

Ph.D. thesis

Preparation of Size and Morphology-controlled Palladium Particles.
Catalytic Probes in Hydrogenations

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1. Introduction and the object of thesis

Nanoclusters -near monodisperse particles that are generally less than 10 nm- have generated intense interest in science and technology over the past decade. The reason for this is the belief that nanoclusters will have unique behavior, their properties lie somewhere between those of bulk and single-particle or molecular species. In the interval of 1 to 10 nm, the conductivity, the optical or catalytic properties of particles can be optimized for a given problem by changing the size and morphology. These particles have many potential uses, including quantum dots, chemical sensors, light-emitting diodes and magnetized liquids. Nanoclusters also have significant potential as new types of higher activity and selectivity catalysts.

The nanoparticles of different noble metals have been found to catalyze a wide range of reactions: hydrogenation, hydrosilylation, hydrogenolysis, Heck-type coupling, oxidation reactions, etc. Beside the key role of metallic properties, the other reason for that the nanoparticles are more active and selective catalysts is that the large percentage of a nanocluster's metal atoms lies on the surface. They are highly dispersed particles.

Nowadays, the development of the controlled colloid synthesis methodologies and the transmission electron microscopes with atomic resolution make possible to optimize the application of metal nanoclusters in catalysis. In case of the classical impregnated supported catalysts the size, morphology and surface statistics of metal particles are accidental. Under certain circumstances, near monodisperse particles with defined morphology can be synthesized which possess a minimum number of surface uncertainties (holes, adatoms). The size and morphology of reduced noble metal particles (Pd, Pt, Rh, Au etc.) in liquid phase can be influenced by the choice of precursors and stabilizing agents (solvents, electrolytes, ligands, polymers and surfactants), by the relative concentration of precursor and stabilizing agent and by the temperature. Nucleation and growth and the relative growth rates of the different sort of crystallite faces determine the habit of particles. The shape of particles can be cubooctahedral, icosahedral, octahedral or cubic depending on the reaction conditions. Electronmicroscopy measurements uniquely determine the crystallographic orientation of particles from the atomic lattice structure, which determines the 3-dimensional geometry of particles.

Recently, the colloid chemistry and material science managed to offer potential possibilities to synthesize particles with preplanned size and morphology (catalyst engineering/tailoring) by which the disputed fundamental phenomena of catalysis (for example the active sites or the structure-sensitivity of reactions) can be examined.

Despite the high preparation cost and the high price of precursors the application of noble metal catalysts is quite widespread because of their

outstanding catalytic activity. The recover of homogen catalysts, their regeneration and the removal of reaction products from the reaction slurry are difficult and expensive therefore the synthesis of heterogen catalysts is preferential in practice. The Pd is one of the most active and selective catalysts that is why we set the development of size and morphology controlled colloid synthesis of Pd particles as well as the investigation of the kinetics of formation of Pd clusters. Since the majority of liquid phase hydrogenation reactions are conducted in nonaqueous media (organic dispersions), the choice of supports with hydrophobic surface, which possess favorable colloid chemical properties in organic phase, is useful. Organophilized montmorillonite and Al/Mg layered double hydroxide were chosen as supports because the layered structure organoclays undergo wetting, swelling and disaggregation in organic media. Besides the instrumental investigations of Pd particles immobilized onto the organophilic clays, our object was to qualify their surface with a simple catalytic test reaction in which no byproduct is formed. The styrene is good probe molecule because its transformation into ethyl benzene possesses zeroth-order kinetics over the whole range of conversion.

Applying a series of supported metal catalyst with different particle size of the metal but otherwise with the same morphology is a fundamental possibility to *in situ* probe the active sites (dispersion) of metal nanoparticles, under the reaction conditions and to probe if the reaction is structure-sensitive.

2. Experimental methods

Nano-sized Pd particles were prepared and dispersed onto the surface of clay minerals.

Before the reduction, the solution of the precursor and the stabilizing surfactant was investigated by titration microcalorimetry, UV/VIS and photon correlation spectroscopy. The stoichiometry of the precipitated organic salt, which formed via interactions between the precursor and the surfactant, was determined by total organic content analyzer, IR, Raman, $^1\text{H-NMR}$ and inductively coupled plasma atom emission (ICP-AES) spectroscopy. The kinetics of the formation of Pd particles was examined by diode-arrayed UV/VIS spectroscopy.

The organic ion-exchange capacity of the supports (sodium montmorillonite and hydrotalcite nitrate) was determined by thermic and total organic compound analysis. The supports were also characterized by nitrogen sorption measurements.

