Sulfate-promoted Titania Photocatalyst for High Efficiency Gas Phase Toluene Degradation

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A regenerable, halide-free, sulfate-promoted titania photocatalyst was developed for the high-efficiency, room temperature gas phase photodegradation of toluene at higher than trace concentrations.

We report on the use of a halide-free sulfate promoted titania photocatalyst for the high efficiency room temperature photodegradation of gaseous toluene at high concentration level under a continuous flow stream. The use of sulfated TiO_2 was recently reported as being non beneficial for the gas phase toluene oxidation,[1] but a more systematic control of the synthesis is reported here and resulted in a higher efficiency.

Within the target to meet strict anti-pollution legislation required by the environmental pressure, the photocatalytic oxidation is very promising for the purification of contaminated wastewater containing organic pollutants and the removal of air contaminants at room temperature.[2] Its application to gaseous toluene only leads to moderate conversions with apparent deactivation.[3,4] A recent approach consists of adding chloride at the TiO_2 surface by HCl pretreating, leading to highly reactive and oxidizing chlorine radicals which act in the same way as OH• radicals and thus react with adsorbed aromatics.[4] However, the benefit is only effective for low concentrations (ca. 14 ppm, i.e. 50 mg/m^3) and during the very early stage of the process, depletion of chloride radicals occurring on stream.

Sulfated titania (SO_4^{2-}–TiO_2) catalysts are prepared following the two-step method used by Arata for sulfated oxides.[4] It consists first of the sol–gel preparation of an amorphous $Ti(OH)_4$ hydroxide by putting the $Ti[OCH(CH_3)_2]_4$ precursor into water and ethanol at a basic pH, kept at 9 by dropwise addition of ammonia. After drying overnight at 22 °C and further at 110 °C, the hydroxide is sulfated by sulfuric acid in water (0.25–5 M concentrations using 1.5 mL for 1 g of solid) and then calcined in air between 400 and 800 °C for 5 h.

For a 0.5 M sulfation solution, Figure 1 shows a maximum of surface sulfation for materials calcined at 500 °C, the S/Ti atomic surface ratio being determined by XPS. Atomic absorption spectroscopy showed a content in sulfate species of 3.5 wt % in agreement with thermal gravimetry analysis (TGA), which displayed a similar total weight loss in air starting at 550 °C and instability of sulfate species at temperatures higher than 550 °C (not shown). Higher calcination temperatures led to a decrease in the S/Ti atomic surface ratio down to zero at 800 °C, due to progressive desulfation of the catalyst. Performing Ar^+ bombardment on 0.5 M-sulfated-titania led to remove the top-layers and resulted in a drastic decrease in the S/Ti atomic surface ratio down to zero, proving the exclusive surface location of SO_4^{2-} species.

A maximum in BET surface area was obtained for a calcination temperature of 500 °C, i.e. 117 m^2/g, together with an anatase mean particle size of 14 nm. Higher calcination temperature led to a drastic decrease in surface area down to 8 m^2/g with a strong increase in the particle size, corresponding to the material sintering. By contrast, a low calcination temperature (e.g. 400 °C) resulted in a low surface area of 49 m^2/g with no difference in the particle size, which could be attributed to the low cristallinity of the sulfated material with a different pore structure. Indeed, incorporation of sulfates into oxides has already been reported to delay its crystallization compared to non-sulfated materials.[5] Sulfation of titania shifted towards higher temperatures the anatase → rutile phase transition, as rutile phase appeared after calcination at 600 °C on similar sulfate-free sol–gel TiO_2[6] compared to 800 °C for SO_4^{2-}–TiO_2, in agreement with the work of Colon et al.[7] Inset of Figure 1 shows the increase in S/Ti atomic surface ratio with increasing the sulfation solution molarity, following a non-linear behavior from 0.1 to 0.2 as a function of the molarity, whereas the overall sulfate content increased from 2.5 to 21 wt %. This behaviour is characteristic of SO_4^{2-}–TiO_2 with strong sulfate surface anchorage at low concentration, and for which complete bulk sulfation requires a high molarity solution as reported by Ecormier et al. for SO_4^{2-}–ZrO_2.[8] Low molarity led exclusively to surface sulfation, while increasing the molarity solution led progressively to the formation of polysulfates and finally to bulk sulfation as supposed with the 5 M-sulfated sample, for which no drastic decrease in the S/Ti atomic surface ratio was observed after Ar^+ bombardment compared to low molarity sulfation solution materials. The

