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Article

Heterogeneous interfacial engineering of Pd/TiO₂ with controllable carbon content for improved direct synthesis efficiency of H₂O₂

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ABSTRACT

Series of heterogeneous interfacial engineered TiO₂ (C-TiO₂) with controllable carbon content were facilely synthesized by incipient-wet impregnation using glucose and subsequent thermal carbonization. The obtained C-TiO₂ were used as catalytic supports to load Pd nanoparticles for H₂O₂ direct synthesis from H₂ and O₂. The as-prepared samples were systematically studied by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), air isothermal microcalorimeter, temperature-programmed reduction of H₂ (H₂-TPR), and so on. The catalytic results showed that H₂O₂ productivity and H₂O₂ selectivity of Pd/C-TiO₂ firstly rose with increasing carbon content and then declined. Pd/C-TiO₂ catalyst with 1.89 wt% of carbon content showed the best catalytic performance that had 61.2% of selectivity and 2192 mmol H₂O₂/g_{Pd}/h of productivity, which were significantly better than those of pristine Pd/TiO₂ (45.2% and 1827 mmol H₂O₂/g_{Pd}/h). Various characterization results displayed that the carbon species were heterogeneously dispersed on TiO₂ surface. Moreover, no obvious geometric transformation in supports and Pd nanoparticles were observed among different catalysts. The superficial hydrophobicity of Pd/C-TiO₂ was gradually promoted with increasing carbon content, which led to the corresponding decrease in adsorption energy of H₂O₂ with catalysts. According to structure-performance relationship analyses, the heterogeneous interfacial engineering of carbon could maintain the interaction of Pd nanoparticles with TiO₂ and simultaneously accelerate the H₂O₂ desorption. Both factors further determined the excellent H₂O₂ direct synthesis performance of Pd/C-TiO₂.

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1. Introduction

Hydrogen peroxide (H₂O₂) is one of the most typical green oxidants, which has been widely applied in the fields of textile,

cosmetics, medical/dental, wastewater treatment, military and aerospace [1–5]. Nowadays, H₂O₂ is generally produced by a consecutive hydrogenation and oxidation of anthraquinone [4,6]. Driven by environmental limitation, several clean ap-

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proaches have been developed to be candidates for replacing the anthraquinone process [7]. Among them, direct synthesis of H_2O_2 from hydrogen and oxygen is conceptually the most straightforward and therefore most attractive process [4]. However, H_2O_2 is an unstable intermediate of hydrogen-oxygen reaction, where H_2O is the thermodynamically preferred product [8–10]. To date, achieving both high conversion and selectivity of H_2O_2 has been the most major target for H_2O_2 direct synthesis.

In the past decades, considerable efforts were devoted to improving the utilization of H_2 and O_2 of H_2O_2 direct synthesis. Preliminarily, the reaction conditions were optimized, including reaction temperature, H_2/O_2 ratio, solvent species, incorporation of liquid acids or halogens, and so on [2,6,7,11]. In comparison, most attentions were focused on the design of novel catalyst. The related researches could be divided into two main categories, construction of new active site and exploration of suitable catalytic support. Up to now, some noble metals, e.g. Pd, Au, Pt, etc., were confirmed to have the catalytic activity of H_2O_2 direct synthesis [12]. In recent years, composition of two or more metals to be an alloy could integrate the advantages of various metals, which effectively inhibited H_2O_2 decomposition or further hydrogenation [3,13–16]. Moreover, some metal oxides or ligands were incorporated to be the promoters, which could shield active sites or increase activation energy of the side reaction of H_2O_2 [17–19]. On the other hand, numerous materials e.g. activated carbon, TiO_2 , SiO_2 , etc., are chosen to be the candidate for industrial support of H_2O_2 direct synthesis [9,20–23]. Further, the surface composition of support was precisely regulated to influence active sites or remove some groups for decreasing H_2O_2 side reaction rate [24–27]. These approaches could make significant progress in H_2O_2 direct synthesis performance of catalysts. However, it still requires continuous development for industrial application of H_2O_2 direct synthesis.

Actually, these approaches mentioned above were mainly focused on the structural adjustment in active sites of catalysts to inhibit the side reactions. This strategy has been demonstrated to be effective in numerous researches. However, note that active site adjustment sometimes may have a negative effect on the formation of H_2O_2 , which is adverse to the reaction conversion of H_2 and O_2 [25]. According to the reaction network of H_2 and O_2 , the H_2O_2 formation has a cascade relationship with two side reactions of H_2O_2 decomposition and H_2O_2 hydrogenation. Provided that the intermediate H_2O_2 was rapidly transferred away from catalyst by some method, two side reactions would be inhibited due to the shortage of reactants. This strategy could achieve the same effect of limiting side reaction to those mentioned above, whose feasibility has been demonstrated by our previous works. Density functional theory (DFT) calculation results showed that the easy desorption of H_2O_2 from Au-Pd surface was responsible for high selectivity of H_2O_2 direct synthesis [28,29]. Moreover, the adsorption strength of H_2O_2 with catalysts could be decreased by altering the crystal or elemental composition of TiO_2 surface [30,31]. Different from active site adjustment, the approach of accelerating H_2O_2 desorption theoretically could not interfere with the

previous hydrogen-oxygen reaction. That is to say, the strategy of improved H_2O_2 desorption could potentially accomplish both excellent selectivity and conversion of catalyst for H_2O_2 direct synthesis.

