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# Studies of new magnesium fluoride supported nickel catalysts for toluene hydrogenation

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## ABSTRACT

$Ni/MgF_2$ (1 wt.% Ni) catalysts were prepared by introduction of nickel nitrate into hydrogel of magnesium fluoride or impregnation of calcined $MgF_2$ with $Ni(NO_3)_2$. The samples were reduced with $H_2$ without or after calcination in air or helium. The catalysts were characterized by BET, $H_2$-TPR, $H_2$-adsorption, XRD and gas phase hydrogenation of toluene.

The catalysts obtained with magnesium fluoride as a support for nickel has enabled to obtain a catalyst of high activity for hydrogenation of toluene to methylcyclohexane under atmospheric pressure. Their catalytic activity was influenced by the method of the nickel phase introduction and was higher when calcined $MgF_2$ was used as a support. The physicochemical characterization and activity testing showed that the catalyst reduced without previous calcination exhibits the highest dispersion of metallic Ni and most excellent catalytic performance in toluene hydorgenation.

## 1. Introduction

Hydrogenation of aromatic compounds is an industrially and environmentally interesting reaction. The major applications of aromatic hydrogenation are in the production of aromatic-free fuels and solvents. Health risks related to aromatic compounds, such as benzene and some polyaromatic compounds, have encouraged legislators to tighten the restrictions on aromatic compounds content in end products. In diesel fuel aromatic compounds are responsible for undesired particle emissions in exhaust gases [1].

The catalytic activity in the process of hydrogenation substantially depends on the type of catalyst's active phase, properties of the support used and methods of preparation.

According to literature a large number of catalysts can be used in toluene hydrogenation – e.g. $Pt/Al_2O_3$ [2–4], $Ni/Al_2O_3$, $Ir/Al_2O_3$ [4,5], Ni/ZSM-5 [6], $Co/SiO_2$ [4,7], $Ni/SiO_2$, $Pt/SiO_2$ [8], $Pt/TiO_2$ [9,10], Ni/MCM-41 [11], $Pt/SiO_2–Al_2O_3$, $Pd/SiO_2–Al_2O_3$ [12], $Ni–Pd/SiO_2–Al_2O_3$ [13], $Ir/SiO_2–Al_2O_3$ [5], $Ni/SiO_2–TiO_2$ [8,14,15]. Among these, nickel supported catalysts are currently used in industry [16]. The choice of nickel is mainly due to its availability and reasonable cost compared to noble metals. Industrial catalysts very often contain larger amount of nickel supported on various oxides [17].

An important factor influencing the hydrogenation catalyst activity is method of preparation [18]. The most often used is conventional impregnation of the support with a salt solution, e.g., nickel nitrate or nickel acetate. The other methods are mixing of Ni salt solution with hydrogel of the support; decomposition of one precipitate onto another, co-precipitation or hydrotermal treatment of mixed precipitates. These methods are employed to produce industrial catalysts Euro-Ni-1 with the active phase content of up to 25 wt.% Ni or the catalyst with Ni content of 30–45 wt.% supported on $Al_2O_3$ [18].

We have decided to propose and test a very interesting new nickel catalyst with magnesium fluoride as the support [19]. Magnesium fluoride was obtained in the reaction of the basic magnesium carbonate with hydrofluoric acid. The use of magnesium carbonate permits obtaining $MgF_2$ of high purity, free from impurities that remain when magnesium fluoride is obtained, e.g., from magnesium sulphate. $MgF_2$ has almost chemically inert surface, good thermal stability up to ~773 K and high hardness. Its mesoporous surface is relatively large (~45 $m^2\,g^{-1}$). Its successful use has prompted derivation of highly active metallic catalysts of hydrodesulphurization of thiophene and its derivatives [20], selective hydrogenation of chloronitrobenzene to chloroaniline [21,22] or hydro-dechlorination of chlorofluorohydrocarbons [23].

The present study has been undertaken to examine the performance of nickel supported on $MgF_2$. Catalytic properties of metal-support systems can be modified by applying suitable precursors of active phase and by the method of preparation. The precursor and method of preparation influence dispersion of the active component and modify its electronic interactions with a support. We have used in our study nickel nitrate as a precursor. Our objective was to compare two methods of catalyst preparation: the

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conventional impregnation of the support and the mixing of Ni salt solution with hydrogel of the support. The nickel precursor was introduced into $MgF_2$ hydrogel or onto calcined $MgF_2$. The content of the active phase in both catalyst systems obtained was 1 wt.%. Both series of samples were then thermally activated. In this study the catalytic properties of nickel supported catalysts were tested in toluene hydrogenation reaction.

## 2. Experimental

### 2.1. Support and catalysts preparation

Magnesium fluoride was obtained by progressively adding of powdered $MgCO_3{\cdot}Mg(OH)_2{\cdot}H_2O$ at room temperature upon intense stirring to an aqueous solution of hydrofluoride (40%, POCH – Polish Chemicals Reagents) to obtain pH = 7, and acidifying it by introduction of a few additional drops of the acid to obtain pH = 6.

$$MgCO_3{\cdot}Mg(OH)_2{\cdot}H_2O + 4HF \rightarrow 2MgF_2\downarrow + CO_2 + 4H_2O$$

The resulting dense gels was aged at room temperature for a couple of days under stirring, at pH = 6 maintained, and than dried at 353 K. The dried samples were calcined for 4 h at 673 K. After the calcination, $MgF_2$ was ground to obtain particles of 0.2–0.5 mm mesh size.

