SYNTHESIS, CHARACTERIZATION AND CATALYTIC PROPERTIES OF CARBON NANOTUBE-NANOPARTICLE NANOCOMPOSITES

András Sápi
Supervisor: Prof. Zoltán Kónya

Ph. D. School of Chemistry
University of Szeged, Faculty of Sciences
Department of Applied and Environmental Chemistry
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1. Introduction and aims

Mankind usually associates nanotechnology and nanoscience with microelectronical and informatical instruments. To improve fastness and high density microchips more than 1000 billion dollars have been investigated into these industrial stages. However, it is not clearly known that similar amount and type of investigation into the catalytic industry and research has been going on.

Catalysis is one of the most dynamically improving fields of the chemical industries due to expectations of green and economical chemistry which demand for catalysts with high activity and selectivity. Nanoscience with the possibility of production of novel catalyst supports and nanoparticles with different size and shape can be the answers for these increasing claims.

The nanoparticles showed dissimilarity to the bulk counterparts in the field of heterogeneous catalysis due to their tiny size and special, controllable shape. Beside the high surface-to-volume ratio non-metallic properties can be risen up in the nanometer scale where the fusion of the valence and conductive band does not occur. Furthermore, the outstanding catalytic properties of the nanoparticles can be attributed to the low coordination of the atoms, excess electronic charge and to the special nanoparticle-support interactions. Carbon nanotubes are promising candidates for novel catalyst supports due to their unique thermal, electric, mechanical and adsorption properties. New phenomena arisen from the combination of nanoparticles and carbon nanotubes can be resulted in novel nanocomposite based catalysts.

In the past few years several researches are focused on heterogenous catalytic reaction and on the synthesis, characterization and application of carbon nanotubes and 0D metallic or non-metallic nanoparticles at the Department of Applied and Environmental Chemistry.

The main objective of our research was to synthesize, characterize and catalytic test of novel carbon nanotube based nanoparticle nanocomposites. Furthermore, our aim was the investigation of the support-nanoparticle interactions and the support effect on the different catalytic processes.
2. Experimental

Multiwalled carbon nanotubes for catalyst support was synthesized on alumina supported Fe-Co catalysts with catalytic chemical vapor deposition (CCVD) optimized at the Department of Applied and Environmental Chemistry. Beside pristine nanotubes nitric acid functionalized and ball-milled counterparts with redundant surface chemistry were also prepared.

Wet impregnation method was used for preparation of different 0D metal or metal-oxide (Ni, Co, Pt, Pd, Rh and their oxides)/carbonaceous material (MWCNT, ball-milled MWCNT, amorphous carbon, graphite) nanocomposites. Benzene and toluene were applied as impregnation media due to the preferable wetting properties. Furthermore, transition metal acetylacetonates and acetates served as catalyst precursor since their adequate solubility and thermal stability. The metal content was adjusted to 5-35 w%. After the impregnation process the samples were dried and thermally treated in air or hydrogen at different temperature (180 °C – 380 °C) dependent upon precursor properties.

Morphology of the pristine and modified carbon nanotubes and the average particle diameter, size distribution and dispersion were characterized by transmission electron microscopy (TEM) as well as scanning electron microscopy (SEM). X-ray diffractometry (XRD) and electron diffraction (ED) technique were used for crystal structure, crystallinity and average particle diameter determinations.

Measurements of the adsorption/desorption isotherms, specific surface area, pore size distribution and pore volume of the different catalysts and supports were carried out in an automatic N₂ sorption equipment. Metal content of the catalysts were determined with energy dispersive spectroscopy (EDS) and thermogravimetry (TG). The number of the acidic sites of the different carbonaceous material supported palladium catalysts were calculated from temperature programmed desorption (TPD) studies. In case of the investigation of the nickel-oxide-carbon nanotube interactions extensive thermal analysis (TG-DTG-DTA) was used for decomposition temperature, rate and enthalpy determination.

The as-prepared catalysts were tested in cyclohexene and propene hydrogenation-dehydrogenation and ethanol steam reforming reactions. Activity, stability and selectivity were monitored by gas chromatography (GC) and infrared spectroscopy (IR).
3. New scientific results

**T.1. Preparation and characterisation of nickel catalysts supported on different carbon allotropes**

1.1 Nickel catalysts supported on different carbon based materials such as multiwalled carbon nanotubes, ball-milled multiwalled carbon nanotubes, graphite and amorphous carbon were synthesized by wet impregnation. The average diameter and size distribution of NiO and Ni nanoparticles were characterized by TEM and XRD techniques. In spite of the chemical similarity the nanoparticles, their diameters were found to depend strongly on the structure of the carbon-based supports.