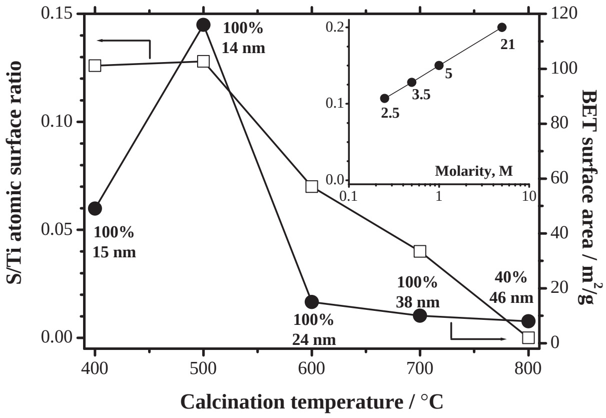

Figure 1. Influence of the calcination temperature of 0.5 M-sulfated-titania on the S/Ti atomic surface ratio (●), the BET surface area (□), the mean particle size derived from the XRD peak broadening using the Scherrer calculation and the anatase molar content in wt % of the resulting materials. Inset: influence of the sulfation solution molarity on the S/Ti atomic surface ratio (●) and the overall sulfate content in wt %. (indicated below the points) for a calcination at 500 °C.

0.5 M-SO_4^{2-}–TiO_2 catalyst calcined at 500 °C can thus be seen as a high surface area partially sulfated material with strong sulfate anchorage and a S/Ti atomic surface ratio of 0.128.

Photocatalysis was conducted in a cylindrical concentric tubular photoreactor.[9] The reactant mixture flows between the internal and the external concentric tubes, set 4 mm apart. Illumination is provided by a 8-W black light tube located inside the inner tube of the reactor. 440 mg of photocatalyst is evenly coated on the internal side of the external tube by evaporating a catalyst-containing aqueous slurry to dryness. The toluene content is set at ≈110 ppm (≈400 mg/m^3), with a relative humidity ratio of 30%[9] in 200 cm^3/min flowing air. Before photocatalysis, the catalyst is exposed to the polluted air stream with no illumination until dark-adsorption equilibrium is reached. Afterwards the UV illumination is switched on. The on-stream efficiency of SO_4^{2-}–TiO_2 depending on the calcination temperature and the sulfation solution molarity were compared to the widespread commercial TiO_2 P25 (Degussa) in Figure 2.

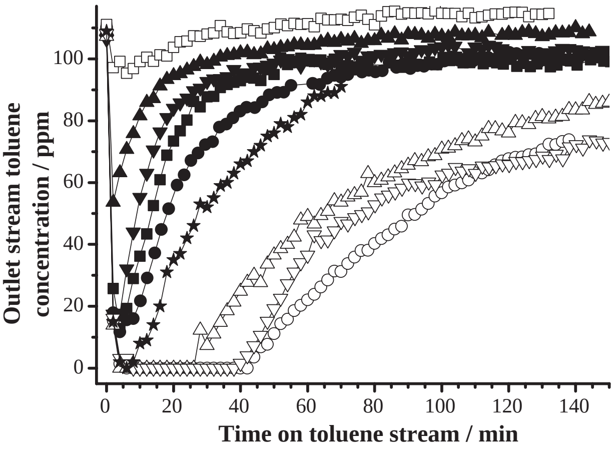

Figure 2. Photocatalytic activity in terms of outlet toluene concentration as a function of time on stream over the commercial Degussa P25 reference catalyst (■), sol–gel TiO_2 (★) and 0.5 M-sulfated titania catalysts calcinated at 400 (●), 500 (○), 600 (▼), 800 °C (▲), and SO_4^{2-}–TiO_2 calcinated at 500 °C using 0.25 M (△), 1 M (▽) and 5 M (□) solutions.

