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XPS STUDY OF THE NICKEL OXIDATION STATE IN THE REDUCED (Ag)NiMg/SiO₂ VEGETABLE OIL HYDROGENATION CATALYSTS

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Abstract

Two series of (Ag)NiMg/SiO₂ catalysts are synthesized on SiO₂ support derived from two silica sources: diatomite activated at 800°C (Series **a**; Mg/Ni=0.1 and SiO₂/Ni=1.07) and synthetic water glass (Series **b**; Mg/Ni=0.1 and SiO₂/Ni=1.15). The modification with silver is made at three molar Ag/Ni ratios, namely 0.0025, 0.025 and 0.1.

The effect of the source of SiO₂ support as well as of the Ag presence and content on the nickel oxidation state in the co-precipitated (Ag)NiMg/SiO₂ catalysts after reduction-passivation procedure are studied by XPS.

The peak-fitting of the composite Ni2p level confirms that nickel on the surface is presented in Ni⁰ and Ni²⁺ oxidation states. The higher content of Ni⁰ on the surface of the diatomite supported catalysts shows that the metallic nickel is more stable to oxidation in comparison of the water glass supported ones.

Introduction

Nickel supported on a SiO₂ carrier is the most commonly used catalyst for hydrogenation of vegetable oils. It has been published that Ni-Mg catalysts, supported on SiO₂ derived from two siliceous sources, either diatomite or water glass, demonstrate both high soybean oil hydrogenation activity and high quantity of detrimental *trans* fatty acids (TFAs) production [1]. According to our data, the addition of Ag to the nickel/diatomite catalyst suppresses the TFAs formation in the hydrogenated products [2].

It is known that the metallic Ni is the active component in the vegetable oil hydrogenation catalysts. The X-ray photoelectron spectroscopy (XPS) supply useful information about the changes in the oxidation state of the components on the catalyst surface.

It presents some interest to study the effect of the source of SiO₂ support as well as of the silver presence and content on the nickel oxidation state in (Ag)NiMg/SiO₂ catalysts after reduction-passivation procedure. The last procedure is applied with purpose to monitor the stability of surface metallic Ni to oxidation.

Experimental

Sample preparation

(Ag)NiMg samples were synthesized on two silica sources of SiO₂ support: diatomite activated at 800°C (Series **a**; Mg/Ni=0.1 and SiO₂/Ni=1.07) and synthetic water glass (Series **b**; Mg/Ni=0.1 and SiO₂/Ni=1.15). Co-precipitation of corresponding metal nitrates with Na₂CO₃ at 90°C and pH=10.00±0.05 was applied. The modification with silver is made at three molar Ag/Ni ratios, namely 0.0025, 0.025 and 0.1. These ratios are noted as a number at the sample denotation. The both Ag free samples are marked by zero (AgNiD-0 and AgNiWG-0).

The reduction-passivation procedure was performed by: (i) dry reduction at 430°C for 5 h with a H₂:Ar (1:1) gas mixture; (ii) cooling down to room temperature in the same gas mixture; (iii) passivation of the reduced precursors with a mixture of 350 ppm O₂/N₂ at room temperature.

Sample Characterization

The electronic properties of the reduced precursors were investigated by X-ray photoelectron spectroscopy (XPS). The measurements were performed in a VG ESCALAB II electron spectrometer using AlK_α radiation with energy of 1486.6 eV. The binding energies (BE) were determined with an accuracy of ± 0.1 eV utilizing the C1s line at 285.0 eV (from an adventitious carbon) as a reference. The composition and chemical surrounding of the films were investigated on the basis of the areas and binding energies of C1s, O1s, Ni2p_{3/2}, Ag3d, Mg2p and Si2p photoelectron peaks (after linear subtraction of the background) and Scofield's photoionization cross-sections.

Results and Discussion

The general view of the Ni2p level evidences two types of the nickel oxidation states. The binding energy (BE) values Ni2p_{3/2} peak reveal that nickel is present as Ni²⁺ oxidation state in all reduced samples in the range of 855.4–857.1 eV for Series **a** and 855.4–856.7 eV for Series **b**. These values characterize Ni²⁺ state in Ni-O species. The asymmetry of the main Ni2p_{3/2} peak towards lower binding energy values presumes the presence of Ni⁰ oxidation state (BE=853 eV). This oxidation state is supported by X-ray diffraction and magnetic susceptibility data.

Table 1. XPS data of the (Ag)NiMg/D samples (Series **a**)

Sample	Ni2p _{3/2} binding energy (eV)		Nickel oxidation state contribution (%)		Ni ⁰ /Ni ²⁺ ratio
	Ni ⁰	Ni ²⁺	Ni ⁰	Ni ²⁺	
AgNiD-0	853.5	856.6	5.6	94.4	0.059
AgNiD-0.0025	852.2	854.8	6.5	93.5	0.070
AgNiD-0.025	851.9	855.2	11.0	89.0	0.124
AgNiD-0.1	853.5	856.7	13.9	86.1	0.161

The peak-fitting of the composite Ni2p level (Tables 1, 2) confirms that nickel on the surface is presented in Ni⁰ and Ni²⁺ oxidation states. The obtained data manifest that Ni⁰ contribution of the samples on diatomite support (Table 1) changes within a wider range of 5.6–13.9 %, while its contribution in the samples on water glass support varies in the 3.6–6.3 % range (Table 2). The silver presence and content increase the Ni⁰ oxidation state contribution on the (Ag)NiMg/D samples. On contrary, this effect is not clearly pronounced in the (Ag)NiMg/WG samples.

Table 2. XPS data of the (Ag)NiMg/WG samples (Series b)

Sample	Ni2p _{3/2} binding energy (eV)		Nickel oxidation state contribution (%)		Ni ⁰ /Ni ²⁺ ratio
	Ni ⁰	Ni ²⁺	Ni ⁰	Ni ²⁺	
AgNiWG-0	853.6	856.6	3.6	96.4	0.037
AgNiWG-0.0025	852.5	855.0	6.1	93.9	0.065
AgNiWG-0.025	852.8	856.0	4.5	95.5	0.047
AgNiWG-0.1	852.3	854.9	6.3	93.7	0.067

The higher content of Ni⁰ on the surface has been demonstrated by diatomite supported samples, where the metallic Ni crystallites possess larger size (chemisorption data). Obviously, the lower dispersed Ni⁰ particles are more stable to oxidation. On contrary, the higher dispersed Ni⁰ particles on water glass are more susceptible to oxidation.

Conclusions

In conclusion, the source of SiO₂ support as well as of the silver presence and content affect the nickel oxidation state. The surface metallic Ni on (Ag)NiMg/diatomite catalysts is more stable to oxidation.

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