Chemical Engineering Journal 210 (2012) 529–538

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Synthesis of TiO_2/SBA-15 photocatalyst for the azo dye decolorization through the polyol method

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HIGHLIGHTS

- The TiO_2 was synthesized via polyol method to increase the quantitative effect.
- By immobilizing the nano-sized TiO_2 on hydrophilic SBA-15, the aggregation was avoided.
- The crystalline size and surface charge of TiO_2 have influences on AR1 degradation.
- The 2,3-butanedione was adsorbed on the surface of TiO_2 during the polyol process.
- The electrophilic at carbon of ketone may attributed to the adsorption of AR1.

ARTICLE INFO

Article history:
Received 12 May 2012
Received in revised form 16 August 2012
Accepted 5 September 2012
Available online 20 September 2012

Keywords:
Immobilized TiO_2
SBA-15
Photocatalyst
Polyol method
Acid red 1

ABSTRACT

The nano-sized TiO_2 powder and immobilized TiO_2/SBA-15 photocatalysts were synthesized via a polyol method with an attempt to increase the quantitative effect by reducing the particle size and avoid the aggregation by immobilizing on hydrophilic SBA-15 support. The effect of reduction temperature on the TiO_2 crystalline size was investigated. The X-ray diffraction (XRD) and Field-emission scanning electron microscopy (FE-SEM) results showed that the crystallite size of the TiO_2 particles is in the nano-regime and indicated that depended on the nucleation and growth process, different sizes and shapes of monodisperse or polydisperse TiO_2 powders are formed. The photocatalytic activities of the samples were evaluated for the decolorization of an ano dye, acid red 1 (AR1) were studied in aqueous solution under UV light irradiation. The effect of different parameters such as catalyst dosage, solution pH, TiO_2 loading weight, and different support materials Al_2O_3 and glass bead on the decolorization efficiency of AR1 were studied. The results indicated that the self-synthesized TiO_2 showed comparable decolorization efficiency than commercial P25, and the efficiency can be significantly improved by using SBA-15 as support material due to its hydrophilicity.

1. Introduction

Acid red (AR) dyes are a type of azo dyes characterized by a nitrogen-to-nitrogen double bond (—N═N—). AR dyes are the largest and most important class of synthetic organic dyes widely used in industries today because they are cheap to synthesize, firm, and have a great variety of colors compared with natural dyes [1,2]. Yearly, 800,000 tons of dye is produced worldwide, and about 50% of these are azo dyes [3]. Azo dyes, however, are not biodegradable by aerobic treatment processes [4]. In addition, they are reducible to potentially carcinogenic aromatic amines under anaerobic condition, thereby causing long-term health concerns [5,6].

In recent years, there has been extensive interest in the use of semiconductors, such as TiO_2, as photocatalysts for azo dye decolorization [7–9]. In this photocatalytic process, UV light was usually used to stimulate the semiconductor surface to generate photo-induced holes or reactive oxygen species, such as $^{\cdot}OH$ and $^{\cdot}O_2^-$ radicals, which further interact with organic pollutants and lead to oxidation and overall mineralization [10–13]. The destruction and/or mineralization efficiency of this process depends on the TiO_2 surface properties and, more importantly, on the quantum yield and its recombination rate [13–15].

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http://dx.doi.org/10.1016/j.cej.2012.09.036

However, from a practical point of view, the scale-up applications of this process may not be possible mainly due to the agglomeration of ultrafine TiO_2 powders or the separation of TiO_2 from aqueous solution [16,17]. To overcome these disadvantages, many researchers have focused on the immobilization of TiO_2 on different substrates [18–20]. As proposed by Chun et al. [21], alteration of the adsorption characteristics of dye on photocatalysts plays an important role in determining the overall reaction rate. Therefore, to increase the adsorption capacity between photocatalysts and dye molecular, support materials possessing high surface area, such as quartz labyrinth flow reactor [22] and porous ceramic membrane tube [23], have been evaluated to investigate their influence on the photocatalytic process. The results obtained thus far indicate that the surface characteristics (e.g., surface acidity/basicity, surface charge, and hydrophilicity) and pore structures significantly affect the adsorption behavior of dye [21].

Zeolites are one of the catalyst supports that have been widely applied in the field of catalysis due to their uniquely developed pore structure and high stability. However, these materials have severe limitations. For example, the adsorption limitation is very intense for microporous materials [23,24] when large reactant molecules are involved, especially in a liquid-phase system. This strategy may be accomplished by the use of supports with appropriate textural properties, because the diffusion limitation of the large dye molecules can be neglected.

