

Improved catalyst performance of Ni/SiO₂ in vegetable oil hydrogenation: impact of Mg dopant

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Mg-doped co-precipitated Ni/SiO₂ precursors were studied as edible sunflower oil hydrogenation catalysts applying two types of commercial silica gels (SIG) as supports of different texture characteristics: a microporous type (SIG-A) and a mesoporous type (SIG-C). It was found that texture parameters of both the silica gels and magnesium addition allow obtaining of catalysts of various hydrogenation activities and fatty acid composition of the products. The results reveal the highest hydrogenation activity of MgNi/SiO₂-C catalyst because of higher amount and accessibility of metal nickel particles on the catalyst surface generated through reduction procedure. A dominant activity of MgNi/SiO₂-C catalyst is ascribed to appropriate mesoporosity, which controls diffusion. It was established that Mg-doped Ni/SiO₂-C possessed a capacity for use as an efficient edible vegetable oil hydrogenation catalyst due to high hydrogenation activity, high saturation level of linoleic acid (C18:2*cis*), moderate amounts of C18:1*trans* fatty acids, and C18:0 stearin acid formation in the partially hydrogenated sunflower oil.

Key words: Ni catalyst; silica gel; Mg additive; hydrogenation; sunflower oil; *trans*-isomers.

INTRODUCTION

Metal nickel (21–25 wt.% Ni) supported on silica represents one proven and thereat widely produced and practiced catalyst in the partial hydrogenation of vegetable oils. The process continues to be applied as universal method in modern food industry to enhance oxidation and thermal stability of the hydrogenated products by decreasing unsaturation of the naturally occurring triacylglycerides and changing solidification characteristics and plasticity of the hydrogenated oils [1]. Nickel has been selected due to its high activity, inert nature relative to oil, availability, and economic price, which makes it superior over other metals [2].

During hydrogenation of fatty acids (FAs), several simultaneous processes can be distinguished, such as saturation, migration, and geometric isomerisation of double bonds. Some unsaturated FAs that are normally in *cis*-configuration may be isomerised into *trans*-FAs [3]. In the light of recent recommendations issued by international food associations, the formation of *trans*-FAs during hydrogenation using conventional nickel catalysts is considered undesirable. Conventional partial hydro-

genation results in the formation of up to 40% of *trans*-FAs in the hardened products. None of the commercially available catalysts enable the production of partially hydrogenated sunflower oil having insignificant *trans*-FAs content [4].

While numerous studies have been focused on improving catalyst preparation, there are only scarce attempts to elucidate the role of additives or modifiers on the structural and textural properties of nickel catalyst precursors, particularly those, which might form compounds similar to those of the parent metal [4,5]. Moreover, the effect of dopants on the catalytic performance in vegetable oil hydrogenation is rarely discussed in the literature [6].

To promote *cis*-FA selectivity it is necessary to dope Ni-containing catalysts with a suitable promoter or modifier [7].

Alkaline, alkaline earth, and rare earth metals are generally employed as promoters. The impact of promoters is mostly related to the following aspects: altering catalyst surface acid-base property, improving dispersion of active species, and considering the type and extent of active species-support interactions. An alkaline earth metal could affect the reducibility, the morphology, and the electronic properties of catalysts [8]. In this connection, doping Ni-based catalysts by Mg alkaline earth

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metal may alter the structure, texture, basicity, and reducibility of the Ni²⁺ ions, the overall impact on catalyst hydrogenation activity, and its *cis/trans*-selectivity.

Based on these considerations, a partial isomorphous replacement of Ni²⁺ with Mg²⁺ ions in Ni-phyllsilicate structure was accomplished aimed at improving the performance of Ni/SiO₂ catalyst in sunflower oil hydrogenation by increasing hydrogenation activity and oleic acid selectivity, tuning the level of *cis-trans* isomerisation, and minimising stearic acid content in the products of hydrogenation.

EXPERIMENTAL

Sample preparation

Two types of commercial silica gels (SIG) of different texture characteristics, microporous SIG-A and mesoporous SIG-C [9] of 0.8–1.0-mm size, were applied as supports for sample synthesis.

The precursors were obtained with identical composition (SiO₂/Ni = 1.0 and Mg/Ni = 0.1) by coprecipitation of aqueous solutions of nickel nitrate hexahydrate, Ni(NO₃)₂·6H₂O, and magnesium nitrate hexahydrate, Mg(NO₃)₂·6H₂O, with anhydrous sodium carbonate, Na₂CO₃, over silica gels suspended in distilled water. The initial salts of analytical grade, provided by Alfa Aesar (USA), were used as received without further purification.