The obtained support was impregnated (denoted as S) with aqueous solution of nickel(II)-nitrate hexahydrate (crystalline, Aldrich). The Ni content was 1 wt.% Ni. The impregnated samples were dried in air at 383 K for 24 h and subjected directly to reduction with hydrogen or then they were subjected to reduction after thermal decomposition in helium or after calcination in air.

The second series of catalysts were prepared by mixing aqueous solution of $Ni(NO_3)_2$ with hydrogel of $MgF_2$ (denoted as G). The impregnated hydrogel was left to age prior to thermal treatment. The amount of nickel(II)-nitrate hexahydrate introduced was chosen so that in the final catalyst the active phase content of nickel was 1 wt.%. The mixing lasted for 48 h and next the catalyst were dried in air at 383 K for 24 h and subjected to thermal treatment in helium or in air.

The codes of the catalysts, methods of their preparation and temperatures of pre-treatment are listed in Table 1.

### 2.2. Determination of surface area and porosity

The surface area and porous structure were determined by the low temperature (77 K) nitrogen adsorption carried out on ASAP 2010 analyzer (Micromeritics GmbH). The samples were degassed at 623 K at 0.5 Pa until the static vacuum. Specific surface area was determined by using the BET method. Total pore volume and average pore diameter were established on the basic of the Barrett–Jayner–Halenda method using a desorption isotherm.

### 2.3. X-ray powder diffraction

The X-ray powder diffraction was performed on Bruker AXS D8 Advance diffractometer with Ni-filtered Cu Kα radiation over a $2\Theta$ range 20–80°.

### 2.4. Hydrogen chemisorption

Prior to hydrogen chemisorption, the samples were reduced with $H_2$ at 673 K for 2 h. The reduced samples were placed in an ASAP 2010C sorptometr and were evacuated for 15 min at room temperature and then at 623 K for 60 min, followed by additional reduction in hydrogen flow (40 $cm^3\,min^{-1}$) at 623 K and evacuation for 120 min at 623 K.

Hydrogen chemisorption measurements were carried out at 308 K. Nickel dispersion was calculated from total chemisorbed hydrogen.

Metallic surface area $S$ was calculated based on the following equation [24]:

$$S = \frac{v_m \cdot N_A \cdot n \cdot a_m \cdot 100}{22414 \cdot m \cdot wt}\,(\mathrm{m^2 g_{Ni}^{-1}})$$

where $v_m$ is expressed in $cm^3$, $N_A$ is the Avogadro's number ($6.022 \times 10^{23}\,mol^{-1}$), $n$ is the chemisorption stoichiometry, $a_m$ is the surface area ($m^2$) occupied by a metal atom, $m$ is the mass of the sample (g), $wt$ is the metal loading (%).

The dispersion of active phase can be calculated from the formula:

$$D = \frac{S \cdot M}{a_m \cdot N_A}$$

where $S$ is the metallic surface area, $M$ is the nickel atomic weight, $N_A$ is the Avogadro's number and $a_m$ is the surface covered by one nickel atom.

### 2.5. TPR-$H_2$

The temperature programmed reduction experiments were carried out with an ASAP ChemiSorb 2705 (Micromeritics). Portions of 100 mg of the catalyst were reduced in a mixture of 10 vol.% $H_2$ in Ar (99.999%, Linde) at the flow rate of 30 $cm^3\,min^{-1}$ and at 10 $K\,min^{-1}$ heating rate up to a final temperature of 1073 K. The calibration for the determination of hydrogen consumed was performed by introducing a specified volume of hydrogen (using a sample loop) into the stream of argon.

### 2.6. Catalytic activity measurements

Prior to the catalytic test some of the samples were pre-treated for 4 h in air or helium at 673 K, in order to decompose the precursor. Fresh or pre-treated catalyst (0.05 g) was placed in the reactor

**Table 1**
Characterization of $Ni/MgF_2$ (1 wt.% Ni) catalysts.

| Symbol | Method of preparation | Method of activation | Surface area ($m^2\,g^{-1}$) | Average pore diameter (nm) | Pore volume ($cm^3\,g^{-1}$) |
|---|---|---|---|---|---|
| MF | Reaction: $MgCO_3 + 2HF$ | Calcination (air, 4 h, 673 K) | 39.7 | 18.0 | 0.18 |
| Ni/MF-S-R | Impregnation of support | Reduction ($H_2$, 2 h, 673 K) | 31.0 | 21.0 | 0.17 |
| Ni/MF-S-DR | Impregnation of support | Decomposition (He, 4 h, 673 K)/reduction ($H_2$, 2 h, 673 K) | 28.8 | 23.5 | 0.17 |
| Ni/MF-S-CR | Impregnation of support | Calcination (air, 4 h, 673 K)/reduction ($H_2$, 2 h, 673 K) | 30.5 | 22.2 | 0.17 |
| Ni/MF-G-R | Impregnation of hydrogel | Reduction ($H_2$, 2 h, 673 K) | 45.5 | 20.6 | 0.23 |
| Ni/MF-G-DR | Impregnation of hydrogel | Decomposition (He, 4 h, 673 K)/reduction ($H_2$, 2 h, 673 K) | 39.4 | 21.4 | 0.21 |
| Ni/MF-G-CR | Impregnation of hydrogel | Calcination (air, 4 h, 673 K)/reduction ($H_2$, 2 h, 673 K) | 38.1 | 23.3 | 0.22 |