

Hydrogen production by thermocatalytic decomposition of methane over Ni-Al and Ni-Cu-Al catalysts: Effect of calcination temperature[☆]

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Abstract

Thermo catalytic decomposition of methane using Ni-Al and Ni-Cu-Al catalyst prepared by fusion of the corresponding nitrates is studied. The effects of catalyst calcination temperature on the hydrogen yields and the characteristics of the carbon obtained are studied. The role of copper has been also analyzed. Whatever the calcination temperature, all the catalysts show a high and almost constant hydrogen yield without catalyst deactivation after 8 h on stream, which confirms the good performance of this kind of catalysts. The presence of copper enhances the hydrogen production and the best results were obtained using catalysts calcined at 600 °C. Cu has a strong influence on the dispersion of Ni in the catalysts and inhibits NiO from the formation of nickel aluminate even at high calcinations temperatures, which facilitates the formation of the metallic Ni active phase during the subsequent catalyst reduction step. All catalysts tested promote the formation of very long filaments of carbon a few tens of nanometers in diameter and some micrometers long. The structural properties of these carbon filaments highly depend on the presence of Cu: Ni-Cu-Al catalysts promote the formation of a well-ordered graphitic carbon while Ni-Al catalysts enhance the formation of a rather turbostratic carbon. © 2007 Elsevier B.V. All rights reserved.

Keywords: Hydrogen production; Ni catalysts; Calcination temperature

1. Introduction

Hydrogen is an emerging alternative to conventional fuels to reduce CO₂ emissions. It is considered a clean energy source and its market demand is steadily increasing [1–3]. It is generally accepted, that in the near-to-medium term hydrogen production will rely on fossil fuels, primarily natural gas. At present reforming of hydrocarbons is the technique most widely used for hydrogen production, generally using catalysts based on metals like Ni [4–6], Cu [7] or Co [8], but this production could be considered clean only applying techniques of capture and storage of the CO₂ obtained during the process.

In the near-to-medium term, hydrogen will be produced in small-to-medium decentralised installations located near to use in order to minimise the important concerns derived from hydrogen transport. If methane is reformed in these “on site” installations, the transport of the CO₂ produced to a sink will increment

significantly the cost of the hydrogen production. In this scenario, thermo catalytic decomposition of natural gas, TCD, with carbon being captured as a solid of added value product appears as a very interesting alternative to steam reforming [9].

Feasibility of TCD in economical terms is very sensible to the carbon selling price which depends on the properties of the carbon obtained. The quality of carbon produced from TCD largely depends on the operation conditions and the type of catalyst used. Using metal-based catalysts lead to the production of carbon forms of high quality whose high selling price would compensate the high cost of the catalyst. Several prior studies on methane decomposition using mainly transition metals have been reported in the literature [10]. TCD of methane using Ni and Ni-Cu catalysts to produce hydrogen and novel carbonaceous materials was first reported by Muradov [11] and Parmon et al. [12]. Although other many metals have been tested for TCD, most of the reported studies have used Ni and Ni-Cu catalysts [13–18].

In a previous work [19], it has been shown that the catalyst life mainly depends on the morphology of the deposited carbon which appears either as long filaments a few nanometres in diameter emerging from Ni particles or as uniform coatings. Formation of filaments enlarges the catalyst life. The influence

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of presence of Cu on the characteristics of the carbon produced using Ni-Cu-Al catalyst prepared by co-precipitation has been extensively studied by Monzón et al. [20] and Suelves et al. [21]. It has been shown that presence of Cu has an important effect on the size and shape of the Ni particles, which affects to the catalyst behaviour.

Among the different methods of catalyst preparation described in the literature, co-precipitation and impregnation are the most used. These methods include washing and filtering steps which are time and energy consuming and involve the use of huge amounts of water. These could be important drawbacks for their use at an industrial scale because in TCD the catalyst is withdrawn from the reactor with carbon. For that reason an easier preparation method based on the fusing of the metallic nitrates was reported in a previous paper [21]. The use of this kind of catalyst was first reported by BIC's researchers [17]. However, in that work, the fusing catalysts were subjected to an additional stabilization with silica and the effect of calcination temperature was not included.

In this work, Ni and Ni-Cu catalyst have been prepared by the fusing method using different calcination temperatures in order to study its influence on methane conversion, catalyst deactivation and the amount and characteristics of the carbon produced. The role of copper has also been analyzed. A wide range of calcinations temperatures covering temperatures up to 1000 °C has been studied in order to simulate the regeneration step of an industrial installation where catalyst was submitted to high temperatures to burn the carbon layer coating the catalyst particle.

2. Experimental

2.1. Catalysts preparation

In a previous work [22] the influence of Ni and Cu concentrations for the catalysts prepared by co-precipitation were studied. For this work, two catalysts were selected: Ni:Al—2:1 and Ni:Cu:Al—78:6:16 (molar ratio). The catalysts were prepared by fusing nitric salt of nickel and copper (when necessary) with nitric salt of aluminium followed by decomposition of the mixtures at 350 °C for 1 h and calcination for 8 h. Four different calcination temperatures were studied: 450, 600, 800 and 1000 °C.

