

## Article

# Photocatalytic degradation of 2,4-dichlorophenol with V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts: Effect of catalyst support and surfactant additives

Eda Sinirtas, Meltem Isleyen, Gulin Selda Pozan Soylu\*

Chemical Engineering Department, Faculty of Engineering, Istanbul University, Avcilar 34320, Istanbul, Turkey

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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<sub>2</sub> 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<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>) was higher than those of pure V<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, and P25. Interactions between V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> affected the photocatalytic efficiencies of the binary oxide catalysts. Cetyltrimethylammonium bromide (CTAB) and hexadecyltrimethylammonium bromide (HTAB) significantly enhanced the efficiency of the 50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> 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 (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-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<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub>.

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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<sub>2</sub> as a semiconductor photocatalyst. TiO<sub>2</sub> 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.

<sup>\*</sup> Corresponding author. Tel: +90-212-4737070; Fax: +90-212-4737180; E-mail: gpozan@istanbul.edu.tr

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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 photoproduced 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 nonmetals, 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  $(V_2O_5-TiO_2)$  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 catalysts structure and photocatalytic activity was examined.

#### 2. Experimental

#### 2.1. Materials

The starting materials for catalyst preparation were  $V_2O_5$  (Merck), TiO<sub>2</sub> P25 (Degussa), ammonium vanadium oxide (Alfa Aesar, 99%), ethanol (absolute), titanium tetrachloride ( $\geq$  99%), TiCl<sub>4</sub> (carbon tetrachloride; Merck), cetyltrime-

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),  $\geq$  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.

 $V_2O_5$ -doped TiO<sub>2</sub> catalysts were prepared using a solid-state dispersion method.  $V_2O_5$  and TiO<sub>2</sub> samples were mixed in specific weight percentage proportions, namely 10:90, 50:50, 70:30, 90:10; for example,  $10V_2O_5$ -TiO<sub>2</sub> denotes the catalyst nominally containing 10 wt%  $V_2O_5$ . 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.

 $V_2O_5$ -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  $N_2$  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  $K_{\alpha}$  ( $\lambda$  = 1.540 Å) radiation. Samples were scanned from 10° to 80° (2 $\theta$ ) 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  $\lambda$  is the X-ray wavelength (Å), *B* is the full width at half maximum,  $\theta$  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  $BaSO_4$  as the reference.

Photoluminescence (PL) spectra were recorded at room temperature using a fluorescence spectrophotometer (Agilent Technologies-Cary Eclipse), with a xenon lamp as the excitation source. The sample was dispersed in ethanol using an ultrasonic bath and the excitation wavelength used in the PL measurements was 530 nm.

## 2.4. Evaluation of photocatalytic activity

Photoactivity studies were performed at atmospheric pressure and room temperature (25 °C). In a typical experiment, the catalyst (100 mg) was dispersed in 2,4-dichlorophenol solution (50 mL) of initial concentration 25 mg/L and neutral pH (pH 5) under magnetic stirring. Phenol photooxidation runs were performed using a cylindrical quartz batch photoreactor. A Luzchem LZC-5 photoreactor system was used in all experiments. The light source was a 64-W UV-B lamp (Luzchem LZC-UVB), with a maximum light intensity at 312 nm and illumination distance 18 cm from the target. The light intensity of the UV lamp used for degradation experiments was recorded using a UV/vis power meter (Smart Sensor-AR823). The photoreactor system had a magnetic stirrer, which was used to achieve uniform conditions in the reaction mixture. Before the UV light was turned on, the solution was stirred for 1 h to ensure good adsorption equilibrium between the catalyst and the solution. After irradiation for 5 h, the 2,4-dichlorophenol solution was filtered through a membrane filter (pore size 0.45 mm) and the filtrate was used for total organic content (TOC) measurements (TOC-V, Shimadzu).

The concentrations of 2,4-dichlorophenol and products were determined using an HPLC (Thermo Finnigan) system equipped with a C-18 column. The mobile phase was a methanol/water (70/30, v/v) mixture at a flow rate of 1 mL/min.

