

Ph.D. thesis

**PRE-PREPARED PLATINUM NANOPARTICLES SUPPORTED ON SBA-15:  
PREPARATION, CHARACTERISATION AND CATALYTIC PROPERTIES**

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## 1. Introduction and the object of thesis

Over the past decade, nanosized materials generated intense interest in science and technology. The reason is the unique behavior of these nanoclusters consisting of 100-1000 atoms. Their properties lie somewhere between those of bulk and single-particle or molecular species. The metal particles located on the surface may have specific physical and chemical properties that are more intensive at the limit of metallic character cessation in the interval of 1-10 nm.

Nanoparticles of different noble metals have been found to catalyze a wide range of chemical reactions. Catalysis in the 20th century focused primarily on activity, increasing turnover rates to produce more molecules per unit time. Recently, the aim has shifted towards reaching 100% selectivity. In this respect it is important that the preparation method of the catalyst influences the activity and selectivity substantially.

In order to obtain high selectivity (with the ultimate goal being 100% selectivity), synthetic methods that enable molecular control over the size, location and structure of the metallic nanoparticles and catalyst promoters must be developed. Under certain circumstances, nearly monodisperse particles with defined morphology can be synthesized. The size and morphology of reduced noble metal particles can be influenced by the choice and the relative concentration of precursors and stabilizing agents and by the temperature. Nucleation, growth and the relative growth rates of the different sorts of crystallite faces determine the properties of the particles. Electronmicroscopic measurements uniquely reveal the crystallographic orientation of particles from the atomic lattice structure, which in turn determines the 3-dimensional geometry of particles.

Due to the high surface/volume ratio, the particles have high surface energy and can easily aggregate in colloidal suspension. The linkage of the nanoclusters can be limited by their immobilization on some sort of support. Due to the small particle size, the noble metal particles dispersed on the surface of the support guarantee high surface available for catalytic reactions. Evidently, the aggregation can not be excluded in this case. The mobility of nanoparticles depends on the raggedness of surface and the strength of the bonding.

High dispersity and homogeneous distribution can be reached using materials with high surface area (e.g.  $\text{Al}_2\text{O}_3$ , silicagel, zeolites, mesoporous materials like SBA-15). The support not only stabilizes these small metallic particles, but may also influence the chemistry through a bifunctional mechanism that provides active sites on the support or at the support-metal interface in addition to the active sites on the metal.

Single crystals of transition metals are utilized as model systems in heterogeneous catalysis; their surface structure is well defined yet easily modifiable, allowing the study of surface effects on adsorption, reaction and desorption phenomena. The techniques and practices of ultra high vacuum

(UHV) have enabled surface cleaning and characterization in order to obtain a wealth of information on the influence of surface structure on heterogeneous reaction kinetics and dynamics. The kinetic measurements of *McCrea et al.* have shown that the selectivity during cyclohexene hydrogenation/dehydrogenation reactions is influenced by the surface structure. Considering the fact that catalytic behavior of single crystals is influenced by the atomic level structure of the crystal faces, research to develop supported metal catalysts mimicking the characteristics of single crystals in nanometer scale was initiated.

On the score of these considerations, the aims of our work are (a) the preparation of platinum nanocrystals with well-defined shape, size and homogeneous size distribution, (b) their deposition on a well-organized silicate support SBA-15, (c) the characterization of these 3-dimensional model catalysts and (d) studying the influence of particle shape and size of platinum particles and the role of the support and catalyst preparation in the cyclohexene hydrogenation/dehydrogenation test reaction investigated by IR spectroscopy.

## 2. Experimental methods

Platinum nanoparticles with controlled shape and size were prepared and dispersed on the surface of the well organized mesoporous silicate support SBA-15. Control over the size- and shape-distribution of platinum nanoclusters was achieved by varying the type of capping and reducing agents and the synthesis temperature.

The size and the shape of nanocrystals and the morphology of the SBA-15 silicate were determined by transmission electron microscopy. The crystal structure of the support and the size of the platinum inside the channels were characterized by Small Angle X-ray Diffraction measurements, while the Pt content of the samples was measured employing X-ray fluorescent analysis. To investigate the thermal behavior of specimens, a Derivatograph Q thermobalance was utilized.

