SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF MESOPOROUS OXIDE MATERIALS SYNTHESIZED USING SOFT AND HARD TEMPLATES

Ph.D. thesis

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1. Background and objectives

Nanostructured materials are becoming increasingly important today because of certain benefits they offer over bulk phases. Nanotechnology is the science of synthesizing, characterizing and using these materials. Increasing demand for nanostructures has recently put their reproducible and economically feasible synthesis, as well as their rapid and accurate characterization into the focus of scientific attention.

Porous solid materials are characterized into microporous (pore diameter below 2 nm), mesoporous (2–50 nem pore diameter) and macroporous (pore diameter above 50 nm) according to IUPAC. The term "nanoporous material" is used frequently to refer to materials witha characteristic pore diameter below 100 nm. The synthesis, characterization and application of nanoporous materials has been a continuously developing field of materials science in the past few decades. The main reason for this attention is that the high specific surface area (~100-1000 m^2 g^{-1}) of nanoporous materials makes them excellent candidates for catalytic and adsorption applications. The specific surface area can even be controlled and increased further by reducing the pore diameter.

The objective of my doctoral research work was the synthesis of various mesoporous materials by using soft and hard templates. I was particularly interested in uncovering the relationships between the synthesis conditions and the properties of the products. My secondary objective was to find practical applications for the new materials.

One of my major research directions was the creation of core-shell nanostructures and the functionalization of hollow inorganic nanospheres. Further research efforts were devoted to the synthesis and catalytic applications of mesoporous oxides and to the synthesis and nanocomposite applications of silica foams.

2. Experimental

Two groups of mesoporous materials were synthesized. Hollow silica nanospheres (HSNS) were obtained by first creating polystyrene–silica core-shell structures and then removing the hard polystyrene (PS) template by heat treatment. The morphology of the HSNS was governed by that of the PS. The size and morphology of the resulting nanostructures was assessed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). HSNS samples featuring adequate stability and the desired morphology were chemically functionalized by substituting their surface OH groups with aminopropyl groups both in toulene and in methanol. FTIR and Raman spectroscopy were used to verify the presence of functional groups after the modification.

The other group of materials investigated in this thesis work was that of mesoporous oxides created by using various soft and hard templates. The former were used to synthesize the materials SBA-15 (Santa Barbara), SF (Silica Foam), MCF-17 (Mesostructured Cellular Foam) and KIT-6 (Korea Institute of Technology). KIT-6 also served as a hard template in the synthesis of mesoporous metal oxides (Co_3O_4, CeO_2, MnO_2, NiO). The structure and morphology of all samples were studied by transmission electron microscopy (TEM), and some materials were also characterized by X-ray diffraction (XRD) and small angle X-ray scattering (SAXS) measurements. The pore structure of the mesoporous oxides was assessed by measuring nitrogen adsorption–desorption isotherms. Specific surface area and pore size distribution data were obtained from the adsorption branch using the BET model and the desorption branch using the Barrett-Joyner-Halenda (BJH) model, respectively.

SBA-15, MCF-17 and SF porous silicas were converted into active heterogeneous catalysts by decorating their surface with size controlled platinum nanoparticles. Moreover, SF based nanocomposites featuring either phosporescent strontium-aluminates or titanate nanowires were also created. Platina/silica catalysts were tested in the ethanol vapor decomposition reaction and in the hydrosililation reaction between phenylacetylene and triethyl-silane.

3. New scientific results

T.1. Results related to the synthesis of meso- and macroporous oxides

1.1. We were the first to prove that the aminopropyl functionalization of hollow silica nanospheres can be accomplished in toulene without any adverse effects on the product morphology. Core-shell nanostructures consisting of polystyrene and SiO_2 were synthesized first, then converted into hollow silica nanospheres by thermal template removal. Afterwards, some surface OH groups were substituted by aminopropyl groups. Raman and FTIR spectroscopy were utilized to confirm the successful functionalization, TEM was used to verify the conservation of the spherical morphology, and nitrogen adsorption-desorption isotherms were used to obtain the specific surface area of the hollow silica nanospheres.

1.2. We contributed to the development of practical applications based on macroporous silica foams (SF) by conducting exploratory research on the relationship between their synthesis conditions and pore structure. We were the first to prove that the Triton X-114 surfactant suggested by the original SF recipe can be replaced by the considerably cheaper Tween X-20 while maintaining an adequate foam structure. We developed methods to add two different functional modifiers (titanate nanowires, phosphorescent strontium-aluminates) into silica foams.

