

# The Effect of Preparation of Ni/MgF<sub>2</sub> Catalysts on the Hydrogenation of Benzene Activity

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## Abstract

The use of magnesium fluoride as a support for nickel has permitted us to obtain a catalyst of high activity and selectivity for hydrogenation of benzene to cyclohexane under atmospheric pressure. The effect of nickel content and metal precursor on the nickel catalysts surface structures and their catalytic behavior in the benzene hydrogenation reaction has been studied. A series of catalysts obtained by impregnation from different precursors, i.e. Ni(CH<sub>3</sub>COO)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub> and NiCl<sub>2</sub> with Ni contents 0.5, 1, 5 and 10 wt.% have been deposited on magnesium fluoride support. Their surface areas and pore size distributions were investigated using BET and BJH methods, respectively. Dispersion of nickel and the mean size of the crystallites have been determined on the basis of hydrogen chemisorption. The activity of the catalysts in the hydrogenation reaction of benzene at 75-225°C under atmospheric pressure was measured. The results show that the maximum activity was obtained at 175°C for all catalysts. The activity of the catalysts in benzene hydrogenation was found to strongly depend on the precursor of Ni and increases with increasing dispersion. From the nickel catalysts supported on MgF<sub>2</sub> the one based on nickel acetate was the most active.

**Keywords:** magnesium fluoride, MgF<sub>2</sub>, nickel, BET, XRD, hydrogen chemisorption, TEM, benzene hydrogenation

## Introduction

Nickel catalysts have been of great interest because of their applications in hydrogenation, hydrodechlorination, and hydrotreating reactions [1]. Special attention has recently been focused on the hydrogenation of aromatic compounds, which permits elimination of carcinogenic aromatic content from fuels.

The catalytic activity in the process of hydrogenation depends on the type and properties of the support used. The most important features of the support in this respect are its crystalline structure, chemical character of surface and porous structure, which influences the character of dispersion of the active component and determines its reducibility.

The commonly used supports of nickel are: Al<sub>2</sub>O<sub>3</sub> [2], SiO<sub>2</sub> [3], TiO<sub>2</sub> [4], and binary systems such as SiO<sub>2</sub>-TiO<sub>2</sub> [5] or SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> [6]. Different surface character (acidic, neutral, basic) of the above supports have substantial effect not only on the development of the surface area of the phases deposited but also on the type of metal-support interactions, so on catalytic behaviour.

We have decided to propose and test another support of nickel catalysts: magnesium fluoride [7]. It has an almost chemically inert surface, good thermal stability up to ~500°C and high hardness. Its mesoporous surface is relatively large (~45 m<sup>2</sup>·g<sup>-1</sup>). Earlier attempts at using MgF<sub>2</sub>-supported systems have brought about active and selective catalysts for the NO reduction in the presence of hydrocarbons [8] as reducing agents, in CO oxidation [9],

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Table 1. Catalyst characterization – symbol, precursors, surface areas and nickel dispersion after hydrogen (2h, 400°C, 100 ml·min<sup>-1</sup>) pretreatment.

Catalyst symbol	Nickel precursor	BET surface area (m <sup>2</sup> ·g <sup>-1</sup> )	Ni dispersion (%)	Average size of particles (nm)
MF	-	39.7	-	-
1NiMF-Ac	Ni(CH <sub>3</sub> COO) <sub>2</sub> ·4H <sub>2</sub> O	35.1	20.7	4.9
5NiMF-Ac	Ni(CH <sub>3</sub> COO) <sub>2</sub> ·4H <sub>2</sub> O	36.8	9.2	10.9
10NiMF-Ac	Ni(CH <sub>3</sub> COO) <sub>2</sub> ·4H <sub>2</sub> O	34.8	3.6	27.8
1NiMF-N	Ni(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	31.0	22.8	4.4
5NiMF-N	Ni(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	35.9	13.0	7.8
10NiMF-N	Ni(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	30.5	6.9	14.6
1NiMF-Cl	NiCl <sub>2</sub> ·6H <sub>2</sub> O	28.6	0.4	282.1
5NiMF-Cl	NiCl <sub>2</sub> ·6H <sub>2</sub> O	21.0	0.3	401.6
10NiMF-Cl	NiCl <sub>2</sub> ·6H <sub>2</sub> O	16.9	0.1	838.2

hydrodesulfurization of thiophene [10] and hydrodechlorination of chlorofluorocarbons [11].

The present study has been undertaken to examine the performance of nickel supported on MgF<sub>2</sub>. The influence of the type of nickel precursor, nickel content, the nickel catalyst surface structure and their catalytic behaviour in benzene hydrogenation reaction has been studied.

