Palladium decorated anatase for photocatalytic partial oxidation of methane to ethane

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1. Introduction

Large reserves of methane (CH4) are a promising alternative for a clean fuel and dependable fundamental building block for chemical production [1]. To date, the industrial-scale technology for CH4 conversion is a two-step process, where CH4 is firstly transformed into syngas and followed by Fischer-Tropsch synthesis to produce C2+, hydrocarbons. However, such a reaction requires huge energy input and strict reaction conditions (e.g., 15–40 atm and 900–1200 K) [2,3]. The low efficiency of carbon-atom utilization causes large greenhouse gas emissions [4]. In contrast, direct C–H bond coupling of CH4 into ethane (C2H6) and further dehydrogenation to ethylene (C2H4) are economical, environmentally friendly and important especially in the background of carbon neutrality [5]. The direct CH4 conversion is initiated by the activation of the C–H bond, which is difficult due to the high C–H bond energy (439 kJ/mol) and low electron affinity (−1.9 eV) [6]. Moreover, the selectivity of desired products is also moderate in CH4 conversion since the products are thermodynamically more reactive than CH4 due to the weaker C–H bond in products. There are two main routes for direct C–C bond coupling of CH4 partial oxidation of CH4 (POM) and non-oxidative coupling of CH4 (NOCM). The change in Gibbs free energy of POM (−320 kJ/mol) is much lower than that of NOCM (68.6 kJ/mol), indicating that POM is thermodynamically more favorable than NOCM and can take place under mild conditions [7]. In addition, catalyst deactivation caused by coking is a fatal issue of NOCM [8]. The mostly used oxidant in POM is O2, leading to the production of C2H6, C2H4 and H2O [9]. For example, MnOx-Na2WO4/TiO2-SiO2 was used to efficiently convert CH4 to C2-C4 with a methane conversion of 22% at 650 °C. However, the C2-C3 selectivity of 62% was moderate due to the introduction of oxygen and high temperature, which inevitably cause over oxidation [10]. The replacement of O2 with other oxidants such as CO2 is one frequent strategy to restrain over oxidation. A recent work used a CaO-based oxide to convert CO2 and CH4 to C2H6 at 950 °C with C2-C3 yield of 6.6% [11]. However, the low selectivity of C2 products remains a major challenge because the product stream is diluted with CO2, which increases capital investment and energy costs associated with gas separation units for the removal of by-products [12].

Photocatalysis has been regarded as a clean and sustainable strategy...
to break the C–H bond to drive CH₄ direct conversion under very mild conditions [13]. Integrating photocatalysis and POM may theoretically ameliorate harsh reaction conditions, over-oxidation, and the deposition of coke. In addition, the majority of photocatalytic methane conversion reactions were carried out in batch reactors [14]. Such systems are easy to operate, but it is theoretically hard to avoid over-oxidation as the long residence time in the batch reactor favours the production of thermodynamically more stable overoxidation products (e.g., CO₂). Flow reactors can effectively avoid the overoxidation process due to the readily-controlled reaction time. The flow reactor can also enable to maintain the stable reaction conditions, including feedstock and products concentration. In addition, large-scale operation is only possible in the continuous-flow reactors.

Recently, several relevant works have been reported. CuOₓ-Pt-TiO₂ was used for photocatalytic POM in a flow reactor to convert CH₄ to C₂H₆ for the first time, showing the highest yield of C₂ product at 6.8 μmol/h with a moderate selectivity [14]. Later, Ag–AgBr/TiO₂ catalyst was used to selectively convert CH₄ to C₂H₆ under 6 bar pressure, the yield of C₂ product was increased to 35.4 μmol/h [15]. However, the highly selective photocatalysis for valuable C₂ production from methane conversion is still challenging due to the low separation rate of photoinduced carriers in the intrinsic semiconductor and inappropriate residence time of reactants in the reactor.

In this work, an optimized Pd₁₁.₈-anatase TiO₂ photocatalyst was used for continuous photocatalytic POM in a flow reactor under mild conditions. The C₂H₆ yield achieved is 40.9 µmol/h, which is 13 times higher than that of the pure TiO₂ and comparable to the results of traditional thermal catalysis at high temperatures. The C₂H₆ selectivity of 80.4% is also remarkable owing to the regulation of the gas ratio in the flow reactor. Moreover, diverse characterizations unveil Pd nanoparticles function as photogenerated holes acceptors, increasing the decay lifetime of photogenerated charges, so to largely enhance the activity of Pd₁₁.₈-TiO₂ catalyst.

