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## Article

# Photocatalytic degradation of 2,4-dichlorophenol with $V_2O_5$ - $TiO_2$ catalysts: Effect of catalyst support and surfactant additives



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## ABSTRACT

Binary oxide catalysts with various weight percentage  $V_2O_5$  loadings were prepared by solid-state dispersion and the nanocomposites were modified with surfactants. The catalysts were analyzed using X-ray diffraction, diffuse-reflectance spectroscopy, Fourier-transform infrared spectroscopy, scanning electron microscopy, and  $N_2$  adsorption-desorption. The photocatalytic activities of the catalysts were evaluated in the degradation of 2,4-dichlorophenol under ultraviolet irradiation. The photocatalytic activity of 50 wt%  $V_2O_5$ - $TiO_2$  (50 $V_2O_5$ - $TiO_2$ ) was higher than those of pure  $V_2O_5$ ,  $TiO_2$ , and P25. Interactions between  $V_2O_5$  and  $TiO_2$  affected the photocatalytic efficiencies of the binary oxide catalysts. Cetyltrimethylammonium bromide (CTAB) and hexadecyltrimethylammonium bromide (HTAB) significantly enhanced the efficiency of the 50 $V_2O_5$ - $TiO_2$  catalyst. The highest percentage of 2,4-dichlorophenol degradation (100%) and highest reaction rate (2.22 mg/(L·min)) were obtained in 30 min with the (50 $V_2O_5$ - $TiO_2$ )-CTAB catalyst. It is concluded that the addition of a surfactant to the binary oxide significantly enhanced the photocatalytic activity by modifying the optical and electronic properties of  $V_2O_5$  and  $TiO_2$ .

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## 1. Introduction

Chlorophenols are toxic organic compounds and are listed by the Environmental Protection Agency as priority water pollutants [1]. They have been used extensively in many industrial products such as petrochemicals, pharmaceuticals, dyes, pulps, pesticides, and paints [2–6]; therefore, chlorophenols are common chloroaromatic pollutants [7]. Removing these contaminants from water is a significant challenge because of ever-increasing pollution and the shortage of high-quality fresh water [8]. The removal of these hazardous organic pollutants has become necessary and important for environmental safety. These organic compounds can be oxidized using chemical, photochemical, and microbiological processes.

Heterogeneous photocatalytic oxidation has aroused considerable interest as a potential efficient method for degrading recalcitrant environmental contaminants. Semiconductors, which have a filled valence band and an empty conduction band, are important materials because of the electronic structures of the metal atoms in chemical combinations [9]. A wide range of chloroaromatics have been eliminated by this process, mainly using  $TiO_2$  as a semiconductor photocatalyst.  $TiO_2$  is the most widely used photocatalyst because of its low cost, abundance, high chemical stability, and low toxicity [10]. However, it has two main defects. First, it is a relatively high energy band gap material ( $E_g \approx 3.2$  eV), which can be excited under ultraviolet (UV) irradiation ( $\lambda < 387$  nm). This practically rules out the use of sunlight to induce photocatalytic reactions efficiently.

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Secondly, the low rate of electron transfer to reducible species (e.g., oxygen in oxidation reactions, protons in hydrogen production from water) and high recombination rate of the photo-produced electron-hole pairs limit the rates of photocatalytic reactions [11]. Research to find alternative high-performance, low-cost photocatalysts is therefore important [12–14]. Among the strategies adopted to minimize the effects of these drawbacks of TiO<sub>2</sub> photocatalysts, coupling TiO<sub>2</sub> with another metal oxide is a promising route.

Improvement of the photocatalytic activity of TiO<sub>2</sub> by doping with transition metals such as Pt, Fe, Mo, Ru, and V or non-metals, and mixing with other metal oxides to form composite semiconductors has been investigated. The combination of a semiconductor substrate and metal cluster improves the photocatalytic activity by trapping the photoinduced charge carriers, thereby improving the charge-transfer processes, as a result of the recombination of electrons and holes prior to the superoxide activation process [15]. Additionally, surfactants have often been used to increase the photodegradation efficiencies of UV-TiO<sub>2</sub> systems [16,17]. Several attempts have been made to enhance the efficiencies of TiO<sub>2</sub> catalysts using visible light [18–20]. For example, V-doped TiO<sub>2</sub>, which has a band gap of 3.0–3.2, compared with 2.5–2.7 eV for TiO<sub>2</sub>, is a promising visible-light-driven photocatalyst [21,22]. Catalytic systems based on vanadium oxides are highly active and selective for a number of industrially relevant chemical transformations. It has already been established that the catalyst support plays an important role in both the activity and selectivity [23–26]. ZrO<sub>2</sub>-TiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>-TiO<sub>2</sub> composite photocatalysts are examples of mixed metal oxides used in the degradation of chlorophenols [27,28]. This type of catalyst has been thoroughly investigated in the treatment of organic wastewater. Catalysts are usually prepared using sol-gel and hydrothermal methods. There are no reports of photocatalysts for 2,4-dichlorophenol removal prepared by solid-state dispersion. The synthesis of inexpensive, active, and nanosized photocatalysts using simple methods therefore needs to be investigated.

