

In accordance with the project proposal and the plan of implementation, the following objectives have been solved in the phase II/2013:

O1/ Identification of parameters that affect the physicochemical properties of non-noble bimetallic nanoparticles (Cu, Ni) deposited on SBA-15 support.

A1.1. Preparation of CuNi/SBA-15 materials by MDI method.

A1.2. Preparation of CuNi/SBA-15 materials with various Cu:Ni ratios.

On the basis of previous investigations carried out in phase I/2012 on the texture of mesoporous supports of SBA-15 type (various supports were prepared at different temperatures of hydrothermal treatment to control the ratio between micropores and primary mesopores), at this stage it was prepared a SBA-15 support with optimal textural properties from the point of view of pore diameter and volume. Freshly prepared support was calcined and stored under controlled moisture up to the preparation of catalytic materials by MDI method.¹ A special attention was paid to the following influences: (i) the effect of the degree of loading with metal (1, 2, 5, 10% by mass, with weight ratio Cu:Ni = 1:1 (activity A1.1) and (ii) the effect of mass ratio M1: M2 (M1 = copper, M2 = nickel; M1: M2 = 10:0, 8:2, 5:5, 2:8 and 0:10) at a constant loading of 5% in metal (activity 1.2) on the physico-chemical and catalytic properties of bimetallic CuNi/SBA-15 system. To prepare these materials, copper and nickel nitrates were used as metal precursors. The obtained samples were dried at 25 °C for 48 h and then calcined at 500 °C (ramp of 1.5 °C/min, 6 h at the final temperature).

O2/ Preparation of CuNi/SBA-15 catalysts by conventional methods.

A2.1. Preparation of CuNi/SBA-15 catalysts by coprecipitation method.

A2.2. Preparation of CuNi/SBA-15 materials by deposition-precipitation method.

Studies on the influence of the mass ratio Cu:Ni have highlighted that the progressive introduction of copper to nickel changes the adsorption mode of cinnamaldehyde molecules, thus modifying the chemoselectivity in the hydrogenation reaction. Consequently, the highest selectivity to unsaturated alcohol was obtained at a mass ratio Cu:Ni = 4:1.² To investigate the influence of preparation method as a tool to control the chemoselectivity, a series of catalysts of Cu₄Ni/SBA-15 type was prepared by two precipitation methods which lead to a stronger interaction between the support and the active centers. For this purpose, catalysts have been prepared by: (i) co-precipitation (CP) at pH ~ 7, using *sodium carbonate* as precipitating agent (activity A2.1), and (ii) deposition-precipitation (DP) using *urea* as precipitating agent. In both cases, the precipitation of cations was done from nitrate precursors. The obtained samples were dried at 60 °C and then calcined at 500 °C (ramp of 1.5 °C·min⁻¹, 6 h at the final temperature).

O3/ Advanced characterization of CuNi/SBA-15 materials.

A3.1. Characterization of CuNi/SBA-15 materials in relation to the structural and textural properties.

A3.2. Characterization of bulk and surface chemical composition of CuNi/SBA-15 materials.

A3.3. Characterization of reducibility, the stability and the nature of the active centers of CuNi/SBA-15 materials.

After calcination, CuNi/SBA-15 materials obtained by MDI, CP and DP have been systematically analyzed by various techniques such as ICP-OES, XRD (large and small angles), nitrogen physisorption, HRTEM/EDX, TPR, XPS. Metal forms of catalysts were analyzed by *in-situ* XRD after thermo-programmed reduction, *in-situ* XPS and chemisorption of hydrogen.

Selection of the most significant results

(i) A first study had as objective the investigation of influence of the metal loading degree (1, 2, 5, 10 wt. %, with a constant mass ratio of 1 between copper and nickel).³

Table 1. Structural and textural properties of the SBA-15 support and calcined CuNi/SBA-15 materials.

