
Theses and Dissertations

Spring 2011

Copper adsorption on functionalized molecular sieves

Melissa Christine Torres
University of Iowa

Copyright 2011 Melissa Christine Torres

This thesis is available at Iowa Research Online: <http://ir.uiowa.edu/etd/1096>

Recommended Citation

Torres, Melissa Christine. "Copper adsorption on functionalized molecular sieves." MS (Master of Science) thesis, University of Iowa, 2011.
<http://ir.uiowa.edu/etd/1096>.

Follow this and additional works at: <http://ir.uiowa.edu/etd>



Part of the [Chemistry Commons](#)

COPPER ADSORPTION ON FUNCTIONALIZED MOLECULAR SIEVES

by

Melissa Christine Torres

A thesis submitted in partial fulfillment of the requirements for the Master of Science degree in
Chemistry in the Graduate College of The University of Iowa

May 2011

Thesis Supervisor: Professor Sarah C. Larsen

Graduate College
The University of Iowa
Iowa City, Iowa

CERTIFICATE OF APPROVAL

MASTER'S THESIS

This is to certify that the Master's thesis of

Melissa Christine Torres

has been approved by the Examining Committee
for the thesis requirement for the Master of Science degree in Chemistry
at the May 2011 graduation.

Thesis Committee:

Sarah C. Larsen, Thesis Supervisor

Ned Bowden

Edward Gillan

To My Parents:
Frank and Elida Torres

To My Sister:
Frances Torres

To My Mentor:
Vinç

TABLE OF CONTENTS

LIST OF TABLES	v.
LIST OF FIGURES	vi.
CHAPTER	1
1. INTRODUCTION	1
1.1. Molecular Sieves	1
1.1.1. Zeolites	1
1.1.2. Mesoporous Silica	3
1.2. Functionalization	4
1.2.1. Post Synthesis Grafting	5
1.2.2. Co-Condensation Functionalization	6
1.3. Metal Adsorption	7
1.4. Thesis Overview	7
2. SYNTHESIS, CHARACTERIZATION, AND FUNCTIONALIZATION OF SILICALITE-1	8
2.1. Introduction	8
2.2. Experimental Section	9
2.2.1. Synthesis	9
2.2.2. Functionalization of Silicalite-1	9
2.2.3. Characterization	10
2.3. Results and Discussion	10
2.4. Conclusions	13
3. SYNTHESIS, CHARACTERIZATION, AND FUNCTIONALIZATION OF MCM-41	14
3.1. Introduction	14
3.2. Experimental Section	14
3.2.1. Synthesis	14
3.2.2. Functionalization of MCM-41	14
3.2.2.1. Post Grafting	14
3.2.2.2. Co-Condensation	15
3.2.3. Characterization	15
3.3. Results and Discussion	15
3.4. Conclusions	18

4. COPPER ADSORPTION	20
4.1. Introduction	20
4.2. Experimental Section	20
4.3. Results and Discussion	20
4.4. Conclusions	26
5. CONCLUSIONS AND FUTURE WORK	27
5.1. Conclusions	27
5.2. Future Work	27
REFERENCES	28

LIST OF TABLES

Table 2.1	Surface Area and Functional Group Loading of Silicalite-1	12
Table 3.1	Surface Area and Functional Group Loading of MCM-41	18
Table 4.1	Analysis from Langmuir Data where q_{\max} represents mmol of Cu(II) per gram of sample; ^a shows the standard deviation in parenthesis, ^b is the R value of q_{\max} .	24
Table 4.2	Literature Review where loading refers to functional group loading and q_{\max} represents mmol of Cu(II) per gram of sample. Author of article is give with references.	26

LIST OF FIGURES

Figure 1.1	Zeolite framework scheme with aluminum and silicon tetrahedrals	1
Figure 1.2	Functionalized scheme with aminopropylsilane groups	5
Figure 1.3	Functionalization scheme for co-condensation method	6
Figure 2.1	MFI framework with 10-membered ring formation	8
Figure 2.2	MFI Pore openings	8
Figure 2.3	Representative pXRD of functionalized Silicalite-1	11
Figure 2.4	Representative TGA of functionalized Silicalite-1	12
Figure 3.1	Representative pXRD of functionalized MCM-41	16
Figure 3.2	Representative TGA of functionalized MCM-41	17
Figure 4.1	Adsorption of CuSO ₄ scheme	21
Figure 4.2	Langmuir copper adsorption with 1N-, 2N-, and 3N- Silicalite-1 functionalized samples	22
Figure 4.3	Langmuir copper adsorption with 1N-, 2N-, and 3N- MCM-41 functionalized samples by post grafting synthesis	23
Figure 4.4	Langmuir copper adsorption with 1N-, 2N-, and 3N- MCM-41 functionalized samples by co-condensation synthesis	23

