

DESIGN OF BIMETAL CATALYSTS ON MAGNETIC POROUS SILICA SUPPORT FOR FENTON-LIKE AOP WASTEWATER PURIFICATION

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ABSTRACT

A new push to solve the problems related to purification of industrial wastewaters was given by advanced oxidation processes (AOPs) and their advantage to generate highly reactive free hydroxyl radicals, which decompose organic molecules to non-harmful H₂O, CO₂ and inorganic species. On the basis of previous promising results for manganese containing porous silica supported catalyst for heterogeneous catalytic Fenton-like AOP at neutral pH we designed copper and manganese containing catalysts on magnetic porous silica supports. The catalysts were prepared via direct solvothermal synthesis. Two different procedures (extraction-calcination and calcination) for template removal were applied in order to investigate the influence of the procedure to the textural and catalytic properties of the obtained materials. Prepared catalysts were tested for removal of different dyes in cationic, anionic and zwitterionic forms as model pollutants. Catalytic results show that prepared catalysts are more suitable for removal of anionic and zwitterionic dyes if compared to cationic dyes. The result is due to the surface charge of the catalysts.

Keywords: bimetal catalyst; manganese and copper active sites; porous silica support; magnetic support; dye degradation.

INTRODUCTION

In the last few decades, wastewater purification and total degradation of organic pollutants (dyes, antibiotics, pesticides, etc.) has been the main object of many academic and industrial research groups not only for environmental issues but also for recycling water sources. The most commonly used AOP is iron based Fenton AOP, but its application as a homogeneous catalytic process is limited because of its drawbacks such as i) optimum efficiency is typically achieved under acidic pH (pH=3), ii) formation of large amounts of ferrous iron sludge and iii) the presence of iron ions after the reaction in the effluents [1].

In order to solve the above problems we designed Fe₃O₄/porous silica composites with magnetic properties as supports for the Mn and Cu catalytically active species working at pH close to neutral.

EXPERIMENTAL

Preparation of the catalysts

Mn and Cu porous silica supported catalysts with magnetic properties were synthesized following a previously reported procedure for the disordered, amorphous, mesoporous silica material type KIL [2] with some modifications. In the first step manganese acetate tetrahydrate (Mn(CH₃COO)₂·4H₂O, Acros) and copper acetate monohydrate (Cu(CH₃COO)₂·H₂O, Acros) with theoretical molar ratios of Mn/Si=0.01 and Cu/Si=0.01 were mixed with 25 g TEOS (Acros, 98 %) and stirred for 10 minutes. Triethanolamine (8.86g, Fluka, 99 %) and distilled water (16.4 g) were later added to the above mixture during

continuous stirring at room temperature and stirred for another 30 min. Tetraethylammonium hydroxide (8.66 g, Acros, 20 %) was added at the end. The solution was stirred with a magnetic stirrer till firmation of homogeneous gel. The final gel was later aged overnight at room temperature and then dried in a furnace for 24 h at 50°C. In the second step, the gel was treated in a Teflon-lined stainless steel autoclave at 150°C for 48 h in ethanol. For the samples containing Fe₃O₄, previously prepared magnetic nanoparticles were dispersed into TEOS and ultrasonicated for 30 minutes. The solid product was decanted and washed with ethanol. For the template removal two different procedures were used: 1) extraction with ethanol at 80°C overnight followed by calcination at 450°C for 6 h using a ramp rate of 1°C/min in the flow of air or 2) calcination at 450°C for 6 h using a ramp rate of 1°C/min in the flow of air. The synthesized materials were denoted as FeKILCuMn—ExC, KILCuMn—ExC and KILCuMn—C, FeKILCuMn—C, respectively.

Characterization

X-ray powder diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO high-resolution diffractometer using CuK α 1 radiation ($\lambda=1.5406$ Å).

Nitrogen physisorption isotherms were measured on a Quantachrom autosorb iQ₃ apparatus recording at -196 °C. The samples were outgassed at 200°C for 2 h.

The morphology of surface of the synthesized catalysts was examine by SUPRA 35VP (Carl Zeiss, Germany) field-emission scanning electron microscope operating at 1 kV and using a 10 μ m aperture.

