HYDROGENATION OF BENZENE ON NICKEL CATALYSTS SUPPORTED ON SPHERICAL CARBON AEROGEL

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Introduction

Catalysis is the one of the most important elements of the modern chemical industry. Because of that research are carried out to find out new catalysts which are characterized by better conversion, selectivity and stability than catalysts currently used. Among many other new types of catalysts, the catalysts based on carbon materials like active carbons, soot, graphite or graphitized materials attracts the attention of researchers.

The reason for this is large surface area and porosity of carbon materials which ensures good dispersion of the active phase (metal) on their surface and their natural resistance to the acidity of the environment. An additional advantage of using these materials as catalyst supports is the possibility of relatively easy recovery of metals, especially precious metals from spent catalyst, by simply burning the support and recover metal from ash. Platinum, palladium and nickel catalysts supported on carbon materials are used in many reactions, such as hydrogenation [1] or hydrogenolysis of organochlorine compounds, including polychlorinated biphenyls [2-6].

Carbon aerogels (CA) patented by Pekala in 1989 [7] are mesoporous carbon materials with numerous interesting properties, such as relatively low mass densities, high surface areas, pore volumes and electrical conductivities. These properties enable the wide possible applications of carbon aerogels which can be used as materials for catalyst supports, adsorbents, chromatographic packings, thermal insulators, electrodes for supercapacitors and rechargeable batteries or in deionization processes and gas separation [8–10].

Some researchers have paid their attention to the synthesis of carbon aerogels in form that could be easily used in industrial applications. As a result of that studies Mayer et al. have patented synthesis method of spherical carbon aerogels (SCA) which size vary from about 1 μm to about 3 mm [11]. This method has involved stirring the aqueous organic phase in mineral oil or other hydrophobic medium at elevated temperature until the dispersed organic phase has polymerized and formed non-sticky gel spheres. The obtained spheres are treated similarly to the monolithic gels (i.e. they are supercritically dried and carbonized).

In the present study activity of spherical carbon aerogel supported nickel catalyst in the hydrogenation of benzene was tested. The content of metal was vary from 2.5 to 10 % wt. Obtained activity test results for Ni/SCA catalysts were compared with hydrogenation activity of 10% wt. Ni/Al_2O_3 catalyst.

Experimental

Spherical carbon aerogel support was synthesized by sol-gel polycondensation of resorcinol and formaldehyde using an inverse emulsion polymerization method in presence of potassium hydroxide as polycondensation catalyst and mineral oil as suspension medium. After curing (48 h) at 65 ^{o}C and acetone supercritical drying (HTSCD method) obtained organic gel was carbonized in gravimetric apparatus at temperature 600 ^{o}C in argon atmosphere at a heating rate of 5 ^{o}C/min.

Before catalyst preparation spherical carbon aerogel (SCA) was demineralized with 5 % water solution of HCl in order to remove potassium catalyst residuum. The nickel catalysts containing 2.5, 5.0 and 10 % wt. of Ni, were prepared using dry impregnation method in which adequate amounts of nickel (II) nitrate hexahydrate were dissolved in water volume equal to water absorbing capacity enlarged by 10%. After impregnation, catalysts were dried at 110 ^oC for 4 hours and calcined at 400 ^oC for 3 hours under argon flow (20 dm^3/h).

Nitrogen adsorption at -196 ^oC measured by QUANTACHROME AUTOSORB 1-C was used to determine textural properties of support and catalysts..

The activity of nickel catalysts prepared on a spherical carbon aerogel and alumina was studied in the benzene hydrogenation reaction. Before the activity test, catalysts were reduced under the hydrogen flow for 4 hours at 400 ^oC with the heating rate 100 ^oC/hour and cooled down to room temperature. Hydrogenation of benzene was carried out in a fixed bed microreactor (Fig. 1) under atmospheric pressure, at: 100, 125, 150, 175 and 200 ^oC.. The reaction mixture was fed to the reactor from benzene saturator, thermostated at 10 ^oC, at a rate of 2.4 dm^3/h (WHSV≈1,9h^{-1}). The composition of the reaction products was determined by gas chromatography using Hewlett-Packard HP 4890D gas chromatograph equipped with FID detector and PONA capillary column.