1.3. We have shown that the pore surface of SBA-15 (a material consisting of mesoporous channels arranged into ordered blocks) differs significantly from that of silica foams (SF, MCF-17) where the mesopores are integrated into a macroporous system. This was done by analyzing the surface fractal dimension data obtained from small angle X-ray scattering measurements. The characteristic surface fractal dimension of foams and SBA-15 is 2 and 3, respectively.

1.4. We demonstrated that it is possible to synthesize mesoporous metal oxides (NiO, Co_3O_4, CeO_2, MnO_2) with a morphology that mimicks the pore structure of the KIT-6 silica hard template inversely. Up-scaling of the synthesis of KIT-6 and metal-oxide were performed by tuning of the reaction parameters. Altering the time of the NaOH assisted washing process, the morphology of the mesoporous metal-oxide could be varied from 3D to 2D nannowire structures.

T.2. Results related to the application of meso- and macroporous oxides

2.1. We have shown that porous silica supports are not necessarily inert in heterogeneous catalytic reactions even though this assumption is very common in the scientific literature. SF, SBA-15 and MCF-17 supports were decorated by precisely size-controlled platinum nanoparticles (average diameter 6.6 nm), and the performance of the obtained catalysts was compared in the vapor phase ethanol decomposition reaction in the 100–300 °C temperature range. The SBA-15 supported system was considerably more active (x2 factor in turnover frequency) than the other two, which can be explained by the known differences (see 1.3 above) in their pore wall surfaces.

2.2. We were the first to measure the catalytic activity of SBA-15 decorated with platinum nanoparticles in the hydrosililation reaction between phenylacetylene and triethyl silance in liquid phase (tetrahydrofurane) at 70 °C. Catalysts prepared with large Pt nanoparticles (average diameter 7.0 nm) significantly overperformed their small Pt nanoparticle (average diameter 1.6 nm) counterparts: conversion and selectivity towards the main products were larger by one order and magniture and 20%, respectively.

3. Publications related to the present thesis

3.1. Morphology conserving aminopropyl functionalization of hollow silica nanospheres in toluene

Dorina G. Dobó, Dániel Berkesi, Ákos Kukovecz

JOURNAL OF MOLECULAR STRUCTURE 1140 pp. 83-88. (2017)

IF (2016): 1,753 independent cite: 1

3.2. Silica-Based Catalyst Supports Are Inert, Are They Not?: Striking Differences in Ethanol Decomposition Reaction Originated from Meso- and Surface-Fine-Structure Evidenced by Small-Angle X-ray Scattering

András Sápi, **Dorina G. Dobó**, Dániel Sebők, Gyula Halasi, Koppány L. Juhász, Ákos Szamosvölgyi, Péter Pusztai, Erika Varga, Ildikó Kálomista, Gábor Galbács, Ákos Kukovecz, Zoltán Kónya

JOURNAL OF PHYSICAL CHEMISTRY C 121 (9) pp. 5130-5136. (2017)

IF (2016): 4,536 independent cites: 2

3.3. Photoelectrical response of mesoporous nickel oxide decorated with size controlled platinum nanoparticles under argon and oxygen gas

Juan Gómez-Pérez, **Dorina G. Dobó**, Koppány L. Juhász, András Sápi, Henrik Haspel, Ákos Kukovecz, Zoltán Kónya

CATALYSIS TODAY 284: pp. 37-43. (2017)

IF (2016): 4,636 independent cites: 2

3.4. Tuning the activity and selectivity of phenylacetylene hydrosilylation with triethylsilane in the liquid phase over size controlled Pt nanoparticles

Dorina G. Dobó, Dániel Sipos, András Sápi, Gábor London, Koppány L. Juhász, Ákos Kukovecz, Zoltán Kónya

CATALYSTS 8 (1) pp 22. (2018)

IF (2016): 3,082 independent cite:-

4. Presentations and posters related to the present thesis

4.1. Morphological characterization of inorganic nanocomposites

D. Dobó, A. Sápi, Á. Kukovecz

9th Students' Meeting Processing and Application of Ceramics (2011; Novi Sad, Serbia)-Book of Abstracts, ISBN 978-86-80995-97-7, p. 82 (2011) (presentation)

