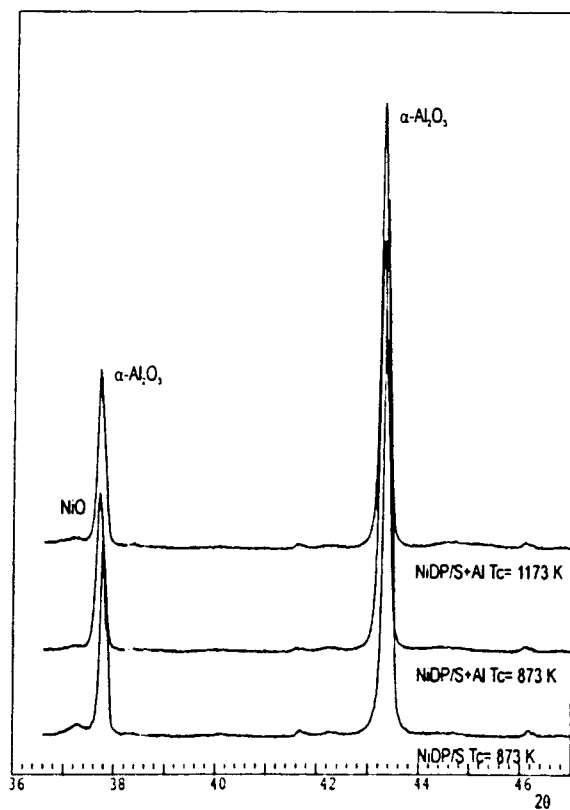

Fig. 12. XRD patterns for the NiDP/S and NiDP/S + Al samples.

to suppose that developed phases on the support are also similar to the ones detected in the bulk system.

XRD diagrams (Fig. 12) of NiDP/S and NiDP/S + Al show, after calcination at 873 K, the presence

of NiO. It is more difficult to observe diffraction peaks in these samples because the Ni concentrations are lower. However, the lower NiO cristallinity showed by NiDP/S + Al with respect to NiDP/S is indicative of a
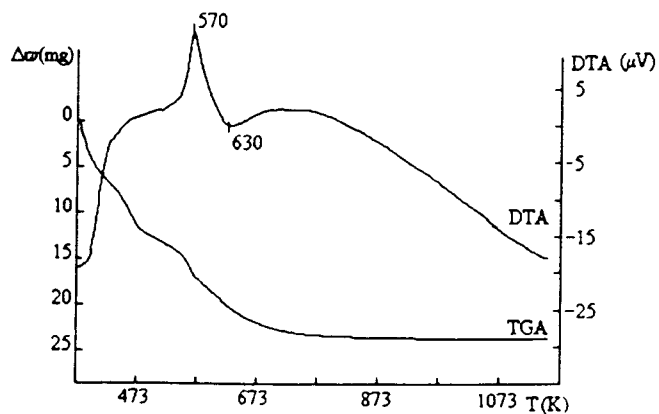

Fig. 11. DTA–TGA diagrams for NiDP/S + Al samples. Initial mass = 395 mg.

higher dispersion of the mentioned phase on the modified support. These results lead to sustain hypotheses presented from DTA–TGA experiments, indicating that this technique leads to a strong interaction between nickel and aluminium.

4. Conclusions

The use of DTA–TGA techniques complemented with XRD is a very useful tool to analyze the evolution of active phases during calcination stage of these materials.

The thermal conditions for total decomposition of nitrate precursors were determined for bulk and supported catalysts.

The Ni and Al co-precipitation by urea hydrolysis leads to phases of the type of mixed hydroxides (hydrotalcites according to XRD) interesting in catalysis whose approximate stoichiometry was established from TGA. These results allowed us to define an experimental route to obtain catalysts by deposition–precipitation on α-Al$_2$O$_3$ and α-Al$_2$O$_3$ modified by Al.

Acknowledgements

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