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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 2Θ 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]:

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

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

and reduced in a flow (100 $cm^3 min^{-1}$) of pure hydrogen (99.99% purchased from Messer) at 673 K for 2 h.

The reaction of toluene hydrogenation was studied at atmospheric pressure using a fixed-bed flow reactor and H_2 as carrier gas. The H_2 stream passed through a saturator filled with toluene and equilibrated at 273 K ($p_{toluene}$ = 0.9 kPa). The catalytic tests were carried out at various temperatures (348–498 K) over the same catalyst. The sample was heated or cooled at the rate of 10 K min^{-1}. The reaction products were mixture was analyzed on a gas chromatograph equipped with a capillary column RESTEK-MXT-1. The catalytic activity was presented as TOF (calculated using the amount of metallic nickel) or as percent of toluene conversion.

3. Results and discussion

3.1. Surface area

Surface areas of calcined MgF_2 and reduced 1 wt.% Ni/MgF_2 catalysts are presented in Table 1. Significant differences were observed between the catalysts obtained by impregnation of calcined MgF_2 (support) and those obtained by impregnation of hydrogel MgF_2. Samples of the former group had the surface areas by about 25% smaller than that of the initial support, while those of the latter group had surface areas greater or close to that of the initial support. The probable reason is the influence of water introduced with the nickel solution onto the calcined MgF_2 and repeated thermal treatment (in hydrogen, helium or air). When impregnation of hydrogel is performed the thermal treatment is applied only once. Moreover, the presence of nickel in hydrogel can inhibit crystallisation of MgF_2 upon thermal treatment. Such a phenomenon has been observed for MgF_2 admixtured with magnesium oxide [25].

3.2. H_2-chemisorption study

Activation of the nickel catalysts was realised by three different ways: by direct reduction with hydrogen of dried samples, by a similar reduction with hydrogen of the catalysts after decomposition in a neutral gas and by reduction of samples calcined in air (Table 1). The three procedures were applied to differentiate the properties of the supported nickel. It is well known that the dispersion of active phase and level of the metal reduction depend on many parameters, such as the pre-treatment steps (drying, decomposition or calcination) and the conditions of the reduction (temperature, heating rate and reducer space velocity). The H_2-chemisorption was used for determination of dispersion and particle size of the nickel active phase after reduction. The results obtained are displayed in Table 2.

Blank experiments proved that the H_2 pre-treated magnesium fluoride support did not adsorb hydrogen. The nickel surface area was calculated assuming the stoichiometric adsorption of hydrogen, i.e., one atom of hydrogen is attached to one surface nickel atom. For both series of catalysts the amount of hydrogen adsorbed (per gram of catalyst) decreased after air or helium pre-treatment.

The highest dispersion (22.8%) and the smallest nickel particle sizes were found for noncalcined catalyst supported on MgF_2 (Ni/MF-S-R). Moreover, the dispersion of this catalyst is 3.5 times higher than that previously decomposed in He (Ni/MF-S-DR) and 5 times higher than that calcined in air (Ni/MF-S-CR). As follows from the above, the thermal treatment in air or helium prior to the reduction with hydrogen leads to decreased degree of dispersion, which is related to the growth of crystallites during calcination. Treatment in air leads to the greatest sintering of nickel crystallites. A similar effect for the nickel catalysts supported on Al_2O_3 has been reported in [26].

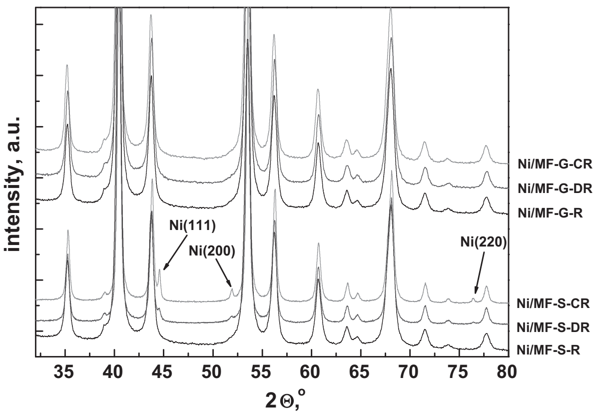

Fig. 1. XRD profiles of reduced Ni/MgF_2 catalysts.

