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Nature of Ni–Al developed phases during thermal activation in relation to the preparation techniques. Part II: reduction and catalytic properties

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Abstract

The reducibility of different catalysts based on Ni (bulk and supported) used to obtain syngas is studied in this work. Taking as test reaction the steam reforming of methane, it was possible to prove that the stability of catalytic systems is closely related with the reduction temperature determined by TGA–DTG. Higher difficulty in reduction of metallic phase implies higher interaction between Ni and Al oxides; this leads to higher stability of catalytic system exposed to severe thermal treatments.

Keywords: TGA–DTG; H_2 reduction; Ni catalyst; Methane steam reforming

1. Introduction

Due to the great demand of hydrogen, both for petroleum refining processes and petrochemical industry, its production by reforming of methane has increased in importance. While most syngas is produced by steam reforming of methane, some other routes as partial oxidation or CO_2 reforming of methane may be more attractive, depending on factors such as H_2/CO ratio, environmental restrictions, etc.

Catalysts based on Ni are widely used for steam reforming, partial oxidation or CO_2 reforming [1–4].

In Part I it was studied the evolution of different systems (bulk and supported catalysts) during calcination step by using differential thermal analysis (DTA) and thermogravimetry analysis (TGA–DTG), complemented with X-ray diffraction (XRD).

In this work the H_2 reducibility of calcined phases in function of preparation method is studied by TGA–DTG. The relation between nature and reducibility of active phase (Ni) with catalytic properties (stability) is analysed, taking as reaction test the methane steam reforming.

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Table 1
Nomenclature of the catalytic systems

Start solution	Method	Bulk systems	Supported systems	
			α-Al_2O_3	α-Al_2O_3 + Al
Ni nitrate	Heat treatment	NiEV	–	–
Ni nitrate + Al nitrate	Heat treatment	NiAlEV	–	–
Ni nitrate + urea	Precipitation	NiCOPU	–	–
Ni nitrate + Al nitrate + urea	Co-precipitation	NiAlCOPU	–	–
Ni nitrate	Impregnation	–	Ni/S	–
Ni nitrate + Al nitrate	Co-impregnation	–	NiAl/S	–
Ni nitrate + urea	Deposition–precipitation	–	NiDP/S	NiDP/S + Al

2. Experimental methods

Catalytic systems were prepared following the methodology presented in Part I. Table 1 summarizes prepared catalytic systems and their nomenclature.

The Ni reducibility was studied following the weight change observed (TGA–DTG) when previously calcined samples (calcination temperature, 1173 K) were exposed to hydrogen flow. Samples were placed in alumina crucibles and α-Al_2O_3 was used as a reference. The equipment was evacuated and then filled with N_2 to eliminate the oxygen present. The experiments were performed in H_2 atmosphere at a flow rate of 30 cm^3 min^{-1}, between 373 and 1273 K with a heating rate of 10 K min^{-1}. A Netzsch STA 409 equipment, model 414/2 was used.

Catalytic tests and stability measures of catalysts were performed in a conventional microreactor of fixed bed at atmospheric pressure with the following program:

1. Reduction in N_2/H_2 (20/80) flow during 1 h at 1023 K.
2. Reaction test in $N_2/H_2/CH_4/H_2O$ (55/20/5/20) flow at 873 K (180 $cm^3 min^{-1}$, catalyst mass = 0.05 g).
3. Deactivating treatment in $N_2/H_2/H_2O$ (58/21/21) flow during 2 h at 1023 K.
4. Reaction test item 2.
5. Deactivating treatment, item 3, during 5 h.
6. Reaction test item 2.
7. Deactivating treatment, item 3, during 5 h.

The stability of catalytic systems was determined through the evolution of activity coefficient (κ) with deactivation time. This coefficient is defined as the ratio between the specific constant of reaction rate at time t and the specific constant of initial reaction rate ($\kappa = k_t/k_0$, supposing reaction of first order).

3. Results and discussion

3.1. Reduction step

The reduction of supported metallic catalysts is considered of great interest because of: (i) the reaction temperature must be known to obtain the adequate active phase and (ii) the reduction temperature may be related with the nature of this phase and with the interactions generated with the support and/or promoters.

Fig. 1 shows the TGA–DTG diagrams of the reduction step for the NiEV solid achieved by calcination of nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$). In these conditions the solid phase represents a NiO bulk [5], without interaction with other components. The NiO reduction ($NiO^{solid} + H_2 \rightarrow Ni^{solid} + H_2O$) occurs in a narrow temperature range (between 473 and 773 K), with a peak temperature at 574 K, where the maximum rate of weight loss by reduction is produced.