4.2. Correlation of morphological and Raman spectroscopic properties in inorganic nanocomposites

Dorina Dobó, András Sápi, Ákos Kukovecz

31st European Congress on Molecular Spectroscopy (2012; Cluj-Napoca, Romania)-Book of Abstracts, ISBN: 978-973-647-912-0 p. 117 (2012) (presentation)

4.3. Titanát nanoszerkezetekkel módosított kerámiák előállítása és jellemzése

Dobó Dorina, Sápi András, Dr. Kónya Zoltán

Helyi Tudományos Diákköri Konferencia, Kémia Szekció II. (2012; Szeged)

Elért helyezés: II. hely (presentation)

4.4. Synthesis and characterisation of porous silica foam based phosphorescent stroncium-aluminate composites

Dorina Dobó, Zoltán Győri, Viktor Havasi, Dr. Ákos Kukovecz, Dr. Zoltán Kónya

HSM Annual Meeting, 2013.05.23-25, Siófok (presentation)

Díj: A Magyar Mikroszkópos Társaság Konferenciáján tartott kiváló előadásért

4.5. Foszforeszcens stroncium-aluminát adalékolt mezopórusos szilika habok szintézise és karakterizálása

Dobó Dorina, Győri Zoltán, Havasi Viktor, Dr. Kukovecz Ákos, Dr. Kónya Zoltán

XXXVI. Kémiai Előadói Napok, 2013.10.29. (presentation)

4.6. Synthesis and characterisation of mesoporous silica foam based titanate nanostructure composites

Dorina Dobó, Tamás Somogyi, Dr. Ákos Kukovecz, Dr. Zoltán Kónya

HSM Annual Meeting, 2014.05.31, Siófok (presentation)

4.7. 3D Mesoporous Oxide Supported Platinum Nanoparticles For Heterogenous Catalytic Applications – Gas vs. Liquid Phase Reactions,

Andras Sapi, H. Wang, C. Thompson, K. Juhasz, **D. Dobo,** M. Szabo, G. A. Somorjai, Z. Konya

11th Conference for Young Scientists in Ceramics, Novi Sad, 2015.10.22.

4.8. Synthesis and Characterization of Platinum Nanoparticles with Controlled Size for Heterogen Catalytic Processes

K. L. Juhasz, M. Szabo, A. Szamosvolgyi, **D. Dobo,** A. Sapi, A. Kukovecz, Z. Konya

11th Conference for Young Scientists in Ceramics, Novi Sad, 2015.10.23.

4.9. Pt nanorészecskékkel dekorált mezopórusos oxidok szintézise, karakterizálása, valamint felhasználása különböző felületkémiai reakciókban

Dobó Dorina, Juhász Koppány, Szabó Mária, Sipos Dániel, Boda László, Lázár Enikő, Szamosvölgyi Ákos, Dr. Sápi András, Dr. Kukovecz Ákos, Dr. Kónya Zoltán

XXXVIII. Kémiai Előadói Napok, 2015.10.26-28., Szeged (presentation)

ISBN 978-963-9970-64-9, p.76. (2015)

4.10. Synthesis and characterization of platinum nanoparticles with controlled size for heterogeneous catalytic processes

Koppány Levente Juhász, **D. Dobó,** D. Sipos, M. Szabó, A. Sápi, Á. Kukovecz, Z. Kónya

MMT Conference, Siófok, 21 May 2016

4.11. Synthesis and characterization of functionalized silica nanospheres

Dorina G. Dobó, Dániel Berkesi, Ákos Kukovecz, Zoltán Kónya

33st European Congress on Molecular Spectroscopy 30 Jul-4 August 2016., Szeged, Hungary, ISBN: 978-963-9970-68-7 p. 67 (2016) (presentation)

4.12. Silica based catalyst support are inert, aren't they?-Study of the 1.8 nm Pt nanoparticles anchored on different amorphous silica supports in ethanol decomposition reaction

Dorina G. Dobó, András Sápi, Gyula Halasi, Dániel Sebők, Koppány L. Juhász, Ákos Kukovecz, Zoltán Kónya

13th Pannonian International Symposium on Catalysis, 19-23. September 2016. Siófok, Hungary, ISBN: 978-963-9970-56-4 p. 51 (2016) (presentation)

4.13. Synthesis and characterization of functionalized silica nanospheres

Dorina G. Dobó, Dániel Berkesi, Dr. Ákos Kukovecz, Dr. Zoltán Kónya

HSM Annual Meeting, 2017.05.12. Siófok (presentation)