Nitrogen adsorption was measured at 77 K. The BET surface area and pore size distribution were determined from the isotherms. These curves were calculated from the adsorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) method.

The removal of organic compounds and the catalytic activity of the samples were confirmed by IR spectroscopy. The catalytic test reaction was the hydrogenation/dehydrogenation of cyclohexene.  $^{13}\text{C}$ - and  $^{29}\text{Si}$  MAS (Magic Angle Spinning) NMR spectroscopic measurements were used to gather information about the structure of the support after mechanical stability testing.

### 3. New scientific results

#### T.1. *Controlling the shape of Pt nanoparticles*

1.a. Different capping agents have been used to synthesize platinum nanoparticles. TEM images have suggested that in the presence of poly(vinyl-pyrrolidone) (PVP) the particles had tetrahedral shape. If poly(N-isopropyl-acrylamide) (NIPA) was used, the most frequently shape has been cubic while in case of sodium polyacrylate (SPA) polyhedral nanoparticles were formed. Systems featuring homogeneous size distribution and morphology were obtained when using PVP or NIPA as capping agent.

1.b. While increasing the temperature or applying stirring has scarcely influenced the particle size, they affected preferably the shape distribution. Without using a capping agent only broad shape and size distributions could be obtained.

#### T.2. *The influence of the catalyst preparation method*

2.a. Impregnation and ultrasonic treatment were used to distribute metal particles over the support. At optimal time of the treatment and concentration of nanoparticles the sonication resulted in a better distribution of particles on the surface and in the pores. The impregnation did not destroy the support, neither were any changes in the surface area or in the crystal structure detectable.

2.b. We have examined the influence of the platinum content increase on the structure of the support. It was demonstrated by X-Ray diffraction and N<sub>2</sub> adsorption that platinum nanoparticles arriving to the vicinity of pore openings cause the mechanical breaking of the ordered straight pores. The presence of a capping agent hardly contributes to the decreasing of the specific surface area. Experiments proved that the ultrasonic treatment destroys the support when the platinum content is above 0,1 wt%.

#### T.3. *The stability of the catalysts*

3.a. Removing of organic compound from the samples was optimized with the aim that either the shape and size of platinum nanoparticles or the structure of SBA-15 support should remain unchanged. IR spectroscopic investigations showed that neither a simple evacuation of the silicate at 450 °C for 2 hours nor leaching the “as-synthesized” SBA-15 in ethanol for several hours have resulted in organic free material. Oxidation with hydrogen peroxide in aqueous solution proved to be ineffective as well. By treating the sample with O<sub>3</sub> the CH residues could be

eliminated at 300 °C but the activity of the catalyst has also been lost. The only procedure that led to an organic free sample was treatment in O<sub>2</sub> at 500 °C.

3.b. XRD and BET measurements revealed that it takes a heat treatment above 800 °C to cause significant changes in the SBA-15 structure. We have confirmed by using TEM pictures that the platinum particles have preserved their shape and size and have not aggregated at 500 °C.

3.c. In order to check the applicability of SBA-15 in IR spectroscopic measurements, we have investigated its resistance against pressure. The support exhibited poor pressure resistance since the ordering of the structure started deteriorating above 5 bar. The pore size distribution has shown the formation of a bimodal pore system and decreasing mean pore diameter from around 6 nm to 3,5 nm due to increasing pressure. At 100 bar pressure exclusively small pores were found in the sample and the hexagonal structure has collapsed completely.

#### *T.4. IR spectroscopic investigations of the catalytic reaction*

4.a. The catalytic activity of different samples was tested in the hydrogenation/dehydrogenation of cyclohexene. Although the IR spectra of cyclohexene and potential products overlapped to some extent, we were able to find several bands suitable for species identification. The rather small shift of the bands after adsorption indicated weak interactions between the adsorbate and the support. The shift of OH band of the silicate to lower wavenumbers was significant and different in the presence of different reactants.