2.2. Activity tests

Runs were carried out in a fixed-bed quartz reactor 1.7 cm i.d., 42.5 cm height, using pure CH₄ as feeding gas. The decomposition tests were carried out at a reaction temperature of 700 °C using a pure methane flow rate of 20 ml min⁻¹. Samples of 0.3 g of catalyst were used. Prior to activity tests, all catalysts were subjected to a reduction treatment using a flow rate of pure hydrogen of 20 ml min⁻¹ for 3 h at 550 °C.

The composition of the outlet gas from the reactor was determined by gas chromatography: two packed columns, Molecular Sieve 13× and Porapack, and TCD detector were used. No methane decomposition products other than hydrogen were detected in the gas phase.

2.3. Characterization techniques

The actual metallic content in the catalysts was determined by ICP-OES. Studies of the homogeneity degree of Ni dispersion in the fresh catalyst and the morphological appearance of the deposited carbon have been carried out in a scanning electron microscope (SEM) Hitachi S-3400 coupled to a Si/Li detector for energy dispersive X-ray (EDX) analysis.

Powder X-ray diffraction measurements were performed at room temperature on a Bruker AXS D8 Advance diffractometer with a θ - θ configuration. Cu K α radiation was used, and graphite was the secondary monochromator. An exit slit window of 0.5°, antiscattering slit of 1.0 mm and a divergence slit of 0.2 mm were used in all the experiments. The Bragg angle step was 0.05°, and the time per step was 5 s.

The qualitative and semi-quantitative analysis of the different species was performed using the powder diffraction files 2002 (PDF) database in the DIFFRAC^{plus} EVA8.0 software. The crystallite size of the different crystalline phases was obtained using the Scherrer equation on the fitting software TOPAS 2.1.

Transmission electron microscopy (TEM) studies were made on a Philips TEM/STEM CM200 LaB₆ apparatus operating at 200 kV.

The reducibility of the catalysts was studied by temperature programmed reduction (TPR). The sample (100 mg) was heated at the rate of 5 °C min⁻¹ in a TPR system equipped with a TCD, from room temperature to 800 °C, under a H₂(5%)/N₂ mixture with a flow of 100 Nml min⁻¹.

3. Results and discussion

3.1. Hydrogen production

Fig. 1(a) shows the hydrogen yields obtained as a function of calcination temperature for the Ni:Al catalyst. Catalyst deactivation did not occur after 8 h on stream. In fact, catalyst activity only slightly decreased in spite of the increasing amount of carbon deposited. A significant variation of the hydrogen yields is observed. The highest yield was obtained for a calcination temperature of 600 °C: a hydrogen yield close to those expected from thermodynamics at 700 °C is observed. At 450 and 800 °C slightly lower hydrogen yields were obtained whereas a noticeable decrease in the methane conversion was observed when the calcination temperature was increased up to 1000 °C. Fig. 1(b) shows the results obtained for the Ni-Cu-Al catalyst. The same tendency than for the Ni-Al catalyst is observed. However, the effect is less noticeable in the case of the catalyst with copper, so that a high hydrogen yield is obtained even after calcination at 1000 °C.

3.2. Catalysts characterization

3.2.1. Nickel domain size

Table 1 shows the composition of the fresh catalysts determined by ICP. Ni is the active phase for the thermal decomposition of methane. Al₂O₃ is inactive and is only present to increase the degree of dispersion of the Ni-containing phases

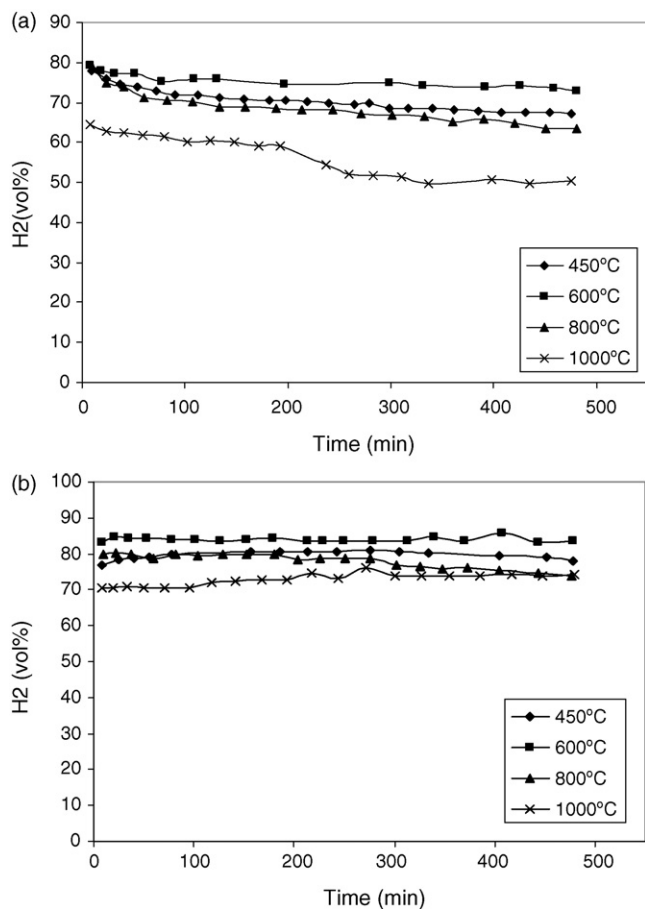


Fig. 1. Effect of the calcination temperatures on the hydrogen production. (a) Ni:Al catalysts. (b) Ni:Cu:Al catalysts.

