



Combined TiO₂/SiO₂ mesoporous photocatalysts with location and phase controllable TiO₂ nanoparticles

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ABSTRACT

Combined TiO₂/SiO₂ mesoporous materials were prepared by deposition of TiO₂ nanoparticles synthesised via the acid-catalysed sol–gel method. In the first synthesis step a titania solution is prepared, by dissolving titaniumtetraisopropoxide in nitric acid. The influences of the initial titaniumtetraisopropoxide concentration and the temperature of dissolving on the final structural properties were investigated. In the second step of the synthesis, the titania nanoparticles were deposited on a silica support. Here, the influence of the temperature during deposition was studied. The depositions were carried out on two different mesoporous silica supports, SBA-15 and MCF, leading to substantial differences in the catalytic and structural properties. The samples were analysed with N₂-sorption, X-ray diffraction (XRD), electron probe microanalysis (EPMA) and transmission electron microscopy (TEM) to obtain structural information, determining the amount of titania, the crystal phase and the location of the titania particles on the mesoporous material (inside or outside the mesoporous channels). The structural differences of the support strongly determine the location of the nanoparticles and the subsequent photocatalytic activity towards the degradation of rhodamine 6G in aqueous solution under UV irradiation.

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1. Introduction

TiO₂ is one of the most studied photocatalysts, because of its low cost, high photocatalytic activity and chemical/photocorrosion stability under reaction conditions [1]. TiO₂ can be used as heterogeneous photocatalyst for water or air purification [2–4]. For a heterogeneous catalyst it is important to have a high surface area, with a high number of reactive sites. Therefore researchers often use TiO₂ with small particle sizes, leading to a high surface area and photocatalytic activity. The industrial interest for this material is however limited, because it is difficult and expensive to separate the catalyst from the liquid or gas. Therefore, a lot of research is done to increase the surface area of the TiO₂ catalyst without decreasing the particle size in order to easily separate and reuse the photocatalyst. The scientific research in this field can be divided into two classes: (1) On one hand researchers attempt to make TiO₂ itself mesoporous, similarly to mesoporous silica

materials. Nevertheless, the high hydrolysis and condensation rates of Ti- precursors make it difficult to prepare mesoporous titania. When the high reactivity of the Ti-precursor is not tempered, synthesis will lead to ill-defined mesoporous structures. There are a lot of possibilities to control the reactivity of the precursor: working in non-aqueous solvents, using a complexed titania precursor or working in strong acidic medium [5–7]. A second problem in making TiO₂ mesoporous, is the phase transformation that could happen upon calcination, necessary to remove the surfactant. Therefore the mesostructured material should be stabilised before calcination: modification with NH₃, NH₄OH or NaOH can be executed to increase the thermal stability of the synthesised materials [8–11].

(2) On the other hand, a silica material can be activated with titania. The activation can be carried out immediately, during the formation of the silica material (in-situ activation). This way, combined TiO₂/SiO₂ materials, like aerogels [12–18], films [19,20] and mesoporous materials (MCM-41, MCM-50 and SBA-15) [21–26] have already been prepared. Irrespective of the type of material, the reactivity of the Ti- and Si-precursor have to be adjusted to each other. Most of the times, the Si-precursor is

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prehydrolysed, before the Ti-precursor is added. The reactivity of the Ti-precursor is tempered by adding extra organic complexators, like acetylacetone or a surfactant [12,13,19,20]. The hydrolysis of the Ti-precursor can also be adjusted by a careful pH-control. The pH can be controlled by using urea, which is decomposed upon temperature increase, resulting in an elevated pH [23,24]. Another method to adjust the reactivities of the precursors is by first preparing an inverted microemulsion of TiO₂ particles, which are then used in the preparation of combined TiO₂/SiO₂ materials like MCM-41, MCM-50 and SBA-15. Depending on the applied Ti-precursor, different crystalline TiO₂ phases can be formed [22]. For in-situ synthesis methods, the anatase formation is influenced by the SiO₂ content and the calcination temperature. Therefore, anatase is not always present, which implies that in some cases the materials are not suited as catalyst for photocatalytic degradation reactions [23,24,27].

A second way to produce SiO₂/TiO₂ materials is to introduce TiO₂ in a pre-synthesised silica support by applying post-synthesis methods. Here, the SiO₂ support material is first prepared and then loaded with TiO₂. Commercial SiO₂ [28,29], β -zeolite [30], clays [2,3,30,31], SiO₂ spheres [32,33] and ordered SiO₂ materials, like MCM-41 [1] and SBA-15 [1,34–39] have already been activated with TiO₂. The TiO₂ loading can be varied ranging from 3 to 80 wt% [1,28,30]. Different post-modification methods have been described in literature to deposit crystalline TiO₂ on different supports: acid-catalysed sol-gel method [29,30], chemical solution deposition [40], internal hydrolysis [40] or multistep deposition [37,38,41]. By post-modification of porous materials, titania can be situated at different places in the porous network: the particles can be inside or outside the porous channels, whereby possible blocking of the pores occurs [42]. Nevertheless, many studies are not so detailed. Some studies do not even determine the amount of effectively deposited TiO₂ [1,34]. The discussion of the position of the TiO₂ nanoparticles (in- or outside the mesoporous channels) is often lacking or interpretation of data is incomplete [1,34,36]. However it is important to know the position of the TiO₂ nanoparticles towards applications. If the TiO₂ photocatalyst will be incorporated in e.g. wall paper or textile for the goal of air purification such as elimination of indoor odours and pollutants, it is important that the TiO₂ particles are located solely inside the mesoporous structure, so that the outer surface of the TiO₂ particles remains inactive. This way, the degradation of the colour of the wall paper and textile upon illumination with UV-light is prevented. So, the wall paper or textile can be used as catalyst themselves, to degrade air components.

