



PHYSICAL CHEMISTRY 2016

*13th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry*

*Proceedings
Volume I*

BELGRADE
September 26-30, 2016

ISBN 978-86-82475-34-7

Title: Physical Chemistry 2016 (Proceedings)

Editors: Željko Čupić and Slobodan Anić

Published by: Society of Physical Chemists of Serbia, Studentski trg 12-16, 11158, Belgrade, Serbia.

Publisher: Society of Physical Chemists of Serbia

For Publisher: S. Anić, President of Society of Physical Chemists of Serbia

Printed by: "Jovan", Printing and Publishing Company; 200 Copies.

Number of pages: 6+502; Format B5; printing finished in September 2016

Text and Layout: "Jovan"

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C - Kinetics, Catalysis

EFFECT OF NICKEL SALTS ON THE DISPERSION OF NICKEL AND REDUCIBILITY OF SUPPORTED Ni-Mg CATALYST PRECURSORS PREPARED BY PRECIPITATION-DEPOSITION

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ABSTRACT

Diatomite supported Ni-Mg catalyst precursors (Ni-Mg/D) with a constant Ni/Mg ratio, prepared by the precipitation-deposition method using different nickel salts, sulfamate, nitrate, chloride, acetate or formate, were studied by hydrogen chemisorptions and temperature programmed reduction (H₂-TPR). The results showed that the dispersion of nickel and the reducibility of the prepared catalyst precursors were different depending upon the counter ion of nickel salt. Among the studied nickel salts, the best results for the dispersion of metallic Ni and reducibility of Ni-Mg/D catalyst precursors were achieved using nickel sulfamate salt.

INTRODUCTION

The common procedure for the preparation of supported nickel catalysts requires different successive operations: (i) introduction of suitable nickel salt on the support by the appropriate preparative method, (ii) drying, and (iii) reduction. Precipitation-deposition (PD) is the simplest method of preparation for supported catalysts with high nickel loading. Although this method allows a homogeneous distribution of nickel salt on the support, the best dispersion of nickel does not achieve due to its high loading in the catalyst.

In the hydrogenation processes, a catalyst with high activity and selectivity is required. To meet these requirements, the catalyst support should provide sufficient surface area for the metal to disperse, and there must be an adequate metal-support interaction. The nickel phase on different support surfaces exhibits different extents of metal-support effects. The

metal-support interaction is generally affected by the identity of the nickel salt and the thermal treatment reduction procedure used in preparation. This implies that the surface properties of a catalyst could be changed by the nature of the supported Ni phase, thus acquiring different characteristics and exhibiting different performances toward activity and selectivity.

In this paper, Ni dispersion and reducibility in Ni-Mg/D hydrogenation catalyst precursors, prepared according to the same preparation procedure using different Ni salts, were studied by H₂-chemisorption and H₂-TPR to elucidate the effect of nickel salt on the studied characteristics.

EXPERIMENTAL

Diatomite supported Ni-Mg catalyst precursors were prepared by the PD method, using five different nickel salts: nickel(II) sulfate, nickel(II) nitrate, nickel(II) chloride, nickel(II) acetate or nickel(II) formate. The catalyst precursors derived from these Ni salts were designated as follows: NiS-Mg/D, NiN-Mg/D, NiC-Mg/D, NiA-Mg/D and NiF-Mg/D. A detailed description of the preparation procedure of studied catalyst precursors was given in our previous paper [1].

Hydrogen chemisorption - Pretreatment procedure: The first step was cleaning the gas line with argon. The second step is pretreatment with 4.9% H₂/Ar (flow: 20 cm³ min⁻¹; heating rate: 2 °C min⁻¹) at 430 °C. Finally, temperature programmed desorption at 425 °C is carried out with argon.

Analysis: After pretreatment, the catalyst precursor sample was subjected to a known number of calibrated pulses of pure H₂ at 45 °C.

Temperature programmed reduction - H₂-TPR runs were performed with 4.9 vol% hydrogen in argon (flow: 20 cm³ min⁻¹; heating rate: 2 °C min⁻¹), the hydrogen consumption was measured by thermal conductivity detector (TCD) in temperature range 50-900 °C. TPR profiles were normalized to the same catalyst precursor mass.

Hydrogen chemisorption and temperature programmed reduction (H₂-TPR) measurements were performed in an automatic apparatus Thermo Scientific TPDRO 1100.

RESULTS AND DISCUSSION

H₂ chemisorption results

Nickel loading, BET surface area, and nickel phase characteristics obtained from H₂-chemisorption data are given in Table 1. The chemisorption results show that the nickel phase characteristics are affected by the counter ion of the Ni salt. From the data presented in Table 1, all prepared catalyst precursors can be divided in two groups: group A containing the catalyst precursors having acceptable dispersion characteristics (NiS-Mg/D, NiN-

Mg/D and NiC-Mg/D), and group B with the catalyst precursors having poor dispersion features (NiA-Mg/D and NiF-Mg/D).

