

Catalytic behavior of nanoparticle α -PtO₂ for ethanol oxidation

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Abstract

Fusion method is used to prepare α -PtO₂ and has a special needle-like microcrystalline morphology, with a diameter of ca. 6 nm and a length of ca. 50 nm. The two Pt–O bonds of α -PtO₂ are different in strength and α -PtO₂ decomposes thermally to Pt⁰ in two steps. α -PtO₂ is a p-type oxide semiconductor with a band-gap of 1.84 eV. α -PtO₂ is easily reduced by ethanol, its reduction product, Pt⁰, can directionally catalyze the oxidation of ethanol to acetic acid in the presence of air, while acetaldehyde, acetal and ethyl acetate are intermediates.

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1. Introduction

In the 1970s, Calvin [1], Kiwi and Gratzel [2] used PtO₂ as catalyst to study photocatalytic splitting of H₂O [3]. Recently, the behavior of PtO₂/TiO₂ in photocatalytic dehydrogenation reaction of alcohols was investigated by Ohtani et al. [4]. Vorontsov compared the catalytic ability of α -PtO₂ with Pt⁰ in CO oxidation reaction and found that the activity of α -PtO₂ in the dark is about 20 times higher than that of Pt⁰/TiO₂ under UV light illumination [5]. PtO₂ has two crystalline forms: α and β [6]. α -PtO₂, which can be prepared easily, is sometimes called Adam's catalyst [7]. PtO₂ can form on the surface of n-type semiconductors, CdS and TiO₂, through photoinduced reaction in H₂PtCl₆ aqueous solution [8,9]. Stabilized by carbo- or sulfo-betaines, water-soluble colloidal PtO₂ can also be obtained from the aqueous solution of

PtCl₄ in the presence of excess NaOH [10]. Although, α -PtO₂ was used as catalyst for different reactions, its structure and physicochemical properties have not been reported in detail yet. In our research, we found that α -PtO₂ has a special needle-like microcrystalline morphology. It is a p-type oxide semiconductor with a band gap of 1.84 eV. Its thermal stability is good but its chemical stability is poor (e.g. it is easily reduced by ethanol). The reduction product Pt⁰ of α -PtO₂ in aqueous ethanol, can catalyze the oxidation of C₂H₅OH directionally to produce CH₃COOH at room temperature, its mechanism is different from that of dark oxidation of CH₃OH on Pt/TiO₂ proposed by Thomas and co-workers [11].

2. Experimental

Fusion method is used to prepare α -PtO₂ by, 2 g H₂PtCl₆·6H₂O and 8 ml distilled water were added

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into a crucible, then 20 g NaNO₃ was added under stirring [7]. The paste-like mixture was dried at ca. 100 °C, then it was put into a temperature controllable muffle furnace, the temperature rising from room temperature to 400 °C was ca. 30 min, from 400 to 600 °C ca. 40 min and was kept at 600 °C for 1 h; after cooling, the melt was dissolved in distilled water and washed by decantation until it was free from Cl⁻, Na⁺ (monitored by AgNO₃ and UO₂ (COOCH₃)₂ solution spot tests, respectively), after being dried at ca. 100 °C for 8 h, a dark crown powder α-PtO₂ was obtained.

Transmission electron microscopy (TEM) of α-PtO₂ was taken in Boreskov Institute of Catalysis, Russia. X-ray diffraction (XRD) spectrum was obtained on a Rigaku D/Max-rB X-ray diffractometer. X-ray photoelectron spectroscopy analysis (XPS) was conducted on a PHI-550 Multitechnique spectrometer. O₂ (charge:mass ratio, $M = 32$) measurement was performed on a Finnigan Mat 700 ITD ion trap detector. Scanning tunneling spectroscopy (STS) was conducted on a Strues Scope Type 2400 STM apparatus. In order to obtain current versus voltage curve ($I-V$), the distance between tip and substrate should be held constant, with an initial bias of 1.0 V, a tunneling current of 0.1 nA, a scanning rate of 100 mV/S and a scanning range from -3.0 to +3.0 V [12,13]. UV-VIS diffuse reflectance spectrum (DRS) and thermo-gravimetric analysis (TGA) were taken on a Shimadzu UV-365 Spectrometer and a TGA 2950 apparatus of TA Instruments, respectively.

