



NEW COMPOSITE Ni/MULTI-WALLED CARBON NANOTUBES CATALYST IN HYDROGENATION OF CHLOROACETOPHENONE

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Development of new kinds of catalysts based on carbon materials is promising area of catalytic chemistry because of the possibility of obtaining materials with improved characteristics. Carbon nanofibers, multiwalled or singlewalled carbon nanotubes reveal such important properties as thermal and chemical resistance due to crystal and common electronic structure, so they can be used under hard reaction conditions (high temperature and pressure, different organic solvents and strong oxidizing agents). Also structure of carbon nanotubes provides better dispersion and bonding of metal nanoparticles and prevents aggregation of them during reaction.

In this work we used multi-walled conic carbon nanotubes as support for controlled insertion of metallic catalytic phases (i.e. nickel phase). This choice was imposed by morphology and regular structure of conic nanotubes: edges of conical graphite layers makes possible carboxylation of material almost for total surface of MWCNT. Carboxylation results in better loading and dispersion of metal particles joined with surface group by means of ionic or electrostatic forces. Moreover globules of MWCNT provide high surface value for composite material.

Before catalyst preparation nanotubes were treated by HNO₃ for 6 hours followed by washing up to pH=7. Four methods were applied for insertion of nickel into agglomerates of conic MWCNT: **a)** ion exchange of protons in surface –COOH groups with Ni²⁺ ions from excess of Ni(CH₃COO)₂ and **(b)** Ni(COO)₂ solution followed by H₂ reduction at 500°C; **c)** ion exchange of protons in –COOH groups with Ni²⁺ ions from excess of Ni(CH₃COO)₂ solution, followed by



reduction with hydrazine hydrate under the room temperature, **d**) sonochemical deposition of metallic nickel from Ni(CO)₄ solution on MWCNT surface. As a reference commercial catalyst Ni/SiO₂ (Südhemie) with 60 wt. % nickel content and “parent sample” of MWCNT were used.

The results obtained for Ni/MWCNT materials in reaction of hydrogenation of chloroacetophenone demonstrate strong dependence of catalyst activity on nickel dispersion and particles location. The lowest activity was measured for the "parent MWCNT" where most of nickel was in form of large (80 nm) particles at the external surface of MWCNT and small (8 nm) nickel particles encapsulated inside the channels and hardly accessible to reacting molecules. Deposition of nickel by ion-exchange with carboxyl groups protons with H₂-reduction yielded nanoparticles of 15-20 nm decorating the external surface of MWCNT. Increasing of loading of nickel increases the catalysts activity per gram of catalyst by 4-9 times. But increasing of nickel loading from 10.5 wt. % for sample **(a)** to 33.5 wt.% for sample **(b)** leads to decreasing of the activity of metal (per gram) because of lowering the metal dispersion. The reduction of the ion-exchange products by hydrazine hydrate yields to the catalyst **(c)** with less activity than "parent CNT". The reasons for this fact is formation of nickel chloride and hydroxide instead Ni⁰. The sonochemical deposition of nickel **(d)** yielded to catalyst with highest activity, which is a result of a combination of high nickel dispersion and metal loading. The sonochemical deposition of nickel decorated the external surface of MWCNT with small 4-6 nm nanocrystals of metallic nickel or their agglomerates of 8-10 nm. The efficiency of nickel calculated per gram of active metal in this Ni/MWCNT material is about 2 times higher compared with that in the commercially available catalyst.