

# ***In-situ* Incorporation of Pd-MPTES Complex in Zeolite and MCM-41 type Silica**

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## **ABSTRACT**

Monodispersed Pd nanoparticles have been successfully synthesized by controlled reduction of Pd(II) complexes. In the first step, the Pd(II) complexes were obtained by using mercaptopropyltriethoxysilane (MPTES) or aminopropyltriethoxysilane (APTES) as ligands. In a subsequent step, these Pd-complexes were *in-situ* incorporated to different nanostructured silica materials. Finally, the Pd complex was thermally decomposed to produce Pd nanoparticles homogeneously dispersed in nanostructured silica. The resulting materials can be used as catalysts for a variety of reactions. In addition, we have studied the possibility to use this method with others metals.

The method herein described yields novel nanostructured silica materials having highly dispersed and strongly anchored Pd nanoparticles into their structures. Consequently, these materials are expected to be highly active and stable catalysts.

**Keywords:** Pd complex, zeolites, nanostructured materials, MCM-41, catalysis, nanoparticles

## **1 INTRODUCTION**

The widespread use of Pd and other noble metal catalysts in many industrial processes, especially in the fine-chemical industry, has lead to several efforts devoted to improve their activity and stability.

In recent years, most studies have been focused on the use of soluble Pd complexes with various types of ligands with the aim of increasing the activity and selectivity of the catalysts. [1] These homogeneous catalysts have been successfully used in numerous processes including C–C bond formation and oxidation reactions. The main limitations are the catalyst recovery and recycling, and the catalyst deactivation due to the aggregation of the nanoparticles formed *in situ* during reaction.

To overcome these problems, heterogeneous catalysts are used because they limit the loss and agglomeration of metal and to make their handling and recovery easier. [2]

Nowadays, two different approaches are used to prepare heterogeneous catalysts. First, many Pd complexes have been heterogenized by covalently bounding their ligands

to various solid supports. Most of the novel heterogenized catalysts are based on silica. [3] Nanostructured silica materials are widely used as catalyst support because their large surface area, controllable surface chemistry and porosity, excellent stability (chemical and thermal) and good accessibility.[4]

On the other hand, Pd nanoparticles are typically loaded on porous supports. The high surface area-to-volume ratio of noble metal nanoparticles makes them highly attractive for catalysis. Usually, supported Pd catalysts have lower activity than the homogeneous ones and require more drastic reaction conditions. However, they are often more stable and can be recovered and reused. These advantages overcome their lower activity in comparison with the homogeneous catalysts.

Conventional synthesis techniques of supported metal nanoparticles such as wet or dry impregnation, deposition-precipitation, deposition-reduction, and ion-exchange methods, still have considerable limitations, mainly in terms of homogeneity, dispersion and reproducibility. It is highly desirable to develop heterogeneous Pd catalysts more homogeneous and stable for industrial applications.

In last years, many examples of new Pd heterogeneous catalysts have been described, as Kobayashi's incarcerated catalysts [5], ionic gels [6], Pd-containing perovskites [7], and physically immobilized catalysts using a zeolite shell [8].

In 2007, J.D. Webb et al. synthesized mesoporous silica functionalized by mercaptopropyltrimethoxysilane [9]. After Pd loading, the resulting catalyst showed optimal characteristics when used for the Suzuki–Miyaura coupling reaction.

Recently, we described a simple method to incorporate Pd nanoparticles in porous materials by functionalization of the nanoparticles with trialkoxysilanes. This strategy is based on three steps: first, the metal nanoparticles were produced by controlled reduction in toluene and phase transfer to water, then they were functionalized with mercapto-terminal trialkoxysilanes, and finally they were incorporated into the porous material by co-polymerization with a silica alkoxide (tetraethoxysilane).[10]

Herein, a novel method to obtaining nanostructured silica materials supported Pd catalyst with high loading and dispersion by means *in situ* Pd complex incorporation is brought forward. This approach does not require the preparation of metal nanoparticles because the Pd precursor

is directly incorporated in the silica support using a Pd complex. Moreover, as herein described, this method allows for *in situ* incorporation the Pd complex in several nanostructured silica materials i.e. MCM-41 type silica, zeolite A and zeolite Y during their synthesis.

