Synthesis and characterization of carbon/silicate nanocomposites

Ph.D. Thesis

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1. Introduction

Natural and artificial carbon forms (graphite, active carbon, fullerenes, carbon fibers, carbon nanotubes etc.) possess many advantageous properties. One of their major fields of application in contemporary materials science is as components of inorganic composite materials.

The synthesis of carbon/silicate composites as selective adsorbents has been receiving enhanced attention recently. Due to their polar and apolar component, carbon/silicate composites are considered as novel hydrophilic-hydrophobic adsorbents capable of adsorbing both polar and apolar molecules. Consequently, they may become important elements of e.g. selective adsorption, gas and liquid purification and industrial by-product and waste removal processes as well as in valuable reactant recovery. Traditional carbon/silicate composite synthesis paths are (i) the catalytic decomposition of hydrocarbons and (ii) the partial or total carbonization of an adsorbate on a support surface. A third method emerging nowadays is hydrothermal synthesis.

Some laboratories have prepared carbon/zeolite composites in order to improve diffusion efficiency in zeolites by introducing mesopores (diameter: 2-50 nm) into the microporous (diameter < 2 nm) zeolite crystals. Because of their paramount importance in the heterogeneous catalytic and adsorption processes of the petrochemical industry, the persistent study of zeolite-based materials with novel structural and surface properties remains an important research challenge.

Carbon nanotubes have been receiving a constantly increasing attention as polymer fillers and composite components recently. However, carbon nanotubes must be purified of catalyst particles and amorphous carbon particles after synthesis. Since their surface properties and consequently, their applicability as polymer fillers are modified during purification, it is necessary to develop a protocol for the reliable characterization of nanotube surface hydrophilicity-hydropbobicity.

2. Experimental

We synthesized several mesoporous carbon (active carbon, graphite, nanotube) – Si-MCM-41 nanocomposites under hydrothermal conditions. The template molecules required for Si-MCM-41 synthesis were removed by either solvent extraction or heat treatment at 540 ºC in N_2 atmosphere. The obtained template-free samples were characterized by IR spectroscopy, XRD, TEM, SEM, N_2 adsorption, organic vapor adsorption and ethanol/cyclohexane mixture adsorption.

We prepared MWNT/LTA, FAU and MSI composites in various carbon/silicate mass ratios with the aim of obtaining zeolites possessing a bimodal pore structure. Multiwall carbon nanotubes served as templates for the secondary pore system in these reactions. The nanotubes were removed by heat treatment in air at 600 ºC. Both the composites and the calcined zeolites were characterized by XRD, ^{29}Si and ^{27}Al-MAS-NMR, TEM, TG and N_2 adsorption.

We utilized ethanol/cyclohexance mixture adsorption excess isotherms for the quantitative assessment of the surface properties of carbon nanotubes and carbon-containing composites. Multiwall carbon nanotubes prepared by CCVD (catalytic chemical vapor deposition) and purified by an acidic oxidative method were annealed in inert atmosphere at 400, 700, 1000 and 1400 ºC. Besides studying the effect of the annealing temperature to the surface properties, the heated samples were also characterized by TEM, XRD and N_2 adsorption.

Results

1.1. It was proven that ethanol/cyclohexane binary solvent adsorption excess isotherms are applicable to quantify the surface hydrophilicity-hydrophobicity of multiwall carbon nanotubes.
1.2. It was shown that the amount of oxygen containing functional groups generated by acidic purification treatment of MWNTs decreased with thermal annealing of the samples.

2.1. Carbon/MCM-41 mesoporous nanocomposites with various carbon/silicate mass ratios were successfully synthesized by hydrothermal treatment, where the carbon compound was activated carbon, graphite or multiwall carbon nanotube.
2.2. It was shown by morphological analysis of the samples, that during the synthesis the silicate and carbon compounds retained their original properties.
2.3. Using ethanol/cyclohexane binary solvent adsorption excess isotherms it was proven that the composites possess hydrophilic and hydrophobic properties simultaneously. Moreover, the experiments indicate that in order to reach higher hydrophobicities in carbon/Si-MCM-41 composites one must introduce a large amount of carbon to compensate for the hydrophilic nature of Si-MCM-41.

3.1. We prepared MWNT/NaA(LTA)-, NaX(FAU) and ZSM-5(MFI) composites in various mass ratios where cut multiwall carbon nanotubes were applied as mesoporous templates. Removing the nanotubes from the composites at 600 ºC in air zeolites with secondary mosoporosity were obtained.

3.2. In each sample the zeolite components retained their original properties and no new phase could be identified.

3.3. We succeeded in introducing mesopores of 3-13 nm in diameter into LTA, FAU and MFI zeolite matrices by synthesizing various MWNT/carbon nanotube composites.

4. Exploitation of the results

We consider the development of the ethanol/cyclohexane mixture adsorption method for the quantitative assessment of the surface hydrophilicity-hydrophobicity of carbon nanotubes to be the most important practical achievement of our work.

The synthesis of the carbon/silicate nanocomposites can be classified as fundamental research. Future applications are anticipated in the fields of energetics, gas storage and environmentally friendly processes.