4.b. Investigations of the hydrogenation and dehydrogenation of cyclohexene over SBA-15 support in the absence of platinum nanoparticles have revealed the inactive behavior of the support in the reaction. Neither the cyclohexene nor the potential products were transformed on the surface.

#### *T.5. Catalytic features of the 3D model catalysts*

5.a. Even the sample with 0.05 wt% Pt exhibited some catalytic activity. We observed that the catalytic performance of the samples was very sensitive to the reaction temperature. Hydrogenation takes place at 25 °C while dehydrogenation needs a higher temperature. The transformation speed depends on the particle size, particle shape and the catalyst preparation method.

5.b. In contrast to previous observations reported on single crystals, the maximum turnover rate for hydrogenation was found to be higher on Pt (100) and lower on Pt (111) faces. In case of dehydrogenation the reaction rates were identical.

5.c. The influence of the particle size was examined in the case of hexagonal particles. As the size increased, the reaction speed decreased.

5.d. No observable hydrogenation reaction rate differences were found over the different platinum nanoparticle shapes above 50 °C reaction temperature.

5.e. The lowest catalytic activity was found on the sample with 0.01% Pt loading. The shape of the kinetic curve exhibited a saturation character indicating the deactivation of metal after a very short reaction time. Between 0.05-0.1 wt% Pt content the reaction could be monitored well, whereas above 0.5 wt% Pt loading the transformation was too fast.

5.f. The samples prepared by ultrasonication were more active in both reactions than the samples prepared by impregnation. The reason for this is the more even distribution of the particles on the surface and in the channels of the support.

5.g. A strong influence of the hydrogen pressure was observed for both catalysts. The kinetic curves for hydrogen/cyclohexene = 1 molar ratio run to saturation. Reaction mixtures containing more hydrogen exhibited much better catalytic performances. 100 % conversion could be achieved over cubic particles at hydrogen/cyclohexene = 5 ratio and over tetrahedral ones at 10:1 ratio.

5.h. Intermediates were not detectable by changing either the particle size and shape or the concentration of platinum nanoparticles on SBA-15 support.

#### T.6. *Deactivation*

6.a. The life time of catalysts was examined by reproducibility experiments. The activity decreased with time indicating the deactivation of the catalyst. Since no traces of aggregation were visible on the TEM images of the deactivated catalyst, this phenomenon is believed to be caused by the deposition of organic compounds on platinum surface.

#### 4. Publications related to the Ph. D. thesis

1. **É. Molnár**, Z. Kónya, I. Kiricsi:

Thermal stability of platinum particles embedded in mesoporous silicates

*Journal of Thermal Analysis and Calorimetry* 79 (2005) 573-577,

IP:1,425

2. **É. Molnár**, G. Tasi, Z. Kónya, I. Kiricsi:

Infrared Spectroscopy Studies of Cyclohexene Hydrogenation and Dehydrogenation Catalyzed by Platinum Nanoparticles Supported on Mesoporous Silicate (SBA-15).

*Catalysis Letters* 101 (3-4) (2005) 159-167

IP:2,088

3. **É. Molnár**, Z. Kónya, G. Tasi, I. Kiricsi:

IR spectroscopic investigation of the particle size and morphology of platinum nanoparticles supported on mesoporous silicate

*Studies in Surface Science and Catalysis* 158 (2005) 1351-1358

IP:0,307

4. Z. Kónya, **É. Molnár**, G. Tasi, K. Niesz, G. A. Somorjai, I. Kiricsi:

Pre-prepared platinum nanoparticles supported on SBA-15-preparation, pretreatment conditions and catalytic properties

*Catalysis Letters* 113 (1-2) (2007) 19-28

IF: 1,772 (2006.)

