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Use of Nb_2O_5 as nickel passivating agent: characterisation of the $Ni/Nb_2O_5/SiO_2$ system

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Abstract

Niobia-modified silica was used as support for nickel-based catalysts. Catalysts with different nickel loading were prepared by successive incipient-wetness impregnation of toluenic nickel octanoate solutions. The samples were characterised after both calcination and reduction by TEM-EDX techniques and tested in the ethane hydrogenolysis. Their catalytic behaviour was compared to that of related silica-supported nickel catalysts. A high suppression of hydrogenolysis activity (93–99%) was determined for the niobia-modified silica-supported nickel catalysts which do not show nickel particles on silica.

Keywords: Nb_2O_5; Nickel-based catalysts; Incipient-wetness method

1. Introduction

Nickel can be considered a pollutant of fluid catalytic cracking (FCC) catalysts, since it promotes the formation of dehydrogenated products. If oil with a high nickel content is used, a large amount of hydrogen is formed and the process can be affected due to limitations in the volume of the compressor of the unit. Niobia has been proposed as a passivating agent of nickel [1]. Nickel niobate would be present when Ni/Nb_2O_5 is treated at high temperature in an oxidising atmosphere [2]. Under reducing atmosphere, a strong metal–support interaction would exist; consequently, a decrease of nickel catalytic activity is to be expected [3,4].

In early works, the Nb_2O_5/SiO_2 system and its interaction with nickel has been studied as has the behaviour of $Ni/Nb_2O_5/SiO_2$ in the cyclohexane reactions, hydrogenolysis and dehydrogenation [5,6]. Significant differences were found in the catalytic behaviour as a function of the preparation method of the sample [5]. The aim of this work was to contribute towards a better understanding of these systems. The nickel–niobia interaction in the catalyst seems to be crucial in determining the nickel reduction properties and consequently its activity in hydrogenolysis and dehydrogenation reactions. According to previous works, different Nb_2O_5/SiO_2 samples prepared by grafting or impregnation of niobium compounds on silica were used as supports [5–7]. $Ni/Nb_2O_5/SiO_2$ samples were prepared and characterised by transmission electron microscopy (TEM), energy dispersive X-ray (EDX) analysis, and electron diffraction (ED).

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Table 1
Ni(*a*)/SiO_2 and Ni(*a*)/Nb_2O_5(b)/SiO_2 catalysts, a = % w/w Ni, b = % w/w Nb_2O_5

Catalyst	Niobium precursor	Number of nickel impregnations
Ni(0.43)/SiO_2	–	1
Ni(0.87)/SiO_2	–	2
Ni(1.30)/SiO_2	–	3
Ni(0.36)/Nb_2O_5(0.5)/SiO_2	$Nb(OC_2H_5)_5$[a]	1
Ni(0.77)/Nb_2O_5(0.5)/SiO_2	$Nb(OC_2H_5)_5$[a]	2
Ni(0.5)/Nb_2O_5(13)/SiO_2	$NH_4[Nb(C_2O_4)_3]$[b]	1
Ni(0.85)/Nb_2O_5(13)/SiO_2	$NH_4[Nb(C_2O_4)_3]$[b]	2
Ni(1.14)/Nb_2O_5(13)/SiO_2	$NH_4[Nb(C_2O_4)_3]$[b]	3

[a] Nb_2O_5(0.5)/SiO_2 preparation according to [7].

[b] Nb_2O_5(13)/SiO_2 preparation according to [1].