P25 titania only reached 90% of conversion and was rapidly deactivated on stream. The SO_4^{2-}–TiO_2 catalyst shows the best efficiency for a 0.5–1 M sulfation solution molarity and a calcination temperature of 500 °C, with total conversion during 42 min before deactivation, while a bare sulfate-free sol–gel TiO_2 method showed lower performances. Sulfated and non-sulfated TiO_2 are deactivated due to sp^2-bound carbon by-products/intermediates such as benzaldehyde and benzoic acid remaining strongly adsorbed on the TiO_2 surface after the reaction (not shown FTIR), as reported by Marci et al.[10]

Taking into account the surface area of the 0.5 M-SO_4^{2-}–TiO_2 calcinated at 500 °C and the saturation coverage of sulfate species of 2.4 * 10^{18} atom/m^2,[11] the sulfate equivalent monolayer coverage corresponds to 4.4 wt % SO_4^{2-}. Thus, the optimum efficiency photocatalysts correspond to a near monolayer surface coverage of the TiO_2 surface by SO_4^{2-} species, the 0.5 M- and 1 M-SO_4^{2-}–TiO_2 corresponding to 3.5 and 5 wt % SO_4^{2-} respectively. Lower and higher coverages, obtained by varying the sulfation solution molarity decreased the toluene removal efficiency, indicating that a partial sulfation of TiO_2, i.e. the presence of TiO_2 and well-dispersed SO_4^{2-} with optimized contact between SO_4^{2-} and TiO_2 domains, is required for obtaining a high efficiency. The main role of TiO_2 is the reactant adsorption, the band gap excitation and the transformation, while the sulfates could play a double role: (i) better desorption of the e$^-$-rich sp^2-bound carbon aromatic poisons on the e$^-$-rich sulfates, thus limiting deactivation; (ii) positive electron trap effect[12] hindering the e$^-$-hole recombination which is one of the most limiting photocatalytic factors, thus increasing the photocatalytic efficiency. Sulfating TiO_2 already led to an electron transfer from bulk TiO_2 to sulfate, causing a delocalisation and a new electron distribution on the TiO_2 surface.[13] An irreversible shift in Ti_{2p} binding energies for SO_4^{2-}–TiO_2 under the XPS electron beam confirmed that sulfation induced an irreversible charge transfer. A similar electron trap effect was observed on WO_3/TiO_2.[9] Excessively high SO_4^{2-} surface coverage decreases the number of TiO_2 surface sites available for the reaction while a low SO_4^{2-} content reduces the connection between sulfated and non-sulfated TiO_2 zones, and thus limits both positive roles. The optimum calcination temperature of 500 °C can result from the highest surface area and a good cristallinity, obtained without desulfation of the material, thus leading to higher adsorption capacity and photoefficiency.

The stability in air of the sulfates at the TiO_2 surface up to 550 °C (not shown TG-DTA) allowed regeneration of the photocatalyst to be performed by combusting into CO_2 in air for 2 h at 450 °C the strongly adsorbed sp^2-bound carbon intermediates, without destroying the sulfate-containing surface and modifying the anatase-to-rutile ratio.

We think that the halide-free sulfated TiO_2 catalyst is thus a regenerable and highly efficient alternative for improving the on-stream gas phase toluene photodegradation for which the commercial TiO_2 and other alternatives lack of efficiency.[4]

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