As mentioned above, it is necessary to meet both requirements of enhanced H_2O_2 desorption and no negative effect on active sites in the practical catalyst design for H_2O_2 direct synthesis. In detail, the heterogeneous characteristic of support surface is considered to be very crucial for combined consideration to two above factors. In our previous works, this strategy has been successfully applied to improve the hydrosulfurization performance of TiO_2 -supported catalyst and water tolerance of solid superacid [32,33]. Herein, the present work reports a heterogeneous interfacial engineering of carbon using glucose as carbon source for H_2O_2 direct synthesis. This is a facile approach and a quantitative relation of carbon amount with glucose usage is established, which could controllably regulate the carbon content of catalyst. A typical Pd/ TiO_2 is chosen as the research object. Heterogeneously dispersed carbon species could accelerate the H_2O_2 desorption and simultaneously maintain the synergetic effect between Pd nanoparticles and TiO_2 . The obtained Pd catalyst shows an enhanced H_2O_2 selectivity and a constant H_2 conversion.

2. Experimental

2.1. Materials and synthesis

The heterogeneous interfacial engineering of carbon over TiO_2 (C- TiO_2) was carried out by a combination of incipient-wetness impregnation and high-temperature carbonization. Briefly, 2 g of TiO_2 (P25, Degussa) was immersed in an aqueous solution containing specified glucose amount. After stirring evenly, mixed powder was then placed in an oven at 110 °C. Carbonization of samples was performed at 500 °C in pure N_2 atmosphere (40 mL/min) for 2 h. The obtained sample was entitled as C- TiO_2 -x, where “x” was the mass ratio of glucose to TiO_2 .

The corresponding Pd catalyst was prepared by incipient-wetness impregnation. PdCl_2 was selected as the Pd precursor, and the Pd content of catalyst was 3 wt%. In detail, a certain amount of PdCl_2 was preliminarily dissolved into hydrochloric acid (36%–38%). Then, the obtained solution was added into C- TiO_2 powder. Continuous stir accompanied with heating was performed until the formation of paste. The impregnated sample was transformed to the oven and dried at 110 °C for 12 h. After being reducing at 300 °C in H_2 flow (40 mL/min) for 1 h, the final catalyst was achieved and entitled as Pd/C- TiO_2 -x.

2.2. Characterization

X-ray diffraction (XRD) spectrum was collected by the Bruker D/8 Advance X-ray diffractometer. The operating voltage of $\text{Cu K}\alpha$ radiation was 40 kV and its electric current was controlled at 100 mA. The structural information of carbon species was provided by Horiba HR800 Raman spectrometer

and the wavenumber of Ar⁺ laser was 514.5 nm. Surface area, pore volume and pore size of supports were determined by the TriStarII 3020M system (Micromeritics) at −196 °C. The nanoscale information analyses of catalysts were performed by transmission electron microscopy (JEOL JEM-2100). Axis AXIS Ultra DLD with the light source of Al K_α X-rays was used to provide the X-ray photoelectron spectroscopy (XPS) spectra of samples, which could obtain the superficial information of catalysts. The interaction between H₂O₂ and supports was measured at 10 °C by TAM air isothermal microcalorimeter. The hydrophobicity of various samples was studied using a JC2000D1 contact angle analyzing instrument at ambient temperature. Before the test, each sample needed to be ground and then dried at 100 °C for 2 h. The dried powders were pressed into a smooth sheet (~30 MPa), which was finally used for the test of water contact angle. Temperature-programmed reduction (TPR) experiments were conducted on TP-5000 equipment. The sample was preliminarily pretreated at 300 °C in pure He for 0.5 h. Then, the test temperature was increased at a rate of 10 °C/min. The gas mixture of 10% H₂/N₂ with a flowing rate of 30 mL/min was introduced into the quartz reactor and that was also used as a reference gas. Temperature-programmed desorption (TPD) using different probe gas molecules were carried out on a Quantachrome ChemBET to analyze the corresponding adsorption properties of catalysts. For O₂-TPD experiments, the sample was pretreated in He at 300 °C for 2 h (60 mL/min) and then cooled down to 40 °C. Then, adsorbents of 5% O₂/He (60 mL/min, 3 h) were introduced into the system. After purging of the system with He for 1 h (20 mL/min), the temperature was ramped from 40 to 800 °C at a rate of 10 °C/min with the pure He gas flowing at a rate of 20 mL/min. The off-gas signal at this stage was recorded by TCD detection. Furthermore, the process of H₂-TPD experiment is in accordance with that of O₂-TPD. The only difference between them is the probe gas molecule. CO-diffuse reflectance infrared Fourier transformed spectroscopy (CO-DRIFTS) was carried out on a Thermo Electron Nicolet-360 spectroscopy apparatus equipped with a diffuse reflectance accessory and a MCT detector. The catalyst was pretreated in pure He at 300 °C

for 0.5 h, and then cooled down to room temperature. CO was introduced into the chamber at 30 °C for 0.5 h and excessive gaseous CO was removed by He purge. Also, the spectra were recorded after 32 scans with a resolution of 4 cm^{−1}.

