Applied Catalysis B: Environmental 203 (2017) 731–739

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Elucidation of structures of surface sulfate species on sulfated titania and mechanism of improved activity

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ARTICLE INFO

Article history:
Received 18 August 2016
Received in revised form 17 October 2016
Accepted 24 October 2016
Available online 25 October 2016

Keywords:
Sulfated TiO_2
Superacid
Sulfate species
Brønsted acid
Lewis acid

ABSTRACT

Sulfated SO_4^{2-}/TiO_2 superacid photocatalysts were synthesized and investigated for their photocatalytic activity and the structures of surface sulfate species. Six structures of sulfate species were elucidated using Fourier-Transform Infrared Spectroscopy. Correlation between the photocatalytic activity and structures of surface sulfate species were studied. The neutral Structures (IV) and (V) promoted the photocatalytic activity for the degradation of organic pollutants in reverse osmosis concentrate (ROC). Structure (II) was inactive. The acidic Structure (I) converted to (IV) when calcined at 600 °C or to (V) when neutralized. Brønsted acid amounts did not correlate to the photocatalytic activity while Lewis acid sites promoted the activity. Sulfated species-bonded Brønsted acid sites and Lewis acid sites and their transformation were observed with pyridine adsorption. Impact of surface area, crystal size and sulfate density on activity was also discussed. Mechanism of improved activity due to neutral sulfate species (IV) and (V) was also proposed. This study sheds some light on the mechanism of improved activity of sulfated photocatalysts and may also provide some clues to mechanism of other superacid catalysts.

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1. Introduction

Reverse osmosis (RO) membrane technology has wide applications in wastewater recovery processes and desalination processes [1]. However, it also produces a certain quantity (15–25%) of reverse osmosis reject, i.e. reverse osmosis concentrate (ROC) [2]. ROC contains an increased amount of effluent organic matter (EfOM). Although EfOM is not considered to be a pollutant, it might be associated with undesirable organic compounds such as natural organic matter (NOM) and endocrine disruptors which limits reuse application. EfOM has been widely studies due to its promotion of membrane fouling [3]. Since ROC is not considered as a pollutant, currently ROC is usually discharged to water bodies, such as rivers, lakes, sea, and so on [4]. Many conventional methods (activated carbon, alum coagulation, air stripping) and advanced oxidation methods (AOPs) have been investigated to purify ROC, while results are still not satisfactory due to harmful by-products, low efficiency, high chemical cost or high capital investment cost [1,3–10]. Recently we reported high activity of internally sulfated TiO_2 photocatalysts for the degradation of organic pollutants in ROC [11–13]. In this study, we further investigated the possible relationship between the photocatalytic activity and the structure of surface sulfate species.

Sulfation has been studied in many solid oxide catalysts, such as ZrO_2, Al_2O_3, SiO_2, Fe_2O_3 and TiO_2 [14–20]. It is known that sulfation creates Brønsted acid sites on the oxide surface. The ring-opening isomerization of cyclopropane is catalysed by Brønsted acids [21]. TiO_2/SO_4^{2-} was used as solid superacid photocatalyst for several substrates, such as ethylene, hexane, methanol, benzene, and trichloroethylene (TCE), etc. [22–25]. Sulfation may improve the catalytic activity from its increased Brønsted acid sites. Sulfation could be usually achieved by impregnating TiO_2 with 0.5 or 1.0 M H_2SO_4 or $(NH_4)_2SO_4$, or treating it with gases SO_2, SO_3 or H_2S and further oxidation with air or O_2 at elevated temperature [14,26]. After sulfation of ZrO_2 or TiO_2, surface Brønsted acid sites were increased which could be part of the reasons for the improved activity [27]. The electron withdrawing O=S=O groups at the surface of sulfated titania might function as electron traps [28]. Sulfation of TiO_2 extended its photocatalytic life and improved its thermal stability till 700 °C although no more SO_4^{2-} content at this temperature [27,29,30]. However, past reports on TiO_2/SO_4^{2-} mainly focused on activity, characterization and Brønsted acid amount but did not address the structures of surface sulfate species and the activity of individual sulfate species. In this study we report the structures of surface sulfate species, the activity of individual

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http://dx.doi.org/10.1016/j.apcatb.2016.10.068
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sulfate species, and the inter-conversion among different sulfate species.

2. Experimental

2.1. Materials

Titanyl sulfate (99.5%, AR), ethanol (95%, Reagent grade), absolute ethanol (99.9%, AR), Degussa P25 TiO_2, pyridine (99.9%, AR) and ammonia 25% (AR) were obtained from Sigma-Aldrich (St Louis, MO). Municipal ROC sample (5 l) was obtained from a Singapore water treatment plant and stored in fridge at 4 °C for all photocatalytic experiments here. Characteristics of the ROC samples were similar to those given in our previous work (see Supplemental Information) [12].

2.2. Preparation of sulfated titania

The sulfated titania photocatalysts were prepared through hydrolysis of $TiOSO_4 \cdot xH_2O$ in ethanol/water solution. In a typical preparation, 4 g of titanyl sulfate was dissolved in 100 ml mixture of ethanol/water and hydrolysed for 6 h, followed by filtration and DI water rinsing. When the ethanol/water ratio was different, the dissolution time need for the 4 g of $TiOSO_4 \cdot xH_2O$ was different. The slurry after rinsing was dried and calcined for 1 h. The synthesis conditions of 8 samples S1 to S8 are listed in Table 1.