## 2 EXPERIMENTAL SECTION

### 2.1 Materials

Reagents were purchased from the following suppliers: mercaptopropyltriethoxysilane (MPTES), aminopropyltriethoxysilane (APTES) and sodium metasilicate were obtained from Fluka. Tetraethylorthosilicate (TEOS), cetyltrimethylammonium bromide (CTAB), sodium silicate solution (27% SiO<sub>2</sub>), tetrapropylammonium bromide (TPABr), sodium hydroxide, and sodium tetrachloropalladate(II) were supplied by Aldrich. Sodium aluminate was obtained from Riedel-de Haën. All chemicals were used as received without further purification.

### 2.2 Synthesis of Pd-MCM-41 type silica

Parent silica-based MCM-41 was synthesized as described elsewhere [11] taking into account that Pd-complexes are unstable in ammonia solutions. NH<sub>4</sub>OH was therefore avoided as a base to prevent the formation of Pd ammonia complexes. Pd/MCM-41 2 wt% was typically prepared dissolving 0.24 g NaOH, 0.099 g Na<sub>2</sub>PdCl<sub>4</sub> and 0.164 ml MPTES in 54 ml of distilled water under orbital stirring. A brown-red solution was obtained after a few minutes. Then, 2.19 g CTAB was dissolved. When a clear solution was obtained, 6.25 g TEOS was added dropwise under vigorous stirring to ensure its complete hydrolysis. After that, the solution was transferred to a 100 ml Teflon-lined stainless steel autoclave and heated at 100 °C for 24 h. After cooling to room temperature, the solid product was water washed, filtered out, and air dried overnight. The surfactant was removed by calcination at 550°C for 8 h.

### 2.3 Synthesis of Pd-zeolite A

Zeolite Type A was prepared according to the procedure reported by R.W. Thompson and M.J. Huber [12]. For 1 g Pd/zeolite A 2 wt%, 0.072 g sodium hydroxide, 0.055 g Na<sub>2</sub>PdCl<sub>4</sub> and 0.164 ml MPTES were dissolved in 8 ml of distilled water. The solution, which took a brown-red, was divided into two equal volumes in polypropylene bottles. 0.826 g sodium aluminate was dissolved in one of these parts and 15.48 g sodium metasilicate in the other. The silicate solution was added to the aluminate solution quickly under vigorous stirring. A thick orange gel was obtained after 6 hours of orbital stirring. This product was transferred to a Teflon-lined stainless steel autoclave and heated at 99 °C for 4 h. The solid product was water washed, filtered out, and air dried overnight.

### 2.4 Synthesis of Pd-zeolite Y

Zeolite Type Y was synthesized using a gelling process described by D. M. Ginter, A. T. Bell and C. J. Radke [13]. Pd incorporated in zeolite Y was obtained using a three-step synthesis procedure. A typical synthesis solution for zeolite Y seeds was prepared by dissolving in a plastic bottle 0.204 g sodium hydroxide, 0.02 ml MPTES, 0.012 g Na<sub>2</sub>PdCl<sub>4</sub> and 0.105 g sodium aluminate in 0.997 g distilled water. Finally, 1.136 g sodium silicate was added. After 10 min of mild stirring a orange gel was obtained. Finally, the bottle was capped and the solution let age at room temperature for 1 day.

The second step is the preparation of a feedstock gel. 0.007 g sodium hydroxide, 0.125 ml MPTES, 0.077 g Na<sub>2</sub>PdCl<sub>4</sub> and 0.655 g sodium aluminate were dissolved in 6.55 ml of distilled water. Then, 7.122 g sodium silicate solution was added under vigorous stirring.