2.3. Catalytic performance evaluation

The direct synthesis reaction of H₂O₂ from H₂ and O₂ was carried out in a 100 mL of triphase reactor at 10 °C under atmospheric pressure. The mixed gas (H₂:O₂:N₂ volume ratio: 9:36:15) with a flowing rate of 60 mL/min was introduced into the reactor. In a typical run, 50 mg of catalyst was dispersed in ethanol/H₂SO₄ mixed liquid (60 mL of ethanol and 0.38 mL of H₂SO₄), which was vigorously stirred with a speed of 1000 rpm to minimize mass transfer limitations. H₂ conversion of various catalysts was determined by external standard method through online SP-6890 gas chromatograph equipped with thermal conductivity detector and TDX-01 column. A TiOSO₄/H₂SO₄ reagent was used to complex with H₂O₂ produced in reaction liquid. The H₂O₂ concentration was analyzed by the colorimetric method using UV-vis spectrophotometer. The selectivity of H₂O₂ (*S*_{H₂O₂}) could be calculated by following formula [34,35]:

$$S_{H_2O_2} = \frac{\text{Rate of } H_2O_2 \text{ formation (mole/min)}}{\text{Rate of } H_2 \text{ conversion (mole/min)}}$$

Moreover, the hydrogenation of H₂O₂ and H₂O₂ decomposition were also studied in triphase reactor at 10 °C under atmospheric pressure. The initial H₂O₂ concentration of solution was 0.5 wt%. Two above reactions were proceeding in flowing gas of H₂/N₂ (9 mL/min / 51 mL/min) and pure N₂ (60 mL/min), respectively. Analysis of H₂O₂ concentration was identical to the process mentioned above.

3. Results and discussion

3.1. Structural properties

The content of carbon species on TiO₂ is confirmed by TG tests and the corresponding results are shown in Fig. 1. Each sample experiences two obvious stages of weight loss. The first

Fig. 1. TG curves (A) and fitting result (B) of various C-TiO₂.

Fig. 2. N₂ adsorption-desorption isotherms of various C-TiO₂.

stage (room temperature ~ 300 °C) is mainly ascribed to the removal of physically adsorbed water and strong-bonding water or hydroxyls on C-TiO₂. The second one at above 300 °C is attributed to the decomposition of carbon species [36]. Through quantitative calculation of weight loss at the second stage, the resulting carbon contents in C-TiO₂-0.15, C-TiO₂-0.45, C-TiO₂-0.75 and C-TiO₂-1.05 are 0.23 wt%, 1.89 wt%, 3.20 wt% and 4.85 wt%, respectively. The mass ratio of glucose to TiO₂ displays a linear relationship with the carbon content, whose fitting equation is shown in inset of Fig. 1(B). Accordingly, it could carry out the controllable synthesis of C-TiO₂ with specified carbon content.

Fig. 2 shows the isotherms of various C-TiO₂ and TiO₂. All the samples exhibit a kind of type IV with a H₃ hysteresis loop, suggesting the presence of typical mesoporous structure [37,38]. As listed in Table 1, carbon interfacial engineered TiO₂ have surface areas of 49.9–56.4 m²/g, pore volumes of 0.29–0.33 cm³/g and average pore sizes of 17.0–22.7 nm. There is no evident trend in structural transformation among these C-TiO₂. Moreover, all the C-TiO₂ have similar porous data to those of the pristine TiO₂.

The crystal structure of TiO₂ and other species was analyzed by XRD. As shown in Fig. S1, diffraction peaks at $2\theta = 25.3^\circ$, 37.8° , 48.0° , 53.9° and 55.1° , which are assigned to anatase phase TiO₂ [39]. Moreover, the diffraction peaks ascribed to rutile phase TiO₂ are appeared at $2\theta = 27.4^\circ$, 36.1° and 41.2° [39]. Series of Pd/C-TiO₂ exhibit same diffraction peaks to that

Table 1
Structural data of various samples.

