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PHYSICAL CHEMISTRY 2014

12th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

The Conference is dedicated to the
25. Anniversary of the Society of Physical Chemists of Serbia

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September 22-26, 2014
Belgrade, Serbia

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Volume I

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Fundamental and Applied Aspects of
Physical Chemistry

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with

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PREPARATION OF Ni/DIATOMITE HYDROGENATION CATALYST PRECURSORS: EFFECT OF COUNTER IONS ON TEXTURAL CHARACTERISTICS

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ABSTRACT

Diatomite supported nickel catalyst precursors (Ni/D) were prepared by the precipitation-deposition (PD) method using different nickel salts such as nitrate, chloride, acetate and formate. The effect of counter ions (NO_3^-, Cl^-, CH_3COO^-, and $HCOO^-$) on the texture of prepared samples was studied. For determination of the textural characteristics mercury intrusion porosimetry (MIP) and N_2 physisorption techniques were used. MIP and physisorption data (pore volume, pore size distribution, porosity as well as N_2 adsorption-desorption isotherms and BET surface area) showed that counter ions were found to have a profound effect on the microstructure and porosity characteristics of Ni/D precursors. An order of the counter ions effect on the textural characteristics of prepared precursors was determined.

INTRODUCTION

High loading silica supported nickel catalysts are used extensively in processes of edible oils hydrogenations. These catalysts are often prepared by Ni ion deposition from aqueous solutions onto proper support, followed by a suitable thermal activation procedure corresponding to reduction step.

The nature of deposition method and the choice of precursor complex control the formation of isolated supported phases (nickel basic carbonate) or of supported intermediate phases (nickel hydrosilicates). The hydrogenation activity of the catalysts depends not only on the distribution of nickel as basic carbonate and silicate, but also on the accessibility of free metal surface area in suitable pore dimension [1]. The pore structure of supported catalyst controls transport phenomena and governs selectivity in edible oils hydrogenations.

The choice of nickel precursor salt, in other terms, the choice of the counter ions accompanying Ni cation, is crucial as it governs the solubility of salt and its ability to decompose during reduction. In the following activation step the precursor must be fully transformed into metal particles without leaving side species that may modify the properties of the support. For transition metals nitrate, chloride and sulfate anions are generally selected as counter ions, due to their commercial availability and low price.
The aim of this work was to prepare Ni/D catalyst precursors by DP method with well developed textural parameters. The effect of four Ni salts containing NO_3^-, Cl^-, CH_3COO^-, and $HCOO^-$ anions on the textural characteristics of catalyst precursors was examined.

EXPERIMENTAL

Catalyst precursors were prepared using PD method. Precipitation of nickel was performed by addition of anhydrous sodium carbonate (Na_2CO_3) to a solution containing corresponding nickel salt and magnesium nitrate. The deposition of formed Ni-precipitates onto diatomite support (D) was carried out by addition of hot aqueous suspension of D to slurry containing Ni-precipitates. The same preparation procedure was employed for all the samples. Afterwards, the samples were aged, filtered, washed and finally dried at 110°C overnight. The resultant pale green materials were used as catalyst precursor samples. The sample code, Ni content and yield of the samples as well as preparation procedure are summarized in Table 1.

Table 1. Ni content, yield and PD procedure used to obtain Ni/D samples

Sample				PD procedure				
Code[a]	$Ni_{content}$[b] /wt%	Yield /g	Ni salt[c]	Ni/SiO_2[d] /molmol^{-1}	Ni/Mg /molmol^{-1}	T_P[e] /°C	T_A[f] /°C	t_A[g] /h
Ni-N/D	36.3	7.89	[1]$Ni(NO_3)_2$	1.00	10	90	90	1
Ni-Cl/D	36.2	8.26	[2]$NiCl_2$	1.00	10	90	90	1
Ni-Ac/D	36.6	7.99	[3]$Ni(CH_3COO)_2$	1.00	10	90	90	1
Ni-F/D	36.6	7.96	[4]$Ni(HCOO)_2$	1.00	10	90	90	1

[a] N: nitrate, Cl: chloride, Ac: acetate, F: formate; [b] Ni content was determined gravimetrically with dimethylglyoxime; [c 1] Carlo Erba reagents min. assay: 99%, For analysis; [c 2] Carlo Erba reagents min. assay: 98%, For analysis; [c 3] Alfa Aesar: 99+%; [c 4] Alfa Aesar: CAS 3349-06-2; [d] SiO_2 content in diatomite was: 97.9wt%; [e] Precipitation temperature; [f] Aging temperature; [g] Aging time.

Mercury porosimetry was performed on a Porosimeter Model 2000 equipped with the Macropore unit Model 120 manufactured by Carlo Erba. Nitrogen adsorption-desorption isotherms were measured at -196°C on a Sorptomatic 1990 (Thermo Finnigan) after the sample had been degased at 110°C for 16 h.

RESULTS AND DISCUSSION

Porosimetry Results

Table 2 presents MIP data for prepared precursor samples and diatomite support. The intrusion curves of all precursors, which correspond to cumulative pore volume of the precursors and histograms of the chosen precursors Ni-N/D and Ni-F/D, are presented in Fig. 1. The histograms are used to elucidate distribution of pore sizes in a selected range.

