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Full Length Article

Rapid Degradation of Methyl Orange by Ag Doped Zeolite X in the Presence of Borohydride

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Abstract

A series of Ag nanoparticles impregnated on zeolite X (Ag-ZX) containing various amounts of Ag (in wt%) were prepared via impregnation method. The pristine zeolite X and Ag-ZX catalysts were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), N_2 adsorption desorption analyses and atomic absorption spectroscopy (AAS). The prepared catalysts were employed for the decolourization of methyl orange (MO) in the presence of potassium borohydride (KBH_4). Various parameters such as the amount of Ag impregnated, MO concentration, KBH_4: MO mole ratios, pH and catalyst reusability were investigated. It was found that the best decolourization efficiency was obtained when 0.06 g of Ag-ZX (6.7) catalyst was employed using a KBH_4: MO mole ratio of 731: 1 at pH 5. The degradation process obeyed pseudo first-order kinetics.

Keywords: Methyl Orange; Decolourization; Zeolite X; Silver Nanoparticles; Potassium Borohydride

1. Introduction

Industries based on textile paint and food consume more than 70% of the dyes produced worldwide [1]. This high demand leads to environmental hazards because dyes do not easily degrade in water bodies. Such lack of degradation is directly harmful to aquatic organisms and indirectly harmful to humans [2]. In this regard, various physical and chemical approaches have been developed for the removal of dyes to improve the quality of the environment. Adsorption processes using activated carbon [3], chitosan [4] as well as charcoal [5], has been reported as a promising technique for the removal of dyes. However, these approaches produce secondary pollutants and the need for the regeneration of the adsorbents may limit the practical application of this technique in industry.

The chemical approach using catalysts can be more favourable for dye degradation and removal. To date, the potential use of nanoparticles, such as silver metal (Ag), as catalysts in the degradation of dyes has gained attention. A major advantage of Ag nanoparticles is their strong absorbance in the visible region band gap. This

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promotes high activity under both UV and visible light [6]. However, the easy agglomeration of Ag nanoparticles in the absence of supports or stabilizers is one of the main limitations for their practical use [7]. Therefore, much attention has been directed to the synthesis of fine and discrete Ag nanoparticles. For example, Rajan et al. [8] synthesized Ag nanoparticles using *Areca catechu nut*, while Vidhu and Philip [9] proposed the use of dried *Saraca indica* flower to synthesize Ag nanoparticles for catalytic purposes. While these methods may obtain fine nanoparticles, the particles may suffer from reusability problems because the nanoparticles are synthesized in colloidal form. To address this issue, the use of inorganic supports such as clay materials can be an alternative pathway for the synthesis of fine Ag nanoparticles.

Zeolites are crystalline aluminosilicate minerals that have been widely used in various areas such as gas and liquid separations [10] as well as scaffolds [11] for biomedical applications. The open cage frameworks with well-defined porous structure (pore diameter <2 nm) make zeolites suitable for use as supports to encapsulate smaller particles. These smaller particles are dispersed in the zeolite intracrystalline area [12]. Recently, zeolite supported metal and metal oxide nanoparticles have been extensively studied. An enormous number of works have focused on zeolites as potential supports for catalytic systems such as zeolite/TiO_2 [13], zeolite X/CuO [12], zeolite/Pt [14] and zeolite/Cu [14]. It was found that the zeolite/Pt catalyst exhibited superior performance for the catalytic combustion of toluene [14]. In contrast, Chen et al. [15] found that zeolite/Cu was active for the selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with NH_3. Zeolite-supported metal oxides such as TiO_2 as well as CuO have also been employed. However, these are commonly used for the photocatalytic degradation of dyes and organic pollutants under UV exposure [12,13,16–18]. To date, few studies on the use of zeolite/Ag as catalysts have been reported. Colar et al. [19] focused on the preparation of Ag-modified natural zeolite for the decolourization of methylene blue (MB) under visible irradiation. In addition, Hatamifard et al. [20] investigated the ability of natural zeolite/Ag as a catalyst for various dyes in the presence of borohydride. Although the authors demonstrated the effectiveness of the catalyst, they focused solely on the reduction of different organic dyes with a high Ag loading (approximately 1.29 wt%) [20].

In this study, we propose a simple and easy method to synthesize Ag-doped zeolite X (Ag-ZX) catalysts for the decolourization of methyl orange (MO) dye in the presence of KBH_4. It is important to mention here that finite amounts of Ag (1.9 to 6.7×10^{-3} wt%) were employed unlike in the previous study [20]. Furthermore, various parameters were studied and the kinetics of degradation were investigated. The performance of the Ag-ZX catalyst was compared with that of the parent zeolite to verify its superior reduction ability.

2. Experimental

2.1. Materials

Methyl orange, MO, with the chemical formula of $C_{14}H_{14}N_3NaO_3S$ was supplied by Hopkins & William Chemicals (United States), while silver nitrate ($AgNO_3$) was obtained from R&M Chemicals (Malaysia). Potassium borohydride (KBH_4) and sodium aluminate anhydrous ($Na_2O{\bullet}Al_2O_3$) were purchased from Sigma Aldrich (United States). Sodium silicate (Na_2SiO_3) solution was supplied by Merck (United States), and a sodium hydroxide (NaOH) pellet was obtained from QReC (New Zealand). All materials were used as purchased without further purification.

2.2. Synthesis the Zeolite X

Zeolite X was synthesized based on previous work [21]. Solutions A and B were prepared as follows: For solution A, as much as 14.1 g of NaOH pellet and 37.0 g of Na_2SiO_3 were dissolved in 179.7 g of distilled water. Solution B was prepared by dissolving 31.8 g of NaOH pellet and 6.40 g of $Na_2O{\bullet}Al_2O_3$ in 215.5 g of distilled water. Subsequently, solution B was slowly added to solution A under vigorous magnetic stirring. The mixture was further stirred for an additional 10 minutes before ageing at room temperature for 24 hours and then placed in an oven at 50 °C for 48 hours. The solid was extracted via centrifugation at 8500 rpm for 10 minutes followed by re-dispersion in double distilled water until the final colloidal suspension achieved pH 7. The colloid solution was then freeze-dried in order to obtain zeolite powder.

2.3. Preparation of Ag-ZX Catalysts

These catalysts were prepared by impregnation method. Various amounts of 2.0×10^{-3} M $AgNO_3$ stock solutions were mixed with the zeolite X in order to prepare Ag-ZX (*n*), where *n* is the wt % of Ag in the power of 10^{-3}. Typically, to prepare the Ag-ZX (1.9) catalyst, 46 μL of 2.0×10^{-3} M $AgNO_3$ was mixed with 1.0 g of zeolite X powder. The mixture was mechanically stirred