By analogy with non-modified Ni/SIG samples, the same preparation procedure was used which is described in detail elsewhere [10]. It should be noted that because of magnesium presence synthesis procedure was performed at pH = 10.0.

After drying at 120 °C for 20 h the precursors were designated as (Mg)Ni/SIG-X, where X is A or C and represents the type of used silica gel.

This paper reports refined preliminary partially published results [11–13] and new data on FA composition and *cis/trans*-selectivity of non-doped and Mg-doped Ni/SIG catalysts. The properties of the Mg-doped precursors and catalysts were compared with the non-doped counterparts. The effects of magnesium modification on the structure, texture, reducibility, and catalytic performance of the materials will contribute to select a promising candidate for an active edible vegetable oil hydrogenation catalyst.

Sample characterization

Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance powder diffractometer employing CuK α radiation. The crystalline phases were identified using International Centre for

Diffraction Data (ICDD) powder diffraction files.

FTIR spectra within the range of 4000–400 cm⁻¹ were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Electron Corporation, USA) at 0.4 cm⁻¹ resolution and 50 scans, using KBr pressed disk technique with sample concentration of ~0.5 wt.%.

Texture characteristics were determined by nitrogen adsorption–desorption measurements conducted at a low temperature (77.4 K) with a Sorptomatic 1990 (Thermo Finnigan) apparatus. Specific surface area (S_{BET}) values were calculated according to the BET method from the linear part of the N₂ adsorption isotherms. Mesopore volume (V_{meso}) data were acquired from isotherms adsorption branch by means of the Dollimore-Heal method. Micropore volume (V_{micro}) values were calculated using the Dubinin-Radushkevich method.

Temperature-programmed reduction (TPR) experiments were accomplished using a Thermo Scientific TPRDO1100 system by a 5% H₂/Ar gas mixture at a flow rate of 20 cm³/min and a heating rate of 10 °C/min in the temperature range 50–900 °C. Two TPR approaches were used: (i) normal TPR and (ii) reTPR – TPR after reduction of the samples at 430 °C for 2 h.

‘Dry reduction’ of preliminary dried precursors (110 °C/16 h) was performed in a laboratory set-up with a gas mixture of H₂/N₂ (1/1 v/v), flow rate of 10 L/h, and a heating rate of 1.5 °C/min from 110 to 430 °C and held constant for 5 h to avoid sintering of the reduced metal nickel. After cooling down to room temperature in H₂/N₂ stream, the gas line was switched to argon. Then, the reduced precursors were impregnated with argon-purged paraffin oil to prevent oxidation of metal nickel. Finally, after vacuum filtration of paraffin oil excess, the resulting catalysts (reduced precursor coated with some amount of paraffin oil) were collected.

Partial hydrogenation of commercially available refined edible sunflower oil was performed in a 1000-cm³ jacketed glass reactor Series 5100 (Parr, USA) with a computer coupled with Mass Flow Controller F-201C and Pressure Meter F-502C (Bronkhorst, Netherlands). In all experiments, the conditions were the same: oil mass - 900 g; catalyst concentration - 0.06 wt.% of Ni with respect to oil amount; stirring rate of 1200 rpm; hydrogenation temperature – 160 °C, and H₂ pressure of 0.2 MPa. FA composition of a starting sunflower oil (mol%) was: C16:0 = 7.2; C18:0 = 4.0; C18:1-*cis* = 26.0; C18:1-*trans* = 0.02; C18:2-*cis* = 62.2; C18:2-*trans* = 0.06; C18:3-*cis* = 0.10; C20:0 = 0.22; C22:0 = 0.20. The hydrogenation activity of the catalysts was evaluated by measuring the changes in the Refraction Index (RI) at 50 °C [13] (RX-5000 α ,

Atago) of the starting oil and periodically collected samples of partially hydrogenated oil in conformity with ISO 6320:2017 [14]. The quantity of the consumed hydrogen during the hydrogenation process was determined by post processing through integrating the differential data from the mass flow controller.

FA composition of the starting and partially hydrogenated sunflower oils was quantitatively determined using a Thermo Scientific Trace GC Ultra gas chromatograph equipped with a FID and a TriPlus auto sampler. The triglycerides were first converted into their fatty acid methyl esters (FAME) following the standardised procedure according to AOCS Official Method Ce 2-66 (1997) [15]. Split injection (split ratio of 1:80) of prepared 1 µl FAME was performed with helium as a carrier gas at a flow rate of 0.8 ml/min. The column temperature (fused silica capillary column HP-88, 100 m x 0.25 mm i.d. with a 0.20-µm film thickness, J&W Scientific – Agilent) was maintained at 170 °C for 75 min of analysis time. The injection part and detector temperatures were 240 and 250 °C, respectively.

