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Effect of silver modification on component interaction in Ni-Mg/SiO_2 vegetable oil hydrogenation catalysts

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Seventh National Conference on Chemistry
International Conference on Green Technologies and Environmental Protection
26–29 May 2011, Sofia, Bulgaria

This study represents part of our investigations realized in the frame of a joint research project between Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, and Department of Catalysis and Chemical Engineering, Institute of Chemistry, Technology and Metallurgy, University of Belgrade: "Ni/SiO_2 catalysts for edible vegetable oil hydrogenation with controlled pore structure".

The catalytic partial hydrogenation of vegetable oils

continues to be applied as one of the most universal methods in the modern chemical industry, aimed at:

➲ decreasing the unsaturation of the high fatty acids;

➲ modifying the physical properties of the oils;

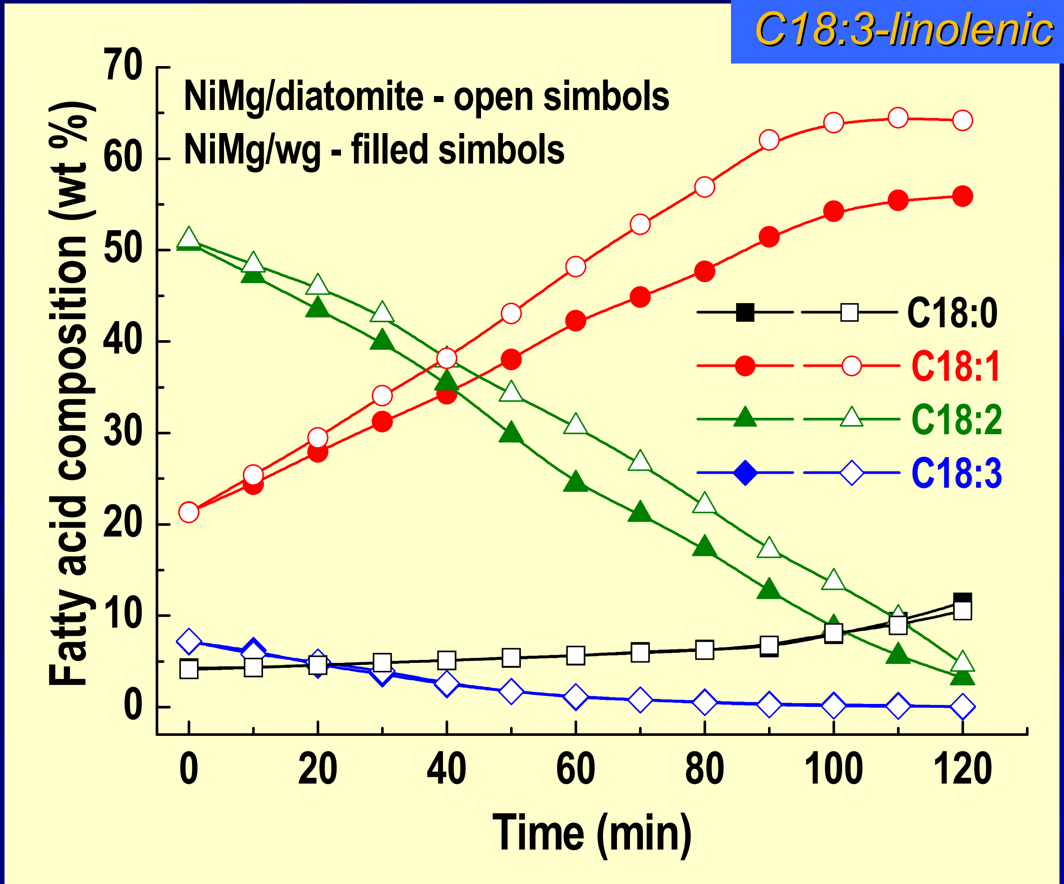
➲ enhancing the oxidation and thermal stability of the hydrogenated products: raw materials for the manufacture of margarines, cooking, frying and salad oils, chocolates, ice creams, shortenings and bakery products.

Currently, metallic nickel (22–25 wt.%) supported on different sources of silica and impregnated with hardened oil, represents the commonly applied commercial catalyst for the process because of the high activity, inert nature relative to oil and low cost.

We studied Ni-Mg hydrogenation catalysts supported on two types of silica sources, diatomite (a natural product) and water glass (a synthetic commercial product) and established that both catalysts manifested similar soybean oil hydrogenation activity *(Gabrovska et al., Applied Catalysis A: General 299 (2006) 73–83)*

P_{H2}=0.16 MPa
T = 160°C

C18:0-stearic
C18:1-oleic
C18:2-linoleic
C18:3-linolenic



We should note that crude diatomite has some disadvantages such as:

⇨ variation of composition from batch to batch;

⇨ presence of different impurities.

Therefore, a number of mechanical, chemical and thermal treatments are necessary to obtain a pure and activated support.

Water glass, as an alternative source of silica, allows the preparation of low cost catalyst. Thus, the prolonged and expensive procedures for purification of the crude diatomite can be avoided.

It is well known that metallic silver as a member of IB group metals decreases the reduction temperature of the transition metal ions.

