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Synthesis and characterisation of novel titania impregnated kaolinite nano-photocatalyst

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ABSTRACT

Nano-sized titanium dioxide (TiO_2) has received a great attention in the field of research and development as a promising photocatalyst to promote the degradation of organic contaminants in water. One of the key technical challenges involved in separation and recovery of the photocatalyst particles from the water treatment system makes this technology unviable as an industrial process. A novel titania impregnated kaolinite (TiO_2/K) photocatalyst was synthesized by a modified two step sol–gel method: hydrolysis of titanium(IV) butoxide and heterocoagulation with pre-treated kaolinite (K) clay. The TiO_2/K photocatalysts were characterised using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and BET specific surface area measurements (BET). The photocatalytic activity was evaluated by the degradation of Congo red in aqueous solution. The TiO_2/K photocatalyst had a rigid porous layer structure and promising nano-size properties, and demonstrated an enhanced adsorption and photocatalytic ability for the removal of Congo red. The TiO_2/K photocatalyst can be easily separated and recovered from the water treatment system. The TiO_2/K photocatalyst is expected to deliver a true engineering solution for an industrial water/wastewater treatment process.

1. Introduction

Heterogeneous photocatalysis employing nano-sized titanium dioxide (TiO_2) has been an attractive research and development subject in water treatment owing to its proven capability in the degradation of bio-recalcitrant organic contaminants [1–9]. The high specific surface area (SSA) of the photocatalyst as a result of its nanometer size has rendered its high efficiency in degrading indiscriminately any organic contaminants [10–12]. However, there are still some technical challenges that impede this novel technology towards large scale implementation. One of the most prominent challenges is the post separation and recovery of the photocatalyst particles after water treatment due to the very fine particle size and hence the reusability of the particles [1–3,6]. It was reported that the small size (4–30 nm) of the TiO_2 (Degussa P25) can easily form aggregates in suspension, resulting in a significant reduction in both its effective surface area and photocatalytic efficiency [3].

In recent years, numerous researches have been devoted in searching for the suitable substrates that could be used as an immobiliser to alleviate the problems involved in the post separation and aggregation. The immobiliser substrates, including glass matrix, Raschig rings, fibre optics, silica, stainless steel plates, synthetic membranes, and clay minerals were used in a number of investigations [9,13–17]. Direct coating of the TiO_2 on the internal surface of the photoreactor has been studied [18,19]. The selection criteria for an ideal substrate for the immobilised-catalysts seem to be a compromise of one another and depend on the reactor configuration. For instance, inorganic immobilisers such as clay minerals (i.e., zeolites and montmorillonite) are meant for application in suspension reactor system, while stainless steel plates and membranes are suitable for continuous operation processes.

TiO_2 supported on inorganic clay minerals has received wide attention. The natural structure and adsorption ability of the clay materials can maintain large SSA, stability and consequently enhance the photocatalytic efficiency of the photocatalysts [1,3,6,13,20–23]. This is because the photocatalytic reaction occurs on the particles surface through the generated hydroxyl radicals ($OH^{\cdot}$). The enhanced adsorption provided by the clay minerals could direct more contaminants to the surface of the particles prior to photocatalysis. Therefore, the selection for the suitable clay minerals is the key step for the success in developing the immobilised-catalysts.

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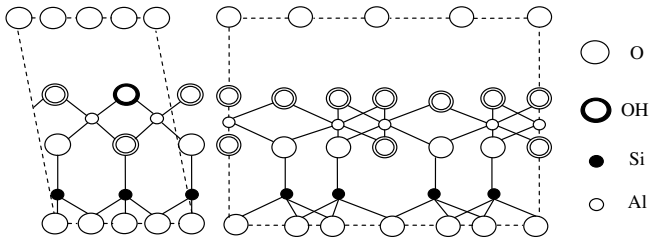

Fig. 1. The crystal structure of kaolinite, viewed on the left hand side along *b*-axis and on the right hand side along *a*-axis. The *c*-axis is vertical. (Reproduction from Barrer [3]).

The physical properties of the immobilised-catalysts used in the suspension reactor system have to be considered. For instance, montmorillonite shows a high capability in adsorption. However, the clay minerals may be swelled rapidly in the suspension system, resulting in particle sedimentation and poor hydrodynamics in the photoreactor [3,13,24,25].

In this work, Australian kaolinite (K) clay was used as the TiO_2 immobiliser. K (Fig. 1) belongs to the kandites mineral group and is a clay mineral with the chemical composition of $Al_2Si_2O_5(OH)_4$ [26,27]. It is a layered silicate mineral with one layer of octahedral, which reacts with one sheet $(Si_2)_3(OH)_2)_n$, resulting in a two-layer sheet structure [24,27]. The siliceous side of K presents a surface of oxygen, while the aluminous side provides a surface of hydroxyl groups. These double layers are then stacked upon one another with the –OH groups of one such sheet against the oxygen of the next sheets [28]. The interaction between the stacked layered in K are bonded covalently to each other, rather than Van der Waals or electrostatic forces [24]. This interaction force makes K suitable as a structurally rigid substrate for supporting and immobilizing the TiO_2. The strong interaction forces make the immobilized particles chemically stable from swelling and can endure high temperature of up to 950 °C (Fig. 2). To our knowledge, no investigation using the K clay as an inorganic support for TiO_2 in photocatalysis was reported in the literature.

