

PhD. Thesis

**New types of heterogeneous palladium loaded catalysts  
(Synthesis and application)**

**Attila Papp**

Supervisor:  
Dr. Árpád Molnár



University of Szeged  
Department of Organic Chemistry  
Szeged  
2010.

## **Introduction**

The organic reactions are, generally, carry out catalytic condition. Main features of frequently used homogeneous catalysts are having great activity and selectivity. Furthermore forming catalyst libraries are able to increase reaction and product specificity. However they have some disadvantages: some of them needs specific condition ie. inert atmosphere, water free solvents, needs expensive ligands; they are instable thereby strongly or can not separate from the reaction mixture thus hinder its from reusability. The heterogenization of the catalysts can eliminate these disadvantages.

The heterogeneous catalysts can remove from the reaction mixture by simple separation techniques like as filtration or centrifugation thus it easy to regenerate and recycle into a new reaction. The heterogeneous form of sensitive homogeneous catalyst can be stable or do not need special storage and reaction conditions. However the heterogeneous catalyst has less advantageous features too. The catalytically active centers, in many cases, have different catalytic activity and admittance to the active centers are different. The activity of heterogeneous catalyst less then homogeneous form whereas the efficient number of impacts are less and the effects of diffusion phenomena become remarkable.

At the Department of Organic Chemistry, University of Szeged has been studied the heterogeneous catalysis since many decades. My doctoral studies organically connect to the Department investigation area thus this doctoral thesis demonstrate the preparing the new type of heterogeneous palladium loaded catalyst and its activity in organic transformation. Within the frame of our studies we synthesized MCM-41, SBA-15 structured, surface grafted silica and montmorillonite supported Pd catalysts. These catalysts were compared with commercially available palladium loaded heterogeneous catalysts ie. Pd/C és Pd-ENCAT<sup>®</sup>. The synthesized catalysts were characterized physically by accessible apparatus. Its catalytic activity was studied in carbon–carbon coupling reaction and in the selective hydrogenation of alkynes respectively.

## Experimental methods

Our studies four methods have been used for preparing palladium loaded supported catalysts:

- (i) Immobilization of palladium on organically modified silica surface (Pd-SiO<sub>2</sub>).
- (ii) Palladium deposition by sodium borohydride onto SBA-15 and MCM-41 structured silica (Pd-B/MCM and Pd-B/SBA).
- (iii) Simultaneous immobilization of palladium with synthesis of MCM-41 structured silica (Pd-MCM).
- (iv) Montmorillonite supported Pd catalysts by ion exchange (Pd-montm1) and intercalation (Pd-montm2)

The catalyst's mean pore volume and pore diameter were determined by BET method. The palladium dispersity and morphology of particles were determined by H<sub>2</sub> chemisorption and Transmission Electron Microscopy (TEM). The structure of the supports, the degree of order of structure and the interplanar spacing were determined by X-ray diffraction. The palladium contents of the catalysts were determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The surface methyl, methoxy and phenyl groups) on organically modified silica (Pd-SiO<sub>2</sub>) were characterized by <sup>29</sup>Si MAS NMR and <sup>13</sup>C CP-MAS NMR techniques.

The catalytic activities of the catalysts were studied in the Heck and Suzuki-Miyaura carbon-carbon cross coupling reactions and in the selective hydrogenation of alkynes. In case of coupling reactions same experimental equipments were used (5 ml, heavy-walled, closed glass tube, heater), while for the selective hydrogenation reaction an automated hydrogenation apparatus was applied. The reaction was monitored by gas chromatography (Hewlett Packard 5980). And the identification of the products commercially available standards or some case Hewlett Packard 5970 mass selective detector equipped Hewlett Packard 5890 gas chromatograph was used .