The Pd-MM and Pd-LDH catalysts were characterized by ICP-AES, transmission and high-resolution transmission electron microscopy, X-ray diffraction and hydrogen sorption measurements. Their catalytic activity was tested in liquid-phase hydrogenation of olefins.

3. New scientific results

1. The real precursor of Pd particles formed in the postmicellar region of $\text{K}_2\text{PdCl}_4/\text{C}_n\text{TABr}$

1.a We have determined that PdCl_4^{2-} is not the real precursor of Pd particles reduced in the aqueous solution of K_2PdCl_4 and the cationic alkyl trimethyl ammonium bromides C_nTABr ($n=8,10,12,14,16$) in the postmicellar region. The reduction is preceded by a ligand exchange reaction ($\text{PdCl}_4^{2-} \rightarrow \text{PdBr}_4^{2-}$) and the formation of the organic salt $[\text{C}_n\text{TA}]_2[\text{PdBr}_4]$ as confirmed by IR, Raman, $^1\text{H-NMR}$ and ICP-AES spectroscopy, titration microcalorimetry and TOC measurements.

1.b In the premicellar region of the aqueous solution of C_nTABr surfactant, C_nTA^+ associates with PdBr_4^- to form the ion pairs $[\text{C}_n\text{TA}]_2[\text{PdBr}_4]$ with a 2:1 stoichiometry, confirmed by UV/VIS spectroscopy and titration microcalorimetry. Upon storage, microphase separation occurs according to solubility, and the organic salt slowly precipitates. Above the critical micellar concentration (cmc), the alkyl chains of organic salt incorporate into the hydrophobic core of micelles

according to solubilization capacity. The real precursor of reduced Pd particles is the organic salt.

1.c Because of the specific interactions between PdCl_4^{2-} and C_nTABr both below and above the cmc, the palladate complex is a suitable spectral indicator for rapid measurement of the cmc's of cationic surfactants by UV/VIS spectroscopy.

2. Controlling the size of Pd nanoparticles

2.a The size of Pd particles can be controlled in the range of 1 to 7 nm by systematic variations of the concentrations of K_2PdCl_4 and C_nTABr in the postmicellar region. TEM images suggested that by increasing the alkyl chain length of cationic surfactant homologues, the mean particle diameter decreased and the size distribution became narrower. The particle size increased significantly when increasing the precursor concentration. By increasing the surfactant concentration, the increase in size was not so obvious. The particle size decreased when the strength of the reducing agent was increased (ethanol < hydrazine hydrate < sodium borohydride).

2.b On the basis of corresponding data in the literature and our dilution experiments, we suggested that the long-life stability of Pd hydrosols when stabilized by cationic surfactants is ensured by a vertically oriented surfactant bilayer adsorbed onto the surface of the Pd particles (electrostatic and steric stabilizations). The particle growth is limited by the rapid adsorption of surfactant molecules at a very early stage of the aggregation process. The ultrafine Pd particles are generated via the arrested growth mechanism.

3. Kinetics of formation of Pd colloids

We obtained quantitative information on the formation kinetics of Pd nanoparticles stabilized by cationic surfactants through time-resolved, diode-arrayed UV/VIS spectroscopy. The intensities of the absorption bands at 251 and 342 nm are proportional to the concentration of unreduced precursor species and hence characteristic of nucleation. The intensity of the absorption band at 229 nm is related to the size of the Pd clusters formed and characteristic of the growth mechanism. Nucleation is a very fast process that is completed in seconds. Growth is nearly two-orders of magnitude slower than nucleation. This marked difference in rate favoured the formation of small, nearly monodisperse particles in the presence of the stabilizing agent.

4. Structure and morphology of Pd particles

The Pd crystallites have a face-centred cubic structure, as proved by XRD measurements. The TEM images of surfactant-free, precipitated Pd particles indicated a characteristic hexagonal periphery. The HRTEM measurements of a hydrosol particle also revealed a hexagonal periphery. From the atomic lattice structure, the crystallographic orientation is uniquely determined to be [110]. Since only the cubooctahedron has a hexagonal outer shape in this crystallographic orientation, the dominant morphology of the Pd particles can be identified as cubooctahedral.