Sample	XRD small angles		Physisorption of N ₂			XRD large angles	
	<i>d</i> ₁₀₀ ^a (nm)	<i>a</i> ₀ ^b (nm)	<i>S</i> _{BET} ^c (m ² ·g ⁻¹)	<i>V</i> _p ^d (cm ³ ·g ⁻¹)	<i>D</i> _p ^e (nm)	<i>D</i> _{CuO} ^f (nm)	<i>D</i> _{NiO} ^f (nm)
SBA-15	9.71	11.22	713	1.14	8.1	-	-
CuNi/SBA-15(1)	9.52	10.99	628	0.996	7.0; 8.1	-	-
CuNi/SBA-15(2)	9.42	10.87	592	0.977	7.0; 8.1	-	-
CuNi/SBA-15(5)	8.89	10.27	566	0.971	7.0; 8.1	28.5	8.3
CuNi/SBA-15(10)	8.99	10.38	515	0.949	7.0; 8.1	33.5	14.0

^a*d*₁₀₀ interplanar distance; ^b*a*₀ = 2*d*₁₀₀/√3. ^c*S*_{BET} = specific surface area by BET equation (P/P₀ = 0.1–0.25). ^d*V*_{total} = pore volume determined at P/P₀ = 0.97; ^e*D*_p = pores diameter determined by NL-DFT method for cylindrical pores; ^fcrystallite size by Scherrer equation: *d*_{hkl} = K(λ/β)cosθ.

Structural (*a*₁₀₀, *a*₀, *D*_{MO}) and textural (BET surface area, porous volume and pore diameter) properties of the calcined parent SBA-15 support and CuNi/SBA-15 materials were determined from XRD at small and large angles and nitrogen physisorption. The values of the structural and textural properties for SBA-15 (Table 1) are typical for this type of material, confirming the formation of a hexagonal 2D mesostructure with a *p6mm* symmetry.^{2,4} After impregnation with metal nitrates and calcination, it can be observed a reduction of textural parameters due to the location of nanoparticles of copper and nickel oxide (as identified by XRD at large angles) within the pores of SBA-

15. It is interesting to note that a process of mesopores blocking was observed for oxide materials from the isotherms of nitrogen physisorption, which was also confirmed by the pore size distribution.⁵ Thus, the desorption branch shows a new step at the relative pressures of 0.5-0.6, which leads to a delay in closing the hysteresis loop, associated with the presence of some new "ink-bottle" type mesopores⁵ (Fig. 1A) with average diameter of 7.0 nm besides the primary mesopores (average diameter of 8.1 nm). This additional type of mesopores is just the result of partial blocking of the primary mesopore system by oxide nanoparticles with sizes equal to the mesopores diameter, a phenomenon known as oxide particle confinement. Indeed, transmission electron microscopy

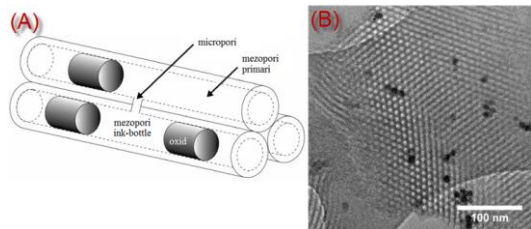


Fig. 1. Schematic representation of the formation of "ink-bottle"-type mesopores A); TEM for CuNi/SBA-15(5) (B).

confirms this confinement of oxide nanoparticles in the primary mesopores of SBA-15 support (Fig. 1B). Reducibility of metal cations has been determined by TPR, the analysis being performed on a Pulsar ChemBet TPR/TPD (Quantachrome) apparatus, purchased in phase I/2012 of the project. As depicted in Fig. 2, a typical TPR profile shows two maxima of reduction. For example, in the case of CuNi/SBA-15 sample (1:1, 5%) the first maximum temperature is identified at 270 °C, and the second at 290 °C. According to the literature, bulk CuO and NiO are reduced at temperatures above 300°C⁶ and 400 °C⁷, respectively. Under these circumstances, it is obvious that the reducibility of the two oxides deposited on SBA-15 is improved, especially of NiO, this effect being correlated with a good dispersion of oxide particles. Also, these reducibilities indicate that copper and nickel atoms are located in the same particle and in a strong interaction. In addition, there are two very small peaks at temperatures above 400 °C, which are assigned to a small fraction of bulk oxides formed on the external surface of the support grains.

