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**EFFECT OF THE METAL LOADING DEGREE AND THE
IMPREGNATION METHOD ON THE STRUCTURAL,
TEXTURAL AND CATALYTIC PROPERTIES OF
CuNi/SBA-15 MATERIALS**

BY

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Abstract. CuNi/SBA-15 catalysts with different metal loadings (1, 2, 5 and 10 wt.%) and constant Cu:Ni weight ratio of 1:1 were prepared by wet impregnation (WI) and incipient wetness impregnation (IWI) of the SBA-15 silica support with the corresponding aqueous solutions of the metallic nitrate precursors. Structural, textural and catalytic properties of these samples are reported in the present study. According to the low-angle XRD patterns and nitrogen physisorption isotherms, all the CuNi/SBA-15 catalysts have highly ordered 2D hexagonal mesostructure while XRD at high angles revealed the formation of the specific phases of NiO and CuO with crystallites size slightly larger for the samples prepared by WI than those prepared by IWI. Liquid phase hydrogenation of *trans*-cinnamaldehyde was used to evaluate the catalytic properties of the bimetallic supported catalysts. Depending on the preparation method, differences between the catalytic behaviors of the two series of catalysts at the same metal loading degree were noticed, especially at low metal loadings. Improvements of the catalytic activity with the increasing of the metal loading from 1 to 5 wt.% were observed. Further increasing of the metal loading up to 10 wt.% did not considerably change the catalytic behavior

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of the materials. Therefore, a loading degree of 5 wt.% in metals was found to be optimum value in relation to the dispersion of metal nanoparticles (NPs) as well as the activity and selectivity of the catalysts.

Key words: CuNi/SBA-15, impregnation, *trans*-cinnamaldehyde, hydrogenation.

1. Introduction

Selective catalytic hydrogenation of organic substrates containing unsaturated functional groups is a key step in the preparation of fine chemicals and therefore, the related researches are of particular interest (both from economic and ecologic reasons), especially when the molecule has two or more unsaturated bonds. An example is that of the synthesis of cinnamyl alcohol (CNOL), one of the products of partially hydrogenated cinnamaldehyde (CNA), an α,β -unsaturated aldehyde. The interest in the production of CNOL comes from its applications in food, cosmetics and pharmaceutical industries (Hajek *et al.*, 2005; Reddy *et al.*, 2006; Saudan, 2007; Xi *et al.*, 2008; Mahata *et al.*, 2008). However, high selectivity to this unsaturated alcohol is difficult to achieved because the hydrogenation of other double bond of CNA (C=C) is thermodynamically favored. Accordingly, many efforts were dedicated to the design of new catalytic systems to improve the selectivity towards the unsaturated alcohol (Maki-Arvela *et al.*, 2005).

So far, the noble metal based materials proved to be the best catalysts for the selective hydrogenation of α,β -unsaturated aldehydes (Shirai *et al.*, 2001; Chatterjee *et al.*, 2002) while only few studies are reported on the catalytic applications of non-noble metals supported on ordinary silica (*i.e.*, Cu, NiCu) (Maki-Arvela *et al.*, 2003; Marchi *et al.*, 2003; Chambers *et al.*, 1997). Regardless of the solid material, the catalytic behavior depends on the method of preparation, the nature of support and/or the promoter, the dispersion and the crystal size of the catalytic active phases, the catalyst activation procedure before test, the reaction conditions etc. (Ma *et al.*, 2007; Plomp *et al.*, 2008; Mahata *et al.*, 2008; da Silva *et al.*, 1997; Mercadante *et al.*, 1996). Usually, the most part of the metal-supported catalysts are prepared by deposition of the suitable precursor on the surface of the support. In the particular case of impregnation, several steps are involved: (i) support impregnation by a soluble salt of the catalytic active metal, (ii) the controlled drying of the supported precursor, (iii) the decomposition of the deposited salts to the corresponding oxide and (iv) the reduction of oxide to the catalytic active metal. The properties of the catalytic active phase (*i.e.*, particles size and dispersion of metal NPs) are strongly depending on the impregnation and drying steps.

The objective of the present work is to study the influence of (i) the metal loading degree and (ii) the method of impregnation (*i.e.*, incipient wetness *versus* wet) of an ordered porous support with the copper and nickel precursors

on the structural and textural properties of the calcined CuNi/SBA-15 materials. The catalytic performance of the reduced CuNi/SBA-15 was evaluated for the hydrogenation of *trans*-cinnamaldehyde. To this aim, SBA-15 mesoporous silica was chosen as support because of its well-defined geometry, monodispersed pore diameters in the range of 4 – 14 nm and high surface areas ($> 700 \text{ m}^2 \cdot \text{g}^{-1}$) that allow better control of both the dispersion and particle size in comparison with a non-ordered silica (Meynen *et al.*, 2009).

