Chemical Engineering Journal 153 (2009) 206–210

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Preparation and catalytic properties of platinum dioxide nanoparticles: A comparison between conventional heating and microwave-assisted method

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ARTICLE INFO

Article history:
Received 13 March 2009
Received in revised form 31 May 2009
Accepted 5 June 2009

Keywords:
Platinum dioxide nanoparticle
Microwave irradiation
Conventional heating
Catalytic performance
Hydrogenation
Cyclohexene

ABSTRACT

Using platinum chloride, sodium hydroxide, sodium acetate, and polyvinylpyrrolidone as starting materials, platinum dioxide nanoparticles with small particle diameter and narrow distribution were prepared by microwave irradiation and conventional heating, respectively. UV–vis spectrophotometer was used to trace the hydrolytic decomposition of platinum chloride and the formation of platinum dioxide nanoparticles. X-ray powder diffraction and transmission electron microscopy were employed to characterize the crystalline structure and the morphologies of the obtained nanoparticles. Gas chromatography was performed to investigate their catalytic properties for hydrogenation of cyclohexene. The results revealed that (i) the obtained nanoparticles have the same crystalline structure; (ii) the nanoparticles obtained by microwave irradiation were smaller and more narrowly distributed than those obtained by conventional heating; (iii) the activation time of the catalyst markedly influences the catalytic activity; (iv) the particles obtained by microwave irradiation showed higher catalytic activity than those obtained by conventional heating for hydrogenation of cyclohexene.

1. Introduction

Platinum dioxide is an important catalyst used not only for production of hydrogen by splitting H_2O, but also for reduction of many organic substrates such as phenol and certain substituted phenols, certain pyridine derivatives, vanillin and salicyl aldehyde, aromatic nitro compounds, methyl ethyl ketone, and certain heterocyclic compounds [1–3]. With the advancement of nanoscience and nanotechnology, nanosized platinum dioxide is becoming increasingly interesting due to its unique properties which differ significantly from bulk material and several methods have been developed to synthesize nanosized platinum dioxide. Jin et al. [4] developed a fusion method originated by Adams and Shriner [1] to obtain needle-like α-PtO_2 nanoparticles with a diameter of about 6 nm and a length of about 50 nm. Reetz and Koch synthesized water-soluble colloidal platinum dioxide with an average diameter of 1.9 nm by hydrolysis/condensation of $PtCl_4$ or H_2PtCl_6 for several days in presence of carbo- or sulfobetaines [5]. He and co-workers prepared size-controlled platinum dioxide nanoparticles by conventional heating by tuning the mole ratio of the starting materials [6]. However, although nanosized platinum dioxide nanoparticles could be prepared by the mentioned methods, the preparation procedures were performed either time-wasting or at high temperature. Therefore, it is imperative to explore more practical approaches for preparation of platinum dioxide nanoparticles.

Microwave irradiation, as a fast, simple, uniform and energy-efficient heating method, has been used extensively in chemistry since 1986 [7,8]. In recent years, microwave-assisted synthesis has been used for rapid preparation of nanosized metal [9–13], metal oxide [14–16], and other kind materials [17–22] because small and homogeneous nanoparticles can be achieved. However, as we could ascertain, platinum dioxide nanoparticles synthesized by microwave-assisted method and influences of activation time on catalytic activity have not been reported to date. In this work, platinum dioxide nanoparticles were obtained by microwave-assisted method and conventional heating, respectively. The catalytic properties for hydrogenation of cyclohexene of the as-prepared nanoparticles were also investigated.

2. Experimental

2.1. Materials

The main starting materials were $H_2PtCl_6{\cdot}6H_2O$, polyvinylpyrrolidone (PVP, MW = 30,000), sodium hydroxide, sodium acetate, methanol and cyclohexene. Cyclohexene was of chemical grade

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doi:10.1016/j.cej.2009.06.009

purity and was purified according to the previous work [23] before use. The other reagents were of analytical grade purity and used without further purification.