Generally, under the selected experimental conditions for all prepared

Table 1. Nickel loading, BET surface area and H₂-chemisorption data

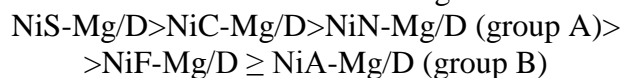
Catalyst precursors			Nickel phase characteristics (Ni ⁰)				
Designation	Ni ^a wt%	S _{BET} ^b m ² g ⁻¹	H ₂ uptake ^c μmol g _{cat p} ⁻¹	S _{Ni} ^d m _{Ni} ² g _{Ni} ⁻¹	Ni _{mpd} ^e nm	Ni _s × 10 ⁻²³ g At _{Ni acc} g _{cat p} ⁻¹	D ^h %
NiS-Mg/D	34.99	255	161.7	36.2	18.6	1.95	5.4
NiN-Mg/D	36.32	224	132.7	28.6	23.6	1.60	4.3
NiC-Mg/D	36.20	208	158.3	34.2	19.7	1.91	5.1
NiA-Mg/D	36.64	223	94.8	20.3	33.3	1.14	3.0
NiF-Mg/D	36.57	177	89.1	19.1	35.3	1.07	2.9

^a Determined gravimetrically; ^b N₂-physisorption; ^c Hydrogen chemisorbed; ^d Nickel surface area; ^e Mean particle diameter of nickel (spheres) assuming stoichiometry H/Ni_s=1; ^hNumber of accessible nickel atoms; ^hDispersion degree.

catalyst precursors, a low Ni dispersion was achieved. It is more likely that the main reason is the high nickel loading of prepared catalyst precursors [2]. A good agreement between the BET surface areas of catalyst precursors and active metal surface areas of metallic nickel phase suggests that larger total surface areas allow better distribution of metallic nickel phase.

H₂-TRP results

The TPR profiles of catalyst precursors, including the deconvolution curves, are shown in Fig. 1. It is very complicated to attribute the reduction peaks to the transformation of corresponding nickel(II) phases by analyzing the reduction profiles. It is more likely that different extents of metal-support are responsible for the complicated profiles. A peak due to the reduction of the Ni²⁺ phase, which corresponds to the basic nickel carbonate (BNC) decomposition, was seen only in the catalyst precursors of group A (Fig. 1a). Among the prepared catalyst precursors, the relative content of Ni²⁺ phase from BNC decreased in the following order:



The stronger interaction of Ni²⁺ phase with support hinders the reduction of catalyst precursors. This leads to a shift in the T_{max} value of peaks corresponding to the reduction of Ni²⁺ phases interacting with the support from 320 °C over NiS-Mg/D catalyst precursor to 462 °C over NiA-Mg/D catalyst precursor (Fig. 1a and b). From TPR study, it can be concluded that

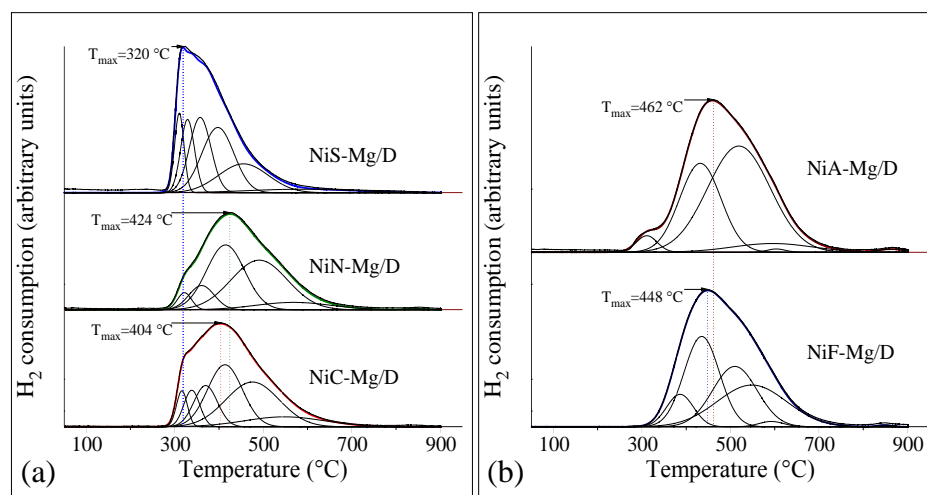


Figure 1. TPR profiles of prepared Ni-Mg/D catalyst precursors

two kinds of Ni^{2+} phase were observed on the diatomite support, one in which Ni^{2+} interacts with support and the other as Ni^{2+} (BNC) with no or very weak metal-support interaction.

CONCLUSION

H_2 -chemisorption and H_2 -TPR characterization methods were utilized for determining metallic nickel phase characteristics and reducibility of prepared diatomite supported Ni-Mg hydrogenation catalyst precursors by precipitation-deposition using different nickel salts. The chemisorption results showed that the metallic Ni phase properties in the catalyst precursors are affected by the counter ion of nickel salt. The TPR study revealed that the reduction features depend on the nature of nickel salt and its interaction with the support. An order of the nickel salts effect on the reducibility of catalyst precursors was established.

Acknowledgement

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project III 45001).

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