1.2 Catalysts supported on carbon nanotubes showed higher activity than amorphous carbon and graphite based catalysts in cyclohexene hydrogenation reactions below 1:9 hydrocarbon:hydrogen ratio. The catalytic activity dissimilarities observed between pristine and ball-milled carbon nanotube supported catalysts can be attributed to the effects of unequal number of surface defects and functional groups.

**T.2. Preparation and characterisation of carbon based palladium catalysts**

2.1 Pristine and acid-functionalized carbon nanotube, amorphous carbon and graphite supported palladium catalysts were also prepared. TEM studies revealed that smaller (1-2 nm) nanoclusters are agglomerated into larger (7-8 nm) nanoparticles in case of the pristine carbon nanotube based samples. Such phenomenon was not observed on functionalized carbon nanotube supported catalysts due to the oxygenated surface functional groups/nanoparticle interactions. Unlike Ni/carbon nanocomposites, the type of the carbonaceous supports does not appear to effect the average diameter of supported palladium nanoparticles.

2.2 Both carbon nanotube supported catalysts exhibited high and long-lasting activity in the hydrogenation of cyclohexene. The rapid decline of the initial 100% conversion measured on the amorphous carbon based catalyst can be attributed to the deactivation step taking place on Broensted acidic sites found to be present in relatively high amounts as determined by NH₃ TPD. In case of the functionalized carbon nanotube based catalyst no significant deactivation
was observed despite the high number of active sites. This phenomenon can be assigned to the stable, stacky structure of the support.

**T.3. Hydrogen production over multiwalled carbon nanotube supported catalysts**

3.1 Nickel, cobalt, platinum and rhodium catalysts supported on acid functionalized multiwalled carbon nanotubes were also synthesized. The nanoparticles decorating the nanotubes were identified as metallic (Pt and Rh) as well as oxide (NiO and Co₃O₄) phases by XRD after the oxidative precursor decomposition process. In case of the cobalt catalyst, the presence of the reduced, mixed oxide form and the relatively high metal content determined by EDS can be attributed to the reductive behavior of the carbon nanotube support. TEM images indicated that the nanoparticle size distributions on the carbon nanotube surfaces are polydisperse in case of cobalt and platinum catalysts. On the other hand, the CNT supported nickel and rhodium catalysts are monodisperse, although the rhodium nanoparticles are partially agglomerated into larger (20-50 nm) nanoclusters.

3.2 Steam reforming of ethanol (SRE) for hydrogen was studied using CNT-based nickel, cobalt, platinum and rhodium catalysts and the results were compared to those measured on commercial Ni/Al₂O₃. The Ni/CNT and Co/CNT catalysts exhibited the highest activity and selectivity in hydrogen production and were found to outperform the reference commercial catalyst. Complete ethanol conversion is achieved over Ni/CNT at around 400 °C. Co/CNT produces the highest hydrogen yield at 450 °C with low CO and CH₄ selectivity. Pt and Rh CNT-based catalysts were found to have low activity and selectivity in the SRE reaction.

**T.4. 3D CNT scaffolds as catalyst support**

4.1 Palladium decorated aligned carbon nanotubes grown on microstructured SiO₂/Si chips were also produced by wet impregnation followed by either solely reductive or oxidative plus reductive precursor decomposition. The nitrogen adsorption behavior could be described as a Type II isotherm with a pronounced multilayer condensation region at high relative pressures. The pore size distribution curve was found to be bimodal: while the majority of the pores were macropores over 10 nm in diameter, there was also a well-defined mesoporous contribution at ~3 nm pore diameter. The larger pores correspond to the general
voids formed by the intercrossings of carbon nanotubes in the membrane, whereas the smaller ones are related to the V-shaped channels defined by the cylindrical outer surfaces of two quasi parallel neighboring multiwalled carbon nanotubes.

4.2 The larger average size of the palladium nanoparticles supported on the CNT surface in case of the samples calcined in air can be attributed to the surface diffusion and coalescence of the nanoparticles during the treatment with longer duration at high temperature. A significant difference between the obtained catalysts is that the nanotube support was partially consumed in calcined samples because the catalyst nanoparticles drilled nano-sized holes and cavities into the CNT walls due to palladium catalyzed carbon oxidation processes.