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)	Crystal particle size ^a (nm)	I _D /I _G
C-TiO ₂ -1.05	56.4	0.26	18.3	19.4, 29.8	1.00
C-TiO ₂ -0.75	54.6	0.30	20.6	20.0, 29.4	0.94
C-TiO ₂ -0.45	49.9	0.33	22.7	19.2, 29.5	0.94
C-TiO ₂ -0.15	52.4	0.29	17.0	19.8, 29.5	0.97
TiO ₂	52.3	0.35	26.7	19.7, 29.4	—

^a Crystallite sizes of anatase and rutile were calculated by Scherrer equation according to the half-peak width of peak at 25.3° and 27.4° , respectively.

of the pristine Pd/TiO₂, suggesting the identical crystal phase of TiO₂ in C-TiO₂. Furthermore, Table 1 displays that all Pd/C-TiO₂ catalysts have almost the similar crystal particle sizes to that of TiO₂. This demonstrates the interfacial engineering of carbon does not influence the crystal structure of catalytic support, which is accordance with that of BET analysis results.

Furthermore, it is difficult to observe the diffraction peaks assigned to Pd nanoparticles and carbon species. No obvious signal of Pd nanoparticles might be mainly due to low Pd loading under XRD detection limits or their good dispersions [22,31]. As for carbon species, no diffraction peak could be attributed to the amorphous state of carbon species or relatively weak intensity of corresponding peaks [40]. By contrast, the structural information of carbon species could be more clearly provided by Raman spectra [41].

As displayed in Fig. 3, Raman bands at 1350 cm⁻¹ (D band) and 1600 cm⁻¹ (G band) represent the amorphous and graphitic carbon in Pd/C-TiO₂, respectively [42,43]. The intensities of both D band and G band of Pd/C-TiO₂ are heightened as their carbon content increases. The ratio values in two band intensity (I_D/I_G) of Pd/C-TiO₂ are calculated and corresponding results are listed in Table 1. I_D/I_G value is nearly equal to 1, suggesting the equivalent content of amorphous and graphitic carbon. Moreover, similar I_D/I_G values demonstrate the same composition of carbon species in these Pd/C-TiO₂ catalysts even though they have different carbon contents [44].

The nanoscale structure of various Pd catalysts was characterized by TEM. As shown in Fig. S2(A–D), all Pd/C-TiO₂ catalysts and Pd/TiO₂ are uniformly consisted of spherical particles with dozens of nanometers. No remarkably morphological differences are observed among them. Moreover, each catalyst contains numerous well-dispersed dark spots. One dark spot in Pd/C-TiO₂-3 is randomly selected to be analyzed in high resolution. As displayed in Fig. S2(E), the lattice fringe of $d = 0.23$ nm ascribed to Pd (111) plane is clearly visible [31]. That is to say, dark spots in various catalysts are confirmed to be the Pd nanoparticles. The particle sizes of Pd nanoparticles are statistically analyzed and the results are located in corresponding insets. The most probable particle sizes of Pd/C-TiO₂-0.15, Pd/C-TiO₂-0.45, Pd/C-TiO₂-0.75 and Pd/TiO₂ catalysts are 2.4, 2.3, 2.4, and 2.5 nm, respectively. According to their particle

Fig. 3. Raman spectra of catalysts. (a) Pd/TiO₂; (b) Pd/C-TiO₂-0.15; (c) Pd/C-TiO₂-0.45; (d) Pd/C-TiO₂-0.75; (e) Pd/C-TiO₂-1.05.

Fig. 4. (A) XPS spectra of catalysts. (a) Pd/TiO₂; (b) Pd/C-TiO₂-0.15; (c) Pd/C-TiO₂-0.45; (d) Pd/C-TiO₂-0.75; (e) Pd/C-TiO₂-1.05. (B) The atomic percentage of Pd⁰ and Pd²⁺.

size, their corresponding Pd dispersions are calculated based on hemisphere model [35]. As displayed in Table S1, all the catalysts have the Pd dispersion of 43.7%–48.5%. These results indicate that interfacial engineering of carbon does not significantly influence, at most slightly improve, the dispersion state of Pd nanoparticles.

Besides Pd nanoparticles information, Fig. S2(E) also shows a lattice fringe of $d = 0.35$ nm, which corresponds to d_{101} of anatase phase TiO₂. By contrast, there is no observation of lattice fringes ascribed to carbon species in visual field. This may be attributed to the weak crystallite of carbon species. Additionally, the relative less content may be another factor for invisibility of carbon species in Pd/C-TiO₂. The content of carbon species in present work indeed could not completely coat such high surface area of TiO₂. In our previous work [32,41,43], the C-TiO₂ has been confirmed to possess a certain proportion of TiO₂ surface exposure when the carbon amount per surface area was 0.004–0.147 wt%/nm². The corresponding values of C-TiO₂ in present work are 0.005–0.114 wt%/nm², which demonstrates the existence of exposed TiO₂ surface. Simultaneously, several TiO₂ lattice fringe in version field of Fig. S2(E) also illustrates the exposure of TiO₂ surface. Therefore, the present surface modification over TiO₂ is a technique of heterogeneous interfacial engineering of carbon.