2. Main

Pd decorated TiO₂ was synthesized via an in situ photo-deposition method with (1 wt.%) K₂PdCl₄ as the precursor. The resulting catalysts are denoted as Pdₓ-TiO₂ (x stands for the weight percentage of loaded Pd species on TiO₂). The morphology of Pd₁₁.₈-TiO₂ was investigated using transmission electron microscopy (TEM), as shown in Fig. 1A. No obvious Pd particles are observed on Pd₁₁.₈-TiO₂. The distributed Pd particles were visible in the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image (Fig. 1B). Energy-dispersive X-ray (EDX) mapping images also show a homogeneous distribution of Pd (Fig. 1C), O (Fig. 1D), and Ti (Fig. 1E) species. The crystalline structures of the photocatalysts were identified by powder X-ray diffraction (XRD), as shown in Fig. 1F. Only anatase TiO₂ (JCPDS no. 84–1272) signals are observed after the deposition of Pd, indicating that the structure of TiO₂ remains unchanged during the photodeposition process [16]. Furthermore, no new diffraction peaks attributed to Pd species are observed, suggesting that the metal species are highly dispersed on the surface of TiO₂. The optical absorption of TiO₂ and various Pdₓ-TiO₂ samples were studied by the ultraviolet–visible (UV–vis) absorption spectra (Fig. 1G). TiO₂ exhibits a typical photo-absorption edge at 400 nm. All the photocatalysts display

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**Fig. 1.** (A) TEM image of Pd₁₁.₈-TiO₂, (B) HAADF-STEM of the region in the red dashed box in Fig. 1(A) and the corresponding EDX results of Pd (C), O (D), and Ti (E). (F) XRD patterns and (G) UV–VIS absorption spectra of TiO₂ and Pdₓ-TiO₂. (x = 0.9, 1.2, 1.5, 1.8, 2.1).
similar bandgaps around 3.1 eV [17] (Fig. S1). Stability tests indicated that TiO$_2$ and Pd$_{1.8}$-TiO$_2$ are stable under the reaction condition (room temperature) (Fig. S2). The DSC signals at 329 K of TiO$_2$ and Pd$_{1.8}$-TiO$_2$ exhibit typical endothermic feature caused by adsorbed water. The broad feature ranging from 750 to 900 K is caused by the transformation of the crystalline phase of TiO$_2$ [18].

Then, the performance of POM over TiO$_2$ and Pd$_{x}$-TiO$_2$ photocatalysts was evaluated in a flow reactor. The actual Pd loading was verified by inductively coupled plasma atomic emission spectrometry (ICP-AES). As shown in Fig. 2A, C$_2$H$_6$, CO$_2$ and CO are detected in the products. Bare TiO$_2$ shows a low C$_2$H$_6$ production rate of 2.8 µmol/h, while the production rates of CO$_2$ and CO are 1.8 µmol/h and 0.2 µmol/h, respectively. The C$_2$H$_6$ yield significantly increases from 2.8 µmol/h to 34 µmol/h after loading with 0.9 wt.% Pd. In addition, the selectivity of C$_2$H$_6$ increases from 74% to 82.3%. With increasing Pd content, the yield of C$_2$H$_6$ further increased to 37.6 µmol/h with 1.2 wt.% Pd content, and reached the highest value over Pd$_{1.8}$-TiO$_2$ at 41.0 µmol/h. Further increases in Pd loading results in decreased photocatalytic activity, as observed with yields of 40.9 µmol/h and 36.5 µmol/h for Pd$_{1.5}$-TiO$_2$ and Pd$_{2.1}$-TiO$_2$, respectively. Meanwhile, the selectivity of C$_2$H$_6$ also exhibits an inverted volcanic trend, with values of 80.8%, 79.7%, 80.4% and 82.1% for Pd$_{1.2}$-TiO$_2$, Pd$_{1.5}$-TiO$_2$, Pd$_{1.8}$-TiO$_2$ and Pd$_{2.1}$-TiO$_2$, respectively. The morphology of Pd$_{2.1}$-TiO$_2$ was investigated by TEM. As shown in Fig. S3, the yellow circle representing an agglomerated Pd particle with a particle size exceeding 50 nm. Thus, excessive Pd loading causes the aggregation of Pd species, resulting in decreased photocatalytic activity. Based on the results, Pd$_{1.8}$-TiO$_2$ was selected as the optimized catalyst for subsequent experiments due to its similar C$_2$H$_6$ yield compared to Pd$_{1.5}$-TiO$_2$, but with the higher selectivity. In addition, as shown in Table S1, compared with the reported photocatalysts, the well-designed Pd$_{1.8}$-TiO$_2$ catalyst shows a high C$_2$H$_6$ production rate of 40.9 µmol/h in photocatalytic methane oxidation with a selectivity of 80.4% under mild conditions. The effect of CH$_4$ to O$_2$ ratio was then investigated at a total pressure of 200 MPa, with a flow rate of 50 ml/min, molar ratio of CH$_4$ to O$_2$ is 96:1, the data was recorded at 30th minute.