## **New scientific results**

### **1. The results of structure analysis**

- 1.1 The BET area of the organically modified silica catalysts decreased in contrast of starting silica and the rate of decrementation is depend on the amount of the surface function group and they character. The surface features of the Pd-SiO<sub>2</sub> catalysts - by the silylhydride reduction induced palladium deposition - (BET area, size of particles) also depend on the amount of the surface function group and they character.
- 1.2 The mean surface area, pore volume and interplanar spacing of the Pd-MCM samples are change by palladium loading. The mean surface area 1.39 % Pd-MCM > 3 % Pd-MCM > 5.85 % Pd-MCM increasing while the interplanar spacing and the pore volume are reverse.
- 1.3 The degree of order of Pd-MCM catalysts decreasing by increasing of palladium content and the size of palladium particles did not change proportionally with Pd content. But the dispersity changed like 5.85 % Pd-MCM > 1.39 % Pd-MCM > 3 % Pd-MCM by H<sub>2</sub> chemisorption investigation.
- 1.4 The mean surface area dramatically reduced during the sodium borohydride reduction. The degree of the decreasing in case of Pd-B/MCM 96 %, while in case of Pd-B/SBA 47 % in contrast of the starting materials.
- 1.5 The Pd-B/MCM sample lost its ordered structure by the treatment, while the Pd-SBA keeps its structure due to the flexible skeleton.
- 1.6 Varied size of palladium particles and clusters can be prepared by the sodium borohydride reduction.

Publications in connections with these topics: (1) (2) (4)

### **2. Results of the Heck coupling**

- 2.1 The Pd-SiO<sub>2</sub> samples have great catalytic activity in reaction with iodo- and activated bromo derivatives. These activity in the reaction of iodobenzene–styrene are depend on the palladium content and it decreasing with decreasing of the loading of Pd and the one phenyl group containing Pd/SiO<sub>2</sub>Ph catalyst is the most active.
- 2.2 The effect of the surface functional groups come to the front in case of the low loaded Pd-SiO<sub>2</sub> catalysts in the reaction of iodobenzene–methyl acrylate. Thus the activity of Pd/SiO<sub>2</sub>Ph, Pd/SiO<sub>2</sub>Me and Pd/SiO<sub>2</sub> are highest than the same function groups containing catalysts in contrast with the more Pd loaded sample.

- 2.3 The region selectivity of the Heck reaction is not influenced by Pd-SiO<sub>2</sub> catalysts, thus it depends on the substrate–reactant connection.
- 2.4 In case of Pd-SiO<sub>2</sub> catalysts the palladium leached from the supports into the reaction mixture due to these catalysts reusable only 5 times same as the 10 % Pd/C catalyst.
- 2.5 The activity of Pd-MCM catalysts increasing with increasing of dispersity of Pd.
- 2.6 The 1.39 % Pd-MCM catalyst is active in case of normal and activated bromo derivatives and the Pd-MCM type catalyst in general have suitable activity with deactivated bromo derivatives.
- 2.7 The Pd-MCM samples are reusable in 20 times without loss of activity independently of palladium content.
- 2.8 The Pd-montm catalysts have high activity with deactivated iodo and bromo derivatives in Heck reaction.
- 2.9 The Pd-montm samples have very high activity (TON = 6000–17000) in low concentration (0.0008–0.005 mol%), which activity same as the homogenous Pd(OAc)<sub>2</sub>. Same high activity were observed in case of activated chloro derivatives (0.0016–0.005 mol %, TON = 18000–32500).
- 2.10 Pd-montm catalysts (in contrast the Pd-SiO<sub>2</sub> and Pd-MCM catalysts) have major *E* selectivity in case of electron rich alkenes.
- 2.11 Pd-montm catalysts lost their activity due to reusability.

Publications in connection with these topics: (1) (2) (4) (6)

### **3. Results of the Suzuki coupling**

- 3.1 Among our synthesized catalysts the 1.39 % Pd-MCM has the highest activity in the Suzuki cross coupling reaction. This activity is same as the commercially available Pd-ENCAT<sup>®</sup> catalyst. The reduction pre-treatment of the catalyst increases the activity in 3 times.

Publications in connection with this topic: (5)

### **4. Results of selective hydrogenation**

- 4.1 The Pd-MCM samples have highest activity than the (4 – 5 times) than the Pd-B/MCM and Pd/Cabosil. The activity of Pd-MCM depends on the size of Pd particles and the Pd content. The less Pd loaded and the lower Pd particles content 1.39 % Pd-MCM more active than the biggest particles content 5.85 % Pd-MCM catalyst.

