Synthesis and Characterization of the Pd/SiO₂ Nanocomposite by the Sol-Gel Method

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Abstract The silica supported palladium nano particle were synthesized by using the sol-gel method. The possibility of using palladium (II) nitrate dehydrates as Pd precursor and effect of metal precursor concentration on the final Pd nanoparticle size was investigated. A stable silica sol was prepared via hydrolysis of tetraethyl orthosilicate (TEOS) as a metal alcoxide and condensation reaction. Subsequently, Palladium (II) nitrate dehydrates was added to sol to form the Pd/silica sol. After drying and calcination of the sol, the Pd/SiO₂ nanocomposite has been obtained. Crystallographic information and crystalline size of the synthesized Pd/SiO₂ were determined by X-ray diffraction (XRD) method. Morphology of the nanoparticles and hydrogen-bonding interaction between silanol groups and amine ligands were characterized by SEM and Fourier transform infrared (FTIR) spectra, respectively. Finally, the distribution and size of the palladium nanoparticles in the silica was evaluated.

Keywords Pd Nanoparticle; Palladium (II) Nitrate Dehydrate; Sol-Gel; XRD; SEM; FTIR

1. Introduction

A new type of automobile catalyst based on an active Pd layer is presently being introduced into the European market. Accordingly, this work is trying to assess the magnitude of Pd emissions by automobile catalysts up to now in order to establish baseline information [1]. Additionally, one of the important pollutant elements is Pd and it's a big threat for the urban life. Several workers have reported accumulation of Pt, Rh and Pd in road dusts and soils, Pd is discovered in influents of:

Exhaust emissions from motor vehicles using catalytic converters (both petrol and diesel) and subsequent runoff from road surfaces and roadside soils;

Emissions in effluents from hospitals using the anti-cancer drugs cisplatin and carboplatin,

Industrial uses including jewellery manufacture, electronics and glass manufacture.

Since Pd is increasingly used in several different aspects of industry, this study focused on synthesis new nanocomposite. In further study, new Pd nanocomposite applications in different industry aspects may be examined.

Nanotechnology has been the thrust area of research, which requires the development of novel engineered materials that can be successfully integrated into the existing technology [1-6]. In recent years much attention has been concentrated to metal nanocatalysts due to their novel characteristics and wide application in numerous reactions [7-9]. The synthesis and selective application of such engineered materials are of critical importance for the development of functional nano devices. Nanocomposites of metal-polymer or metal oxide-polymer are expected to be an important class of materials in the area of nanotechnology [10-16]

The sol-gel method is based on the phase transformation of a sol obtained from metallic alkoxide or organometallic precursors. This sol which is a solution containing particles in suspension is polymerized at low temperature, in order to form a wet gel. The solvent is removed by drying the gel and the next step is a proper heat treatment [17].

In this research work, we described a simple route for preparing Palladium nanoparticles supported by silica using the sol-gel method. Palladium (II) nitrate dehydrate; [Pd(NO₃)₂ .2H₂O] was used as Pd precursor and the effect of precursor concentration on the size of particles was investigated.

2. Experimental

2.1. Materials and Methods

Palladium (II) nitrate dehydrate; [Pd (NO₃)₂ .2H₂O] purchased from Sigma-Aldrich Co was used as Pd precursor. Tetraethyl orthosilicate (TEOS), ammonia and ethanol were obtained from Merck and were used as a silica source, base

catalyst and homogenizing agent, respectively. All materials used without further purification.

2.2. Characterization

The XRD measurements of synthesized samples were carried out using a Philips X-pert PRO powder diffractometer with Cu-K α radiation ($\lambda = 1.54060 \text{ \AA}$) in the scan range 0-1000. The morphology of synthesized sample was studied using scanning electron microscopy (Philips-XL30) by a sputtering technique with gold as covering contrast material. The FTIR spectra were recorded using Bruker spectrometer with KBr pellets in the range from 400 to 4000 cm^{-1} .

