CARBON NANOSTRUCTURES WITH DIFFERENT DIMENSIONALITY – FROM SYNTHESIS TO APPLICATIONS

Ph.D. thesis

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1. Introduction

One of the key sectors nowadays is nanotechnology that produced a considerable amount of results in its few decades of existence, most of which are now widespread in everyday life. Examples include information technology, transportation, detergents, sports equipment, etc.

A lot of effort has also been made to utilize the benefits of nanotechnology in the field of catalysis for the production of catalysts with higher stability and selectivity. Zero dimension nanoparticles exhibit properties missing from bulk phase which are attributed to the high surface to volume ratio of nananoparticles, unstably coordinated atoms and particle-support interactions. Particle-support interaction greatly depends on both the position of nanoparticles on the support and on the presence of surface moieties, like minute amounts of foreign elements, functional groups or impurities.

Several attempts have been made in the past decades to transfer the beneficial properties of nanomaterials into macroscopic scale, which was mostly achieved by creating different composites. These solutions however are not capable of utilizing the possibilities provided by nanomaterials completely, as composites only allow the improvement of the properties of bulk materials; the full utilization of all beneficial properties of nanomaterials however remain unsolved. For this reason in recent years an increasing amount of research has been conducted for creating bulk phase materials purely from nanostructures, which in turn should be able to combine the beneficial properties of nanomaterials with the ease of handling of macroscopic objects.

Several studies already dealt with the production, characterization and utilization of porous, 0D and 1D nanostructures at the Department of Applied and Environmental Chemistry, which opened an opportunity for the production and modification of new kinds of carbon nanostructures on the basis of knowledge already acquired in the past. The aim of my work was to expand this knowledge in the following ways:

1. The control of specific surface area and total pore volume of mesoporous carbons within a wide range.

2. The modification of mesoporous carbon materials with palladium nanoparticles and trace amount of elements with different techniques. Testing the catalytic properties of supported nanoparticles in a hydrogenation model reaction.

3. Revealing the effects of different functionalization times on the carbon structure and formation of metallic and oxide nanoparticles.

4. Better understanding the effects of surface moieties forming at carbon nanotube synthesis and functionalization.

5. Assembly of self-supported 3D nanostructures purely made of carbon nanotubes, where the assembly process does not hinder the modification of nanotubes themselves.

2. Experimental

The carbon nanotubes used for all experiments were synthesized by the widely known catalytic chemical vapor deposition method (CCVD) on alumina supported iron-cobalt catalysts. Oxidation modified, Soxhlet-extractor washed and Pd nanoparticle modified versions of nanotubes were also created.

Mesoporous amorphous carbon structures exhibiting high specific surface area were created by the chemical vapor infiltration (CVI) method using silicon-dioxide as template. For the removal of the silica template both hydrofluoric acid and sodium-hydroxide solutions were employed. Both carbon nanotubes and mesoporous carbon structures were modified with the widely employed wet impregnation method.

The physical properties like average diameter, length, dispersion or structure of carbon nanotubes, amorphous carbon structures and supported nanoparticles were determined by using transmission electron microscopy (TEM). The crystal structure and in some cases the crystallite size of supported nanoparticles and carbon structures was determined by X-ray powder diffractometry (XRD) and/or electron diffraction (ED). The specific surface area, pore size distribution and total pore volume of carbon structures were determined by nitrogen adsorption-desorption analysis, while their thermal stability with thermogravimetry (TG). The concentration of metal on nanoparticle modified structures were determined by energy dispersive X-ray spectroscopy (EDS). Prepared samples were also subjected to catalytic testing in a continuous flow reactor, where the ratio of product and reactant was determined by gas chromatography (GC).

For the preparation of 3D carbon nanotube structures we used the centrifugation method developed in our laboratory. This method allows the preparation of nanotube objects with different size and shape without incorporating additional materials or the need for post-synthetic treatments. The mechanical properties of carbon nanotube assemblies were determined by dynamic mechanical analysis (DMA) and a simple elasticity test, while the thermal properties were determined by thermogravimetry.

3. New scientific results

T.1. Synthesis of Pd/CMH systems and the testing of their catalytic activity in cyclohexene hydrogenation

1.1. Mesoporous carbon structures with high thermal and mechanical stability, specific surface area and total pore volume were synthesized with the hard template method on mesoporous silica templates of different particle size. The free changing of specific surface area and total pore volume within broad limits with relative ease was successfully demonstrated by selecting and mixing appropriate templates. This method also does not show some of the disadvantages found in other methods devised for changing these attributes.

1.2. The modification of mesoporous carbon structures with Pd nanoparticles was done by the widely known wet impregnation method as well as with the "Pd-sol" method developed in our laboratory. By studying the prepared samples, it was found that while the size of nanoparticles made by the Pd-sol method showed dependence on the carbonization temperature, the nanoparticles made with the wet impregnation method did show such relationship with temperature. The etching agents used did not affect particle size significantly.