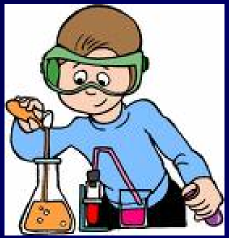
It may be supposed that introduction of silver to Ni-Mg/SiO_2 system could diminish the reduction temperature of the Ni^{2+} ions, which may be a precondition for better reduction to the metallic nickel state. This will contribute to the formation of a large number of catalytic active centers (Ni^0) on the surface, hence, higher hydrogenation activity may be expected.

This fact directed us to improve the activity of the Ni-Mg/SiO_2 catalyst by the following steps:

(i) modifying the system by addition of Ag

(ii) preparing the precursor samples by co-precipitation, thus achieving a more strong contact between the Ni and Ag species and favoring their interaction.

Preparation procedure



Constant composition

Mg/Ni = 0.1

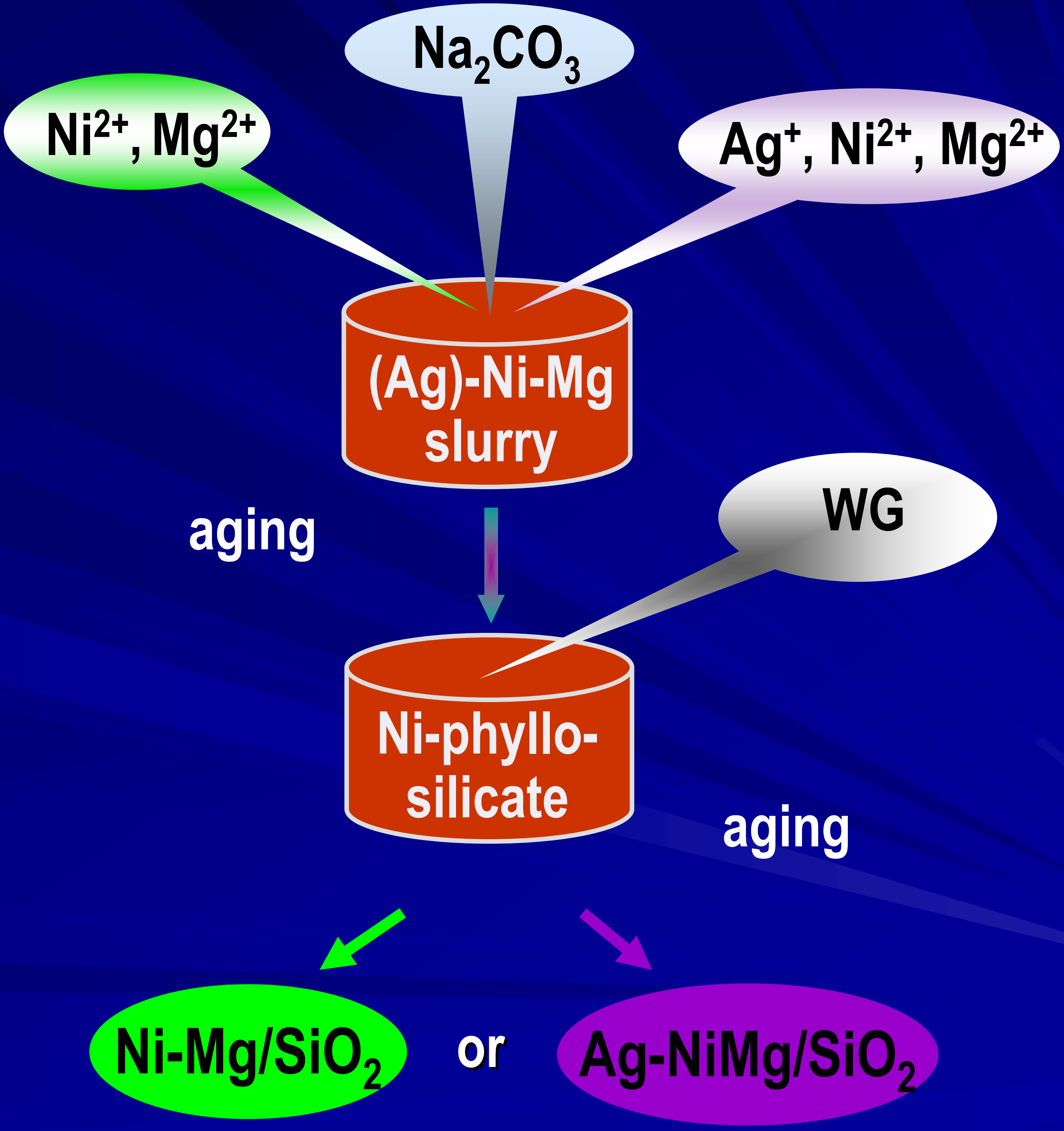
SiO_2/Ni = 1.0-1.15

Variable composition

Ag/Ni = 0.0025 = 0.1 at.% Ag

Ag/Ni = 0.025 = 1.0 at.% Ag

Ag/Ni = 0.1 = 4.0 at.% Ag



Ni^{2+}, Mg^{2+}

Na_2CO_3

Ag^{+}, Ni^{2+}, Mg^{2+}

(Ag)-Ni-Mg slurry

aging

WG

Ni-phyllo-silicate

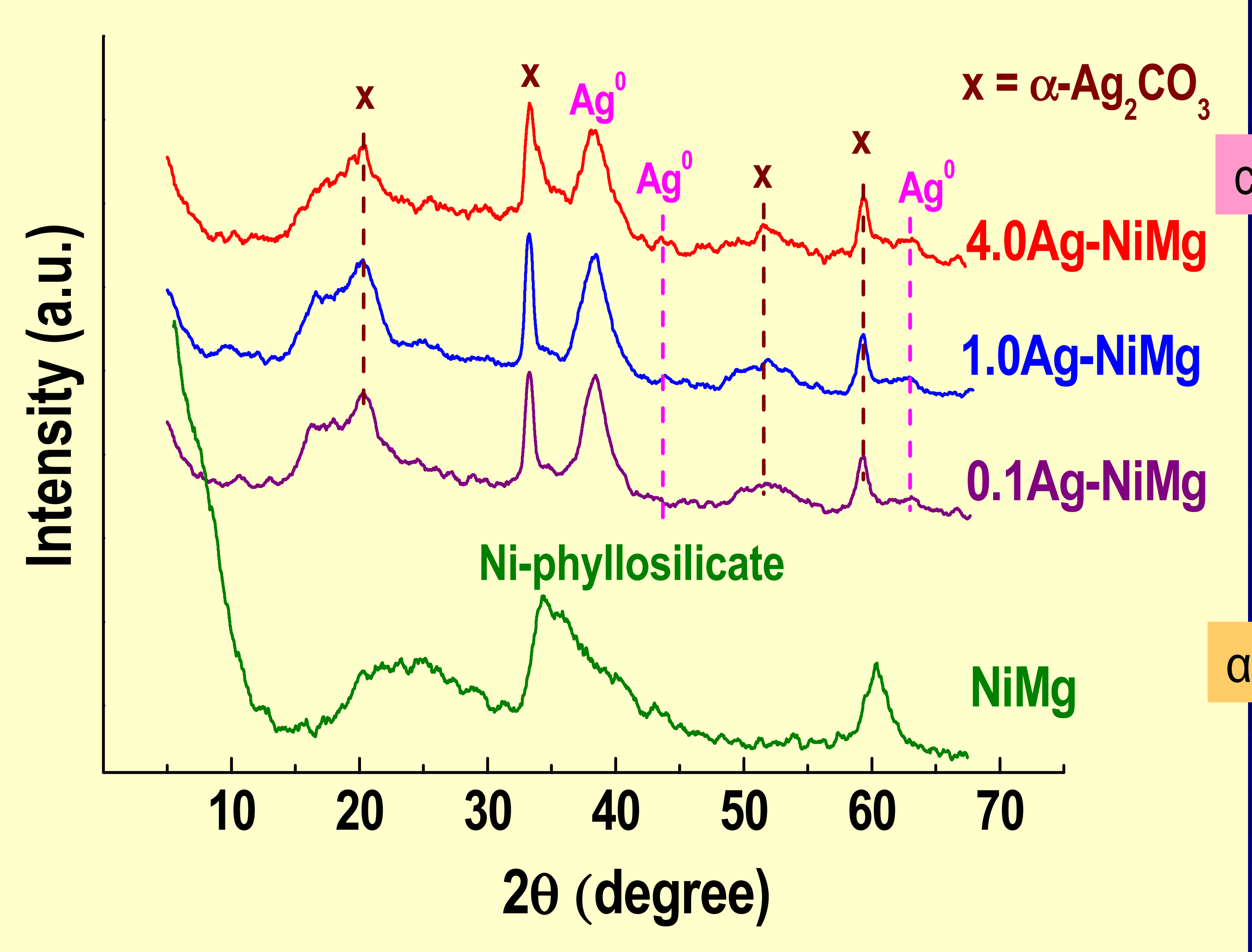
aging

Ni-Mg/SiO_2 or **Ag-NiMg/SiO_2**

Sample	SSA (m^2 /g)	Color $Ag^+ \longrightarrow Ag^0$	Chemical composition (atomic %)			
			Ni	Mg	Ag	Si
Ni-Mg	198	green	44.45	4.45	–	51.10
0.1Ag-NiMg	151	green	44.40	4.43	0.11	51.10
1.0Ag-NiMg	164	pale-grey	43.95	4.38	1.10	50.57
4.0Ag-NiMg	217	grey	42.56	4.26	4.26	48.92

What is the effect of silver presence and silver content on the interaction between the components in the as-synthesized and reduced at 430°C solids?