CHAPTER 1: INTRODUCTION

1.1 Molecular Sieves

1.1.1 Zeolites

Zeolites are a family of inorganic crystalline materials. At present, there are 192 known zeolite frameworks that each has unique pore structures of tetrahedrally coordinated atoms.¹ The framework consists of interconnected aluminosilicate building blocks, AlO_4 or SiO_4 tetrahedra shown in Figure 1.1 which forms 3D frameworks with linked channel systems and well-defined micro and mesopores as shown in Figure 1.1.

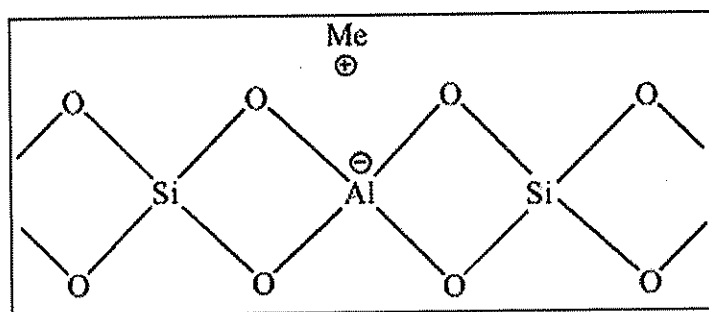


Figure 1.1 Zeolite framework scheme with aluminum and silicon tetrahedrals.

Though the silicon tetrahedra are neutral, introduction of tetrahedral aluminum atoms into the framework results in a negative charge that needs to be balanced by another cation. The zeolite composition follows the following formula:

where Me^{m+} denotes a cation with the charge m , needed for each aluminum tetrahedron and is electrostatically bound to the host framework. The different zeolite frameworks are made up from the number of tetrahedra per unit cell ($x+y$) and the silicon to aluminum ratio (y/x), where y and x are numerical values taken from the zeolite composition formula.

Zeolite synthesis involves a reaction of both silicon and aluminum sources with a structure directing agent under basic conditions. The templating agent directs the overall zeolite structures which can exhibit well-defined micropore openings ($<20 \text{ \AA}$). This high degree of open porosity gives rise to an exceptionally high surface area. The large internal and external surface areas have made modification of zeolites much easier.^{2,3}

Zeolites can be synthesized in the nanoscale with small crystal sizes ($<100 \text{ nm}$) which can be controlled by adjusting the synthesis gel composition, crystallization temperature or time, or recycling of synthesis solution.⁴ Nanocrystalline zeolites are of particular interest in industry and exhibit new properties relative to conventional sized zeolites. Advantages of the nanoscale are: better materials than commercial available, with more uniform, more controlled size and site distributions; ability to form dense, uniform nanostructures like thin films; and an increased external surface area where 30% of total surface area is on the external surface providing an additional reactive surface.

Crystal size, channel structure and silicon/aluminum ratio can all be the cause of the different properties observed in zeolites. The ability to synthesize zeolites with tailored properties makes them amenable to various applications such as catalysis, ion exchange, separations, and metal adsorption.^{5,6} Commercially, zeolites are frequently used to exchange hard calcium and magnesium ions with soft sodium ions for water

softeners and in powdered laundry detergents. More recently and thoroughly studied in our research group is metal adsorption, with emphasis on chromate and arsenate adsorption from aqueous solutions onto functionalized zeolites.²

1.1.2 Mesoporous Silica

As more applications of zeolites continuously expanded so did a need for property and characteristic changes. In the early 1990s, scientists at Mobile Oil Company discovered a new family of molecular sieves, mesoporous silica M41S. Mesoporous silicas are highly ordered materials with large uniform cylindrical pores with diameters ranges from 20-500 Å; which are larger than zeolite pores and can accommodate larger molecules in the pores. This molecular sieve is an amorphous siliceous system with very high surface areas (700-1000 m²/g). The mesoporous structure can be controlled by using different self-assembled surfactants, organic chemicals, and changing reaction parameters such as temperature.⁷ Different templating agents can provide different mesophases: hexagonal, cubic, and lamellar. The specific phase present in a surfactant aqueous solution not only depends on the critical micelle concentration (cmc) but also the length of the hydrophobic carbon chain, hydrophilic head group, and counter-ion.