In this article two different SiO₂ materials (SBA-15 and MCF) will be modified by post-synthesis deposition based on the acid-catalysed sol-gel method. The amount of Ti-precursor and the temperature at which the particles are formed and deposited will be varied. Special attention will be paid to the location of the TiO₂ particles in the mesoporous structure and the influence of its location on the photocatalytic activity of the material. The importance of the type of support will be demonstrated.

2. Experimental

2.1. Synthesis

2.1.1. Support

For the synthesis of the mesoporous SiO₂ supports (SBA-15 and MCF), the triblock copolymer P123 (EO₂₀PO₇₀EO₂₀, Aldrich) was used as structure directing agent and tetraethyl orthosilicate (TEOS, 98%, Acros Organics) as silica source. SBA-15 was synthesized according to the procedure described earlier by Van Bavel et al. [43]. 4.0 g of Pluronic P123 was dissolved in 150 mL

1.6 M HCl. Subsequently, 9.14 mL of TEOS was added. The obtained suspension was stirred at 45 °C for 8 h and then aged at 80 °C for 15 h. Afterwards the solid product was filtered, washed with distilled water and dried.

The synthesis method of MCF was based on the method, reported by Schmidt-Winkel et al. [44]. 4.0 g of Pluronic P123 was dissolved in 150 mL 1.6 M HCl solution at 35–40 °C. Then, 46.7 mg NH₄F and 2 g 1,3,5-trimethylbenzene (mesitylene, 99% Acros) were added and vigorously stirred for 1 h. Subsequently, 9.14 mL of TEOS was added. After 20 h stirring at 35–40 °C, the slurry was transferred into an autoclave and aged at 100 °C for 24 h. The obtained precipitate was filtered, washed with distilled water and dried.

2.1.2. Post-modification

Prior to modification of the supporting materials, the samples were calcined at 550 °C with a heating rate of 1 °C/min and an isothermal period of 6 h. The post-modification of these supporting materials is based on the acid-catalysed sol-gel method of Battacharyya et al. [30]. Different amounts of Ti-isopropoxide (TTIP) (Ti(OⁱPr)₄, 97% Aldrich), ranging from 0.6 mL to 7.4 mL, were added gradually to 30 mL of an aqueous 1 M HNO₃ solution under continuous stirring for 2.5 h. Subsequently, the colloidal solution was diluted with 50 mL of water and the pH was adjusted to 3 with 1 M NaOH. At pH 3, there is an electrostatic interaction between the positively charged TiO₂ particles and the negatively charged SiO₂ support. Then, 0.5 g of the supporting material (SBA-15 or MCF) was added and the mixture was stirred for 2 h at room temperature. The obtained catalyst was separated by centrifugation, washed with water and dried. Finally, it was calcined at 300 °C for 6 h, with a heating rate of 1 °C/min.

2.2. Characterisation

For all samples, the surface area and the porosity were determined by a Quantachrome Autosorb-1-MP automated gas adsorption system. Prior to N₂-sorption, all samples were degassed at 200 °C for 16 h. The N₂-sorption was carried out at liquid nitrogen temperature (–196 °C). The specific surface area was calculated using the Brunauer-Emmet-Teller (BET) method. The pore size distribution was determined from the adsorption branch using the Barret-Joyner-Halenda (BJH) model. The total amount of N₂ adsorbed at $p/p_0 = 0.95$ was used to estimate the total pore volume.

X-ray diffraction (XRD) measurements were carried out on a PANalytical X'Pert PRO MPD diffractometer using filtered CuK α radiation. Measurements were done in the 2 θ mode using a bracket sample holder with a scanning speed of 0.04°/4 s continuous mode.

The titania loading was determined with electron probe microanalysis (EPMA). The measurements were carried out on a JEOL JXA-733 apparatus.

High angular annular dark field-scanning transmission electron microscopy (HAADF-STEM) images were recorded using a JEOL 3000 F operating at 300 kV.

2.3. Adsorption and catalysis

For all catalysts, the adsorption and catalytic activity were investigated. Therefore, the rhodamine 6G concentration (initial concentration 0.00004 M) was measured at distinct time intervals by means of UV-vis spectroscopy (thermo-electron evolution 500). 0.32 mg catalyst per mL dye solution was used in all experiments. For the adsorption and catalysis experiment, 50 mL resp. 25 mL dye solution with 16 mg resp. 8 mg of catalyst was used. The

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