![Fig. 2. (A) The product distribution and C$_2$H$_6$ product selectivity over TiO$_2$ and Pd$_{x}$-TiO$_2$ (x = 0.9, 1.2, 1.5, 1.8, 2.1). (B) The product distribution and C$_2$H$_6$ product selectivity over Pd$_{1.8}$-TiO$_2$ with different molar ratios of CH$_4$ to O$_2$. Reaction conditions: 50 mg catalyst, 365 nm light irradiation, under room temperature and 0.1 MPa, with a flow rate of 50 ml/min, molar ratio of CH$_4$ to O$_2$ is 96:1.](image-url)
activity of the Pd$_{1.8}$-TiO$_2$ catalyst. Overall, this work provides an effective and green route toward continuous methane conversion to value-added products.

4. Methods

4.1. Chemicals and materials

Titanium dioxide (TiO$_2$, 60 nm, anatase, 99.8%, Alfa Aesar), potassium tetrachloropalladate (II) solution (1 wt.% Pd) were applied in the experimental studies.

4.2. Preparation of Pd$_x$-TiO$_2$

300 mg TiO$_2$ was suspended in 30 mL aqueous methanol solution (10 vol.%), where a certain amount of K$_2$PdCl$_4$ was then added. The suspensions were sealed and irradiated for 4 h after purging with ultrapure Ar for 30 min. Then, the products were washed with DI water and collected by centrifugation. The obtained products were named Pd$_x$-TiO$_2$, where $x$ represented the wt. percentage of Pd to TiO$_2$ substrates.

4.3. Characterisation

TEM images were acquired via FEI Talos F200X, equipped with an Energy-dispersive X-ray Detector. XRD patterns were obtained on a Bruker D8 Advance fitted with a solid-state X’Celerator detector (2.2 kW) using Cu Kα radiation from 5 to 80°. The UV–Vis absorption spectra were acquired using a Shimadzu UV 3600 plus spectrophotometer with BaSO$_4$ as the reference. In-suit XPS was performed on a Thermo Scientific ESCALAB 250Xi system with an Al Kα source, where a 365 nm LED light was utilized as the excitation source. All XPS spectra were calibrated using C 1s line at 284.6 eV. The contents of Pd species were measured by an ICP-MS (Agilent 7900). Photoluminescence and transient-state photoluminescence were collected on an FLSP920.

Fig. 3. (A) Pd 3d XPS spectra and (B) EPR spectra under 100 K of Pd$_{1.8}$-TiO$_2$ in dark and under light irradiation. (C) Time-resolved photoluminescence (TPL) spectra, (D) Photoluminescence (PL) spectra, and (E) I-T curves of TiO$_2$ and Pd$_{1.8}$-TiO$_2$. (F) Proposed reaction mechanism of photocatalytic POM on Pd decorated TiO$_2$. 
spectrofluorometer. The excitation and emission wavelength of TPL were 310 and 470 nm, respectively. The electron spin resonance (ESR) measurements were carried out on a Bruker E500–9.5/12 spectrometer operating at the X-band frequency at room temperature, where a 365 nm LED was applied as the irradiation source. TGA-DSC was performed on a NETZSCH STA449C under Ar atmosphere

4.4. Photocatalytic test

50 mg sample powder was suspended in 50 mL water and filtered with a nylon membrane (diameter 35 mm) to produce a uniform film. The film was placed on the top-irradiated flow reactor with a temperature probe. For each experiment, the system was purged with Ar (50 mL min⁻¹) for 30 min. Subsequently, the reactor was irradiated by a LED light source (365 nm Beijing Perfect Light, PLS-LED 100B) with a CH₄ flow rate of 50 mL/min. The outlet gasses were detected by an SP-3420A GC equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID).

4.5. Calculation of selectivity

The selectivity for C₂H₆ was calculated as below:

\[ \text{C}_2\text{H}_6\text{ selectivity} = \frac{2 \times n(\text{C}_2\text{H}_6)}{2 \times n(\text{C}_2\text{H}_6) + n(\text{CO}_2) + n(\text{CO})} \]

Data availability

The authors declare that the data supporting the findings of this study is available in the main text or the supplementary materials.

CRediT authorship contribution statement

Jianlong Yang: Investigation, Formal analysis, Writing – original draft, Visualization. Chao Wang: Formal analysis, Writing – original draft, Visualization. Jialiang Xing: Formal analysis, Writing – original draft. Junwang Tang: Supervision, Conceptualization, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials


References