



# A novel route for the synthesis of nanosize particles of metallic palladium

Stjepko Krehula\*, Svetozar Musić

Division of Materials Chemistry, Ruđer Bošković Institute, P.O. Box 180, HR-10002 Zagreb, Croatia

## ARTICLE INFO

### Article history:

Received 30 June 2008

Accepted 20 July 2008

Available online 24 July 2008

### Keywords:

Nanosize particles

Palladium

Tetramethylammonium hydroxide

Catalysts

X-ray techniques

Electron microscopy

## ABSTRACT

A novel route for the synthesis of metallic palladium consisting of nanosize particles has been reported. The synthesis is based on (a) the addition of tetramethylammonium hydroxide (TMAH) to the aqueous solution of  $\text{PdCl}_2$ , and (b) autoclaving of this precipitation system at 160 °C. The distribution of the nanosize particles of metallic palladium has its mean value at about 18 nm. The mechanism of the metallic palladium formation is briefly discussed.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

Metallic palladium is a well-known catalyst for many chemical reactions. Unsupported palladium and other platinum group metal catalysts find a wide use in laboratory hydrogenations and are particularly preferred in small-scale hydrogenation where any loss of product should be avoided [1]. Palladium often shows a particularly high selectivity among the six platinum metals in various hydrogenations. Metallic palladium can be used as the catalyst in ethylene hydrogenation, where specific adsorption of ethylene on Pd(111) plane plays an important role [2]. It was also investigated as a catalyst in the oxidation of methane into methanol [3]. In this way methanol can be easily produced at the location where natural methane is exploited. Bovkun et al. [4] found conditions for the hydrodechlorination and hydrodearomatization of various chlorophenols to cyclohexane using as the catalyst a mixture of nanosize palladium particles and chloro(1,5-cyclooctadiene)rhodium dimer. Ishikawa and Iglesia [5] used Pd, Rh and Pt clusters deposited on  $\text{ZrO}_2$ ,  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{SiO}_2$  carriers in the combustion of dimethyl ether to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  at 400–600 K without any detectable formation of byproducts. Palladium deposited on a  $\gamma\text{-Al}_2\text{O}_3$  carrier was used [6] to catalyze the decomposition of  $\text{CF}_2\text{Cl}_2$  which is currently prohibited for use due to its participation in the destruction of ozone layer. The Pd/ $\gamma\text{-Al}_2\text{O}_3$  catalyst was also used in total oxidation of *n*-hexane [7]. Metallic palladium has been found to be more active at low combustion temperatures than PdO. Grunwaldt et al. [8] also found that metallic palladium is more active than palladium in the oxidized state in the selective oxidation of benzyl alcohol. Pisanu and Gigola [9] used the

Pd/ $\alpha\text{-Al}_2\text{O}_3$  catalyst in the reduction of NO to  $\text{N}_2$  with CO gas at 150–300 °C. Greca et al. [10] investigated the effect of the preparation route on the catalytic efficiency of the Pd/ $\alpha\text{-Al}_2\text{O}_3$  catalyst. Ortega Zarcosa et al. [11] investigated the formation of Pd aggregates in the amorphous silica gel upon calcination. The phase composition of this composite depended on temperature, and metallic palladium appeared at 1000 °C. Other phases such as quartz, cristobalite and PdO were also found in dependence on temperature.

In the present work we report on a novel route for the synthesis of the nanosize particles of metallic palladium. The synthesis is based on the precipitation of palladium (hydr)oxide particles with tetramethylammonium hydroxide (TMAH) at high pH value and hydrothermal processing of the suspensions obtained.

## 2. Experimental

### 2.1. Sample preparation

$\text{PdCl}_2$  supplied by Acros Organics, TMAH solution (25% w/w, electronic grade 99.9999%) supplied by Alfa Aesar® and twice-distilled water prepared in our own laboratory, were used. During the dissolution of  $\text{PdCl}_2$  a small amount of concentrated HCl was added to accelerate the dissolution of the starting chemical. To a 0.1 mol  $\text{dm}^{-3}$   $\text{PdCl}_2$  aqueous solution the TMAH solution as received was added to achieve the alkaline pH value. The aqueous suspension thus formed was vigorously shaken for about 10 min, then heated at 160 °C for 24 h, using the Parr general-purpose bomb (model 4744), comprising a Teflon vessel and a cup. The precipitate was cooled to RT (mother liquor pH=13.5) and subsequently washed with twice-distilled water to remove the “neutral electrolyte”. The ultraspeed Sorvall RC2-B centrifuge was used. After drying, the precipitate was characterized by X-ray powder diffraction (XRPD) and high-resolution scanning electron microscopy (FE-SEM).

