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SHORT COMMUNICATION

Large-scale production of titania nano-coated silica-gel beads by fluidized bed chemical vapor deposition

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Abstract−A new technique of thermal fluidized-bed metal-organic chemical vapor deposition (FB-MOCVD) was developed to prepare titania nano-coated silica-gel beads on a large scale (20 kg/batch) at different deposition temperatures of 450, 500, 550, and 600 °C. Titanium tetra iso-propoxide (TTIP, $Ti[OCH(CH_3)_2]_4$, Aldrich Chemical Co.) was used as a precursor of titania. The titania nano-coated silica-gel beads prepared by FB-MOCVD apparatus were hardly breakable compared to other common coating techniques in liquid phase such as sol-gel and dipping method. It was found that, from the FE-SEM/EDXS analysis and XPS results, the surfaces of silica-gel beads were covered with particle forms of titania. The photocatalytic degradation of acetaldehyde into CO_2 and H_2O was not much affected by deposition temperature.

Key words: Fluidized Bed Chemical Vapor Deposition, Photocatalyst, Titania, Nano-coating

INTRODUCTION

We have developed the FB-CVD techniques on a lab-scale [1,2] for the preparation of titania nano-coated beads (i.e., silica-gel beads, alumina beads, glass beads). The fundamental research and application development of the technology could be enhanced by scale-up for large-scale production. The main purpose of the study was to produce photocatalyst nano-coated silica-gel beads on a large scale and at low cost. Those photocatalyst deposited beads could be used effectively for the removal of pollutants in gas and liquid phases.

Volatile organic compounds (VOCs), such as aldehydes, aromatic compounds and chlorinated ethylenes are hazardous pollutants emitted from paints, solvents, industrial facilities, etc. [3] These VOCs become the main sources of environmental pollution in the world [4]. Nowadays, Advanced Oxidation Technologies (AOTs) [5] are researched and developed for air purification and waste water treatment, and photocatalytic degradation of VOCs on UV-illuminated titanium dioxide (TiO_2) is proposed as an alternative AOT [6]. In an ideal photocatalytic mineralization of VOCs, they are oxidized into CO_2 and H_2O (and HCl when the VOC contains chlorine) [7,8].

Fluidized beds have been utilized for several decades in many chemical and environmental industries. One of the most processes with potential is Fluidized Bed Chemical Vapor Deposition (FB-CVD). In this process, each particle is coated with a thin film of a new material, thus changing the properties of particles. FB-CVD is a useful method in catalyst preparation for the improvement of physicochemical properties such as catalytic activity, hardness, and mechanical stability since it deposits nano size particles of the catalytic compound possibly on selective sites of the substrate. This process can uniformly coat metal or metal oxide on small, three-dimensional objects such as beads, powders, fiber, and small pieces of equipment, which is not possible in conventional chemical vapor deposition, because entire surface area is not come out to the activated gas.

Field-Emission Scanning Electron Microscope/Energy-dispersive X-ray spectroscopy (FE-SEM/EDXS) system was used to image the surfaces of titania-coated beads for confirmation of uniform coating. The major chemical compositions of the particle surface were analyzed by X-ray photoelectron spectroscopy (XPS). The photocatalytic activities were evaluated by measuring the change in concentrations of evolved CO_2 under UV lamp in a batch-type reactor.

EXPERIMENTAL

1. Preparation of Titania Nano-Coated Beads

TiO_2 photocatalysts nano-coated silica-gel beads were prepared by FB-CVD method and titanium tetra iso-propoxide (TTIP, Ti[OCH

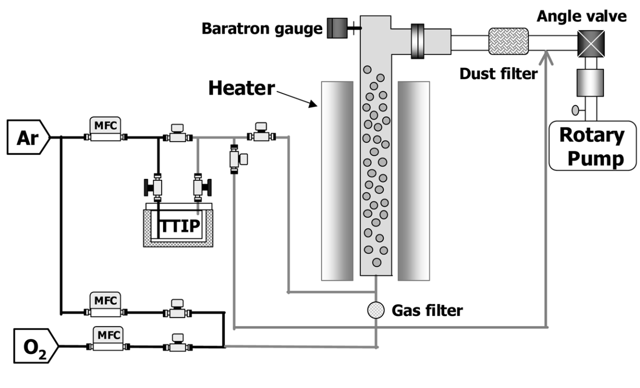

Fig. 1. Schematic of fluidized bed chemical vapor deposition (FB-CVD).