5. Synthesis of organophilic Pd-MM and Pd-LDH catalysts

An *ex-situ* preparation method was developed for the preparation of organophilic, supported Pd catalysts. The particles of a stable, surfactant-stabilized Pd hydrosol were dispersed onto the surface of sodium montmorillonit and hydrocalcite nitrate, both supports are ion-exchanger clays. The Pd hydrosol stabilized by the cationic surfactant $C_nTA^+Br^-$ was added to an aqueous suspension of Na^+MM^- . The cation-exchange reaction between Na^+ and C_nTA^+ rendered the MM surface hydrophobic. Simultaneously, the released Pd particles were restabilized by adhesion to the silicate layers. In a similar way, the Pd hydrosol stabilized by an anionic surfactant ($C_{12}SO_4^-Na^+$) was added to the aqueous suspension of hydrocalcite $^+NO_3^-$. The anion exchange reaction between NO_3^- and $C_{12}SO_4^-$ rendered the LDH surface organophilic and was accompanied by the adhesion of the naked Pd particles to the surfaces of the LDH lamellae. In this way, hydrophobic Pd-MM and Pd-LDH materials were formed, which are readily dispersible in organic solvents. In addition, the catalysts may undergo disaggregation and swelling. The Pd content of the catalysts can be controlled. The higher the Pd concentration and the lower the surfactant concentration of hydrosols, the higher the Pd content of the catalysts.

6. Activities of the Pd-MM and Pd-LDH catalysts

The activities of the Pd-MM catalysts are significantly higher, those of the Pd-LDH catalysts are moderately higher than the previously reported hydrophilic Pd-MM and heterogenized homogen Pd-MM catalysts in the olefin (styrene, 1-hexene, cyclohexene) hydrogenations in organic media. Beside the high activity of the Pd particles, we attributed this efficiency to the different colloid chemical behaviour (wetting, disaggregation and swelling) of organophilic and hydrophilic clays in organic solvents.

7. The active sites of Pd particles in the liquid-phase hydrogenation of styrene

7.a Seven Pd-MM catalysts were synthesized with control over the size of the Pd particles in the range of 1.5 to 6.2 nm. The metal content (0.15 m/m%) and the morphology of the particles (cubooctahedral) were otherwise identical for each sample. The surface statistics of cubooctahedral Pd particles in terms of high-coordination terrace sites (face atoms), low-coordination defect sites (edge and corner atoms) and all the surface sites (face, edge and corner atoms) were computed and the dispersions were calculated as functions of the Pd particle size.

7.b The initial reaction rates of catalysts in the liquid-phase hydrogenation of styrene were converted to turnover frequencies by using the calculated dispersion data. The analysis of the dependence of the TOF values for different surface sites on the particle size, led to the conclusion that it is the edge and corner atoms which are the catalytically active centers of styrene hydrogenation and that the face atoms are inactive.

7.c The decisive role of the corner and edge atoms was confirmed by systematic poisoning of the active sites by CS₂. The hydrogenation rate of styrene decreased in proportion with increasing the CS₂ concentration in the slurry. When the CS₂ concentration corresponded to the number of edge and corner atoms of the cubooctahedral Pd particles, the reaction was not started.

7.d We pointed out that the dispersion of Pd particles determined by hydrogen sorption is proportional to the dispersion of all the surface atoms of a cubooctahedral particle and not just the catalytically active edge and corner atoms. The hydrogen chemisorption onto the Pd particle is followed by the formation of β -hydride phase. The β -hydride phase formed more readily for Pd-MM62 than for Pd-MM15. The activities of Pd-MM15 and Pd-MM62 are not influenced by difference in the magnitude of the β -hydride phase.

4. Publications in connection with the Ph.D. thesis

[A1] Z.Király, **B.Veisz**, Á.Mastalir, Zs.Rázga, I.Dékány:
Preparation of Organophilic Palladium Montmorillonite Catalyst in a Micellar System
Chemical Communications **1999**, 1925
IF: 3,695

[A2] Z.Király, **B.Veisz**, Á.Mastalir, Gy.Kőfaragó:
Preparation of Ultrafine Palladium Particles on Cationic and Anionic Clays, Mediated by Oppositely Charged Surfactants. Catalytic Probes in Hydrogenations.
Langmuir **2001**, *17*, 5381
IF: 3,045

[A3] **B.Veisz**, Z.Király, L. Tóth, B. Pécz:
Catalytic Probe of the Surface Statistics of Palladium Crystallites Deposited on Montmorillonite
Chem. Mater. **2002**, *14*, 2882
IF: 3,580

[A4] **B.Veisz**, Z.Király:
Size-Selective Synthesis of Cubooctahedral Palladium Particles Mediated by Metallomicelles
Langmuir **2003**, *19*, 4817
IF: 3,045

ΣIF:13,365

5. Other publications

Á.Tóth, **B.Veisz**, D.Horváth:
Diffusion-Driven Front Instability in a Three-Dimensional Medium
J. Phys.Chem. A **1998**, *102*, 5157
IF: 2,754