As-synthesized



cubic metallic Ag phase

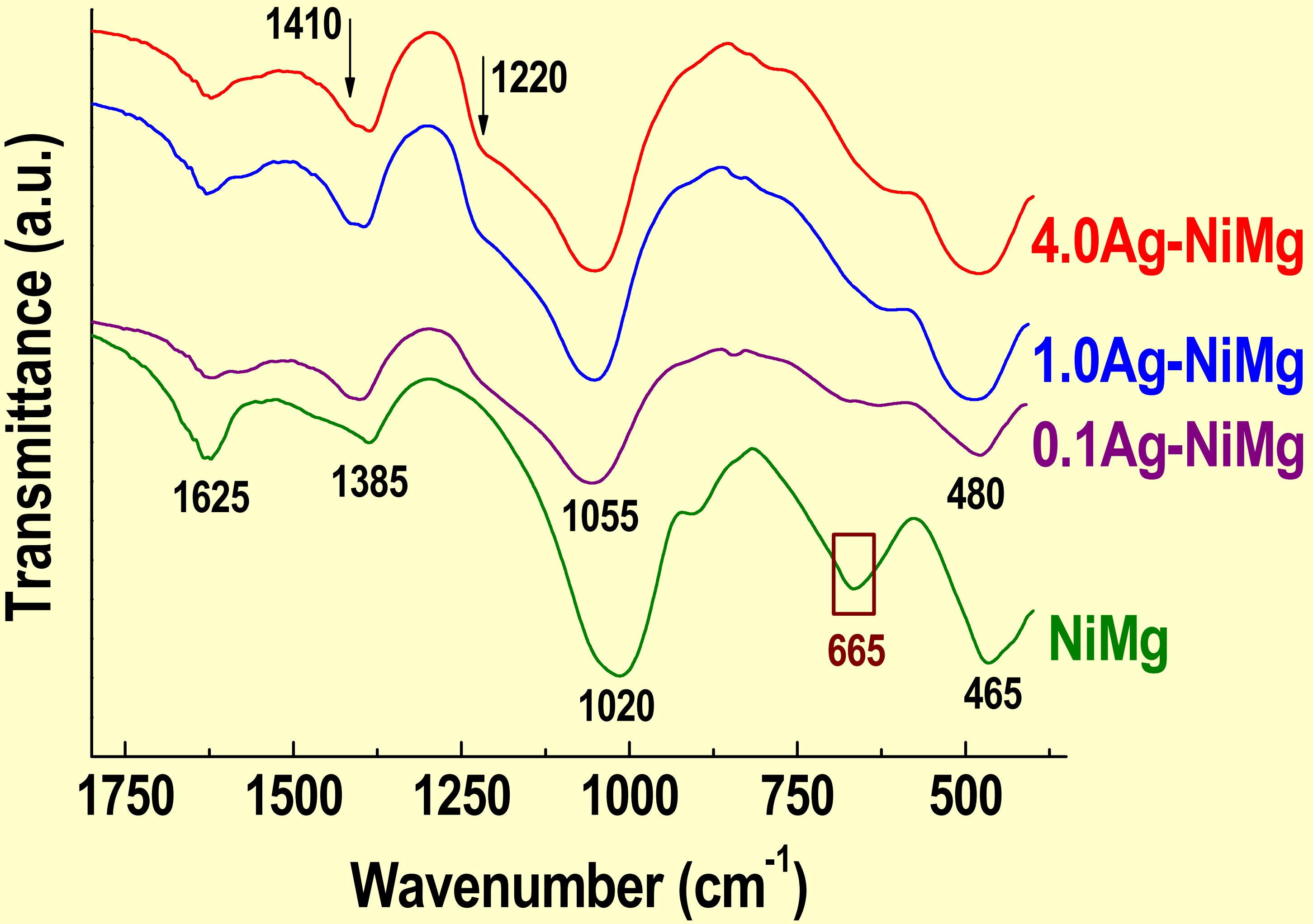
Ag^+ ions are weakly bonded to the surface of the silica and as a result partly the Ag^+ ions are readily reduced to the metallic state during the preparation

α-Ag_2CO_3 phase

Ni-phyllosilicate phase is fully amorphizated or “covered” by the Ag-containing entities

Interaction between Ni+Mg+SiO_2 leads to the formation of Ni-phyllosilicate layers with antigorite-like structure which covers the surface of the silica particles

As-synthesized



The IR spectra of the solids demonstrate absence of the typical vibrations of the silica network:
asymmetric Si–O–Si (~1100 cm^{-1}); symmetric Si–O–Si (~800 cm^{-1}); free Si–OH groups (~970 cm^{-1}); Si–O–Si bending vibration (~470 cm^{-1}).

NiMg

➲ The bands at ~1020 cm^{-1}, ~665 cm^{-1} and ~465 cm^{-1} are attributed to Ni-phyllosilicate linkages (–Ni–O–Si–) with antigorite structure

The presence of Ag causes

⇨ absence of the bands typical of Ni-phyllosilicate ;