RESULTS AND DISCUSSION

PXRD patterns of the as-prepared non-Mg doped samples (Fig. 1a) reveal the presence of a single phase that can be attributed to nickel silicate hydroxide (Pecoraite, Ni₃Si₂O₅(OH)₄, ICDD-PDF file 00-049-1859), a nickel analogue of Chrysotile. Chrysotile (Mg₃Si₂O₅(OH)₄), a monoclinic Mg-silicate represents a group of polymorphous minerals of the same chemical composition but different crystal system, namely Lizardite Mg₃Si₂O₅(OH)₄ (hexagonal), Antigorite, Mg₃Si₂O₅(OH)₄ (monoclinic), Pecoraite, Ni₃Si₂O₅(OH)₄ (monoclinic), etc.

The concept of Ni substitution for Mg is an important phenomenon in the structure of nickel-bearing minerals. Having isomorphous substitution because of identical charge and close ionic radii of Ni²⁺ (r = 0.069 nm) and Mg²⁺ (r = 0.072 nm) ions [16] it may be expected that Ni²⁺ ions can readily replace six-coordinated Mg²⁺ entities in hydrous Ni-Mg silicates, such as Nepouite, (Ni,Mg)₃Si₂O₅(OH)₄ (orthorhombic). Nepouite and Pecoraite possess a layered structure that consists of a tetrahedral sheet joined to an octahedral one. In octahedral sites, a complete solid solution is possible between divalent cations of Mg and Ni with a general formula (Mg,Ni)_{3-x}Si₂O₅(OH)₄ [17]. Therefore, the patterns of Mg-doped samples (Fig. 1a) show a simultaneous occurrence of the Pecoraite and Nepouite phases (ICDD-PDF file 00-025-0524). Because of turbostratic structure of the registered phases [18], the

diffraction lines of all XRD patterns were not clearly organised, however, they were better defined with the Mg-doped samples, particularly in MgNi/SIG-A.

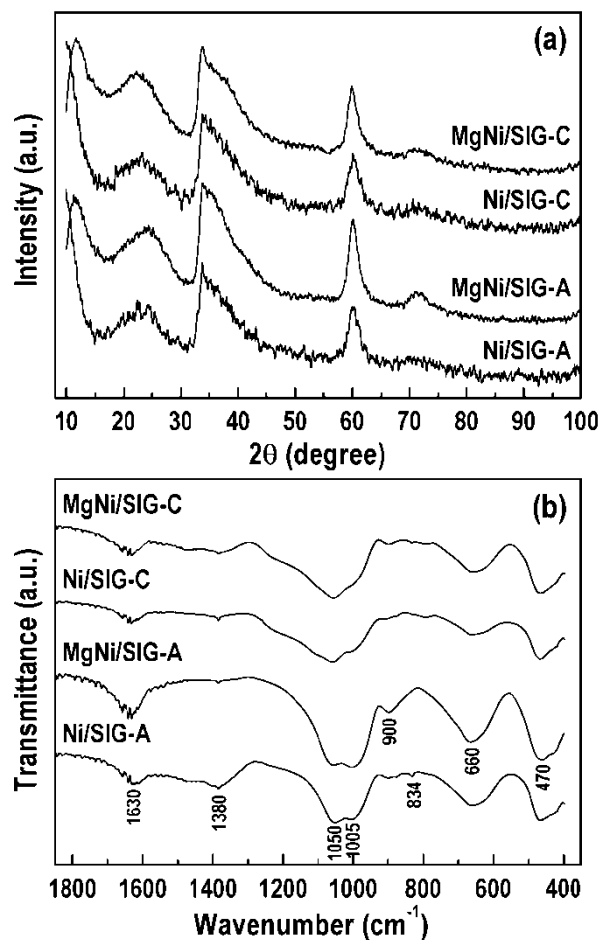


Fig. 1. PXRD patterns (a) and FTIR spectra (b) of the as-prepared precursors.

FTIR spectra of the studied precursors are displayed in the frequency range of 1800–400 cm⁻¹ since variations in the absorption profiles characterising the Ni-O-Si interactions are observed in this region (Fig. 1b). Typical bands of the silica network are absent [10]. A doublet at 1050 and 1005 cm⁻¹, and a band at ~660 cm⁻¹ are related to generated Ni-phyllsilicate structure (-Si-O-Ni-), which covers the surface of the support particles [17,19], formed most significantly in MgNi/SIG-A. A low intensity band at ~900 cm⁻¹ can be ascribed to the stretching vibrations of free Si-OH groups on the solid surfaces. Bands assigned to CO₃²⁻ anions (~1380 cm⁻¹) and to bending vibrations of H₂O molecules at ~1630 cm⁻¹ were also detected [19,20].