Finally, 0.165 g seed gel was slowly added to the feedstock gel under vigorous hand stirring, the composition molar of the mixture is 10SiO<sub>2</sub>:1Al<sub>2</sub>O<sub>3</sub>:4.62Na<sub>2</sub>O:180H<sub>2</sub>O. The beaker was energetically shaken to improve the mixing.

The crystallization was carried out in a Teflon-lined stainless steel autoclave at 100°C for 5 h. An orange-brown solid and a clear supernatant were obtained. This solid was water washed, filtrated out, and air dried overnight.

### 2.5 Instrumentation

Transmission Electron Microscopy (TEM) studies were carried out using a JEOL JEM-2010 instrument operated at 200 kV. The Pd-nanoparticles-containing silica was suspended in ethanol, sonicated and a few drops placed over a carbon-coated copper grid. In combination with TEM studies, chemical analysis was carried out using a INCAEnergyTEM – EDS Microanalysis system. The porous texture of the samples was characterized by N<sub>2</sub> adsorption at 77 and 273 K in an AUTOSORB-6 apparatus. The samples were previously degassed for 4 h at 523 K at 5\*10<sup>-5</sup> bars. The nanostructure of these materials were characterised by X-ray powder diffraction (Bruker D8-Advance) using a CuK $\alpha$  radiation. The scanning velocity was 0.1°/min from 1.7 to 50 2theta (°).

## 3 RESULTS AND DISCUSSION

### 3.1 TEM images of the Pd containing zeolite and MCM-41 type silica

Two TEM micrographs at of a Pd/zeolite A are presented in Figure 1. More specifically, Figure 1.b) shows a magnification of the area indicated in Figure 1.a) with a red square. It is possible to distinguish Pd nanoparticles in this zoomed-in image as dark spots. The analysis of this image indicates that these nanoparticles are a very small size (around 1.5 nm) and high dispersion in the support.

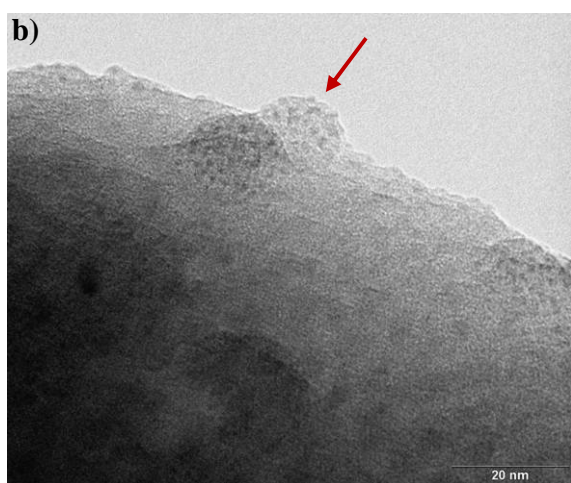
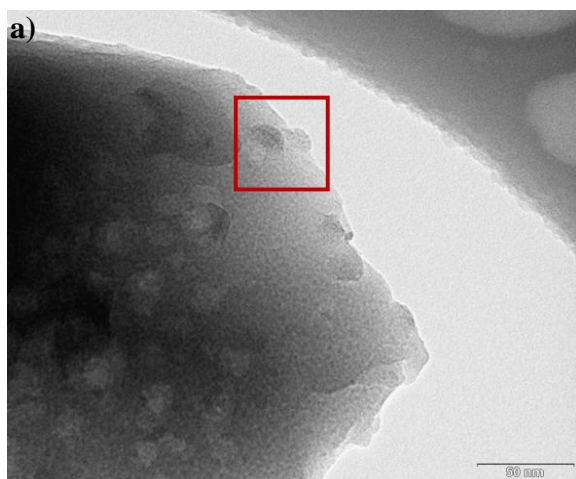


Figure 1: Two transmission electron micrographs at two different magnifications of the same sample of Pd-zeolite A.