The chemical valence of Pd nanoparticles is one of the important factors for influencing catalytic performance of H₂O₂ direct synthesis [45]. XPS spectra of Pd 3d for various catalysts are exhibited in Fig. 4. Each XPS spectrum could be resolved into two pairs of peaks. One pair at 341.8 and 336.3 eV is assigned to Pd²⁺ 3d_{3/2} and Pd²⁺ 3d_{5/2}, respectively. Another pair at 340.3 and 334.9 eV is ascribed to metallic Pd⁰ 3d_{5/2} and Pd⁰ 3d_{3/2}, respectively [38,46]. The atomic percentage of Pd⁰ and Pd²⁺ could be calculated quantitatively according to fitting peak area. As seen in Fig. 4(B), there are 53.8 ± 0.8% of Pd⁰ existed in Pd/C-TiO₂-0.15, Pd/C-TiO₂-0.45 and Pd/TiO₂. This tiny difference in metallic Pd percentage suggests the similar chemical valence of Pd nanoparticles in these three catalysts. CO-DRIFT spectra (Fig. S3) shows that the bands at about 2115 and 2170 cm⁻¹ are assigned to the linear adsorption of CO onto oxidic Pd^{δ+}, and the band at 2060 cm⁻¹ is ascribed to the linear adsorption of CO onto metallic Pd⁰ [45,47]. The similar CO-DRIFT

spectra of Pd/C-TiO₂-0.45 and Pd/TiO₂ demonstrate the similar chemical valence of Pd nanoparticles, which is in accordance with XPS analysis results. However, the Pd/C-TiO₂-0.75 catalyst possesses 44.5% of Pd⁰, which is obviously lower compared with other three catalysts. Similar observations are appeared in the Pd catalysts using carbon species-TiO₂ composite as the catalytic support. They almost attributed the high Pd²⁺ content to the improvement of carbon species on electron transfer from Pd to support [48,49]. Apparently, the heterogeneous interfacial engineering does not influence chemical valence of Pd nanoparticles when carbon content is below 1.89 wt%. Excessive carbon species could instead decrease the metallic Pd content of Pd/C-TiO₂ catalyst.

3.2. Catalytic performance

The direct synthesis of H₂O₂ from H₂ and O₂ was carried out at 10 °C under atmospheric pressure to comparatively study the catalytic performance of various Pd/C-TiO₂ and Pd/TiO₂. Fig. 5 displays the H₂ conversion, H₂O₂ selectivity and H₂O₂ productivity of catalysts. For Pd/TiO₂, the H₂O₂ productivity is 1825 mmol/g_{Pd}/h, the H₂O₂ selectivity and H₂ conversion are 45.2% and 25.02%, respectively, which is similar to the refer-

Fig. 5. H₂ conversion and H₂O₂ selectivity, H₂O₂ productivity of catalysts.

enced result (1857 mmol/g_{pd}/h) [35]. As expected, the heterogeneous interfacial engineering of carbon over TiO₂ could exert a significant influence on catalytic performance of Pd/C-TiO₂. The H₂O₂ selectivity of Pd/C-TiO₂ could increase to 61.2%, and meanwhile their H₂ conversions negligibly change when the carbon content is below 1.89 wt%. As exceeding 1.89 wt% of carbon content, the H₂O₂ selectivity of corresponding catalyst declines gradually whereas its H₂ conversion shows a very slight increase. To sum up, C-TiO₂-0.45 (1.89 wt% of carbon content) supported Pd catalyst has the optimal performance of H₂O₂ direct synthesis, which has a H₂O₂ productivity of 2192 mmol/g_{pd}/h. Noteworthy is that the catalytic performance of a series of Pd/C-TiO₂ catalysts (Table 2) in present work could be comparable to other catalysts reported in literatures. Moreover, the carbon interfacial engineered Pd catalyst could be structurally stable after five times of reaction. As shown in Fig. S4, there is no observable difference in crystal phase between catalysts before and after reaction. TEM (Fig. S5) and XPS (Fig. S6) analysis results also display ignorable change in Pd particle size (2.6 versus 2.3 nm) and chemical valence of (53.0% versus 55.5% of Pd⁰) catalyst after reaction compared with that of the pristine one. Therefore, the heterogeneous interfacial engineering of carbon is an effective approach to improve H₂O₂ direct synthesis efficiency of catalyst.

3.3. Structure-performance relationship discussion

From above results, it can be seen that the catalytic performance of series Pd/C-TiO₂ is significantly influenced by heterogeneous interfacial engineering of carbon. Generally, the surface modification would alter many factors, including porous structure, surface properties of support, dispersion state and chemical valence of metal nanoparticles, and so on. These are more or less related to the intrinsic reaction, absorption/adsorption of reactants, and mass transfer [6,8,9,32]. Thus, it is necessary for clarifying their relationship to definite the mechanism of heterogeneous interfacial engineering of carbon on H₂O₂ direct synthesis performance of Pd catalyst.