## Experimental Section

### Support and Catalyst Preparation

Magnesium fluoride was obtained by adding small portions of MgCO<sub>3</sub>·2H<sub>2</sub>O to an aqueous solution of hydrofluoric acid until neutralization, and acidifying it by introduction of a few additional drops of the acid. The precipitate was then aged at room temperature for a couple of days under stirring, dried at 80°C and calcined at 400°C for 4 h. After calcination, MgF<sub>2</sub> was ground to obtain particles of 0.2-0.5 mm mesh size.

Nickel acetate Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, nickel nitrate Ni(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and nickel chloride NiCl<sub>2</sub>·6H<sub>2</sub>O were purchased from Aldrich. The catalysts were prepared with 0.5, 1, 5 and 10 wt.% Ni loading by the conventional method of impregnation of magnesium fluoride with nickel acetate denoted as xNiMF-Ac, nickel nitrate - xNiMF-N and nickel chloride - xNiMF-Cl, where x = 0.5, 1, 5 or 10 wt.% Ni content. The catalysts were air dried at 110°C overnight.

### Physico-Chemical Characterization

The low-temperature adsorption of nitrogen was performed on a Micromeritics ASAP 2010 sorptometer. Specific surface area was determined using the BET method.

The X-ray powder diffraction was performed on Bruker AXS D8 Advance diffractometer with Ni-filtered CuKα radiation over a 2θ range 20-80°.

The JEOL 2000 instrument with 80kV electron beam was used for TEM studies. Ethanol suspension of NiMF catalysts particles was prepared by means of ultrasonic waves and then the suspension was supported as a thin film on the holey carbon.

### Hydrogen Chemisorption

Prior to hydrogen chemisorption, samples were pretreated in situ to remove the molecules adsorbed from the nickel surface. Samples were evacuated for 15 min. at room temperature and then at 350°C for 60 min, followed by reduction in hydrogen flow (40 ml·min<sup>-1</sup>) at 400°C and evacuated again for 120 min. at 350°C.

All chemisorption experiments were performed on an ASAP 2010C sorptometer. Hydrogen chemisorption measurements were carried out at 35°C.

### Catalytic Test

The benzene hydrogenation reaction was performed with a mixture containing 1 vol.% of benzene in hydrogen, prepared by passage of an H<sub>2</sub> stream through benzene placed in a saturator. The total flow rate was 50 ml·min<sup>-1</sup>. A 0.05 g of a catalyst was placed in the reactor and reduced in a flow of pure hydrogen (flow rate = 100 ml·min<sup>-1</sup>) at 400°C for 2h. The catalytic test was carried out at various temperatures (75-225°C temperature range) on the same catalyst. The sample was heated or cooled at a rate of 10°C·min<sup>-1</sup>. The post reaction mixture was analyzed on a gas chromatograph equipped with a capillary column RESTEK-MXT – 1.

## Results and Discussion

On the basis of the low temperature nitrogen adsorption, the texture of xNiMF-y (where x = wt.% of nickel, y = type of precursor) catalyst reduced at 400°C was characterized. The symbol of the catalyst, type of precursor, surface

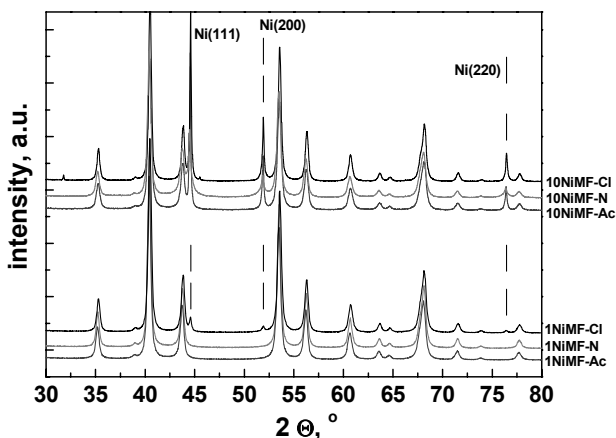


Fig. 1. Diffraction patterns of the nickel catalysts supported on MgF<sub>2</sub> after reduction ( $H_2 = 100 \text{ ml}\cdot\text{min}^{-1}$ ; 400°C; 2h).