[15,23–25]. Additionally, most of the mechanical properties exhibited by the prepared catalysts are due to the presence of this inactive phase. The catalyst composition determined by ICP is highly correlated with the nominal composition, the results obtained at higher calcination temperatures are not so accurate due to the presence of nickel aluminate that has not been completely dissolved by the digestion method previous to the analysis.

Fig. 2(a) shows the powder XRD patterns of the Ni–Al catalyst calcined at different temperatures. It reveals the presence of NiO as the only nickel-containing crystalline phase for the catalyst calcined at 450 and 600 °C. At higher calcination tem-

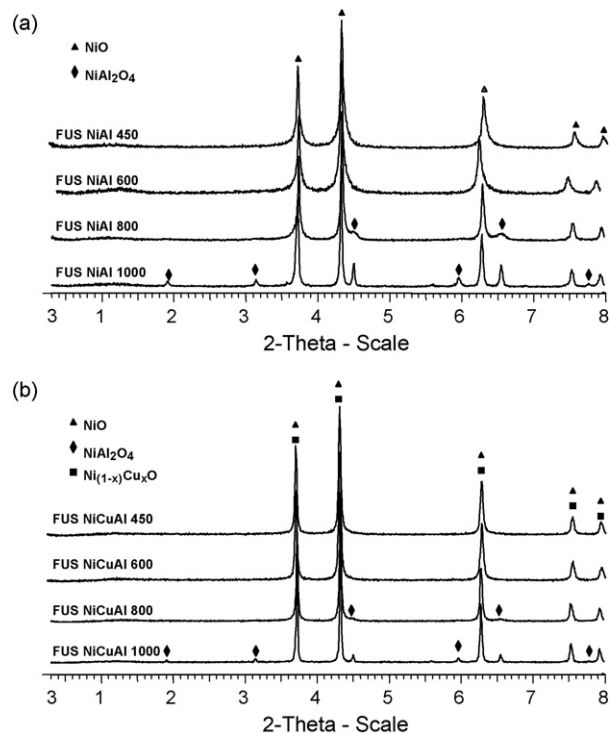


Fig. 2. Powder XRD patterns of the fresh calcined catalysts. (a) Ni:Al catalysts. (b) Ni:Cu:Al catalysts.

peratures new reflections appear due to the presence of nickel aluminate, NiAl₂O₄. Fig. 2(b) shows the XRD patterns for the Ni:Cu:Al—78:6:16. A similar trend is observed: nickel aluminate appears only at the highest calcination temperatures. It should be noted that Cu is in these samples in the form of a mixed oxide Ni_(1-x)Cu_xO, with identical structure than NiO. As a consequence, Cu oxide cannot be resolved by this technique. Alumina was only detected through the presence of some characteristic broad reflections in some samples since it is microcrystalline. The XRD results indicate that NiO interacts strongly with the inactive Al₂O₃ through the formation of the spinel phase NiAl₂O₄ at calcination temperature higher than 600 °C and that presence of Cu inhibits the formation of this phase.

Fig. 3(a) shows the powder XRD patterns of the Ni:Al catalysts calcined at different temperatures after the reduction treatment under hydrogen. In all cases, the most prominent reflections are assigned to metallic Ni, which obviously comes from hydrogen reduction of the NiO present in the calcined cat-

Table 1
Composition of the catalysts calcined at different temperatures determined by ICP

Catalyst	Calcination temperature (°C)	Molar ratio (Ni:Cu:Al; nominal)	Molar ratio (Ni:Cu:Al; determined by ICP)
Ni:Al—2:1	450	67:0:33	67.2:0:32.8
	600	67:0:33	65.2:0:34.8
	800	66:0:33	74.0:0:26.0
	1000	66:0:33	92.8:0:7.2
Ni:Cu:Al—78:6:16	450	78:6:16	78:6.7:15.3
	600	78:6:16	77.3:6.7:16
	800	78:6:16	80.3:7.7:12
	1000	78:6:16	88.5:7.8:3.7