\* Corresponding author. Tel.: +385 1 4561 094; fax: +385 1 4680 098.

E-mail address: [krehul@irb.hr](mailto:krehul@irb.hr) (S. Krehula).

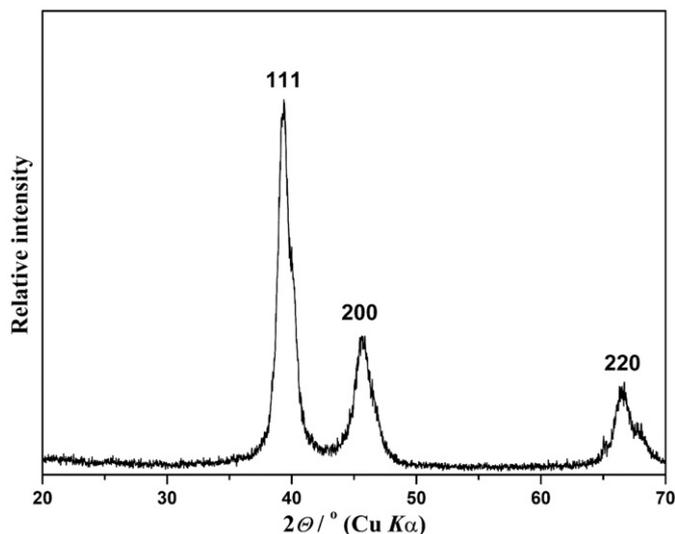


Fig. 1. XRPD pattern of metallic palladium. A significant broadening of diffraction lines is noticeable.

## 2.2. Characterization

X-ray powder diffractometer APD 2000 (Cu  $K\alpha$  radiation, graphite monochromator, NaI-Tl detector) manufactured by *ItalStructures* (Riva Del Garda, Italy) was used.

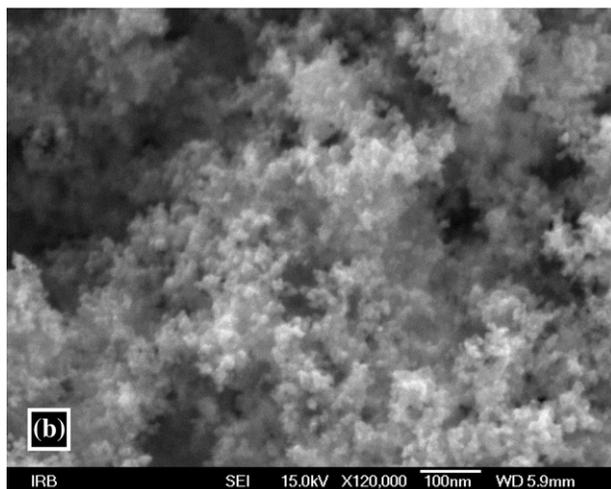
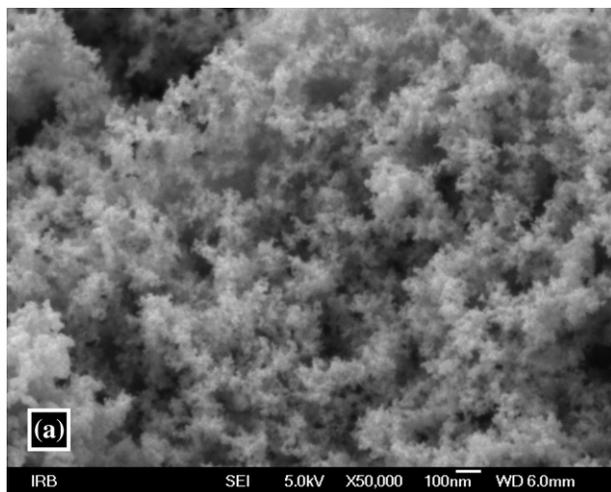


Fig. 2. FE-SEM image of nanosize particles of metallic palladium at (a) lower and (b) higher magnification.