4.14. Controlled Synthesis of Copper Nanocrystals with Various Shapes

M. Mohl, **D. Dobo,** P. Pusztai, A. Dombovari, A. Kukovecz, Z. Konya and K. Kordas

The Annual meeting of the NGS-NANO 18-19.09.2012, Åbo Akademi, Turku, Finland (2012)

4.15. Dramatically different mechanism and kinetics at solid/gas and solid/liquid interfaces for alcohol oxidation over size-controlled Pt nanoparticles,

András Sápi, Hailiang Wang, Chris Thompson, Koppány Juhász, **Dorina Dobó,** Mária Szabó, Gabor A. Somorjai, Zoltán Kónya

MCM 2015 Multinational Congress on Microscopy, Eger, 2015.08.23-28.

4.16. Synthesis and Characterization of Pt Nanoparticles with Controlled Size for Catalytic Applications,

Koppany Levente Juhasz, M. Szabo, **D. Dobo,** A. Szamosvolgyi, E. Lazar, T. Varga, A. Sapi, A. Kukovecz, Z. Konya

21st International Symposium on Analytical and Environmental Problems, Szeged, 2015.09.28.

4.17. Study of 1.8 nm Pt nanoparticles anchored on different amorphous silica supports in ethanol decomposition reaction

Dorina G. Dobó, András Sápi, Gyula Halasi, Dániel Sebők, Koppány L. Juhász, Ákos Kukovecz, Zoltán Kónya

22nd International Symposium on Analytical and Environmental Problems Szeged, Hungary October 10, 2016. (poster)

4.18. Liquid Phase Hydrosilylation over Size-Controlled Pt Nanoparticles

Dániel Sipos, **Dorina Dobó,** András Sápi

22nd International Symposium on Analytical and Environmental Problems Szeged, Hungary October 10, 2016. (poster)

4.19. Investigation of Pt/SiO_2 nanoparticles by solution and single particle mode ICP-MS

Albert Kéri, Ildikó Kálomista, Ákos Szamosvölgyi, **Dorina Dobó,** Koppány Juhász, András Sápi, Ákos Kukovecz, Zoltán Kónya, Gábor Galbács

22nd International Symposium on Analytical and Environmental Problems Szeged, Hungary October 10, 2016. (poster)

4.20. Room temperature ethanol sensor with sub-ppm detection limit: improving the optical response by using mesoporous silica foam

Dániel Sebők, László Janovák, András Sápi, **Dorina G. Dobó,** Ákos Kukovecz, Zoltán Kónya, Imre Dékány

22nd International Symposium on Analytical and Environmental Problems Szeged, Hungary October 10, 2016. (poster)

4.21. Synthetisation and characterization of platinum nanoparticles in a wide range of size

Ákos Szamosvölgyi, Koppány Levente Juhász, András Sápi, Mária Szabó, **Dorina Dobó,** Ákos Kukovecz, Zoltán Kónya

22nd International Symposium on Analytical and Environmental Problems Szeged, Hungary October 10, 2016. (poster)

4.22. Understanding the photoelectical response of mesoporous nikkel oxide decorated with controlled size platinum nanoparticles in different atmospheres

Juan Gómez-Perez, **Dorina G. Dobó,** Koppány L. Juhász, András Sápi, Henrik Haspel, Zoltán Kónya, Ákos Kukovecz

SIWAN7, 7th Szeged International Workshop on Advances in Nanoscience, Szeged, Hungary October 12-15, 2016. (poster)

4.23. Size-controlled platinum nanoparticles: fabrication, characterization and application in heterogenous catalytic processes

Koppány L. Juhász, **D. Dobó,** M. Szabó, A. Sápi, Á. Kukovecz, Z. Kónya

SIWAN7, 7th Szeged International Workshop on Advances in Nanoscience, Szeged, Hungary October 12-15, 2016. (poster)

4.24. **Optimization of SP-ICP-MS instrumental parameters for the measurement of surface modified nanoparticles**

I. Kálomista, A. Kéri, Á. Szamosvölgyi, **D. Dobó,** K. Juhász, A. Sápi, G. Galbács, Á. Kukovecz, Z. Kónya

SIWAN7, 7th Szeged International Workshop on Advances in Nanoscience, Szeged, Hungary October 12-15, 2016. (poster)

4.25. Low ppm-range reflectometric ethanol sensor at room temperature: improving the optical response by using mesoporous materials

