Synthesis and characterization of the Pt/SiO₂ nanocomposite by the sol-gel method

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Abstract

The silica supported platinum nanoparticles was synthesized by using the sol-gel method. The possibility of using diamminedinitro platinum(II) as Pt precursor and effect of metal precursor concentration on the final Pt nanoparticle size was investigated. A stable silica sol was prepared via hydrolysis of tetraethyl ortho-silicate (TEOS) as a metal alchoxide and condensation reaction. Subsequently, diamminedinitro platinum (II) was added to sol to form the Pt/silica sol. After drying and calcination of the sol, the Pt/SiO2 nanocpmposite has been obtained. Crystallographic information and crystalline size of the synthesized Pt/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. Transmission Electron Microscopy (TEM) was employed in evaluating the distribution and size of the platinum nanoparticles in the silica.

1. Introduction

Metal catalysts could be supported by several inorganic supports, such as silica, alumina and zeolites to enhance their stability and high specific area [1]. In recent years much attention has been concentrated to metal nanocatalysts due to their novel characteristics and wide application in

numerous reactions [2-4]. In the nano scale, the control over the size of the particles and their activity and selectivity is accessible. Supported platinum catalysts are used in several heterogeneously catalysed reactions, such as oxidation, hydrogenation, reduction, as well as reforming in petroleum industry [5-8]. The structural characteristics of supported catalysts are affected by the preparation technique. By employing an appropriate method of preparation, a catalyst with the required parameters (e. g. stability, shape of the catalysts and selectivity) would be obtained [9, 10].

There are different synthesis methods for preparation of silica supported Pt nanoparticles, including impregnation [11], strong electrochemical adsorption (SEA) [12], sol-gel [13, 14] and microemulsion [10]. By using the sol-gel technique higher BET surface areas, good homogeneity, better particle distribution and control over the size of the particles could be achieved. On the other hand, because of the strong metal–support interactions, supported catalysts prepared by the sol–gel route usually show better thermal stability compared with those which have been produced by impregnation.

The introduction of guest phase in the sol during gelation allows the metal to have a direct interaction with silica matrix, and the structure and properties of resulting nanocomposite strongly depend on the interactions between the metallic precursor and the gel. To get basic knowledge about such a nanocomposite, an understanding of roles of the metal precursor is strongly required. The platinum sources which have been used thus far are platinum acetylacetonate; $[Pt(acac)_2]$ [15], hexachloroplatinic acid $[H_2PtCl_6]$ [13], platinum tetraammine chloride $[Pt(NH_3)_4Cl_2]$ [16] and platinum tetraammine hydroxide [14].

Eswaramoorthy *et al.* have reported a sol-gel method of preparing Pt/SiO$_2$ using Diamminedinitro platinum $[Pt(NH_3)_2(NO_2)_2]$ as a platinum precursor [17].

In this research work, we described a simple route for preparing platinum nanoparticles supported by silica using the sol-gel method. Diamminedinitro platinum(II); $[Pt(NH_3)_2(NO_2)_2]$ was used as Pt precursor and the effect of precursor concentration on the size of particles was investigated.

2 Experimental

2.1. Materials

Diamminedinitro platinum (II) purchased from Sigma-Aldrich Co was used as Pt 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. Synthesis of Pt/SiO$_2$ nanocomposite

Silica sol formation was based on the method proposed by Lee et al. [14]. This sol synthesized by hydrolyzing TEOS in a mixture of water, ammonia and ethanol. The molar ratio of components was 1: 0.1: 53.6: 40.7, 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 $[Pt(NH_3)_2(NO_2)_2]$ were added to the sol. In order to

study the effect of precursor concentration, three different Pt/SiO$_2$ molar ratio of 0.047, 0.095 and 0.149 were prepared. By adding Pt 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).

2.3. Characterization

FTIR spectra were obtained using a Unicam Galaxy Series FTIR 5000 spectrometer to characterize the bonding formation on the surface using a potassium bromide (KBr) pellet technique (Samples were prepared by diluting with KBr). The crystallographic information and particle size measurement were analyzed via a Philips X-ray diffractometer (XPERT model) using Cu Kα radiation (λ = 1.54 Å).

The micrography of Pt/SiO$_2$ nanocomposite has been investigated by scanning electron microscope (VEGAII, TESCAN) operating at 15 kV. Transmision electron microscopy (TEM) analysis was carried out using a Philips CM10 instrument operated at 100 kV.

3. Results and discussion

Figure 1 shows FTIR spectra of the synthesised pure silica and Pt/SiO$_2$ nanocomposite before calcination or dried samples and after calcination. As can be seen, the pure silica sample illustrated a broad band at 3433 cm^{-1} that correspond to hydrogen-bonded silanol groups with physically adsorbed water, whereas the Pt/SiO$_2$ nanocomposite gave two bands at 3433 cm^{-1} and 3284 cm^{-1}.

