



Framework Cu-doped AlPO₄ as an effective Fenton-like catalyst for bisphenol A degradation



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ABSTRACT

Cu-doped AlPO₄ molecular sieve was prepared by a hydrothermal method and characterized by field emission scanning electron microscope, X-ray diffraction, extended X-ray absorption fine structure, X-ray photoelectron spectroscopy and nitrogen adsorption/desorption isotherms. The Cu(0.05)-AlPO₄ with Cu/Al molar ratio of 0.05 was highly effective and stable for the degradation of bisphenol A (BPA) in the presence of H₂O₂ at room temperature and neutral pH conditions. The characterization results confirmed that Cu(II)/Cu(I) was co-incorporated into AlPO₄ molecular sieve by chemical bonding of Cu—O—T (T for Al or P) in Cu(0.05)-AlPO₄, increasing the BET surface area of AlPO₄ for more active sites. Excessive copper species existed in the form of Cu(II) and located in the extraframework sites, blocking the porous structure to decrease the specific surface area of AlPO₄. The studies of electron spin resonance, *in situ* Raman spectra and other experiments verified that H₂O₂ was predominately converted into •OH and HO₂•/O₂•⁻ in Cu(0.05)-AlPO₄ suspension. Specially, the presence of BPA in Cu(0.05)-AlPO₄ suspension promoted the conversion of H₂O₂ into •OH. A mechanism of heterogeneous Fenton catalysis was proposed on the basis of the cycle between Cu(I) and phenoxo-Cu(II) complexes during the interaction of Cu(0.05)-AlPO₄, BPA and H₂O₂.

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1. Introduction

Bisphenol A (BPA) is one of the most common endocrine disruptors, which has been widely used as a raw material for producing polycarbonate plastic, epoxy resins, flame retardants, and other chemical products [1,2]. The global demand for BPA was more than 6.5 million tons in 2012 and its annual growth rate is expected to be 4.6% from 2013 to 2019 [3]. Due to its large production and widespread application, BPA has been released into the aquatic environment by direct discharge of effluents from its manufacture processing, wastewater treatment plants [4] and landfill leachates [5]. The presence of BPA in the aqueous environment is harmful to ecosystems and human health. Therefore, it is necessary to develop a proper technique to rapidly and efficiently remove BPA from wastewater, groundwater and even drinking water.

As one of the most effective advanced oxidation processes, Fenton process has unique advantages due to the generation of powerful hydroxyl radical (•OH) by a simple reaction between Fe(II) and H₂O₂ with low cost and environmental benignity. During this process, most organic pollutants can be nonselectively degraded into non-toxic products under ambient temperature and pressure [6,7]. However, the application of conventional homogeneous Fenton processes is limited by the requirement of low solution pH (<4), the difficulty of Fe²⁺/Fe³⁺ cycling, and the formation of ferric hydroxide sludge in wastewater treatment [8]. To overcome these problems, the heterogeneous Fenton-like processes have been recently investigated as a more practical and efficient alternative technique for removing recalcitrant organic pollutants over a wider pH range with reduced catalyst loss. Specially, many iron-free catalysts, such as copper [9], Au [10], manganese [11], titanium [12], and carbon materials [13], have sprung up as Fenton-like catalysts to activate H₂O₂ into reactive oxygen radicals for the degradation of organic pollutants in water.

