Contents lists available at ScienceDirect

Advanced Powder Technology

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

Original Research Paper

Enhancement of photocatalytic activity and stability of Ag_2CO_3 by formation of $AgBr/Ag_2CO_3$ heterojunction in mordenite zeolite

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ARTICLE INFO

Article history:
Received 31 May 2016
Received in revised form 2 October 2016
Accepted 4 October 2016
Available online xxxx

Keywords:
Hybrid material
Photocorrosion
Photocatalysis
Cocatalyst
Fe-mordenite

ABSTRACT

Two serious problems for semiconductor photocatalysts are their poor photocatalytic activity and low stability. In this work, Ag_2CO_3 nanoparticles incorporated in mordenite zeolite (MOR) by a facile precipitation method. Silver bromide (AgBr) with different weight percentage (20%, 40% and 50%) was coupled into Ag_2CO_3-MOR composite and producing a series of novel $AgBr/Ag_2CO_3$-MOR nanocomposites. The effects of AgBr on the Ag_2CO_3–MOR catalyst for the photocatalytic degradation of methyl blue (MB) under visible light irradiation have been investigated. The structure, composition and optical properties of nanocomposites were investigated by UV–Visible diffuse reflectance spectroscopy (UV–Vis DRS), X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM). The prepared $AgBr/Ag_2CO_3$-MOR photocatalyst with the optimal content of AgBr (50 wt%) indicated higher photocatalytic activity than that of the Ag_2CO_3-MOR and Ag_2CO_3 for degradation of methylene blue (MB) under visible light irradiation. For studying of stability of nanocomposites, Fe^{+3} ions, as a cheap and available cocatalyst, was inserted into mordenite matrix (Fe^{3+}/MOR) by impregnation method. The hybrid material ($AgBr/Ag_2CO_3$) was synthesized in the Fe^{3+}/MOR matrix by precipitation method. The cycle experiments on the $AgBr/Ag_2CO_3$-Fe/MOR nanocomposite indicated that cocatalyst, not only to improve photocatalytic activity, but also enhance photoinduced stability of photosensitive silver compounds in all cycles with respect to MOR. On the basis of the experimental results, a possible mechanism for the enhanced photocatalytic activity and photoinduced stability of silver compounds by Fe^{3+} cocatalyst was proposed. The mordenite support played an important role in decreases of recombination of photogenerated electrons-holes and increases of MB absorption. The Fe cocatalyst reduced photocorrosion of silver compounds.

1. Introduction

While the shortage of energy sources becoming severe, photocatalytic degradation based on semiconductors is one of the growing technologies in terms of solar energy conversion for degradation of organic pollutants [1–3]. Traditional semiconductors can only absorb the small amounts of photons in the visible region and need to irradiation of UV light for excitation, while sunlight irradiation is composed of 3–5% UV light and approximately 43% visible light. Moreover, high recombination rate of the photoexcited electrons and holes is their drawback [4,5].

Noble metal nanoparticles such as Au, Pt, Ag, Cu and Sn due to surface plasmon resonance (SPR) exhibit excellent absorption in the visible light region and increase the excitation of electron-hole pairs of semiconductors in this region. When noble metal nanoparticles are deposited on the surface of large band gap photocatalysts, they can act as a heterogeneous photocatalysts to extend the light absorption region. In addition, they can decrease recombination of electrons and holes as an electron trapping [6–8].

Silver containing compounds indicates advantages as photocatalyst due to the remarkable SPR effect of metallic silver nanoparticles that are produced on their surface [9]. Several recent publications were reported that Ag_2CO_3 with visible light photocatalytic performance can be used for photodegredation of organic contaminants in aqueous solutions [10–12]. However, the recombination of electrons and holes can decrease the photocatalytic activity of photocatalyst. Furthermore, the generated electrons can be transferred in interstitial Ag^+ ion and Ag

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http://dx.doi.org/10.1016/j.apt.2016.10.004