Surface charge of the samples was measured by Zetasizer nano ZS instrument (Malvern) using electrophoretic light scattering technology in the pH range of 1–12 adjusted by the addition of either 0.1 M NaOH or 0.1 M HCl.

Catalytic tests

The Fenton-like catalytic reactions were carried out in a 250 mL five-necked glass reactor under continuous stirring (300 rpm). In a typical run, a water solution of dye (methylene blue, plasmocorinth B, resasurin) with concentration of 25 mg/L was transferred into the reactor and 100 mg of catalyst were added. The suspension was thermostated at T=25°C and purged continuously with nitrogen. The suspension was left for 30 min, for adsorption-desorption equilibrium to establish. Then H₂O₂ was added ($c_0=3.3$ %). One mL aliquots were withdrawn at periodic intervals (up to 240 min) and immediately filtered for the removal of the catalyst. The temporal concentration of dyes was determined by means of UV-Vis spectrophotometry (Perkin Elmer, USA).

RESULTS AND DISCUSSION

Diffraction patterns of materials containing iron showed the presence of Fe₃O₄ nanoparticles (Figure 1). Materials prepared by calcination procedure showed presence of CuO in comparison with samples prepared by extraction-calcination.

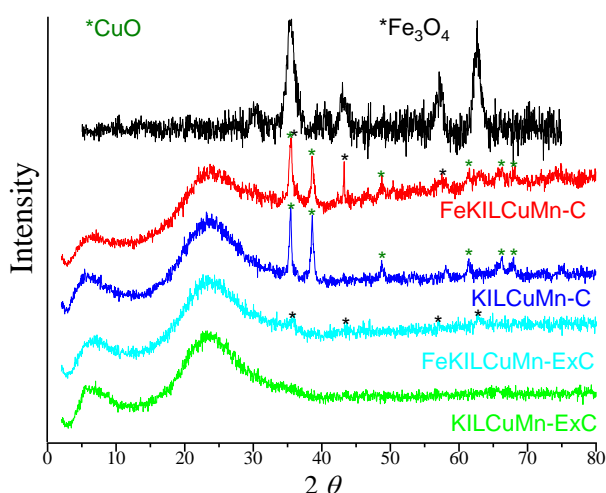


Figure 1. X-ray diffraction patterns of obtained catalysts.

SEM images showed interparticle mesoporosity for all samples (not shown).

Surface charge measurements revealed that the surface of all samples is negatively charged around neutral pH (not shown).

Results from nitrogen physisorption show that all the obtained materials possess high specific surface area ($> 600 \text{ m}^2/\text{g}$), and the use of the extraction-calcination procedure leads to formation of materials with even higher specific surface area and pore volume in comparison with the materials obtained by calcination (Table 1).

Table 1. Textural properties of obtained materials.

Samples	BET (m^2/g)	Total pore volume (cm^3/g)	Pore Diameter (nm)
KILCuMn-Ex.C.	790	1,87	9,2
FeKILCuMn-Ex.C.	701	2,39	18,5
KILCuMn-C.	609	1,52	8,4
FeKILCuMn-C.	523	1,41	10,9

The catalytic activity of the prepared materials was tested in Fenton-like AOP reaction for degradation of methylene blue (MB), plasmocorinth B (PC), resasurin (RZ) where the concentration of the dyes was tracked by UV absorption at wavelengths 664, 527 and 596 nm, respectively. The results for adsorption after one hour of exposure and final removal of the dye after 3 hours of reaction are shown on Figure 2.

Catalytic results show that prepared catalysts are more suitable for removal of anionic (plasmocorinth B) and zwitterionic (resasurin) dyes in comparison to cationic (methylene blue) dye. Furthermore, calcination procedure for template removal leads to efficient catalysts for anionic dye removal while extraction-calcination procedure for template removal leads to efficient catalysts for zwitterionic dye removal.

