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Evaluation of the physical properties and photodegradation ability of titania nanocrystalline impregnated onto modified kaolin

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ABSTRACT

In this study, a microporous layer photocatalyst of titania nanocrystallites heterocoagulated with structurally modified kaolin (TiO_2–K) was synthesised via a modified sol–gel method. Physical properties (particle size, morphology, stability and settleability) and photodegradation capacity of the TiO_2–K catalyst subject to its synthesis, regeneration and use for water treatment were studied. The modified kaolin, as a support for the titania nanocrystallites had a delaminated sandwich silica structure that minimises chemical intercalation within the nanocomposite structure. Microscopic examination revealed that the TiO_2 nanocrystallites were uniformly deposited on the kaolin external surface, resulting in a high degree of photon activation. Compared to the commercial TiO_2 P25, the TiO_2–K demonstrated a superior photocatalytic degradation capacity to remove an anionic Congo red dye. Its removal efficiency and photo-reaction performance were improved when the TiO_2–K was regenerated by a thermal treatment. The TiO_2–K particles can be easily separated from the water system for further reuse. This unique nanocomposite photocatalyst shows promising technical advantages for a continuous industrial process of water treatment.

1. Introduction

The multi-faceted properties and photocatalytic performance of titanium dioxide (TiO_2) for water purifications have received an increasing interest in recent decades owing to its high photostability, non-toxicity and cost effectiveness [1]. Many successes in TiO_2-assisted photodegradation toward recalcitrant organic contaminants in water, including different complexes endocrine disrupting compounds and dyes has been well-documented [2–4]. In reality, however, such heterogeneous photocatalysis processes for water purification utilising commercial TiO_2 are still facing a number of constraints that annihilate its feasibility for an industrial application.

Since the main photo-induced charged separation occurs on the surface of the photocatalysts, a larger specific area would promote a higher photocatalytic reaction rate. Herrmann [5] suggested that adsorption is a pre-dominant step in ensuring rapid photocatalytic surface reaction on the water contaminants. Owing to the large surface area to volume ratio, nanosized photocatalysts (i.e. Degussa P25) present a significant physical advantage that compromises the organic adsorption. These nanosized TiO_2 photocatalysts can lead to a latent difficulty for a downstream process to separate and recover the TiO_2 particles before reaching the consumer-end. Such ultra-fine particle separation usually incurs high operation and capital costs, and thus has seriously impeded the large scale applications of TiO_2 photocatalysts for an industrial treatment process.

Immobilisation of the nanosized TiO_2 photocatalysts can avoid the problem associated with the post downstream process required to separate the TiO_2 catalysts. Such a deposition method is usually technically-subjective, and requires significant experimental efforts to optimise between the surface areas to volume ratio of the supported-photocatalysts with its photoactivity. The exploitation of various titania-supported-photocatalysts to achieve desirable physicochemical properties, photoactivity and stability for water treatment has received a great attention [6]. Deposition of TiO_2 thin films onto a larger catalyst support, such as ferromagnetic cores or silica materials considerably improved both the particle recovery and adsorptive capacity [7]. Different layer silicate materials such as clay minerals were investigated as a possible supporting platform for the TiO_2 nanocrystals [8,9]. A few studies have explored the possibility of clays-supported TiO_2 nanocrystals, with frequent emphasis on the natural montmorillonite subclass. So far, a little attention has been paid how the physicochemical

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properties and photoactivity of the TiO_2 nanocrystals could be varied during the photocatalytic process, especially if the catalysts are repeatedly recovered and reused in a water purification system.

In this study, we synthesized a thin-layer TiO_2 nanocrystalline impregnated onto physiochemically modified kaolin as the immobiliser platform. Natural kaolin, $Al_2Si_2O_5(OH)_4$, is a phyllosilicate (sheet silicates) mineral with a tetrahedral silica sheet alternating with an octahedral alumina sheet. The ideas of exploiting kaolin is owing to its relatively low isomorphous substitution within its lattice structure, that limits the molecular interaction in water system, in which the clay structure can be possibly altered as found in montmorillonite. Such an ordered structure of kaolin, however, can restrict its functional active site to the plane and edge of kaolin particles. To improve the physical surface properties of kaolin as the catalyst platform, we investigated for the first time a series of pre-treatment methods of the kaolin prior to the sol–gel deposition of TiO_2 thin film, including acid dissolution, alkaline treatment and thermal activation. That was followed by controlled heterocoagulation of the TiO_2 sol with the treated kaolin particles, as previously reported by this team [8]. The resultant physicochemical properties of the TiO_2-impregnated kaolin (TiO_2–K) nanocomposites were characterised using X-ray diffractionometry (XRD), Brunauer–Emmett–Teller (BET), and electroscopic techniques of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Such techniques were also used to unveil the variation in physicochemical properties during different thermal regeneration cycles. Photoactivity of the TiO_2–K catalyst was evaluated against the degradation of anionic Congo red dye as a model surrogate compound. The settleability of the photocatalyst particles were also analysed using Kynch's hindered settling conditions, in terms of the single photocatalyst particle terminal settling velocity.