2.2. Preparation of platinum dioxide

In a typical experiment, to obtain small and narrowly distributed nanoparticles, 4×10^{-5} mol H_2PtCl_6, 8×10^{-3} mol (as monomeric unit) PVP and 2.4×10^{-4} mol NaOH were dissolved in 21.0 ml distilled water in a 100-ml flask [6]. An aqueous solution of NaAc was added dropwise while vigorously stirring. For conventional heating, the solution was heated up rapidly to ebullition and kept on refluxing for a period of time. For microwave irradiation, the solution was heated by a modified domestic microwave oven (Galanz, 900W) with 50% output of the power. The microwave oven was modified as described as in Ref. [9]: a water-cooled condenser outside the oven's cavity was connected by a glass joint of a glass round-bottomed flask set inside. A Teflon stirrer was set in the flask and was driven by a motor.

2.3. Hydrogenation of cyclohexene in presence of different platinum dioxides catalysts

For the hydrogenation to be more efficient, the optimal activation time of the catalyst was determined using platinum dioxide obtained by microwave irradiation as a probe. Several samples were prepared by transferring 1.16×10^{-5} mol of the obtained PtO_2 and 10.0 ml methanol into each 30-ml flask. H_2 was used to replace the air in the flask repeatedly while stirring vigorously with a magnetic stirrer. Each sample was activated in a different period of time, during which the temperature was kept constant at 30 °C and the pressure at 0.1 MPa. After activation, 2.0×10^{-3} mol of the purified cyclohexene was injected into the flask rapidly. The activation time was considered to be optimal, at which the maximum conversion of cyclohexene to cyclohexane was reached in 30 min.

To investigate the catalytic properties of the two catalysts, two samples were prepared by transferring 1.16×10^{-5} mol of PtO_2 colloids prepared by microwave irradiation into one flask and the same mol of those prepared by conventional heating into another flask. Each sample was added 10.0 ml of methanol, followed by replacement of the air in the flasks. After the samples were activated for the optimal activation time, 2.0×10^{-3} mol of the purified cyclohexene was injected into each flask rapidly, with the temperature kept constant at 30 °C and the pressure at 0.1 MPa. Samples were transferred for gas chromatography at certain interval of reaction time.

2.4. Instruments and characterization

Ultraviolet–visible absorption spectra were measured with a UV-Lambda-35 spectrophotometer.

X-ray powder diffraction (Hitachi D MAX, R3) with Cu Kα radiation was used for the crystalline structure characterization of the obtained nanoparticles. Scherrer formula, $d = K \cdot \lambda / (B \cdot \cos\theta)$, was also applied to evaluate the particle diameter, in which K is 0.89, λ is 1.54056 Å, B is the half peak width, and θ is the diffraction angle.

Transmission electron microscopy (TEM) photographs were recorded on an FEI Tecnai G2 20 electron microscope. Samples for TEM measurements were prepared by placing a drop of the metal oxide colloidal dispersion on a copper grid. The average particle diameter was determined by measuring the diameters of 300 nanoparticles.

Gas chromatography was recorded on an Agilent 6890 chromatographic instrument (HP-5, 12 m × 0.22 mm). For the measurement, the following formula is given:

$$X_{(COE)} = \frac{C_{0(COE)} - C_{(COE)}}{C_{0(COE)}} \times 100\% \quad (1)$$

where $X_{(COE)}$ is the fractional conversion of cyclohexane, $C_{0(COE)}$ is the initial concentration of cyclohexene, and $C_{(COE)}$ is the reactant concentration.