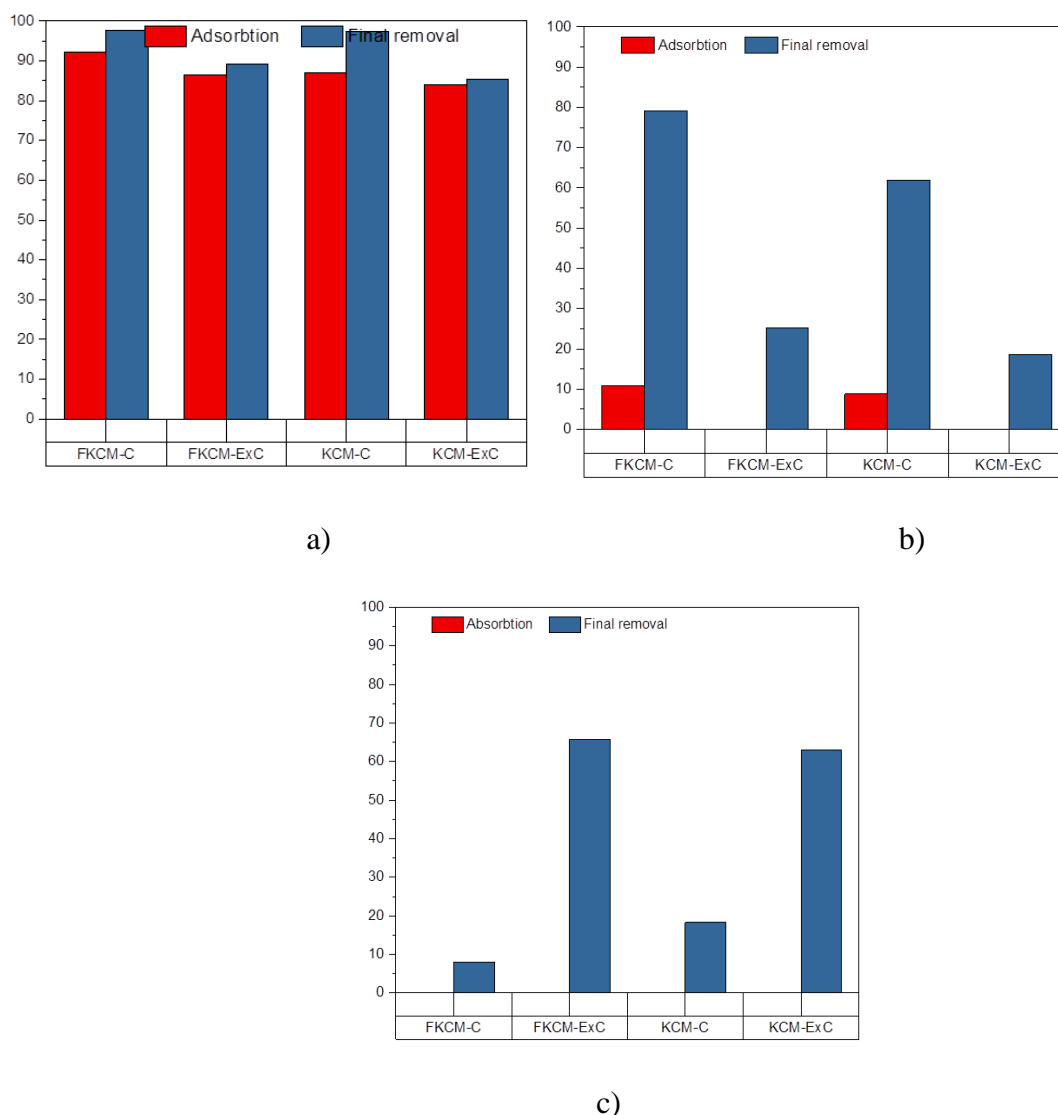


Figure 2. Representation of the contribution of adsorption and final removal of a) methylene blue, b) plasmocorinth B and c) resasurin for the obtained catalysts.

CONCLUSION

Bimetal copper-manganese catalysts on Fe₃O₄/porous silica supports with magnetic properties and negative surface charge in pH close to neutral were successfully synthesized and catalytic tests with dyes with different surface charges were performed. Characterization of the catalysts using transmission electron microscopy (TEM), determination of possible metal leaching from the catalysts and determination of total organic carbon (TOC) after the catalytic reaction are in progress.

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