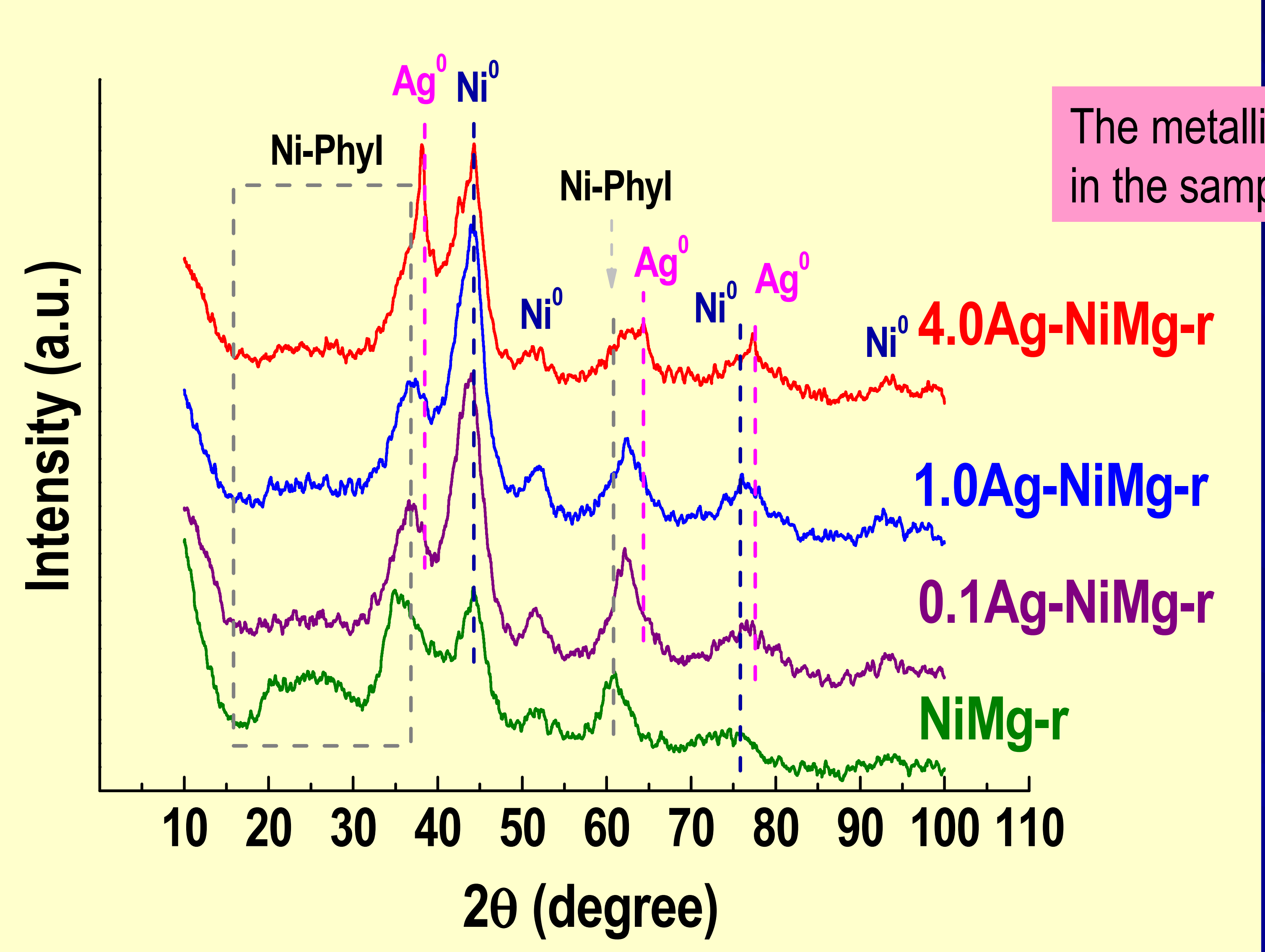
⇨ appearance of bands typical of Ag-containing phases.

In all samples

➲ water molecule deformation vibrations at ~1625 cm^{-1};

➲ CO_3^{2-} anions at ~1385 cm^{-1}.