Please cite this article in press as: A. Asadollahi et al., Enhancement of photocatalytic activity and stability of Ag_2CO_3 by formation of $AgBr/Ag_2CO_3$ heterojunction in mordenite zeolite, Advanced Powder Technology (2016), http://dx.doi.org/10.1016/j.apt.2016.10.004

nanoparticles (Ag NPs) are produced. Then the photocorrosion of Ag_2CO_3 would reduce the photocatalytic activity and stability of photocatalyst [13,14]. The heterojunction can change behavior of photogenerated holes and electrons, such as the separation efficiency, direction of transportation, and the recombination rate of charges [15]. Hybridization and formation of heterojunction between silver semiconductors and other compounds can greatly reduce the recombination of photogenerated electron and hole and thereby increasing their photocatalytic activity and stability. In addition, these photocatalysts with appropriate energy band structures have stronger reduction and oxidation potential than the individual photocatalyst.

AgX species (X = Cl, Br, I) are very important photosensitive materials and show photocatalytic activity for decomposition of organic dyes and disinfect. The coupling of Ag_2CO_3 with other silver halides has been reported [16–18]. Compared with the single-component compounds, these multi-component heterojunctions or hybrid materials could significantly increase the photocatalytic activity.

As mentioned, the other problem in utilization of Ag based compounds as photocatalyst is their inactivation *via* photocorrosion in light irradiation. This means that the interstitial Ag^+ ions combine with the photogenerated electrons to form Ag°. This unwanted photographic process can cause that the pure photocatalyst to be directly used as unstable photocatalyst and corroded by photogenerated electrons ($Ag_2CO_3 + 2e^- \leftrightarrow 2Ag\ NPs + CO_3^{2-}$). The poor structural stability of silver compounds can decrease the catalytic activity during the photocatalytic reaction [19]. For enhancement of stability, some strategies have been developed, such as use to form heterostructures (as be mentioned above), the addition of $AgNO_3$ as an excellent electron acceptor into the reaction mixture [14], the utilization of cocatalysts [20]. The heterostructure compounds often can increase the photocatalytic activity but the stability can't be necessarily increased. In these cases, cocatalysts can be used for inhibition of photocorrosion. There are reports about the utilization of cocatalysts such as Fe^{3+} or Cu^{2+} ions for to improve the photocatalytic performance and stability of photocatalysts [21].

To overcome the turbidity of solution due to dispersion of photocatalyst and also for easy separation of photocatalyst, immobilization of photocatalyst on different matrices were proposed. Meanwhile, the adsorption of pollutants can be increased by matrix [22]. Zeolites have been used in photochemical processes as conventional adsorbents and photocatalytic matrices. The pores and channels of zeolites can be used for synthesizing of nanomaterials. The preparation method and the nature of the matrix can influence size, distribution and morphology of nanoparticles. The nanoparticles SPR are related to these properties. Therefore, the matrix can effect on the photocatalytic degradation efficiency of photocatalysts [23,24]. However, there are few data about the silver halides modified Ag_2CO_3 hybrid materials in matrices.

In our previous work, antibacterial activity of the Ag_2CO_3 in two matrices, montmorillonite and MCM-41 mesoporous material, was demonstrated [25]. In the present work, for increasing of adsorption of pollutants over Ag_2CO_3 photocatalyst, Ag_2CO_3 nanoparticles were synthesized in mordenite (MOR) by precipitation method. For enhancing of photocatalytic activity of Ag_2CO_3-MOR nanocomposite, silver bromide was deposited in Ag_2CO_3-MOR nanocomposite. In the next step, mordenite zeolite was ion exchanged with Fe^{3+} ions to produce Fe/MOR. The Fe/MOR zeolite was used for investigating of stability of AgBr/Ag_2CO_3 hybrid material. The degradation of MB as model dye was selected to evaluate the photocatalytic activity and stability of the synthesized catalysts. The possible photocatalytic mechanisms were discussed in details for nanocomposite.