This study was to synthesize a novel titania impregnated kaolinite (TiO_2/K) nano-photocatalyst through a modified two step sol–gel method. A series of tests were carried out to characterise the surface properties of the prepared photocatalyst. The photocatalytic ability was evaluated through the degradation of Congo red

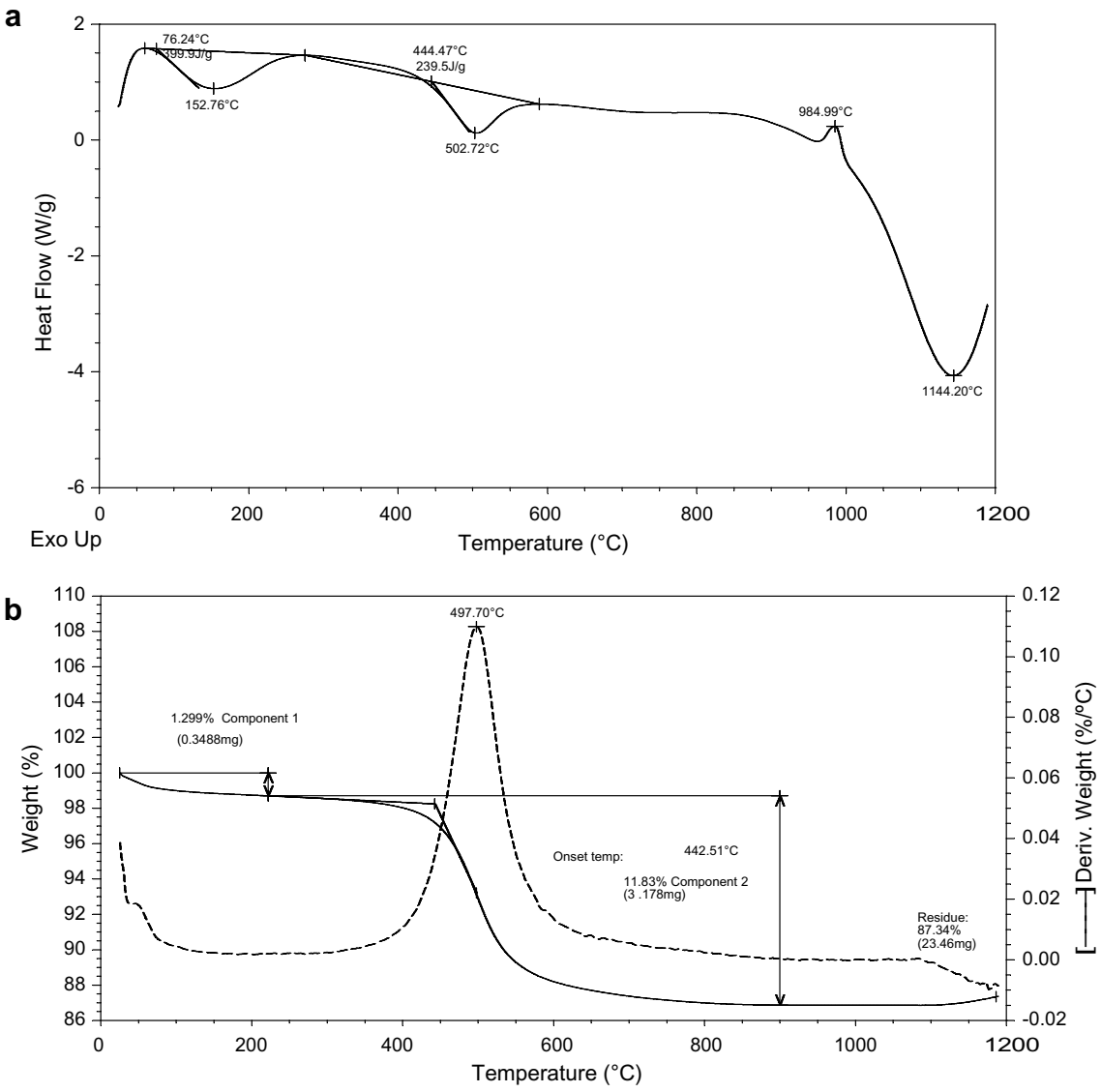

Fig. 2. Differential thermal analysis and thermogravimetric profiles for raw kaolinite. (a) Heat flow against temperature profile. (b) Weight loss against temperature profile.