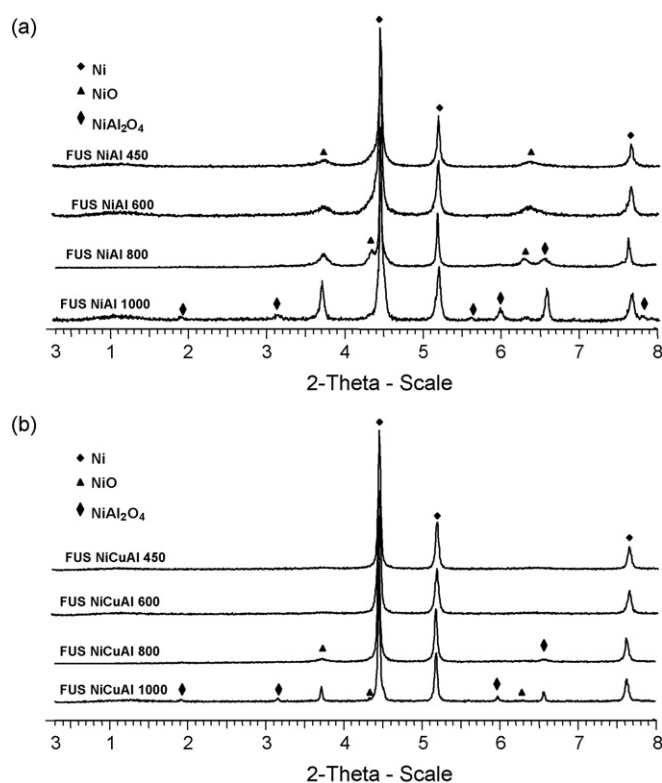


Fig. 3. Powder XRD patterns of the catalysts after the reduction pre-treatment at 550 °C. (a) Ni:Al catalysts. (b) Ni:Cu:Al catalysts.

alysts. It can be observed that NiO is not totally reduced since some peaks related to this compound persist after the reduction treatment. For the catalysts calcined at high temperatures – appear also some peaks of nickel aluminate which cannot be reduced under the conditions used. Fig. 3(b) shows the XRD patterns of the Ni-Cu-Al catalyst after reduction. In Cu-doped catalysts the presence of the spinel phase is not so evident. Apparently, Cu-doping enhances the reducibility of the catalysts, as will be shown in the below TPR study.

These results show that reducibility of the catalysts, i.e., the formation of the metallic Ni active phase, is better for those prepared at low calcination temperature. In addition, the presence of Cu improves reducibility of Ni since it prevents NiO from the formation of not reducible Ni aluminates. It has been reported [26] that Cu^{2+} ions are stabilized by a square plane coordination which differs from the octahedral one for Ni^{2+} . So, the layer structure of the Ni-Al catalysts can be partially distorted or

fragmented by copper ions. Therefore, the introduction of copper could prevent the formation of spinel or its growth during samples calcination.

Table 2 shows the crystal domain size of NiO in the calcined catalysts and Ni in the reduced catalysts. As expected NiO domain size is highly dependent on the calcination temperature: at 450 and 600 °C similar domain sizes are obtained, while at 800 and 1000 °C the domain size increases due to thermal sintering. However, after the reduction step, the domain sizes of Ni are similar for all the calcination temperatures tested. Presence of Cu increases the domain sizes of NiO in Ni-Cu-Al catalysts. A plausible explanation is that Cu-doping reduces the melting point of Ni species enhancing thermal sintering. Again in this case, the domain size of Ni formed after reduction is similar for all the calcination temperatures and all of them are higher than for the Ni-Al catalysts.