1.3. Catalytic tests were also performed on samples by utilizing the hydrogenation of cyclohexene as a model reaction. Samples modified with the Pd-sol method showed the lowest activity which is attributed to the coverage of nanoparticles with amorphous carbon forming during synthesis. The presence of the low conversion rate detected on such samples thus proves that amorphous carbon does not isolate the particles completely, but only serve as a considerably high diffusion limitation. Samples prepared with the wet impregnation method showed average to high conversion rates depending on the etching method used, where samples etched with NaOH showed the highest. This was attributed the presence of surface hydroxide groups formed during etching and trace amounts of Na which is known to have promoting effects.

T.2. The modification and characterization of carbon nanotubes with oxidation and palladium nanoparticles.

2.1. By the systematic oxidation of carbon nanotubes we demonstrated that the size of nanoparticles closely follows Raman G/D ratios regardless of nanoparticles being metallic or oxide in nature. This allows to assume that the change in nanotube surface environment affects the formation of both oxide and metallic nanoparticle identically despite their different electronic properties. It was also demonstrated that nanoparticles initially forming on the nanotube surface are built up of several smaller crystallites, which later during the activation process performed prior to catalytic testing sinter to form coherent particles.

2.2 The systematic oxidation and decoration of nanotubes was then supplemented by Soxhlet-extractor enhanced acetone washing. It was found that impurities left from the synthesis negatively affect supported nanoparticle size and specific surface area. Oxidation debris forming during oxidation also affects specific surface area heavily, but the size of nanoparticles remains unaffected by it. Functional groups forming during oxidation were not found to affect nanoparticle size or specific surface area. Raman spectroscopic measurements also demonstrated that the ratio calculated from graphitic G and disorder induced D bands is only affected by oxidation debris, but not by functional groups or post-synthetic impurities.

2.3 Catalytic performance tests were also performed on palladium modified samples. It was found that post-synthetic impurities and functional groups forming during synthesis have a beneficial effect on conversion, while the oxidation debris affects conversion negatively. The shortening of nanotubes during oxidation has the ability to counter the negative effects of oxidation debris, which is particularly pronounced for particles residing on the inner side of the nanotube walls.

T.3. Low temperature preparation of 3D solids purely from carbon nanotubes with different size and shape.

3.1 A new method has successfully been devised for the preparation of 3D solids purely from carbon nanotubes. This methods allows the preparation of bulk solids from modified nanotubes, as the preparation procedure itself can happen any time after various nanotube modification procedures. Since there is no need for high temperature treatments, nanotubes modified with less stable functionalities could also be used.

3.2 The mechanical properties of nanotube bulks created with this new method has also been investigated, where the stiffness of the material was found to be dependant on the amount of adsorbed water. The material is also capable of adsorbing 2.5 wt% of water from moist air, which is also enough for changing the mechanical properties. By utilizing a simple elasticity test it was found that the bulk nanotube material absorbs more energy during elastic deformation than the aluminum bar used for comparison. This is though to be caused by the friction happening between nanotubes during deformation.

4. Publications the Thesis is based upon

1. **A Novel Catalyst Type Containing Noble Metal Nanoparticles Supported on Mesoporous Carbon: Synthesis, Characterization and Catalytic Properties**
   E. Horváth, **R. Puskás**, R. Rémiás, M. Mohl, Á. Kukovecz, Z. Kónya, I. Kiricsi
   Topics in Catalysis, 2009; 52 (9), 1242-1250
   DOI:10.1007/s11244-009-9277-2
   IF_{2009}: 2.38
2. **Adsorption of C6 hydrocarbon rings on mesoporous catalyst supports**
   R. Rémiás, A. Sápi, **R. Puskás**, Á. Kukovecz, Z. Kónya, I. Kiricsi
   Chemical Physics Letters, 2009; 482 (4-6), 296-301
   DOI: 10.1016/j.cplett.2009.10.016
   IF_{2009}: 2.29
3. **Low-temperature growth of multi-walled carbon nanotubes by thermal CVD**
   N. Halonen, A. Sapi, L. Nagy, **R. Puskas**, A.R. Leino, J. Maklin, J. Kukkola, G. Toth, M.C. Wu, H.C. Liao, W.F. Su, A. Shchukarev, J.P. Mikkola, A. Kukovecz, Z. Konya, K. Kordas
   Physica Status Solidi (b), 2011; 248 (11), 2500-2503
   DOI: 10.1002/pssb.201100137
   IF_{2011}: 1,32
4. **Comparison of Nanoscaled Palladium Catalysts Supported on Various Carbon Allotropes**
   R. Puskás, A. Sápi, A. Kukovecz, Z. Kónya
   Topics in Catalysis 2012; 55(11-13), 865-872
   DOI: 10.1007/s11244-012-9861-8
   IF_{2012}: 2.61
5. **Effects of carbon nanotube functionalization on the agglomeration and sintering of supported Pd nanoparticles**
   R. Puskás, Á. Kukovecz, Z. Kónya
   Adsorption, 2013; 19 (2-4), 501-508
   DOI: 10.1007/s10450-013-9472-0
   IF_{2013}: 1.74