D. Sebők, A. Sápi, **D. G. Dobó**, Á. Kukovecz, Z. Kónya, L. Janovák, I. Dékány

SIWAN7, 7th Szeged International Workshop on Advances in Nanoscience, Szeged, Hungary October 12-15, 2016. (poster)

4.26. Molecular level exploration of the coplexity of hydrogenation of CO_2 over size controlled Pt nanoparticles supported on mesoporous NiO by in-situ DRIFTS and NAP-XPS techniques

Gyula Halasi, András Sápi, János Kiss, **Dorina Dobó,** Kornélia Baán, Koppány Juhász, Zoltán Kónya

33RD European Conference on Surface Science, Szeged, Hungary, 27 Aug-1 Sep 2017.

4.27. Méretkontrollált nanorészecskék alkalmazása heterogén katalitikus folyamatokban

Juhász Koppány Levente, **Dobó Dorina,** Sipos Dániel, Sápi András, Kukovecz Ákos, Kónya Zoltán

XI. Országos Anyagtudományi Konferencia, Balatonkenese, 2017. október 15-17.

5. Other publications

5.1. Interaction between amino-functionalized inorganic nanoshells and acid-autocatalytic reactions

Emese Lantos, Nirmali Prabha Das, Dániel Simon Berkesi, **Dorina Dobó**, Ákos Kukovecz, Dezső Horváth, Ágota Tóth

PHYSICAL CHEMISTRY CHEMICAL PHYSICS (20) pp. 13365, (2018)

IF (2017): 4,123 independent cites: -

5.2. Molecular level exploration of the complexity of CO_2 hydrogenation over size controlled Pt nanoparticles supported on mesoporous NiO by in-situ DRIFTS and NAP-XPS techniques

András Sápi, Gyula Halasi, Janos Kiss, **Dorina Dobó**, Koppány Juhász, Vanessza Kolcsár, Gabor Vari, Vladimír Matolín, András Erdőhelyi, Akos Kukovecz, Zoltán Kónya

JOURNAL OF PHYSICAL CHEMISTRY C 122:(10) pp. 5553-5565. (2018)

IF (2016): 4,536 independent cites: -

5.3. Photoelectrochemistry by Design: Tailoring the Nanoscale Structure of Pt/NiO Composites Leads to Enhanced Photoelectrochemical Hydrogen Evolution Performance

András Sápi, András Varga, Gergely F. Samu, **Dorina Dobó**, Koppány L. Juhász, Bettina Takács, Erika Varga, Ákos Kukovecz, Zoltán Kónya, Csaba Janáky

JOURNAL OF PHYSICAL CHEMISTRY C 121: pp. 12148-12158. (2017)

IF (2016): 4,536 independent cites: 3

5.4. Room temperature ethanol sensor with sub-ppm detection limit:Improving the optical response by using mesoporous silica foam

Dániel Sebők, László Janovák, Dániel Kovács, András Sápi, **Dorina G. Dobó**, Ákos Kukovecz, Zoltán Kónya, Imre Dékány

SENSORS AND ACTUATORS B-CHEMICAL 243: pp. 1205-1213. (2017)

IF (2016): 5,401 independent cites: 2

5.5. Determination of the platinum concentration of a Pt/silica nanocomposite decorated with ultra small Pt nanoparticles using single particle inductively coupled plasma mass spectrometry

András Sápi, Albert Kéri, Ildikó Kálomista, **Dorina G. Dobó**, Ákos Szamosvölgyi, Koppány L. Juhász, Ákos Kukovecz, Zoltán Kónya, Gábor Galbács

JOURNAL OF ANALYTICAL ATOMIC SPECTROMETRY 32: pp. 996-1003. (2017)

IF (2016): 3,379 independent cites: 2

5.6. Formation of CuPd and CuPt Bimetallic Nanotubes by Galvanic Replacement Reaction

Melinda Mohl, **Dorina Dobo**, Akos Kukovecz, Zoltan Konya, Krisztian Kordas, Jinquan Wei, Robert Vajtai, Pulickel M. Ajayan

JOURNAL OF PHYSICAL CHEMISTRY C 115:(19) pp. 9403-9409. (2011)

IF (2011): 4,085 independent cites: 93

Peer-reviewed papers total: 10 out of this, related to the topic of thesis: 4

Cumulative impact factor: 40.068 out of this, related to the topic of thesis: 14.007

Independent cites total: 105 out of this, related to the topic of thesis: 5