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$(CH_3)_2]_4$, Aldrich Chemical Co.) was used as a precursor of titania. Fig. 1 shows the Fluidized Bed Chemical Vapor Deposition (FB-CVD) apparatus (SUS tube: 200 mm i.d. and 1.3 m height) used for the deposition of titanium dioxide photocatalyst on substrate (silica-gel beads). The fluidizing gas is supplied to the bottom of the riser (In a circulating fluidized bed, the particles leave the riser through a horizontal tube at the top, and are separated from the gas in a cyclone. They are recirculated to the riser through a downcomer and L-valve. The flow rate of the aeration gas to the L-valve is the main parameter to control the solid flux. The gas exit of the cyclone is linked to the vacuum unit.). Mixtures of argon, oxygen and TTIP were fed as reaction gases at vacuum and high temperature conditions. The deposition temperature was the main parameter in the study, and was set to 450, 500, 550, and 600 °C. Temperature and pressure were measured above and bottom of the riser. In the thermal CVD of thin TiO_2 films, TTIP is decomposed in the fluidized bed and reacts with oxygen on the surfaces of substrate to form thin films of TiO_2. The films are deposited on the silica-gel beads and reactor wall. A total mass of 20 kg bead particles was handled per batch.

2. Characterization and Activities of Photocatalysts

FE-SEM/EDXS system was used to image the surfaces of titania-coated particles for the confirmation of thin and uniform coating. The major chemical compositions of particle surface were analyzed by XPS. The photocatalytic activities of the photocatalysts coated on substrates were evaluated by measuring the change in concentrations of evolved CO_2 under UV lamp.

RESULTS AND DISCUSSION

1. Characterization of Photocatalysts

The FE-SEM images of the surfaces of titania nano-coated silica-gel beads prepared by FB-CVD at 500 °C of deposition temperature are shown in Fig. 2 (left). From the photographs, it was found that the surfaces of titania nano-coated on beads were covered with particle forms of titania (tens of nanometers in size). From EDXS analysis, it could be verified that the main chemical component on the surface is titanium dioxide. It is shown in Fig. 2 (right).

The surface atomic compositions of TiO_2 films on silica-gel beads were determined by X-ray photoelectron spectroscopy (XPS), shown in Fig. 3. Binding energy spectra were recorded in the regions of Ti 2p (458.8 eV), O 1s (529.8 eV), and C 1s (284.6 eV) originating

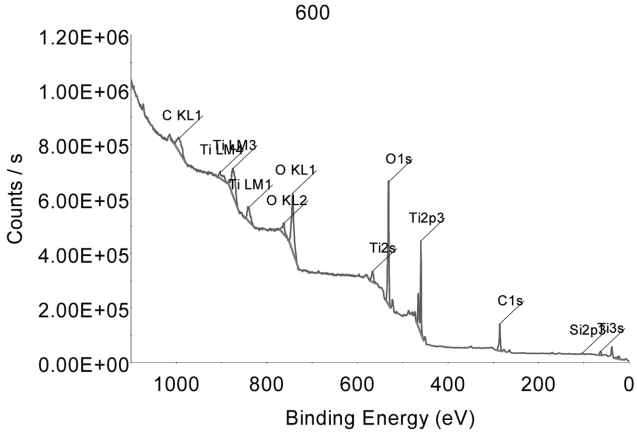

Fig. 3. XPS survey spectra of the TiO_2/silica-gel prepared at deposition temperature of 600 °C.

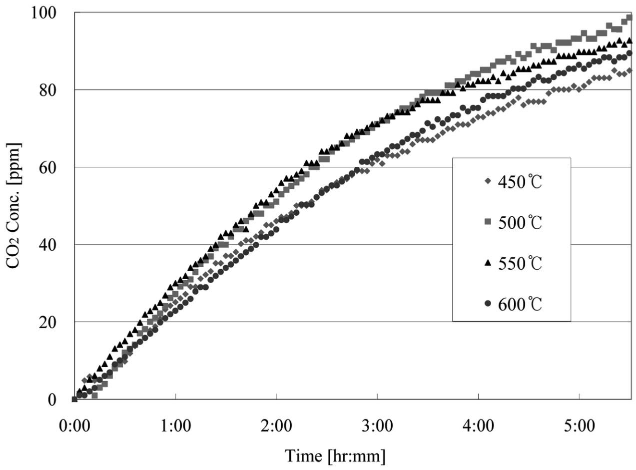

Fig. 4. Photocatalytic activities of TiO_2/silica beads at different deposition temperatures.

from surface impurity carbons.