Preliminarily, XRD analysis results have confirmed that various Pd catalysts possessed the identical crystal structure of supports, which should not be the main factor for influencing catalytic performance of Pd/C-TiO₂. Also, the porous structure, e.g. surface area, pore volume, etc., of supports shows a negligible change as increasing carbon content. As for the dispersion

state of Pd nanoparticles, TEM analysis has exhibited that Pd/C-TiO₂ catalysts possess 2.29–2.40 nm of most probable particle sizes while that of Pd/TiO₂ is 2.54 nm. Lee et al. [51] found that Pd catalyst with 4.2 nm of mean particle size could have 78.4% of H₂O₂ selectivity, which was obviously higher than 48.9% of Pd catalyst with 3.4 nm of mean particle size. This was attributed to the easier dissociation of O-O bond on smaller size of Pd nanoparticles, as also demonstrated by Han et al.'s works [52]. Accordingly, the relatively small particle size of Pd/C-TiO₂ in present work could not be responsible for their improvements in H₂O₂ direct synthesis performance. Thus, these characterization results demonstrate that the geometrical structure of Pd catalyst does not significantly influence their H₂O₂ direct synthesis performance.

As for the influence of chemical valence, XPS results have confirmed that the metallic Pd content in Pd/C-TiO₂-0.75 is obviously lower than that in Pd catalysts with low carbon content. Numerous researches demonstrated that metallic Pd was more active than oxidic Pd in H₂O₂ direct synthesis [53]. Accordingly, the poor catalytic performance of Pd/C-TiO₂ catalysts with high carbon content could be attributed to the relatively low metallic Pd content. However, this viewpoint could not individually account for the improvement in catalytic performance of Pd/C-TiO₂ under low carbon content (<1.89 wt%) due to their similar chemical valence of Pd nanoparticles.

After analyses of above factors, following discussion is focused on the influence of surface properties of various supports on H₂O₂ direct synthesis performance of Pd catalyst. Generally, the adsorption of reactants and desorption of resultants are closely related to the surface properties of catalyst. As shown in Fig. S7, H₂-TPD and O₂-TPD patterns display the increase in adsorption amount of H₂ and O₂ in carbon interfacial engineered Pd catalyst, which should be beneficial to reaction process. However, Fig. 5 has showed that H₂ conversions of various catalysts are almost same. Thus, there may be other factors for influencing the H₂O₂ direct synthesis performance of catalyst. In our previous work, we have demonstrated that the decline in adsorption intensity of resultants with catalyst could accelerate their desorption and improve catalytic performance of catalysts, including hydrodesulfurization, direct synthesis of H₂O₂, and so on [30–32,43]. Herein, the calorimetric measurement technique is applied to achieve the adsorption energy of H₂O₂ with catalyst to analyze their interaction. The corresponding support of various catalysts is used for analysis to exclude the

Table 2
H₂O₂ direct synthesis performance of various catalysts and literature data.

Catalysts	Temperature&Pressure (°C&MPa)	Metallic elements and contents (wt%)	Solvent (s)	Promoters	Conversion& selectivity (%)	H ₂ O ₂ productivity (mmol/g _{pd} /h)	Ref.
Pd/C-TiO ₂ -1.05	10&0.1 (ambient)	3.0 wt%Pd	Ethanol	H ₂ SO ₄	27.7&41	1933	This work
Pd/C-TiO ₂ -0.75	10&0.1 (ambient)	3.0 wt%Pd	Ethanol	H ₂ SO ₄	25.2&52.2	2121	This work
Pd/C-TiO ₂ -0.45	10&0.1 (ambient)	3.0 wt%Pd	Ethanol	H ₂ SO ₄	22.2&61.2	2192	This work
Pd/C-TiO ₂ -0.15	10&0.1 (ambient)	3.0 wt%Pd	Ethanol	H ₂ SO ₄	23.8&47.7	1958	This work
Pd/TiO ₂	10&0.1 (ambient)	3.0 wt%Pd	Ethanol	H ₂ SO ₄	25.0&45.2	1825	This work
Pd/TiO ₂	10&0.1 (ambient)	3.0 wt%Pd	Ethanol	H ₂ SO ₄	26.2&44.6	1922	[35]
Pd/Carbon	2&3.7	5.0 wt%Pd	Methanol/water	None	None, 34.0	220	[50]
Pd-Au/TiO ₂	10&0.1 (ambient)	2.0 wt%Pd1.0 wt%Au	Ethanol	H ₂ SO ₄	29.7&48.1	2330	[45]
Pd-Au/Carbon	2&3.7	2.5 wt%Pd2.5 wt%Au	Methanol/water	None	None, 80	880	[17]

Fig. 6. Calorimetric measurement results of H_2O_2 adsorption.

influence of Pd nanoparticles. As seen in Fig. 6, the adsorption heat, amount and energy of H_2O_2 on support are all decreased with increasing carbon content. To exclude geometrical factors, the adsorption energy could reflect the influence of surface properties of support on H_2O_2 adsorption, which is calculated by dividing adsorption heat by adsorption amount. All interfacial engineered TiO_2 have lower adsorption energy than that of the pristine TiO_2 . This indicates carbon species could indeed decrease the interaction between H_2O_2 and catalysts, which is consistent with the results of our previous work [30,31].