#### 3. Results and discussion

## 3.1. Structures and textural properties of $V_2O_5$ -Ti $O_2$ binary oxides

The BET surface areas of the catalysts are shown in Table 1. The surface areas of the prepared  $V_2O_5$  and  $TiO_2$  are 25 and 40 m<sup>2</sup>/g, respectively. For the  $V_2O_5$ -TiO<sub>2</sub> series, the surface areas decrease with increasing  $V_2O_5$  content. This is because surface coverage by the  $V_2O_5$  particles increases, and this prevents the



Fig. 1. XRD patterns of V<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>,  $50V_2O_5$ -TiO<sub>2</sub>, CTAB-assisted V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>, HTAB-assisted V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> and PVA-assisted V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts.

entry of nitrogen probe molecules. In addition, when CTAB is added to  $50V_2O_5$ -TiO<sub>2</sub>, the surface area decreases 17 to 10 m<sup>2</sup>/g. However, the photocatalytic activity does not only depend on the BET surface area. This point was clarified by a series of detailed experiments.

Fig. 1 shows the XRD patterns of the V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts, and pure V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub>. The diffraction peaks can be indexed to orthorhombic V2O5 (JCPDS 41-1426) and anatase TiO2 (JCPDS 89-4921). No peaks for other phases were detected. The patterns show that the pure V<sub>2</sub>O<sub>5</sub> catalyst consists of an orthorhombic phase and pure TiO<sub>2</sub> has significant peaks from the anatase crystal phase. Orthorhombic V<sub>2</sub>O<sub>5</sub> is the dominant phase in the catalysts prepared using solid-state dispersion, whereas anatase TiO<sub>2</sub> prevails in the catalysts prepared by coprecipitation. XRD confirms the presence of V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> in the composites, confirming the successful introduction of V2O5 onto TiO2. Many studies have confirmed that the photocatalytic activity of anatase-phase TiO2 is higher than those of the brookite or rutile phases [30]. For 50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>, the dominant V<sub>2</sub>O<sub>5</sub> phase is orthorhombic, with some TiO<sub>2</sub> embedded on the V<sub>2</sub>O<sub>5</sub> particles. The phase structure, crystallite size, and crystallinity of V<sub>2</sub>O<sub>5</sub> play important roles in the photocatalytic activity.

Figure 1 shows that the XRD patterns of all the surfac-

Table 1

The crystance sizes, specific surface areas, band gap, not phology of materials and 2,4-dicinorophenor degradation enciencies over 50 mil	The crystallite sizes,	specific surface areas,	band gap,	morphology	of materials and	2,4-dichloropheno	l degradation	efficiencies over	30 min
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Catalyst	V <sub>2</sub> O <sub>5</sub> crystallite size (nm)	$S_{\text{BET}}$ (m <sup>2</sup> /g)	Band gap (eV)	2,4-Dichlorophenol degradation (%)	$k_r (mg/(L \cdot min))$
10V <sub>2</sub> O <sub>5</sub> -TiO <sub>2</sub>	27	22	2.31	60	0.87
50V2O5-TiO2	30	17	2.26	85	1.49
70V2O5-TiO2	33	12	2.24	79	1.19
90V <sub>2</sub> O <sub>5</sub> -TiO <sub>2</sub>	37	8	2.21	75	1.13
(50V2O5-TiO2)-CTAB	35	10	2.21	100	2.22
(50V2O5-TiO2)-HTAB	38	6	2.24	93	1.84
(50V2O5-TiO2)-PVA	42	4	2.26	18	0.12
V <sub>2</sub> O <sub>5</sub>	40	25	2.35	72	1.09
TiO2 (synthesis)	43	40	3.12	66	0.95
TiO <sub>2</sub> (P25)	32	50	3.12	59	0.77

tant-assisted 50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> nanoparticles have similar profiles and all the diffraction peaks can be indexed to orthorhombic V<sub>2</sub>O<sub>5</sub> and anatase TiO<sub>2</sub>. Although all the samples show the same morphologies, the crystallite sizes and relative peak intensities change on addition of a surfactant. The crystallite sizes are 42, 38, and 35 nm for (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-PVA, (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-HTAB, and (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-CTAB, respectively. The size differences may lead to morphological and structural differences [31].