Close inspection of the bands gives evidence for creation of different Ni²⁺ species on sample surfaces. A well expressed band at ~1380 cm⁻¹ and a weak one at ~834 cm⁻¹ in the spectrum of Ni/SIG-A are attributed to the presence of a basic nickel

carbonate phase located on the surface of the Ni-phyllsilicate [10,21]. However, these bands were not registered with MgNi/SIG-A thus signifying the formation of a strongly bonded Ni,Mg-phyllsilicate phase.

The effect of Mg modification on the textural properties of the Ni/SIG precursors was investigated by N₂ adsorption–desorption analysis. It has been shown that the SIG-A support is a microporous material with Ib isotherm while the SIG-C support is typically mesoporous with larger mesopores of IV type with H2 hysteresis loop from interconnected network of pores being different in size and shape [9]. Incorporation of Ni leads to a dramatic texture transformation, therefore, the isotherm of Ni/SIG-A (Fig. 2a) is characterised by complicated hysteresis. Registered hysteresis discloses the formation of mesoporous Ni-phyllsilicate phase on the SIG-A microporous surface. Such isotherms are classified as type IIb with type H3 hysteresis generated from aggregates of plate-like particles, which possess non-rigid slit-shaped pores [22]. Mg dopant provokes widening of H3 hysteresis for MgNi/SIG-A as a bimodal porosity is preserved. This view of isotherm confirms generation of a new mesopore system from the Ni,Mg-phyllsilicate phase. The isotherm type of the SIG-C support [9] was preserved in Ni/SIG-C (Fig. 2b) with observation of a step-wise hysteresis character, namely a combination of H2 and H3 at higher and average pressures, respectively. Isotherm type was preserved after incorporation of Mg in the Ni-phyllsilicate structure (MgNi/SIG-C); however, the isotherm position indicates a better filling of SIG-C pores compared to the Mg non-doped Ni/SIG-C sample.

All these observations were confirmed from the texture characteristics of the precursors collected in Table 1, namely S_{BET} for MgNi/SIG-A increased relative to non-doped Ni/SIG-A due to formation of additional micro- and mesoporous system, which is presented by an increase in V_{micro} and V_{meso} .

Table 1. Textural characteristics of the as-prepared precursors

Sample	S_{BET} (m ² /g)	V_{micro} (cm ³ /g)	V_{meso} (cm ³ /g)	d_{aver} (nm)
Ni/SIG-A	269	0.10	0.32	8.8
MgNi/SIG-A	341	0.13	0.35	9.2
Ni/SIG-C	367	0.13	0.46	10.2
MgNi/SIG-C	197	0.07	0.35	15.1

It can be seen that the S_{BET} surface area of MgNi/SIG-C was diminished approximately twice compared to Ni/SIG-C because of a two-fold decrease in V_{micro} as well as a decrease in V_{meso} .

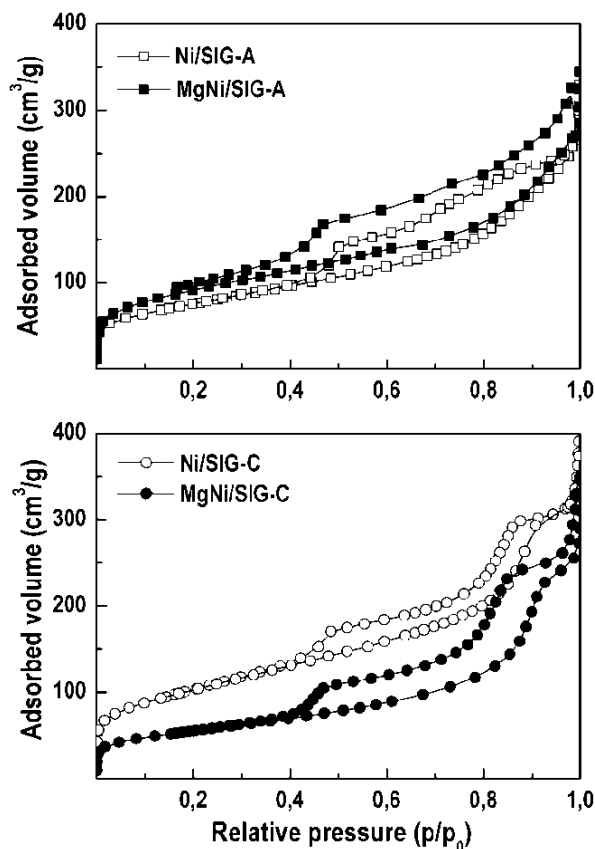


Fig. 2. Adsorption–desorption isotherms of the as-prepared precursors

It is interesting to note that the presence of magnesium provokes enlargement of the average pore diameter (d_{aver}) value to 15.1 nm for MgNi/SIG-C unlike 9.2 nm for MgNi/SIG-A. The explanation of d_{aver} growth in MgNi/SIG-C is illustrated on the differential curves by existence of mesopores having sizes between 15 and 30 nm with two maxima at 18 and 22 nm (Fig. 3). This finding may enable better accessibility of bulky triglyceride molecules to the catalyst surface.