The absorption band at 3284 cm^{-1} indicates the interaction of silanol groups with amine groups of silanol groups with amine groups of the [Pt(NH$_3$)$_2$(NO$_2$)$_2$] precursor by hydrogen-bonding. This absorption band between amine group and silanol group is completely disappeared after heat treatment (Figure1).
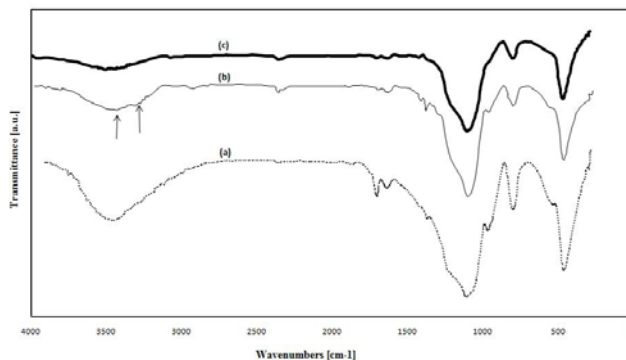

Fig. 1. FT IR spectra of: (a) synthesized silica, (b) Pt/SiO$_2$ nanocomposite before calcination and (c) after calcination.

The band at 1635 cm^{-1} is assigned to vibration of OH group attributable to environmental water; the intensity of this peak was decreased after calcination. The peak at 1099 cm^{-1} which corresponds to Si-O stretching band, shows the presence of silica in sample. This peak is observed at 1107 cm^{-1} for the amorphous silica. Si-O-Si signals are observed around 800 cm^{-1} and 460 cm^{-1}.
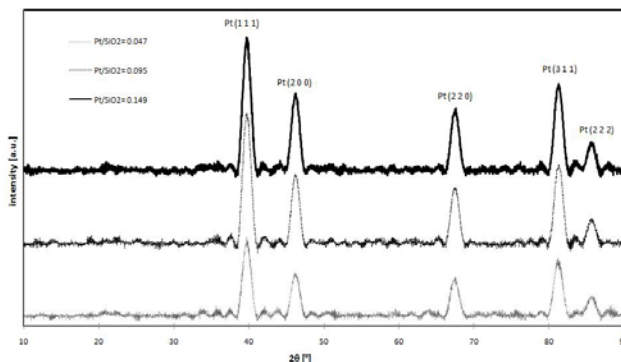
Fig. 2. XRD patterns of Pt/SiO$_2$ nanocomposite.

The XRD patterns are shown in figure 2. Successful reduction of the $[Pt(NH_3)_2(NO_2)_2]$ to Pt of the face centered cubic (fcc) phase was confirmed by diffraction peaks of Pt (111), Pt (200) and Pt (220) observed at 2θ of 39.7°, 46.2° and 67.6°, respectively.
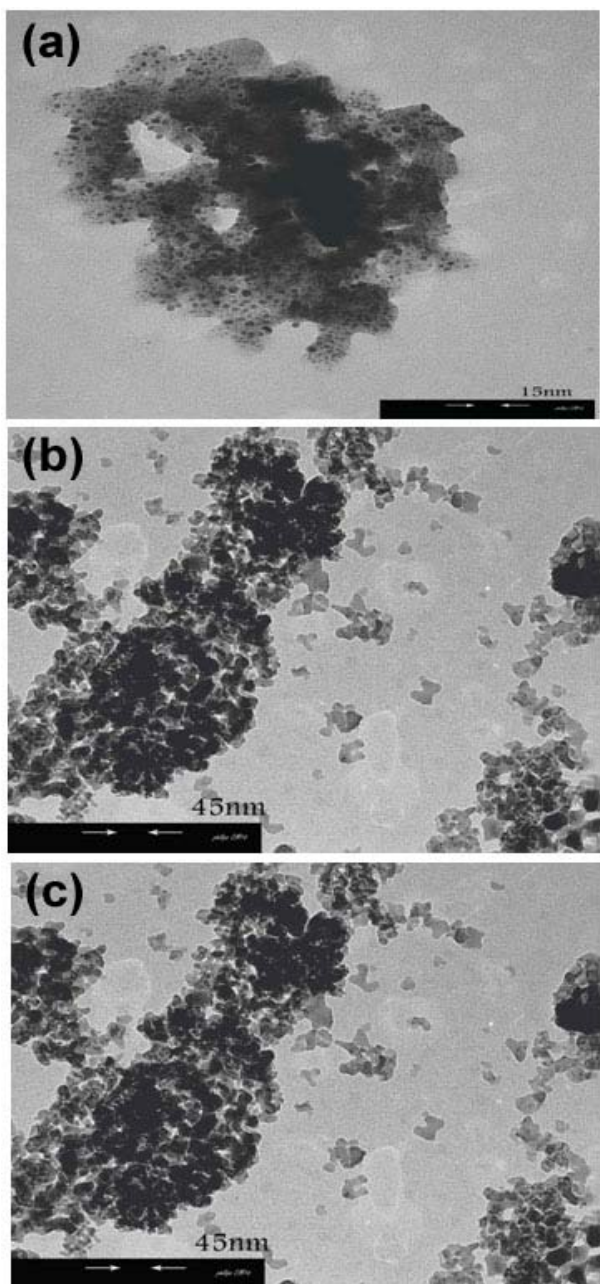
Fig. 3. Transmision electron micrograph of platinum nanoparticles dispersed on silica (a) Pt/SiO$_2$ = 0.047, (b) 0.095 and (c) 0.149.