2. Experimental

2.1. Supports and Catalysts Preparation

The *synthesis of SBA-15* was performed according to the previously reported method (Zhao *et al.*, 1998). The open pore structure was obtained after the removing of surfactant by calcination under air at 550°C for 6 h with a heating rate of $1.5^\circ\text{C} \cdot \text{min}^{-1}$. *CuNi/SBA-15 catalysts* were synthesized by wet impregnation ($V_{\text{solution}} > V_{\text{pore}}$) and incipient wetness impregnation methods ($V_{\text{solution}} \leq V_{\text{pore}}$). The calcined support was impregnated with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (98%, Aldrich) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%, Aldrich) as precursors. Different amounts of precursors were used to obtain a final metal loading of 1, 2, 5, and 10 wt.%, respectively while the Cu:Ni weight ratio was kept constant at 1:1. The resulted materials were dried either at room temperature (samples prepared by - IWI) or 60°C (samples prepared by WI) before the calcination step (500°C for 6 h) when the corresponding Cu and Ni oxides were obtained. The catalysts are denoted as “CN_x%”, where x = the metal loading degree.

2.2. Characterization

XRD measurements were performed at room temperature using a Bruker D5000 apparatus with monochromatic $\text{CuK}\alpha$ radiation. *Nitrogen physisorption* was carried out at -196°C on Autosorb 1-MP (Quantachrome) apparatus. The isotherms were used to quantify the textural properties of the samples by specific equations. *Diffuse reflectance UV-visible* (DR UV-Vis) spectra were recorded on a Shimadzu UV-2450 spectrometer equipped with an integrating sphere unit (ISR-2200). The spectra were collected in the range of 200-800 nm and using BaSO_4 as reference. *Temperature programmed reduction* (TPR) runs were performed on TPR ChemBET PULSAR™ TPR/TPD equipped with TCD (Quantachrome). The calcined samples were introduced in a U-shape microreactor and activated under air flow ($40 \text{ mL} \cdot \text{min}^{-1}$) at 500°C for 1 h (heating ramp of $10^\circ\text{C} \cdot \text{min}^{-1}$). After cooling to 50°C, the 5 vol.% H_2/Ar flow was stabilized ($40 \text{ mL} \cdot \text{min}^{-1}$) and the TPR runs were then performed up to 900°C (heating ramp of $5^\circ\text{C} \cdot \text{min}^{-1}$).

2.3. Catalytic Test

Before test, the calcined catalysts were reduced under a H_2 flow ($1 L \cdot h^{-1}$) at $350^\circ C$ for 10 h (heating rate of $6^\circ C \cdot min^{-1}$) in order to obtain the metallic active sites. The catalytic test was carried out at atmospheric pressure in a three neck glass reactor equipped with reflux condenser and magnetic stirring (900 rpm constant stirring) under the following conditions: 1 mL of reagent, 25 mL of propylene carbonate (PC) as solvent, 0.265 g of catalyst, hydrogen flow of $1 L \cdot h^{-1}$, and constant temperature of reaction of $150^\circ C$. At regular time intervals, samples were taken off and analyzed by GC on a HP-5890 gas-chromatograph equipped with a DB-5 capillary column and a flame ionization detector.

3. Results and Discussions

3.1. Physico-Chemical Characterization

Using tri-block copolymer P123 as organic directing agent under acidic conditions, SBA-15 with ordered two-dimensional hexagonal ($p6mm$) mesostructure was obtained (Zhao *et al.*, 1998). Accordingly, the low-angle XRD patterns (Fig. 1) show the three typical peaks assigned to (100), (110) and (200) reflections.

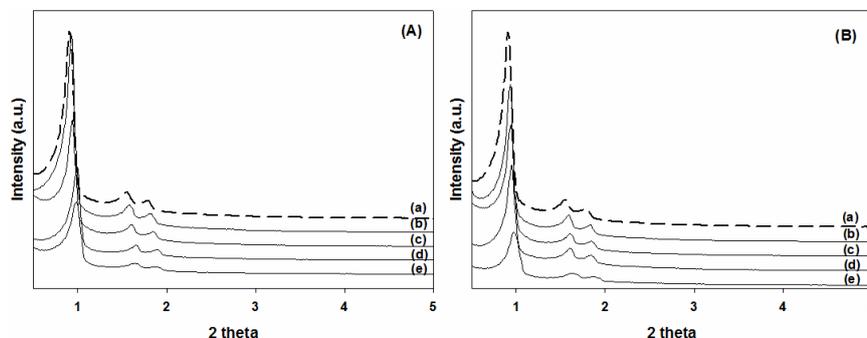


Fig. 1 – Powder X-ray diffraction at low 2θ angle: (A) IWI; (B) WI;
a. SBA-15, b. CN_1%, c. CN_2%, d. CN_5%, e. CN_10%.

