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Full Length Article

Enhanced photo-catalytic activity of TiO_2 films by removal of surface carbon impurities; the role of water vapor

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ABSTRACT

We have studied the photo-catalytic degradation of acetaldehyde over the surface of TiO_2 films under UV light (365 nm) irradiation both at dry and humid air conditions using a high vacuum chamber equipped with on-line gas-chromatography as a batch-type reactor. Changes of TiO_2 surfaces upon the photo-catalysis experiments were studied by X-ray photoelectron spectroscopy. The competitive adsorption of water and acetaldehyde resulted in the reduction of reaction rate of photo-catalytic degradation of acetaldehyde under the UV light irradiation. The photo-catalytic reaction rate of TiO_2 films towards acetaldehyde mineralization increased when the photo-catalysis experiments were performed repeatedly and it was much more pronounced under humid conditions. Our XPS analysis revealed that carbon impurities on the surface of TiO_2 films were removed by UV-light driven photo-catalytic mineralization under humid conditions. Water vapor facilitated the photo-catalytic removal of carbon impurities from TiO_2 surface generating additional active sites of TiO_2 which resulted in the enhanced photo-catalytic activity of TiO_2 films.

1. Introduction

Removal of volatile organic compounds (VOCs) such as formaldehyde and acetaldehyde has been drawing attention, since indoor environments enriched with these molecules as vapor can be harmful to the human-being [1–4]. There are several different strategies to eliminate VOCs from the atmosphere, and one of the most widely used methods is use of high-surface-area adsorbents such as activated carbon [5–11]. Even though use of adsorbent is effective for removal of VOCs, adsorbent has disadvantages; lifetime of adsorbent is limited and saturated adsorbent should be replaced or regenerated. Alternatively, one can use heterogeneous catalysis, which can be semi-permanently used [12–23]. Here, either dark thermal catalysts or photocatalysts can be considered as building-block of VOC removal devices [12–14,24–28].

Photocatalysis uses light and light-harvesting materials to accelerate chemical reactions. When light is absorbed by semiconductive materials, electron-hole pairs can be created, which can interact with O_2 and H_2O to yield strongly oxidizing agents such as O_2^- and OH radicals, which can oxidize organic molecules adsorbed on the surface into CO_2 and H_2O. It is ideal to use solar light, mostly consisting of visible light; however, most of the practically useful photocatalysts (such as TiO_2) exhibits band gaps corresponding to the energy of UV light. Devices consisting of TiO_2-based photocatalysts and UV-light sources can be applied for the air purification; it is particularly worth paying attention that UV light emitting diode (LED) becomes nowadays inexpensive, making such UV-light based photocatalysis more practical [29–35].

It has been widely argued in the literature that humidity can play a pivotal role in photocatalytic activity. On one hand, high humidity can create a larger amount of OH radicals, resulting in high photocatalytic oxidation yield towards VOCs [36–39]. On the other hand, competitive adsorption of H_2O and VOC molecules on the surface can result in reduced photocatalytic oxidation activity upon increased humidity in the atmosphere [40–43]. In the present work, we studied acetaldehyde oxidation driven by UV light and TiO_2 thin film, and the change in the surface structure of TiO_2 was unveiled using photoelectron spectroscopy. We show that H_2O molecules show both positive and negative effects to the photocatalytic oxi-

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dation and acetaldehyde; H_2O competitively adsorb with VOCs and O_2, resulting in decrease in the photocatalytic activity with increasing humidity, however, H_2O is more effective than O_2 in burning carbon deposit impurities on TiO_2 surface, increasing number of active sites of TiO_2.

2. Experimental methods

2.1. TiO_2 films preparation

The film consisting of TiO_2 power (P-25, Degussa) was fabricated by spin-casting of TiO_2-containing isopropyl alcohol (IPA) solution. The TiO_2-containing IPA solution was prepared by dissolving 2 g of the TiO_2 powder in 10 ml of IPA and the TiO_2-containing IPA solution was ultra-sonicated at room temperature for 21 min before the spin-casting process. 1 ml of TiO_2-containing IPA solution was spin-casted on SUS plate with a lateral size of 6 × 6 cm^2 at 3000 rpm for 90 s. Samples were dried at room temperature under dark conditions for 30 min after the spin-casting process. The weights of SUS plates before and after the spin-casting of TiO_2 films were measured using an analytical balance (EL204-IC, Mettler Toledo). The topological and cross-sectional geometric structures of TiO_2 film deposited on SUS plate were characterized by scanning electron microscopy (SEM, JSM-7100F, JEOL).

2.2. Photo-catalytic degradation of acetaldehyde

The photo-catalytic degradation of acetaldehyde over the surface of TiO_2 films on SUS plates was carried out using the vacuum chamber (base pressure of 10^{-5} torr) as a batch-type reactor equipped with an on-line Gas Chromatograph (GC). The entire experimental set-up for photo-catalysis experiments and X-ray photoelectron spectroscopy (XPS) is schematically described in Fig. 1 and the reactor parts are marked with gray dashed line. Two reactors, denoted as reactor S and B in Fig. 1, are connected via a vacuum gate valve. The reactor B is equipped with a vacuum gauge and a gas injection line, which is connected to four gas bottles filled with H_2O, dry air, O_2, and acetaldehyde-containing N_2 (201 μmol/mol) via vacuum leak valves. The composition of the gas mixture in the reactor was monitored using a gas-chromatography (GC, HP 6890 series, Hewlett Packard) equipped with 6-port valve (loop volume: 1 ml). The 6-port valve is connected to the reactor B and S via polytetrafluoroethylene (PTFE) tube. The gas mixture was circulated through the batch-type reactor during the experiments using a diaphragm pump (flow: 7 l/min, DA70EEAC, YLKTECH) connected to the PTFE tube. The total volume of the reactor, including PTFE line is ~5.3 l.