Table 2
Catalytic activity in the ethane hydrogenolysis of Ni/SiO_2 and Ni/Nb_2O_5/SiO_2 samples (mean size of nickel particles on Ni/SiO_2 catalysts (d) was determined by TEM)

Catalyst	d (nm)	Ni (m^2/g_{cat}) ($\times 10^2$)	Activity (mmol ethane converted/g Ni min)
Ni(0.43)/SiO_2	5.4	53.6[a]	17.73
Ni(0.87)/SiO_2	7.9	74.2[a]	12.10
Ni(1.30)/SiO_2	9.8	89.4[a]	8.67
Ni(0.36)/Nb_2O_5(0.5)/SiO_2		2.8[b]	1.06
Ni(0.77)/Nb_2O_5(0.5)/SiO_2		4.5[b]	0.80
Ni(0.5)/Nb_2O_5(13)/SiO_2		0.9[b]	0.25
Ni(0.85)/Nb_2O_5(13)/SiO_2		3.2[b]	0.51
Ni(1.14)/Nb_2O_5(13)/SiO_2		31.0[b]	3.71

[a] Calculated from particle size determined by TEM assuming semi-hemispherical shape.

[b] Calculated from activity value assuming a mean of 0.14 mmol ethane converted/m^2 Ni min.

Samples were tested in the ethane hydrogenolysis and the results related to catalyst characteristics.

2. Experimental

Two series of catalysts were prepared Ni(*a*)/Nb_2O_5(0.5)/SiO_2 and Ni(*a*)/Nb_2O_5(13)/SiO_2 (a = % w/w Ni). Two different supports were used, Nb_2O_5(0.5)/SiO_2, and Nb_2O_5(13)/SiO_2, with 0.5 and 13% w/w Nb_2O_5 on silica, respectively. Nb_2O_5(0.5)/SiO_2 was prepared by the method proposed by Asakura and Iwasawa [7] using $Nb(OC_2H_5)_5$ in hexane solution as precursor. An aqueous solution of $NH_4[Nb(C_2O_4)_3]$

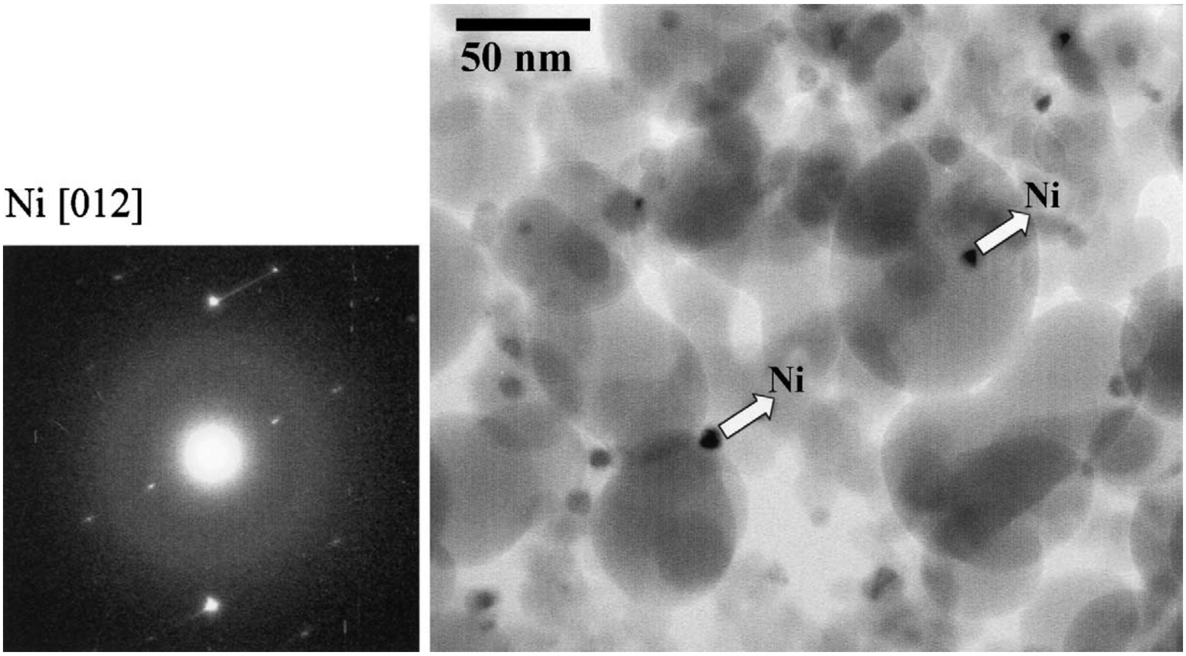

Fig. 1. Transmission electron micrograph of Ni(0.87)/SiO_2 after reduction. The SAED pattern corresponds to an individual Ni crystallite.

was used as niobium precursor for the preparation of Nb_2O_5(13)/SiO_2 [1]. The sample was dried at 273 K, and calcined overnight at 773 K. The procedure was repeated to obtain the final composition.