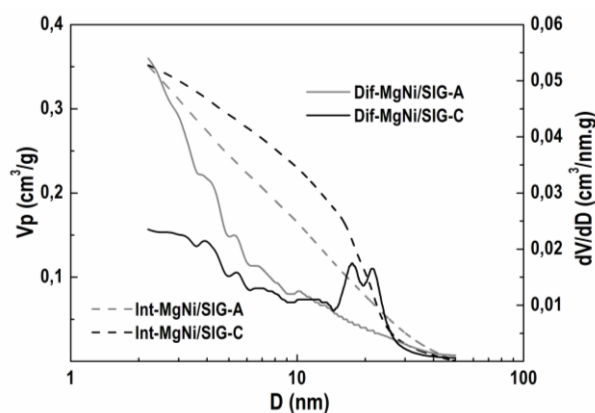


Fig. 3. Integral mesopore curves (Int) and pore size distribution differential curves (Dif) of the Mg-doped precursors.

Pore size distribution (PSD) differential curves (Fig. 3) show a different distribution of pores generated from the created Mg,Ni-phyllsilicate phase. More pores in the range 4–10 nm were recorded for MgNi/SIG-A unlike MgNi/SIG-C, which is in accordance with a higher S_{BET} of MgNi/SIG-A.

Catalyst activity in the sunflower oil hydrogenation was evaluated by measuring the Refraction Index (RI) at 50 °C. Experimental curves expressing the change of crude oil RI (1.46365) as a function of hydrogenation time are displayed in Figure 4. Collected information discloses that the catalysts hydrogenate the oil to different RI levels, consume diverse amount of hydrogen, and need different reaction time. Diminution of the crude oil RI value at the end of the hydrogenation reaction follows the order: MgNi/SIG-C (1.45495) > MgNi/SIG-A (1.45582) > Ni/SIG-A (1.45674) > Ni/SIG-C (1.45783), which corresponds to the quantity of consumed hydrogen (cm³), namely: MgNi/SIG-C (61395) > MgNi/SIG-A (54868) > Ni/SIG-A (48013) > Ni/SIG-C (40632).

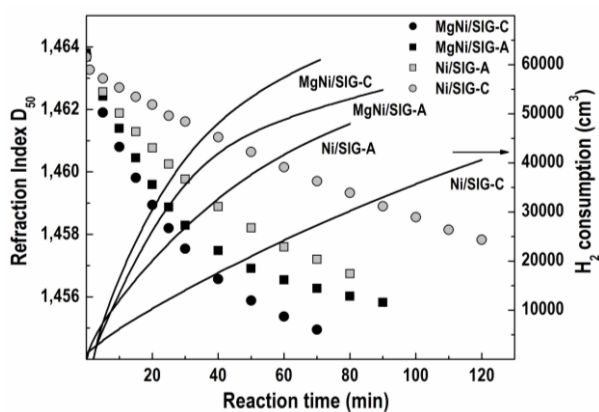


Fig. 4. Changes of RI value and amount of consumed hydrogen vs. reaction time.

Hydrogen consumption of the Ni/SIG-A, MgNi/SIG-A, and MgNi/SIG-C catalysts after 70 minutes of hydrogenation reveals higher values by 1.65, 1.87, and 2.23 times, respectively, with reference to the most inactive Ni/SIG-C catalyst. The data point out a higher activity of the Mg-doped catalysts and show the dominant behaviour of MgNi/SIG-C.