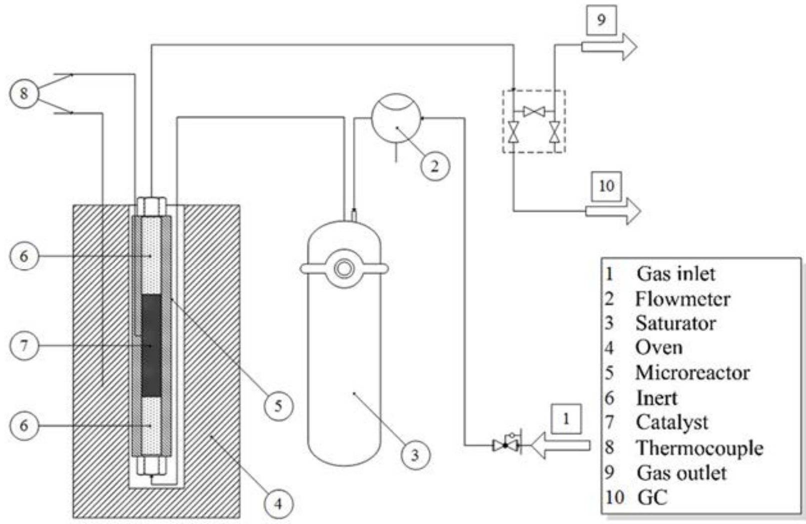

Fig. 1. Schematic of the apparatus for testing catalyst activity in the hydrogenation process.

Results and discussion

Textural properties of spherical carbon aerogel (SCA), Ni/SCA and Ni/Al_2O_3 catalysts are given in Table 1.

Table 1

Textural properties of spherical carbon aerogel (SCA), Ni/Al_2O_3 and SCA supported Ni catalysts

Sample	S_{BET}, m^2/g	V_{total}, cm^3/g	V_{meso}, cm^3/g	V_{micro}, cm^3/g	APD, nm
SCA	718	1.153	0.961	0.192	6,4
2.5 Ni/SCA	650	1.075	0.907	0.168	6.6
5.0 Ni/SCA	695	1.156	0.975	0.181	6.6
10.0 Ni/SCA	700	1.204	1.018	0.186	6.7
10.0 Ni/Al_2O_3	201	0.374	0.369	0.016	7.4

As one can see, both the carbon support and the nickel/SCA catalyst are the mesoporous materials characterized with large surface area in the range of 650-700 m^2/g and total pore volume between 1.075 and 1.204 cm^3/g. Impregnation of spherical carbon aerogel with nickel salt leads to decrease of surface area and porosity of obtained catalyst. With the increase of nickel content the textural properties of materials are improving and in the case of 10.0 Ni/SCA are similar to the properties of support. This phenomena can be related to the interaction between nickel (II) nitrate and carbon structure of support during impregnation step and thermal treating (e.g. calcination of prepared catalyst).

The alumina supported nickel catalyst (10.0 Ni/Al_2O_3) is characterized by lower surface area (201 m^2/g) and pore volume (0,374 cm^3/g) than discussed above carbon supported catalysts.

The average pore diameter (APD) of all tested materials is in range 6.4–7.4 nm. Impregnation of spherical carbon aerogel by nickel salt leads to increase the APD from 6.4 nm to 6.6 nm for 2,5 and 5.0 % wt. of Ni content in catalyst, and to 6.7 nm in case of material containing 10 % wt. nickel.

All prepared catalysts shows virtually the same pore size distribution regardless the amount of metal deposited on support surface (Fig. 2).

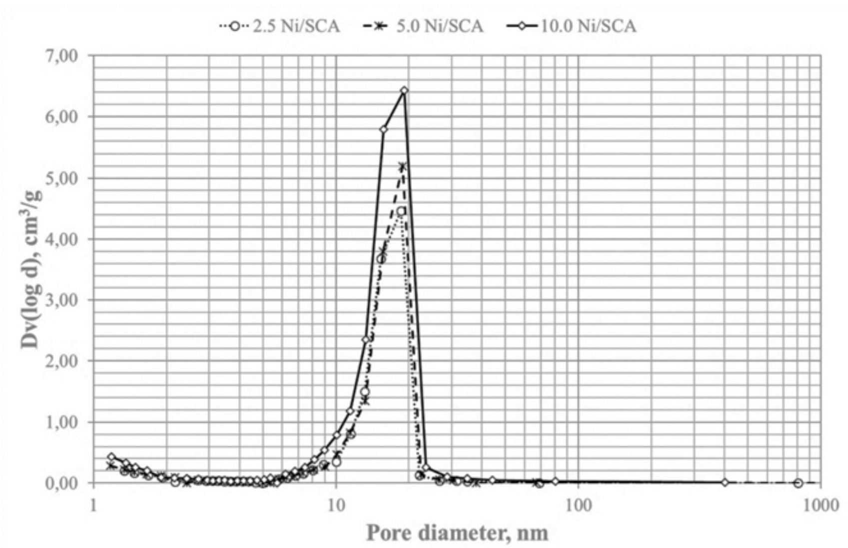

Fig. 2. Pore size distribution of spherical carbon aerogel supported nickel catalyst

The results of the activity tests of nickel catalysts in the benzene hydrogenation reaction are presented in Fig. 3.