Fig. 2 shows the reduction diagram for NiCOPU system, presenting a similar behaviour to the one of the NiEV system. This indicates that Ni precipitation by alkalinization via urea hydrolysis and subsequent calcination leads to formation of nickel oxide bulk.

Fig. 3 shows TGA–DTG diagrams of NiAlEV solid. The weight loss observed is developed within a wider temperature range than for NiEV (between 473 and 1173 K) recording two temperature peaks. The lower temperature peak is well defined at 603 K, while the higher temperature peak is at about 893 K corresponding to a wide not well defined zone.

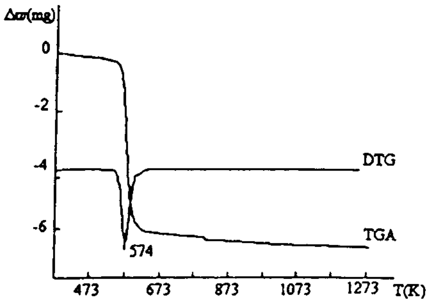

Fig. 1. TGA–DTG diagrams for NiEV samples. Initial mass = 71 mg.

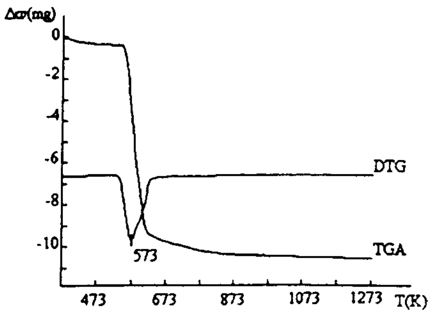

Fig. 2. TGA–DTG diagrams for NiCOPU samples. Initial mass = 72 mg.

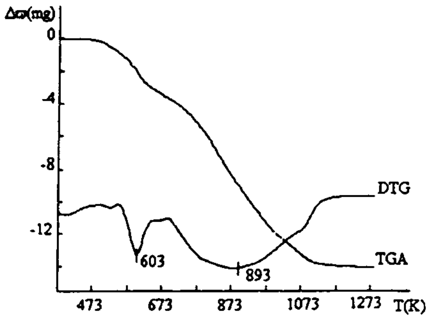

Fig. 3. TGA–DTG diagrams for NiAlEV samples. Initial mass = 71 mg.

The TGA–DTG diagrams for the NiAlCOPU solid (Fig. 4) show a similar behaviour to the one of the NiAlEV system with a reduction shift towards higher temperatures. The temperature range is between 673 and 1173 K. Two temperature peaks are observed at 893 and 1053 K.

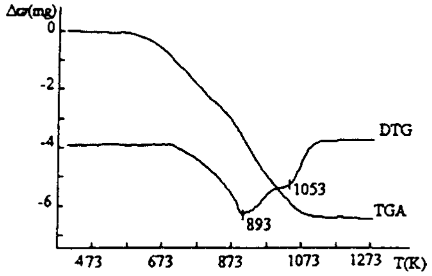

Fig. 4. TGA–DTG diagrams for NiAlCOPU samples. Initial mass = 73 mg.

The shifting of the reduction zone to higher temperatures observed for NiAlEV and NiAlCOPU systems with respect to NiO is in agreement with conclusions of Part I. The existence of a specific interaction between Ni and Al, after calcination step, leads to formation of mixed oxide structures strongly interactive. The presence of two reduction zones may be explained by the existence of two phases: (i) a mixed oxide, $NiAl_2O_4$ type (the reduction temperature of $NiAl_2O_4$ is higher than 1000 K [6,7]); (ii) a NiO interacting with the previous phase (its temperature peak is higher than the one of the NiO bulk). This result is in agreement with the stoichiometric ratio used Al/Ni = 0.5, where the Ni-excess respect to the amount required for spinel ($NiAl_2O_4$) is found as NiO.