Decrease in dispersion as a result of treatment in air or helium was also observed for the series of catalysts obtained by impregnation of pre-support – Ni/MF-G. The highest dispersion was found for the catalyst reduced directly after drying, Ni/MF-G-R, but this dispersion was almost three times lower than for Ni/MF-S-R catalyst. Much lower dispersion of the catalysts obtained by impregnation of pre-support is related to the capturing of nickel in the pores of the support upon preparation and later thermal treatment, which makes it inaccessible to the chemisorbed hydrogen. For the catalysts from this series the treatment in helium or air resulted in over twice decrease in dispersion.

3.3. XRD study

The XRD study was undertaken to identify the phases present in reduced catalysts. The measurements were performed for the catalysts obtained by impregnation of the support and those obtained by impregnation of hydrogel, fresh, decomposed in helium or calcined in air and reduced with hydrogen. Only for the catalysts impregnated and then subjected to treatment in helium (Ni/MF-S-DR) or air (Ni/MF-S-CR) the weak signals assigned to metallic nickel were detected, Fig. 1. The XRD patterns of these catalysts showed three distinct reflection signals at $2\Theta = 44.59^\circ$ (1 1 1), 51.90° (2 0 0) and 76.4° (2 2 0) characteristic of metallic nickel with a *fcc* structure [27]. The intensity of these signals was greater for the catalysts activated in air than for those subjected to decomposition in helium. The lack of signals assigned to metallic nickel in the XRD patterns of Ni/MF-S-R indicates the presence of small (smaller than 5 nm)

Table 2
H_2-chemisorption data and TOFs in toluene hydrogenation of Ni/MgF_2 catalysts.

Symbol of catalyst	Total H_2 adsorbed 10^{-5} (mol g_{cat}^{-1})	Ni dispersion (%)	Ni surface area (m^2 g_{Ni}^{-1})	Mean particle size (nm)[a]	TOF (448 K) (min^{-1})
Ni/MF-S-R	1.943	22.8	152.1	4.4	2.18
Ni/MF-S-DR	0.521	6.1	40.8	16.5	0.30
Ni/MF-S-CR	0.366	4.3	28.6	23.5	0.24
Ni/MF-G-R	0.687	8.1	53.7	12.5	0.80
Ni/MF-G-DR	0.333	3.9	26.1	25.8	0.23
Ni/MF-G-CR	0.263	3.1	20.6	32.7	0.19

[a] Determined by the H_2 adsorption.