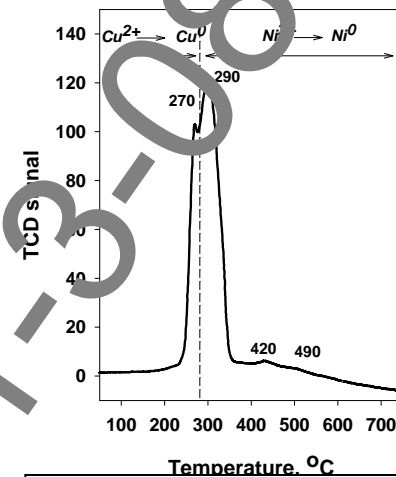


Fig. 2 TPR profile for CuNi/SBA-15(10).

(ii) The second study was focused on the effect of the molar ratio $M_1:M_2$ (M_1 = copper, M_2 = nickel; $M_1: M_2 = 10:0, 8:2, 5:5, 2:8$ and $0:10$) on the structural, textural and reducible properties, as well as on the catalytic performance in hydrogenation of cinnamaldehyde.²

Table 2. Structural and textural properties of SBA-15 support and calcined CuNi/ SBA-15 materials.

Sample	ICP Cu: Ni (Cu/M ^a)	XRD small angles		N ₂ physisorption					XRD high angles	
		d_{100}^b (nm)	a_0^c (nm)	S_{BET}^d (m ² g ⁻¹)	S_{micro}^e (m ² g ⁻¹)	V_{total}^f (cm ³ g ⁻¹)	V_{micro}^g (cm ³ g ⁻¹)	D_p^h (nm)	D_{NiO}^i (nm)	D_{CuO}^i (nm)
SBA-15	-	9.1	10.5	805	183	1.12	0.082	8.4	-	-
Ni/SBA-15	0: 5.6 (0)	8.3	9	613	104	0.91	0.044	7.4; 8.2	9.2	-
Cu ₁ Ni ₄ /SBA-15	1.2: 4.5 (0.20)	8.8	10.2	653	110	0.94	0.047	7.4; 8.2	8.7	-
Cu ₁ Ni ₁ /SBA-15	2.5: 3.0 (0.44)	9.0	10.4	672	129	1.01	0.057	7.4; 8.2	8.1	29.6
Cu ₄ Ni ₁ /SBA-15	5.1: 1.1 (0.81)	9.1	10.5	722	145	1.09	0.066	8.2	14.5	29.5
Cu/SBA-15	6.2: 0 (1)	9.1	10.5	717	142	1.06	0.063	8.2	-	31.5

^aM = Cu+Ni; ^b d_{100} interplanar distance; ^c $a_0 = 2\pi/d_{100}/\sqrt{3}$; ^d S_{BET} = specific surface area by BET equation ($P/P_0 = 0.1-0.25$). ^e S_{micro} = micropores surface by t-plot method; ^f V_{total} = pores volume determined at $P/P_0 = 0.97$; ^g V_{micro} = micropores volume by t-plot method; ^h D_p = pores diameter by NL-DFT method for cylindrical pores; ⁱcrystallite size by Scherrer equation: $d_{hkl} = K(\lambda/\beta)\cos\theta$.

On the basis of the first study, it was established that a loading degree of 5% represents an optimal both in terms of physico-chemical properties and catalytic performances. The calcined samples have been systematically characterized for their physico-chemical properties by the characterization techniques listed above. Because the actual catalysts contain nickel and copper in zero-valence state (M^0), not as cations, the investigations have been also directed on the reduced samples (the methods are listed above). The results of chemical analysis, nitrogen physisorption and XRD (small and large angles) are collected in Table 2. It can be seen that each type of material (Cu)Ni/SBA-15 presents a metal loading close to 5%, which is in agreement with the amount of metal used for preparation. Also, the ratios Cu:Ni are close to those desired. X-rays diffraction at small angles and nitrogen physisorption for parent SBA-15 and for mono- and two-component materials (Figs. 3 A and B) confirm, on the one hand, an ordered mesostructure with parallel cylindrical pores for SBA-15 and, on the other hand, show that the order at long distance and the texture of support are maintained after impregnation with copper and nickel nitrates and calcination. Interesting is the fact that in the case when only copper is deposited on support, the metal precursors are quite difficult to be stabilized. This could be explained by the weak interactions between copper precursors and silica, which make these precursors to be mobile and hardly to be stabilized. This effect is very well illustrated by XRD at small angles (Fig. 1A and Table 2), XRD at large angles and TEM, which put in evidence very large particles ($D_{CuO} = 31.5$ nm according to Scherrer equation) mainly located on the external surface of SBA-15 granules (Fig. 3 Cd and Fig. 4Ae). Indeed, the thermo-programmed reduction showed two maxima of reduction at temperatures of ~345 and 500°C. The first maximum is intense and it