With respect to the carbon species accelerating H_2O_2 desorption, surficial hydrophobicity of support should be the key reason brought by heterogeneous interfacial engineering of carbon species. As is known, TiO_2 is a super-hydrophilic metal oxide that could strongly absorb polar molecules [8,32]. This is also supported by high adsorption energy of H_2O_2 with TiO_2 . By contrast, H_2O_2 molecules have a weak interaction with hydrophobic surface [8]. Fig. 7 shows the data of water contact angle of various supports. The pristine TiO_2 has a water contact angle of 23.0° , suggesting the strong hydrophilicity. The water contact angle of support progressively enlarges with increasing carbon content. C- TiO_2 could have 57.8° of water contact angle when the carbon content is 4.85 wt%. Although all C- TiO_2 in

Fig. 7. Water contact angle of supports as a function of carbon content.

present work is hydrophilic, the distinct enlargement in water contact angle compared with that of TiO_2 could demonstrate the increased hydrophobicity of C- TiO_2 .

As mentioned above, the adsorption energy of C- TiO_2 declines and its corresponding hydrophobicity rises when the carbon content is increased. Consequently, the H_2O_2 desorption performance of Pd/C- TiO_2 is gradually improved with increasing carbon content. In our previous work, the easy desorption of H_2O_2 was demonstrated to be very important for achieving high productivity of H_2O_2 [25,28–30]. This is mainly attributed to the instability of H_2O_2 in hydrogen-oxygen reaction, which could further be decomposed or hydrogenated into water. Thus, two major side reactions, H_2O_2 hydrogenation and H_2O_2 decomposition, are performed in the presence of N_2/H_2 and N_2 , respectively. As shown in Fig. 8, all the catalysts have low decomposition activity in pure N_2 flow (<50 mmol/ g_{Pd} /h). However, the hydrogenation rate of H_2O_2 significantly changes along with the carbon content, which is first decreased from 2762 to 2236 mmol/ g_{Pd} /h and then increased to 2567 mmol/ g_{Pd} /h when the carbon content exceeds 1.89 wt%. Two order of magnitude differences in the rate between hydrogenation and decomposition could indicate that H_2O_2 hydrogenation has the up-most effect on H_2O_2 selectivity and H_2O_2 productivity in present work [35,45]. Noteworthy is that when the carbon content is below 1.89 wt%, desorption performance of H_2O_2 improved by interfacial engineering of carbon could be the key reason for interpreting the excellent H_2O_2 selectivity and high H_2O_2 productivity of Pd/C- TiO_2 catalysts. However, as exceeding 1.89 wt% of carbon content, there seems to be some other factors for influencing the final catalytic results. Chuang et al. [8] considered that excessive hydrophobicity of catalysts could achieve the low resistance of mass transfer of H_2 and O_2 onto their active sites, which resulted in the high H_2 conversion and easy hydrogenation of H_2O_2 into H_2O . Therefore, the heterogeneous characteristic of interfacial engineering of carbon is very important for obtaining the excellent H_2O_2 direct synthesis performance of Pd catalyst.

Besides H_2O_2 desorption, the surface properties of support is also responsible for above-mentioned difference in chemical valence of Pd nanoparticles among various catalysts. It is

Fig. 8. H_2O_2 hydrogenation rate and H_2O_2 decomposition rate of catalysts.

Fig. 9. TPR patterns of Pd precursor on various supports.

acknowledged that the reduction of Pd precursors is varying on different supports [44]. Fig. 9 shows the TPR patterns of Pd precursor on various supports. Pd species on C-TiO₂-0.45 could have a similar reduction process to those on the pristine TiO₂. Both of them show one reduction peak of similar shape at 300 °C in TPR patterns, which is ascribed to the reduction of Pd²⁺ to Pd⁰ [32,54]. The area of reduction peak is integrated to calculate the hydrogen consumption of catalysts. Pd species on C-TiO₂-0.45 has almost similar hydrogen consumption to that of Pd species on TiO₂, which is only 10% of difference between them. This could be responsible for the same metallic Pd content of catalysts under low carbon content. By contrast, the Pd species on C-TiO₂-0.75 has a completely different reduction process from those on C-TiO₂-0.45 and TiO₂, which instead is analogous to those on pure carbon. Besides redox properties of catalysts, the obvious change in peak shape is considered to have different synergetic interaction of active species with supports [55,56]. This means the excessive carbon species could cut off the interaction between Pd and TiO₂ so that the Pd/C-TiO₂-0.75 has a relatively low metallic Pd content.