*Cumulative impact factor: 5,592*

## 5. Other publications

1. L. Guzzi, G. Stefler, O. Geszti, Zs. Koppány, Z. Kónya, **É. Molnár**, M. Urbán, I. Kiricsi:  
CO hydrogenation over cobalt and iron catalysts supported over multiwall carbon nanotubes: Effect of preparation  
*Journal of Catalysis* 244 (1) (2006) 24-32  
IF: 4,533
2. I. Kiricsi, Á. Fudala, D. Méhn, Á. Kukovecz, Z. Kónya, M. Hodos, E. Horváth, M. Urbán, T. Kanyó, **É. Molnár**, R. Smajda:  
Tubular inorganic nanoclusters  
*Curr. Appl. Phys.* 6(2) (2006) 212-215  
IF: 1,116
3. Á. Pál, D. Méhn, **É. Molnár**, Sz. Gedey, P. Mészáros, T. Nagy, H. Glavinas, T. Janaky, O. von Richter, Gy Bathori, L. Szente, P. Krajcsi:  
Cholesterol Potentiates ABCG2 Activity in a Heterologous Expression System: Improved in Vitro Model to Study Function of Human ABCG2  
*The Journal of Pharmacology and Experimental Therapeutics* 321(3) (2007) 1085-1094  
IF: 3,956 (2006)
4. H. Glavinas, E Kis, Á. Pál, R. Kovács, M. Jani, E. Vági, **É. Molnár**, Sz. Bánshági, Z. Kele, T. Janáky, Gy. Báthori, O. Von Richter, G. J. Koomen, P. Krajcsi:  
ABCG2 (BCRP/MXR) ATPase assay-a useful tool to detect drug-transporter interactions  
*Drug metabolism and disposition: the biological fate of chemicals* (2007) in press  
IF: 3,638 (2006)

## 6. Conference lectures, posters

### 6.1. Lectures

1. **É. Molnár**, Z. Kónya, I. Kiricsi:

Expansion of 2D surface chemistry and catalysis to 3D. Synthesis and characterisation  
X. Zeolite Forum, 2003.

2. **É. Molnár**, Z. Kónya, Gy. Tasi, I. Kiricsi:

IR spectroscopic investigation of the particle size and morphology of platinum nanoparticles supported on mesoporous silicate  
3rd International FEZA Conference, 2005.

3. **É. Molnár**, R. Rémiás, Á. Kukovecz, G. Tasi, Z. Kónya, I. Kiricsi:

Reactions taking place on supported metal surfaces  
XXVIII. European Congress on Molecular Spectroscopy 2006.

### 6.2. Posters

1. **É. Molnár**, J. Halász, I. Kiricsi:

Application of catalytic wet air oxidation (CWAO) in the wastewater treatment: removal of phenol in the presence of Cr-containing mesoporous catalysts  
VI. International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe and the Commonwealth of Independent States 2003.

2. **É. Molnár**, M. Hodos, Z. Kónya, I. Kiricsi

Spectroscopic studies on the transfer of surface chemistry from 2D to 3D systems  
VIIth International Conference on Molecular Spectroscopy 2003.

3. **É. Molnár**, J. Halász, I. Kiricsi

Application of catalytic wet air oxidation (CWAO) in the wastewater treatment: removal of phenol in the presence of Cr-containing mesoporous catalysts  
Interfaces Against Pollution 2004.

4. **É. Molnár**, Z. Kónya, I. Kiricsi

IR spectroscopic investigation of the particle size and morphology of platinum nanoparticles supported on mesoporous silicate

XXVII. European Congress on Molecular Spectroscopy 2004.

5. **É. Molnár**, Z. Kónya, I. Kiricsi

IR spectroscopic investigation of the particle size and morphology of platinum nanoparticles supported on mesoporous silicate

SIWAN 2004 2nd Szeged International Workshop on Advances in Nanoscience

6. R. Rémiás, A. Gazsi, **É. Molnár**, T. Tóth, Á. Kukovecz, Z. Kónya, I. Kiricsi

Hydrogenation activity of Pt/SBA-15 catalysts in the conversion of cyclohexene to cyclohexane

*Proc. 8th. Pannon Int. Symp. on Catal. Szeged, 2006 (Editor: I. Pálinkó) ISBN 963 06 0138 9, 227-232.*

7. Á. Pál, D. Méhn, **É. Molnár**, E. Kis, M. Jani, Gy. Báthori, P. Krajcsi

Excipients may modulate the pathway in ADME/TOX via ABC transporters

MDO 2006 16<sup>th</sup> International Symposium on Microsomes and Drug Oxidation, Budapest 2006.