can be assigned to the reduction of Cu^{2+} to Cu^0 in bulk CuO , barely dispersed, while the second one is less important and it is considered that it would be due to the reduction of Cu^{2+} in silicates or CuO confined in micropores (Fig. 4Be).

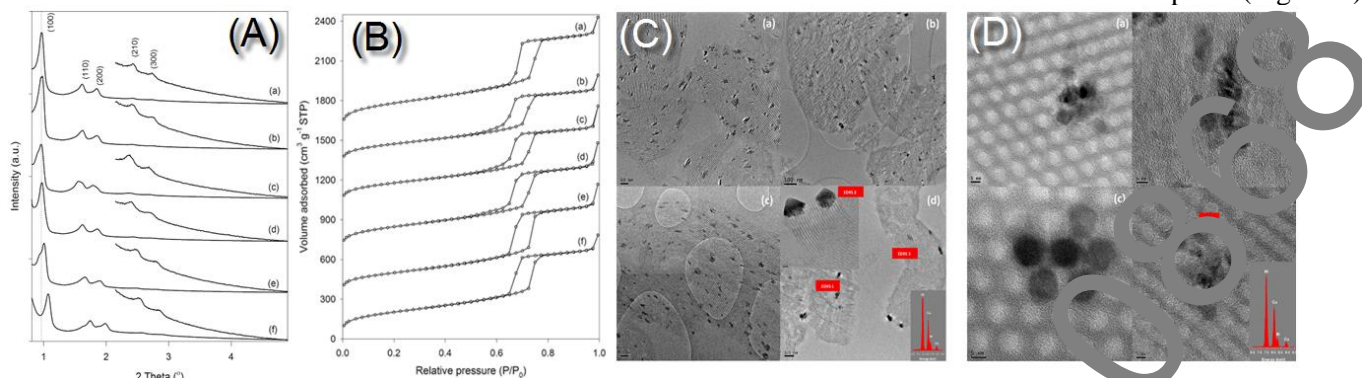


Fig. 3 Isotherms of physisorption (A) and the curves of pore size distribution (B) for SBA-15(a) and Cu/SBA-15(b), $\text{Cu}_1\text{Ni}_4/\text{SBA-15}$ (c), $\text{Cu}_1\text{Ni}_1/\text{SBA-15}$ (d), $\text{Cu}_4\text{Ni}_1/\text{SBA-15}$ (e) and Ni/SBA-15(f); TEM images (C) for Ni/SBA-15(a), $\text{Cu}_1\text{Ni}_4/\text{SBA-15}$ (b), $\text{Cu}_1\text{Ni}_1/\text{SBA-15}$ (c) and $\text{Cu}_4\text{Ni}_1/\text{SBA-15}$ (d) after calcination. HR-TEM images (D) for Ni/SBA-15 (a,b) and $\text{Cu}_1\text{Ni}_1/\text{SBA-15}$ (c,d) after calcination (Inset images: EDS spectra).

For copper-free nickel sample, it was observed a better stabilization of NiO by comparison with CuO. Thus, the nickel oxide crystallites identified by XRD have an average size of 9.2 nm, value that is very close to the mean pore diameter of SBA-15. This result indicates a good dispersion of NiO particles, and their confinement within the pores of support. Indeed, this assertion is supported by nitrogen physisorption data, which indicate the blocking of the main mesopores and the generation of a new system of pores of the “ink-bottle” type whose diameter is of 7.4 nm, as well by TEM images clearly showing well dispersed NiO particles which are confined in mesopores. Simultaneous deposition of both metals (in various mass ratios) on SBA-15 support showed interesting influences, the most important being the stabilizing effect, which is very well illustrated by X-rays diffraction at large angles. Thus, it could be observed the decrease in intensity of the diffraction peaks and the increase of their width at half height, as the ratio Cu:Ni tends to 1: 1. A second interesting effect was observed on the reducibility of Cu^{2+} and Ni^{2+} cations (Fig. 4B). In particular, the catalytic effect of copper on the reducibility of nickel could be noted. Hence, the reduction temperature of nickel decreased progressively from 530 to 245 °C and from 345 to 190 °C for copper (sample $\text{Cu}_1\text{Ni}_1/\text{SBA-15}$). This behavior indicates the presence of both elements in the same particle and that between them there is a strong and synergistic interaction.