According to the characterization results and discussion, we could clarify the relationship between heterogeneous interfacial engineering of carbon and H₂O₂ direct synthesis performance of Pd catalyst. With increasing carbon content, the superficial hydrophobicity of support gradually rises and their interaction with H₂O₂ correspondingly declines. This could give rises to the improvement in H₂O₂ desorption performance of corresponding catalyst. By accelerating mass transfer, the increase in carbon content is beneficial to improving H₂O₂ direct synthesis reaction. On the other hand, the chemical valence of Pd nanoparticles turns high as carbon content increases, which leads to the decrease in catalytic activity of catalyst. Simultaneously, the hydrogenation reaction of H₂O₂ into H₂O is more liable to occur under high carbon content. That is to say, the increasing carbon content instead is adverse to H₂O₂ direct synthesis reaction. Therefore, it is crucial for H₂O₂ direct synthesis performance of Pd catalyst to control a moderate coverage of heterogeneous interfacial engineering of carbon over TiO₂.

4. Conclusions

The present work reported a controllable approach to heterogeneous interfacial engineering of carbon over TiO₂ for improving the H₂O₂ direct synthesis performance of Pd catalyst. The carbon content in Pd/C-TiO₂ could be controllably determined by the glucose usage in the preparation process. The catalytic performance of Pd/C-TiO₂ was not monotonously increased as increasing carbon content. There was an optimal carbon content (1.89 wt%) in Pd/C-TiO₂ for H₂O₂ direct synthesis, which could weaken the adsorption energy of H₂O₂ on catalyst and simultaneously maintain the synergistic effect between Pd nanoparticle and TiO₂.

Acknowledgments

Chang Liu and Licheng Li established the framework of present work and supervised the project. Wei Yan and Licheng Li contributed to the writing of manuscript. Wei Yan and Fan Pan synthesized all samples and conducted the analysis of catalytic performance. All authors discussed the results and made comments on the manuscript.

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Graphical Abstract

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Heterogeneous interfacial engineering of Pd/TiO₂ with controllable carbon content for improved direct synthesis efficiency of H₂O₂

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Heterogeneous interfacial engineering of carbon could maintain the interaction of Pd nanoparticles with TiO₂ and simultaneously accelerate the H₂O₂ desorption, which improves the H₂O₂ direct synthesis performance of catalyst.

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可控碳改性Pd/TiO₂用于直接合成双氧水：非均相界面对催化性能的影响

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摘要: 双氧水(H₂O₂)是一种重要的绿色氧化剂, 广泛应用于纺织、医疗、废水处理、军事等重要领域。目前, H₂O₂的工业生产以蒽醌法为主, 该法设备投资大、运行成本高, 同时工艺涉及大量的有机溶液, 活性中间体蒽醌也会发生缓慢降解, 产生有毒副产物。与蒽醌法相比, 通过负载型贵金属催化剂催化H₂与O₂反应直接合成H₂O₂, 过程绿色环保且生产工艺简单, 引起了各界广泛关注。然而, 从热力学上分析, H₂和O₂更容易反应生成H₂O, H₂O₂只是该反应的中间产物, 会继续发生加氢和直接分解反应生成H₂O, 导致H₂和O₂的低效利用, 开发高H₂O₂选择性且高反应效率的催化剂已成为氢氧直接合成H₂O₂研究的重点与难点。目前大部分研究策略旨在通过调控或影响反应中心结构、价态来抑制H₂O₂的副反应, 进而提升H₂O₂的选择性和反应效率; 尽管已取得了良好的进展, 但仍需发展新的调控策略来满足工业应用的要求。

本课题组前期研究表明, 促使H₂O₂从催化剂上脱附可以有效地提升H₂O₂的选择性和产率。相比于针对反应中心的调控, 不稳定的H₂O₂从催化剂上快速脱附同样起到抑制H₂O₂参与副反应的作用。为此, 本文提出一种炭量可控的非均一界面改性方法, 以常规的Pd/TiO₂作为研究对象, 借助各种结构表征, 发现炭物种在TiO₂表面呈非均一分散状态, 而且改性对于催化剂的几何结构影响较小; 另外, 催化剂表面的疏水性会随着碳含量的增加而增加, 导致其与H₂O₂间的吸附能相应变小。反应结果显示, 表面非均一的炭化改性技术可以显著提升Pd/TiO₂催化剂的H₂O₂选择性和产率。通过构效关系分析, 可知这种改性技术可以保持Pd颗粒与TiO₂间相互作用的同时, 还可以促进H₂O₂的快速脱附, 进而提升改性Pd/TiO₂催化剂的H₂O₂直接合成效率。该改性方法简单、易控, 可拓展应用到其他类型催化剂的H₂O₂直接合成性能调控与改进。

关键词: H₂O₂直接合成; 二氧化钛; 炭; 非均一界面改性; 钯

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