6. Conference lectures, posters

6.1 Lectures

1. **B.Veisz**, Z.Király:
Investigations of Pd-montmorillonite Catalysts Prepared in Micellar Solutions
Chemical Lecture Days (KEN), Szeged, Hungary, 1-3 November, 1999

2. Z.Király, **B.Veisz**, I.Dékány, Á.Mastalir:
Surfactant-Mediated Synthesis of Palladium Particles in Layer Structured Materials
10th International Conference on Colloid and Interface Science
Bristol, UK., 23-28 July, 2000, Abstracts p.149

3. **B.Veisz**, Z.Király:
Preparation of Size-quantized Pd, Pt and Pd/Pt Alloy Particles in Surfactant
Solutions. Investigations in Heterogeneous Catalytic Reactions
PORANAL, Eger, Hungary, 13-14 September, 2001

4. **B.Veisz**, Z.Király:
The Active Sites of Pd-montmorillonite catalysts
The Day of Hungarian Science, Szeged, Hungary, 5 November, 2001

5. **B.Veisz**, Z.Király:
The Surface Statistics of Pd Particles Generated in Cationic Surfactant Solutions
14th International Symposium on Surfactants in Solution
Barcelona, Spain, 9-14 June, 2002, Abstracts O-056

6. Á.Mastalir, Z.Király, **B.Veisz**:
Novel Pd-hydrotalcite clays as highly selective catalysts in alkyne
semihydrogenation under mild conditions
8th North American Catalysis Society Meeting
Cancun, Mexico, 1-6 June, 2003, Abstracts O128

6.2 *Posters*

1. Á.Mastalir, **B.Veisz**, Zs.Rázga, Z.Király, I.Dékány:
Preparation of Palladium-Organoclay Catalysts
10th International Symposium on Intercalation Compounds
(ISIC 10)
Okazaki, Japan, 30 May-3 June, 1999, Abstracts p.93.

2. **B.Veisz**, Gy.Szöllösi, Á.Mastalir, Z.Király, M.Bartók, I.Dékány:
Clay-Supported Noble Metal Catalysts: Preparation and Application
5th Pannonian International Symposium on Catalysis
Kazimierz Dolny Nad Wisla, Poland, 31 June- 3 July, 2000, Abstracts P-36

3. **Á.Mastalir, Z.Király, B.Veisz, J. Walter, I.Dékány, M.Bartók:**
The Controlled Synthesis and the Catalytic Application of Organophilic Pd-Montmorillonite

14th International Symposium on the Reactivity of Solids
Budapest, 27-31 August, 2000, Abstracts p.133

4. **B.Veisz, Á.Mastalir, Gy.Kőfaragó, Á.Patzkó, Z.Király, I.Dékány:**
Preparation of Palladium and Platinum Particles on Ion-Exchanging Layer-Structured Materials Mediated by Oppositely Charged Ionic Surfactants

3rd International Conference of the Kolloid-Gesellschaft e. V.
Budapest, 25-28 September, 2000, Abstracts P62

5. **I.Dékány, B.Veisz, Gy.Kőfaragó, Á.Patzkó, Á.Mastalir, Z.Király:**
Preparation of Palladium and Platinum Particles on Charged Surfaces Mediated by Oppositely Charged Ionic surfactants

13th International Symposium on Surfactants in Solution.
Florida, U.S.A., 11-16 June, 2000, Abstracts p.98.

6. **B.Veisz, Z. Király, Á.Mastalir:**

Preparation of Pd, Pt and Pd/Pt Nanoparticles on Cationic and Anionic Clays.
Catalytic Probes in Hydrogenations

8th European Conference on Solid State Chemistry
Oslo, Norway, 4-7 July, 2001, Abstracts P064

7. **B.Veisz, Z. Király:**

Surfactant-mediated Synthesis of Size-quantized Pd, Pt and Pd/Pt Nanoparticles

8th European Conference on Solid State Chemistry
Oslo, Norway, 4-7 July, 2001, Abstracts P065

8. **B.Veisz, Z.Király, O.Berkesi, G. Galbács:**

Size-tailoring of Pd, Pt, Pd/Pt Nanoparticles in Normal Micellar Solutions

14th International Symposium on Surfactants in Solution
Barcelona, Spain, 9-14 June, 2002, Abstracts P-075-B

9. **Z.Király, B.Veisz, Á.Mastalir:**

Catalytic Probes of the Surface Statistics of Palladium Crystallites Deposited on Montmorillonite

8th North American Catalysis Society Meeting
Cancun, Mexico, 1-6 June, 2003, Abstracts P-204