6. **Mesoporous carbon supported Pd nanoparticles with high specific surface area for cyclohexene hydrogenation; Outstanding catalytic activity of NaOH treated catalysts**
   R. Puskás, T. Varga, A. Grósz, A. Sápi, A. Oszkó, Á. Kukovecz, Z. Kónya
   Submitted
7. **On the role of post-CCVD synthetic impurities, functional groups and functionalization-based oxidation debris on carbon nanotubes**
   R. Puskás, A. Sápi, Á. Kukovecz, Z. Kónya
   Submitted

5. Lectures, posters, conference participations

1. **Synthesis and characterisation of large pore volume mesoporous carbon**
   E. Horváth, **R. Puskás**, M. Mohl, Á. Kukovecz, Z. Kónya, I. Kiricsi
   Carbon for Energy Storage and Environment Protection, Krakow, Poland 2007 (poster)
2. **Synthesis and characterization of noble metal nanoparticles supported in the ordered pore system of mesoporous carbon**
   E. Horváth, **R. Puskás**, R. Rémiás, Z. Kónya, I. Kiricsi
   IX. Pannonian International Symposium on Catalysis, Strbske pleso, Slovakia, 2008 (poster)
3. **Different carbon allotrope supported metal nanoparticles in catalysis**
   R. Puskás, Á. Kukovecz, Z. Kónya
   Annual conference of Hungarian Society for Microscopy, Siófok, Hungary, 2011 (lecture)
4. **Carbon nanotube functionalization and its effects on agglomeration and sintering of Pd nanoparticles**
   R. Puskas, Á. Kukovecz, Z. Kónya
   VIII. Symposium on Effects of Surface Heterogeneity in Adsorption and Catalysis, Kraków, Poland, 2012 (lecture)
5. **The effect of surface defects and functional groups on the sintering and agglomeration of Pd nanoparticles**

R. Puskás, Á. Kukovecz, Z. Kónya

V. Szeged International Workshop on Advances in Nanoscience, Szeged, Hungary, 2012 (poster)

6. **A systematic study of carbon nanotube functionalization and purification on catalytic activity and surface properties**

   R. Puskás, Á. Kukovecz, Z. Kónya

   Annual conference of Hungarian Society for Microscopy, Siófok, Hungary, 2014 (lecture)

7. **A systematic study of carbon nanotube functionalization and purification on catalytic activity and surface properties**

   R. Puskás, Á. Kukovecz, Z. Kónya

   Hungarian Academy of Sciences Work Committee for Environmental Chemistry, 3rd Symposium for Environmental Chemistry Lajosmizse, Hungary, 2014 (lecture)

   (MTA Környezeti Kémiai Munkabizottság 3. Környezetkémiai Szimpóziuma)

8. **Formation and characterization of gold nanoparticles on titanate nanotubes and nanowires**

   P. Pusztai, **R. Puskás**, L. Nagy, E. Varga, A. Erdőhelyi, Á. kukovecz, Z. Kónya, J. Kiss

   Joint Vacuum Conference, 2014. Wien, Austria (lecture)

9. **Nanokompozitok vizsgálati lehetőségei (Possibilities for the investigation of nanocomposites)**

   R. Puskás, Á. Kukovecz, Z. Kónya

   Joint event of Hungarian Academy of Sciences Regional Committee in Szeged and TÁMOP-4.2.2.C-12/1/KONV-2012-0012: Nanocomposites: From basic research to industrial applications, Szeged, Hungary, 2014 (lecture)

   (MTA SZAB Kémiai Szakbizottság Anyagtudományi Munkabizottság és a TÁMOP-4.2.2.C-12/1/KONV-2012-0012 közös rendezvénye: Nanokompozitok: alapkutatástól az ipari alkalmazásokig)

6. Other publications

1. **In situ synthesis of catalytic metal nanoparticle-PDMS membranes by thermal decomposition process**