Reduced at 430°C/5h

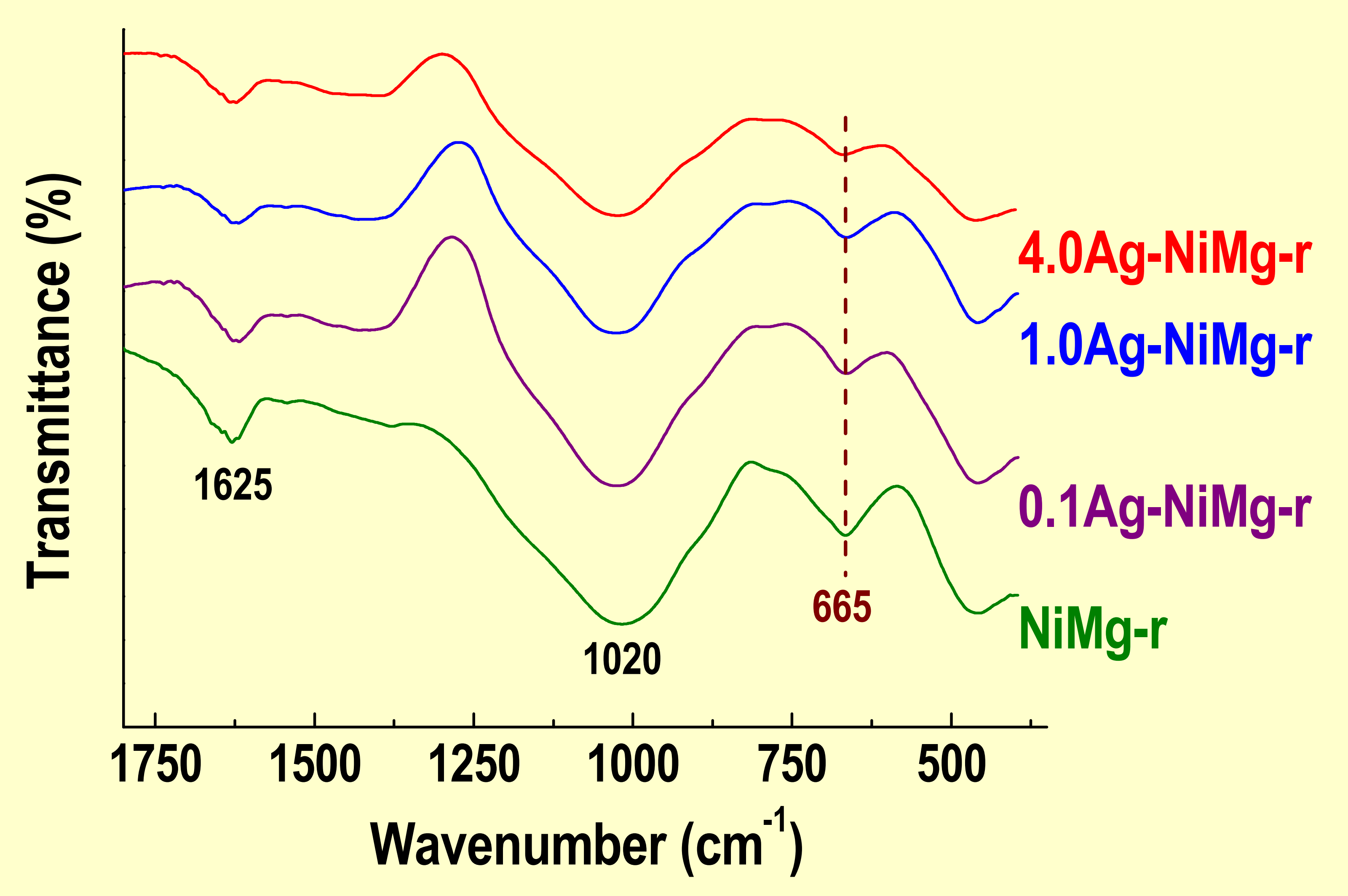


The metallic Ag phase is better organized in the sample of the highest Ag loading

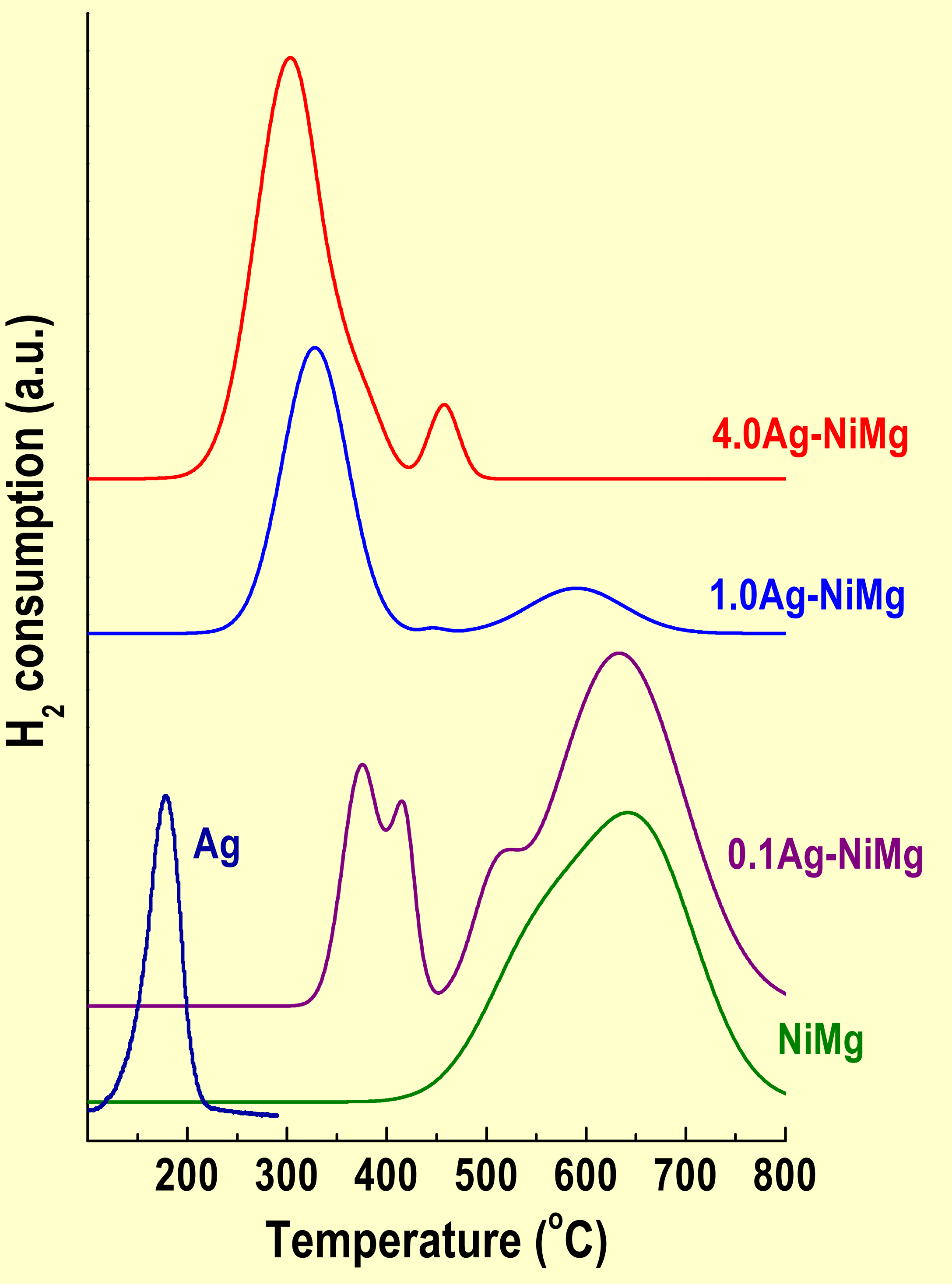
The presence of silver diminishes the intensity of the Ni-phyllosilicate phase, indicating facilitated reduction of the Ni^{2+} ions, which is better expressed with the increase of silver loading in the samples.

