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Electroreduction as a facile method for one-pot synthesis of CuZSM-5 nanostructures

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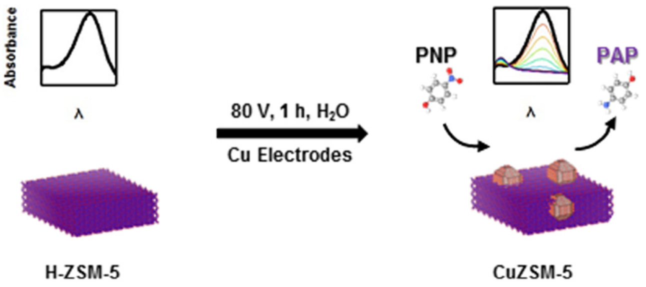
GRAPHICAL ABSTRACT



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ABSTRACT

Materials composed of earth abundant first-row transition metal nanoparticles supported upon zeolites serve as both fundamentally interesting and useful nanostructures. Examples such as Cu-functionalized zeolites have shown high activity for partial oxidation of methane to methanol. Currently wet impregnation serves as the most popular method for the production of these nanostructures, however the resultant metal nanoparticles are often irregular and aggregated. Here, we describe a comparably facile process for *in situ* formation of Cu-rich nanoparticles on the surface of commercial ZSM-5. This green, one-pot, process is carried out through simplified two-electrode electroreduction of Cu wire with minimal purification in aqueous solution. The produced materials were found to have Cu content as high as 1.60 wt. % while maintaining high surface area. High resolution transmission electron microscopy and energy dispersive X-ray spectroscopy mapping show evenly dispersed 3–5 nm Cu-rich nanoparticles on the surface of the zeolite support. These materials exhibit first order rate constants up to -5.2×10^{-3} s^{-1} for the reduction of 4-nitrophenol indicative of readily accessible catalytic sites. X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analysis, and nitrogen physisorption are also employed to characterize the catalytic material. The robust synthesis method was applied over various times, voltages, and supports.

1. Introduction

Heterogeneous catalyst composed of earth-abundant first-row transition metals supported upon zeolites are both fundamentally interesting nanostructures as well as pragmatic materials. As a material regime for interesting nanostructures, Fe, Co, and Ni nanoparticles supported upon a variety of zeolites are composed of varying size and shapes for $[M]^{0+}$nanoparticles, diverse metal chemistries at the particle–zeolite interface, and the ordered internal pores structure of the zeolite support [1–3]. From a pragmatic angle, these materials have shown potential and promise in Fischer–Tropsch synthesis, hydrogenolysis of cyclic-ethers, hydroconversion of aryl ethers, low-temperature oxidative upgrading of short-chain alkanes, oxidation of hydrocarbons, and in general serve as methods to build tandem catalytic systems [3–7]. In addition to Fe, Co, and Ni, Cu is a first-row transition metal with comparable abundance and Herfindahl— — Hirschman Index

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reserve values that could also serve as a worthwhile candidate for exploration in these hierarchical systems [8].

Various types of wet impregnation and ion-exchange remain the most ubiquitous methods for producing metal nanoparticles upon zeolites [2,3,5,6,9,10]. This typically involves incorporation of a metal precursor rich solution within the zeolite support, followed by a reduction step [11–14]. Unfortunately, electron microscopy reveals that both of these methods can produce irregular particle morphology with low dispersion across the zeolite support and, while ion-exchange can minimize this, it limits the metal content of the final product [1–3,15]. Since the relative ease of wet impregnation likely drives its widespread implementation, an alternative method which could improve regularity and dispersion of nanoparticles must be equally facile. Electroreduction is a synthetic technique which employs electrolysis of a sacrificial anode combined with electrochemical reduction to produce metal nanoparticles [16,17]. It has been used to functionalize supports such as carbon black and mesoporous silica [16,18]. Since the size of the formed particles can be tuned by the current intensity and the technique can be readily applied to easily oxidized earth abundant first-row transition metals like Cu we believe electroreduction can provide a facile route to these zeolite supported materials [19].

Herein, we disclose a reagent-free method to produce a dual functionality, CuZSM-5 nanostructure. Through a simplified two-electrode electroreduction process using Cu wire, commercial ZSM-5, and water; we produce 3–5 nm nanoparticles rich in Cu dispersed across the surface of the ZSM-5 support. The use of aqueous solvents, commercial support, and robust reagents we believe we provide a facile approach whose execution is comparable to wet impregnation, but with improved nanoparticle dispersion and morphology. We describe the physicochemical attributes of our CuZSM-5 system through HR-TEM, EDAX mapping, ICP-OES, XRD, FTIR, TGA, and N_2 physisorption methods with emphasis on the structure of the material. To show the accessibility and reactivity of Cu nanoparticle functionalized ZSM-5 materials, we demonstrate its performance in the model reduction of 4-nitrophenol to 4-aminophenol.