   A. Goyal, M. Mohl, A. Kumar, **R. Puskas**, A. Kukovecz, Z. Konya, I. Kiricsi, P.M. Ajayan

   Composites Science and Technology, 2010; 71 (2), 129-133

   DOI: 10.1016/j.compscitech.2010.10.010

   IF_{2010}: 2.86

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

   N. Halonen, A. Sapi, L. Nagy, **R. Puskas**, A.R. Leino, J. Maklin, J. Kukkola, G. Toth, M.C. Wu, H.C. Liao, W.F. Su, A. Shchukarev, J.P. Mikkola, A. Kukovecz, Z. Konya, K. Kordas

   Physica Status Solidi (b), 2011; 248 (11), 2500-2503

   DOI: 10.1002/pssb.201100137

   IF_{2011}: 1.32

3. **Effect of planetary ball milling process parameters on the nitrogen adsorption properties of multiwall carbon nanotubes**

   I.Z. Papp, G. Kozma, **R. Puskás**, T. Simon, Z. Kónya, Á. Kukovecz

   Adsorption, 2013; 19 (2-4), 687-694

   DOI: 10.1007/s10450-013-9493-8

   IF_{2013}: 1.74

4. **Palladium Nanoparticle–Graphene Catalysts for Asymmetric Hydrogenation**

   K. Szőri, **R. Puskás**, Gy. Szőllősi, I. Bertóti, J. Szépvölgyi, M. Bartók

   Catalysis Letters, 2013; 143 (6), 539-546

   DOI: 10.1007/s10562-013-1006-6

   IF_{2013}: 2.29

5. **Synthesis and characterization of polyvinyl alcohol based multiwalled carbon nanotube nanocomposites**

   E.Y. Malikov, M.B. Muradov, O.H. Akperov, G.M. Eyvazova, **R. Puskás**, D. Madarász, L. Nagy, Á. Kukovecz, Z. Kónya

   Physica E Low-dimensional Systems and Nanostructures, 2014; 61, 129–134.

DOI: 10.1016/j.physe.2014.03.026

IF_{2014}: 1.86

6. **Influence of gold additives on the stability and phase transformation of titanate nanostructures**

   P Pusztai, **R Puskás**, E Varga, A Erdőhelyi, A Kukovecz, Z Kónya, J Kiss

   Physical Chemistry Chemical Physics, 2014; 16 (48), 26786-26797

   DOI: 10.1039/c4cp04084h

   IF_{2014}: 4.20

7. **Microphysical properties of carbonaceous aerosol particles generated by laser ablation of a graphite target**

   T. Ajtai, N. Utry, M. Pintér, G. Kiss-Albert, **R. Puskás**, Cs. Tápai, G. Kecskeméti, T. Smausz, B. Hopp, Z. Bozóki, Z. Kónya, G. Szabó

   Atmospheric Measurement Techniques, 2015; 8 (3),1207-1215

   DOI: 10.5194/amt-8-1207-2015

   IF_{2014}: 3.21

8. **Synthesis and characterization of CdS nanoparticle based multiwall carbon nanotube–maleic anhydride–1-octene nanocomposites**

   E.Y. Malikov, M.C. Altay, M.B. Muradov, O.H. Akperov, G.M. Eyvazova, **R. Puskás,** D. Madarász, Á Kukovecz, Z. Kónya

   Physica E Low-dimensional Systems and Nanostructures, 2015; 69, 212-218

   DOI: 10.1016/j.physe.2015.01.040

   IF_{2014}: 1.86

9. **Synthesis of tungsten carbide and tungsten disulfide on vertically aligned multi-walled carbon nanotube forests and its application as non-Pt electrocatalyst for the hydrogen evolution reaction**

   J.F. Lin, O. Pitkänen, J. Mäklin, **R. Puskás**, A. Kukovecz, A. Dombovari, G. Toth, K. Kordas

   Journal of Materials Chemistry A, 2015; 3, 14609-14616

   DOI: 10.1039/C5TA02908B

   IF_{2014}: 7,44

10. **Propionic Acid Produced by Propionibacterium acnes Strains Contributes to Their Pathogenicity.**

    G. Tax, E. Urbán, Zs. Palotás, **R. Puskás**, Z. Kónya, T. Bíró, L. Kemény, K. Szabó

    Acta Dermato-Venereologica 2015;

    DOI: 10.2340/00015555-2154

    IF_{2014}: 4.24

11. **Facile synthesis of CuS nanoparticles deposited on polymer nanocomposite foam and their effects on microstructural and optical properties**

    M.C. Altay, E.Y. Malikov, G.M. Eyvazova, M.B. Muradov, O.H. Akperov, **R. Puskás**, D. Madarász, Z. Kónya, Á. Kukovecz

    European Polymer Journal, 2015; 68, 47-56

    DOI:10.1016/j.eurpolymj.2015.04.036

    IF_{2014}: 3.24

Number of reviewed articles: 17	related to the thesis: 7
Cumulative impact factor: 43.18	related to the thesis: 10.34
Total independent citations: 57	related to the thesis: 19