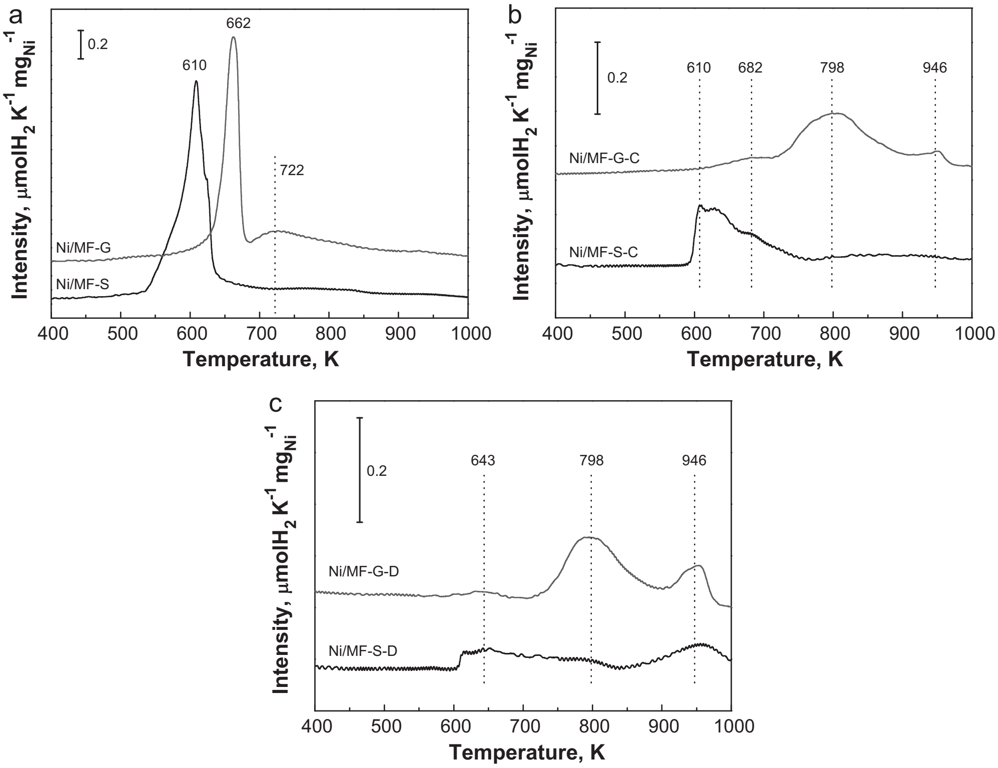

Fig. 2. TPR-H_2 – profiles for Ni/MF-S and Ni/MF-G catalysts after drying (a), calcination in air (b) and decomposition in helium (c).

nickel crystallites, that are undetectable by this method (Table 2). For the catalysts obtained by impregnation of hydrogel, the lack of signals assigned to metallic nickel, even after the treatment in air or helium, suggests amorphous state or well-dispersed nickel particles. The relatively low chemisorption of hydrogen at the absence of XRD signals assignable to nickel suggests that nickel particles are surrounded by magnesium fluorine.

3.4. *Temperature programmed reduction – TPR-H_2*

Additional information on the state of the supported nickel phases has been provided by the temperature-programmed reduction with hydrogen. The catalysts reducibility was studied by TPR-H_2 method after various pre-treatments. Fig. 2 presents the reduction profiles of the Ni/MgF_2 catalysts obtained by impregnation of the support dried (Fig. 2a), calcined (Fig. 2b) and after decomposition (Fig. 2c) pre-treatment. Table 3 presents the data on total H_2 consumption and degree of reduction calculated on the basis of the peaks of reduction from the range 500 to 1000 K.

Fig. 2a shows the TPR-H_2 profiles of the dried catalysts. According to literature data, in dried catalysts the first process is decomposition of the metal salt and reduction of the liberated nitrogen oxides and then reduction of the nickel phase [26]. This sequence of processes is confirmed by unusual high consumption of hydrogen, for Ni/MF-S and Ni/MF-G catalysts, and the degree of reduction calculated on the basis of this hydrogen consumption of 325 and 252%. For Ni/MF-S sample, the maximum peak assigned to a single-stage reduction of Ni^{2+} to Ni^0 was recorded at 610 K. According to literature information [28–30] below 700 K, the amorphous overlay of NiO or Ni_2O_3 whose interaction with the support is poor, undergoes reduction. The shift of the peak maximum observed for the catalyst obtained by impregnation of hydrogel (Ni/MF-G) by 50 K with respect to that recorded for Ni/MF-S can be interpreted as poorer accessibility of Ni^{2+} species. For the latter catalyst the second reduction signal was noted at 722 K, which implies that there are two types of active centres on the catalysts surface. The first peak at 662 K corresponds to reduction of Ni^{2+} interacting weakly with magnesium fluoride or easier accessible; while the peak near 722 K can be attributed to the reduction of Ni^{2+} captured in the support.

Table 3
TPR-H_2 study of Ni/MgF_2 catalysts.

Symbol of catalyst	Total H_2 consumption (μmol g_{cat}^{-1})[a]	Degree of reduction (%)
Ni/MF-S	55.26	–
Ni/MF-S-D	9.42	85.2
Ni/MF-S-C	16.22	95.4
Ni/MF-G	43.12	–
Ni/MF-G-D	16.47	96.9
Ni/MF-G-C	16.66	97.8

[a] Calculated from the area of the TPR-H_2 peak in the range of 500–1000 K.