The procedure for two sets of dark reaction experiments were:

- (i) Under Ar atmosphere: 73.0 mg of α-PtO₂ and 16.7 ml of aqueous ethanol (25 vol.%) were added into a ground-glass stoppered flask, after bubbled with high purity Ar (99.999%) for 15 min, flask was closed.
- (ii) Under air: 72.4 mg of α-PtO₂ and 16.7 ml of aqueous ethanol (50 vol.%) were added into a ground-glass stoppered flask, shaken, then closed. The flask was opened for few minutes, every 3–4 days to supplement fresh air.

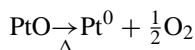
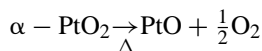
Nanoparticle α-PtO₂ suspended in aqueous ethanol. In the course of dark reaction, the suspensions were not stirred. After 20 days, the reaction liquids (with solid particles filtered out) were analyzed on SQ 208 gas chromatograph (Beijing factory of analytical

instruments) with a high performance capillary column (LZP-930, made by Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences). The chromatographic peaks of the products were calibrated by known compounds.

Anhydrous ethanol (99.5%), H₂PtCl₆·6H₂O and NaNO₃ were analytically pure reagents made in China.

3. Results and discussion

Fig. 1 gives the TEM image of α-PtO₂, its needle-like microcrystals are ca. 6 nm in diameter, ca. 50 nm in length. The XRD pattern shows that the diffraction peaks are broadened (Fig. 2a) and they belong to the hexagonal crystal system (a_0 3.10 Å, c_0 4.29–4.41 Å) but with poor crystallinity [6]. After 3 h treatment in N₂ at 350 °C, the pattern of α-PtO₂ is unchanged (Fig. 2b), which indicates that the bulk structure of α-PtO₂ is stable at $T \leq 350$ °C. The oxygen free basis elementary analysis indicated that α-PtO₂ contains almost 100 wt.% Pt, with trace Na and Cl. In the XPS spectrum the symmetry of Pt_{4f} peaks is good. The binding energies (E_b) of Pt_{4f} (7/2) and Pt_{4f} (5/2) equal to 74.5 and 77.8 eV, respectively, ($\Delta E_b = 3.3$ eV) which shows that the valence of surface Pt atoms on α-PtO₂ is +4 [14] (Fig. 3). Siegel et al. reported that two Pt–O bond lengths of β-PtO₂ (prepared under high O₂ pressure and high temperature) equal to 2.02 and 1.98 Å, respectively, [15]. In α-PtO₂ two different Pt–O bonds are also observed, which is demonstrated by TPD curve (Fig. 4), there are two oxygen evolving peaks at 600 and 685 °C, respectively. The thermal decomposition of α-PtO₂ proceeds in two steps:



In first step the solid state structure might change from hexagonal (α-PtO₂) to tetragonal (PtO) [6]. TGA result of α-PtO₂ indicate that the total weight loss equals 17.5%, after subtraction of the weight of desorbed water, it equals to ca. 14%, which is close to the theoretical value of O₂ contained in PtO₂ molecules (14.1%). So far as we know, the data of the energy