The nanostructural morphology has an important effect on the photocatalytic activity. The SEM images of 50V2O5-TiO2 and surfactant-assisted V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts are shown in Fig. 2. Fig. 2(a) shows a SEM-energy dispersive X-ray spectroscopy (EDS) image of the 50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst. The figure shows that the sample has a mixed morphology consisting of micro- and macro-clusters. EDS analysis indicates the presence of Ti, V, and O on the 50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> surface. The SEM-EDS results clearly show that the synthesized 50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> consists of particles. Fig. 2(b) shows that on CTAB addition the particle morphology changes to rod-like and significant particle interactions occur. However, agglomeration is seen in the SEM photograph of the (50V2O5-TiO2)-PVA and (50V2O5-TiO2)-HTAB catalysts. There are irregular and coarse grains in addition to agglomeration in the morphology of (50V2O5-TiO2)-HTAB. These nanoparticles gradually self-assemble into aggregates with a specific morphology as a result of van der Waals interactions with surfactant molecules adsorbed on the nanocrystal surfaces and the tendency to minimize the interfacial energy [32,33].

The surfactants act as structure-directing agents and can reduce the particle size; therefore, they influence the particle morphology [34]. Surfactants greatly affect the morphology of  $V_2O_5$ -TiO<sub>2</sub>, and the crystal structure, as shown by the XRD results.

### 3.2. Optical properties of V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> binary oxides

The optical absorption properties of a semiconductor, which are related to the electronic structure, are key factors in deter-



Fig. 2. SEM images of (a)  $50V_2O_5$ -TiO<sub>2</sub>, (b)  $(50V_2O_5$ -TiO<sub>2</sub>)-CTAB, (c)  $(50V_2O_5$ -TiO<sub>2</sub>)-HTAB, and (d)  $(50V_2O_5$ -TiO<sub>2</sub>)-PVA catalysts.

mining its photocatalytic activity [35]. The UV-vis DRS spectra of various samples are shown in Fig. 3. The band gaps of the samples were calculated from the onset of the absorption edges to be 2.26, 2.21, 2.24, and 2.26 eV for 50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>, (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-CTAB, (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-HTAB, and (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-PVA, respectively (Table 1). The band gaps are close to each other.

The absorption of visible light by V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts is better than that by TiO<sub>2</sub>. V<sub>2</sub>O<sub>5</sub> loading therefore significantly improves visible-light absorption by TiO<sub>2</sub> photocatalysts. Surfactant addition has a minor impact on the catalyst band gap energy. However, doping of the pure catalyst with a surfactant such as CTAB decreases the absorption wavelength into the visible region. In solution, CTAB, which is a cationic surfactant, ionizes and is selectively adsorbed on the crystal surfaces. This changes the growth rates of different crystal surfaces, and different morphologies are formed [36]. This change in the band gap energy positively affects the photocatalytic activity. (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-CTAB therefore shows strong absorption in the UV region, indicating that this material would show photocatalytic activity under UV irradiation.

Fig. 4 shows the FT-IR spectra in the range 450-4000 cm<sup>-1</sup> for various samples. The samples all have similar FT-IR spectra, indicating that the structures of V2O5 and TiO2 did not change after surfactant loading. The Ti-O-Ti bending vibration at 420-650 cm<sup>-1</sup> confirms the formation of anatase TiO<sub>2</sub>. This is in agreement with the XRD results. The band at 1016 cm<sup>-1</sup> from the V-O (vanadyl oxygen) stretching vibration and the bands at 844 and 580 cm<sup>-1</sup> from O-V-O stretching modes are observed for pure V<sub>2</sub>O<sub>5</sub>. The bands at 1000–1030 cm<sup>-1</sup> represent the O-V-O stretching vibration and the bands at 800-830 cm<sup>-1</sup> due to Ti-O-V linkage [37] was observed for V2O5-TiO2 and surfactant doped V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> nanocomposites. Furthermore, the sharp bands at about 2850, 2918 and 1474 cm<sup>-1</sup> are assigned to the C-H and C=C stretches. The absorption bands at 2918 and 2850 cm<sup>-1</sup> are due to the C-H asymmetric and symmetric stretching vibrations of CTAB and HTAB, respectively [38]. The IR spectra show two intense bands, assigned to asymmetric (2918 cm<sup>-1</sup>) and symmetric (2850 cm<sup>-1</sup>) stretching vibrations of C-CH<sub>2</sub> in methylene chains. The sharp bands in the region 1450–1500 cm<sup>-1</sup> are attributed to deformation of  $-CH_2-$  and -CH<sub>3</sub> [39] of the incorporated surfactants. These results indi-



Fig. 3. UV-vis DRS spectra of  $50V_2O_5$ -TiO<sub>2</sub> and surfactant loaded  $50V_2O_5$ -TiO<sub>2</sub> catalysts.



