Self-assembled ZnAl-LDH/PMo$_{12}$ nano-hybrids as effective catalysts on the degradation of methyl orange under room temperature and ambient pressure

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ABSTRACT

ZnAl-layered double hydroxide/H$_3$PMo$_{12}$O$_{40}$ (ZnAl-LDH/PMo$_{12}$) nano-hybrids were prepared by self-assembly between positively charged LDH nano-sheets and negatively charged PMo$_{12}$ nano-clusters. The catalytic performance of ZnAl-LDH/PMo$_{12}$ (ZAM) nano-hybrids on methyl orange (MO) degradation under room temperature and ambient pressure was investigated. The self-assembly process was evidenced by various characterization results, including X-ray diffraction, scanning electron microscopy, transmission electron microscopy, N$_2$ adsorption measurements, and X-ray photoelectron spectroscopy, which also suggested that the structure and morphology of the ZnAl-LDH/PMo$_{12}$ hybrids played a critical role in their catalytic performance. The ZAM nano-hybrid with a 1:1.59 M ratio of ZnAl-LDH to PMo$_{12}$ exhibited an excellent catalytic activity for MO degradation, with a 74.2% discoloration rate and a 66.2% total organic carbon (TOC) removal efficiency. After five cycles of reactions, the discoloration rate remained at 62.5%. This high catalytic activity might be attributed to the formation of O$_2$$^{\cdot-}$, which was generated from the reduction of the dissolved oxygen by PMo$_{12}$. Overall, the results show that the formation of novel nano-hybrid catalysts through self-assembly of LDH nano-sheets with PMo$_{12}$ nano-clusters leads to a significant improvement in the catalytic activity and stability of Mo based catalysts under room temperature and ambient pressure.

1. Introduction

Catalytic wet air oxidation (CWAO) technology has been widely adopted for the commercial treatment of organic wastewater as a highly effective and simple process, with short residence time and minimal secondary pollution [1,2]. However, a significant disadvantage of CWAO is that the process typically requires a high temperature and pressure condition, consequently increasing operational costs and limiting its practical applications. With an aim to overcome these current constraints of CWAO, extensive researches have been directed at exploring novel catalysts with a high catalytic activity under room temperature and ambient pressure [3,4].

A series of molybdenum based catalysts exhibited adequate catalytic performance for dye wastewater treatment under mild conditions and were thereby noted as prospective candidates for use in CWAO processes [4–16]. Recently, Wang et al. investigated a series of Mo-based catalysts, such as Na$_2$Mo$_4$O$_{13}$/α-MoO$_3$, which demonstrated high catalytic activity on the degradation of cationic red GTL [15]. In previous studies, a Mo-Zn-Al-O heterogeneous catalyst was prepared with a ZnAl-layered double hydroxide (ZnAl-LDH) carrier. The catalytically active molybdate ions were intercalated into the interlayer space and adsorbed onto the surface of ZnAl-LDH. Under room temperature and ambient pressure, cationic red GTL and cationic orchid X-BL were readily adsorbed on the Mo-Zn-Al-O catalyst and degraded, with a discoloration rate of 80.1% and 94.6%, respectively [10,17]. However, Mo$_7$O$_{24}$$^{6-}$ anions have a tendency to leach out in weakly acidic to basic conditions due to their hydrolytic instability. This usually results in the co-formation of an impurity phase accompanying the reactions. Due to charge repulsion existing between the anionic dye and the negatively charged Mo-Zn-Al-O catalyst, the degradation of anionic dye wastewater by this catalyst is negligible.

In recent years, inorganic 2D nanostructured materials have been widely used in the field of catalysis [18,19]. For example, LDHs can be exfoliated into positively charged nano-sheets for use as building

blocks, along with anionic substances, in the construction of various inorganic/organic nanostructured hybrids [20]. Cavani et al. reported that the glycine intercalated LDHs could be exfoliated into single-layer nano-sheets in formamide solution [21]. Mesoporous layer-by-layer ordered nano-hybrids were prepared by electrostatically driven self-assembly between the positively charged ZnCr-LDH nano-sheets and the negatively charged titanate nano-sheets [22,23]. The resulting hetero-layered nano-hybrid structure exhibited improved stability and photocatalytic activity under visible light. Although various types of hybrid catalysts consisting of sheet-structured materials have been reported [22,24–28], the combination of nano-sheets and nano-clusters to form heterogeneous nano-hybrids is expected to be equally, if not more, effective compared to those consisting solely of nano-sheets, because heterogeneous nano-hybrids such as LDH/PMo_{12} may open more actives sites for the direct contact with reactants. In comparison to $Mo_7O_{24}^{6-}$ anions, PMo_{12} clusters with faster reversible multi-electron redox behavior and more stable performance under mild conditions [29], are expected to be able to better assemble with LDH nano-sheets. Patterning of Mo_{12} clusters on LDH nano-sheets is expected to enhance both the catalytic activity and stability. This complementary combination of both nano-sheets and nano-clusters may potentially broaden the scope and application of molybdenum based catalysts.

In this work, we designed a group of novel heterogeneous catalysts comprised of PMo_{12} nano-clusters and ZnAl-LDH nano-sheets. Positively charged LDH nano-sheets and negatively charged PMo_{12} nano-clusters were self-assembled to form heterogeneous nano-hybrids. By this approach, PMo_{12} can be effectively immobilized, thus minimizing the issue of leaching, but the nano-hybrid remains highly active. The catalytic activity and chemical stability of these hybrid catalysts for the degradation of MO under room temperature and ambient pressure were systematically evaluated in conjunction with their structural and physicochemical properties.