Nickel was impregnated by the incipient-wetness method from a solution of nickel octanoate in toluene [8]. Samples were treated under vacuum at 373 K for 2 h, dried at 393 K for 12 h and calcined at 873 K for 3 h. Successive impregnations were carried out to yield catalysts with a nickel content higher than 0.5% w/w, after each impregnation samples were calcined at 1073 K by 2 h. For purposes of comparison, Ni/SiO_2 catalysts were prepared similarly.

Catalysts were reduced in a 10% v/v H_2/N_2 mixture with a flow rate of 60 ml/min using a heating rate of 10 K/min up to 773 K for 2 h. Table 1 shows catalysts prepared and the main features of their preparation. After reduction, the temperature of the reactor was decreased to 613 K and the reaction mixture, 20 ml/min of 10% v/v ethane in hydrogen, introduced. The analysis of products were carried out on line after 2 and 18 min on stream, using a Shimadzu 17 A chromatograph equipped with a chrompack KCl alumina column and an FID detector. In all cases, only methane was observed as product. The catalysts were characterised by TEM combined with EDX using a Philips CM-30 electron microscope working at 300 kV and equipped with a Link analytic system. The X-rays emitted upon electron irradiation were acquired in the range 0–20 keV with a ca. 8–10 nm probe. ED was carried out in selected-area mode (SAED). Particle size determination was calculated over 200 particles from bright-field images taken at different magnifications.