The presence of Ni-phyllosilicate phase in all samples signifies incomplete reduction of the Ni^{2+} entities.

Reduced at 430°C/5h



The intensity of the bands at 665 cm^{-1} typical of the antigorite-like structure decreases with the increase of Ag loading, thus showing enhanced reduction of the Ni^{2+} species.

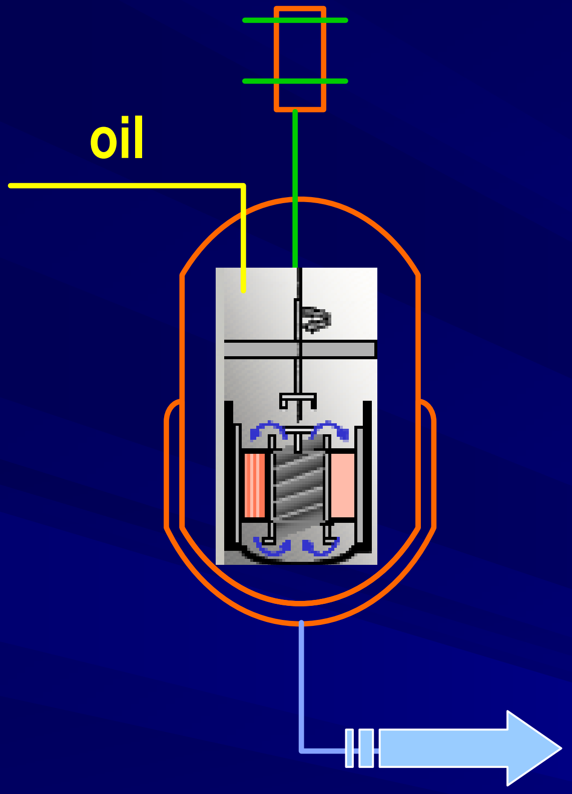


Temperature-programmed reduction study shows gradual shifting of the T_{max} to lower temperatures on increasing the silver concentration.

The main part of the Ni^{2+} ions in the NiMg sample is reduced at ~630°C, while that in 4.0Ag-NiMg at ~300°C. Consequently, the highest quantity of modifier readily promotes the reduction of Ni^{2+} ions.

