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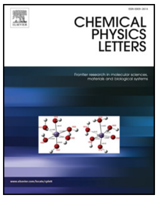

Research paper

Pd nanoparticles on carbon layer wrapped 3D TiO_2 as efficient catalyst for selective oxidation of benzyl alcohol

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HIGHLIGHTS

- The 2D carbon layers homogeneously cover the flower-like TiO_2 skeleton (CFT).
- Ti—O—C bondings are observed in CFT.
- Ti—O—C bond permits strong interactions between PdNPs and CFT.
- PdNPs remain strongly anchored and highly dispersed on CFT after reaction.

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ABSTRACT

In this work, a uniform thickness of a two-dimensional carbon layer wrapping a three-dimensional flower-like TiO_2 (CFT) is used to support Pd nanoparticles (Pd/CFT) as efficient catalyst for selective oxidation of benzyl alcohol in a three-phase reaction system. The results of characterization reveal that the Ti—O—C bond plays a key role in establishing interactions between the CFT and Pd. In comparison to the Pd/AC catalyst, Pd nanoparticles (PdNPs) with active phases can be effectively anchored on the surfaces of CFT without obvious dynamic change under reaction conditions.

1. Introduction

Conversion of alcohols to aldehydes is an important reaction in chemical industries. Benzaldehyde, as an important aldehyde product, is primarily produced by the following two methods, i.e., the hydrolysis of benzal chloride and toluene oxidation [1,2]. However, these methods have their limitations for large scale applications due to chlorine contamination and relatively poor selectivity [3]. Oxygen, as an oxidant, can not only avoid chlorine participation but also improve oxidation contact on catalyst surfaces in liquid phase oxidation.

In a three-phase reaction system, design of heterogeneous catalysts plays a key role in promoting optimal gas-liquid contact and determines efficient reaction pathways. Palladium-based catalysts have been widely studied for selective oxidation of alcohols into corresponding aldehydes [4]. However, in this reaction process, size-sintering is one of the main reasons for the deactivation of the Pd-based catalyst caused by heat supply during reactions [5,6].

Carbon materials are widely applied as supports in catalysis, examples include activated carbon (AC) [7], multi-walled carbon nanotubes (MWCNTs) [8], graphene oxide [9], reduced graphene oxide (RGO) [10]. Graphene can not only be used as a support, but also in composite systems owing to the enhanced electron transmission efficiency. However, the complex preparation method limits its production efficiency, agglomeration or stacking between graphitic layers take place due to the van der Waals force [11]. Therefore, design of two-dimensional (2D) carbon materials that are similar to graphene in structure and surfaces is required for avoiding agglomeration during catalytic applications. Metal oxides nanostructures with various morphologies have been widely studied in different fields [12,13], as one of the most common metal oxides, various preparation technologies can produce different morphologies of TiO_2, such as nanoparticles [14], nanorods [15], nanobelts [16], nanosheets [17], hollow nanospheres [18], and urchin-like spheres [19,20]. Therefore, using designed structures of TiO_2 as skeletons for depositing carbon layers on top can

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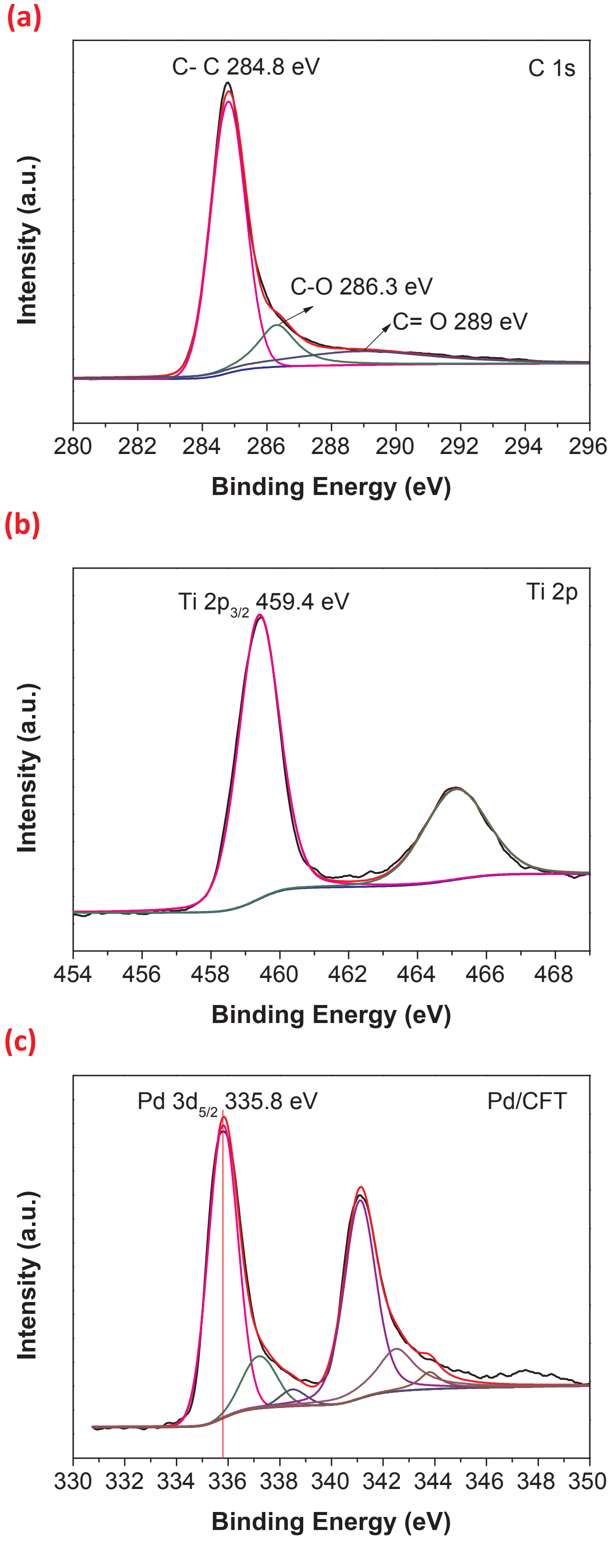