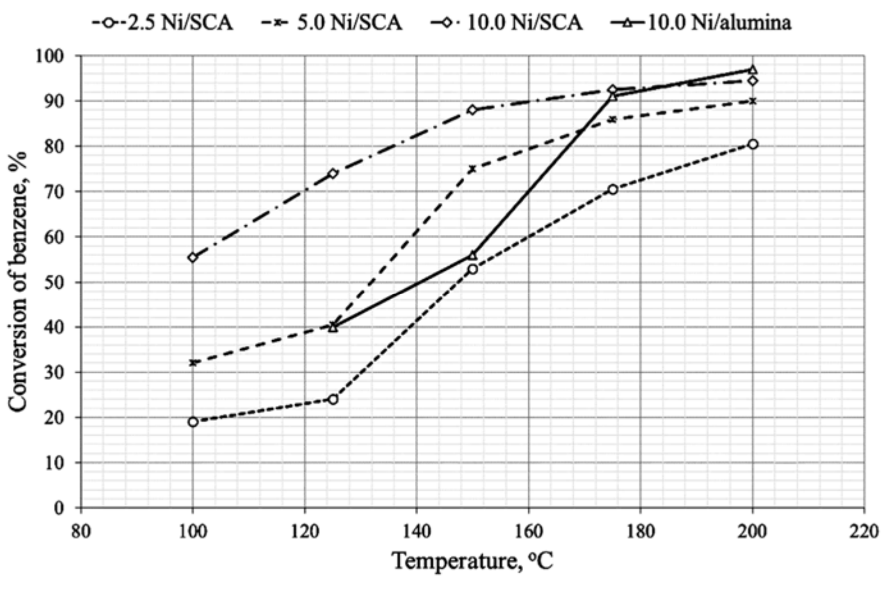

Fig. 3. Influence of the temperature on the conversion of benzene to cyclohexane over the SCA and Al_2O_3 supported nickel catalysts

One can see that there is a clear relationship between nickel content, temperature of the process and the conversion of benzene to cyclohexane. In case of spherical carbon aerogel supported catalysts activity increases with increase of metal content. Maximum conversion of benzene at 200 ^oC changes from 80.5%, through 90%, to 94.5% respectively for 2.5, 5.0 and 10.0 Ni/SCA. Similar relationship is observed at lower temperature. It is worth notice that at 100 ^oC hydrogenation of benzene reaches 55% when the SCA supported catalyst containing 10% wt. of nickel is used.

In comparison to above discussed materials Ni/alumina catalyst is characterized by slightly better maximum conversion of 97 % at 200 ^oC, but its performance at lower temperature (e.g. 125 and 150 ^oC) is similar to that of 2.5 Ni/SCA and 5.0 Ni/SCA catalysts.

When comparing results obtained by “classic” nickel/alumina catalyst and “modern” Ni/SCA catalysts one should keep in mind that because of adopted methodology actual catalyst load vary. As it was said before in all tests the same volume ($1cm^3$) of catalyst was placed in microreactor. However, due to the differences in bulk density the mases of tested catalysts were different. In case of Ni/alumina catalyst it was 0.82 g, and in case of Ni/SCA only 0.34 g. As a result WHSV for the first catalyst is 0.8 h^{-1}, and for the latter 1.9 h^{-1}. Keeping that in mind the results obtained by nickel spherical carbon aerogel supported nickel catalysts make an even bigger impression.

Conclusions

Based on the obtained results, it was found that spherical carbon aerogels is an excellent material for the support of hydrogenation catalysts.

The nickel catalysts produced on SCA showed high activity in the hydrogenation reaction of benzene. Despite of 2.4 times higher WHSV the conversion rates of benzene in a wide range of reaction temperatures (125–200 ^oC) were comparable or higher than the conversion rates obtained on nickel catalysts based on commercial alumina. A 10.0 Ni/SCA catalyst proved to be a particularly active catalyst with conversion 88–94.5% in temperature range 150–200 ^oC.

The obtained test results show that spherical carbon aerogel can be a competitive material for commonly used active carbons. The main advantage of carbon aerogel materials is the ability to "tune" their capillary structure during the synthesis stage. Its allows to design material with properties selected for specific reactions. Moreover spherical carbon aerogels supported nickel catalysts are characterized by good mechanical properties.

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