4.3 Both reduced and oxidized-reduced CNT scaffold supported palladium catalyst exhibited stable and high catalytic activity in propene hydrogenation because of the ordered macrostructure. The highest activity (TOR = 1.1 molecules·s⁻¹·Pd active site⁻¹) was achieved at 120 °C. Apparent activation energies calculated from the Arrhenius-type diagram were 27.8 ± 0.6 kJ·mol⁻¹ in the intrinsic-kinetic regime, 12.0 ± 0.2 kJ·mol⁻¹ in the internal diffusion regime and 4.8 ± 0.2 kJ·mol⁻¹ in the external diffusion regime.

T.5. CNT-nanoparticle interactions study

5.1 The structure of the carbon nanotube support deteriorated with increasing temperature during the Ni(acac)₂/carbon nanotube calcination. The initially tiny (1-2 nm) Ni(acac)₂ nanoparticles coalesced into larger (2-4 nm) particles through surface diffusion. The catalytic carbon oxidation reactions responsible for the graphitic layer destruction occurred simultaneously. NiO nanoparticles drilled into the walls of the CNTs agglomerated due to the extensive destruction of the carbon nanotube support during calcinations at higher temperature (653 K).

5.2 In situ TEM studies showed that the nickel salt particles decomposed and that CNT oxidation due to the high energy of the incident electron beam suppressed the surface diffusion phenomenon. The surface of the observed nanotubes was completely destroyed and their outer diameter decreased to approx. 75% of the initial value after 7 minutes of electron beam exposure. The dominant process is the radial movement of particles towards the
nanotube axis, however, particle migration parallel with the CNT axis was also observed. The depth and width of the drilled pits both increased with irradiation duration.

5.3 Thermogravimetric measurements showed that in the presence of the carbon nanotube support the decomposition temperature of the Ni(acac)$_2$ precursor decreased from 614 K to 580 K. This can be attributed to the small size of the nickel based particles and the special interactions between the carbon nanotubes and the complex electron system of the Ni(acac)$_2$ precursor. The carbon decomposition started at 680 K in case of pristine carbon nanotubes, while in the presence of the nickel the carbon oxidation occurred immediately after the nickel precursor decomposition (580 K). Carbon oxidation was both faster and more complete in the presence of NiO nanoparticles.

5.4 The activation energy of the Ni(acac)$_2$ precursor decomposition as calculated from DTA measurements was 28.11 kJ·mol$^{-1}$ and 26.35 kJ·mol$^{-1}$ in the case of raw and carbon supported Ni(acac)$_2$ precursor, respectively. The lower value measured for the carbon supported precursor can be attributed to the interaction between the CNT surface and d orbitals of the nickel atoms. The significant difference in the activation energy of pristine and Ni(acac)$_2$ decorated carbon nanotube decomposition is explained by the carbon oxidation reactions catalyzed by the NiO formed.

4. Publications related to the present thesis

1. Synthesis and catalytic application of metallic nanoparticles

   A. Sápi, Z. Kónya, Á. Kukovecz, and I. Kiricsi

   *Ed.: Tamás Szőrényi: Nanoparticles: Production pathways and appealing applications,*  


   IF$_{2012}$: 0.000, independent citations: 0
2. Fundamental aspects of the synthesis, modification, characterization and catalytic testing of various silicate forms and metal nanoparticle-mesoporous silicate composite materials

A. Sapi, R. Remias, A. Kukovecz, I. Palinko, Z. Konya, I. Kiricsi


IF2010: 0,000, independent citations: 0

3. Adsorption of C6 hydrocarbon rings on mesoporous catalyst supports

R. Remias, A. Sapi, R. Puskas, Z. Konya, Á. Kukovecz, I. Kiricsi


IF2009: 2,291, independent citations: 0

4. Low temperature growth of multi-walled carbon nanotubes by thermal CVD


IF2010 = 1,344, independent citations: 0

5. Synthesis and characterization of nickel catalysts supported on different carbon materials

A. Sápi, R. Rémiás, Z. Kónya, Á. Kukovecz, K. Kordás, I. Kiricsi

*RKCL 96 (2009) 379-389

IF2009 = 0,557, independent citations: 0
6. CNT-based catalysts for \( \text{H}_2 \) production by ethanol reforming