After impregnation with copper and nickel salts by IWI and WI and calcination of the solids to the corresponding oxides, the X-ray diffraction at low angles displays the same type of diffraction planes as for the pure SBA-15. However, the attenuation of the (100) intensity accompanied by the shift towards higher 2θ values (lower d_{100} and a_o , Table 1) with the increasing of the oxides loading were observed. Taking into account the amorphous nature of the walls of ordered mesoporous SBA-15, these decrease of the intensity could be attributed either (i) to the formation of copper and nickel oxides

nanoparticles inside the pores of SBA-15 (Chen *et al.*, 2009) or (ii) to the large oxide particles formed at the pore entrance. The first case is the most probable for the samples with 1, 2 and 5 wt.%, while the second one seems to be more appropriate for the samples with 10 wt.% as it will be discussed below. The calculated crystallites sizes for the two oxides (Table 1) suggest the formation of CuO particles predominantly outside the pores whereas the NiO particles are mostly formed inside the mesopores of SBA-15. X-Ray patterns registered at high-angle (Fig. 2) indicate the presence of Cu and Ni oxides (CuO - monoclinic and NiO - cubic) with characteristic diffraction peaks (Reddy *et al.*, 2006). The crystallites size of both oxide NPs increases with the amount of copper and nickel in the sample, regardless of the impregnation method. For the samples with metal loading of 1 and 2 wt.%, the application of the Scherer equation is difficult to accomplish because the diffraction peaks are too small.

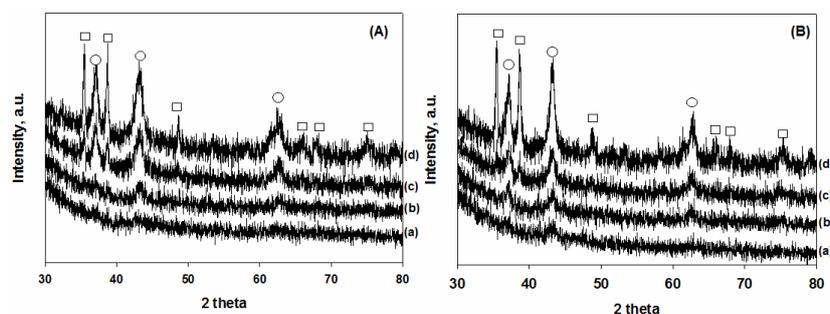


Fig. 2 – Powder X-ray diffraction at high 2θ angle: (A) IWI; (B) WI; a. CN_1%, b. CN_2%, c. CN_5%, d. CN_10%; CuO (\square), NiO (\circ).

By contrary, for the samples with 5 wt.%, crystallites with average sizes of ~ 30 nm and ~ 8.4 nm were obtained for CuO and NiO, respectively (Table 1). Taking into account the impregnation methods (*i.e.*, IWI and WI) that suppose the use of different volumes of the impregnation aqueous solution, these results are quite interesting and suggest that (i) the volume of solvent does not significantly affect the size of the particles prepared by impregnation and (ii) the copper and nickel precursors present different mobility inside the mesopores of SBA-15. Therefore, copper precursors seem to have higher mobility in comparison with nickel precursors that result in larger crystallites of CuO than NiO. Additionally, it can be pointed out that all samples were dried in gentle conditions. Therefore, the samples prepared by IWI were dried at 25°C while the samples prepared by WI were dried at 60°C . As observed, these temperatures are much lower than the usually reported of 120°C , the last temperature favoring the migration of the metallic precursors outside the pores when will gather into large oxide particles (de Jong *et al.*, 2009). When the amount of metal loading is two times higher (10 wt.%), the crystallite size of CuO and NiO are even larger but the size ratio between CuO and NiO remains

unchanged. Thus, the CuO crystallites are larger than NiO crystallites reinforcing the idea of different mobility of the two precursors.

The texture of SBA-15 and CuNi/SBA-15 materials was examined by nitrogen physisorption at -196°C . Fig. 3 illustrates the corresponding nitrogen adsorption–desorption isotherms and NL-DFT pore size distributions, calculated from the desorption branch of the isotherms. According to IUPAC classification, the registered isotherms are of type IV, typical for the mesoporous materials, with hysteresis loop of type H1 characteristic to cylindrical and parallel pores (Zhao *et al.*, 1998; Ravikovitch *et al.*, 2001). As observed in Fig. 3, the desorption branch of the isotherms for the calcined CuNi/SBA-15 materials displays a delay in the closing of the hysteresis loop at relative pressures of ~ 0.5 - 0.6 . This shape suggests the development of a new porous system due to the metal oxide nanoparticles which are confined within the mesopores of SBA-15 (Sietsma *et al.*, 2009).