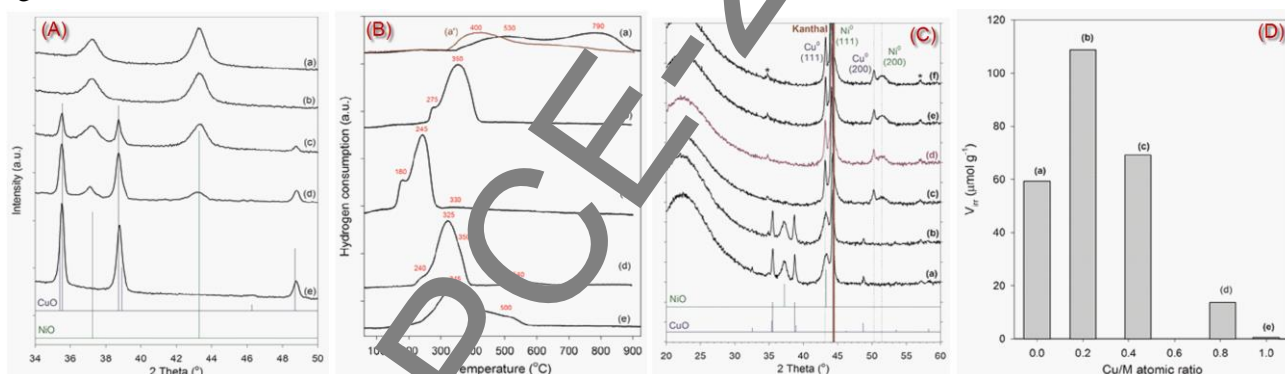


Fig. 4 (A) – XRD diffractograms for Ni/SBA-15(a), $\text{Cu}_1\text{Ni}_4/\text{SBA-15}$ (b), $\text{Cu}_1\text{Ni}_1/\text{SBA-15}$ (c), $\text{Cu}_4\text{Ni}_1/\text{SBA-15}$ (d) and Cu/SBA-15(e); (B) –TPR profiles for Ni/SBA-15(a), $\text{Cu}_1\text{Ni}_4/\text{SBA-15}$ (b), $\text{Cu}_1\text{Ni}_1/\text{SBA-15}$ (c), $\text{Cu}_4\text{Ni}_1/\text{SBA-15}$ (d) and Cu/SBA-15(e); (C) – XRD diffractograms recorded *in-situ* after thermo-programmed reduction of $\text{Ni}_1\text{Cu}_1/\text{SBA-15}$ at 30 °C (a), 150 °C (b), 250 °C (c), 350 °C (d), 450 °C (e) and 550 °C (f); * = 1:1 Ni PS; (D) – Capacity of H_2 chemisorption for (bi)metallic catalysts reduced at 350 °C for Ni/SBA-15(a), $\text{Cu}_1\text{Ni}_4/\text{SBA-15}$ (b), $\text{Cu}_1\text{Ni}_1/\text{SBA-15}$ (c), $\text{Cu}_4\text{Ni}_1/\text{SBA-15}$ (d) and Cu/SBA-15(e).