2. Materials and methods

2.1. Preparation of reactor

Synthetic apparatus for CuZSM-5 catalyst consisted of an Erlenmeyer round-bottom flask fitted with a custom electrolytic cell, as pictured in Figure S1. This cell was prepared by placing two metallic electrodes (14-gauge Cu wire) through a septum and isolating the ends with a natural rubber spacer or hot-melt adhesive. Before installation, the electrodes were mechanically polished to remove surface oxides using a commercial carborundum abrasive. An electrode gap of 1–3 mm was necessary to minimize solution resistance as the electrolytic reduction reaction proceeded. While ambient $O_{2\ (g)}$ was not found to impact results, to control the atmosphere, the 100 mL flask was fitted with a Schleck adaptor and septa for N_2 purging. Except where noted reagents were acquired from Sigma-Aldrich and used without further purification.

2.2. Electrolytic modification of ZSM-5

Within the cell described in Fig. S1, a variety of porous silica nanoparticles (PSN) or PSN precursors were suspended within the chosen solvent. Within this work, we primarily explored modification of commercial microporous H-ZSM-5 in aqueous media; however, we found similar results when modifying well-studied mesoporous silica SBA-15 possessing 5.4 nm pores and *in-situ* during the synthesis of MCM-41 [20,21]. Support material was suspended by stirring the solution at 450 RPM and the reactor atmosphere was purged with N_2. Finally, to modify the suspended support, voltage, current, and heat were applied to the cell for a set amount of time to produce nanoparticles on the PSN surface, although solution temperature and atmosphere appeared to have negligible impact on modification.

To modify commercial H-ZSM-5, 75 mL nanopure H_2O was used as the solvent for 1 g H-ZSM-5 (Zeolyst International, CBV3024E, silica to alumina molar ratio of Si/Al = 30), which was calcined at 550 °C for 5 h prior to modification to convert it from the nominal ammonium form to protonic H-ZSM-5. The cell was then purged with high purity N_2 for four reactor volumes. The suspension was held at 50 °C and stirred at 450 RPM for the duration of the reaction. The two electrodes were connected to a DC power supply (BIOrad PowerPac Basic 75 W) providing a constant voltage of 80 V. The reaction was run for 60 min under $N_{2\ (g)}$, after which centrifugation recovered the catalyst, and dried under ambient conditions overnight. During the reaction, pH was measured at several points using a pH meter (Fisher Accumet XL15). The dried recovered catalyst appeared light turquoise in color, reminiscent of $Cu(OH)_2$ or $Cu_2CO_3(OH)_2$. Modified catalysts are denoted as CuZSM-5-Duration-Voltage. Additional information on the pH ranges during synthesis can be found on Table S1.

To show robustness of our method, two mesoporous silica support systems were used in addition to microporous H-ZSM-5. CuMSN, copper modified mesoporous silica nanoparticles, was prepared in a similar fashion as described for Cu-ZSM-5 samples. A voltage of 80 V was held for 60 min across a solution of SBA-15 prepared according to Zhao et al. [21]. In the case of CuMCM-41, the MCM-41 synthesis was carried out in the presence of our electrolytic cell [20]. Tetraethyl orthosilicate (TEOS, 4.7 g, 2.26×10^{-2} mol), cetyltrimethylammonium bromide surfactant (1 g, 2.74×10^{-3} mol), nanopure H_2O (480 mL, 26.6 mol), and 2 M NaOH (3.5 mL, 7.00×10^{-3} mol) were combined in a 1000 ml round bottom flask. Initially, the surfactant, solvent, and base were combined at 80 °C and allowed to dissolve over 3 h stirring at 600 RPM. The electrolytic cell was placed within the solution and 80 V was triggered. Immediately upon initiation of the voltage across the cell, 4.7 g of TEOS was delivered by syringe pump at 120 mL h^{-1}. The reaction continued stirring for 1 h under constant voltage, with the final product recovered by filtration. The prepared CuMCM-41 was dried in air over night and calcined at 550 °C for 5 h to remove the surfactant template. All samples were labeled as *Metal-Support–Voltage(V)–Duration(min)–Iteration*, for example CuZSM-5 60 80 01 was the first preparation of electrolytically modified ZSM-5 prepared by applying 60 V for 80 min. For mesoporous samples where there is no ambiguity, the voltage and duration are dropped for brevity.

2.3. Characterization of electrolytically modified catalyst

Transmission Electron Microscopy (TEM) images were acquired on a Phillips CM200 transmission electron microscope operating in bright-field (BF) mode equipped with a LaB_6 cathode operating at 200 kV accelerating voltage. A FEI TALOS F200X TEM/STEM (HRTEM) equipped with Schottky field emission gun operated at 200 keV was operated in BF and dark-field (DF) modes. The instrument was equipped with a Super-x energy dispersive spectrometer (EDS) for acquisition of spectral images. Images were processed using *ImageJ* software. All samples were prepared by casting dilute suspensions of as-prepared catalyst in methanol upon lacey-carbon coated Cu grids.

XRD patterns for samples were acquired on a PANALYTICAL PW3040 X-ray diffractometer. $\theta/2\theta$ scans were acquired between 20-50° 2θ with a 4 s dwell time. Samples were prepared by packing of powder within a 0.317 cm thick, 2.54 cm by 2.54 cm aluminum holder.