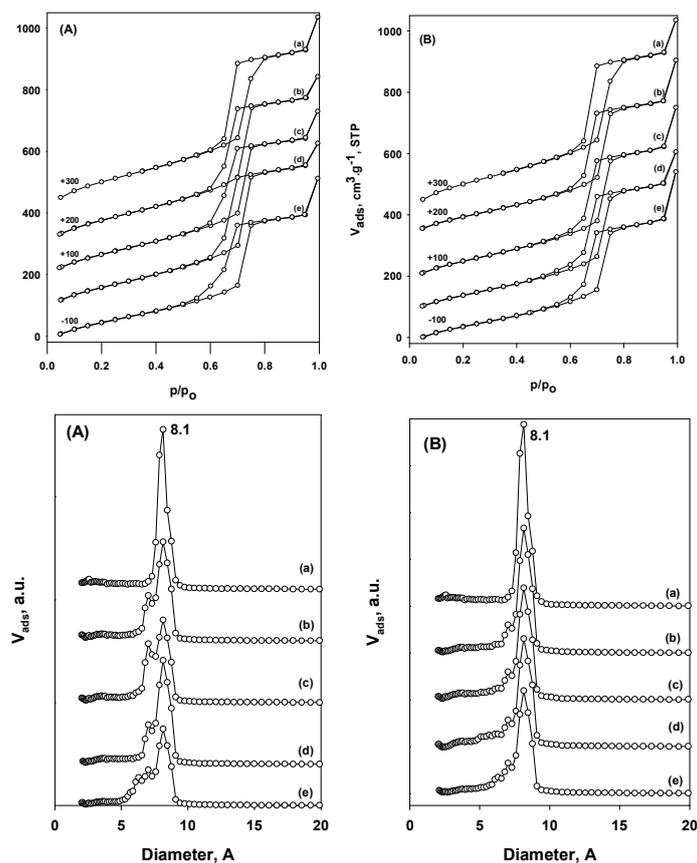


Fig. 3 – N_2 physisorption isotherms (up) and pores size distribution curves (down): (A) IWI; (B) WI; a. SBA-15, b. CN_1%, c. CN_2%, d. CN_5%, e. CN_10%.

This new porous system is clearly observed from the pore size distribution curves depicted in Fig. 3. The curve corresponding to the original SBA-15 support (Fig. 3, down, curves a) displays only one maximum at 8.1 nm which denotes the average pore size for this support. For all calcined CuNi/SBA-15 samples, a new maximum is observed at ~7.0 nm (Fig. 3, down, curves b-e) and represents the average pore size of the secondary porous system mentioned above. However, differences between the samples prepared by the two impregnation methods as well as the various loading degrees were noticed. Thus, for the samples prepared by IWI method, the amount of the secondary porosity increases with the amount of copper and nickel from 1 to 10 wt% (Fig. 3A, down). In contrast, for the samples prepared by WI, the shape of the hysteresis loops does not depend on the metal loading and suggests that the new porous system is less developed. It can be firstly assumed that the impregnation of mesopores with a volume of solution equal to the pores volume (the case of IWI method) allows as higher amount of the metallic precursors to be stabilized inside the mesochannels of SBA-15. Secondly, these results show that higher amount of metallic precursors can be stabilized inside the mesopores by IWI method than WI method. If these data are correlated to the XRD results, it can be stated that a loading of 5 wt.% represents the optimal loading at which the most part of the precursors is located inside the pores. Once the loading degree is increased to 10 wt.%, a considerable amount of precursors is still inside the pores but a sufficient high quantity of the precursors goes out through the pores and the generated oxides are located outside the grains of the support as shown by XRD.

Table 1
Structural and Textural Properties of the Support and the Catalytic Materials

Sample	S_{BET} [m ² .g ⁻¹]	V_p [cm ³ .g ⁻¹]	APS [nm]	d_{100} [nm]	a_0 [nm]	D_{CuO}^a [nm]	D_{NiO}^a [nm]
SBA-15	713	1.14	8.1	9.71	11.22	–	–
IWI-samples							
CN 1%	628	0.996	7.0; 8.1	9.52	10.99	–	–
CN 2%	592	0.977	7.0; 8.1	9.42	10.87	–	–
CN 5%	566	0.971	7.0; 8.1	8.89	10.27	28.5	8.3
CN 10%	515	0.949	7.0; 8.1	8.99	10.38	33.5	14.0
WI-samples							
CN 1%	515	1.015	7.0; 8.1	9.50	10.97	–	–
CN 2%	533	1.008	7.0; 8.1	9.42	10.87	–	–
CN 5%	491	0.938	7.0; 8.1	9.33	10.77	31.0	8.3
CN 10%	483	0.992	7.0; 8.1	9.06	10.46	37.5	14.0

V_p = pore volume determined at $p/p_0 = 0.995$; APS = average pore size obtained by the maximum/maxima of the pore size distribution curves on desorption branch; a_0 = lattice parameter ($a_0 = 2d_{100} / \sqrt{3}$); D = particle size determined by Scherrer equation.