Fig. 4. FT-IR spectra of 50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> and surfactant loaded 50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts.

cate that the higher catalytic activities of CTAB- and HTAB-doped  $V_2O_5$ -TiO<sub>2</sub> can be attributed to higher concentrations of methylene chains compared with that in pure  $V_2O_5$ -TiO<sub>2</sub>.

Fig. 5 shows the PL spectra of  $V_2O_5$ -TiO<sub>2</sub>, (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-CTAB, (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-HTAB, and (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-PVA. The PL emission is the result of separation and recombination of excited electrons and holes [40]. A lower PL intensity implies decreased recombination, and possibly higher photocatalytic activity [41]. This is reasonable because CTAB and HTAB addition can improve the separation of photogenerated electron-hole pairs and provide faster transport of charge carriers, thereby enhancing the photocatalytic performance [42,43]. As shown in Fig. 5, all the samples exhibited a strong emission peak at around 530 nm. The intensities varied, and those for (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-CTAB and (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-HTAB were much lower than those for the other catalysts. This suggests that the addition of CTAB or HTAB inhibits electron-hole recombination and improves the photocatalytic activity. These results are in good agreement with the activity results.

#### 3.3. Photocatalytic activity

The photocatalytic activities of the samples were investi-



Fig. 5. PL spectra of  $50V_2O_5\mathchar`-TiO_2$  and surfactant loaded  $50V_2O_5\mathchar`-TiO_2$  catalysts.

gated based on degradation of 2,4-dichlorophenol in aqueous solution in the presence of a small amount of  $H_2O_2$  under UV-B irradiation. The reactions follow pseudo-first-order kinetics. The rate constants are listed in Table 1.

In general, the diffusion rate of adsorbed reactive species on the surface is faster than the photocatalytic reaction rate. The photocatalytic reaction is therefore the rate-controlling step. Photocatalytic degradation can be described using the Langmuir-Hinshelwood equation [44]:

$$r = -dC/dt = k_r K_{ads} C/(1 + K_{ads} C)$$

where *r* is the initial reaction rate (mg/(L·min)),  $k_r$  is the Langmuir-Hinshelwood reaction rate constant (mg/(L·min)) and *K* is the Langmuir adsorption constant (L/mg).

Heterogeneous photocatalytic processes involve many steps such as diffusion, adsorption, and reaction. An appropriate pore distribution promotes diffusion of reactants and products, and this favors the photocatalytic reaction [45]. Before the photocatalytic reaction, dark reactions were performed, i.e., in the presence of a catalyst without irradiation, to ensure adsorption-desorption equilibrium. The effects of strongly oxidizing additives such as H<sub>2</sub>O<sub>2</sub> are controversial and depend on the substrate type and various experimental parameters [46]; their usefulness should be carefully checked under the operating conditions. In our case, the highest degradation rate was achieved with addition of 0.15 mL of H2O2. The improved catalytic activity of V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> in the presence of H<sub>2</sub>O<sub>2</sub> is attributed to the reactive radical intermediates (•OH) formed from the oxidants by reaction with photogenerated electrons; these intermediates can themselves act as strong oxidants and as electron scavengers, inhibiting electron-hole recombination at the semiconductor surface. The activities were calculated and are given in Table 1.

The photocatalytic degradation performances of V<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, and V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> binary oxide catalysts in the oxidative degradation of 2,4-dichlorophenol were monitored; the results are shown in Fig. 6. The data in Table 1 show that 72% degradation of 2,4-dichlorophenol was achieved with the pure V<sub>2</sub>O<sub>5</sub> catalyst under UV-B irradiation for 30 min. Under the same conditions, the photodegradation rate was only 66% for the synthesized



Fig. 6. Degradation activities of  $V_2O_5$ ,  $TiO_2$  (synthesis),  $TiO_2$  (P25) and  $V_2O_5$ -TiO<sub>2</sub> catalysts.

TiO<sub>2</sub> catalyst. The 50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst gave the highest percentage of 2,4-dichlorophenol degradation (85%); however, higher weight percentages (70–90 wt%) did not noticeably change the reactivity and the value decreased slightly with further loadings of V<sub>2</sub>O<sub>5</sub>. 2,4-Dichlorophenol degradation decreased to 60% for 10 wt% V<sub>2</sub>O<sub>5</sub> mixed with TiO<sub>2</sub>.

