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Full Length Article

Graphitic carbon nitride induced activity enhancement of OMS-2 catalyst for pollutants degradation with peroxymonosulfate

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ABSTRACT

Low valent manganese species and surface oxygen vacancies in OMS-2 play an important role in catalytic reactions, and it is highly desirable and challenging to develop a feasible strategy of increasing the Mn(II) and Mn(III) species concentration in the oxide. Herein, the OMS-2/g-C_3N_4 hybrids (OMS-2/CN) were prepared by a facile refluxing approach. It was found that the MnO_x precursor from the reaction of $KMnO_4$ and $MnSO_4$ was transformed into OMS-2 nanofibers with the formation of more Mn(II) and Mn(III) species in OMS-2 and the destruction and oxidation of g-C_3N_4. The hybrids exhibited higher efficiency for pollutants degradation in the presence of PMS than the pure OMS-2 or g-C_3N_4. There was a linear correlation between the specific initial rate and the ratio of Mn(II + III)/Mn(IV). Mechanism investigation indicated that high active manganese species or caged radicals were produced through the oxidation of Mn(II) and Mn(III) by PMS and contributed to the degradation reaction. During five consecutive cycles, the catalyst exhibited good reusability and stability. Therefore, the OMS-2/CN hybrids are promising catalysts for wastewater treatment with PMS as the oxidant.

1. Introduction

Sulfate radical-based advanced oxidation processes have attracted extensive attention for organic pollutants degradation in recent years [1]. The radicals can be generated through persulfate or peroxymonosulfate (PMS) activation by UV, heat, base and especially homogeneous and heterogeneous catalysts [2]. Cobalt and copper solid catalysts such as Co_3O_4, CuO, $CoFe_2O_4$, $CuFe_2O_4$ and $Fe_xCo_{3-x}O_4$ are efficient PMS activators [3–7]. However, leaching of cobalt and copper from the solid catalysts during reaction usually occurs and is considerably toxic and potentially carcinogenic [3,4,7,8]. The use of other environmental friendly Mn and Fe-based metal oxides and metal-free catalysts has become more attractive [9–14]. Recently, we found that cryptomelane-type manganese oxide (OMS-2) showed excellent activity and stability for organic dyes decompositions in the presence of PMS [15–17]. Though OMS-2 is an inexpensive and environmentally benign catalyst, its catalytic performance is strongly influenced by solution pH, and the activity decreases dramatically under neutral condition [15,16]. However, the average pH of wastewater is about 7. Thus, developing a strategy to improve the performance of OMS-2 catalyst for the activation of PMS, particularly under neutral condition, is of significance for theory and practical application.

OMS-2 is a form of manganese dioxide with a one dimensional tunnel structure composed of 2 × 2 edge-shared MnO_6 octahedral chains, which are corner-connected to form 4.6 × 4.6 Å tunnels [18]. It has been widely reported as an easily regenerable catalyst for oxidation of volatile organic compounds and alcohols [19–21]. In view of the related researches, a general conclusion can be found that low valent manganese species, Mn(II) and Mn(III), or surface oxygen vacancies in manganese oxides play an important role in the catalytic reactions [22]. Several strategies have been reported to improve the catalytic activity of OMS-2. For example, Hou et al. prepared OMS-2 by hydrothermal redox reactions under different temperatures, and found that lower preparation temperature resulted in higher the oxygen vacancies and then higher catalytic activity for the oxidation of benzene [23]. Increasing K^+ concentration or using $MnAc_2$ as a Mn^{2+} precursor also lead to higher atomic ratio of Mn^{3+}/Mn^{4+}, and thus increased the catalytic activity of benzene oxidation or ozone decomposition [24,25]. However, current methods are based on the adjustment of synthesis conditions, while the formation of organic-inorganic hydrids has not received any attention, in which the distribution of manganese species in OMS-

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2 might be conveniently controlled through the reaction between OMS-2 and the reductive organic polymers.

Recently, the polymeric semiconductor graphite-like carbon nitride (g-C_3N_4), has stimulated scientists' interest in photocatalytic reactions, due to the unique properties such as excellent chemical and thermal stability, cost-effective, simple synthesis process and appealing electronic structure [26]. The composite materials of g-C_3N_4 coupled with different metal oxides has been shown to enhance e^-/h^+ separation and increase light absorption in the visible region, presenting superior photocatalytic activity than pure g-C_3N_4 [27,28]. In the current work, we prepared the OMS-2/g-C_3N_4 hybrids by a simple reflux method, and evaluated the influence of g-C_3N_4 on the valance change and catalytic performance of OMS-2 for PMS activation under neutral conditions. To the best of our knowledge, the improvement of the catalytic activity of OMS-2 by turning the ratio of Mn(II + III)/Mn(IV) with the formation of inorganic/organic hybrids has not been reported.

2. Experimental

2.1. Materials

Acid orange 7 (AO7) was obtained from Aldrich. Other materials such as Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, containing 47% $KHSO_5$, i.e PMS), $KMnO_4$, $MnSO_4$, urea, melamine, pyromellitic dianhydride, benzoic acid (BA) and sodium pyrophosphate (PP) were purchased from Aladdin Industrial Inc.