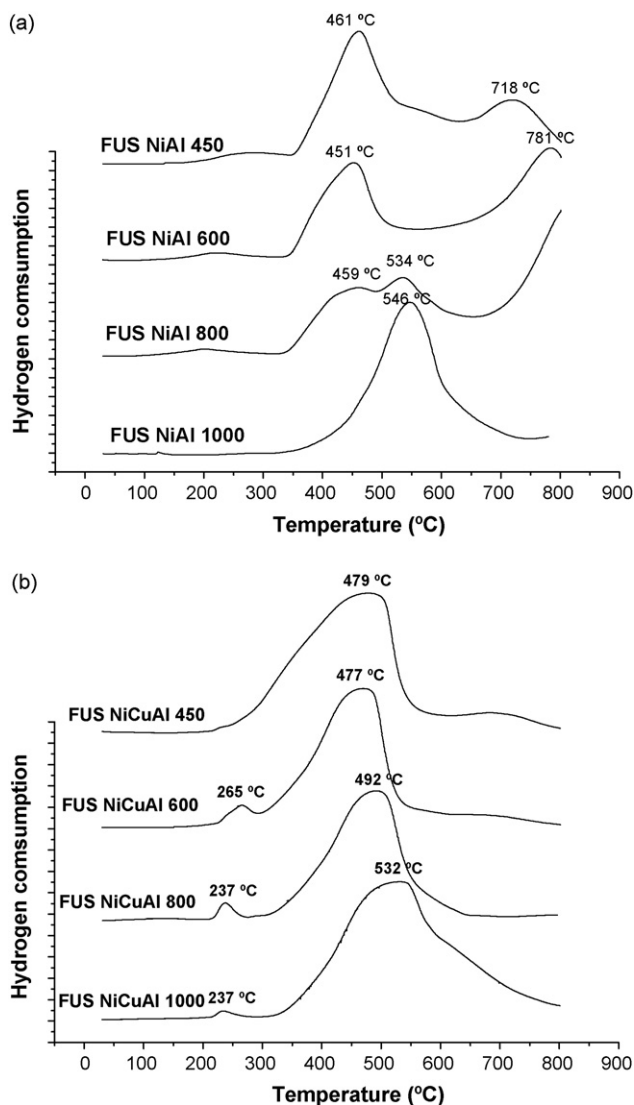
3.2.2. Nickel reduction temperature

As Ni is the active phase in the TCD catalyst, it is important to determine the temperature of reduction of the different Ni compounds present in the calcined catalysts. The reducibility of the oxidic species of Ni involved in the catalysts can be studied in depth by TPR. Fig. 4(a) shows the TPR curve for the Ni:Al catalyst calcined at 450 °C. Two reduction zones are observed. The first one at 450–460 °C corresponds to the reduction of NiO and the second one at 718 °C corresponds to the reduction of the NiAl_2O_4 phase. The reduced species have been assigned in basis on the XRD study although the spinel phase was not found in the sample calcined at this low temperature. Aluminium oxides do not reduce below 900 °C. The catalyst calcined at 600 °C has the same reduction regions, the first one corresponds to the reduction of NiO, but in this case, the reduction peak corresponding to NiAl_2O_4 displaces to higher temperatures (781 °C). By increasing the calcination temperature, the TPR profiles of sample calcined at 800 °C reveal the appearance of a second reduction peak of NiO centred around 540 °C coexisting with the first peak at 450 °C. These two reduction peaks of two NiO species was reported earlier by Li and Chen [27] in TPR profiles of catalysts prepared by co-precipitation with high Ni loadings and calcined at 450 °C. Authors suggest that this could be due to an increase in the nucleation rate of large NiO crystallites. At the same time the reduction peak of the NiAl_2O_4 phase is shifted to higher temperatures almost out of the range of the temperature scanned. This peak shifting is more clearly evidenced in the TPR profile of sample Ni-Al calcined at

Table 2

NiO domain size in fresh catalysts and Ni domain size in pre-reduced catalysts determined by XRD

Catalyst	Calcination temperature (°C)	NiO domain size (nm; fresh catalyst)	Ni domain size (nm; reduced catalyst)
Ni:Al–2:1	450	14.8 ± 0.2	21.5 ± 0.6
	600	14.0 ± 0.3	17.9 ± 0.5
	800	24.0 ± 0.6	32.6 ± 1.7
	1000	51.3 ± 2.0	23.9 ± 1.0
Ni:Cu:Al—78:6:16	450	41.6 ± 0.9	40.7 ± 0.9
	600	40.4 ± 0.8	30.4 ± 0.6
	800	60.0 ± 1.6	42.3 ± 1.2
	1000	124.8 ± 6.0	48.0 ± 1.7



nickel is in the form of NiO, that could be reduced at the operating temperatures. Metallic Ni, the active phase in the TCD of methane, is obtaining easier, leading to a higher hydrogen production.

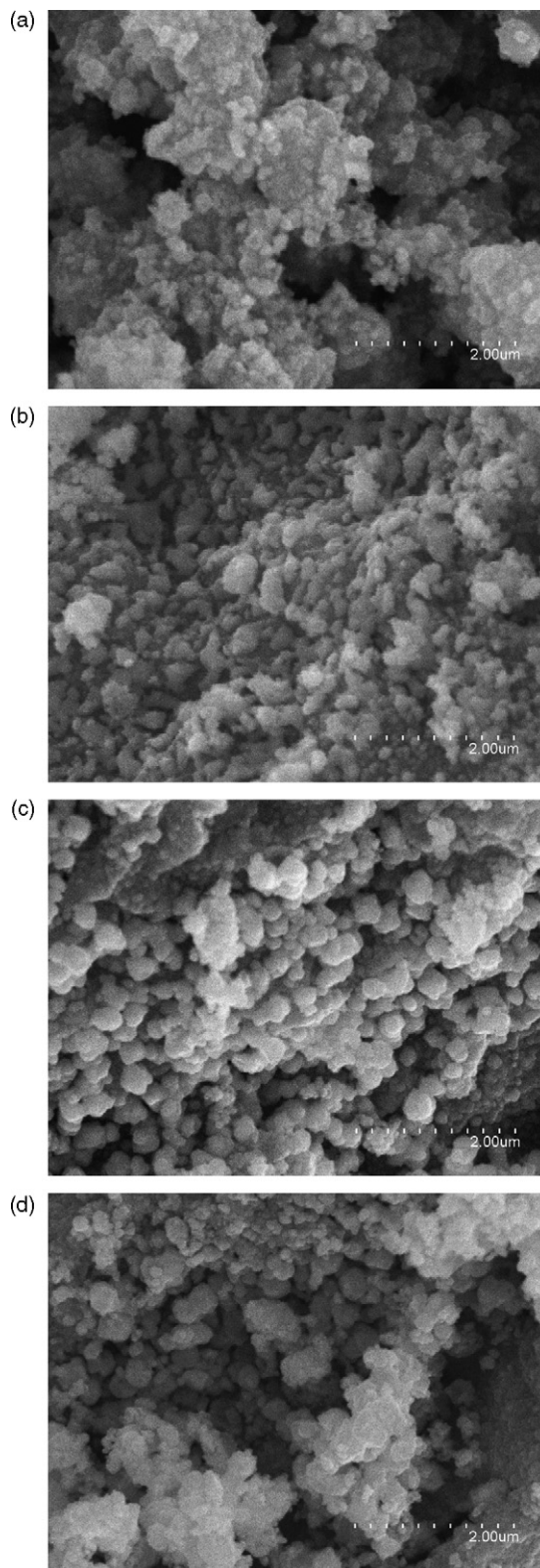


Fig. 5. SEM micrographs of fresh NiAl catalysts after reduction pre-treatment. Calcination temperature: (a) 450 °C. (b) 600 °C. (c) 800 °C. (d) 1000 °C.