\( \text{IF}_{2010} = 4.053, \) independent citations: 1

7. Three-Dimensional Carbon Nanotube Scaffolds as Particulate Filters and Catalyst Support Membranes


\( \text{IF}_{2010} = 9.855, \) independent citations: 9

5. Presentations, posters, attending conferences

1. Low temperature CVD synthesis of multiwall carbon nanotubes

A. Sápi, L. Nagy, Á. Kukovecz, K. Kordás, G. Tóth, Z. Kónya

*IWEPNM 2011, Kirchberg in Tirol, Austria, 2011 (poster)*

2. Tungsten oxide and titanium dioxide nanowires – Preparation, doping and application

M. Szabó, M. C. Wu, M. Mohl, A. Sápi, G. Tóth, K. Kordás, Á. Kukovecz, Z. Kónya

*IWEPNM 2011, Kirchberg in Tirol, Austria, 2011 (poster)*
3. Mechanical resistance of titanate nanowires
A. Sápi, G. István, L. Nagy, Á. Kukovecz, Z. Kónya
10th Multinational Congress on Microscopy, Urbino, Italy, 2011 (presentation)

4. One dimensional titanate nanostructures
A. Sápi, Á. Kukovecz, Z. Kónya
EuroNanoForum, Budapest, Hungary, 2011 (presentation)

5. Synthesis of nanoparticles based on high energy methods
A. Sápi, Á. Kukovecz, Z. Kónya
TÁMOP-4.2.1/B-09/1/KONV-2010-0005 project lectures; Szeged, Hungary, 2011 (presentation)

6. Synthesis and catalytic applications of metallic nanoparticles
A. Sápi, Á. Kukovecz, Z. Kónya, I. Kiricsi
TÁMOP-4.2.2.-08/1/08/1/2008-0016 project lectures; Dunaújváros, Hungary, 2011 (presentation)

7. Ex situ and In situ TEM examination of CNT modification
A. Sápi, Á. Kukovecz, Z. Kónya, I. Kiricsi
Magyar Mikroszkópos Konferencia, Siófok, Hungary, 2010 (presentation)

8. Synthesis and characterisation of various NiO/CNT nanocomposites
A. Sápi, Á. Kukovecz, Z. Kónya, I. Kiricsi
Magyar Mikroszkópos Konferencia, Siófok, Hungary, 2009 (presentation)

9. Moderate electrical anisotropy in aligned multi-walled carbon nanotube forests and carbon nanotube/epoxy composites
NGS Meeting, Jyväskylä, Finland, 2009 (poster)
10. Electrical properties and gas sensitivity of nickel-palladium nanowire thin films
_Nanoscience days, Jyväskylä, Finland, 2009 (poster)_

11. Multi-walled carbon nanotubes grown in 3-dimensional templates: Facile route towards novel membrane-type catalyst support materials
_Nanoscience days, Jyväskylä, Finland, 2009 (poster)_

12. Carbon nanotube based catalysts for ethanol reforming and hydrogen fuel cells
_Nanoscience days, Jyväskylä, Finland, 2009 (poster)_

13. Preparation and catalytic activity study of Ni/C nanocomposites
A. Sápi, Á. Kukovecz, Z. Kónya, I. Kiricsi
_MTA Katalízis Munkabizottság gyűlése, Szeged, Hungary, 2008 (presentation)_

14. On the morphology and transport properties of HDPE-titanate nanowire nanocomposites
_IWEPNM 2007, Kirchberg in Tirol, Austria, 2007 (poster)_

15. System for thermal properties measurements
A. Sápi, J. Szél, Á. Kukovecz, Z. Kónya, I. Kiricsi
_XXVIII. OTDK, Szeged, Hungary, 2007 (presentation)_

16. Developing a system for measuring thermal properties of nanocomposites
A. Sápi, J. Szél, Á. Kukovecz, Z. Kónya, I. Kiricsi
_XI. Természettudományi ETDK, Temesvár, Romania, 2006 (presentation)_
17. Spectroscopic studies on self-supporting multi-wall carbon nanotube based composite films for sensor applications
R. Smajda, Z. Győri, A. Sápi, M. Veres, A Oszkó, J. Kis-Csitári, Á. Kukovecz, Z. Kónya, I. Kiricsi
XXVIII. EUCMOS (2006), Istanbul, Turkey, 2006 (poster)

18. System based on a periodic method for thermal analysis of nanocomposites
A. Sápi, J. Szél, Á. Kukovecz, Z. Kónya, I. Kiricsi
VIII. Temesvári Műszaki TDK, Temesvár, Romania, 2006 (presentation)