Among these iron-free catalysts, Cu-containing catalysts have attracted considerable attention in recent years, because of the

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high natural abundance and low cost of Cu, and the practical multiple methods to prepare Cu-based materials [14]. In particular, the reduction of Cu^{2+} by H_2O_2 ($4.6 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$) is more easy than that of Fe^{3+} ($0.001\text{--}0.02 \text{ M}^{-1} \text{ s}^{-1}$), and Cu^+ can react efficiently with H_2O_2 to form $\cdot\text{OH}$ with a higher reaction rate ($1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$) than Fe^{2+} ($76 \text{ M}^{-1} \text{ s}^{-1}$) [15–17]. Due to the mobilization of $\text{Cu}^{2+}/\text{Cu}^+$ in water, copper has been suggested to be supported on a porous solid substrate. Cu-containing MFI zeolites [18], Cu/SBA-15 [19], Cu-ZSM-5 [20,21], Cu-impregnated zeolite Y [22] and Cu/TUD-1 [23] have been reported for Fenton-like oxidation of different organic pollutants. The oxidation of organic compounds by the reported Cu-based heterogeneous Fenton-like systems was often followed by the release of Cu ($0.5\text{--}10 \text{ mg L}^{-1}$) [24] and the invalid decomposition of H_2O_2 to O_2 [9]. AlPO_4 was proven to be a robust support material that produces optimum interactions with metal-based species, facilitating high dispersion and thermal stabilization [25]. Moreover, the incorporation of transition metal cations into the Al and P framework of AlPO_4 molecular sieves could markedly enhance the redox catalytic activity [26]. The presence of Cu(I) in the framework of ZSM-5 has been proposed to promote the decomposition of H_2O_2 and the formation of $\cdot\text{OH}$ [27]. This paper intends to introduce Cu(I) and Cu(II) into the framework of AlPO_4 , investigate the performance of Cu-containing AlPO_4 for BPA removal through Fenton-like oxidation, and the corresponding $\cdot\text{OH}$ formation mechanism by the interaction of BPA with framework Cu(II) and the Cu redox transformation.

In this paper, Cu-doped AlPO_4 was prepared, characterized, and assessed for Fenton catalysis. Cu(0.05)- AlPO_4 was found to be highly effective and stable for the degradation of BPA at room temperature and neutral pH conditions in the presence of H_2O_2 . The possible catalytic mechanism was also discussed.

2. Experimental

2.1. Materials

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), aluminium isopropoxide ($\text{Al}(\text{O}_i\text{Pr})_3$), orthophosphoric acid (H_3PO_4 , 85 wt%), diisopropylamine and hydrogen peroxide (H_2O_2 , 30%, w/w) were purchased from Sinopharm Chemical Reagent Co., Ltd. 5-Tert-butoxycarbonyl-5-methyl-1-pyrroline-*N*-oxide (BMPO) was provided by Sigma Ltd. Bisphenol A (BPA) was obtained from Acros (Geel, Belgium). All chemicals were at least analytical grade.

2.2. Preparation of catalysts

Cu-doped AlPO_4 was synthesized using a hydrothermal method. In a typical procedure, 7.08 g $\text{Al}(\text{O}_i\text{Pr})_3$ was dissolved in 15 mL of deionized water, and stirred at 35°C for 1 h. Then, 7.4 mL 27.5 wt% H_3PO_4 , 5 mL of an aqueous solution containing a certain amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and 2.5 mL diisopropylamine were added to the $\text{Al}(\text{O}_i\text{Pr})_3$ homogeneous gel in order. Next, the resulting solution was continuously stirred magnetically for 22 h and then transferred to a 50 mL Teflon-lined autoclave and heated in an oven at 180°C for 72 h. After natural cooling, the obtained solids were filtered, washed with deionized water and dried at 120°C . The solid product was calcined in air at 550°C for 8 h. The synthesized samples were denoted as AlPO_4 , Cu(0.005)-, Cu(0.01)-, Cu(0.015)-, Cu(0.025)-, Cu(0.05)-, Cu(0.075)-, and Cu(0.1)- AlPO_4 , where the number referred to the Cu/Al molar ratio in the precursor solution ($\text{Cu}/\text{Al}_{\text{pre}}$) of 0, 0.005, 0.01, 0.015, 0.025, 0.05, 0.075, and 0.1, respectively.