4.2 The Pd-MCM catalysts have a superior selectivity in the alkene propagation, and their have great selectivity in the transformation of the asymmetrical alkyne to the Z-alkene in contrast of Pd-B/MCM and Pd/Cabosil samples.

Publications in connection with this topic: (3)

#### A. Referated literatures

- (1) Á. Molnár, A. Papp, K. Miklós, P. Forgo:  
Organically modified Pd–silica catalysts applied in the Heck coupling  
*Chem. Commun.*, 2626 (2003).
- (2) A. Papp, K. Miklós, P. Forgo, Á. Molnár  
Heck coupling by Pd deposited onto organic–inorganic hybrid supports  
*J. Mol. Catal. A: Chem.*, **229**, 107 (2005).
- (3) A. Papp, Á. Molnár, Á. Mastalir  
Catalytic investigation of Pd particles supported on MCM-41 for the selective hydrogenations of terminal and internal alkynes  
*Appl. Catal., A*, **289**, 256 (2005).
- (4) A. Papp, G. Galbács, Á. Molnár  
Recyclable ligand-free mesoporous heterogeneous Pd catalysts for the Heck coupling  
*Tetrahedron Lett.*, **46**, 7725 (2005).
- (5) A. Papp, D. Tóth, Á. Molnár  
Suzuki–Miyaura coupling on heterogeneous palladium catalysts  
*React. Kinet. Catal. Lett.*, **87**, 335 (2006).
- (6) A. Papp, Á. Molnár  
Efficient heterogeneous palladium–montmorillonite catalysts for Heck coupling of aryl bromides and chlorides  
*Synlett*, 3130, 3360 (2006).

#### B. International lecture

- (1) Attila Papp, Ágnes Mastalir, Péter Forgó, Árpád Molnár  
Preparation of novel Pd-MCM catalysts, characterization and application in organic reactions  
*19th North American Catalysis Society Meeting*, Philadelphia, USA, 2005  
Technical Program, O-247.

#### C. Lectures and posters

- (1) A. Papp, B. Rác, Á. Molnár:  
Organic transformations with functionalized solids  
*6<sup>th</sup> Pannonian Int. Symposium on Catalysis*, Obergurgl, Austria, 2002  
Book of Abstracts, P-44, p. 176.
- (2) Á. Molnár, A. Papp, K. Miklós:  
Organically modified Pd-on-silica catalysts applied in the Heck coupling

*Indo-Hungarian Workshop on Surface Chemistry and Catalysis on Nanoparticles*,  
Budapest, 2003

Abstracts, pp. 17–18.

- (3) Papp Attila, Miklós Krisztina, Molnár Árpád, Kiricsi Imre:  
Heck-reakció új típusú heterogén katalizátorokkal  
*Vegyészkonferencia*, Hajdúszoboszló, 2003  
Program és előadásösszefoglalók, P-87, p.5
- (4) A. Papp, K. Miklós, Á. Molnár:  
Preparation and characterization of palladium-grafted amorphous and mesoporous silica supports  
*EUROPACAT VI*, Innsbruck, 2003  
Programme, A2.034.
- (5) A. Papp, D. Tóth, Á. Molnár:  
Preparation and application of new Pd catalysts in organic synthesis  
*7<sup>th</sup> Pannonian Int. Symposium on Catalysis*, Srní (Czech Republic), 2004  
Abstracts, p. 79.
- (6) A. Papp, Á. Mastalír, Á. Molnár:  
Heck coupling and semi-hydrogenation of alkynes over supported Pd catalysts  
*5<sup>th</sup> International Conference of PhD Students*, Miskolc, 2005  
pp. 361–366.
- (7) A. Papp, G. Galbács, Á. Molnár:  
Reusable Pd loaded MCM-41 catalysts in the Heck coupling reaction  
*Frontiers in Catalysis Symposium*, Visegrád, 2005  
Book of Abstracts, P-11, p. 45

### Impact Factors (i)

#### The base publications of the doctoral theses

1. publication	i = 4.031
2. publication	i = 2.348
3. publication	i = 2.728
4. publication	i = 2.477
5. publication	i = 0.514
6. publication	i = 2.838

---

$\Sigma i = 14.936$