The TEM micrographs shown in the Figure 2 and 3 of the Pd/MCM-41 type silica materials confirm their mesoporosity. These images show a sample containing 2 wt% Pd, before (Figure 2) and after calcination (Figure 3). The sample before calcination, Figure 2, has the Pd incorporated in atomic form as Pd-MPTES complex, therefore, it is impossible to recognize at the image. Nevertheless, the Pd presence was confirmed by microanalysis with EDS system. Figure 3 shows a micrograph of the same sample after calcinations. In the case, highly disperse Pd nanoparticles formed during the thermal treatment were observed, the size of these particles change between 4 and 8 nm. It is likely that the Pd was partially oxidised producing an incomplete PdO.

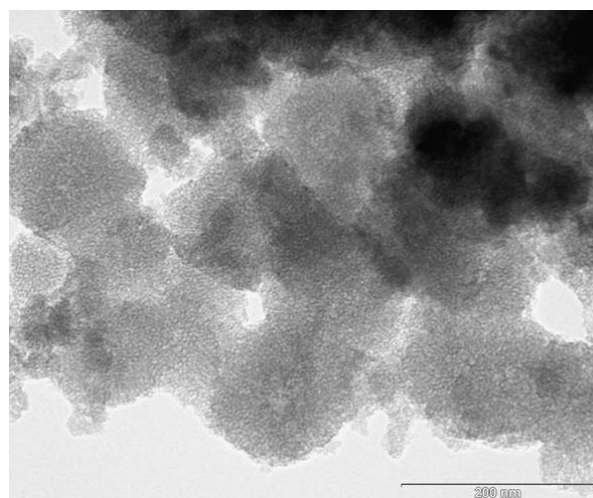


Figure 2: TEM micrograph of a 2 wt% Pd/MCM-41 type silica sample, before surfactant removal.

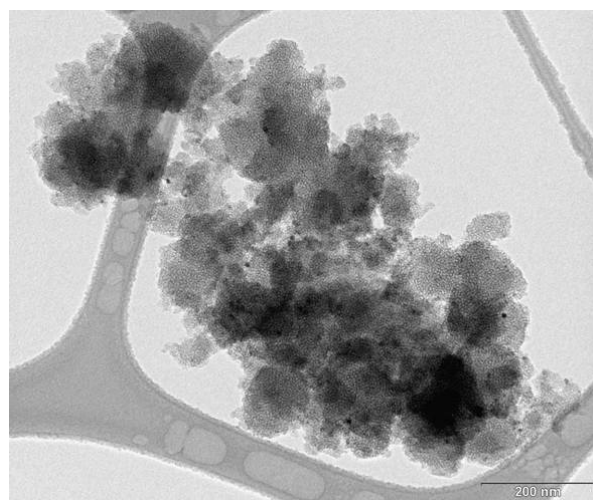


Figure 3: TEM micrograph of a 2 wt% Pd/MCM-41 type silica sample, after calcination treatment to remove the surfactant.

### 3.2 XRD of Pd containing nanostructured silicas

The X-ray diffraction (XRD) patterns of the Pd-MPTES incorporated zeolite Y and A are shown in Figure 4. For comparison purposes, the XRD patterns of conventional zeolites have been added. The XRD patterns of all the Pd-MPTES incorporated zeolites present well-defined peaks with similar intensities to the original zeolites. No shift was observed in the position of the Pd containing zeolite, suggesting that the unit cell of the zeolites (U.C.S zeolite Y = 24.794 Å, zeolite A = 12.283 Å) was not changed due to the presence of Pd (U.C.S Pd/zeolite Y = 24.757 Å, Pd/zeolite A = 12.283 Å). No other phases were identified as no spurious peaks were observed, neither broad peaks nor change in the baseline due to amorphous material. Also, no peaks that could be indexed to Pd metal were observed.

which is in agreement with the very small size of the Pd nanoparticles and Pd content in the sample. All these observations are consistent with the TEM analysis. These results suggest that Pd nanoparticles were successful *in situ* incorporated in zeolites without damaging their structural integrity.