Fig. 1. (a) C 1s XPS patterns of the CFT and (b) Ti 2p XPS patterns of the CFT, (c) Pd 3d XPS patterns of the Pd/CFT.

form a well-distributed two-dimensional composite for supporting metal nanoparticles as catalysts for efficient alcohols conversion.

2. Experimental section

The encapsulation of flower-like rutile TiO_2 with a 2D carbon layer was accomplished basing on our previous work [21]. By the following processes: 5.86 g of cetyltrimethyl ammonium bromide (CTAB) was mixed with n-hexane and n-pentanol at a volumetric ratio of 6:1 at 65 °C under stirring for 5 min in a water bath. Then, 20 mg of carbon dots and 1 mL of $TiCl_3$ was added and stirred for 2 min. Subsequently, the solution was loaded into a Teflon-lined stainless-steel autoclave with a capacity of 100 mL and heated at 200 °C for 6 h. After cooling to room temperature, the flower-like TiO_2 was dispersed in the solution by ultrasonication and then transferred into a beaker with stirring at 80 °C until solution evaporated completely. Next, 2D carbon layer shells were patterned onto the flower-like TiO_2 cores and obtained by calcination conducted in a tube-furnace at 800 °C for 2 h in a He atmosphere. The obtained 2D carbon layer/flower-like TiO_2 shell-core structures (CFT) were washed with ethanol and ultra-pure water several times and dried at 60 °C for 12 h in a vacuum oven. 0.1 g CFT and 60 μL $Pd(NO_3)_2$ (10 wt% in 10 wt% nitric acid) were dispersed in 20 mL ethanol, after impregnation, the Pd/CFT was reduced at 250 °C for 2 h under H_2/He (25 sccm/100 sccm).

X-ray photoelectron spectroscopy (XPS) was performed with a Thermo ESCALAB 250 instrument with monochromatic Al Kα radiation. The morphologies and structures of the catalysts analyzed by transmission electron microscopy (TEM) (JEOL JEM-2100F). Measurement of BET surface area were performed using N_2 adsorption/desorption isotherms (Tristar 3020). The Pd content of the Pd/CFT and Pd/AC collected with an inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Optima 8000). X-ray diffraction (XRD) patterns were conducted on a Bruker D8-Advanced X-ray diffractometer with Cu-Kα radiation. Raman spectra were carried on a Horiba Scientific LabRAM HR Evolution system with an Ar-ion laser at an excitation wavelength of 633 nm.

3. Results and discussion

X-ray photoelectron spectroscopy (XPS) was used to characterize the surface and sub-surface properties of CFT. Fig. 1a shows that the C 1s XPS spectra for CFT has peaks at 284.8, 286.3, and 289 eV, which are ascribed to C—C, C—O, and C═O, respectively [22,23]. The emergence of peaks from C—O and C═O indicate that the flower-like TiO_2 surface was modified by carbon species [24]. In Fig. 1b, the Ti $2p_{3/2}$ peak of CFT is located at 459.4 eV, a significant shift toward higher binding energy compared with that of the pure rutile [25]. This phenomenon shows an electron transfer from the flower-like TiO_2 to the surface carbon layer due to the presence of Ti—O—C bonds [26–28]. The Pd 3d XPS spectra for Pd/CFT is shown in Fig. 1c. Comparing with the reported characteristic binding energy of monometallic Pd $3d_{5/2}$ peak located at 335 eV [29,30], the peak at 335.8 eV with 0.8 eV positive shift indicates that there was electronic transfer between the support and PdNPs.

Fig. 2a shows flower-like structure of the Pd/CFT Pd nanoparticles with average diameters of 6.4 ± 0.2 nm are highly distributed on the surface of CFT. The HRTEM image of the PdNPs shows clear lattice fringes of 0.23 nm, which corresponds to the interplanar spacing distance of the Pd (1 1 1). 2D carbon layer shows clear lattice fringes of 0.34 nm, which corresponds to the interplanar spacing distance of the graphene structure. In addition, the thickness of the carbon layer is approximately 2.4 to 3.2 nm, and it tightly wraps the surfaces of TiO_2 to form a contact interface between the two phases. For comparison, Pd/AC was shown in Fig. 2b and 2d. The PdNPs on AC shows an average diameter of 6.8 ± 0.2 nm. The crystalline structural properties of PdNPs on AC exhibited similar lattice distribution of Pd (1 1 1). BET surface area of CFT and Pd/CFT are 22.0 m^2g^{-1} and 27.5 m^2g^{-1}, respectively, which were measured by N_2 adsorption-desorption isotherms (Fig. S1).

Oxidation of benzyl alcohol test was performed with a 0.05 M benzyl alcohol solution using hexamethylene as the solvent, and a continuous-flow reactor (Thales-Nano Phoenix Flow Reactor™) was applied to test the performance of the catalysts. In this reaction system,