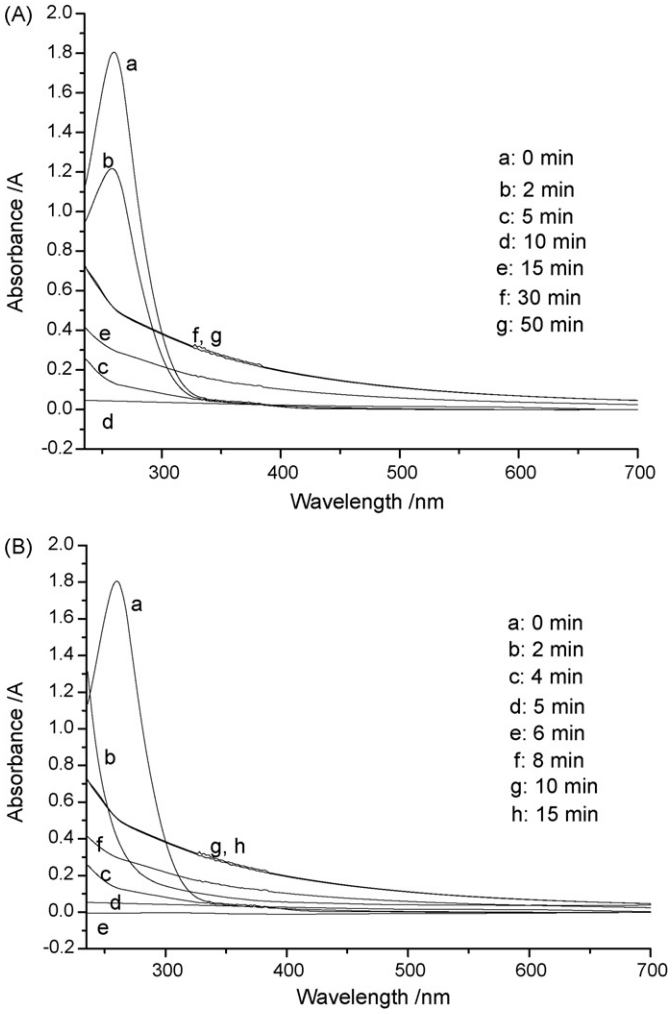

Fig. 1. UV–vis spectra of the colloids obtained by (A) conventional heating and (B) microwave irradiation.

3. Results and discussions

3.1. UV–vis spectra analysis of the hydrolytic decomposition of platinum chloride

The hydrolytic decomposition of platinum chloride and the formation of platinum dioxide nanoparticles were traced by using UV–vis spectra. As shown in Fig. 1A and B, the initial solution showed prominent absorbance at ~270 nm due to ligand to metal charge transfer transitions of Pt ions. With further heating, the absorption peak decreased distinctly till the weakest absorbance at 10 min for conventional heating and 6 min for microwave irradiation, respectively, suggesting that all the metal ions might have been hydrolyzed. Hereafter, the absorbance was observed enhancing because of the nucleation and growth of the platinum dioxide nanoparticles. When the reaction was carried out for about 30 min for conventional heating and 10 min for microwave irradiation, the absorbance nearly became constant, indicating that the formation

of platinum oxide nanoparticles could have completed (see curve f, g in Fig. 1A and curve g, h in Fig. 1B). It is evident that it took less time to synthesize nanosized platinum dioxide by microwave-assisted process in comparison with the conventional method.

3.2. XRD examination of the obtained platinum dioxide nanoparticles

The XRD patterns of the platinum dioxide nanoparticles obtained by both conventional heating and microwave irradiation are showed in Fig. 2. It reveals that both the particles have the same crystalline structure. The diffraction peaks of the particles matched well with the diffraction data from the JCPDS card. The peaks at 21.32, 33.44 and 39.85 corresponded to the (0 0 1), (1 0 0) and (0 1 1) planes of the platinum dioxide crystal [24], respectively. The particle diameters were calculated to be about 2.2 nm for those obtained by conventional heating and 1.8 nm for those by microwave irradiation based on (1 0 0) plane, respectively.

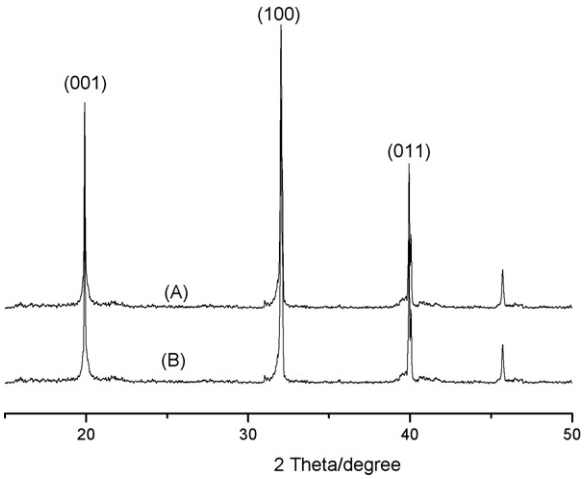

Fig. 2. XRD patterns of the platinum dioxide nanoparticles obtained by (A) conventional heating and (B) microwave irradiation.