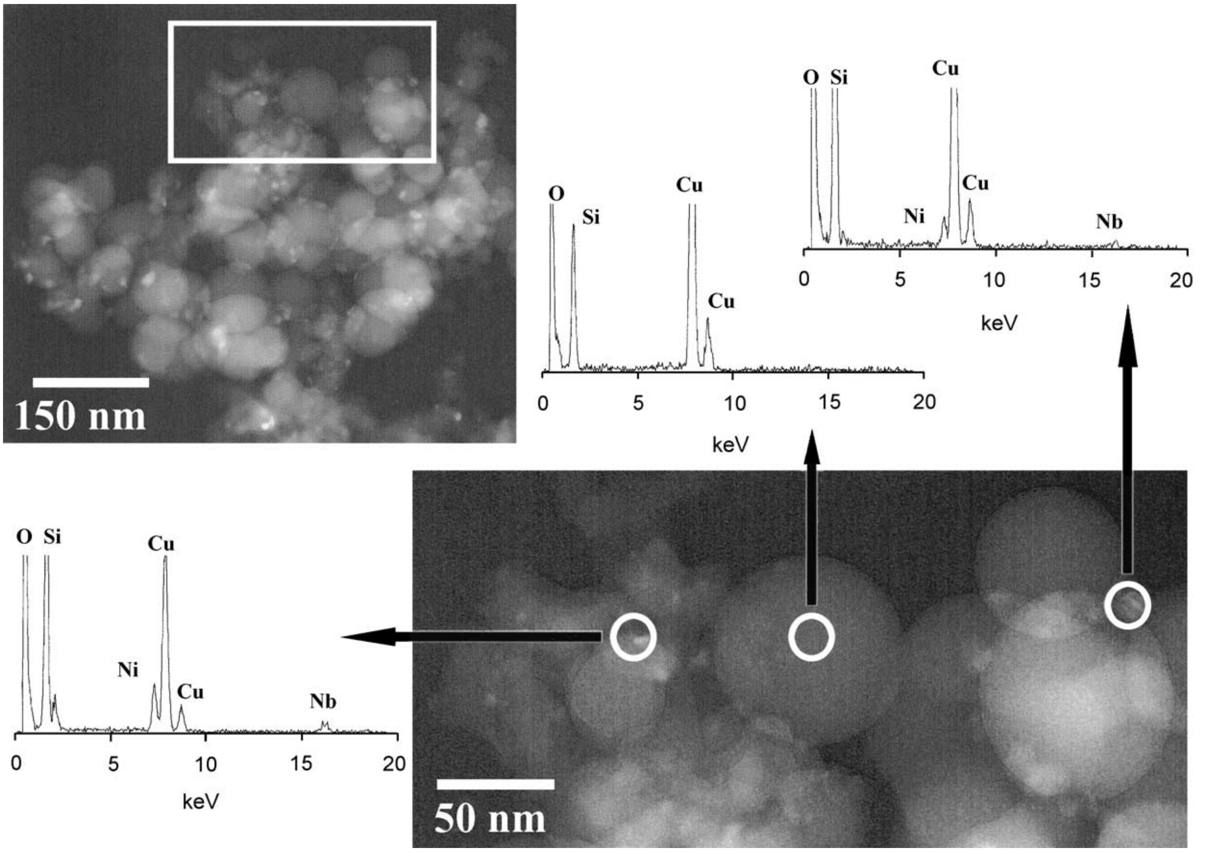

Fig. 2. Transmission electron micrograph of Ni(0.77)/Nb_2O_5(0.5)/SiO_2 after calcination and EDX analysis of marked areas. The Cu signals in EDX profiles are due to the grid used for TEM sample preparation.

3. Results and discussion

Results of ethane hydrogenolysis at 743 K and atmospheric pressure appear in Table 2. Ni/SiO_2 samples showed higher activity values than $Ni/Nb_2O_5/SiO_2$ samples. In an attempt to rationalise these results, the characterisation of catalysts was carried out. TEM studies of reduced silica-supported nickel catalysts showed the presence of homogeneously distributed nickel crystallites. As an example, Fig. 1 shows a representative transmission electron micrograph of $Ni(0.87)/SiO_2$ and an SAED pattern which shows single spots corresponding to metallic nickel. The mean particle size of nickel for silica-supported catalysts increased with the nickel content of catalysts (see Table 2), we recall that catalysts with a nickel content higher than 0.5% w/w were prepared by successive impregnations and they were calcined at 1073 K before each new nickel impregnation. The mean area of nickel for Ni/SiO_2 catalysts was calculated from TEM measurements and assuming a semi-hemispherical model and a density equal to that of metallic nickel ($8.9\ g\ cm^{-3}$) (Table 2).

For Ni/SiO_2 samples, the activity per gram of catalyst increased with the nickel content according to the increase in nickel area (see Table 2). On the other hand, the values of activity per square meter of nickel for Ni/SiO_2 catalysts prepared in this work were in a narrow interval around 0.14 mmol ethane converted/m^2 Ni min. If this mean value is assumed, it is possible to calculate the nickel area related to the activity shown by $Ni/Nb_2O_5/SiO_2$ samples. In Table 2, the calculated nickel areas are also compiled, which represent the active surface nickel of $Ni/Nb_2O_5/SiO_2$ catalysts. A comparison of these areas with those of Ni/SiO_2 catalysts with a similar nickel content indicates a high suppression of the number of active surface nickel centres for $Ni/Nb_2O_5/SiO_2$ systems;