6. Other publications

1. One-pot liquid phase catalytic conversion of ethanol to 1-buthanol over aluminium oxide – The effect of the active material on the selectivity
Catalysts 2 (2012) 68-84
IF2010 = 0.000, independent citations: 0

2. Characterization of carbon thin films prepared by the thermal decomposition of spin coated polyacrylonitrile layers containing metal acetates
M. Darányi, I. Sarusi, A. Sápi, Á. Kukovecz, Z. Kónya, A. Erdőhelyi
Thin Sol. Films 520 (2011) 57-63
IF2010 = 1.909, independent citations: 0

3. Thermal diffusivity of aligned multi-walled carbon nanotubes measured by the flash method
IF2010 = 1,344, independent citations: 0
*Nano Research* 4 (2011) 360-369
IF$_{2010}$ = 5,071, independent citations: 1

5. Nervous system effects of dissolved and nanoparticulate cadmium in rats in subacute exposure
E. Horvath, G. Oszlánczi, Zs. Máté, A. Szabó, G. Kozma, A. Sápi, Z. Kónya, E. Paulik, L. Nagymajtényi, A. Papp
*J. Appl. Toxicology* 31 (2011) 471-476
IF$_{2010}$ = 2,322, independent citations: 0

6. Nervous system effects in rats on subacute exposure by lead-containing nanoparticles via the airways
G. Oszlánczi, A. Papp, A. Szabó, L. Nagymajtényi, A. Sápi, Z. Kónya, E. Paulik, T. Vezér
*Inhalation Toxicology* 23 (2011) 173-181
IF$_{2010}$ = 2,295, independent citations: 0

7. Nitrogen-Doped Anatase Nanofibers Decorated with Noble Metal Nanoparticles for Photocatalytic Production of Hydrogen
*ACS NANO* 5 (2010) 5025-5030
IF$_{2010}$ = 9,855, independent citations: 1
8. Subacute exposure of rats by metal oxide nanoparticles through the airways: general toxicity and neurofunctional effects
*Acta Biologica Szegediensis* 54 (2010) 165-170
IF$_{2010}$ = 0,000, independent citations: 0

9. Increasing chemical selectivity of carbon nanotube-based sensors by fluctuation-enhanced sensing
*FNIL* 9 (2010) 277-287
IF$_{2010}$ = 0,317, independent citations: 0

10. Moderate anisotropy in the electrical conductivity of bulk MWCNT/epoxy composites
*CARBON* 48 (2010) 1918-1925
IF$_{2010}$ = 4,893, independent citations: 1

11. Synthesis and properties of novel Ba(II)Fe(III) layered double hydroxides
D. Sranko, A. Pallagi, E. Kuzmann, S. E. Canton, M. Walczak, A. Sápi, Z. Kónya, Á.
Kukovecz, P. Sipos, I. Pálinko
IF$_{2010}$ = 2,303, independent citations: 4
12. Carbon nanotube based sensors and fluctuation enhanced sensing
IF$_{2010}$ = 0,000, independent citations: 0

13. Chemical synthesis of poly(3-thiophene-acetic-acid)/magnetite nanocomposites with tunable magnetic behaviour
IF$_{2010}$ = 1,871, independent citations: 2

14. Neurotoxic effects of metal oxide nanoparticles on the somatosensory system of rats following subacute intratracheal application
CEJOEM 14 (2008) 277-290
IF$_{2008}$ = 0,000, independent citations: 0

15. More attention to the plastics!
A. Sápi
A Kémia Tanítása 1 (2008) 16-26
IF$_{2008}$ = 0,000, independent citations: 0

16. Spectroscopic studies on self-supporting multi-wall carbon nanotube based composite films for sensor applications
R. Smajda, Z. Győri, A. Sápi, M. Veres, A. Oszkó, J. Kis-Csírá, Á. Kukovecz, Z. Kόnya, I. Kiricsi
IF$_{2007}$ = 1,440, independent citations: 8
17. Building up a system based on periodic method for measuring thermal properties of nanocomposites

A. Sápi

ISBN: (10)973-638-254-0 April, 2006
IF$_{2006}$ = 0,000, independent citations: 0

Peer-reviewed papers total: 24 out of this, related to the topic of the thesis: 7
Cumulative impact factor: 51,720 out of this, related to the topic of the thesis: 18,100
Independent cites total: 26 out of this, related to the topic of the thesis: 10