As reported in own papers [9,10,23], differences in hydrogenation activity of non-Mg doped catalysts are ascribed to texture parameters of the carriers which induce creation of two types of Ni²⁺ species in the precursors: Ni-phyllsilicate situated in the pores of the supports and basic carbonate-like nickel located on the Ni-phyllsilicate surface [9]. Such an effect leads to a diverse coordination level of the Ni²⁺ ions by the surface oxygen atoms resulting in different Ni-O and Ni-O-Si bond strength, and

hence, different reducibility [10]. Thus, a lower activity of the Ni/SIG-C catalyst was attributed to hardly reducible or non-reducible Ni²⁺ species from the Ni-phyllsilicate phase and to the catalyst pore system, which does not favour accessibility of the reactant molecules to the active Ni⁰ sites. A higher activity of the Ni/SIG-A catalyst was attributed to facilitated reduction of the Ni²⁺ species at 430 °C and to creation of adequate number of accessible Ni⁰ active sites on the catalyst surface. Obviously, the SIG-A support (microporous-type) contributes to the formation of readily reducible Ni²⁺ species from the basic nickel carbonate-type phases, which after reduction at 430 °C generate a sufficient number of accessible Ni⁰ active sites on the catalyst surface.

A possible understanding of the demonstrated activity of the Mg-containing catalysts could be found in TPR experiments accomplished by two consecutive procedures: normal TPR and TPR after reduction of the samples at 430 °C for 2 h denoted as ReTPR. The former procedure with MgNi/SIG-A precursor resulted in a symmetric profile with a temperature maximum T_{max} at 445 °C as well as a high-temperature shoulder at ~600 °C (Fig. 5).

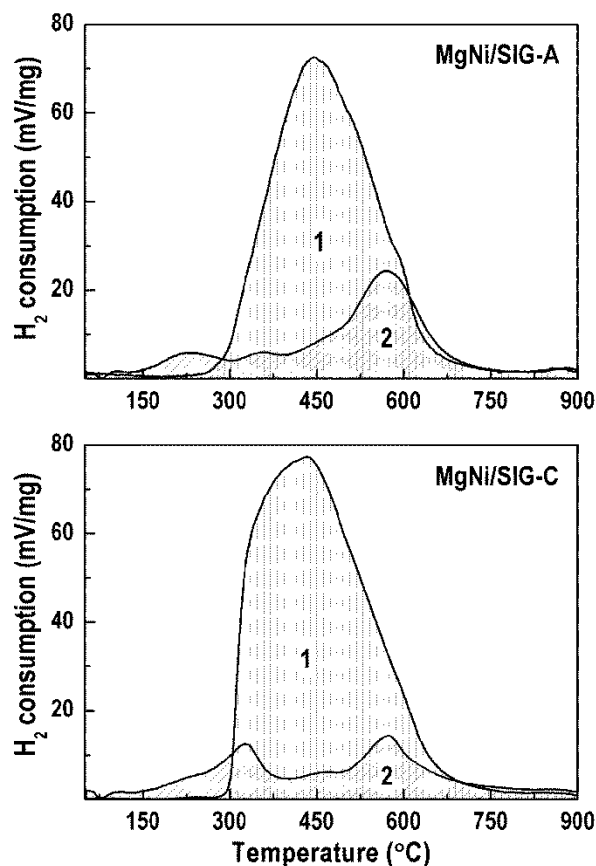


Fig. 5. Normal TPR (1) and ReTPR (2) profiles of the Mg-doped precursors.

The normal TPR profile of MgNi/SIG-C is asymmetric and displayed a well-resolved T_{max} at

430 °C and a negligible high-temperature shoulder also at ~600 °C. Calculated total peak area of both precursors showed higher reducibility of the Ni²⁺ species in MgNi/SIG-C by 17.1% compared to MgNi/SIG-A. Considering that chemical analysis of the precursors confirmed a similar concentration of Ni²⁺ for both samples, a likely interpretation is the existence of hardly reducible Ni²⁺ species in MgNi/SIG-A.

The aim of the ReTPR procedure was to indicate catalyst status after reduction at 430 °C for 2 h, namely the presence of unreducible or hardly reducible species, and their quantity, etc. Actually, ReTPR profiles propose a facilitated reduction of the Ni²⁺ species in MgNi/SIG-C up to 430 °C. A smaller area of the ReTPR curve signifies a lesser amount of unreducible species. This phenomenon specifies higher reducibility efficiency in first run (up to 430 °C) and a greater quantity of readily reducible species. Calculations showed that only 11.8% of the Ni²⁺ species in MgNi/SIG-C precursor remained unreduced vs. 26.1% for MgNi/SIG-A. Bearing in mind that the final catalyst was obtained after reduction also at 430 °C, it is correct to assume that the higher MgNi/SIG-C activity originates from a higher amount of metal Ni⁰ particles generated during reduction.

