

Chromate adsorption on amine-functionalized nanocrystalline silicalite-1

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ABSTRACT

Nanocrystalline silicalite-32 nm, which has a large external surface area ($\sim 100 \text{ m}^2/\text{g}$), was functionalized with aminopropyltriethoxysilane (APTES). The functionalized nanocrystalline silicalite was characterized by powder X-ray diffraction to verify crystallinity, solid state ^{29}Si MAS NMR and thermal gravimetric analysis to quantify the functionalization, and zeta potential measurements of surface charge. As the amount of APTES functionalization increased, the zeta potential increased and this led to increased chromate ($\text{Cr}_2\text{O}_7^{2-}$) adsorption. Chromate adsorption on the APTES functionalized silicalite-32 nm was attributed to external surface adsorption by an electrostatic interaction between the positively charged amine groups and the negatively charged chromate anions.

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1. Introduction

Nanocrystalline zeolites have crystal sizes of less than $\sim 100 \text{ nm}$ and very large external and internal surface areas [1–6]. A nanocrystalline zeolite with a crystal size of 50 nm has an external surface area of $>100 \text{ m}^2/\text{g}$. For comparison, a 500 nm zeolite crystal has less than $10 \text{ m}^2/\text{g}$ of external surface area. The increased external surface of nanocrystalline zeolites results in enhanced adsorptive properties and additional surface area available for adsorption and reaction of molecules. In principal, bifunctional nanocrystalline zeolites may be obtained by incorporating one functionality into the internal zeolite surface and a second functionality onto the external zeolite surface. The objective of the work described here is to functionalize and characterize the external nanocrystalline zeolite surface with amine groups. Future work will focus on preparing and demonstrating bifunctional nanocrystalline zeolite materials by combining internal and external surface reactivity.

Through surface functionalization, the properties of the nanocrystalline zeolite external surface can be tailored for specific applications [7–11]. For example, the hydrophobicity of the external surface of the zeolite can be increased through functionalization with long chain hydrocarbons, such as octylmethyltrichlorosilane [9]. Similarly, specific functional groups, sulfonic acid groups ($-\text{SO}_3\text{H}$) or amine groups ($-\text{NH}_2$) can be placed on the external surface to promote acid catalyzed reactions or adsorption of DNA, respectively.

Methods used for functionalization of silanol groups in silica based materials, such as mesoporous silica [12–16], can be readily

adapted for zeolites with the main difference being that the functionalization occurs exclusively on the external zeolite surface due to the zeolite pore sizes that restrict access to the internal zeolite surface for most organosilane reactants [7,8]. The advantage of nanocrystalline zeolites in this regard is the extremely high external surface area relative to micron-sized zeolites. The reaction of a surface silanol group on the zeolite external surface with APTES results in an amine-functionalized zeolite as shown schematically in Fig. 1. This method is versatile because many different organosilane reagents can be used to introduce different functionalities to the zeolite surface.

Hexavalent chromium is highly toxic and strictly regulated by the EPA ($50 \mu\text{g}/\text{L}$ limit in drinking water) [17–19]. Hexavalent chromium is found in industrial waste effluents (electroplating, tannery and textile), such that the effluent must be treated before being discharged into the environment to be compliant with EPA regulations. Adsorption is a relatively easy and efficient way to remove hexavalent chromium from waste water effluents and many different adsorbents have been investigated including activated carbon, clays, ion-exchange resins, zeolites and mesoporous silica [10,20–31].

Recently, there have been several studies of chromate adsorption on amine-functionalized mesoporous silica (MCM-41 and SBA-15) [21,26,27,30,32] and studies of chromate adsorption on organic functionalized natural zeolites [10,24,26–29]. Surface modification is accomplished through reaction of surface silanol groups with organosilane reagents. This strategy has been widely adopted to functionalize mesoporous silica materials [12,13,15] with catalytically active or biologically compatible functional groups [14,33]. SBA-15 and MCM-41 have been functionalized with amine functional groups using organosilanes, such as amino-

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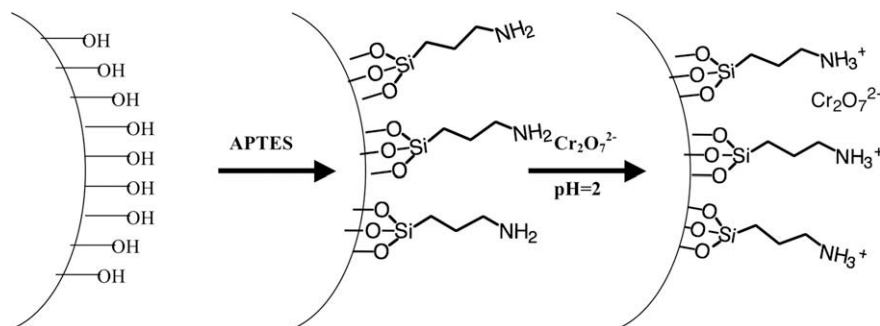


Fig. 1. Schematic diagram showing the functionalization of a nanocrystalline silicalite with aminopropyltriethoxysilane (APTES) and the protonation of the amine group in acidic solution followed by the adsorption of chromate ($\text{Cr}_2\text{O}_7^{2-}$).

propyltriethoxysilane (APTES) [21,30,34]. The amine functionalized mesoporous silica samples exhibited very high adsorption capacities for chromate.