Fig. 2b and c shows the TPR-H_2 profiles for the catalysts after calcination in air at 673 K and after decomposition in helium at 673 K. The calcination in air provokes the decomposition of nickel precursor and nickel oxidation to NiO. For Ni/MF-S-C catalysts the presence of the two nickel species was detected, most probably, isolated NiO (range 600–620 K) or Ni^{2+} (for example – $Ni(OH)_2$) and bulk NiO (range 650–700 K). In a similar range of temperatures the reduction of bulk NiO in oxidised Ni/Nb_2O_5 was reported [31,32]. The profiles of the catalysts obtained by impregnation of hydrogel after calcination in air, differ from those of the catalysts prepared by impregnation of support. For Ni/MF-G-C catalysts (Fig. 2b) two maxima of reduction were recorded: at 798 and 946 K. The peak at 798 K, which is the main peak, can be assigned to the reduction of nickel oxide in the bulk. The shift of the reduction peak towards higher temperatures – from 610 to 798 K – relative to the position for Ni/MF-S-C catalyst, is related to the method of preparation and incorporation of nickel oxide in the support lattice. This nickel oxide is not so easily accessible and hence higher temperatures are

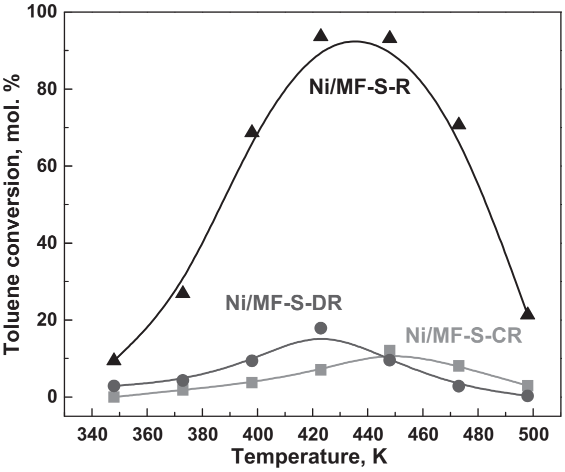

Fig. 3. The effect of reaction temperature on toluene conversion over reduced Ni/MgF_2 catalysts, prepared by impregnation of support.

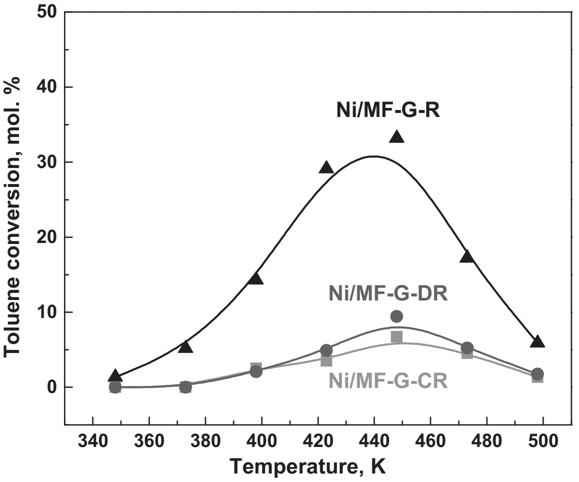

Fig. 4. The effect of reaction temperature on toluene conversion over reduced Ni/MgF_2 catalysts prepared by impregnation of hydrogel.

needed for its reduction. The peak near 950 K can be attributed to the reduction of nickel species incorporated into the magnesium fluoride framework. The nickel atoms reducible at this temperature are supposed to be linked to the support surface by Mg–O–Ni bonds. Most probably such connections are formed in the process of impregnation of hydrogel as no such peaks are detected in the TPR profiles of the catalysts obtained by impregnation of support.

The TPR reduction profiles of the Ni/MF-G-C (Fig. 2b) and Ni/MF-G-D (Fig. 2c) catalysts are very similar and show maxima at 798 and 946 K. Intensity of the second signal at ~950 K increases after pretreatment in helium. The degree of reduction calculated for these two samples on the basis of total H_2 consumption is 98 and 97%, so indicates total reduction of Ni species. For the series of the catalysts obtained by impregnation of support the situation is similar. In the TPR-H_2 profile of Ni/MF-S-C (Fig. 2b) the intensity of the peak at 643 K is greater for the sample subjected to treatment in air than for that subjected to decomposition in helium (Fig. 2c). The degree of reduction calculated for the latter sample indicates incomplete reduction of the active phase.