Fig. 5 shows TGA–DTG diagrams for the supported Ni/S system. This catalyst presents a behaviour similar to the one of NiO bulk although the temperature range (Δ*T*) is more prolonged (473–973 K) and the peak temperature is at 613 K shifted in 40 K with respect to the one of NiO. These results would indicate

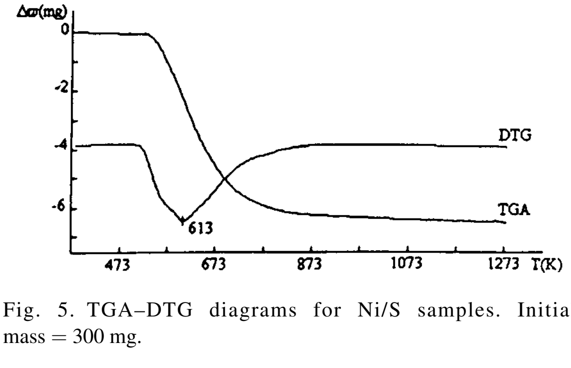

Fig. 5. TGA–DTG diagrams for Ni/S samples. Initial mass = 300 mg.

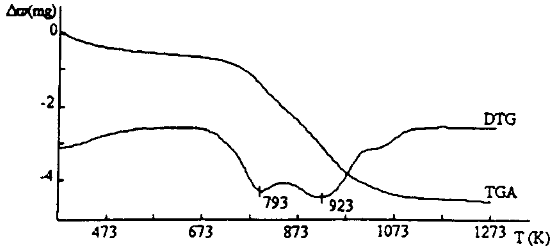

Fig. 6. TGA–DTG diagrams for NiAl/S samples. Initial mass = 300 mg.

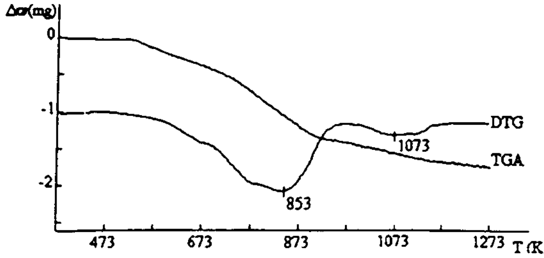

Fig. 8. TGA–DTG diagrams for NiDP/S + Al samples. Initial mass = 300 mg.

that the Ni phase interacts with the support, although the interaction would be slightly weak [8,9].

For the case of NiAl/S co-impregnated systems (Fig. 6), the behaviour is similar to the one of the NiAl bulk solids ($\Delta T = 573$–1173 K; two temperature peaks at 793 and 923 K). The peak at 923 K is assigned to mixed oxide phase of $NiAl_2O_4$ type. The peak at 793 K may be interpreted as the one corresponding to the reduction of a NiO phase presenting a high interaction degree with the mentioned mixed oxide or with the support.

The systems prepared for deposition–precipitation showed different behaviours. Two reduction peaks appear in Fig. 7 for the catalyst prepared on α-Al_2O_3 without modification (NiDP/S); the first peak at the same temperature of NiO bulk (573 K), indicative of a phase without interaction with the support, while the second peak around 860 K corresponds to a wide reduction zone ($\Delta T = 573$–1173 K). This last peak evidences that even in the case of support without modification, a part of deposited Ni by this method interacts with the support.

TGA–DTG diagrams for the NiDP/S + Al system are shown in Fig. 8. In this case, the reduction occurs in a wide temperature range ($\Delta T = 673$–1173 K). These diagrams are similar to the ones obtained for the NiAlCOPU solid bulk, in agreement with results of Part I, where it was stated that active phases, obtained on modified supports (NiDP/S + Al), are similar with the ones achieved by co-precipitation (NiAlCOPU). In both solids, the interaction between Ni and Al surely occurs. With respect to NiAl/S systems (co-impregnation), the shifting of the reduction temperature towards higher values would indicate a more efficient interaction between Ni and Al, for NiDP/S + Al catalyst.

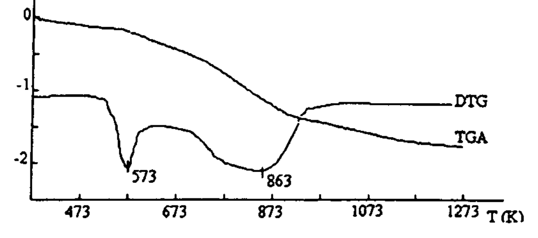

Fig. 7. TGA–DTG diagrams for NiDP/S samples. Initial mass = 300 mg.

Through weight loss measured (Δw), it is possible to estimate the reduction degree reached. In all cases this value is compatible with a reduction degree of NiO near 100%. Table 2 shows the coincidence existing between the weight change achieved by TGA (Δw^{exp}) and the theoretical one estimated for total reduction from NiO composition determined by atomic absorption (Δw^{theor}).