With a growing interest in expanding pore size to the mesopore region mesoporous silicas are heavily used in industries such as protein separation and selective adsorption of large organic molecules from waste water.⁷ The catalytic activity of the mesoporous silica, MCM-41, with chromium for olefin oligomerization to produce lube oil additives has also shown promising research.⁸

1.2 Functionalization

The large internal and external surface areas have made modification of the molecular sieve much easier and functionalization of the surface can be tailored to specific needs.^{5,3} Silanol groups (Si-OH) on MCM-41 and Silicalite-1 can act as an anchoring site for the functional groups and occurs through a reaction between the Si-OH groups on the external surface and an organosilane containing the target organic group. Functionalization methods can be tailored to the specific molecular sieve, though a difference is seen on zeolites since the functionalization occurs mainly on the external surface due to small pores sizes which restrict functional groups access to the internal surface area.⁹ Functional groups, such as sulfonic acid (-SO₃H) and amine (-NH₂), have been attached to the external surface of a zeolite to improve adsorption, catalytic reactions and drug delivery.⁶ In particular, aminopropylsilane functionalization for modification of silica surfaces has shown great potential for various biomedical applications such as imaging, disease diagnosis, cell type recognition and heavy metal removal.¹⁰⁻¹³ Amine derivatives such as mono-, di-, and tri- aminopropyl ligands can be grafted on a zeolite or mesoporous silica surface for heavy metal adsorption.^{2,14} The amine group is not affected by the functionalization process though an appropriate amount of water is needed to keep the silane activated.

In this research both Silicalite-1 and MCM-41 were functionalized with aminopropylsilanes and were further studied. The functional groups used in these experiments are 3-Aminopropyltrimethoxysilane (APTMS, 1N), N-[3-(trimethoxysily)propyl]ethylenediamine (AAPTMS, 2N), and N-[3-(trimethoxysily)propyl]diethylenetriamine (AEPTMS, 3N). Functionalization was

performed via two methods: post synthesis grafting (Silicalite-1 and MCM-41) and co-condensation (MCM-41) synthesis.

1.2.1 Post Synthesis Grafting

In the post synthesis grafting method, MCM-41 and Silicalite-1 samples were refluxed in toluene, a nonpolar anhydrous solvent that is used to prevent a reaction of the organosilanes with anything but the silica material, and an appropriate amount of functional group at 115 °C for 5 hours. The samples were collected, washed, and dried. The reaction takes place between the silanol groups on the surface and the organosilanes via hydrolysis and subsequent condensation as shown in Figure 1.2. The advantage of this method is that the silanols located on the exterior surface and at the openings of the mesopores maybe more accessible than the silanols located on the interior pore walls. There may be limited loading since this is directed mainly on the external surface and not much functional group can enter the channels and may clog the entrance of the pores.