3.3. TEM examination of the obtained platinum dioxide nanoparticles

Fig. 3 shows the TEM photographs and particle diameter distributions of the obtained platinum dioxide nanoparticles. As shown in Fig. 3, it was observed that both the obtained nanoparticles were spherical and the average particle diameter was calculated to be 2.10 nm for the particles obtained by conventional heating whereas when the reaction was carried out under microwave irradiation, the average diameter of the obtained nanoparticles was 1.68 nm. The result corresponds well with that calculated according to Scherrer formula. Moreover, the particles prepared under microwave irradiation were of narrower distribution than those prepared by conventional heating. It is well known that the formation of nanoparticles prepared by either conventional heating or microwave irradiation depends strongly on the heating condition [25]. Efficient and uniform heating would result in rapid and homogeneous nucleation and growth of nanoparticles. Hence the reasons

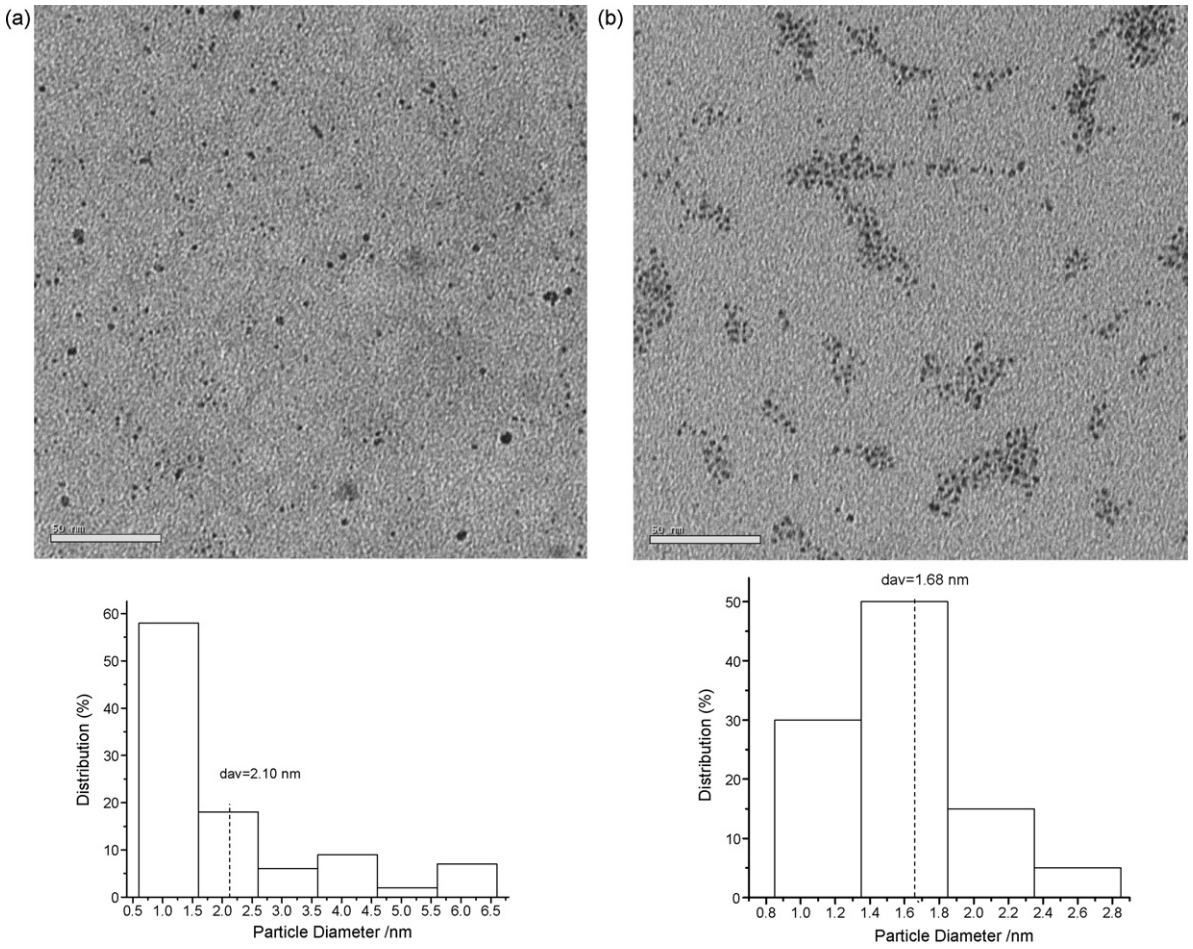

Fig. 3. TEM photographs and particle diameter distributions of the platinum dioxide nanoparticles obtained by (a) conventional heating and (b) microwave irradiation.