2.3. Characterization

Morphological studies were carried out using a field emission scanning electron microscope (FESEM, Hitachi, S-5500) at acceleration voltage of 5 kV. The crystal structure was analyzed by X-ray diffraction (XRD, Scintag-XDS-2000) equipped with Cu $\text{K}\alpha$ radiation ($\lambda = 1.540598 \text{ \AA}$) at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) data were measured on an Kratos AXIS-Ultra instrument with monochromatic Al $\text{K}\alpha$ radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. The C1s photoelectron binding energy was set at 284.8 eV and used as reference for calibrating other peak positions. The Fourier transforms of the extended X-ray absorption fine structure (EXAFS) signals were analyzed from Cu K-edge (8.979 keV) X-ray absorption spectra collected at room temperature in transmission mode on the BL14W1 beam line at the Shanghai Synchrotron Radiation Facility (SSRF), China. The background removal, atomic absorption normalization and the EXAFS part extraction were performed using the Winxas 3.1 program. The EXAFS oscillation $\chi(k)$ was extracted using spline smoothing, weighted by k^3 in the high k range, and then transformed to R space with a Hanning function window. The Brunauer-Emmett-Teller (BET) surface area measurements were carried out by N_2 adsorption at 77 K using an ASAP 2020 HD88 instrument. The samples were previously outgassed for 30 min at 150°C and 4 Pa and then heated for 120 min at 350°C . For the electron spin resonance (ESR) spectra measurement, 0.01 g of the catalyst was dispersed in 1 mL of water or methanol, following by the addition of 10 μL of H_2O_2 (30%, w/w). Then, 100 μL of the above suspension was quickly mixed with 10 μL of BMPO (250 mM). To test the effect of BPA, 1 mL BPA (100 mg L^{-1}) with water or methanol as solvent was used to disperse the catalyst. The ESR spectra with BMPO as a spin trap agent were recorded to detect reactive oxygen radicals on a Bruker A300-10/12 ESR spectrometer (microwave frequency: 9.86 GHz; microwave power: 2.29 mW; center field: 3504.07 G; sweep width: 100.00 G; modulation frequency: 100.00 kHz; conversion: 80.00 ms; time constant: 40.96 ms; and sweep time: 81.92 s). The *in situ* Raman spectra were recorded on a LabRAM HR Evolution (HORIBA, France) equipped with a CCD detector using a laser source at an excitation line of 532 nm. In a typical procedure, 0.05 g of the catalyst was mixed with 3 mL of water or BPA aqueous solution (100 mg L^{-1}), and then 100 μL of H_2O_2 (30%, w/w) was added. The mixture was placed into the reaction cell, which was scanned from 200 to 2000 cm^{-1} .

2.4. Procedures and analysis

The Fenton-like catalytic experiments were carried out under ambient conditions by using BPA as a model contaminant. In a typical experiment, 1 g L^{-1} catalysts were dispersed in the 25 mg L^{-1} aqueous solution of BPA (pH 7.0). The mixture was vigorously stirred for 30 min to establish the adsorption/desorption equilibrium. Then, 10 mM H_2O_2 was added into the suspension to initiate the reaction. At fixed time intervals during the degradation process, the analytical samples were taken out and immediately filtered through a 0.22 μm millipore filter to remove the catalyst particles. The solution concentration of BPA was measured by high-performance liquid chromatography (HPLC, 1200 series; Agilent) with an autosampler and a Zorbax SB-Aq column ($4.6 \times 250 \text{ mm}$, 5 μm ; Agilent), and equipped with an UV detector at the wavelength of 225 nm. The mobile phase was a mixture of 70/30% (v/v) methanol/water and was operated at a flow-rate of 1.0 mL min^{-1} . The total organic carbon (TOC) was determined by a TOC-V_{CPH} analyzer (Shimadzu) using high-temperature combustion. The metal content in the catalysts after dissolving by nitric acid and hydrofluoric acid and the amount of metallic ions releasing from the

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