Major applications of zeolites with double pore structure are expected in the petrochemical industry. It is assumed that the high selectivity assured by the zeolite will be complemented by enhanced catalytic activity because of the reduced diffusion barrier.

Publications

Papers:

1. Binary solvent mixture adsorption as a characterization tool to determine the hydrophilic/hydrophobic properties of multiwall carbon nanotubes,
Kanyó T., Kónya Z., Berger F., Dékány I., Kiricsi I.,
Chem. Commun., 2003, 2746-2747

2. Quantitative Characterization of Hydrophilic-Hydrophobic Properties of MWNTs Surfaces,
Kanyó T., Kónya Z., Kukovecz Á., Berger F., Dékány I., Kiricsi I.,
Langmuir, 20(5) 2004, 1656-1661

3. Thermal behavior of multiwall carbon nanotube – zeolite nanocomposites,
Kónya Z., **Kanyó T.**, Kiricsi I.,
Journal of Thermal Analaysis and Calorimetry (submitted)

4. Morphological characteriyation of mesoporous carbon/silicate nanocomposites,
Kukovecz Á., **Kanyó T.**, Kónya Z., Kiricsi I.,
Langmuir, (submitted)

5. Synthesis of zeolites containing mesopores using carbon nanotubes as templates
Kanyó T., Kónya Z., Forgó P., Kukovecz Á., Kiricsi I.
Phys. Chem. Chem. Phys., (in preparation)

6. Elongated ball-milling of multi-wall carbon nanotubes,
Kukovecz Á., **Kanyó T.**, Kónya Z., Kiricsi I.,
Carbon (in preparation)

Posters:

1. IR and multinuclear NMR spectroscopic studies of zeolite multiwall carbon nanotube composites,
T. Kanyo, Z. Kónya, P. Forgó, I. Kiricsi, *XXVII Eurpean Congress on Molecular Spectroscopy*, Krakow, Poland, 5-10 September, 2004 *(poster)*

2. Surface property of active carbon-silicate composite,
T. Kanyó, Z. Kónya, I. Kiricsi, *X Zeolite Forum,* Tuczno, Poland, 21-26 September, 2003 (*oral)*

3. Spectroscopic study of carbon-silicate composites,

T. Kanyó, Z. Kónya, I. Kiricsi, *VII International Conference on Molecular Spectroscopy*, Wroclaw-Ladek Zdrój, Poland, 11-14 September, 2003 *(poster)*

4. Szén/Si-MCM-41 kompozitok szintézise és spektroszkópiás vizsgálatai,
Kanyó T., *46. Magyar Spektrokémiai Vándorgyűlés,* Szeged, Június 30-Július 2, 2003. *(oral)*

5. Szén-mezopórusos szilikát nanokompozitok szintézise és adszorpciós tulajdonságainak jellemzése,
Kanyó T., Horváth Z., Kónya Z., Biró L. P., Kiricsi I., *XXV Kémiai Előadói Napok,* Szeged, október 28-30, 2002. *(oral)*

6. Synthesis and characterization of carbon-MCM-41 composites for adsorption and catalytic purposes,
T. Kanyó, Z. Horváth, Z. Kónya, L.P. Biro, I. Kiricsi, *IX Zeolite Forum*, Wysowa-Zdrój, Poland, 22-26 September, 2002 *(oral)*

7. Synthesis and characterization of carbon-silicate nano-composites for adsorption purposes,
T. Kanyo, Z. Horváth, Z. Kónya, L. P. Biro, I. Kiricsi, *5th Conference on Solid State Chemistry*, Bratislava, Slovakia, 7-12 July, 2002 *(poster)*

8. Szén szilikát nanokompozitok (Szintézis, jellemzés, alkalmazási lehetőségek),
Kanyó T., Kónya Z., Urbán M., Méhn D., Kiricsi I., *VIII Nemzetközi Vegyészkonferencia,* Kolozsvár, Románia, November 15-17. 2002.

Others:

9. Hidrotalcit eredetű keverékoxid katalizátorok alkalmazása klórtartalmú szerves vegyületek oxidative lebontásában,
Kanyó T., Halász J., *The 8th Symposium on Anayitical and Environmental Problems,* Szeged, 1 October, 2001 *(oral)*

10. Klórbenzol oxidatív lebontása hidrotalcit eredetű katalizátorokon,
Kanyó T., Halász J., *XXIV Kémiai Előadói Napok,* Szeged, Október 29-31, 2001. *(oral)*

11. Oxidative and reductive destruction of halogenated organics over mixed oxide and zeolite catalysts,
J. Halász, B. Imre, **T. Kanyó**, A. Gungle, I. Kiricsi, *Plenary Lecture, Romanian Academy: Timisoara's Academic Days*, Timisoara, Rumania, May, 2001

12. Oxidative destruction of chlorobenzenes over hydrotacite originated catalysts, **T. Kanyó,** J. Halász, *Scientific Symposium in Chemistry for Students* Timisoara, Rumania, 28 October, 2000 *(oral)*

13. Klórbenzol oxidatív lebontása hidrotalcit alapú katalizátorokon, **Kanyó T.,** Halász J., *VI Nemzetközi Környezetvédelmi Szakmai Diákkonferencia*, Mezőtúr, Július 5-7, 2000. *(oral)*