2.2. Catalyst synthesis

The OMS-2/g-C_3N_4 hybrids (OMS-2/CN) were prepared by a refluxing method [29]. Typical 2.22 g $KMnO_4$ was dissolved in 100 ml deionized water in a beaker under ultrasonic vibration, named as A; 3.33 g $MnSO_4$, 7 ml nitric acid and g-C_3N_4, which was prepared by a thermal polycondensation of urea at in a muffle furnace at 500 °C for an hour with a heating rate of 4 °C/minute, were placed in 50 ml deionized water, named B. Then A was subsequently added dropwise into B under vigorous stirring to form a dark brown precipitate at a room temperature. The resultant slurry was then heated at a reflux temperature of 110 °C for 24 h, washed with deionized water to neutral, and finally dried at 80 °C for 24 h. The obtained product was denoted as OMS-2/CN-n (n = 1, 2) with g-C_3N_4 dosages of 0.33 and 1 g respectively. For comparison, pure OMS-2, metal doped OMS-2 (Cu, Co, and Fe, 5 wt%), other OMS-2 hybrids including OMS-2/graphite and OMS-2/polyimides were prepared with the same procedure. The polyimides were prepared with a same process described in literature [30].

2.3. Catalyst characterization

X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 powder X-ray Diffractometer with Cu Ka radiation. Fourier transform infrared (FT-IR) spectra were obtained on a Bruker Vector 22 spectrometer. The morphology of catalysts was observed by a Hitachi S-4800 scanning electron microscope (SEM) instrument (Hitachi Ltd., Japan) and field-emission transmission electron microscope (FETEM, Tecnai G2 F20). The catalyst composition was investigated by energy dispersive spectroscopy (EDS). N_2 adsorption isotherm was measured at 77 K using a Quanta chrome Autosorb-1. X-ray photoelectron spectra (XPS) measurements were conducted on a VG Multilab2000 spectrometer (Thermo Electron Corporation) with Al Ka radiation as the exciting source. Charging effects were corrected by adjusting the binding energy of C 1s to 284.6 eV. The average oxidation state (AOS) of the prepared samples was obtained using a potentiometric titration method that has been described in detail elsewhere [31].

2.4. Catalyst activity

Catalyst activities of OMS-2/CN hybrids were performed by the degradation of Acid Orange 7 (AO7) in the presence of PMS. In a typical procedure, a 50 ml aqueous solution with 0.13 mM AO7 and 0.65 mM PMS was adjusted to a pH of 7.2 by NaOH. The degradation reaction was initialized by adding 0.01 g catalyst. The reaction was carried out at a room temperature of 8 °C. To monitor the degradation process, solution samples were taken out at given time intervals, filtered by a 0.45 μm film to remove the catalyst, and measured immediately on a Varian Cary 50 Scan UV–vis spectrophotometer under an absorption wavelength of 484 nm. The degradation extent was described as C/C_0, where C_0 was refer to dye absorbance before degradation. In the experiment of active species detection, 1 ml quenching agent was added in the system, and the degradation was evaluated as above. For the recycling experiment, the catalyst was separated without any treatment after each recycle, and the next reaction was started by adding fresh AO7 and PMS.

3. Results and discussion

3.1. Catalyst characterization

The powder XRD patterns of the prepared catalysts are shown in Fig. 1. The peaks for pure OMS-2 at 12.7, 18.0, 28.7, 37.5, 41.9, 49.8, 56.5, 60.1, 65.4 and 69.5° can be indexed to (110), (200), (310), (211), (301), (411), (600), (521), (002) and (541) (JCPDS 29-1020), respectively [25]. For the pure g-C_3N_4, the typical (002) interlayer-stacking peak at 27.6° and another week peak at 13.0° corresponding to the (100) plane were observed [28]. For the hybrids of OMS-2/CN, the structure of OMS-2 kept unchanged, but the main peaks of g-C_3N_4 disappeared. In the enlarged figures shown in Fig. S1 in Supplementary material, only an increase of the intensity at 2theta = 27.6° was observed in OMS-2/CN-2. The absence of g-C_3N_4 reflections is most likely due to its low amount. In addition, it may be also resulted from that the g-C_3N_4 particles became smaller during preparation and well dispersed in the hybrids.

In order to analysis the forming mechanism of OMS-2/CN, the XRD patterns of OMS-2 and OMS-2/CN-2 precursors, prepared by mixing $KMnO_4$, $MnSO_4$ and HNO_3 at room temperature with and without g-C_3N_4 respectively, were examined. As given in Fig. 1(B), the patterns show that a poorly ordered manganese oxide phase (MnOx) was obtained, with two main peaks at 2theta of about 37.7° and 65.9° [31]. Moreover, the peak attributed to g-C_3N_4 at 2theta = 27.6° can be distinguished clearly in OMS-2/CN-2 precursor. The results suggest that in the mixture of $KMnO_4$, $MnSO_4$ and g-C_3N_4 at room temperature, $KMnO_4$ will react first with Mn^{2+} to form MnO_x. For the MnOx/CN sample, prepared by mixing $KMnO_4$, HNO_3, and g-C_3N_4 at room temperature and then refluxing at 110 °C for 24 h, there are two broad peaks at 2theta around 11.6 and 23.4° appeared, in addition of those observed in OMS-2/CN-2 precursor. This might be probably caused by the partial oxidized product of g-C_3N_4 by $KMnO_4$ at a high temperature. While without refluxing, the XRD patterns of the solid products from $KMnO_4$, HNO_3, and g-C_3N_4 were the same as that of pure g-C_3N_4. However, the two peaks were not observed in all of the OMS-2/CN catalysts, suggesting that the strong oxidation of g-C_3N_4 by $KMnO_4$ did not occur during refluxing procedures.

Fig. 2 shows SEM images of the obtained samples. Pure OMS-2 was nanofibers with a diameter of about 20–30 nm, as also indi-