2. Materials and methods

2.1. Materials

Physicochemical properties of kaolin may be varied, depending upon the geographic source of origin. Natural white dry-milled kaolin obtained from Unimin, Australia was used in this study. The kaolin consisted of SiO_2 (48.7%), Al_2O_3 (34.6%), TiO_2 (1.3%), Fe_2O_3 (0.9%) and other trace compositions of K_2O, CaO, MgO and Na_2O. The details of the physical and chemical properties of the kaolin materials were reported in our previous work [10]. Commercial TiO_2 P25 (Degussa, Germany) was used as received for comparison study. The Degussa P25 has a surface area of $50 \pm 5\ m^2\ g^{-1}$ and composes of 80% anatase and 20% rutile with elementary particle size of 25–85 nm, respectively.

Titanium (IV) butoxide (tetrabutyl orthotitanate AR grade $\geq$ 97% gravimetric, Sigma–Aldrich), absolute ethanol (AR grade, Labserv Pronalys, Australia), and sodium pyrophosphate (AR grade, BDH VWR, England) were used as received. Congo red (CR) ($C_{32}H_{22}N_6Na_2O_6S_2$, Labchem Ajax Finechem, Australia), sulphuric acid (AR grade, 98 wt%, BDH VWR, England), nitric acid (AR grade, 69 wt%, BDH VWR, England), sodium hydroxide (AR grade, BDH VWR, England) were prepared using double-deionised water with 18.2 M-ΩM, resistivity.

2.2. Pre-treatment on natural kaolin clay

Natural kaolin was first pre-treated, in order to purify and augment the surface availability prior to the subsequent heterocoagulation process with TiO_2 sol. A series of acid–alkaline-thermal treatment was performed to alter the surface properties of the clay. Kaolin suspension (ca. $20\ g\ L^{-1}$) was magnetically suspended in a 20 cm high jar that fills with deionised water for particle size screening. At a certain stirring extent, the suspension was allowed for settling within 0.5 h. Supernatant from the jar containing particles with a size range <10 μm was decanted and filtered. The filtrate cake was then resuspended in 1 M sulphuric acid solution with continuous stirring up to 10 h before being filtered and washed repeatedly with deionised water. Following this, the kaolin particles were treated by 2 M sodium hydroxide at pH 10 for 0.5 h. The final kaolin filtrate cake was washed and dried at 70 °C for 4 h before firing at 750 °C for 1 h.

2.3. Synthesis of TiO_2–kaolin Catalysts

Deposition of TiO_2 thin film onto surface-augmented kaolin was prepared according to our previously reported method [9]. Twenty-five millilitre titanium (IV) butoxide was vigorously mixed with 30 mL of absolute ethanol for 0.5 h. The mixture was then acid catalysed via backdrop into a controlled-molar nitric acid solution. After the acid catalysed reaction a transparent homogeneous TiO_2 sol was then attained under continuous stirring for 0.5 h. Following this, the homogeneous TiO_2 sol was carefully heterocoagulated with the treated kaolin (ca. 10% w/v) via slow addition of the sol into the vigorously-stirred kaolin suspension. The stirring flask was kept at 37 °C in a water bath. Heterocoagulated TiO_2–kaolin was continually stirred for 4 h, before aging for 14–16 h at room temperature. The aged nanocomposites were then filtered and washed repeatedly with deionised water to remove any excess chemical impurities. Then, the nanocomposites were dried at 70 ± 2 °C for 2–4 h to remove any surface-bound water molecules before calcination at 600 °C at a heat ramping rate of 4–5 °C min^{-1} for 3 h. The final product of TiO_2–K particles was readily used as photocatalysts for the following experiments.

2.4. Characterisation of kaolin and TiO_2–K catalysts

The following analytical methods were conducted to characterise both the raw kaolin and TiO_2–K particles. This information is useful to gain insight into the physical, chemical and photochemical characteristics of the TiO_2–K particles using surface-augmented kaolin as a support platform.

Differential temperature analysis coupled with thermogravimetric analyser (DTA–TG) (TA Instruments) was performed on the raw kaolin to obtain the weight loss of kaolin as a function of temperature. During the analysis, the raw kaolin sample was heat-treated from room temperature to 1200 °C at a ramping rate of 10 °C min^{-1} under highly nitrogenised condition to avoid any possible oxidation.

Particle size of pre-treated kaolin was then measured using a static light scattering laser diffraction particle sizer instrument (Malvern Mastersizer 2000), covering the detection range from 0.02 to 2000 microns. The kaolin particles were first dispersed in sodium pyrophosphate solution, with constant agitation and sonication until a stable dispersion was attained. The particle size distribution of the pre-treated kaolin particles from the particle size screening are as shown in Fig. 1.

Morphological and surface characteristics of the resultant TiO_2–K particles were analysed using SEM (Philips XL30 SEM) at an accelerating voltage of 10 kV. Thin platinum coating was applied on the particle sample prior to analysis. TEM was also performed using Philips CM-100 TEM at an accelerating voltage of 100 kV. Before the analysis, the TiO_2–K particles were minimally suspended in ethanol solution (ca. 0.01% w/v), followed by ultrasonic dispersion and subsequent immobilisation on the copper measurement grids of 2 mm diameter.

BET specific surface area and pore size measurements on the resultant nanocomposites were performed using a micrometrics