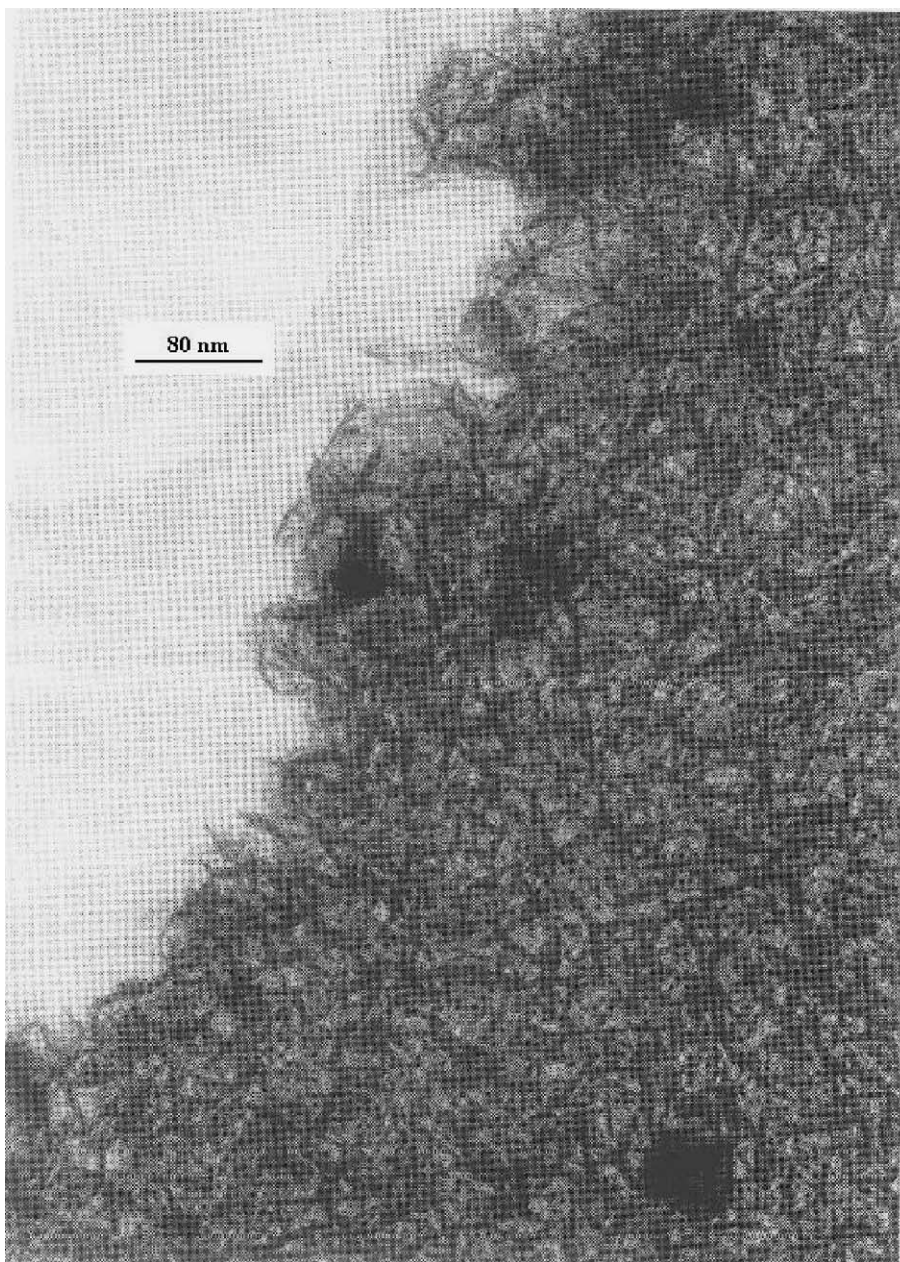


Fig. 1. TEM image of α -PtO₂ (150,000 \times).

band structure of α -PtO₂ have not been reported [16]. Fig. 5 gives the STS spectra of I - V and dI/dV - V of as-prepared α -PtO₂. The statistical average value of 14 α -PtO₂ particles shows that the E_g (surface band gap energy), V_{cb} (conduction band potential), V_{vb} (valence

band potential) are 1.84 eV, -1.35 , and $+0.49$ V, respectively. Its Fermi level (E_{FS}) is situated at the position of $V = 0$ near the edge of the valence band, which implies that α -PtO₂ is a p-type semiconductor. From the onset absorption wavelength ($\lambda_{onset} = 690$ nm), E_g

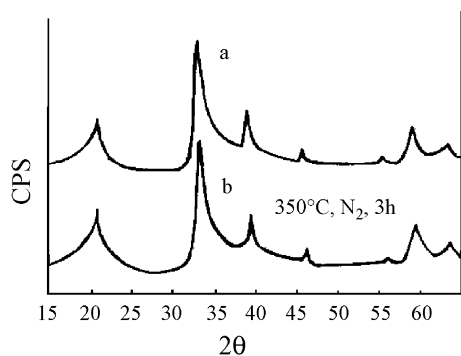


Fig. 2. XRD spectra of α -PtO₂: (a) as-prepared and (b) treated at 350 °C in N₂ flow for 3h.

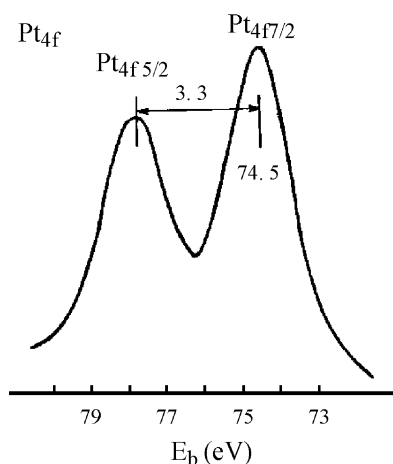


Fig. 3. XPS spectrum of as-prepared α -PtO₂.

