

BIMETAL (Cu/Fe) MODIFIED MESOPOROUS SILICA AS AN EFFICIENT FENTON-LIKE CATALYST FOR BISPHENOL A REMOVAL

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ABSTRACT

The immobilization of metals in/on the structure of mesoporous silica has been proved challenging due to leaching problems and the accessibility of metal sites for catalytic reactions. We synthesized bimetal modified mesoporous SiO₂ via direct synthesis of Cu and Fe. The catalysts were tested for the removal of bisphenol A (BPA), a model molecule for contaminants of emerging concern (CEC), from water under neutral pH conditions. Additionally, photocatalytic effect of each metal was studied. The incorporating of metals in/on the silica support did not significantly affect the specific surface area nor the pore volume of mesoporous silica structure. The combination of Cu and Fe was proved most effective for the BPA removal, with Cu being the most active site (Cu/Si = 0.02). Iron showed photocatalytic activity under visible light and its optimum molar concentration was Fe/Si = 0.01. The most successful catalyst completely removed BPA in less than 90 min in a photo-Fenton reaction and its activity was stable for up to four consecutive loadings of fresh BPA.

Key words: Water treatment; Photo-Fenton-like systems; Photocatalyst; Sunlight

INTRODUCTION

The demand for clean drinking water is increasing from year to year due to the growing world population and the associated increase in industrial and agricultural activities, while drinking water supplies are diminishing, partly due to climate change. The reuse of wastewater poses some challenges as it is a source of contaminants of emerging concern (CECs). More efficient removal of these pollutants from wastewater is crucial, while the simultaneous reduction of their emission, e.g. through quaternary wastewater treatment, is also critical. A prime example of such pollutants are e.g. bisphenols (BPs), a group of industrial chemicals with a common basic structure containing two phenol rings linked by a C–H bridge [1]. Their best-known representative is bisphenol A (BPA), which is used in the production of polycarbonate plastics and epoxy resins. Due to the hormone disruption caused by BPA, the European Food Safety Authority banned the use of BPA in the manufacture of baby bottles as a precautionary measure in 2011 and lowered the tolerable daily intake from 4 µg/kg body weight to 0.2 ng/kg body weight in 2023, based on scientific evidence of the toxic effects of the compound [2].

The removal of BPA from water can be achieved by using advanced oxidation methods, one of which is the Fenton reaction. The homogeneous Fenton reaction uses iron salts at low pH. Due to the production of iron sludge and the need for acidic pH values, a switch to heterogeneous Fenton-like systems operating under quasi-neutral conditions is highly desirable. In this case, several metals can be used, of which Cu and Fe are the most important. Mesoporous silica can be used as a support for anchoring the metals to the surface due to its good tunability and high chemical stability. We have already shown that for bimetallic Cu/Mn catalysts on silica support, convincing BPA removal is most efficient at a near-neutral pH of 6.5 [3]. However, using SiO₂ as a support suffers from relatively insufficient binding of metal sites, resulting in low reusability [4].

Herein, iron and copper were incorporated onto/into the SiO₂ support during the solvothermal synthesis of mesoporous silica with a direct source of both metals in the form of metal acetates. The samples were tested for the removal of BPA in their powder form at quasi-neutral pH conditions and under visible light irradiation.

EXPERIMENTAL

25 g of silica source (Aldrich, 98%) and 0.324 g iron (III) acetate hexahydrate (Sigma Aldrich, 95%), with theoretical molar ratio of Fe/Si = 0.02, 0.01 and 0.005 was stirred for 10 min. After that 0.475 g of copper acetate monohydrate (Aldrich) with theoretical molar ratio of Cu/Si = 0.02 was stirred for 10 min. Triethanolamine (8.86 g, Sigma Aldrich, 99%) as a structure directing agent (directs the polycondensation of silicate species) was added dropwise after 10 min of stirring. Distilled water (16.16 g) was also added dropwise to the mixture under continuous stirring at room temperature. After 30 minutes of continuous stirring, tetraethylammonium hydroxide (8.66 g, Acros, 20%) was added as a pH moderator. The formed gel was aged overnight at room temperature then furnace dried for 24 h at 50 °C.