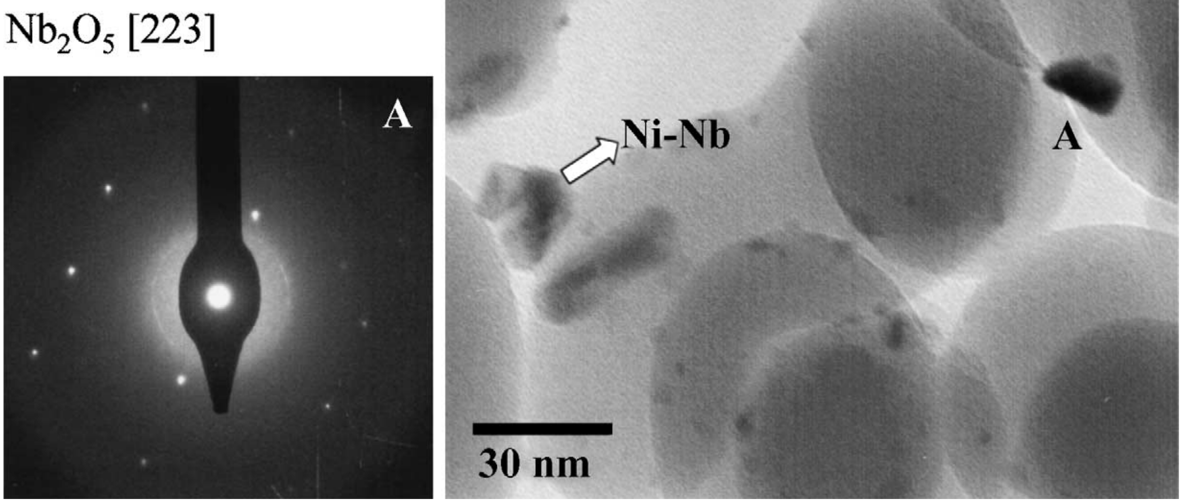

Fig. 3. Bright-field image of $Ni(0.77)/Nb_2O_5(0.5)/SiO_2$ after reduction and SAED pattern of a Nb_2O_5 crystal (marked by A).

this diminution is higher for Ni/Nb_2O_5(13)/SiO_2 (96–99%) than for Ni/Nb_2O_5(0.5)/SiO_2 (93–94%) catalysts at least till 0.85% w/w Ni content.

After calcination and reduction steps, Ni/Nb_2O_5/SiO_2 catalysts were characterised by TEM, and the presence of different phases was determined, depending on the support and metal loading.

After calcination, Ni(0.77)/Nb_2O_5(0.5)/SiO_2 showed a homogeneous distribution of particles of ca. 10 nm (see Fig. 2). The EDX analysis of some of them indicated the simultaneous presence of nickel and niobium. However, the EDX analysis of some particles was inconclusive, since they showed Nb signals at the detection limit when Ni was clearly visible (Fig. 2). Fig. 3 shows a TEM micrograph of Ni(0.77)/Nb_2O_5(0.5)/SiO_2 after reduction. Some particles were identified as Nb_2O_5 by SAED, in other particles the simultaneous presence of nickel and niobium was clearly determined by EDX analysis. However, as in the case of calcined catalyst, EDX analysis of some particles do not show clearly the simultaneous presence of nickel and niobium although this cannot be discarded.

The analysis of Ni(0.85)/Nb_2O_5(13)/SiO_2 sample after calcination shows the presence of particles of ca. 24 nm. These particles are in fact aggregates constituted by multiple crystallites which have growth without a preferential orientation, as determined by the lattice fringe imaging mode. In all cases, EDX analysis of these particles shows the simultaneous presence of nickel and niobium. When Ni(0.85)/Nb_2O_5(13)/SiO_2 was reduced, the presence of Nb_2O_5 particles was determined by SAED (see Fig. 4). EDX of particles which contained nickel always evidenced the simultaneous presence of niobium. Fig. 5 shows a representative TEM micrograph