3.5. Catalytic activity

The MgF_2 support did not show any activity in the gas phase toluene hydrogenation, while the reduced Ni-catalysts were active in this process. In all catalytic tests the only product was methylcyclohexane. The activities of the catalysts are given in Figs. 3–6 and reaction rate (TOF) in Table 2. All catalysts exhibit a maximum of activity as a function of the reaction temperature. The temperature of this maximum depends of the method on preparation and activation of catalysts.

For the catalysts from both series, the highest conversion degree was obtained for the dried samples subjected to reduction directly before the reaction, Figs. 3 and 4. Their activity increased with increasing temperature reaching a maximum at about 423 K. Further increase in temperature resulted in decreased activity. Like for benzene hydrogenation, the presence of a maximum activity can have several causes. The reaction of hydrogenation occurs in low temperatures, whereas at higher temperatures the reverse reaction of dehydrogenation occurs [33]. The temperature dependencies of activities of the samples from both series had similar characters but the activities of the series obtained by impregnation of hydrogel were lower. The maximum activities were observed near 448 K, except for Ni/MF-S-DR sample, whose maximum activity was noted at 423 K.

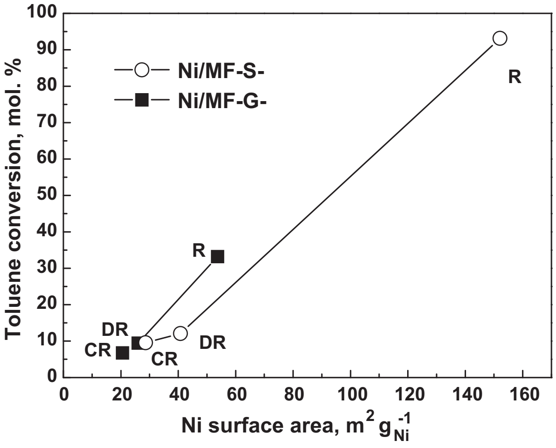

Fig. 5. The effect of nickel dispersion on activity of Ni/MF-R catalysts for hydrogenation of toluene at 448 K.

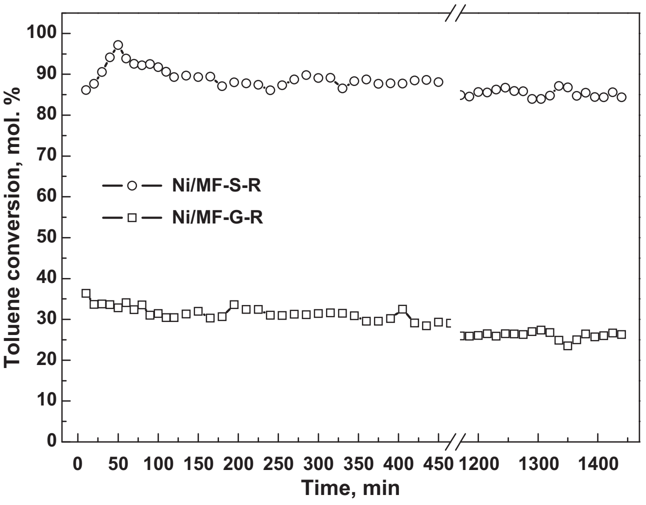

Fig. 6. Changes of catalytic activity in toluene hydrogenation of the most active catalysts with time of reaction at 448 K.

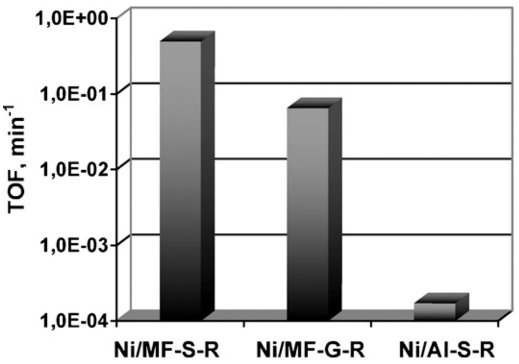

Fig. 7. The effect of nickel support on activity (TOF, min^{-1}) of nickel catalysts for hydrogenation of toluene at 448 K.