2.3. Sol-gel process

Silica sol formation was based on the method proposed by Lee et al. [18]. This sol synthesized by hydrolyzing TEOS in a mixture of water, ammonia and ethanol. The molar ratio of components was 1: 0.2: 44.1: 39.8 respectively. Briefly, under continuous stirring condition TEOS was dissolved in alcohol with later addition of a mixture of deionized water and ammonia drop by drop at 50°C. The ending solution was aged for 3 h under reflux at 50°C to obtain a clear silica sol. Following the formation of transparent and homogenous silica sol the various amounts of $[\text{PdNO}_3)_2 \cdot 2\text{H}_2\text{O}]$ were added to the sol. In order to study the effect of precursor concentration, three different Pd/SiO₂ molar ratio of 0.02, 0.05 and 0.09 were prepared. By adding Pd precursor, the solution, which was transparent, became cloudy.

After that, the mixtures were held in an ultrasonic bath for 30 minutes. The samples were dried at 70°C for 12 h to remove the solvent and then calcined at 500°C for 2 h in air (heating rate = 2 °C/min).

3. Results and Discussion

3.1. FT-IR

FT-IR spectra of the sol-gels are shown in Fig. 1. The low frequency peak near 434 cm^{-1} is assigned to Si-O-Si out-of-plane bending. The band at 819 is ascribed to Si-O-Si symmetric stretching vibrations, respectively. The peaks at 896 and 1250 cm^{-1} are related to Si-OH and Si-O-C, respectively.

Figure 1. FT-IR spectrum of the VB1 and the sol-gel

3.2. X-ray Diffraction

Crystalline size of Pd was calculated by applying the Scherrer's equation from a full-width at half maximum of the reflection of Pd metal ($2\theta = 39.4^\circ$) as follows [19]:

$$t = K\lambda/\beta\cos\theta \quad [1]$$

Where K is the shape factor and taken as 0.9, λ is the x-ray wavelength (0.15405 nm), β is the line broadening at half the maximum intensity (FWHM) in radians and θ is the Bragg angle.

Crystalline sizes of the palladium nanoparticles and FWHM for each sample are reported in Table 1 and Fig. 2 shows X-ray diffraction pattern of Pd/SiO₂ nano composite.

As a result, while Pd/SiO₂ molar ratio increases from 0.02 to 0.09, crystalline size will increase from 4.67 nm to 16.79 nm. Therefore Pd/SiO₂ molar ratio 0.02 was the best ratio for obtaining the lowest particle size.

Table 1. Crystalline size of the palladium nanoparticles dispersed on silica.

Pd/SiO ₂ molar ratio	Peak position(2θ)	D(nm)
0.02	39.4	4.67
0.05	39.00	12.92
0.09	38.8	16.79

Figure 2. XRD pattern of Pd/SiO₂ nanostructure a) XRD pattern of Pd/SiO₂ nanostructure while Pd/SiO₂ molar ratio of 0.02 b) XRD pattern of Pd/SiO₂ nanostructure while Pd/SiO₂ molar ratio of 0.05 c) XRD pattern of Pd/SiO₂ nanostructure while Pd/SiO₂ molar ratio of 0.09.

3.3. Scanning Electron Microscopy (SEM)

The micrograph of Pd/SiO₂ nanocomposite has been investigated by SEM and corresponding results for Pd/SiO₂ = 0.02 molar ratio as a sample is shown in figure 3. Figure 3 shows the SEM images of the nano Pd/SiO₂ composite at different magnifications. The SEM observation clearly illustrates that the nano Pd/SiO₂ composite are formed by sol-gel method. Also it is to be noted that the nanocomposite varied in size from 4 – 10 nm which is in good agreement with that estimated by Debye-Scherrer formula from the XRD pattern.

Figure 3. SEM image of Pd/SiO₂ nanostructure

3.4. Particle Size Distribution

Figure 4 presents the histograms of particle size distribution obtained by the SEM and XRD analysis for

Pd/SiO₂ = 0.02 as a sample. The Pt particle sizes show a narrow range of distribution. The maximum range of the synthesized nano particles is about 4nm.

Figure 4. Particle size distribution of platinum over silica (Pd/SiO₂ = 0.02).

4. Conclusion

The current study describes the synthesis of pure phase Pd/SiO₂ nanocomposite in diameters in the range of about 4-10 nm by the sol-gel method and characterized by XRD, SEM, IR. In this study Palladium (II) nitrate was used as Palladium precursor. It is clear that, the final particle size could be controlled by changing the Pd/SiO₂ molar ratio.

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