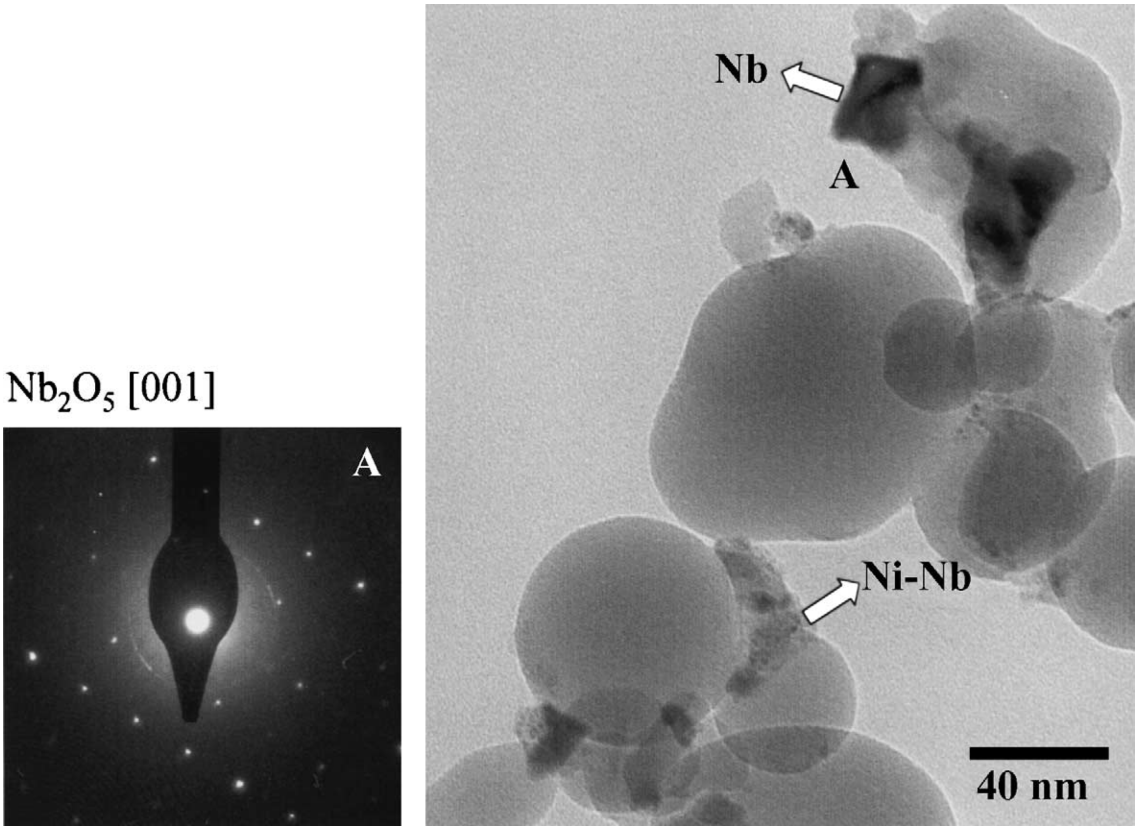

Fig. 4. Transmission electron micrograph of Ni(0.85)/Nb_2O_5(13)/SiO_2 after reduction. The SAED pattern corresponds to a Nb_2O_5 crystal (marked by A in the bright-field image).