Silicalite is the purely siliceous form of the zeolite, ZSM-5 which has the MFI structure with 5.6 Å pore diameters. In this study, nanocrystalline silicalite with a crystal size of 32 nm and an external surface area of $\sim 100 \text{ m}^2/\text{g}$ was functionalized with varying amounts of APTES so that the surface properties (such as zeta potential) could be systematically varied and tailored for chromate adsorption. The functionalized silicalite was characterized by powder X-ray diffraction, ^{29}Si magic angle spinning (MAS) NMR, thermal gravimetric analysis (TGA), nitrogen adsorption isotherms, and zeta potential measurements. Finally, chromate ($\text{Cr}_2\text{O}_7^{2-}$) adsorption on the APTES functionalized silicalite (32 nm) was measured in batch experiments.

2. Experimental section

2.1. Sample preparation

A silicalite-1 sample with a crystal size of 32 nm was synthesized according to the method described previously [2,4]. The external surface area of the uncalcined silicalite-32 nm was $99 \text{ m}^2/\text{g}$. To functionalize the silicalite, 0.5 g of calcined silicalite (32 nm) was added to 60 mL toluene and 0.25 (0.5, 1.0) mL aminopropyltriethoxysilane (APTES). The reaction mixture was heated to 90 °C for 4 h and then was centrifuged. The solids were washed with water and ethanol and dried overnight at 85 °C.

2.2. Characterization

Powder XRD patterns were obtained using a Siemens D5000 diffractometer with Cu K α target and a nickel filter. XRD patterns were collected between $2\theta = 5^\circ$ and 35° . ^{29}Si MAS NMR was conducted using a 300 MHz wide bore magnet with a TecMag Discovery console and a Chemagnetics double-channel 7.5 mm pencil MAS probe (59.6 MHz). 1000 scans were collected with a 60 s pulse delay and a spinning speed of 6 kHz. Thermogravimetric analysis was performed on a TA Instruments Q500 TGA by heating from room temperature at 5.00 °C/min to 1000 °C under N_2 . The results were analyzed using TA Universal Analysis with the amine peak appearing at approximately 300 °C. Zeta potential measurements were obtained using a Malvern Zetasizer Nano. The zeta potential was measured using a 1–2% by weight suspension of the zeolites in deionized water. The samples were sonicated for 60 min prior to the zeta potential measurements and placed in disposable zeta potential cells. Nitrogen adsorption isotherms were obtained on a Quantachrome Nova 4200e multipoint BET apparatus using approximately 0.1 g of sample for each measurement. Prior to the N_2 adsorption, each sample was vacuum degassed at 300 °C

for 2–3 h. The specific surface area was calculated by the BET method using the Nova 4200e instrument software.

2.3. Metal adsorption experiments

Ten milligrams of each zeolite sample was added to 10 mL of 50 ppm solution prepared from $\text{K}_2\text{Cr}_2\text{O}_7$ and controlled at pH 2 with HNO_3 . The zeolite/chromate solution was stirred for 2 h at room temperature. After centrifugation, the solids were separated from the supernatant and both were analyzed for chromium content using a Varian 720-ES Inductively Coupled Plasma/Optical Emission Spectrometer (ICP/OES) spectrometer. The chromium concentrations of the solutions were measured directly using the Cr 205.56 nm line of the ICP/OES. The solids were dissolved in 3 mL HF, 1 mL HNO_3 and 15 mL H_3BO_4 , diluted to 25 mL with deionized water and the resulting solutions were analyzed for chromium concentration by ICP/OES. Calibrations were done before each set of measurements using three solutions of known concentration (25, 50 and 100 ppm) made from standards purchased from Inorganic Ventures. Three sample replicates were run for each sample and were averaged to provide the final chromium solution concentrations. Single component adsorption isotherms for $\text{Cr}_2\text{O}_7^{2-}$ were measured using 10 mg of zeolite and 10 mL of solution with concentrations ranging from 0.1 to 2 mM. The samples were allowed to equilibrate for 2 h at room temperature.

3. Results and discussion

3.1. Characterization of functionalized nanocrystalline silicalite

Nanocrystalline silicalite with a crystal size of approximately 32 nm was synthesized and characterized. The MFI framework was confirmed by powder X-ray diffraction. The external surface areas of the silicalite-32 nm was $99 \text{ m}^2/\text{g}$, as measured by the BET method. The crystal size was calculated from the external surface area: $S_{\text{ext}} = 3214/x$ where S_{ext} is the external surface area in m^2/g and x is the silicalite-1 crystal size in nm, as described previously [4]. The silicalite-32 nm was functionalized with varying amounts of APTES (0.5 and 1.0 mL) to achieve systematically varied external surface functionalization. The XRD powder pattern, characteristic of the MFI zeolite structure, is shown before and after functionalization in Fig. 2a and b. The characteristic peak positions do not change after functionalization, although the relative peak intensities do change slightly. After treatment with the acidic solution used for adsorption measurements, additional decrease of the XRD peaks in the $2\theta = 20^\circ$ – 25° region is observed (Fig. 2c) indicating some loss of crystallinity.

The extent of functionalization was characterized by ^{29}Si MAS NMR as shown in Fig. 3. A framework silicon peak is observed at -113 ppm and a second peak attributed to the silicon atom from

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