Evolution of the crystalline phases and their thermostability during the reduction process was monitored by *in-situ* XRD (Fig. 4C – example: $\text{Cu}_1\text{Ni}_1/\text{SBA-15}$). It can be seen that, in agreement with TPR data, at 350 °C (curve c), the diffraction peaks corresponding to NiO and CuO are no longer identified in diffractogram due to their complete reduction to the corresponding metal phases. Instead, new diffractions appear at (i) ~ 43.2 and ~ 44.5 ° assigned to planes (111) of Ni^0 and Cu^0 and (ii) ~ 50.2 and ~ 51.5 ° attributed to planes (200) of Cu^0 and Ni^0 , respectively. It is interesting to note that at $2\theta \approx 50^\circ$, there isn't a single peak of diffraction, by contrary there are two peaks (those already mentioned). This result indicates that two distinct phases exist in this material, one being enriched in copper and other enriched in nickel. It also indicates a low solubility between copper and nickel due to strong interactions between nickel and silica, which prevents an inter-diffusion of these two metals. Indeed, XRD at high angles, TPR and XPS analyses indicate very clearly the existence of a new crystalline phase besides to that corresponding to the oxide phase, in all the samples containing nickel; it is a nickel phyllosilicate phase, whose formation likely takes place during the final drying step (MDI method). This phase, together with the effect of confinement of the oxide particles, is considered to be responsible for very good thermostability of metal/oxide particles deposited inside the pores of SBA-15. Identification of these phases, as well as their interesting catalytic behavior (see Objective 4, O4), was the origin of a new study as follows.

The third study was focused on the effect of the interaction between metal and support on the physico-chemical and catalytic properties of materials⁸. For this purpose, the catalysts were prepared by two methods of precipitation (CP and DP), as mentioned above. After calcination, these samples were characterized by the techniques mentioned above and compared with the sample obtained by MDI. Selected results are shown in Fig. 5 and Tables 3

and 4. Fig. 5 indicates that the method of preparation has an important influence on the structural, textural and reducible properties. In addition, they confirm the results obtained for Cu/-, Ni/- and Co/SBA-15 prepared by the two methods of precipitation, CP and DP (phase I of the project)⁹.

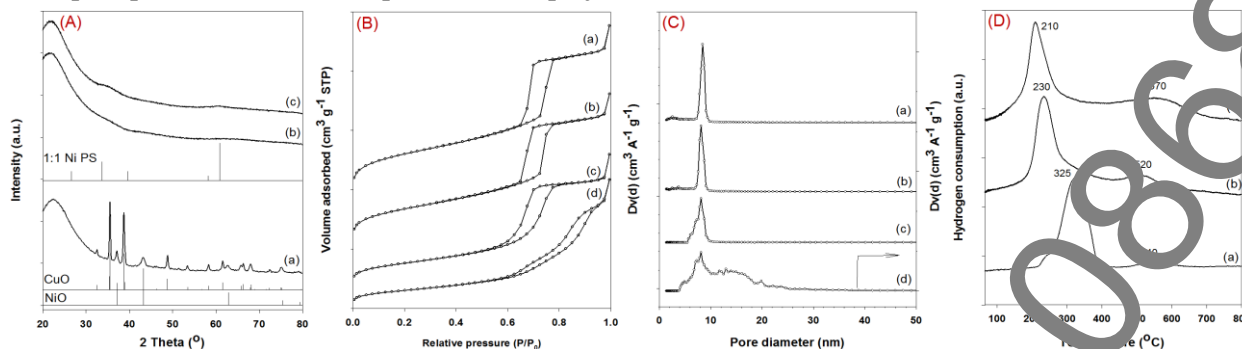


Fig. 5 (A) – XRD diffractograms for CuNi/SBA-15 prepared by MDI(a), CP(b) and DP(c); (B) – Isotherms of nitrogen physisorption for SBA-15(a) and CuNi/SBA-15 prepared by MDI(b), CP(c) and DP(d); (C) – Pore size distributions for SBA-15(a) and CuNi/SBA-15 prepared by MDI(b), CP(c) and DP(d); (D) – TPR profiles for CuNi/SBA-15 prepared by MDI(a), CP(b) and DP(c).

Thus, according to the data of XRD at high angles, the precipitation of cations in solution in the presence of silica support leads to well dispersed crystalline phases with sizes below the limit of detection by XRD (Figs. 5Ab and c). In addition, the texture of the material suffers changes due to the alkaline pH of synthesis media (as it is known basic pH favors the hydrolysis of silica wall, with partial or total loss of mesostructure arrangement)¹⁰.

Table 3. Structural and textural properties of SBA-15 support and calcined CuNi/SBA-15 materials.