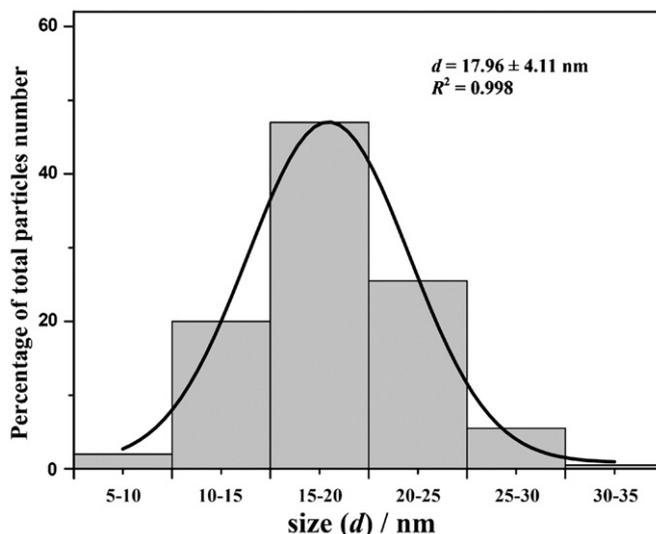


Fig. 3. Particle size distribution of metallic palladium sample.

A thermal field emission scanning electron microscope (FE-SEM, model JSM-7000F, manufactured by *JEOL Ltd.*) was used. The specimens were not coated with an electrically conductive surface layer.

## 3. Results and discussion

Fig. 1 shows the X-ray powder diffraction pattern of the sample prepared. This XRPD pattern corresponds to metallic palladium (JCPDS PDF card no. 46-1043), while a significant broadening of diffraction lines can be taken as a sign of very small crystallites. Crystallite size was estimated as about 13 nm from the width at half height of diffraction line 111 by using the Scherrer equation. FE-SEM inspection of the sample showed the Pd particles to be in the nanosize range (Fig. 2). The particle size distribution of metallic palladium (Fig. 3) is obtained from the FE-SEM images by particle diameter measurements. The distribution shows a good uniformity and corresponds to the bell-shaped curve of a normal (Gaussian) distribution (mean value = 18 nm) which is superimposed on a histogram.

TMAH plays a key role in the metallic palladium formation. Generally, TMAH is a strong organic alkali and a very high pH value can be achieved with it in an aqueous medium. Its advantage over the NaOH (or KOH) alkali is that there is no possibility of product contamination with Na<sup>+</sup> or K<sup>+</sup> ions, which in the next step may affect some product properties, such as its ohmic conductivity. The addition of the TMAH solution to PdCl<sub>2</sub> initiated the precipitation of the amorphous palladium(II) hydrous(oxide) or amorphous Pd(OH)<sub>2</sub>. At the autoclaving temperature utilized in this synthesis TMAH plays an additional role in the formation of metallic palladium, one connected with TMAH decomposition which yields NH<sub>3</sub>, volatile amines and CH<sub>3</sub>OH. Palladium ions in the suspension catalyze the decomposition of NH<sub>3</sub> to N<sub>2</sub> and H<sub>2</sub>, whereas CH<sub>3</sub>OH decomposes to CO and H<sub>2</sub>. The nascent hydrogen formation easily reduces Pd<sup>2+</sup> to metallic palladium. The formation of metallic palladium is accompanied by an acceleration of the above mentioned reactions, and strong reductive conditions in the precipitation system are being created. Similar reductive conditions were recently observed during the formation of magnetite (Fe<sub>3</sub>O<sub>4</sub>) in a highly alkaline medium in the presence of small amounts of ruthenium, initially added as the Ru(NO)<sup>3+</sup> complex [12]. In this case TMAH was also used as a precipitation agent.

The nanosize particles and specifically strong reductive conditions created during the synthesis process thus make a formed metallic palladium suitable for applications in catalytic reactions.

## References

- [1] Nishimura S. Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis. John Wiley & Sons; 2001. p. 29–30.
- [2] Molero H, Stacchiola D, Tysoe WT. Catal Lett 2005;101:145–9.
- [3] Michalkiewicz B, Kałucki K, Sońnicki JG. J Catal 2003;215:14–9.
- [4] Bovkun TT, Sasson Y, Blum J. J Mol Catal A Chem 2005;242:68–73.
- [5] Ishikawa A, Iglesia E. J Catal 2007;252:49–56.
- [6] Ahn BS, Jeon SG, Lee H, Park KY, Shul YG. Appl Catal A 2000;193:87–93.
- [7] Ihm SK, Jun YD, Kim DC, Jeong KE. Catal Today 2004;93–95:149–54.
- [8] Grunwaldt JD, Caravati M, Baiker A. J Phys Chem B 2006;110:25586–9.
- [9] Pisanu AM, Gigola CE. Appl Catal 1999;B20:179–89.
- [10] Greca MC, Moraes C, Segadães AM. Appl Catal 2001;A216:267–76.
- [11] Ortega Zarzosa G, Palomares Sánchez SA, Martínez JR, Ruiz F. J Sol-Gel Sci Technol 2005;35:5–11.
- [12] Krehula S, Musić S. Croat Chem Acta 2007;80:517–27.