It is worth noting that the higher hydrogenation activity of MgNi/SIG-C can be related not only to the presence of a larger number of Ni⁰ active sites on the catalyst surface but also to a larger average pore diameter of the MgNi/SIG-C precursor compared to MgNi/SIG-A (Table 1). A larger pore diameter permits a faster diffusion rate of the reactant molecules through the pore system of the catalyst reflecting on a higher reaction rate. In addition, the polydisperse character of the PSD in the whole mesoporous region for the MgNi/SIG-C precursor (Fig. 3) may further contribute to a faster rate of the reaction and a higher hydrogenation activity. Moreover, a twofold smaller amount of micropores (V_{micro}) with MgNi/SIG-C than MgNi/SIG-A (Table 1) may also affect hydrogenation effectiveness. According to Balakos and Hernandez [2], micropores inhibit the participation of triglyceride molecules in the reaction because of limited access to the active sites. In addition to the diffusion limitations due to the presence of micropore system, which does not contribute to reaction progress, the lower activity of the MgNi/SIG-A catalyst is explained by existence of hardly reducible Ni²⁺ species, which was evidenced by the TPR and ReTPR results.

The different activity of the catalysts reflects on the different FA profiles and different FA composi-

tions obtained during hydrogenation (Fig. 6). The hydrogenation of linolenic acid (C18:3*cis*) was not considered due to its low initial concentration in the sunflower oil (0.1%)

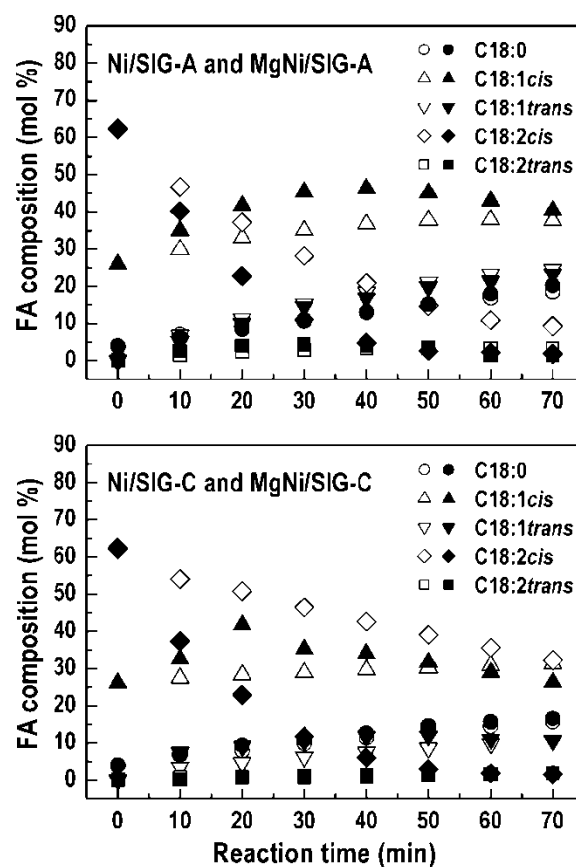


Fig. 6. FA composition obtained during hydrogenation over non-doped catalysts (open symbols) and Mg-doped catalyst (closed symbols).

The overall vegetable oil hydrogenation includes consecutive saturation of linolenic acid (C18:3*cis*) to linoleic acid (C18:2*cis*), then to oleic acid (C18:1*cis*), and finally to stearic acid (C18:0). Except increasing the hydrogenation activity, a goal of this study was to decrease linolenic acid (C18:3*cis*) and linoleic acid (C18:2*cis*) FA contents. From this point of view, FA compositions obtained after 70 min of hydrogenation (end-point of the reaction over the MgNi/SIG-C catalyst) demonstrated a decrease of the linoleic acid C18:2*cis* (mol%) in the order: 1.4 (MgNi/SIG-C) < 1.9 (MgNi/SIG-A) < 9.4 (Ni/SIG-A) << 32.2 (Ni/SIG-C) (Fig. 6). Apparently, modification of the Ni/SIG systems by Mg increases the conversion of C18:2*cis* FA. The results give evidence for a high selectivity of the MgNi/SIG-C catalyst to C18:1*cis*, hydrogenation being almost complete. This finding could be explained by much faster diffusion of the triglyceride molecules through the pores. It is well known that linoleic acid, C18:2*cis*, is one of the essential

fatty acids. Small amounts are sufficient for human nutrition and allowable in the edible hydrogenated oils.

As mentioned above, along with saturation of the double bonds during hydrogenation, two reversible reactions of *cis*-FA to *trans*-FA isomerisation take place: linoleic (C18:2*cis*) → (C18:2*trans*) and oleic (C18:1*cis*) → (C18:1*trans*), which lead to a broad product distribution [1,3]. Due to increasing concern about the negative effect of *trans*-FA on human health, it is desirable to reduce the formation of *trans*-FA isomers [24] and significantly impede stearic acid FA C18:0 formation in the hydrogenated vegetable oil. The latter is better exhibited by the MgNi/SIG-A catalyst than MgNi/SIG-C (Figure 6) and is therefore a promising feature.