TiO_2 covered SUS plate (6 × 6 cm^2) was placed in the reactor B (base pressure of 10^{-5} torr) and four different gases were injected into the reactor B and S through the leak valves. The amount of each gas injected into the chamber was monitored by a vacuum gauge connected to the reactor B. The load-lock chamber connected to the reactor S is equipped with a quadrupole mass spectrometer (QMS, HAL 201, HIDEN), allowing purity check of each gas. Starting from the high vacuum condition of the reactor, dry air was introduced into the chamber until the pressure of the reactor reached 24 Torr. For the photo-catalysis experiments under the humid conditions, 8 Torr of H_2O vapor was introduced into the chamber prior to the dry air injection. Subsequently, 146 Torr of O_2 gas was introduced into the chamber and finally the chamber was filled with acetaldehyde-containing N_2 gas (201 μmol/mol) until the pressure of reactor reached to 760 Torr. The humidity level of the gas mixture containing water vapor with a partial pressure of 8 Torr (humid condition) corresponds to 33.6 relative humidity (RH) % at room temperature.

The vacuum valves connecting the reactor B to gauge and gas injection line were closed after the aforementioned gas injection process and the diaphragm pump was turned on to circulate and evenly distribute the gas mixture through the whole reactor. After the 30 min of pre-circulation process, 1 ml of gas mixture in the reactor was injected into the on-line GC every 15 min to track the changes of the gas composition in the reactor with time. The GC was equipped with a capillary column (30 m × 0.53 μm, HP-PLOT/Q, Agilent Technologies), a methanizer, and a flame ionization detector (FID). For the photo-catalysis experiments, sample surface was illuminated by UV light (365 nm) through a quartz window port at the top part of the reactor B using a UV lamp (4 W, VL-4.LC, Vilber Lourmat). The UV lamp is specified to provide 3.5 W of UV light (365 nm) per unit area (m^2) at 15 cm-distance from the lamp. The distance between the UV lamp and sample was 8 cm during the photo-catalysis experiments in this work. The UV light (365 nm) intensity on the sample was estimated to be 12.3 W/m^2 based on the fact that the light intensity per unit area of the sample is inversely proportional to the square of the lamp-sample distance [44].

2.3. X-ray photoelectron spectroscopy

The changes of TiO_2 surface structure upon the photo-catalysis experiments were studied using XPS system connected to the reactor S (Fig. 1). TiO_2/SUS plate with a lateral size of 1 × 1 cm^2 was mounted in reactor S for the XPS analysis in addition to the TiO_2/SUS plate (6 × 6 cm^2) placed in reactor B. Smaller sized-TiO_2/SUS plate was prepared by cutting the TiO_2/SUS plate (6 × 6 cm^2) prepared by the aforementioned spin-casting process.

XPS analysis chamber with a base pressure of ~ 4.0×10^{-10} Torr is connected to the reactor S through the load-lock chamber (base pressure ~ 10^{-9} Torr). Each chamber can be separated using an ultra-high vacuum gate-valve. Sample with a later size of 1 × 1 cm^2 was transferred back-and-forth between XPS analysis chamber and reactor S using a magnetic transfer-stick without exposure of samples to the external atmosphere. XPS analysis chamber is equipped with an Al/Mg dual X-ray source and a concentric hemispherical analyzer (CHA, PHOIBOS-Has 2500, SPECS). XPS spectra were obtained using a Mg- Kα (1253.6 eV) at room temperature and the binding energy of XPS spectra was calibrated with a Ag sample (Ag $3d_{5/2}$ at 368.3 eV and $3d_{3/2}$ at 374.3 eV) as well as Ti(IV) 2p peaks of our TiO_2 samples.

3. Results and discussion

3.1. SEM results

Topological and cross-sectional SEM images of the TiO_2 film on SUS plate were taken to investigate the geometric structure of TiO_2 film spin-casted on SUS plate (Fig. 2). The rough TiO_2 film with nano-size pores with a diameter of several hundreds nanometers were formed on the SUS plate by the aforementioned spin-casting procedures (Fig. 2a). The enlarged topological SEM image revealed that individual TiO_2 nanoparticles (~20 nm) were connected to each other without suffering the significant aggregation during the film preparation process (inset of Fig. 2a).

The cross-sectional SEM image of the film was also taken to measure the film thickness on SUS plate (Fig. 2b). Some of TiO_2 film was removed from one side of the SUS plate by wiping the side of TiO_2/SUS plate with an ethanol-wetted tissue prior to taking the cross-sectional SEM image and this corresponds to the left side of Fig. 2b). We estimated the film thickness to be ~7 μm by measuring the height difference between bare and TiO_2 covered SUS plate [45].