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Article

Supercritical synthesis of platinum-modified titanium dioxide for solar fuel production from carbon dioxide

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ABSTRACT

This paper investigates the properties of TiO_2-based photocatalysts synthesised under supercritical conditions. Specifically, the characteristics of Pt dispersed on TiO_2 catalysts obtained in supercritical CO_2 are discussed and compared with those of commercial TiO_2. The photocatalytic activity of the synthesised catalysts in the CO_2 photoreduction reaction to produce solar fuel is tested. The main conclusion of the study is that photocatalysts with better or similar features, including high surface area, crystallisation degree, hydroxyl surface concentration, pore volume, absorbance in the visible range and methane production rate, to those of commercial TiO_2 may be produced for the reduction of CO_2 to fuel by synthesis in supercritical media.

1. Introduction

The increasing atmospheric concentration of greenhouse gases, especially CO_2, is a pressing social issue at present [1]. Different processes to capture gas from large point sources such as the flue gases of coal, oil, natural gas and biomass power plants have been patented in recent years [2,3]. The recovered CO_2 can be either stored in natural caves or used as feedstock to produce useful chemicals, especially fuel, which is the only CO_2 conversion product that may substantially lower anthropogenic CO_2 emissions because of its high rate of consumption. However, because the CO_2 molecule is very stable, only a few technologies for its conversion are available. In particular, effective photocatalytic conversion of CO_2 to fuel has been demonstrated [4,5]. Thus, following this previous work, the present study focuses on the synthesis of catalysts for the photocatalytic conversion of CO_2 gas into fuel using solar energy (i.e., catalysts for solar fuel production from CO_2), a process with an enormous future potential despite being in the early stages of development.

The main drawbacks currently limiting photocatalytic CO_2 reduction are low photoconversion speed and efficiency. These problems may be overcome through the design of highly active photocatalysts with favourable reactant adsorption, charge separation and transport, light harvesting and CO_2 activation [6–14]. TiO_2 particles show most of these features along with non-toxicity, high photostability, chemical inertness, environmentally friendly nature and low cost. Thus, TiO_2 is a promising material for use as a catalyst in CO_2 photoreduction.

The main weakness of TiO_2 is that it only uses the ultraviolet (UV) region of the solar spectrum, which is less than 5% of the total solar energy. Moreover, after UV irradiation of TiO_2 with an energy equal or larger than its band gap (3.2 eV), the resulting photogenerated electron–hole pairs rapidly recombine.

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However, both problems can be tackled with appropriate dispersion or doping of TiO_2 with either noble or transition metals [7,9,10,12,15–17]. The dispersion method leads to the scattering of metal particles on the TiO_2 support, while doping involves the inclusion or substitution of foreign metal atoms into the TiO_2 lattice [10,18].

The most commonly ascribed effect of Pt as a dopant for TiO_2 is its ability to promote charge carrier separation because electrons tend to accumulate on the doped Pt and holes remain on TiO_2. Pt also shifts the band edges of TiO_2 to make certain electron transfer processes more favourable in the vicinity of the metal atom. In addition, Pt increases the electron scavenging capability of O_2, removes strongly bound intermediates, promotes hydroxyl (OH) formation and promotes H^+ reduction to adsorbed H atoms [18]. However, the influence of Pt on TiO_2 photocatalysis is not always positive because Pt atoms may act as charge recombination centres or block active sites on TiO_2. Moreover, Pt is a good centre for hydrogen (H_2) generation from H_2O; therefore, it is necessary to take measures to minimise this process [19].

The amount of Pt added to TiO_2 can also play a major role in catalyst performance. The typical optimal Pt loading is around 1 wt% [9,18]. Higher metal contents can induce faster electron–hole recombination and deactivate the photocatalyst [10,20]. Table 1 summarises details of some recent Pt/TiO_2 catalysts. Pt concentration is typically in the range of 0.2–5 wt%.