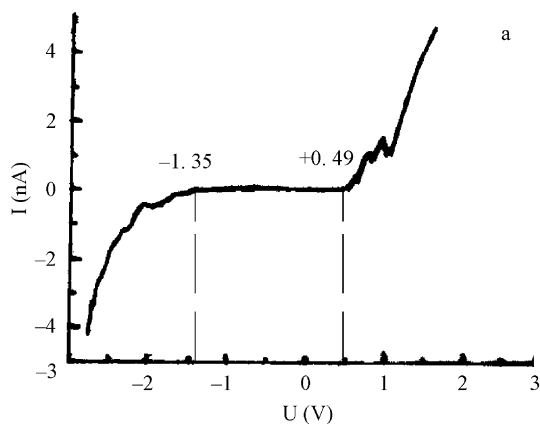


Fig. 5. STS spectra of α -PtO₂: (a) I - V and (b) dI/dV - V curve.

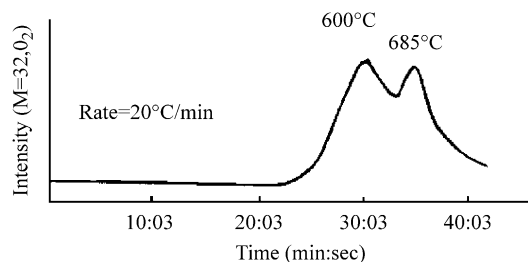
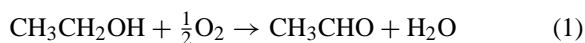


Fig. 4. TPD curve of α -PtO₂ ($M = 32$).

of α -PtO₂ is calculated to be 1.80 eV (Fig. 6), which is identical with that obtained by STS method.

Initially, we tried to utilize α -PtO₂ (a narrow band gap semiconductor) as a photocatalyst of water splitting and ethanol dehydrogenation aimed at the chemical conversion of solar energy, but it failed. Unexpectedly, we found that α -PtO₂ can be easily reduced to Pt⁰ by CH₃CH₂OH (Fig. 7, Pt_{4f} (7/2) = 70.8 eV), in other words, ethanol can be easily oxidized by α -PtO₂. What are the oxidation products of ethanol? Two sets of dark reaction experiments were carried out (Section 2). After 20 days, the reaction products were analyzed (Fig. 8b and c). It was found that there are only four kinds of products to be formed, i.e. acetaldehyde, acetic acid, acetal and ethyl acetate, the yields of which are 0.16, 0.05, 0.51, 0.10 mol%, respectively, (under Ar) and 1.7, 1.7, 2.9, 0.7 mol%, respectively, (under air).



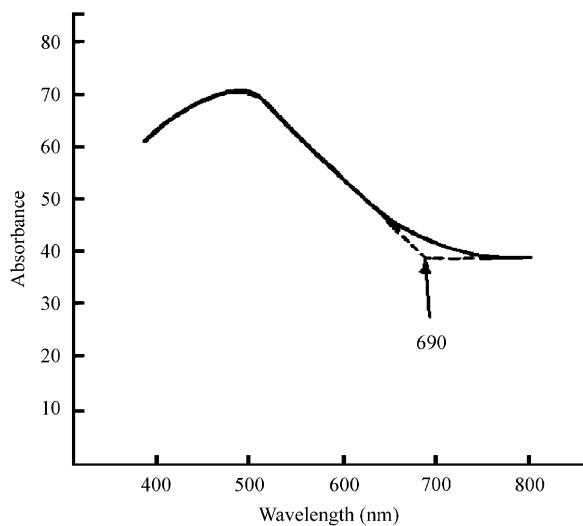


Fig. 6. DRS spectrum of α -PtO₂.

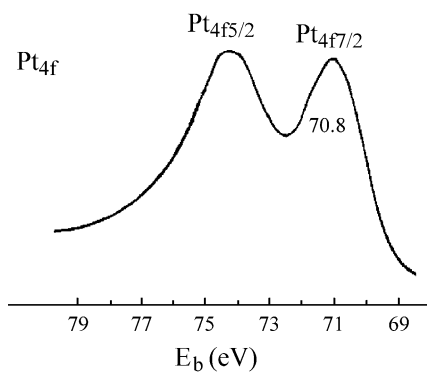
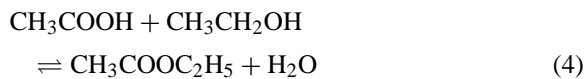
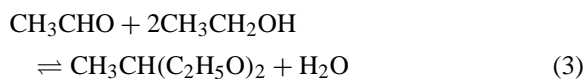
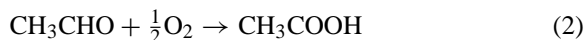


Fig. 7. XPS spectra of α -PtO₂ dispersed in aqueous ethanol (50 vol.%) for 24 h under air.