The obtained product was grinded and solvothermally treated in a Teflon-lined stainless-steel autoclave (45 mL) at 150 °C for 48 h in 30 mL of ethanol. The solid product was separated by filtration and washed with ethanol and finally dried at ambient room temperature overnight.

The pores were freed from organic compounds (structure directing agent triethanolamine and pH moderator tetraethylammonium hydroxide) via calcination: direct calcination at 500 °C for 10 h using a ramp rate of 1 °C/min under continuous air flow. (The heating started from room temperature and the furnace needed 5 h to get 500 °C and 5 h to cool down to room temperature.) The synthesized materials were denoted as CuFeKIL002-C, CuFeKIL001-C and CuFeKIL0005-C for catalysts with Fe to Si molar ratios of 0.02, 0.01 and 0.005, respectively.

X-ray powder diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO MPD X-ray diffractometer using CuK_α1 radiation ($\lambda=1.5406$ Å), in the range from 10 to 70° (2 θ), with the step of 0.034°.

Before measuring the N₂ adsorption/desorption isotherms of prepared catalysts the samples were pretreated by means of the Micromeritics SmartPrep degasser in a stream of nitrogen (purity 6.0, Linde) at 90 °C for 60 min and afterwards at 200 °C for 120 min. To obtain N₂ adsorption/desorption isotherms of the catalysts at 77 K, we employed the Micromeritics TriStar II 3020 analyser. The BET specific surface area was calculated from adsorption data in the relative pressure range from 0.06 to 0.165. The total pore volume was estimated on the basis of the amount adsorbed at a relative pressure of 0.98. The pore size distributions were calculated from nitrogen adsorption data using an algorithm based on ideas of Berrett, Joyner and Halenda (BJH).

X-ray absorption spectra at Cu and Fe K-edge were measured at the P65 beamline of PETRA III, DESY in Hamburg and at the XAFS beamline at Elettra synchrotron radiation facility at Trieste, Italy. The measurements were performed in transmission mode in dark and with continuous visible light illumination (KL 2500 LED, Schott). The catalysts and reference compounds were prepared as homogeneous self-supporting pellets with the total absorption thickness (μ d) of about 2.5 above the corresponding K-edges. Depending on the data quality, up to five spectra were averaged for each sample. Exact energy calibration was established with the simultaneous absorption measurements on corresponding 5 μ m metal (Cu and Fe foil) inserted between the second and third ionization cell. The analysis of XANES spectra was performed with the Athena (IFEFIT) program packages [5]. BPA (10 mg/L) was

degraded in a 100 mL double jacketed batch reactor with a controlled temperature at 25 °C (Julabo). The pH was being monitored (Metrohm) and adjusted constantly by using 0.1 M NaOH. When photocatalytic reactions were performed, visible light was provided externally via KL 2500 LED lamp, (1000 lm of output, $\lambda_{em} = 400\text{--}700$ nm, $\lambda_{max1} = 443$ nm, $\lambda_{max2} = 520$ nm).

RESULTS AND DISCUSSION

Textural properties of the synthesized samples are shown in Table 1. Combination of the two different metals gave slightly different specific surface areas. All catalysts have pores below 10 nm. This means their surface is comparable and any differences in catalytic activity should be ascribed to other factors.

Table 4. Textural properties of various bimetal combinations as determined by N₂ sorption measurements.

| Sample | S _{BET} (m ² /g) | V _p (cm ³ /g) | Average pore size (nm) |
|---------------|--------------------------------------|-------------------------------------|------------------------|
| CuFeKIL0005-C | 667 | 1.231 | 15.9, 5.7 |
| CuFeKIL001-C | 595 | 1.658 | |
| CuFeKIL002-C | 592 | 0.798 | 2.8 |
| CuKIL-C | 558 | 1.486 | 13.3, 12.3 |