On the basis of the adsorption data, textural parameters such as BET surface area, pore volumes and pore diameters were calculated and their values are given in Table 1. The values obtained for SBA-15 sample are consistent with the previous reported data for such high-quality SBA-15 (Zhao *et al.*, 1998; Ravikovitch *et al.*, 2001; Drăgoi *et al.*, 2009). For the CuNi/SBA-15 samples, the values included in Table 1 support the above discussion. Therefore, the textural parameters declined for the calcined CuNi/SBA-15 samples in comparison to the original SBA-15 support due to the localization of the copper and nickel oxides nanoparticles inside the pores of SBA-15. For all the calcined samples, irrespective of the preparation method, the surface areas and pore volumes decreased with the increasing of the amounts of copper and nickel oxides; the obtained values show a reduction of the surface area between ~12% (CN_1%) and ~28% (CN_10%) for IWI samples when compared with that of the initial support. As concern the WI samples, the decrease of surface areas was more significant, percent ranging from 25% (CN_2%) to 32% (CN_10%) being calculated for the surface areas. On the other side, the reduction of the adsorbed nitrogen volumes was not as important as for the surface areas. Thus, reductions ranging from 13 to 17% for the IWI samples and from 10 to 18% for WI samples were noticed. For the samples prepared by IWI, the decrease of the textural parameters is mainly explained by the presence of the metal oxide inside the mesopores while for the samples prepared by WI the decrease could also arise from the pore blocking by the external oxide nanoparticles.

The reducibility of the copper and nickel oxides was evaluated by TPR. The recorded profiles for the samples with 10 wt.% metal loading and prepared by IWI and WI are illustrated in Fig. 4.

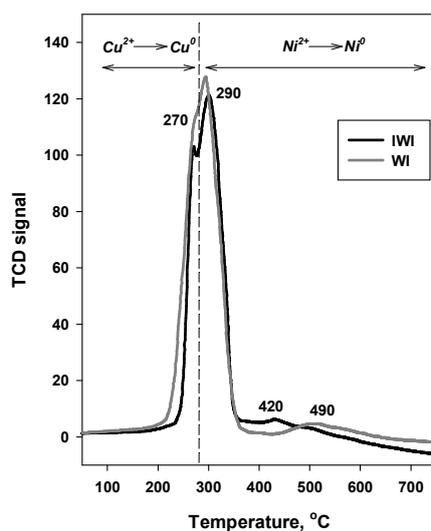
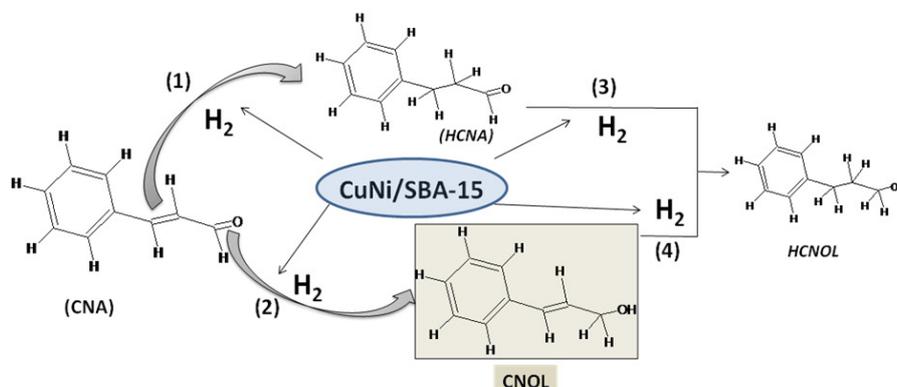


Fig. 4 – TPR profiles for calcined CN_10% samples prepared by IWI and WI.

Two main maxima were observed for each profile of reducibility. The first one is centered at 270°C while the second one is located at 290°C. As it is known, the reduction of the bulk, unsupported copper and nickel oxides takes place at high temperatures (*i.e.*, > 300°C for CuO (Parida & Rath, 2007) and > 400°C for NiO (Ren *et al.*, 2011)). Under these conditions, the TPR profiles show that the reducibility of both oxides supported on mesoporous SBA-15 silica is much improved, especially for NiO. This behavior suggests that most of copper and nickel atoms are found in the same particle and in a strong interaction. Additionally, two minor reduction peaks with maxima at 420 and 490°C were also observed and attributed to bulky oxides grown on the external of the silica grains.

3.3. Catalytic Performances in the Hydrogenation of Cinnamaldehyde

The calcined CuNi/SBA-15 samples were reduced at 350°C under H₂ flow and then evaluated in the liquid phase hydrogenation of *trans*-cinnamaldehyde. As shown in Scheme 1, the hydrogenation of cinnamaldehyde proceeds *via* reaction pathways that involve hydrogenation of C=O and C=C bonds.



Scheme 1 – Reaction pathways for CNA hydrogenation.

