



NH₂-MIL-125(Ti)/TiO₂ composites as superior visible-light photocatalysts for selective oxidation of cyclohexane

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ABSTRACT

Semiconductor-metal-organic framework (MOF) hybrid photocatalysts have aroused increasing interest because of their enhanced photocatalytic activity. In this work, NH₂-MIL-125(Ti)/TiO₂ composites with different molar ratios were successfully prepared by a facile one-pot solvothermal method and used for visible-light driven photocatalytic selective oxidation of cyclohexane. The as-prepared NH₂-MIL-125(Ti)/TiO₂ composites presented better catalytic performances compared with NH₂-MIL-125(Ti). This is due to the energy bands coupling and intimate interfacial contact between NH₂-MIL-125(Ti) and TiO₂, which can improve the photon-generated carrier transfer and minimize the recombination of electron-hole pairs. For the optimum composite photocatalyst, the activity was three times higher than that of NH₂-MIL-125(Ti) in visible-light driven photocatalytic cyclohexane oxidation using molecular oxygen as oxidant at room temperature and under ambient pressure. Additionally, the effects of illumination time on the photocatalytic performance and reusability of the optimum composite photocatalyst were investigated in detail. Finally, a possible reaction mechanism has been proposed based on controlling experiments using different radical scavenger techniques, which prove that the photon-generated holes are significantly involved in the oxidation process.

1. Introduction

Liquid phase selective oxidation of cyclohexane is an important reaction for the production of cyclohexanol and cyclohexanone (known as KA oil), which are the intermediates to fabricate nylon-6 and nylon-66 polymers [1,2]. In recent years, more and more attention has been devoted to photocatalytic selective oxidation of cyclohexane because photocatalysis technique is green, mild and has shorter reaction sequences which can reduce the possibility of side reactions [3]. Titanium dioxide is considered to be the most promising photocatalyst because of its superior photocatalytic activity, chemical stability, low cost, and nontoxicity [4,5]. In 1989, Mu with co-workers used Degussa P25 TiO₂ (consisting of approximately 70% anatase and 30% rutile) as photocatalyst into the selective oxidation of cyclohexane, and high selectivity to cyclohexanone was observed [6]. Subsequently, Almquist and Biswas [7] investigated the effects of different solvents on the catalytic activity and selectivity in cyclohexane photooxidation over TiO₂. Mul and co-workers [8] studied neat cyclohexane photooxidation applying different wavelengths using different reactor setups with varying TiO₂ dosage and constitution. However, some shortages of TiO₂ limit its practical application as photocatalyst for cyclohexane oxidation. One

main drawback is its wide band gap (~ 3.2 eV) which causes it to have no photocatalytic activity in visible light, and another main drawback is poor photocatalytic performance because of the high recombination of photogenerated electron-hole pairs and poor tunability characteristics.

To enable purely UV-active TiO₂ have visible light activity, various modification methods such as impurity doping [9–12], semiconductor coupling [13,14], dye sensitization [15,16], etc., have been employed in recent years. However, the dye-sensitized photocatalysts are usually found to be unstable under irradiation and the metal ion doping of TiO₂ also shows several drawbacks, such as thermal instability and increased electron/hole recombination [17]. By comparison, the coupling with semiconductors with matched band gaps is an efficient method to achieve photocatalysis in visible light. Moreover, this approach is convenient and the matched semiconductors are extensive.