3.2. Stability tests

It is important to take into account the information from the use of these thermal activation techniques to characterize solids and predict their catalytic beha-

Table 2
Weight change determined by TGA and calculated by atomic absorption

Catalyst	Ni (%)	Δw^{exp} (mg)	Δw^{th} (mg)
Ni/S	8.1	6.4	6.6
NiAl/S	5.9	4.5	4.8
NiDP/S	2.6	1.8	2.1
NiDP/S + Al	1.3	1.1	1.1

viour. These catalysts present good levels of initial activity in steam, CO_2 or air reforming of methane to synthesis gas [10–12]. One of the main problems is the deactivation by sintering, mechanism favoured by high temperatures and by the presence of steam. For this reason, steam reforming of methane is a very good stability test.

With the conditions used, NiEV and NiCOPU systems (pure NiO) are completely deactivated after 7 h deactivating treatment. Instead, NiAlEV and NiAlCOPU systems are much more stable and after 7 h deactivating treatment, they maintain approximately more than 80% initial activity ($\tau\sim0.80$). In these last systems, due to the existence of structures where Ni and Al are intimately related, aluminium oxide phases disperse crystallites of the metallic nickel (active phase) acting as barriers inhibiting Ni sintering. This effect favours notably the thermal stability of the system. Although intermediate stages depend on preparation method used (hydrotalcites, nitrates, see Part I), solids obtained at the end of the calcination stage present properties and tendencies qualitatively similar: aluminate phases (XRD), comparable reduction zones (TGA–DTG), stability with respect to sintering.

Figs. 9 and 10 show catalytic results obtained for supported catalysts prepared by impregnation and deposition–precipitation, respectively. For both preparation methods, the Al presence (co-impregnation or deposition–precipitation on modified supports) is essential to generate solids with higher stability. As it was stated for bulk catalysts, the Al presence generates barriers to the sintering mechanism of nickel phase, which improves notably the stability of these catalytic systems. The greatest difficulty in the reduction of nickel in NiDP/(S + Al) solid with respect to NiAl/S (see Figs. 6 and 8) may be explained by the higher interaction between Ni and Al in the system prepared by deposition–precipitation. This fact is in agreement with the higher relative stability observed in curves represented in Figs. 9 and 10. This interpretation is also valid in the supported systems on α-Al_2O_3 without modification since NiDP/S catalyst is more stable than Ni/S catalyst and this result is coherent with TGA–DTG diagrams shown in Figs. 5 and 7.

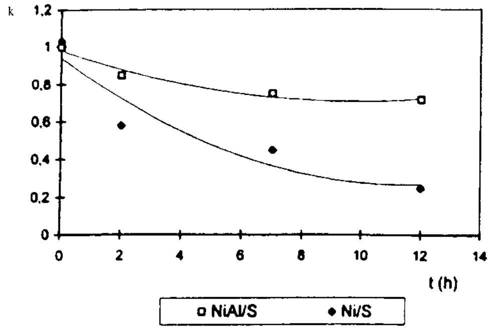

Fig. 9. Activity coefficient evolution (κ) vs. deactivation time (t) for Ni/S and NiAl/S catalysts.

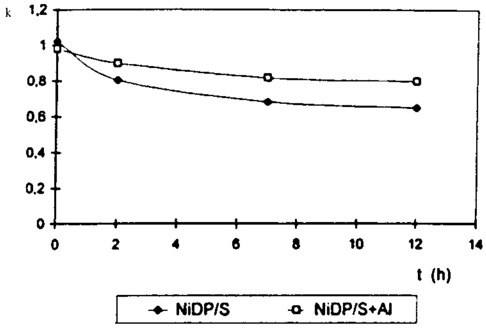

Fig. 10. Activity coefficient evolution (κ) vs. deactivation time (t) for NiDP/S and NiDP/S + Al catalysts.

4. Conclusions

The use of TGA–DTG permits to study the H_2 reducibility of different catalysts based on Ni (bulk and supported), as a function of the different preparation techniques used.

Those preparations that lead to a strong interaction between Ni and Al (co-precipitation, co-impregnation, deposition–precipitation), generate Ni phases more difficult to be reduced. This is produced by the formation of mixed oxides (spinel type non-stoichiometric) when a Al/Ni = 0.5 atomic ratio is used.

The catalytic stability of these systems, in the methane steam reforming process, is related to the catalyst reducibility. When the Ni reduction is more difficult to be performed, there exists higher interaction between Ni and Al and higher thermal stability.

It was possible to fix Ni via alkalinization with the urea on α-Al_2O_3 supports modified by an aluminium oxide layer. This method led to the formation of Ni supported phases more difficult to be reduced and with higher thermal stability.

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