Table 2. Summary of MIP data (macro- and mesoscale pore sizes)

Sample	V_{cum}[a] /cm^3g^{-1}	$D_{average}$[b] /nm	d_b[c] /gcm^{-3}	P[d] /%
Ni-N/D	0.391	220	1.19	47
Ni-Cl/D	0.246	220	1.39	34
Ni-Ac/D	0.228	272	1.48	33
Ni-F/D	0.118	74	1.72	20
D[e]	1.018	692	0.65	66

[a]Cumulative pore volume; [b]Average pore diameter; [c]Bulk density; [d]Total porosity; [e] D support.

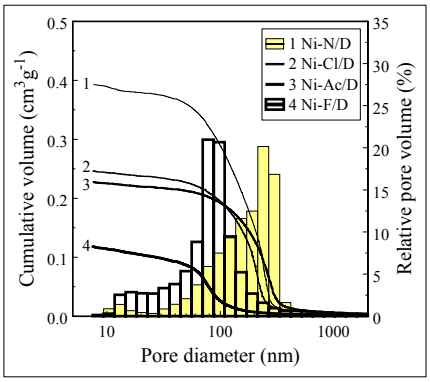

Figure. 1. Pore size distribution (PSD) cumulative and histograms

Significant differences are observed. Sample Ni-N/D shows a much larger cumulative intrusion volume with pores distributed in a pattern resembling a monomodal structure. This sample is very porous (total porosity: 47%, Table 2), with a large percentage (59 vol%) of pores in the 130-320 nm range. In the sample obtained from formate (Ni-F/D), it is obvious an overall decrease in cumulative intrusion volume and a significant reduction in percentage of large pores. In comparison with the support, precursors exhibit reduced porosity and cumulative intrusion volume (Table 2). This is consistent with predictions made for samples with high Ni content (Table 1) that are expected to contain filled pores and reduced pore volumes.

N_2 Physisorption Results In order to obtain porous parameters including specific surface area and pore volume in meso- and microscale pore sizes, N_2 adsorption-desorption isotherms were measured using liquid N_2 (-196°C). Fig. 2 compares the isotherm curves for the diatomite support and samples prepared with the highest (Ni-N/D) and the lowest (Ni-F/D) specific surface area. Values of the specific surface area (BET method), mesopore surface area (t-plot de Boer-Lippens method), micropore volume (Dubinin and Raduskevich method) and total pore volume at $P/P_0 = 0.98$ are listed in Table 3.

As can be seen from Fig. 2, the isotherms of the samples Ni-N/D and Ni-F/D cannot be classified as typical although they mostly resemble type II according to IUPAC classification. Isotherms for the precursors Ni-Cl/D and Ni-Ac/D (not shown) are very similar in shape to those that are shown in Fig. 2. A distinct increase in nitrogen volume in the low P/P_0 region indicates the presence of micropores associated with mesopores. The amount of nitrogen adsorbed increases gradually and hysteresis loops are observed when $P/P_0 > 0.42$, indicating the existence of many meso- and macropores in the precursor samples as determined also by the results of porosimetry studies. Specific surface area (S_{BET}) was greatly enhanced after deposition Ni-precipitates onto diatomite support increasing in the following order Ni-N/D ≥ Ni-Ac/D > Ni-Cl/D > Ni-F/D >> D, as shown in (Table 3).

Table 3. Summary of N_2 physisorption data (meso- and microscale pore sizes)

Sample	S_{BET}[a] /m^2g^{-1}	S_{meso}[b] /m^2g^{-1}	V_{total}[c] /cm^3g^{-1}	V_{micro}[d] /cm^3g^{-1}
Ni-N/D	224	22.8	0.201	0.086
Ni-Cl/D	208	11.6	0.170	0.078
Ni-Ac/D	223	7.8	0.161	0.085
Ni-F/D	177	9.3	0.150	0.071
D[e]	26	–	0.073	0.010

[a]BET surface area; [b]Surface area in mesoscale pore sizes; [c]Total pore volume; [d]Micropore volume, The difference between values of V_{total} and V_{micro} corresponds to the meso-pore volume; [e]D support.

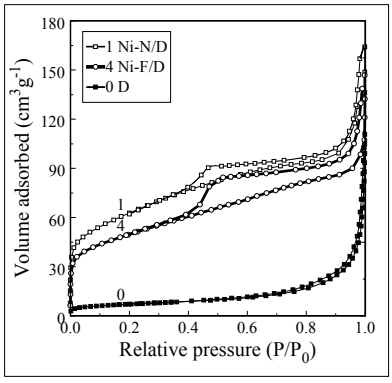

Fig. 2. Nitrogen adsorption-desorption isotherms

CONCLUSION

Nickel precursors supported on diatomite were prepared by PD method. The results showed that Ni-precipitates deposited from different nickel salts significantly affect the textural characteristics of the precursors. The sample from nitrate had the best textural properties among the studied precursors and therefore it can be expected that the catalyst prepared on its basis will show better characteristics in comparison to others.

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