The hydrogenation of C=C double bond generates hydrocinnamaldehyde while the hydrogenation of C=O bond leads to cinnamyl alcohol. Hydrocinnamyl alcohol is the product of the complete hydrogenation of both CNOL and HCNA. Fig. 5 illustrates a typical evolution of cinnamaldehyde hydrogenation on CuNi/SBA-15 catalyst (CN_10%) obtained by IWI method. Fig. 6 shows the evolution of CNA conversion with the metals loading and preparation method.

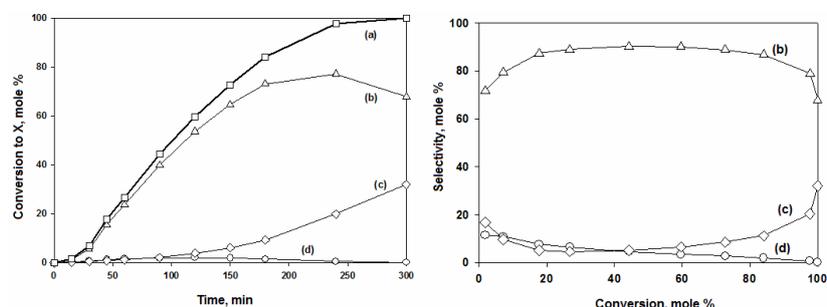


Fig. 5 – Hydrogenation of CNA on CN_10% catalyst obtained by IWI method; conversion vs. time (left); selectivity vs. conversion (right); (a) – CNA conversion, X = [(b) – HCNA, (c) – HCNOL, (d) – CNOL]. (Test conditions: T = 150°C, 0.265 g reduced catalyst; 1 mL of CNA, solvent = propylene carbonate (25 mL), H₂ flow = 1 L·h⁻¹, stirring rate = 900 rpm).

Depending on the preparation method (WI or IWI), differences between the catalytic behaviors of the two groups of catalysts were noticed. However, these differences are more significant up to a metal loading of 5 wt.%. For instance, for 1 wt.% metal loading, the sample prepared by WI is more active in comparison to the sample prepared by IWI (WI/IWI activity ratio is 1.81 after 240 min), whereas for a 10 wt.%, the activities are similar for both preparation methods (WI/IWI activity ratio is 1.02 at 240 min).

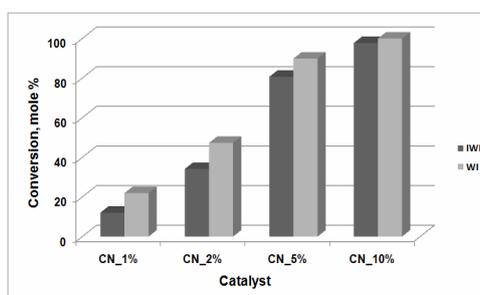


Fig. 6 – CNA conversion over CuNi/SBA-15 (IWI and WI) after 240 min of reaction. (Test conditions: T = 150°C, 0.264 reduced g catalyst; 1 mL of CNA, solvent = propylene carbonate (25 mL), H₂ flow = 1 L·h⁻¹, stirring rate = 900 rpm).

Table 2

Selectivities to CNOL and HCNA vs. CNA Conversion for CN 5% Samples

CNA conversion (mole %)	IWI	WI	IWI	WI
	Selectivity to CNOL (mole %)		Selectivity to HCNA (mole %)	
10	9.9	17.3	81.6	68.4
40	5.0	6.3	89.9	87.8
90	1.4	1.9	83.5	82.7

Table 2 illustrates the selectivities to CNOL and HCNA for CN_5% samples at three different conversions. It is obvious that the main route of reaction is the hydrogenation of C=C bond, which is a typical behavior for the Ni-based catalysts (Jao *et al.*, 2009; Drăgoi *et al.*, 2010). Although the selectivity to CNOL is low, some improvements were observed at low CNA conversions (10 mole%) for WI sample, for which a selectivity to CNOL of 2.7 times higher than for the IWI sample was observed. As the conversion increases up to 90%, the selectivity to CNOL decreases up to 1.5 - 2 mole%. This could be an indication that at low conversion, the particle size effect can be taken into consideration, larger particles obtained by WI method being most favorable than the smaller particles obtained by IWI method to the CNA adsorption *via* C=O bond (Szöllösi *et al.*, 1998; Delbecq & Sautet, 1995; Claus, 1998; Plomp *et al.*, 2008).

4. Conclusions

The results discussed herein on the preparation of CuNi/SBA-15 materials with different metals loadings ranging from 1 to 10 wt.% and constant Cu:Ni weight ratio of 1:1 by two impregnation methods (WI and IWI) allowed to draw the following conclusions:

- Slightly larger crystallites were obtained for the samples prepared by WI than IWI.
- The low temperatures for the drying of the SBA-15 impregnated with the nitrates solutions were favorable for the stabilization of the most part of the metallic precursors, especially for those of nickel, inside the mesopores;
- The CuNi/SBA-15 materials prepared by the two impregnation methods exhibited almost similar catalytic activities in the hydrogenation of CNA;
- For the selectivity to CNOL, the particle size effect was observed only at low conversions of CNA;
- The metal loading degree was the main factor that strongly influences the catalytic activity of the solids; accordingly, a metal loading degree of 5 wt% was optimum in respect of the dispersion of oxides/metals NPs and catalytic performances.