2.3. Determination of Brønsted acid amount

The prepared sulfated titania photocatalysts were acidic. Their Brønsted acid amount were determined by titration with 0.05 M NaOH to pH value 7.0 ± 0.2 monitored with a pH meter. In a typical titration, 1.0 g of the catalyst was dispersed in 100 ml of DI water, then 0.05 M NaOH was dropped into the solution with stirring till pH value 6.8–7.2 while the pH value was monitored with a pH meter. After neutralization, the neutralized catalyst was filtered out and dried at 50 °C for overnight and named as S1N, S2N, S3N, S4N, S5N and S6N accordingly.

2.4. Characterization and photocatalytic reactions

The sulfated photocatalysts were characterized by X-ray diffraction (XRD) (Siemens D5005, Munich, Germany), N_2 sorption (Micromeritics ASAP 2020, Norcross, GA), scanning electron microscope (SEM) (JEOL JSM-6701F, Toyko, Japan), transmission electron microscope (TEM) (JEOL 3010, Toyko, Japan), energy dispersive spectroscope (EDS) (JEOL JSM-6701F, Toyko, Japan), UV–vis diffusive reflectance spectroscopy (UV–vis DRS) (Shimadzu 2450, Kyoto, Japan), Fourier transform infrared spectroscopy (FTIR) (IR Prestige 21 spectrometer, Shimadzu, Kyoto, Japan), X-ray photoelectron spectroscopy (XPS) (Omicron analyser EA125 7-channel spectrometer, Taunusstein, Germany), and photocatalytic reactions. Main characteristic properties of the sulfated titania are listed in Table 1. Photocatalytic reactions were conducted with 50 ml of ROC and 0.05 g of catalysts under monochromatic UV 365 nm irradiation (Mercury lamp, 100 W, 18 mW/cm^2, 6.467×10^{15} photons/s ml) for 6 h. Magnetic stirring was applied. Photocatalytic setup was shown in Fig. S1. Details of the photocatalytic setup, ROC sample analysis and catalyst characterization methods were reported in our previous work [11,12]. Before catalyst was added, the ROC sample had a pH value of 6.75. After catalyst was added, the ROC solution had a pH value range of 3.04–4.07 (Table S2, Supplementary data).

2.5. FTIR

FTIR samples were pre-treated at 110 °C for 8 h to get rid of adsorbed moisture. KBr was baked at 130 °C for 24 h. KBr pellet was pressed on a Shimadzu KBr pellet press equipped with a vacuum pump. The powder sample was vacuumed for 5 min and then pressed at 78.5 kn pressure with continuous vacuum for 15 min. Sample concentration in KBr powder was 0.5–1 %wt. Background spectrum was recorded on a pure KBr pellet in air at room temperature (25 °C) and was subtracted from the sample spectrum at the same temperature. The IR spectra were recorded by accumulating 32 scans at a spectral resolution of 4 cm^{-1}.

2.6. Pyridine adsorption

Pyridine adsorption experiments were conducted to probe the Brønsted and Lewis acid sites on the sulfated titania. A typical procedure was as below: a grinded powder sample (sulfated titania photocatalysts and KBr) was heated at 110 °C for 8 h and then transferred to a vacuum chamber (0.01 Torr or 1.33 Pa) for 16 h, pyridine adsorption was carried out at ambient temperature by allowing a large pyridine dose (10 Torr or 1333 Pa) over the vacuumed sample, and then evacuating at the same temperature to remove the excess pyridine after 30 min of adsorption. Finally the powder sample with adsorbed pyridine was pressed into a pellet as described in Section 2.5 for FTIR analysis.

3. Results

3.1. Photocatalytic activities of SO_4^{2-}/TiO_2

3.1.1. Photocatalytic degradation of organics in ROC

The prepared SO_4^{2-}/TiO_2 photocatalyst samples S1 to S8 were anatase phase with an average crystal size of 4–13 nm, band gap of 3.13–3.26 eV and S content of 1.38–15.76 %wt (Table 1). Four samples (S1, S2, S3 and S8) had higher photocatalytic activity than that of Degussa P25 for the degradation of organic pollutants (mainly natural organic matters (NOM), pharmaceuticals, surfactants, etc.) in ROC (Fig. 1a). However, the other 4 catalysts S4 to S7 were not as good as P25. Among these catalysts, S8 performed the best.

3.1.2. Impact of S content, pH value, crystal size and surface area

The photocatalytic performance was closely, although nonlinearly, related to the sulfur content in the catalysts (Fig. 1b). The catalysts with less S contents had better performance while those with higher than 6% S content (i.e. S4, S5, S6, S7) had low photocatalytic activities.

pH values after catalysts were dispersed in the ROC samples could have some impact on the photocatalytic activities. As shown in Table S2, after sulfated catalysts (S1-S8) were added pH values of the ROC samples dropped from 6.75 to a range of 3.04–4.07. Based on our studies (unpublished data), at pH values of 2.5 and 10.6 degradation of Rhodamine B with TiO_2 were slightly faster than that at neutral pH of 6.3, and at pH 4.2 degradation rate of Rhodamine B with TiO_2 was very close to that at pH 6.3. Therefore, impact of the pH range of 3.04–4.07 on the photocatalytic activities of sulfated TiO_2 should be negligible. In addition, after catalyst neutralization activities of sulfated TiO_2 photocatalysts were improved, which also indicated little activity contribution from the lower pH range of 3.04–4.07.

Photocatalytic activities of the evaluated TiO_2 photocatalyst samples reached maximum with the crystal size of around 12 nm (Fig. 2a). Below 12 nm, the activities became lower due to higher chance of recombination of photogenerated electrons and holes. Above 12 nm, the activities also became lower due to the less photogenerated electrons and holes per crystal unit cell. However, there

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