The difference in activity of the samples from both series – Ni/MF-S and Ni/MF-G could be explained taking into account the results of the TPR-H_2 and H_2 chemisorption studies. When reduction is carried out at 673 K in the hydrogen flow, nickel occurs on the surface of the Ni/MF-S catalyst mainly in the form of metallic species. These active sites are responsible for the activity in the toluene hydrogenation reaction. In Ni/MF-G catalysts, except for Ni/MF-G-R, the total reduction of the catalysts took place at 798 K (Fig. 2), so after activation at 673 K there are NiO and Ni_2O_3 species on the surface, inactive in the hydrogenation reaction. Moreover, part of the active phase is inaccessible for toluene as the nickels species can be captured in the support during preparation.

The best catalytic performances are obtained with Ni/MF-S-R catalyst which is active from 348 K. It could be explained by the higher dispersion and smaller nickel particle size calculated from H_2-chemisorption data for this catalyst as compared with those of Ni/MF-G-R and catalysts after different pre-treatment procedures, Table 2 and Fig. 5.

As mentioned above, the conditions of activation influence the particle size of nickel species, its dispersion and reducibility, which were manifested as the activity in toluene hydrogenation. With increasing dispersion, the activity in toluene hydrogenation increased for the catalysts from both series.

For the most active catalysts from each series, Ni/MF-S-R and Ni/MF-G-R, the stability of their activity in hydrogenation of toluene was tested; the results are given in Fig. 6. For the 24 h test both catalysts showed stable work. The activity of catalyst obtained by impregnation of support was increasing for the first 60 min of the reaction to the level of ~98% of toluene conversion, then it slowly decreased and stabilised after 3 h, while the conversion degree remained at the level of 80–85%. The activity of Ni/MF-G-R sample, showing much lower initial conversion, was also stable. Its activity decreased from 38% of conversion to 28% after 24 h of the reaction. The activity of the best catalysts Ni/MF-S-R and Ni/MF-G-R containing 1 wt.% Ni was compared with that of the nickel catalyst obtained by impregnation of Al_2O_3. Aluminium oxide was prepared by reaction of aluminium isopropoxide with excess of water. The obtained aluminium hydroxide was washed out of isopropyl alcohol, dried at 383 K for 24 h, then calcined at 823 K for 4 h. This support was chosen as it is one of the most often used supports of the nickel phase; its specific surface area was 205 $m^2\,g^{-1}$. The Ni/Al_2O_3 catalyst was prepared by impregnation of Al_2O_3 with an aqueous solution of $Ni(NO_3)_2$ in the same way as the Ni/MF-S-R catalyst and labelled as Ni/Al-S-R. Before toluene hydrogenation catalyst was reduced in situ in hydrogen at 673 K, 2 h. The catalytic activities were presented as TOFs at the reaction temperature of 448 K (Fig. 7). As shown by the results, the activity of the nickel catalysts supported on MgF_2 was by about 3×10^3 higher than that of Ni/Al_2O_3. This low activity follows probably from the formation of nickel aluminate type surface species on the surface of the Ni/Al_2O_3 catalyst inactive in hydrogenation of toluene.

4. Conclusions

1. Magnesium fluoride has been shown to be a good support of the active nickel phase of the catalysts for toluene hydrogenation.
2. The catalysts obtained by impregnation of the earlier calcined MgF_2 show higher activities than those obtained by impregnation of magnesium fluoride hydrogel, which is related to incorporation of part of nickel into support in the latter samples.
3. From among the methods of Ni/MgF_2 catalysts activation, the most effective proved to be the reduction of dried samples. The catalysts obtained in this way were also characterized by very stable work.
4. The catalytic activities of nickel supported on MgF_2 were much higher than those of the analogous catalysts supported on Al_2O_3.

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