These results confirm that the optimum V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> weight ratio is 1:1. This is because few V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> heterostructures can be formed on the surface when the V<sub>2</sub>O<sub>5</sub> content is too low; when it is too high, excess V<sub>2</sub>O<sub>5</sub> can cover active sites on the TiO<sub>2</sub> surface and few V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> heterostructures are formed. V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> nano-heterostructures with a V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> weight ratio of 1:1 show the highest photocatalytic activity.

The activity of the photocatalyst is influenced by its crystallinity and other factors such as surface area, crystal size, synthetic method, band gap, crystal phase, and surface OH groups.

The activity results show that the surface area, particle size, and surface OH groups are not the only factors that contribute to high reactivity in 2,4-dichlorophenol degradation. The interactions in binary oxide catalysts are more important than the surface area, particle size, and surface OH groups. The optimum photodegradation activity was achieved with 50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>. Our XRD observations clearly show that V interacts with Ti.

The specific surface area decreases with increasing  $V_2O_5$  content (70% to 90%) in the binary oxide catalysts because of TiO<sub>2</sub> pore blockage. In addition, a high  $V_2O_5$  content (70% or 90%) prevents TiO<sub>2</sub> crystallization. The results show that the photocatalytic activity of  $V_2O_5$ -TiO<sub>2</sub> was significantly decreased by high loading with  $V_2O_5$  clusters (70% and 90%). These results are in agreement with those in the Refs. [47,48].

Neppolian et al. [49] reported that electron injection was the major factor in the activities of binary oxide catalysts, along with other physicochemical characteristics. The transfer of electrons from  $ZrO_2$  to  $TiO_2$  through chemical interactions between  $ZrO_2$  and  $TiO_2$  to form Ti-O-Zr- bonds was the main process observed in binary oxide catalysts. Wu et al. [50] described mutual chemical interactions between pure oxides when they were coprecipitated (-Ti-O-Zr-), and this profoundly affected the photocatalytic properties.

In this study, the photocatalytic activity of 50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> was higher than those of nano-TiO<sub>2</sub> (synthesized) and Aeroxide P25. Although the surface area of the 50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst was comparable to or even lower than those of  $TiO_2$  and P25, it showed high activity. However, the changes in surface areas were not as great as these in the catalytic activities; therefore, differences among the activities were associated with the active species on the surfaces. 2,4-Dichlorophenol removal of 59% was achieved with Degussa P25. Various synthesized novel catalysts with higher photocatalytic activities than that of Degussa P25 have been reported. Xu et al. [51-53] investigated the photocatalytic activity of TiO<sub>2</sub> supported on ZSM-5, zeolite A, silica, and alumina in the photooxidations of 4-chlorophenol and acetophenone. The photocatalytic activity of TiO<sub>2</sub>/ZSM5 was higher than those of prepared TiO<sub>2</sub> powder and Degussa P25.

The performance data of modified  $V_2O_5$ -TiO<sub>2</sub> catalysts with various HTAB, CTAB, and PVA loadings are shown in Fig. 7(a).

The data in Table 1 show that CTAB and HTAB loading improved the degradation activity of 50V2O5-TiO2. The photocatalytic performance in 30 min over the prepared catalysts decreased in the order  $(50V_2O_5-TiO_2)-CTAB$  (ca. 100%) >  $(50V_2O_5-TiO_2)$ - HTAB (ca. 93%) >  $(50V_2O_5-TiO_2)$  (ca. 85%) > (50V2O5-TiO2)- PVA (ca. 18%). The (50V2O5-TiO2)-CTAB sample achieved complete degradation in 30 min (Table 1) and gave the highest reaction rate (2.22 mg/(L·min)). One explanation of the results is strong interactions between V2O5-TiO2 and HTAB. Only 18% degradation of 2,4-dichlorophenol was achieved in 30 min with the (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-PVA catalyst. The decrease in the activity can probably be explained by partial blocking of the active species of the V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> binary oxide by large PVA particles. The SEM photograph of V2O5-TiO2 loaded with PVA shows particle agglomeration, which would cause a drop in the photocatalytic activity. These results show that surfactant loading changed the surface areas and particle sizes of the samples.