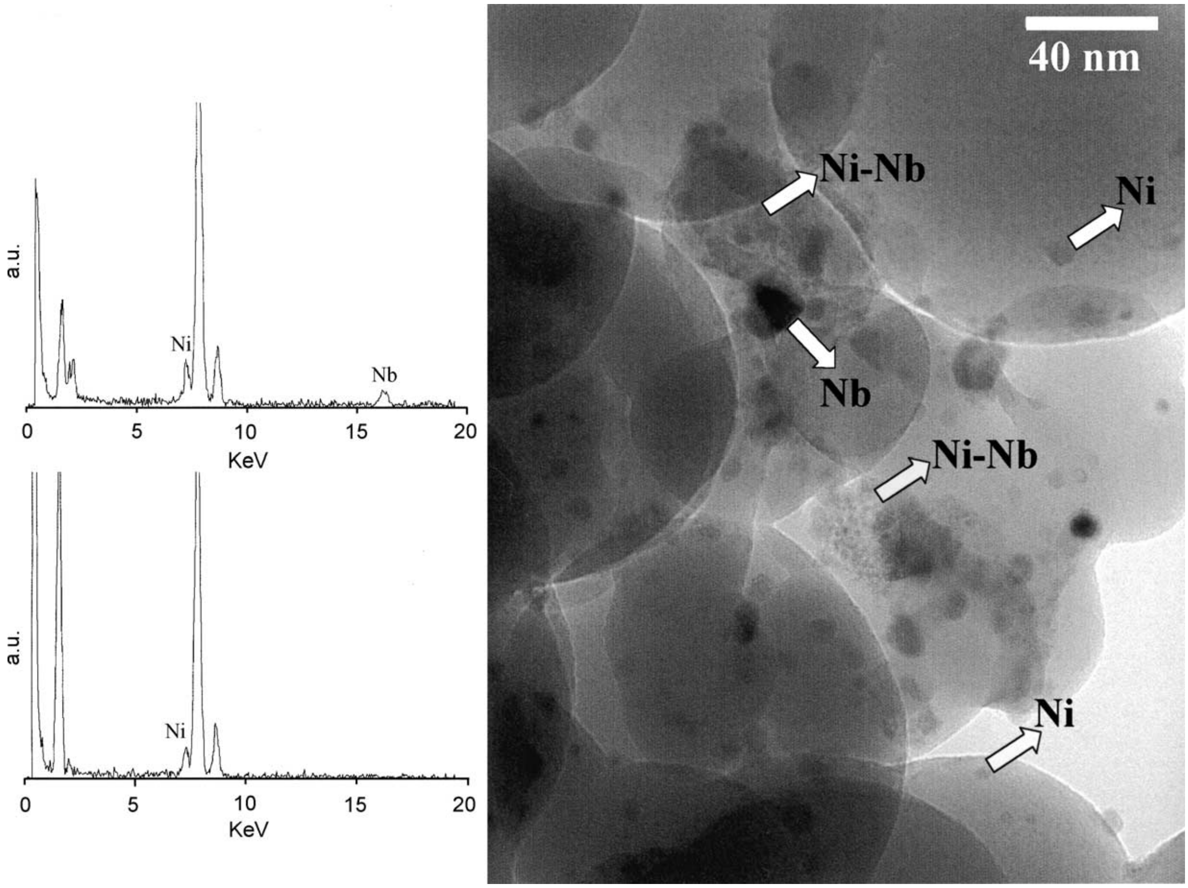

Fig. 5. Transmission electron micrograph of Ni(1.14)/Nb_2O_5(13)/SiO_2 after reduction and EDX analysis of different areas.

of reduced Ni(1.14)/Nb_2O_5(13)/SiO_2 sample, where abundant particles of ca. 6–7 nm can be seen. The EDX analysis of these particles shows the presence of nickel but in none of the cases is niobium present. In addition to these particles, larger aggregates containing niobium and others simultaneously containing niobium and nickel were identified. Among all Ni/Nb_2O_5/SiO_2 catalysts studied, Ni(1.14)/Nb_2O_5(13)/SiO_2 showed the higher number of active nickel centres in ethane hydrogenolysis. The active surface nickel calculated for Ni(1.14)/Nb_2O_5(13)/SiO_2 was a 35% of the corresponding Ni(1.30)/SiO_2 catalyst (see Table 2). According to the characterisation of catalysts discussed above, this is the only Ni/Nb_2O_5/SiO_2 sample in which the presence of silica-supported nickel particles has been evidenced, and these particles are believed to be responsible for this particular catalytic behaviour. The number of active surface nickel centres of the remaining Ni/Nb_2O_5/SiO_2 samples was less than 7% of those of the corresponding Ni/SiO_2 catalysts. Taking into account the characterisation results exposed above, the presence of nickel–niobia interactions, which produce non-active nickel centres, may be proposed in the remainder of the Ni/Nb_2O_5/SiO_2 catalysts.

4. Conclusions

The characterisation by TEM-based techniques of nickel catalysts supported on niobia-modified silica did not reveal nickel particles on silica for contents lower than 0.85% nickel. Their catalytic activity in the ethane hydrogenolysis was less than 7% of that showed by related nickel silica-supported catalysts. The preferential interaction of nickel with Nb_2O_5 is proposed to cause a high suppression of nickel activity in the hydrogenolysis reaction. These results indicate that the hydrogenolysis of ethane is a good tool to determine the ability of niobia-containing catalysts to passivate nickel.

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