Fig. 4. TPR profiles of the catalysts prepared at different calcination temperature. (a) Ni:Al catalysts. (b) Ni:Cu:Al catalysts.

1000 °C in which the reduction peaks of NiO at 450 °C and the NiAl₂O₄ at 781 °C vanish and only a prominent peak at 546 °C is apparent. Consequently, TPR profiles of samples Ni-Al evidence the formation of NiO and NiAl₂O₄ with decreasing reducibility as the calcination temperature increases.

TPR profiles of the copper-doped catalyst Ni-Cu-Al (Fig. 4(b)) show a first small reduction peak at around 237–265 °C assigned to the reduction Cu^{II} → Cu⁰ in CuO suggesting that in the doped catalyst there is a low concentration of CuO not detected by XRD. Similarly to non-doped catalysts, a second reduction peak 479–532 °C is associated with the reduction of copper-nickel mixed oxides. By increasing the calcination temperatures the reduction peaks shift toward higher temperatures indicating the formation of less-reducible NiO species. The peak corresponding to the reduction of nickel aluminate do not appear in the TPR profile scanned up to 800 °C suggesting that copper promotes the formation of less-reducible copper-nickel aluminates, although in lower quantity, as we have seen in the XRD study. In the Ni-Cu catalysts almost all the

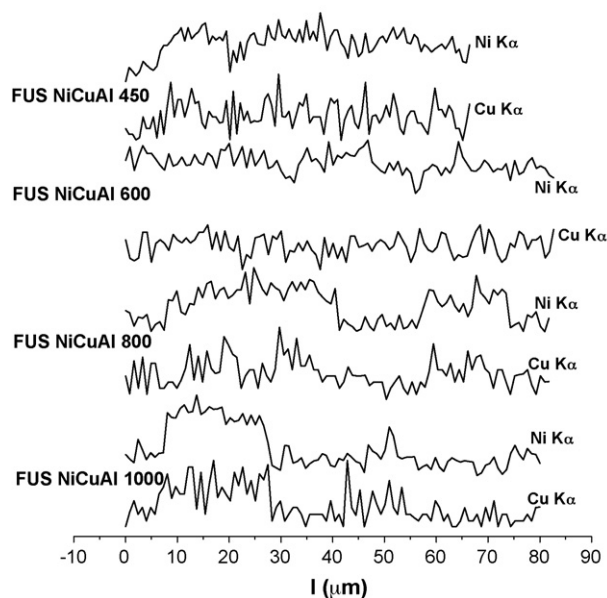
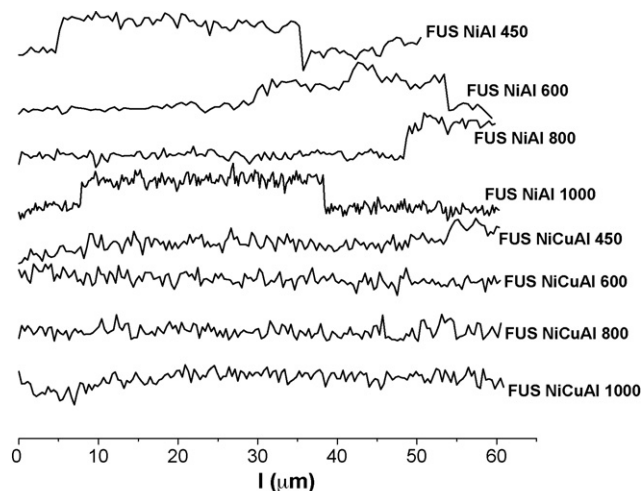


Fig. 6. SEM-EDX line profiles in the catalyst prepared at different calcination temperatures. (a) Ni K α line profiles in calcined fresh samples. (b) Ni K α and Cu K α in NiCuAl catalysts after reduction pre-treatment at 550 °C.

3.2.3. Nickel dispersion

The morphological appearance of the fresh catalysts calcined at different temperatures after the reduction pre-treatment with H₂ is displayed in Fig. 5. All samples appear as large agglomerates of particles whose size increases with the calcination temperature. The real composition of these agglomerates in sample Ni-Al was clearly shown in a previous paper [21] using higher resolution in a TEM study of the Ni-Al 450 revealing these agglomerates are really made of single particles with different sizes always below 50 nm.