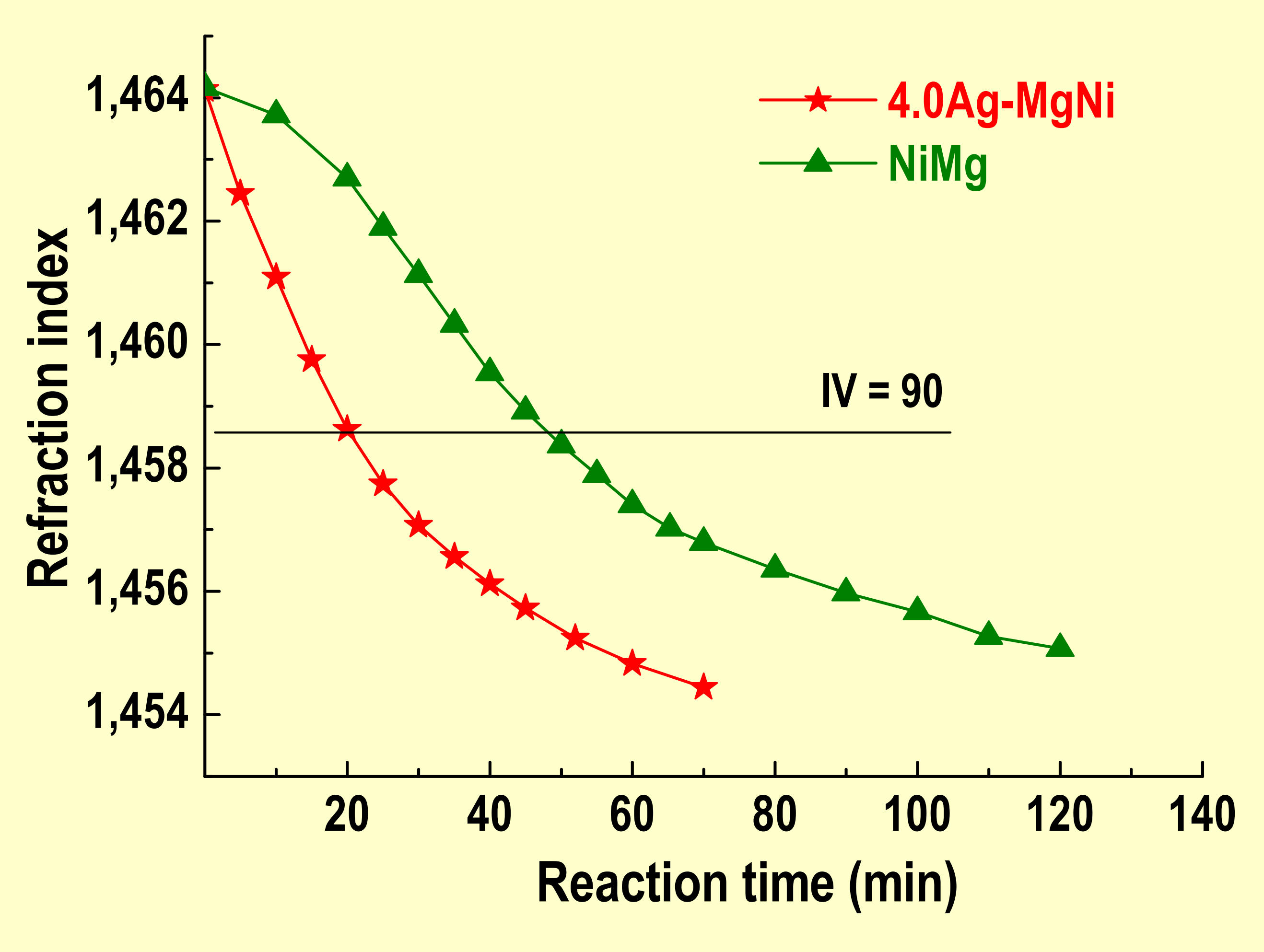
The role of Ag in promoting the reduction of Ni^{2+} is likely associated with the fact that Ag^+ ions are reduced to the metal state at ca. 160° lower than the reduction of the Ni^{2+} ions.

Taking into consideration that silver and nickel do not form a solid solution at any composition under equilibrium conditions, it is assumed that Ag^0 provokes the activation of H_2 and the removal of oxygen atom from the Ni-containing phases *via* weakening the vicinal Ni–O bonds.



hydrogenates

The hydrogenation activity of the reduced (430°C/5 h, a flow rate of 10 dm^3/h and a heating rate of 2°C/min) and impregnated by pure paraffin oil catalysts is estimated by partial hydrogenation of sunflower oil at 150°C, pressure of 0.2 MPa and stirring rate of 1200 rpm in autoclave.



The hydrogenation activity is represented by the change of the refraction index (RI) of the starting liquid oil with reaction time.

RI decreases at the end of the reaction from 1.464 (crude oil) to 1.455 and 1.454 using the NiMg and 4.0 Ag-MgNi catalysts, respectively.

If the criterion for the catalyst activity is the reaction time necessary to attain an iodine value (IV) of about 90, corresponding to the partially hydrogenated oil, the following results are obtained: 20 min (4.0 Ag-NiMg) and 48 min (NiMg).

The shorter reaction time for equal RI indicates a higher activity of the Ag-modified catalyst.

in situ reduction at 430ºC/5h

Sample	*a* (µmol H_2/g_{sample})	Ssp (m^2_{Ni}/ g_{Ni})	d_{Ni} (nm)	Ni^0 dispersion
NiMg-r	205	38	15	5
4.0Ag-NiMg-r	238	50	10	8

The catalytic activity may be explained by the results from H_2-chemisorption measurements, carried out at room temperature, after activation of the precursors. It is well known that Ag^0 does not chemosorb H_2 at room temperature and thus the H_2 chemisorption occurs only on the reduced Ni^0 atoms.

The Ag-modified precursor chemisorbs larger amount of hydrogen, has higher Ni^0 surface area, smaller nanoscaled nickel crystallites and higher Ni^0 dispersion compared to the unmodified sample.

Considering that the hydrogenation reaction takes place on the surface of the catalyst, larger Ni^0 surface area contributes to the formation of a higher number of active sites, namely nickel surface atoms, where the reaction occurs.

Conclusions

It may be concluded that by changing the content of the silver modifier to adjust precursor composition one could control

⇨ the strength of the Ni-O-Si interaction;

⇨ the reducibility of the Ni^{2+} species;

⇨ the degree of Ni^0 crystallization;

⇨ the values of Ni^0 particles, Ni^0 surface area, and Ni^0 dispersion;

⇨ the hydrogenation activity.

The sample of the highest Ag content seems to be a more promising catalyst for vegetable oil hydrogenation.

Thank you very much for your great attention !!!

Acknowledgements: Serbian authors are grateful to the Serbian Ministry of Science (Project 45001).