Metal-organic frameworks (MOFs) consisting of metal clusters interconnected with organic linkers have received considerable attention because of their large surface area, pore volume and tunable pore structure, which have shown potential applications for gas storage, separation, catalysis, electrical conductivity, sensor devices and drug delivery [18–20] etc. In addition, semiconductor MOFs also draw great attention on their utilization as photocatalysts. To date, several

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representative semiconductor MOFs (such as MOF-5, UiO-66(Zr), ZIF-8, and MIL-125(Ti) et al.) have been widely served as photocatalysts, but these semiconductor MOFs showed limited efficiency under solar illumination because of the lack of visible light response. Fortunately, for the semiconductor MOFs, the effective use of solar light can be facilely achieved by the modification of their organic linkers or metal centers [21]. For example, NH₂-MIL-125(Ti) (denoted as NH₂-M125), as the isostructural MOF of MIL-125(Ti), constitutes of cyclic Ti₈O₈(OH)₄ oxoclusters and 2-aminoterephthalate ligands, and it shows extended absorption spectra into the visible-light region (around 550 nm) because of its amino functionality moieties [22]. In 2012, Li et al. [22] first reported that NH₂-M125 reduced CO₂ to HCOO⁻ under visible light irradiation but unfortunately with low activity. In 2015, Yuan's group [23] employed two Ti-based MOFs (MIL-125(Ti) and its derivative NH₂-M125) as multifunctional photocatalysts to reduce Cr(VI). Compared with MIL-125(Ti), the NH₂-M125 exhibited higher photocatalytic activity for Cr(VI) reduction in aqueous solution under visible-light irradiation.

Recently, MOFs as matched semiconductors coupling with traditional inorganic semiconductors such as TiO₂ and CdS, have been proven to be a feasible and effective approach to reduce the recombination probability of photogenerated electrons and holes thus improving the photocatalytic activity [24,25]. In 2014, Lin and co-workers [25] discovered UiO-66/CdS with a photocatalytic hydrogen evolution rate 11.2 times as high as that of pure commercial CdS. The high photocatalytic activity of UiO-66/CdS could be attributed to the increased catalytic sites and reaction centers and the minimized recombination of charge carriers. In 2016, Luo and co-workers [26] prepared TiO₂/ZIF-8 nanofibers which displayed much better performance for the photocatalytic degradation of RhB than either TiO₂ or ZIF-8. The excellent photocatalytic performance was attributed to the formed N-Ti-O chemical bond under sonochemical treatment between TiO₂ and ZIF-8, which may result in reducing recombination of the electron-hole pairs.

In this paper, we have realized the semiconductor coupling of NH₂-M125 and TiO₂. The main purposes are listed below: (i) Narrow the band gap of TiO₂ and extend its absorption spectra toward visible light region; (ii) Reduce recombination of the electron-hole pairs through the transportation of photo-generated electrons of NH₂-M125 to TiO₂ [27]; and (iii) Promote the dispersion of TiO₂ nanoparticles to produce more active centers by taking advantage of the porous structure and large surface area of NH₂-M125. Previously, Jin and co-workers [28] used NH₂-M125/TiO₂ modified glassy carbon electrode (GCE) for the photoelectrochemical detection of pesticide clethodim, and the results implied that the fast photoelectronic communication among clethodim, TiO₂, NH₂-M125 and GCE led to an effective method for the photoelectrochemical detection of clethodim with good analytic performance. In this study, a series of NH₂-M125/TiO₂ composites were prepared via a modified solvothermal method according to the Jin's work [28]. The photocatalytic performance of as-synthesized photocatalysts in the photocatalytic oxidation of cyclohexane were studied in detail, including the effects of illumination time and reusability. The enhanced photocatalytic performance was observed compared with pure NH₂-M125 or TiO₂. The possible reaction mechanism for the selective visible-light photocatalytic oxidation of cyclohexane over NH₂-M125/TiO₂ composites were also proposed and discussed.

2. Experimental section

2.1. Materials

All reagents were analytical grade. 2-Aminoterephthalic acid (H₂ATA) was obtained from Beijing J&K Scientific LTD. Tetrabutyl titanate (TBT) and benzyl chloride were supplied from Tianjin Guangfu Fine Chemical. N,N-dimethyl formamide (DMF) and methanol (MeOH) were purchased from Beijing Chemical Works. P25 (TiO₂) was

purchased from Degussa. Ammonium oxalate (AO), potassium persulfate (K₂S₂O₈) and *tert*-butanol (TBA) were obtained from Tianjin Fuchen Chemical Reagents Factory. Benzoquinone (BQ) and cyclohexane were purchased from Sinopharm. The cyclohexane was purified prior to use by passing through a column filled with neutral alumina to remove traces of possible oxidation products. All other reactants were used without further purification or treatment.