Concerning the content of all C18*trans* FA isomers, the MgNi/SIG-C catalyst demonstrated a lower value by 46% than MgNi/SIG-A under the same operating conditions and for the same activity. In this case, the activity was compared for approximately the same value of H₂ consumption, namely: 41 900 cm³ for MgNi/SIG-A reached for 40 min and 40 723 cm³ for MgNi/SIG-C reached for 30 min. The content of all C18*trans* with MgNi/SIG-A for 40 min was 20.78 mol.%, whereas MgNi/SIG-C manifested 11.22 mol.% for 30 min. It is known that the *trans*-isomers are formed when the triglyceride desorbs from the catalyst surface without being hydrogenated [2]. The increase of *trans*-FA amount with the MgNi/SIG-A catalyst could be explained by mass-transfer limitations due to twofold higher microporosity as compared to MgNi/SIG-C (Table 1). Veldsink et al. [3] who stated that an increase of *trans*-isomer content might be caused by pore diffusion resistance sustained this standpoint.

It was testified that modifying the electronic density of the metallic phase may alter the adsorption-desorption strength of reactants and/or products [7,25]. A lower amount of C18:1*trans* FA isomers formed by the MgNi/SIG-C catalyst relative to the MgNi/SIG-A catalyst can be interpreted also in terms of a greater number of Ni⁰ sites on the catalyst surface, which leads to higher electron density of Ni because of an electron transfer from the basic Mg promotor. The increase in electron density of nickel induces a weak interaction of the adsorbed and hydrogenated molecules, and makes easier their desorption to minimise the transformation from *cis*- to *trans*-FA isomers [7,25].

It may be summarised that Mg-doping has a measurable impact on the characteristics of the catalysts affecting the hydrogenation activity as well as the quality of the hydrogenated products.

CONCLUSIONS

Results obtained in this study reveal that both the application of silica gels of different texture parameters and magnesium addition results in catalysts of different hydrogenation activity and variation in fatty acid composition of the reaction products.

A considerable effect of magnesium dopant was established on the reducibility of Ni²⁺ ions from MgNi/SIG-C precursor thus contributing to a greater quantity of readily reducible Ni²⁺ species and generating a sufficient number of accessible metal nickel active sites on the catalyst surface through applied reduction procedure.

The role of the magnesium on catalyst performance in sunflower oil hydrogenation was clearly demonstrated by the MgNi/SIG-C catalyst. A dominant activity and lower amount of formed C18*trans* isomers could be attributed to formation of suitable catalyst mesoporosity, thereby, restricting diffusion effects.

In conclusion, Mg-doping of Ni/SIG-C is promising for use to obtain an efficient edible vegetable oil hydrogenation catalyst of high activity, high saturation value of linoleic (C18:2*cis*) acid, and moderate amounts of C18:1*trans* and C18:0 stearin FA in partially hydrogenated sunflower oil

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ПОДОБРЕНО КАТАЛИТИЧНО ПОВЕДЕНИЕ НА Ni/SiO₂ ПРИ ХИДРОГЕНИРАНЕ НА РАСТИТЕЛНИ МАСЛА: ВЛИЯНИЕ НА ДОБАВКАТА ОТ Mg

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(Резюме)

Изследвани са Ni-Mg/SiO₂ катализатори за хидрогениране на слънчогледово масло за хранителни цели, получени чрез съутаяване на прекурсори върху носители от търговски силикагели с различни текстурни характеристики - SIG-A (микропорест тип) и SIG-C (мезопорест тип). Установено е, че двата фактора – текстурните параметри на силикагелите и добавката от магнезий – водят до получаване на катализатори с различна хидрогенираща активност и различен състав на масните киселини в реакционните продукти. Получените резултати разкриват висока хидрогенираща активност на Ni-Mg/SiO₂-C катализатор като резултат от по-голямо количество и достъпност на метални никелови частици в катализатора, образувани с процедурата на редукция. По-високата активност на MgNi/SiO₂-C катализатор може да се отдаде на неговата мезопорестост, благодарение на която се избягват дифузионните ограничения. Добавката от Mg подобрява качествата на прекурсора Ni-Mg/SiO₂-C за получаване на ефективен катализатор за хидрогениране на растителни масла за хранителни цели с висока активност, висока степен на насищане на линоловата киселина (C18:2_{cis}) и присъствие на умерени количества от олеинова (C18:1_{trans}) и стеаринова (C18:0) киселини в частично хидрогенираното слънчогледово масло.