These observations indicate that the local structure, crystallinity, surface morphology, and particle shape of the  $V_2O_5$ -TiO<sub>2</sub> powder affect the photocatalytic performance. The crystal structure, crystallinity, morphology, and surface area of a material are important factors in its photocatalytic performance [54–56]. The photocatalytic activity results suggest that the enhanced photocatalytic activity of (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-CTAB can be attributed to an appropriate pore distribution and high separation rate of photoinduced charge carriers. The addition of CTAB to the synthesis system not only alters the surface parameters, especially the pore distribution, but also enhances the photoinduced charge separation rate of  $V_2O_5$ -TiO<sub>2</sub>. These results show that the pore distribution and photoinduced charge separation rate both play important roles in promotion of the



**Fig. 7.** (a) Degradation activities of  $50V_2O_5$ -TiO<sub>2</sub> and surfactant-loaded  $50V_2O_5$ -TiO<sub>2</sub> catalysts. (b) TOC removal for photocatalytic degradation of 2,4-dichlorophenol.



Fig. 8. Concentration profiles for intermediates obtained during the photocatalytic oxidation reaction using (a)  $50V_2O_5$ -TiO<sub>2</sub> (b)  $(50V_2O_5$ -TiO<sub>2</sub>)-CTAB.

photocatalytic activity of (50V2O5-TiO2)-CTAB.

Fig. 7(b) shows the TOC removal results for photocatalytic degradation of 2,4-dichlorophenol with  $50V_2O_5$ -TiO<sub>2</sub>, ( $50V_2O_5$ -TiO<sub>2</sub>)-CTAB, ( $50V_2O_5$ -TiO<sub>2</sub>)-HTAB, and ( $50V_2O_5$ -TiO<sub>2</sub>)-PVA. The ( $50V_2O_5$ -TiO<sub>2</sub>)-CTAB sample achieved complete degradation of 25 mg/L 2,4-dichlorophenol and 97% TOC removal in 30 min. These results show that total mineralization was achieved.

The concentration profiles of 2,4-dichlorophenol, 2-chlorophenol, phenol, catechol, and ring-opening products (others) during photocatalytic oxidation using  $50V_2O_5$ -TiO<sub>2</sub> and ( $50V_2O_5$ -TiO<sub>2</sub>)-CTAB are shown in Fig. 8. The intermediate distributions were also compared.

HPLC results showed that 2-chlorophenol, phenol, and catechol were the main intermediate when  $50V_2O_5$ -TiO<sub>2</sub> was used. Ring-opening products (others) were also detected in low concentrations. When CTAB was added to the pure catalyst, the detected concentrations of 2-chlorophenol, phenol, and catechol were low. It was observed that the concentrations of ring-opening products (others) were considerably higher than those of intermediate products when CTAB was used. These intermediates undergo further photocatalytic oxidation to give ring cleavage and yield carboxylic acids and aldehydes, which give CO<sub>2</sub> and H<sub>2</sub>O by decarboxylation.

It should be noted that some structural features of catalysts play a significant role during photocatalysis. These results confirm that (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-CTAB is more active than some other catalysts. These results also indicate that the photochemical reaction is important in the degradation of 2,4-dichlorophenol under these conditions.

## 4. Conclusions

V2O5-TiO2 binary oxide catalysts prepared using a sol-

id-state dispersion method were used in the photocatalytic degradation of 2,4-dichlorophenol under UV-B irradiation. The photocatalysts showed high photocatalytic activities in 2,4-dichlorophenol degradation. The chemical interactions between V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> to form V–O–Ti– bonds affect the photoefficiencies of binary oxide catalysts. The effects of various surfactants (CTAB, HTAB, and PVA) on the photocatalytic degradation of 2,4-dichlorophenol were also investigated. (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-CTAB gave the highest percentage of 2,4-dichlorophenol degradation (100%) and the highest reaction rate (2.22 mg/(L·min)) in 30 min. The catalytic activity of (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-CTAB was higher than those of nano TiO<sub>2</sub> and P25 photocatalysts. The structural, morphological, optical, and photocatalytic properties of the catalyst play a significant role during photocatalysis. In summary, the effectiveness of using a surfactant such as CTAB to construct an efficient visible-light-driven 50V2O5-TiO2 photocatalyst was shown. The local structure and crystallinity significantly affected the photocatalytic performance. The results indicate that the photocatalytic degradation of wastewater containing chlorophenols can be achieved using (50V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-CTAB. Such heterostructured nanocomposites may help in the design of highly efficient photocatalysts for organic compounds, and have potential technological applications.

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(V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-cetyltrimethylammonium bromide (CTAB) was prepared using a solid-state dispersion method. The dispersion of modified (V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>)-CTAB were successfully enhanced. CTAB was innovatively introduced into the system of V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>. This catalyst efficiently degraded 2,4-dichlorophenol under UV-B light.

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