The degree of Ni dispersion in the fresh catalysts is shown in Fig. 6(a). The respective SEM-EDX line profiles of Ni K α reveal that the Ni dispersion in the calcined fresh catalysts becomes highly correlated with copper in the copper-doped catalysts. In these catalysts Cu increases the degree of Ni dispersion, in clear agreement with the XRD study. Additionally, line profiles of Ni

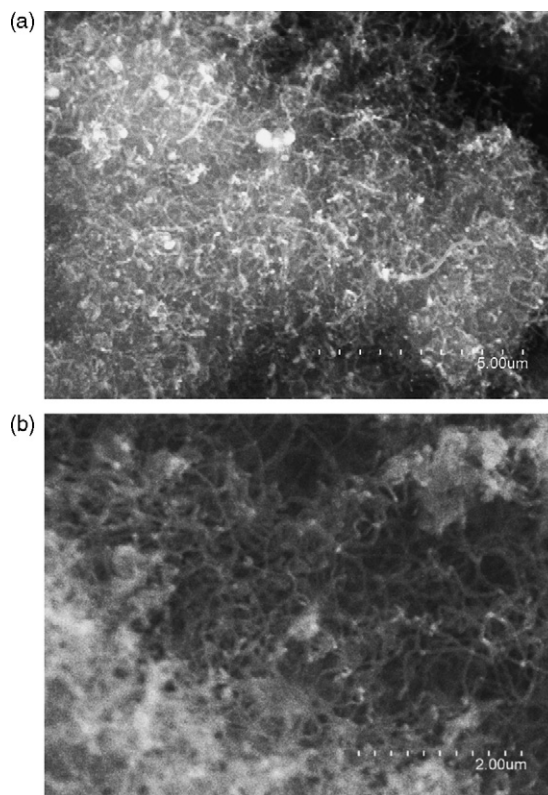


Fig. 7. SEM micrographs of carbons obtained in the thermal decomposition of methane. (a) NiAl 800 catalyst; (b) NiCuAl 600 catalyst.

K α and Cu K α in Ni-Cu-Al of reduced catalysts after H₂ pre-treatment (Fig. 6(b)) reveal that Cu is chemically associated to Ni in the reduced catalysts through the probably formation of an alloy Ni_(1-x)Cu_x not revealed by XRD.

3.3. Carbon characterization

The structural properties of the deposited carbon have been studied by XRD. Their respective powder XRD patterns, shown in Fig. 7, reveal two prominent reflections at 44.34 and 51.76° assigned to metal Ni planes (1 1 1) and (2 0 0) and a third one at 26.24 assigned to graphite basal planes (0 0 2). The graphene distances, $c/2$, of the deposited carbon (Table 3) go from 0.336 nm in sample Ni-Cu-Al 800–0.341 nm in sample NiAl 600. For

Table 3
Quantitative data from the XRD study of the carbon obtained with the different catalysts

Catalyst	Calcination temperature (°C)	Graphite	
		$c/2$ (nm)	L_c (nm)
Ni:Al—2:1	450	0.338	8.3 ± 0.1
	600	0.341	7.6 ± 0.1
	800	0.336	9.5 ± 0.2
	1000	0.337	9.8 ± 0.2
Ni:Cu:Al—78:6:16	450	0.339	10.1 ± 0.2
	600	0.339	11.7 ± 0.2
	800	0.336	13.0 ± 0.2
	1000	0.337	11.5 ± 0.2

comparison a perfect graphite has an interplanar distance of basal planes of 0.3354 nm while interplanar distances as high as 0.3440 nm have been measured in highly disordered turbostratic carbons, in spite of the apparent inherent inaccuracies introduced in dealing with very small domain sizes [29]. Additionally, the domain sizes, L_c , of the carbon deposited in perpendicular direction to the graphene planes vary from 7.6 to 13.0 nm. Low values of L_c are highly correlated with high values of the parameter c , as one would expect for a turbostratic carbon. On the other hand, large values of L_c are correlated with small values of the parameter c corresponding to almost perfect graphite. In this sense, it may be concluded that the presence of copper in the catalysts leads to the formation of a high-order deposited carbon structurally close to a perfect graphite while Ni-Al catalysts, lead to the formation of a low ordered deposited carbon, specially in Ni-Al the sample calcined at 600 °C.

SEM micrographs of catalysts NiAl 800 and NiCuAl 600 after the reaction of methane decomposition at 700 °C are shown in Fig. 8. The presence of filamentous carbon a few nanometers in diameter and some micrometers long are clearly evidenced in the two studied samples. The fiber diameter obtained from the SEM micrographs gives an average diameter of 50–60 nm for the fibers obtained with the catalyst Ni-Al 800 while for the fibers obtained with the Ni-Cu-Al 600 catalyst the average diameter is 70–80 nm. In both cases, this size is a bit higher than that obtained with the XRD after the reduction pre-treatment, probably due to additional thermal sintering undergone by the nickel particles in operation at 700 °C during the TCD of methane. These results agree with the mechanisms proposed in the literature for filament growing which suggest that the diameter of carbon fibres must be approximately equal to the Ni particle size [28]. So, one would expect from data shown in Table 2 obtaining the thinnest carbon fibres with NiAl catalysts, in complete agreement with the experimental results.