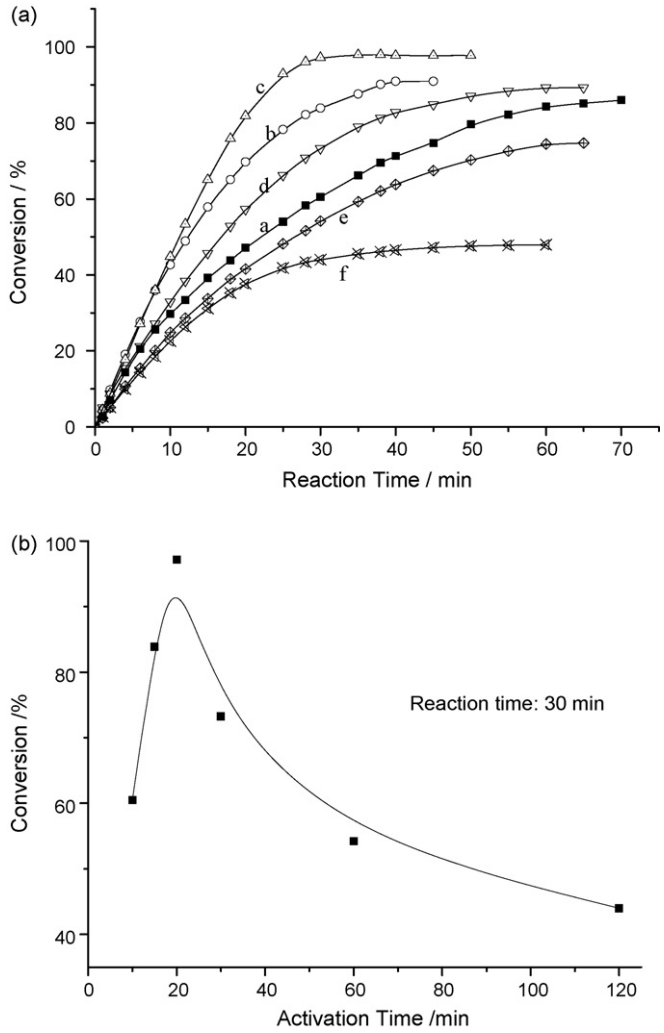

Fig. 4. (a) Influence of activation time on the conversion of cyclohexene in presence of catalyst obtained by microwave irradiation (a: 10; b: 15; c: 20; d: 30; e: 60; f: 120), and (b) variation of conversion to activation time after the reaction was carried out for 30 min.

why the particles prepared by microwave irradiation were smaller and more narrowly distributed than those obtained by conventional heating could be explained based on the time of nucleation and growth period. In general, the greater the speed of nucleation and growth is, the smaller the formed particles will be. It could be observed in Fig. 1 that the reaction was completed after about 30 min for conventional heating whereas under microwave irradiation, it just took only about 10 min. Within this limited time, nucleation, growth and protection by polymer have to be finished hence particles with smaller diameter and narrow distribution are obtained for microwave irradiation. However, for conventionally heating mode, time might be sufficient enough to separate the phases, which lead to the bigger particles and wider distribution.