In the present work, binary metal oxide catalysts (V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>) were prepared by solid-state dispersion. 2,4-Dichlorophenol was used as a model pollutant to evaluate the photocatalytic activities of the catalysts under UV irradiation. The effects of the metal oxide ratio and surfactant additives on the photocatalytic efficiency were examined. The catalysts were analyzed using X-ray diffraction (XRD), diffuse-reflectance spectroscopy (DRS), scanning electron microscopy (SEM), Fourier-transform infrared (FT-IR) spectroscopy, and N<sub>2</sub> adsorption-desorption, and the relationship between the catalyst structure and photocatalytic activity was examined.

## 2. Experimental

### 2.1. Materials

The starting materials for catalyst preparation were V<sub>2</sub>O<sub>5</sub> (Merck), TiO<sub>2</sub> P25 (Degussa), ammonium vanadium oxide (Alfa Aesar, 99%), ethanol (absolute), titanium tetrachloride (≥ 99%), TiCl<sub>4</sub> (carbon tetrachloride; Merck), cetyltri-

thylammonium bromide (CTAB; Merck), hexadecyltrimethylammonium bromide (HTAB; Merck), and poly(vinyl alcohol) (PVA; Merck). The organic compounds used in the photocatalytic experiments were 2,4-dichlorophenol, phenol, 4-chlorophenol, 2-chlorophenol, hydroquinone, catechol, and methanol (for high-performance liquid chromatography (HPLC), ≥ 99%); they were purchased from the Fluka Company and used without further purification. Deionized water was used for the preparation of all the catalysts and to dilute the 2,4-dichlorophenol solution.

### 2.2. Catalyst preparation

Pure TiO<sub>2</sub> was prepared using a sol-gel method [29]. TiCl<sub>4</sub> (1.5 mL) was slowly added dropwise to ethanol (15 mL) at room temperature. A large amount of HCl gas was exhausted during the mixing process. The obtained light-yellow solution was gelatinized for several days to form a sol-gel. The gel was dried in an oven at 105 °C for 1 d, ground to a fine powder, and calcined at 600 °C for 4 h.

V<sub>2</sub>O<sub>5</sub>-doped TiO<sub>2</sub> catalysts were prepared using a solid-state dispersion method. V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> samples were mixed in specific weight percentage proportions, namely 10:90, 50:50, 70:30, 90:10; for example, 10V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> denotes the catalyst nominally containing 10 wt% V<sub>2</sub>O<sub>5</sub>. The binary oxide catalysts were dried at 110 °C for 1.5 h, calcined in air at 450 °C for 6 h, and ball milled.

V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> binary oxides and surfactants (CTAB, HTAB, or PVA) were mixed in weight ratios of 1:1 using a solid-state dispersion method. The resultant catalyst was dried at 110 °C for 1.5 h, heated at 150 °C in air for 5 h at a heating rate of 10 °C/min, and ball milled.

### 2.3. Catalyst characterization

The BET surface areas of the samples were determined from N<sub>2</sub> adsorption-desorption isotherm measurements at -196 °C. The samples were degassed at 200 °C prior to the actual measurements.

Powder XRD patterns of the samples were obtained using a Rigaku D/Max-2200 diffractometer with Cu K<sub>α</sub> (λ = 1.540 Å) radiation. Samples were scanned from 10° to 80° (2θ) at a rate of 2°/min. The sizes of the crystalline domains were calculated using the Scherrer equation,  $t = C\lambda/B\cos\theta$ , where λ is the X-ray wavelength (Å), B is the full width at half maximum, θ is the Bragg angle, C is a factor that depends on the crystallite shape (taken to be 1), and t is the crystallite size (Å).

The morphologies and size distributions of the photocatalysts were determined using SEM (JEOL/JSM-6335F).

Samples for FT-IR spectroscopy were prepared as KBr pellets. All spectra were recorded at a 4 cm<sup>-1</sup> resolution and 100 scans were performed. The surface OH groups of the photocatalysts were detected by FT-IR spectroscopy (Perkin Elmer Precisely Spectrum One).

UV-visible (UV-vis) DRS was performed using a UV-vis spectrophotometer (Shimadzu UV-3600), with BaSO<sub>4</sub> as the reference.

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