Sample	ICP	XRD low angles		N ₂ physisorption				
	Cu: Ni (Cu/M ^a)	d ₁₀₀ ^b (nm)	a ₀ ^c (nm)	S _{BET} ^d (m ² g ⁻¹)	S _{micro} ^e (m ² g ⁻¹)	V _{total} ^f (cm ³ g ⁻¹)	V _{micro} ^g (cm ³ g ⁻¹)	D _p ^h (nm)
SBA-15	-	9.1	10.5	803	183	1.12	0.082	8.4
CuNi_MDI	5.1: 1.1 (0.81)	9.1	10.5	722	145	1.09	0.066	8.2
CuNi_CP	4.5: 0.9 (0.83)	9.1	10.5	488	25	0.87	0.009	7.4; 8.2
CuNi_DP	4.9: 1.1 (0.82)	9.8	11.3	323	11	0.84	0.003	8.2; 15.0

However, when Na₂CO₃ is used as precipitating agent, the pH can be controlled in such a manner that an optimum concerning the mesoporous organization of the material and the dispersion of metallic precursors is obtained. The disadvantage of CP method consists in local super saturation and thus in the punctual precipitation of the cations. For this reason, precipitation by urea is preferred because urea decomposes at 90 ° C gradually releasing HO⁻ ions required for precipitation. In this case, the precipitation takes place uniformly all over the support surface, favoring a more homogeneous deposition of crystalline phases. The disadvantage of this method is the fact that the pH is more difficult to be controlled, and more importantly, textural alterations are more pronounced than in the case of CP method. This statement is supported by the isotherms of nitrogen physisorption and pore-size distribution – Figs. 5B and C (the curves c and d). The textural parameters (S_{BET}, pore volume, pore diameter) of these materials decrease compared with SBA-15 support or with the sample prepared by MDI (Table 3).

Table 4. XPS analyses for calcined and reduced samples.

Sample	Binding (eV)				Cu/Si ^a	Ni/Si ^a	Cu/M ^a
	Cu 2p _{3/2}		Ni 2p _{3/2}				
	Cu ⁰	Cu ^{II}	Ni ²⁺	Ni ⁰			
Calcined samples							
CuNi_MDI	933.2	-	855.7	-	0.01 (0.05)	0.01 (0.01)	0.44 (0.81)
CuNi_CP	933.6; 936.0	-	857.0	-	0.04 (0.05)	0.01 (0.01)	0.72(0.82)
CuNi_DP	933.9; 936.0	-	856.9	-	0.10 (0.05)	0.03 (0.01)	0.75 (0.80)
Samples reduced at 350 °C							
CuNi_MDI	-	933.2	855.7	852.4	0.005 (0.05)	0.006 (0.01)	0.46 (0.81)
CuNi_CP	-	933.0	857.2	852.6	0.03(0.05)	0.01 (0.01)	0.65 (0.82)
CuNi_DP	-	932.8	857.0	852.4	0.05 (0.05)	0.03 (0.01)	0.64 (0.80)

^a Bulk and surface mass ratios (under parentheses)

TPR studies carried out on the bi-component CuNi/SBA-15 materials prepared by the three methods have provided direct information concerning the nature and reducibility of metallic precursors of Cu and Ni generated upon calcination, as well as Cu-Ni and/or metal-support interactions. The sample prepared by MDI contains copper and nickel oxides, poorly dispersed, especially CuO, as indicated by XRD analysis, whose reducibility is relatively low. One can observe that the reducibility of cations is improved for samples obtained by CP and DP, due to very high dispersion of metallic precursors on the surface of support. Moreover, one can see that the reducibility of cations precipitated with Na₂CO₃ is higher than those precipitated with urea, this behavior indicating different chemical natures of crystalline phases formed and hence different metal-support interactions. Thus, it is considered that in the case of CP, the precursors are predominantly of hydroxycarbonate type while in the case of the DP method the precursors are mainly of phyllosilicate type. The nature of the above mentioned precursors was identified by XPS

spectroscopy (Table 4). In the case of the CuNi_MDI sample, binding energies (BEs) for Cu $2p_{3/2}$ and Ni $2p_{3/2}$ are assigned to CuO and NiO phases. It can be seen that BE grows in case of samples synthesized by precipitation, indicating a stronger interaction between metal and support, *via* phyllosilicates, in particular those of nickel. Indeed, after reduction of the samples at 350 °C, both Ni²⁺ and Ni⁰ were identified, clearly indicating that at this temperature there are still nickel cations in a hardly reducible crystalline phase. Moreover, based on studies from the literature, it was established that BE values correspond to those of nickel phyllosilicates, whose reduction temperatures are higher than 500 °C. In terms of distribution of Ni and Cu atoms in the sample, taking into account the atomic ratios, one can notice that there is enrichment in Ni at surface, especially in the case of samples prepared by precipitation.