2. Experimental

2.1. Materials

The chemicals used for this project, including $Zn(NO_3)_2 \cdot 6H_2O$ (99%), $Al(NO_3)_3 \cdot 9H_2O$ (99%), $NaNO_3$ (99%), NaOH (99%), H_2SO_4 (98%), HCl (37%), and PMo_{12} (99%), were purchased from Sinopharm Chemical Reagent Co. Ltd. They were used as received without further purification.

2.2. Synthesis of ZnAl-LDH nano-sheets

Highly crystalline ZnAl-LDH was synthesized by the co-precipitation method reported previously [10,25]. A solution (250 mL) containing 0.40 M $Zn(NO_3)_2$ and 0.20 M $Al(NO_3)_3$ was added drop-wise into 200 mL (0.50 M) $NaNO_3$ aqueous solution. During the synthesis, the pH value was maintained constant at ca. 6.0 by adding a suitable amount of 0.40 M NaOH solution. The obtained slurry was aged at 70 °C for 24 h and the sample was then washed with deionized water and dried in an oven at 60 °C overnight. After drying, 10.0 g of the as-synthesized ZnAl-LDH sample was added into 1.0 L of formamide, and the mixture was shaken until no sediment was observed and the dispersion became transparent. After standing for 24 h, the supernatant containing ZnAl-LDH nano-sheets [21] was collected for the subsequent assembly with PMo_{12} nano-clusters.

2.3. Fabrication of ZnAl-LDH/PMo₁₂ (ZAM) nano-hybrids

Two dispersions, one containing LDH nano-sheets and the other containing PMo_{12} nano-clusters, were mixed directly under vigorous stirring at room temperature and left standing still for 24 h in an N_2 atmosphere. Then, the mixture was hydrothermally treated at 200 °C for 10 h to promote the hybridization [30] between the positively

charged LDH nano-sheets and the negatively charged PMo_{12} nano-clusters. The obtained ZAM nano-hybrids under various ratios were then separated by centrifugation (14,800 g force) and washed thoroughly with an ethanol-water solvent (1:1, v/v), and finally dried under vacuum at 70 °C for 24 h. The molar ratio of ZnAl-LDH to PMo_{12} was varied to adjust the restacking structure of the resultant nano-hybrids on the basis of charge balance (1:1.59). The ratios of ZnAl-LDH to PMo_{12} were 1:1.17 (ZAM-1), 1:1.59 (ZAM-2), 1:2.14 (ZAM-3) and 1:4.67 (ZAM-4). A control sample of self-assembled ZnAl-LDH nano-sheets absent of PMo_{12} was also prepared and labeled as ZAM-0.

2.4. Characterization

X-ray diffraction (XRD) patterns of the as-prepared samples were recorded on a Philips PANalytical X'Pert PRO X-ray diffractometer using Cu K_α radiation (λ = 0.15418 nm) to determine the stacking structures of the respective samples.

Scanning electron microscopy (SEM) images were captured using a JEOL JSM-6700F electron microscope at an accelerating voltage of 10 kV.

The morphology of the nano-hybrids was determined by a transmission electron microscope (TEM, JEOL FEG-STEM 2010) at an accelerating voltage of 200 kV.

The pore structure of the catalysts was analyzed by the N_2 adsorption method on a surface area and porosity analyzer (NOVA-2000E, Quantachrome Instruments). The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method.

X-ray photoelectron spectrometry (XPS) spectra were recorded for each of the catalysts on a Thermo Scientific Escalab 250 X-ray photoelectron spectrometer using a monochromatic X-ray beam from an Al target (15 kV, 10 mA). The charging effect of the samples was corrected by referring to the C 1s peak of adventitious carbon (binding energy (BE) = 284.6 eV) [31].

2.5. Catalytic activity evaluation

The catalytic activity of the ZAM nano-hybrids was evaluated by the degradation of MO under room temperature and ambient pressure. A sample of 0.80 g ZAM nano-hybrids was used to catalyze the degradation of a solution of MO (1.0 L, 100 mg/L). The solution was aerated by an air pump at a rate of 3.5 L/min. The pH of the operating solution was not adjusted in the CWAO process. The adsorption of MO by the ZAM nano-hybrids was tested under N_2 atmosphere (instead of air), where the catalytic reaction can be effectively prohibited [4]. The decoloration rate of MO was estimated on the basis of its maximum absorbance at 462 nm using a UV–vis spectrophotometer (Shimadzu UV 2550). The total organic carbon (TOC) concentration during CWAO process was tested on a TOC analyzer (Shimadzu CPHCN200) to evaluate the mineralization of MO after 10 min of reaction [32]. The leaching rate of Mo from ZAM nano-hydrids was measured.

3. Results and discussion

3.1. Self-assembly of ZnAl-LDH and PMo₁₂

The assembly of ZnAl-LDH nano-sheets and PMo_{12} nano-clusters to prepare ZAM nano-hybrids is illustrated in Scheme 1 . The pristine ZnAl-LDH was exfoliated into nano-sheets and then mixed with PMo_{12} nano-clusters. During the subsequent hydrothermal treatment, ZnAl-LDH nano-sheets provided anchoring sites for the PMo_{12} nano-clusters. Like many other LDHs [33], the ZnAl-LDH can be exfoliated into nano-sheets by agitating in formamide, resulting in formation of a colloidal dispersion. The formation of the colloidal dispersion of exfoliated ZnAl-LDH nano-sheets was evidenced by the apparent Tyndall effect (Scheme 1), confirming the collapse of the layered structure. The size of PMo_{12} nano-clusters was ca. 0.90 nm so that the ZnAl-LDH nano-sheets could