2. Experimental

2.1. Materials

The nitrate salt of silver ($AgNO_3$) and $Fe(NO_3)_3 \cdot 9H_2O$ were used as a source of metal ion and Na_2CO_3, NaCl, KBr was used as a source of anion ions. Hydrochloric acid and sodium hydroxide were applied for a variation of the pH of sample solutions. Sodium silicate and $Al_2\,(SO_4)_3 \cdot 16\ H_2O$ was used in the synthesis of mordenite zeolite. All materials were from Merck. The dye of methylene blue (C.I. name: Basic Blue 9, $C_{16}H_{18}ClN_3S{:}3H_2O$) was purchased from Fluka company. The used reagents were of analytical grade without any further treatment. Ethylene diamine tetraacetic acid (EDTA), benzoquinone (BQ), Isopropyl alcohol (IPA) and catalase (CAT) were purchased from Sigma–Aldrich.

2.2. Preparation of Ag_2CO_3, MOR, Fe/MOR, Ag_2CO_3-MOR, AgBr/Ag_2CO_3-MOR and AgBr/Ag_2CO_3/Fe/MOR

2.2.1. Synthesis of MOR and Fe/MOR as a matrix

Mordenite zeolite (MOR) was prepared by a hydrothermal synthesis method based on the published recipe [26]. For the preparation of Fe/MOR matrix, 0.5 g MOR added to 50 ml of Fe solution (0.05 M), the precipitation was collected and washed with distilled water and dried at room temperature. The color of the solid sample was orange.

2.2.2. Synthesis of Ag_2CO_3 and Ag_2CO_3-MOR photocatalyst

Ag_2CO_3 was prepared via a solid-state method with a slight modification [27]. In a typical synthesis a precursor was prepared by grinding for 5 min 0.08 g of $AgNO_3$ with 0.04 g of Na_2CO_3, followed by mixing powder in 10 ml of deionized water. After grinding for 10 min, the product (Ag_2CO_3) was washed several times with distilled water, and subsequently washed three times with ethyl alcohol (EtOH) to remove $NaNO_3$ and unreacted chemicals. Finally, the product was dried in an oven at 60 °C for 3 h.

For preparing of Ag_2CO_3-MOR nanocomposite in separate batches 0.1–1.00 g of MOR was grounded for 30 min with 0.08 g of $AgNO_3$ and 0.04 g of $Na_2CO_3 \cdot 10H_2O$. After grinding for 30 min, each of the powders was mixed in 10 ml of deionized water for 20 min. The products were washed several times with distilled water, and subsequently washed three times with ethyl alcohol (EtOH) to remove $NaNO_3$ and unreacted chemicals. Finally, the products were dried in an oven at 60 °C for 3 h. The prepared samples were termed as Ag_2CO_3-MOR.

2.2.3. Synthesis of AgBr/Ag_2CO_3-MOR and AgBr/Ag_2CO_3-Fe/MOR photocatalysts

The typical procedure for preparing of AgBr/Ag/Ag_2CO_3-MOR (20 wt%) was as follows: initially, 0.08 g Na_2CO_3 and 0.02 g KBr were dissolved in 20 ml distilled water under stirring. Then, 5 ml $AgNO_3$ solution (containing 0.305 g $AgNO_3$) along with 0.1–1 g MOR was added slowly into the mentioned solution. The obtained suspension was continuously stirred for 1 h. The precipitate was collected by centrifugation, thoroughly washed with distilled water and dried at room temperature. Accordingly, AgBr/Ag_2CO_3-MOR (40 wt%, 50 wt%) photocatalysts were prepared by the same method. The AgBr/Ag_2CO_3-Fe/MOR photocatalyst was fabricated with the same method, only Fe/MOR was used instead of MOR.

2.2.4. Synthesis of bulk AgBr

For preparing of bulk AgBr, 40 mL silver nitrate, aqueous solution (0.02 M) was dissolved in 40 mL of hexadecyltrimethylammonium bromide 0.05 M, separately. The reaction was conducted for 3 h at 25 °C. The resulting sample was thoroughly washed with dis-

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