Catalytic applications of metallic catalysts for chemoselective hydrogenation of cinnamaldehyde

Catalytic materials developed in this phase of the project have been tested in the liquid phase hydrogenation of cinnamaldehyde at 150 °C and atmospheric pressure. In Table 5, some of the experimental results are presented, which clearly illustrate the influence of some important factors (degree of loading with metal, the mass ratio of the two metals, the method of preparation) on the catalytic performance of prepared materials.

Table 5. Catalytic performances of CuNi/SBA-15 materials.

Study	Sample	Reaction time, min	X _{CNA} , % mole	S _{CNOL} , % mole	S _{CNA} , % mole	S _{HCNOL} , % mole
(i) (loading degree of metal)	CuNi/SBA-15(1)	360	21.6	0.6	2.0	6.8
	CuNi/SBA-15(2)		53.5	7.6	0.9	8.6
	CuNi/SBA-15(5)		98.3	0.6	81.9	17.5
	CuNi/SBA-15(10)		100.0	0.7	67.9	31.9
(ii) (ratio M ₁ :M ₂)	Ni/SBA-15	180	86.1	1.4	94.0	4.6
	Cu ₁ Ni ₄ /SBA-15		99.3	5.4	90.8	3.8
	Cu ₁ Ni ₁ /SBA-15		72.0	2.2	88.4	4.4
	Cu ₄ Ni ₁ /SBA-15		11.5	9.7	83.9	6.4
	Cu/SBA-15		1.1	-	-	-
(iii) (method of preparation)	CuNi_MDI	360	21.9	17.1	74.8	8.0
	CuNi_CP		100	24.4	69.3	6.3
	CuNi_DP		100	24.5	65.4	10.1

* CuNi_MDI = Ni₄Cu₁/SBA-15; ^ values calculated at 20 % mole CNA conversion; for the other, the selectivities correspond to maximum conversion.

(i) It can be observed that the catalytic activity increases with the metal loading due to the increase in the number of active sites. Interestingly, this increase has reached a maximum at 5 wt. %, suggesting that this loading represents an optimum in relation to the number of accessible active sites and their dispersion, as well. From the point of view of the catalytic selectivity, these materials, though they contain copper and nickel in equal amounts, they manifest the behavior of solely nickel, the reaction being directed towards the hydrogenation C = C double bond, with the formation of saturated aldehyde.

(ii) Changing the ratio between the two metals has led to specific behaviors. More specifically, it was obtained a conversion of ~ 100 % mole CNA for a ratio Cu:Ni = 1:4, suggesting a positive effect of copper on the dispersion and reducibility of nickel, confirming the results of physico-chemical characterization. Progressive increase of the amount of copper into the material was reflected in a decrease in the catalytic activity down to 1.1% (for the sample containing only copper). At the same time, it is noticed a slight increase in the CNOL selectivity with increasing the amount of copper, indicating the existence of a competition between hydrogenation of C = C and C = O groups, the introduction of copper favoring the adsorption mode of CNA on the active centers *via* C=O.

(iii) Such electronic effects as well as the interaction between metal and support have been further studied on samples prepared by CP and DP. It can be seen that the activity of samples obtained by CP and DP is far greater than that obtained by the MDI method. Also, the properties of chemoselectivity are improved if samples are prepared by precipitation. These results are explained by: (i) the different nature of the active centers generated by reducing of oxides, hydroxy-carbonates and the phyllosilicates of copper and nickel, and in close connection with this, (ii) the mode of CNA adsorption on active centers.

The original results of these studies have been the subjects of 6 communications at international scientific events, 3 articles published in ISI-ranked journals^{2,4}, 1 paper BDI³ and 1 article in preparation⁸ (see Annex at the report).

References

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