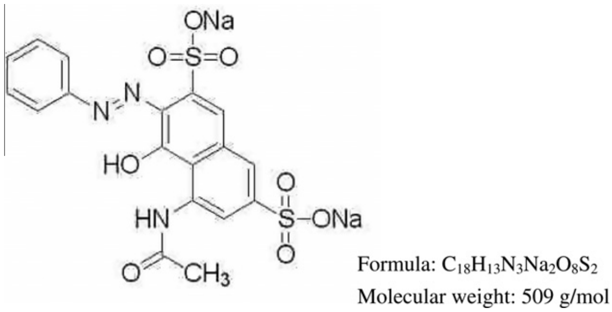
Alternatively, SBA-15 has attracted much attention for its use as a catalyst support due to its relatively large pores, large surface area, and tailorable pore size. These properties facilitate adsorption and contribute to the high loading of active sites. Mesoporous SBA-15 possesses a hexagonal array of uniform tubular channels with tunable pore diameters (5–30 nm) and thick pore walls (3–6 nm) [25]. Despite the application of SBA-15-supported catalysts in various catalysis processes [25–27], however, the available literature on the use of TiO_2/SBA-15 mesoporous catalysts to photocatalyze the dye is very limited.

In the current study, mesoporous SBA-15 is used as support for synthesis the immobilized TiO_2 photocatalyst for decolorization AR1 from an aqueous solution. The TiO_2 powder was self-synthesized through a polyol process, where ethylene glycol (EG) was used as a solvent and as a reducing agent, and polyvinylpyrrolidone (PVP) was used as a stabilizer [28]. In the polyol process, the reduction of metal ions is greatly governed by the difference between the oxidation potential of the solvent and the reduction potential of the metal species at a given temperature. Therefore, anatase and/or rutile TiO_2 with desirable properties can be obtained by adjusting the reduction conditions of the reaction system, such as reduction temperature. The influence of various reaction parameters, including photocatalyst concentration, solution pH, TiO_2 loading weight, and UV irradiation time, on the photocatalytic decolorization of AR1 was examined. Experiments were also conducted to compare the photocatalytic decolorization of AR1 with the use of nonporous glass beads and Al_2O_3 as supports.

2. Experimental

2.1. Materials

Titanium tetraisopropoxide (TTIP, 97%, pharmaceutical grade) purchased from Aldrich was served as the titanium precursor. EG and PVP (K15, $M_w \sim 10{,}000$ g/mol) were purchased from Sigma–Aldrich. TiO_2-P25 was used as received. Tetraethyl orthosilicate (TEOS), non-ionic triblock copolymer pluronic (P123), and a 37% aqueous solution of hydrochloric acid (HCl) were purchased from Sigma–Aldrich (France); these were used for preparing SBA-15 mesoporous materials without further purification. AR1, purchased from Sigma–Aldrich, was used as received. The structure of AR1 is shown in Fig. 1. Al_2O_3 (Sigma–Aldrich) and glass beads (2–3 mm, Pyrex) were used as supports for the deposition of TiO_2. The glass beads were immersed in 0.1 N NaOH for 24 h and washed with deionized water before being used. All other reagents with AR grade were obtained from various well-known suppliers.



Formula: $C_{18}H_{13}N_3Na_2O_8S_2$
Molecular weight: 509 g/mol

Fig. 1. Strucutre of acid red 1.

2.2. Synthesis of TiO_2 powder via polyol method

The detailed procedure for TiO_2 synthesized via the polyol method was described in a previous study [29]. About 3.55 g of the inorganic metallic compound TTIP and 0.25 g of PVP were dispersed in 50 mL of polyol EG. The solution was slowly stirred for 30 min to completely dissolve the reagents. The homogeneous solution was then heated to a series of reduction temperatures in the range of 130–170 °C with a heating rate of 5 °C min^{-1} and refluxed at the desired temperature for 3 h under vigorous stirring. The reduced white Ti powder was obtained once the solution was cooled down in an ice-water bath. The suspension was centrifuged and washed with ethyl alcohol at least five times to remove the remaining solvent and surfactant. The white powder was dried at 105 °C for 24 h, and then ground for further calcinations at 550 °C for 4 h in air. The obtained TiO_2 powder was stored in desiccators before use. Product codes were assigned as T3, T4, T5, T6, and T7, corresponding to reduction temperatures of 130, 140, 150, 160, and 170 °C, respectively.

2.3. Synthesis of SBA-15 substrate via template method

A silica mesoporous support, SBA-15, was synthesized using Pluronic P123 as a direct-structuring agent by following the method given in a previous study [30]. First, Pluronic P123 (5 g) was mixed with HCl and heated at 38 °C for 1.5 h under vigorous stirring. Then, 11.5 mL of TEOS was added to the mixture. The temperature was maintained constant for 24 h under thorough stirring conditions. Subsequently, the slurry was aged at 90 °C in an oven for 72 h. The white precipitate obtained was filtered and washed with abundant deionized water. Finally, the white powder was dried at 105 °C for 24 h and then calcined at 500 °C for 12 h with a heating rate of 0.8 °C min^{-1} to remove the structuring agent and liberate the pores. The obtained SBA-15 was also stored in desiccators before use.

2.4. Synthesis of immobilized TiO_2 photocatalysts

The T3 were then immobilized on the surface of SBA-15, Al_2O_3, and the glass beads substrate through polyol method. The TTIP and 0.2 g of PVP was dissolved in 50 ml of EG solution and mixed with substrate (Ti/substrate = 5 wt.%). The solution was refluxed at 130 °C for 3 h. The precipitate after washing with ethyl alcohol