Many studies have focused on how metal dispersion methods affect the photocatalytic behaviour of catalysts [10,18]. Several techniques have been used to disperse Pt atoms on TiO_2 substrates [21–25,27]. One method is co-precipitation in supercritical fluids because if a metal precursor is added to a reaction medium together with a Ti precursor and a hydrolysis agent, a metal dispersed on TiO_2 catalyst can be obtained in situ [28]. The use of supercritical fluids, mainly CO_2 and H_2O, for particle generation and precipitation is attractive because of their excellent properties [29,30]—they can diffuse through solids like a gas and dissolve materials like a liquid—and their ability to be adjusted by simply changing the operating parameters [31,32]. Both the fluid properties and easy tuning of supercritical fluids allow particle characteristics such as structure, morphology, size and size distribution to be controlled. All of these characteristics are very important for the final application of a catalyst [28]. Moreover, synthesis using supercritical fluids is more environmentally sustainable than classical synthesis procedures, which usually use large amounts of organic solvents.

The objective of this investigation is to use a supercritical medium to synthesise a TiO_2-based catalyst with superior performance to that of a commercial semiconductor in the photocatalytic reduction of CO_2 to fuel molecules. Specifically, Pt dispersed on TiO_2 is synthesised by a hydrothermal method using supercritical CO_2. Pt(II) acetylacetonate and titanium tetraisopropoxide (TTIP) or diisopropoxy titanium bis(acetylacetonate) (DIPBAT) are used as chemical precursors of Pt and TiO_2, respectively, with isopropyl alcohol or ethanol as a hydrolytic agent. The synthesis involves the following process. Once the reagents are in the supercritical phase, precursor decomposition occurs and alcohol decomposition provides the necessary H_2O for the hydrolysis reaction [33,34]. The end products are Pt dispersed on TiO_2 solid particles and carbonaceous contaminants originating from the precursors. The decompressed solvent is in gas phase, which facilitates catalyst drying and recovery at the end of the process. To remove carbon (C) contaminants from the catalyst, a calcination step is performed after supercritical synthesis [35].

The properties of the Pt/TiO_2 catalysts are determined by usual characterisation methods, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), atomic emission spectroscopy with inductively coupled plasma (ICP-AES), X-ray diffraction (XRD), N_2 adsorption-desorption measurements, diffuse-reflectance UV-visible (DRUV-vis) spectroscopy, Fourier transform infrared (FTIR) spectroscopy and laser diffraction, and compared with those of commercial TiO_2. Their photocatalytic activity in CO_2 photoreduction to produce solar fuel is also tested.

2. Experimental

2.1. Chemicals

Various samples of Pt dispersed on TiO_2 powder were synthesised by thermal hydrolysis of two different precursors (DIPBAT and TTIP) with two different alcohols in the presence of Pt(II) acetylacetonate using supercritical CO_2 as the reaction medium. DIPBAT (75 wt% in isopropyl alcohol), TTIP (pure) and Pt(II) acetylacetonate (97 wt%) were provided by Sigma-Aldrich. Analytical reagent-grade ethanol and isopropyl alcohol were provided by Scharlab. In all analyses, Degussa

Table 1
Overview of Pt/TiO_2-based catalysts.

Support	Pt concentration (wt%)	Method	Ref.
TiO_2 anatase	0.5–2	Impregnation + air drying + calcination (450 °C, 4 h) + H_2 reduction	[21]
TiO_2 anatase	5	Mixture of TiO_2 precursor and dopant solutions + drying + gel grinding + calcination (500 °C, 5 h)	[22]
Mesoporous TiO_2 thin films	0.5–3	Evaporation induced self-assembly	[23]
TiO_2	0.2–1	Sol-gel	[24]
TiO_2	0.15	Sol-gel	[25]
TiO_2	1	Two step hydrothermal route	[20]
TiO_2	0.1–0.4	Sol-gel	[26]