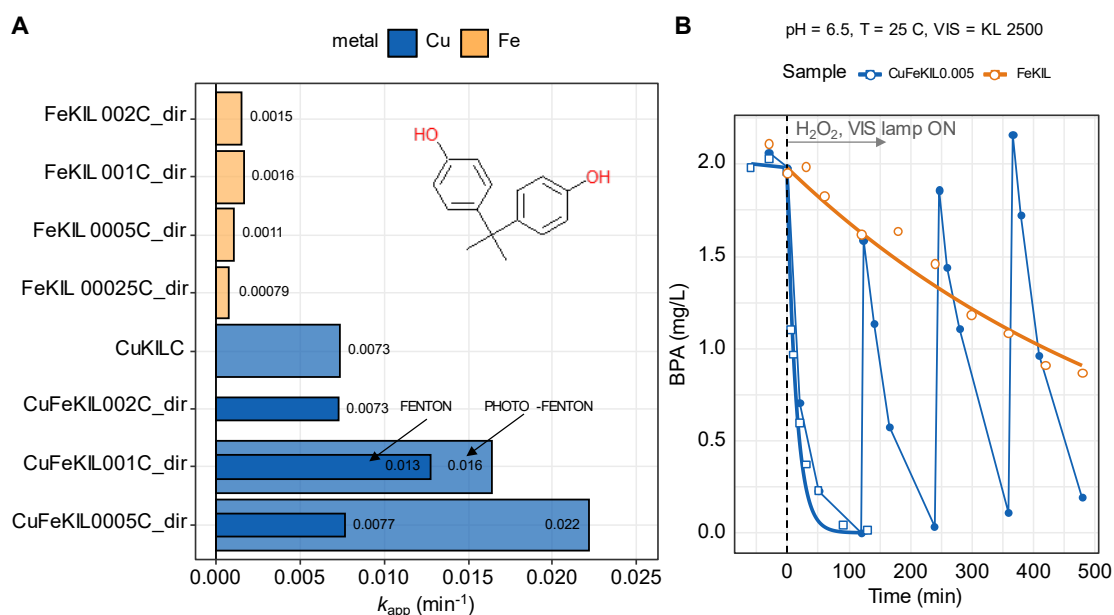


Figure 1. Reaction rate constants of BPA (structure in inset in (A)) removal for several samples (A) and kinetic profiles of BPA removal for experiments at lower BPA initial concentration and longer reaction times (B). The Cu molar ratio is affixed to Cu/Si = 0.02. γ (catalyst) = 400 mg/L, T = 25 °C.

The Fenton-like catalytic activity for the removal of BPA showed that copper was the most active metal under the given conditions (Fig. 1). Monometallic Fe catalysts are less active than Cu. Therefore, the combination of Cu and Fe was further investigated. In these samples CuFeKIL (different molar ratios of Fe/Si), a clear increase in activity can be seen when visible light is introduced into the system (photo-Fenton, Fig. 1a). However, the most significant increase was seen in a sample with a Fe/Si ratio of 0.005. Further increases in Fe content had a detrimental effect on the photo-Fenton activities. When small Fe concentrations are introduced, the positive effect on the photo-Fenton kinetics exceeds the sum of the Fe and

Cu elements alone, indicating the presence of synergy between the cations in such catalysts. The ex-situ and in-situ XAS experiments have shown that irradiation with visible light results in a beneficial structural change between the active sites. On the other hand, long-term stability was also observed (Fig. 1b). The catalyst was repeatedly exposed to fresh doses of BPA in the same experiment, which is close to the conditions in a real application. In addition, the pH was actively adjusted to 6.5, which has proved to be most effective for this type of catalyst in our previous study [3].

CONCLUSIONS

Mesoporous silicas modified with two metals were synthesized and tested as catalysts for the (photo)Fenton removal of BPA at pH 6.5. The experimental results allow the following conclusions:

- Incorporation of the two selected metals does not decrease the specific surface area of the mesoporous silicate support of the catalysts.
- The most photo-Fenton active catalyst is CuFeKIL0005-C, with an optimal Cu/Si molar ratio of 0.02 and for Fe/Si the best ratio is 0.005.
- The synergistic effect between Cu and Fe was demonstrated at the structural level by XAS analysis.
- The most successful catalyst CuFeKIL0005-C is catalytically stable over several rounds of BPA exposure.

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