2. Photocatalytic Activities of Photocatalysts on Beads

In order to investigate the effect of deposition temperature on photocatalytic activities of titania nano-coated silica-gel beads prepared by FB-CVD, photocatalytic decomposition was performed with 100 ppm of acetaldehyde in a batch reactor (16,625 cm^3 inner

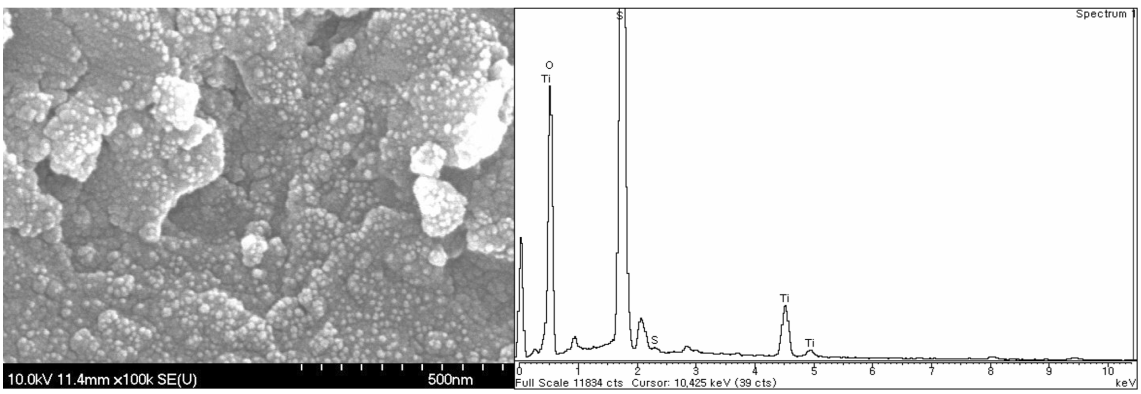

Fig. 2. FE-SEM images of surfaces (left) and EDXS result (right) of TiO_2 on silica-gel beads at deposition temperature of 500 °C.

volume) under UV with CO_2 analyzer. The result is shown in Fig. 4. It was observed that the photocatalytic activities of TiO_2 on silica-gel beads prepared at 500 °C and 550 °C of deposition temperatures were a little higher than those at 450 °C and 600 °C. It is known that the photocatalytic activity of TiO_2 strongly depends on the preparation method and the crystal phase. There are brookite, anatase, and rutile phases in the titania system, among which anatase and rutile are most commonly used as photocatalysts and the crystalline anatase is considered to be the more active form of TiO_2 than rutile. In the case of titania deposited silica-gel beads prepared by FB-CVD, we were not able to identify the crystal phases in XRD analysis due to ultra-thin film of titania. However, in our previous work, crystalline anatase was formed over 400 and the transformation temperature of the deposited titania from anatase to rutile was as high as 600 °C. Therefore, the difference in activity may be due to the phase change from anatase to rutile. However, the difference in activity was too small for us to draw a conclusion. So, it was considered to be due to the experimental error and the deposition temperature did not affect much the photocatalytic activities in the temperature range from 450 °C to 600 °C.

CONCLUSION

Titania was successfully deposited on three-dimensional silica-gel beads on large-scale production (20 kg/batch) by FB-CVD, which was not easy in conventional chemical vapor deposition. The titania nano-coated silica-gel beads prepared by FB-CVD were not easily worn out compared to other common coating techniques such as sol-gel and dipping method, and showed excellent physical properties.

To confirm the even distribution of titania on the surface of silica-gel beads, FE-SEM/EDAX and XPS were used for the analyses and photocatalytic activities in gas phase were studied with acetaldehyde under UV with a CO_2 analyzer. It was observed that the activity of titania on silica-gel beads prepared at different deposition temperatures of 450, 500, 550, and 600 °C showed similar trend and was independent of deposition temperature.

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