Additional information on the graphene orientation in the deposited carbon can be gained from high resolution micro-

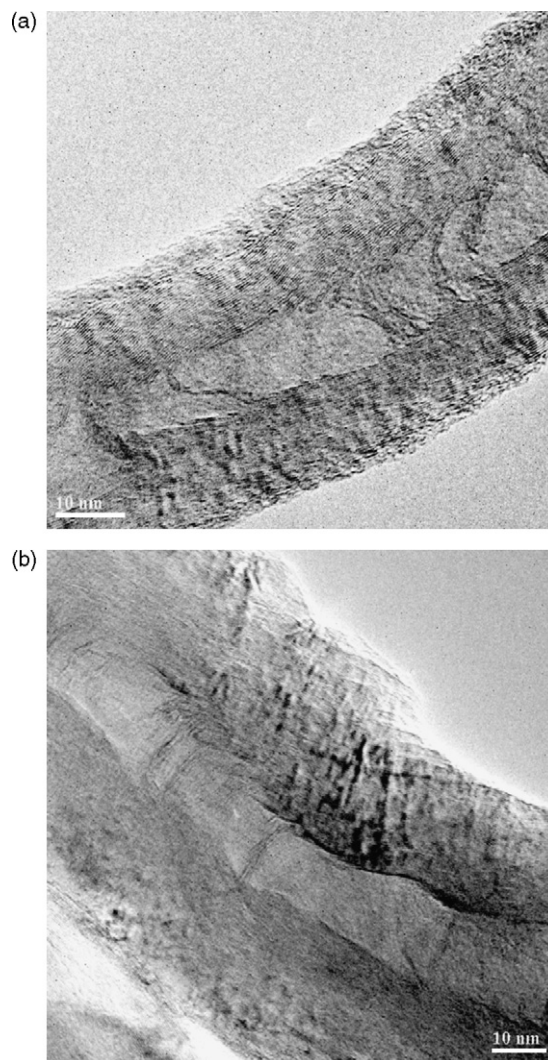


Fig. 9. TEM micrographs of carbons obtained. (a) NiAl 450. (b) NiCuAl 450.

graphs obtained in TEM as shown in Fig. 9. The graphene layers in the deposited carbon obtained from TCD of methane for both Ni-Al (Fig. 9(a)) and Ni-Cu-Al catalysts (Fig. 9(b)) form an angle of around 14° with the fibre axis. Within a fibre, the graphenes reach the fibre surface leaving a rough surface. Other graphenes extend up inside the fibre as a bundle of very thin fibres like steps in a staircase.

4. Conclusions

It can be concluded that presence of copper in the catalysts prepared by fusing the nitric salts and calcined at different temperatures has a strong influence on the degree of dispersion of Ni in the catalysts. In addition, it inhibits the formation of nickel aluminate facilitating the reduction of NiO under hydrogen in the subsequent catalyst reduction step. The calcination temperature has a strong influence on the NiO domain size in the calcined catalysts, so that, the highest the calcination temperature the highest the domain sizes.

Whatever the calcination temperature, all the catalysts show a high and almost constant hydrogen evolution without cata-

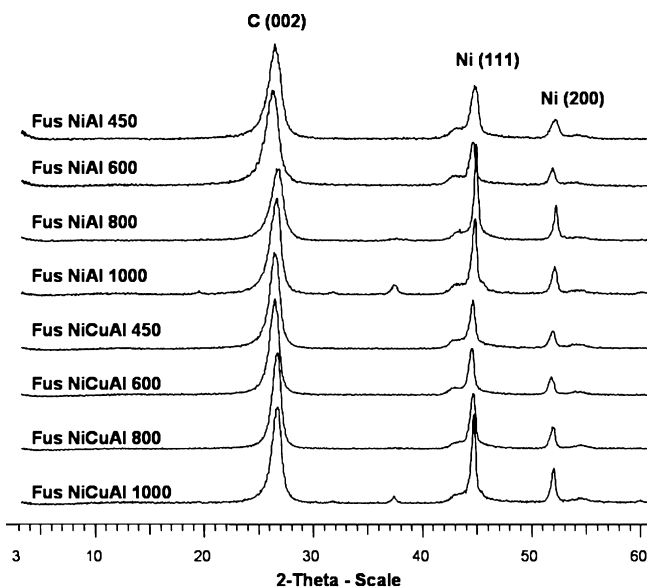


Fig. 8. Powder XRD patterns of carbons obtained with the different catalysts.

lyst deactivation after 8 h on stream. The presence of copper enhances the hydrogen production and the higher hydrogen yields were obtained using catalysts calcined at 600 °C. This behaviour is attributed to the fact that at 450 °C the conversion of the nitric salts into oxides is not complete, while at temperatures higher than 600 °C there is an increment in the metal crystal size. Consistently, the efficiency for methane decomposition decreases.

All catalysts tested promote the formation of very long filaments of carbon a few tens of nanometers in diameter and some micrometers long. The structural properties of these carbon filaments highly depend on the presence of Cu:Ni-Cu-Al catalysts promote the formation of a well-ordered graphitic carbon while Ni-Al catalysts enhance the formation of a rather turbostratic carbon.

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