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REFERENCES

- Chambers A., Jackson S.D., Stirling D., Webb G., *Selective Hydrogenation of Cinnamaldehyde Over Supported Copper Catalysts*. *J. Catal.*, **168**, 301 (1997).
- Chatterjee M., Ikushim Y., Zhao F.Y., *Highly Efficient Hydrogenation of Cinnamaldehyde Catalyzed by Pt-MCM-48 in Supercritical Carbon Dioxide*. *Catal. Lett.*, **82**, 141 (2002).
- Chen L.F., Guo P.J., Zhu L.J., Qiao M.H., Shen W., Xu H.L., Fan K.N., *Preparation of Cu/SBA-15 Catalysts by Different Methods for the Hydrogenolysis of Dimethyl Maleate to 1,4-Butanediol*. *Appl. Catal. A: General*, **356**, 129 (2009).
- Claus P., *Selective Hydrogenation of α,β -Unsaturated Aldehydes and Other C=O and C=C Bonds Containing Compounds*. *Topics Catal.*, **5**, 51 (1998).
- da Silva A.B., Jordao E., Mendes M., Fouilloux P., *Effect of Metal-Support Interaction During Selective Hydrogenation of Cinnamaldehyde to Cinnamyl Alcohol on Platinum Based Bimetallic Catalysts*. *Appl. Catal. A: General*, **148**, 253 (1997).
- de Jong K.P., *Synthesis of Solid Catalysts*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim (2009).
- Delbecq F., Sautet P., *Competitive C=C and C=O Adsorption of α,β -Unsaturated Aldehydes on Pt and Pd Surfaces in Relation with the Selectivity of Hydrogenation Reactions: A Theoretical Approach*. *J. Catal.*, **152**, 217 (1995).
- Drăgoi B., Dumitriu E., Guimon C., Auroux A., *Acidic and Adsorptive Properties of SBA-15 Modified by Aluminum Incorporation*. *Microporous and Mesoporous Mater.*, **121**, 7 (2009).
- Drăgoi B., Ungureanu A., Chiriac A., Hulea V., Dumitriu, E., *Hydrogenation of Unsaturated Carbonyl Compounds on non-Calcined LDHs. I. Synthesis and Characterization of ZnNiCuAl Hydrotalcite-Like Materials*. *Acta Chim. Slov.*, **57**, 677 (2010).
- Hajek J., Kumar N., Salmi T., Murzin DY., *Short Overview on the Application of Metal-Modified Molecular Sieves in Selective Hydrogenation of Cinnamaldehyde*. *Catal. Today*, **100**, 349 (2005).
- Jao K.-Y., Liu K.-W., Yang Y.-H., Ko A.-N., *Vapour Phase Hydrogenation of Cinnamaldehyde Over Nano Ni and Ni/SiMCM-41 Catalysts*. *J. Chin. Chem. Soc.*, **56**, 885 (2009).
- Ma H., Wang L., Chen L., Dong C., Yu W., Huang T., Qian Y., *Pt Nanoparticles Deposited Over Carbon Nanotubes for Selective Hydrogenation of Cinnamaldehyde*. *Catal. Commun.*, **8**, 452 (2007).
- Mahata N., Gonçalves F., Pereira M.F.R., Figueiredo J.L., *Selective Hydrogenation of Cinnamaldehyde to Cinnamyl Alcohol Over Mesoporous Carbon Supported Fe and Zn Promoted Pt Catalyst*. *Appl. Catal. A: General*, **339**, 159 (2008).
- Maki-Arvela P., Hajek J., Salmi T., Murzin DY., *Chemoselective Hydrogenation of Carbonyl Compounds Over Heterogeneous Catalysts*. *Appl. Catal. A: General*, **292**, 1 (2005).
- Maki-Arvela P., Tiainen LP., Lindblad M., Demirkan K., Kumar N., Sjöholm R., Ollonqvist T., Vayrynen J., Salmi T., Murzin DY., *Liquid-Phase Hydrogenation of Citral for Production of Citronellol: Catalyst Selection*. *Appl. Catal. A: General*, **241**, 271 (2003).