2.2. Preparation of photocatalysts

NH₂-M125 was synthesized by a modified solvothermal method according to the literature [22]. Typically, H₂ATA (0.5 g, 3 mmol) and TBT (0.26 mL, 0.75 mmol) were added into the mixed solvent of DMF (9 mL) and dry MeOH (1 mL). The above mixture was stirred at room temperature for 30 min and was transferred to a 50 mL Teflon lined autoclave and heated at 150 °C for 72 h. After reaction, the resulting suspension was filtered, washed twice with DMF to remove the unreacted organic ligands, and then washed again with methanol to exchange DMF with methanol. Finally, the as-prepared yellow powder was dried under vacuum at 60 °C for 6 h to obtain the final yellow NH₂-M125. Similar procedures were used in the preparation of the NH₂-M125/TiO₂ composites except that a certain amount of P25 powder was added into the synthesis mixture of NH₂-M125. The final pale yellow products were labeled as NH₂-M125/P25-X, where X = 2, 4, 8, representing the nominal molar ratio of Ti⁴⁺ ions in P25 and TBT.

2.3. Characterization of catalysts

The XRD patterns were recorded by a Rigaku D/Max-2500 diffractometer with CuK α radiation in the 2 θ range of 5–80° at a scanning rate of 4°/min. Scanning electron microscopy (SEM) images were obtained by SU8010 with an accelerating voltage of 30 kV to confirm the formation and surface morphology of the samples. The FT-IR spectra of synthesized samples were measured as KBr wafers with DIGLAB FTS-3000 spectrometer over a range of 400–4000 cm⁻¹. The BET specific surface areas were measured by nitrogen adsorption at liquid nitrogen temperature in a Micromeritics ASAP 2020 static volumetric gas adsorption instrument. The PL spectra of photocatalysts were detected by a F-7000 spectrometer (2690-002) with a 2400 nm/min scan speed. The XPS measurements were recorded on the Thermo VG Scientific Escalab 250 spectrometer using monochromatized AlK α excitation. The UV-vis spectra of photocatalysts were detected by a Shimadzu UV-4100 spectrophotometer using BaSO₄ as the reference material. All the measurements were operated at room temperature and under ambient pressure.

2.4. Photocatalytic activity testing

The photocatalytic cyclohexane oxidation was carried out in a quartz reactor under irradiation of a PLS-SXE300UV xenon lamp with a 420 nm cutoff filter ($\lambda \geq 420$ nm). Typically, 50 mg catalyst was added into the reactor. Then the reactor was sealed using a quartz septum cap, and evacuated for 2–3 min. After that, 10 mL cyclohexane and 10 mL CCl₄ solvent were injected through the injection port. Prior to test, pure oxygen with the flow rate of 20 mL min⁻¹ was bubbled through the solution for 5 min and the suspension was stirred in the dark for 1 h to ensure the establishment of adsorption-desorption equilibrium. Then photocatalytic reaction was proceeded in the oxygen atmosphere under stirring at 25 °C for 5 h. At the end of the irradiation, 1 mL benzyl chloride as internal standard substance was added into the suspension and stirred for 1 h. The resulting oxidation products cyclohexanol and cyclohexanone were separated from catalysts by centrifugation and analyzed by a gas chromatograph (GC, SP-3420) equipped with an FID detector using a OV-101 column (50 m \times 0.25 mm \times 0.25 mm) and the gas phase product was analyzed by TCD (GC, SP-3420) using a TDX-01 column. The chromatographic conditions were as follows: N₂ constant

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