3.4. Influence of activation time on the catalytic activity for hydrogenation of cyclohexene

To investigate the influence of activation time on the catalytic activity for hydrogenation of cyclohexene, colloidal platinum dioxide obtained by microwave irradiation was chosen as a probe. Fig. 4(a) shows the variation of conversion to reaction time after the catalyst was activated for different period of time. When the catalyst was activated for 10 min, the conversion of cyclohexene to

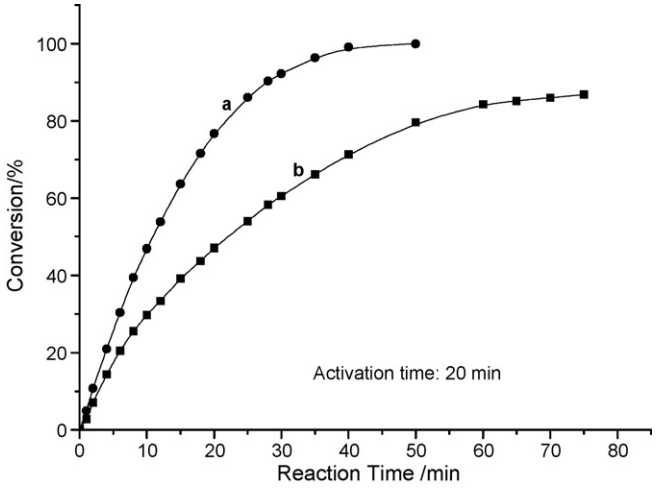

Fig. 5. Hydrogenation of cyclohexene in presence of catalysts obtained by (a) microwave irradiation and (b) conventional heating.

cyclohexane is about 64.5% with the reaction time of 30 min (see Fig. 4(b)). With further activation, the conversion increased initially then decreased after an activation time of 20 min when the reaction was carried out for the same time, indicating the catalytic performance was better when it was activated for 20 min. It is known that the hydrogenation occurs on the surface active sites of the catalyst. When the cyclohexene and hydrogen molecular was adsorbed onto the active sites, the hydrogen bond was broken and the π bond of cyclohexene was weakened, which facilitated the hydrogenation of cyclohexene. The reasons why the conversion increased initially and decreased after 20 min of activation time might be that when the catalyst is activated initially, the hydrogen molecular could be adsorbed onto the active sites of the catalyst, creating an environment of active $H^{\bullet}$. The longer the activation time is, the higher the concentration of $H^{\bullet}$ will be, which in turn facilitates the hydrogenation. However, the nanosized platinum dioxides could also be reduced to metallic platinum with further activation in hydrogen atmosphere [26]. Although metallic platinum also reveals catalytic activity [27,28], it possesses poorer activity for hydrogenation of cyclohexene than α-PtO_2 [26,29] hence supply of oxygen timely would make for the catalytic activity in the hydrogenation of cyclohexene [26]. The longer the activation time is, the more the metallic platinum could be obtained hence the poorer catalytic activity. Therefore, the activation is a competition caused by the adsorption of hydrogen so as to create an advantageous atmosphere for both hydrogenation of cyclohexene and reduction of platinum dioxide to metallic platinum. An optimal activation time would favor the hydrogenation.

3.5. Hydrogenation of cyclohexene in presence of different catalysts

Fig. 5 shows the hydrogenation of cyclohexene in presence of the obtained catalysts. As shown in Fig. 5, the platinum dioxide nanoparticles obtained by microwave irradiation showed higher catalytic activity than those obtained by conventional heating when both the two catalysts were activated for 20 min. It is well known that nanoparticles' properties such as catalytic, electronic, optical properties et al. depend strongly on the size of nanoparticles. Since the catalytic reaction rate is proportional to the surface coverage of nanoparticles, a smaller particle diameter would result in larger surface coverage and better adsorption behavior, which in turn leads to efficient catalysis. The TEM characterization results show that the average diameter of the nanoparticles obtained by microwave irra-

diation is about 1.68 nm and that of those obtained by conventional method is 2.10 nm, indicating the particles prepared by microwave irradiation possess larger surface coverage than those prepared by conventional method, which resulted in higher catalytic activity.

4. Conclusions

Platinum dioxide nanoparticles with different particle diameters and distributions were prepared by conventional heating and microwave irradiation method. The nanoparticles prepared by microwave irradiation were smaller in diameter and more narrowly distributed than those by conventional method. Compared with the conventional heating, microwave assisted method is more time-saving. Both the obtained platinum dioxide nanoparticles have the same crystalline structure. The activation time for the catalyst would influence the catalytic activity because of the reduction of the catalyst. The nanoparticles obtained by microwave assisted method showed greater catalytic activity for hydrogenation of cyclohexene than those obtained by conventional heating.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (Grant No. 20571022).

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