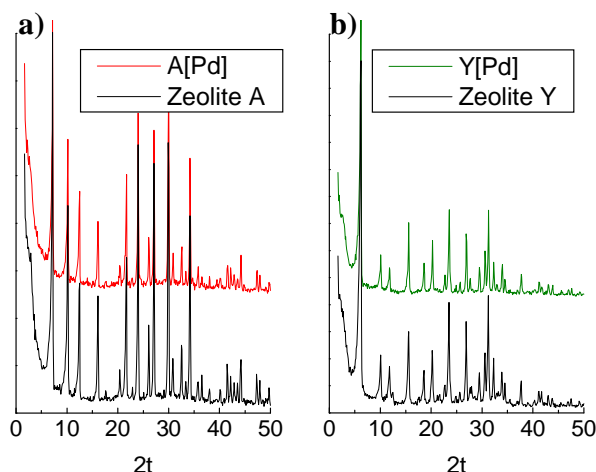


Figure 4: XRD patterns of a) Pd-MPTES zeolite A (2 wt% Pd) (top) compared to a sample of zeolite A (down) and b) Pd-MPTES zeolite Y (2 wt% Pd) (top) compared to a sample of zeolite Y (down).

### 3.3 Nitrogen isotherms at 77K of Pd containing MCM-41 type silica

The mesoporous nature of the calcined materials was confirmed by nitrogen adsorption at 77K, which produces a type IV isotherms (see Figure 5) with a sharp uptake at 0.3 – 0.4  $P/P_0$ .

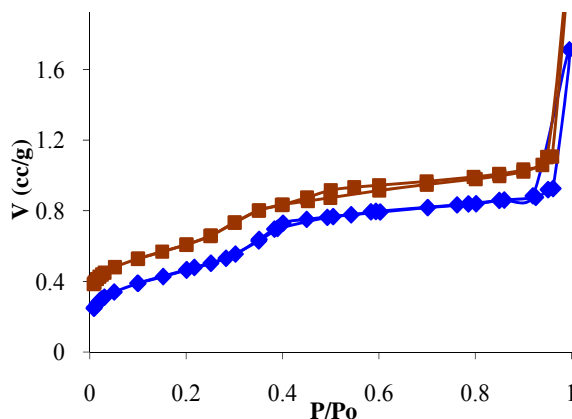


Figure 5:  $\text{N}_2$  isotherms at 77K of a sample prepared with Pd:MPTES molar ratio of: 4 (squares, top) and 1 (rhombus, bottom). The curve at the top is shifted +0.15  $\text{cc/g}$  for clarity.

In the hybrid MCM41-type materials so obtained both the surfactant and the functional group can be removed by

calcination, producing a composite material with Pd nanoparticles incorporated in a mesoporous support.

## 4 CONCLUSIONS

The incorporation of Pd nanoparticles in zeolite A and Y and in MCM-41 type silica has been described using a two step process. The condensation of a Pd-MPTES complex with TEOS under hydrothermal conditions (zeolites) or in a surfactant solution (MCM-41) and complex thermal decomposition. The final materials have highly dispersed fairly small (1-3 nm) Pd nanoparticles.

In this work we have developed an approach to obtain highly dispersed and strongly anchored Pd nanoparticles incorporated in different silica matrices. This method is based on the use of a Pd complex as building blocks for the construction of silica materials, producing composite materials with Pd nanoparticles homogeneously dispersed in nanostructured supports. The cavity, in which the metal nanoparticle is located after the functional groups are removed, inhibits the migration of the nanoparticle and thus the agglomeration/sintering. This method is general and should also serve to incorporate other metal nanoparticles in silica matrices.

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