The results indicate that there are four types of reactions occurred:

Under Ar atmosphere, the O₂ consumed by reactions 1 to 4 came from the reduction of α -PtO₂. 73 mg of α -PtO₂ can provide 0.33 mmol O₂, which is basically in accordance with the amount of O₂ consumed (0.37 mmol). Under air, the total amount of O₂ consumed by reactions 1–4 equals 6.8 mmol, in which only 4.7% O₂ consumed can be obtained from α -PtO₂ and 95.3% of O₂ consumed is provided by air. The results hints that in the course of dark reaction, α -PtO₂

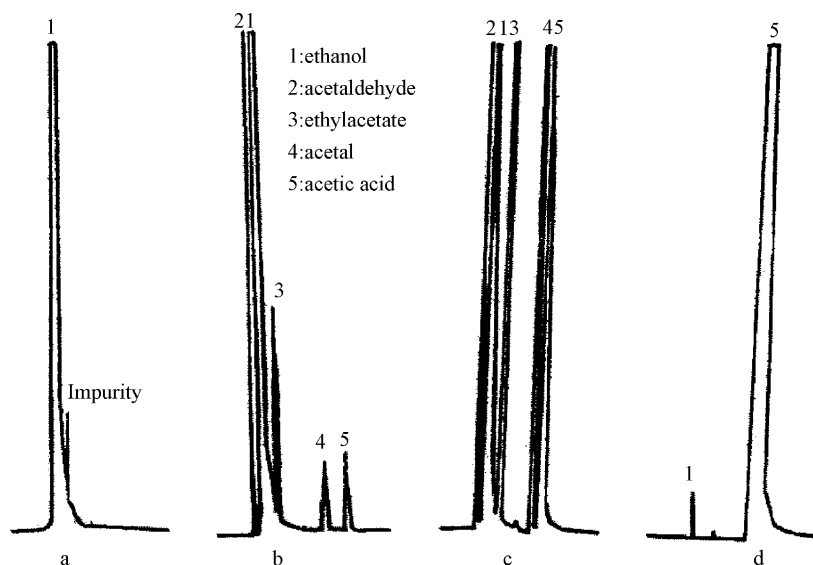


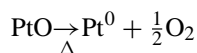
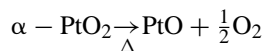
Fig. 8. Chromatogram maps: (a) 50 vol.% aqueous ethanol; (b) dark reaction for 20 days under Ar atmosphere; (c) dark reaction for 20 days under air and (d) dark reaction for ca. 1.5 years under air.

would first be reduced to Pt⁰ by ethanol under mild condition (Fig. 7), then the O₂ dissolved could dissociatively adsorb on the nascent Pt⁰ surface to form a special surface complexes and react with the adsorbed CH₃CH₂OH and CH₃CHO molecules in the similar way as occurred on PtO₂ surface (reaction 1 and 2) [17,18]. CH₃CHO is the initial catalytic oxidation product. CH₃COOH is the final catalytic oxidation product. The mole ratio of CH₃CHO:CH₃COOH equal 1:0.3 (under Ar atmosphere) and 1:1 (under air), respectively, which indicates that with the increase of CH₃CHO concentration, the production rate of CH₃COOH was increases in the presence of air. Acetal and ethyl acetate are the intermediates formed by the reversible reactions 3 and 4, which is verified by the following facts.

In above experiment under air, the sample flask was opened to air at a definite time interval for few minutes. After 1.5 years, C₂H₅OH was almost completely converted to CH₃COOH (Fig. 8d), while CH₃CHO disappeared, acetal and ethyl acetate existed as traces.

4. Conclusions

1. A p-type oxide (α -PtO₂) semiconductor with a E_g of 1.84 eV, has a special needle-like microcrystalline morphology, which is ca. 6 nm in diameter and ca. 50 nm in length.
2. Two Pt–O bonds of α -PtO₂ are different in strength and its thermal decomposition proceeds in two steps:



3. The reduction product Pt⁰ of α -PtO₂ can catalyze the oxidation reaction of ethanol directionally to form CH₃COOH. CH₃CHO is the initial catalytic oxidation product, acetal and ethyl acetate are the intermediate products of reversible reactions

CH₃CHO with C₂H₅OH and CH₃COOH with C₂H₅OH, respectively.

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