- Marchi A.J., Gordo D.A., Trasarti A.F., Apesteguia C.R., *Liquid Phase Hydrogenation of Cinnamaldehyde on Cu-Based Catalysts*. Appl. Catal. A: General, **249**, 53 (2003).
- Mercadante L., Neri G., Milone C., Donato A., Galvagno S., *Hydrogenation of α,β -Unsaturated Aldehydes Over Ru/Al₂O₃ Catalysts*. J. Mol. Catal. A: Chem., **105**, 93 (1996).
- Meynen V., Cool P., Vansant E.F., *Verified Syntheses of Mesoporous Materials*. Microporous and Mesoporous Mater., **125**, 170 (2009).
- Parida K.M., Rath D., *Structural Properties and Catalytic Oxidation of Benzene to Phenol Over CuO-Impregnated Mesoporous Silica*. Appl. Catal. A: General, **321**, 101 (2007).
- Plomp A.J., Vuori H., Krause A.O.I., de Jong K.P., Bitter J.H., *Particle Size Effects for Carbon Nanofiber Supported Platinum and Ruthenium Catalysts for the Selective Hydrogenation of Cinnamaldehyde*. Appl. Catal. A: General, **351**, 9 (2008).
- Ravikovitch P.I., Neimark A.V., *Characterization of Micro- and Mesoporosity in SBA-15 Materials from Adsorption Data by the NLDFT Method*. J. Phys. Chem. B, **105**, 6817 (2001).
- Reddy B.M., Kumar G.M., Ganesh I., Khan A., *Vapour Phase Hydrogenation of Cinnamaldehyde Over Silica Supported Transition Metal-Based Bimetallic Catalysts*. J. Mol. Catal. A: Chemical, **247**, 80 (2006).
- Ren Y, Peter G.B., Zhen M, *Solid-Solid Conversion of Ordered Crystalline Mesoporous Metal Oxides under Reducing Atmosphere*. J. Mater. Chem., **21**, 9312 (2011).
- Saudan L.A., *Hydrogenation Processes in the Synthesis of Perfumery Ingredients*. Acc. Chem. Res., **40**, 1309 (2007).
- Shirai M., Tanaka T., Arai M., *Selective Hydrogenation of α, β -Unsaturated Aldehyde to Unsaturated Alcohol with Supported Platinum Catalysts at High Pressures of Hydrogen*. J. Mol. Catal. A: Chemical, **168**, 99 (2001).
- Sietsma J.R.A., Meeldijk J.D., Versluijs-Helder M., Broersma A., Jos van Dillen A., de Jongh P.E., de Jong K.P., *Ordered Mesoporous Silica to Study the Preparation of Ni/SiO₂ exNitrate Catalysts: Impregnation, Drying, and Thermal Treatments*, Chem. Mater., **20**, 2921 (2008).
- Szöllösi G., Torok B., Szakonyic G., Kuna I., Bartok M., *Ultrasonic Irradiation as Activity and Selectivity Improving Factor in the Hydrogenation of Cinnamaldehyde Over Pt/SiO₂ Catalysts*. Appl. Catal. A: General, **172**, 225 (1998).
- Xi C., Wang H., Liu R., Cai S., Zhao F., *Hydrogenation of Cinnamaldehyde Over Pt/RHCs in Supercritical Carbon Dioxide – Influence of Support Pretreatment and Phase Behavior*. Catal. Commun., **9**, 140 (2008).
- Zhao D., Feng J., Huo Q., Melosh N., Fredrickson G.H., Chmelka B.F., Stucky G.D., *Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores*. Science, **279**, 548 (1998).

EFFECTUL GRADULUI DE ÎNCĂRCARE CU METAL ȘI A METODEI DE
IMPREGNARE ASUPRA PROPRIETĂȚILOR STRUCTURALE, TEXTURALE ȘI
CATALITICE ALE MATERIALELOR DE TIP CuNi/SBA-15

(Rezumat)

Catalizatorii de tip CuNi/SBA-15 cu diferite grade de încărcare cu metal, G, (1, 2, 5 și 10 procente masice) au fost preparați prin impregnarea umedă (WI) și respectiv, cu umectare incipientă (IWI) a unui suport de silice SBA-15 cu soluțiile apoase ale precursorilor metalici de tip azotați de cupru și nichel. În acest studiu sunt raportate proprietățile structurale, texturale și catalitice ale catalizatorilor preparați prin aceste două metode. În acord cu DRX la unghiuri mici și izotermele de fizisorbție a azotului, toți catalizatorii CuNi/SBA-15 au o mezostructură hexagonală ordonată 2D. DRX la unghiuri mari a evidențiat formarea fazelor specifice de tip CuO și NiO, ale căror cristalite sunt doar cu puțin mai mari în cazul probelor preparate prin WI decât prin IWI. Proprietățile catalitice ale materialelor bimetalice au fost evaluate în hidrogenarea în fază lichidă a *trans*-cinamalhidei. În funcție de metoda de preparare s-au observat diferențe între comportamentele catalitice ale celor două serii de catalizatori la același G, în particular la valori mici. Îmbunătățiri evidente ale activității catalitice au fost observate cu creșterea lui G de la 1 la 5% procente masice. O creștere la 10% procente masice nu a mai influențat semnificativ comportamentul catalitic al solidelor. Ca urmare, un G de 5% procente masice s-a dovedit a fi optim în raport cu dispersia NPs precum și cu activitatea și selectivitatea catalizatorului.