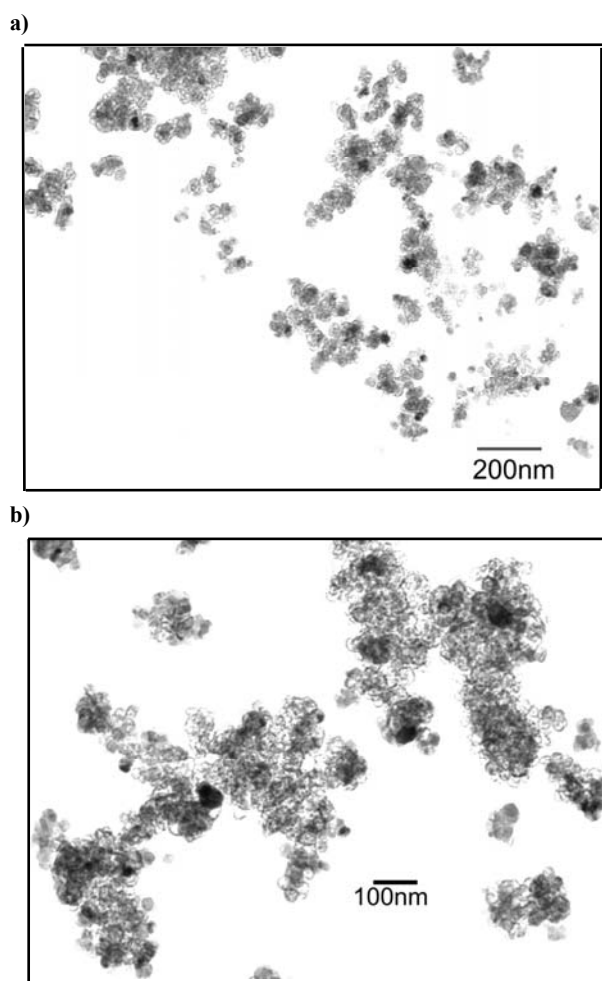


Fig. 2. TEM studies of the 1NiMF-Ac (a) and 1NiMF-Cl (b) catalysts after  $H_2$  pretreatment ( $H_2 = 100 \text{ ml}\cdot\text{min}^{-1}$ ; 400°C; 2h).

area, dispersion and size of particles are presented in Table 1. For the catalysts obtained from nickel acetate and nickel nitrate precursors a decrease in the surface area (between 35 and 30  $\text{m}^2\cdot\text{g}^{-1}$ ) relative to that of magnesium fluoride support (40  $\text{m}^2\cdot\text{g}^{-1}$ ) was observed. The greatest decrease in the surface area was noted as a result of the introduction of nickel from nickel chloride. The loading of 1 wt.% of Ni from nickel chloride reduced the surface area by almost 30%. Introduction of greater amounts of the active phase of 5 or 10 wt.% led to a further decrease in the surface area to  $\sim 17 \text{ m}^2\cdot\text{g}^{-1}$ .

The XRD study was undertaken to identify the phases present in the catalysts prepared (Fig. 1). For the catalysts loaded with 1 wt.% Ni, only the XRD pattern obtained for the chloride catalysts 1NiMF-Cl shows a weak peak which could originate from nickel in metallic form. It should be noted that the XRD method is not able to detect very small particles of nickel. The TEM results (Fig. 2) proved the presence of much greater nickel crystallites in the 1NiMF-Cl catalyst (Fig. 2b) than in the 1NiMF-Ac one (Fig. 2a). Introduction of greater nickel loading led to increasing intensity of the signals assigned to metallic nickel in the XRD spectra. The XRD pattern of the 10NiMF-y catalysts, obtained from different precursors of Ni after reduction by hydrogen showed three reflection signals (as illustrated in Fig. 1) at 44.59° (111), 51.90° (200) and 76.4° (220)  $2\theta$  characteristic of metallic nickel with a *fcc* structure [12].

After  $H_2$  thermal treatment, the catalysts became active and selective in the gas phase hydrogenation of benzene to cyclohexane. The activity of the catalysts in benzene hydrogenation depends on the type of Ni precursor and dispersion of the active phase. Fig. 3 shows a comparison of the benzene hydrogenation activities of NiMF catalysts of different Ni content obtained from the precursors  $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$  and  $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$  denoted as NiMF-Ac, NiMF-N and NiMF-Cl series, respectively. The best precursor is nickel acetate, the second best and not much poorer is nickel nitrate, while the activities obtained when using nickel chloride are much lower. Fig. 4 presents changes in the activity of the NiMF-Ac series catalysts as a function of reaction temperature. The maximum activity in the hydrogenation reaction was

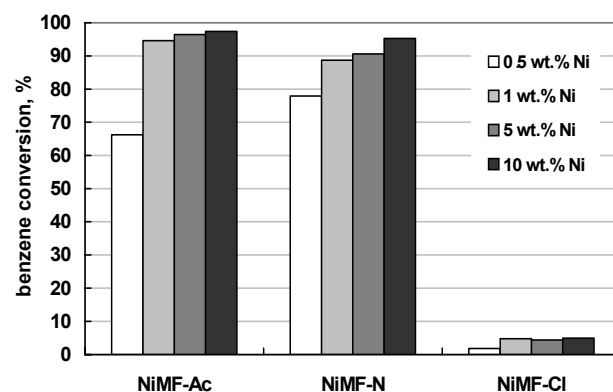


Fig. 3. The effect of nickel precursor and nickel content on hydrogenation of benzene to cyclohexane activity at 175°C (after 30 min of reaction).