Crystalline size of Pt was calculated by applying the Scherrer's equation from a full-width at half-maximum of the (111) reflection of Pt metal (2θ = 39.7°) as follows:

$$t = \frac{K\lambda}{\beta cos\theta} \qquad (1)$$

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 platinum nanoparticles and FWHM for each sample are reported in Table 1. As a result, while Pt/SiO$_2$ molar ratio increases from 0.047 to 0.149, crystalline size will increase from 8.9 nm to 17.98 nm.

**Table 1.** Crystalline size of the platinum nanoparticles dispersed on silica.

Pt/SiO$_2$ molar ratio	Peak Position (°2θ)	FWHM (°2θ)	D (nm)
0.047	39.74	0.94	8.9
0.095	39.71	0.76	11.01
0.149	39.76	0.47	17.98

Figure 3 shows TEM images of Pt/SiO$_2$ nanocomposite with different Pt loadings. In TEM images for all samples, darker spots of the platinum particles with diameters from 4 to 20 nm could be observed.

Figure 4 presents the histograms of particle size distribution obtained by the TEM analysis for Pt/SiO$_2$ = 0.047 as a sample. The Pt particle sizes show a narrow range of distribution.

The micrography of Pt/SiO$_2$ nanocomposite has been investigated by SEM and corresponding

results for Pt/SiO$_2$ = 0.149 molar ratio as a sample is shown in figure 5.
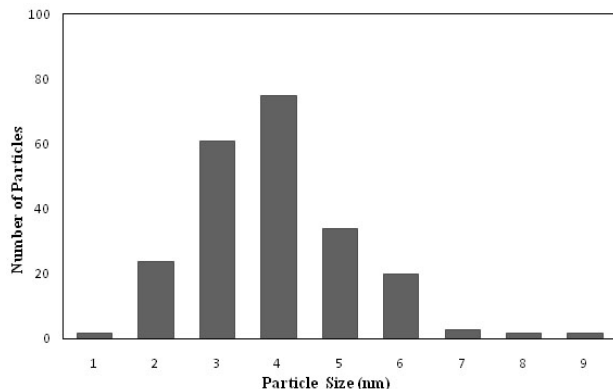
Fig. 4. Particle size distribution of platinum over silica (Pt/SiO$_2$ = 0.047).
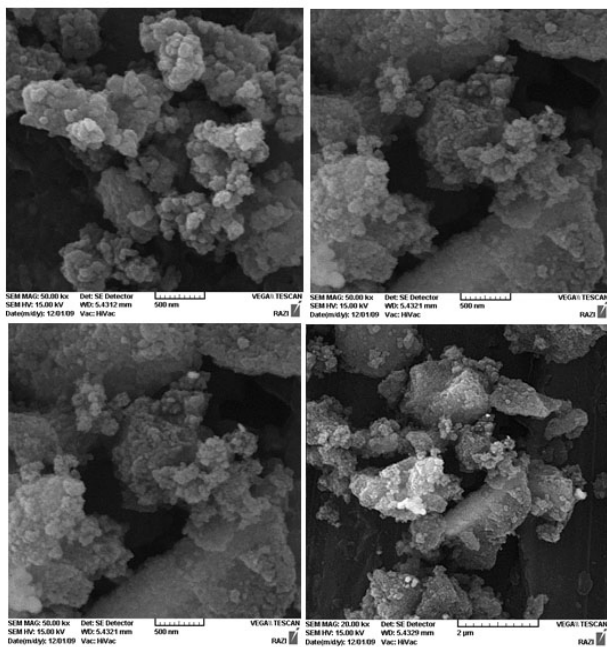
Fig. 5. SEM images of Pt/SiO$_2$ nanocomposite (Pt/SiO$_2$ = 0.149).

The pictures show a sponge-like material and very rough surface that seems to indicate the presence of very large pores in the matrix. The other SEM results showed that the Pt/SiO$_2$ molar ratio has not significant affect on the matrix microstructure.

4. Conclusion

In this study we used [Pt(NH$_3$)$_2$(NO$_2$)$_2$] as platinum precursor and a simple route to synthesis Pt/SiO$_2$ nanocomposite by the sol-gel method. Characterizations of the synthesised nanocmposite prove that diamminedinitro platinum (II) can be used as a good precursor to synthesis Pt/SiO$_2$ nanoparticles. It is verified that, the final particle size could be controlled by changing the Pt/SiO$_2$ molar ratio.

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