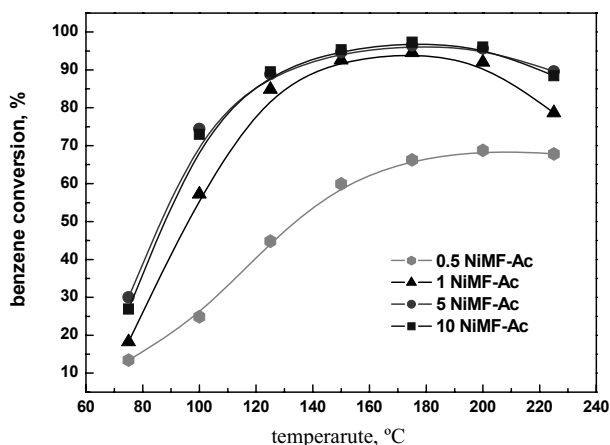


Fig. 4. The effect of the temperature on the benzene hydrogenation activity for NiMF-Ac catalysts (after 30 min. of reaction).

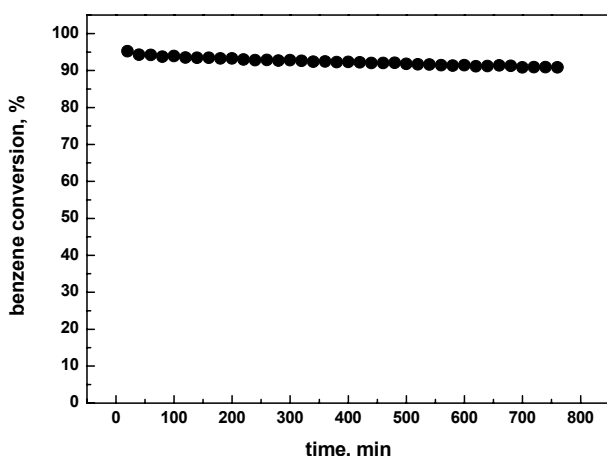


Fig. 5. Changes of catalytic activity in benzene hydrogenation with time of reaction at 175°C for 1NiMF-Ac catalyst.

obtained at 175°C. At the same temperature the maxima of activities of the catalysts based on nickel nitrate and nickel chloride were observed. The content of 1 wt.% Ni is sufficient for getting maximum activity. Such a low Ni content was also enough for catalysts supported on SiO<sub>2</sub>. It should be noted that these two supports have surfaces of very weak acid-base properties. According to literature data, when the support is Al<sub>2</sub>O<sub>3</sub> [13] the maximum activity is achieved for a greater loading with nickel, reaching even 25 wt.% Ni.

Deactivation of the catalysts in the reaction of benzene hydrogenation was studied for the exemplary catalyst 1NiMF-Ac, Fig. 5. The nickel catalysts supported on MgF<sub>2</sub> are highly stable in this reaction; after 13 hours of work their activity decreased by ~4%.

The catalytic activity in the hydrogenation of benzene strongly depends on nickel dispersion. As follows from the dispersion measurements performed by hydrogen chemisorption (Table 1) and for the majority of the known metallic catalysts, the dispersion decreases with increasing

nickel loading. Taking into account the similar performance of nickel catalysts supported on MgF<sub>2</sub> and SiO<sub>2</sub>, it can be expected that the neutral character of the MgF<sub>2</sub> surface has a substantial effect on the strength of the Ni-MgF<sub>2</sub> interactions. The interactions between the silica and metal have been found to be weak [14], so we expect that the interactions of Ni-MgF<sub>2</sub> also are weak. The low activity of the catalysts obtained from NiCl<sub>2</sub>·6H<sub>2</sub>O is explained by the realisation that the chlorine ions are built onto the MgF<sub>2</sub> surface, which changes the character of the surface into acidic and is probably responsible for decreasing dispersion of nickel and changes in the Ni-MgF<sub>2</sub> interactions.

## Conclusions

1. The use of nickel phase and magnesium fluoride as a support has permitted us to obtain new catalysts of high activities in the hydrogenation of benzene.
2. A significant effect of nickel precursors on the activity of NiMF catalysts in benzene hydrogenation to cyclohexane was observed.
3. As small an amount as 1 wt.% of nickel content was enough to obtain a very active catalyst, which was interpreted as related to better nickel dispersion.

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