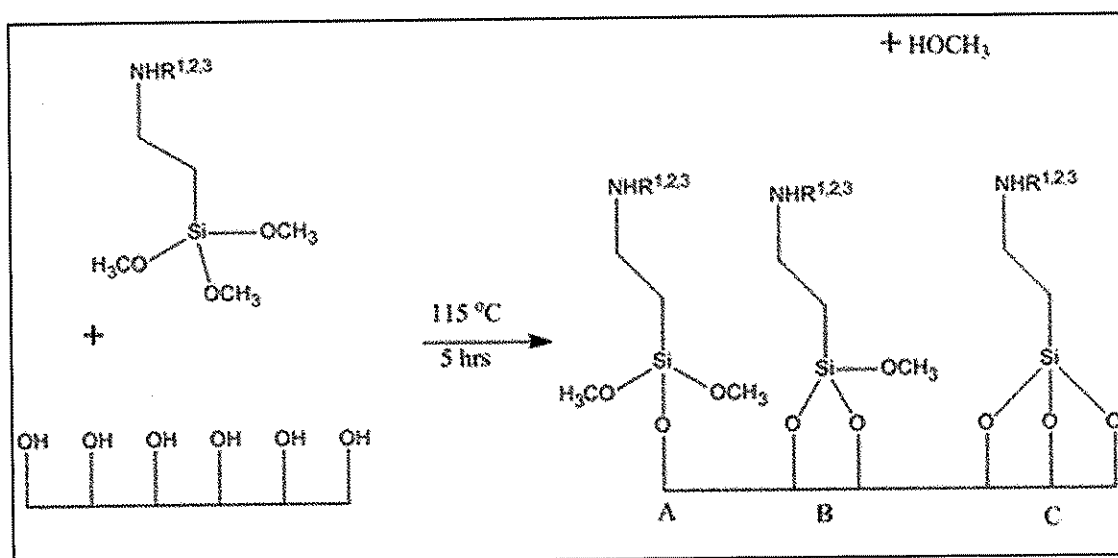


Figure 1.2 Functionalized scheme with aminopropylsilane groups and either scenario A, B, and C can occur. R¹=H, R²=CH₂CH₂NH₂, and R³=CH₂CH₂NHCH₂CH₂NH₂

1.2.2 Co-Condensation Functionalization

Only MCM-41 was functionalized by co-condensation because the Silicalite-1 structure is sensitive to changes in the synthesis and may lead to unwanted products. This functionalization is a direct synthesis method, in which the organosilane is introduced to the basic aqueous solution during the condensation as shown in Figure 1.3. An appropriate amount of functional group is incorporated in the structure during synthesis then the samples are collected, washed, and dried. This one step synthesis can lead to higher functional group loadings and access to the internal surface area. However, the homogeneity of distribution is not guaranteed and the organic groups may become buried within the silica wall, thereby decreasing the stability of the silica.

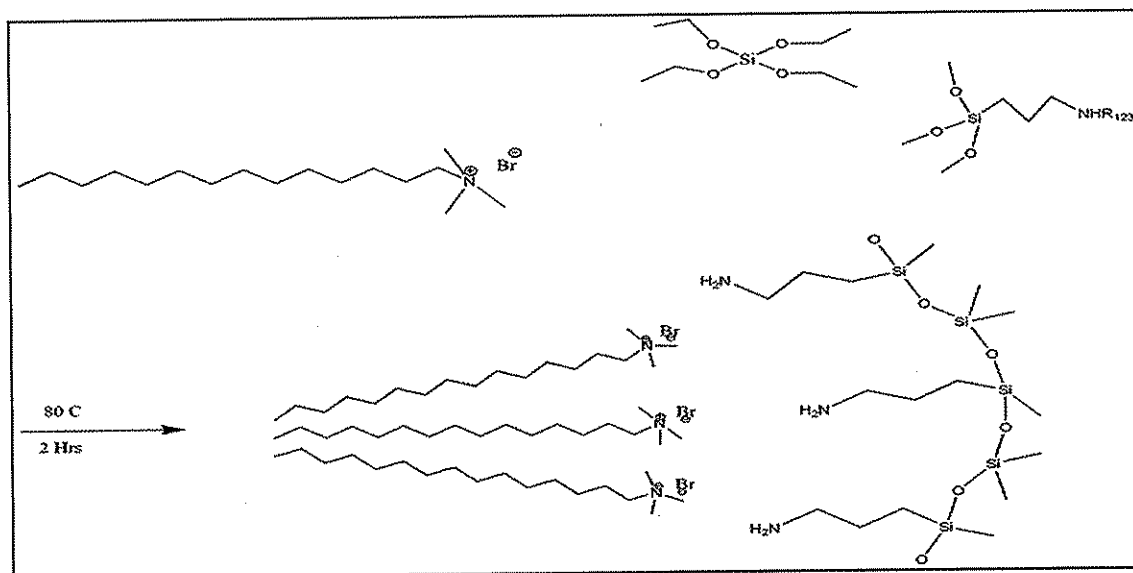


Figure 1.3 Functionalization scheme for co-condensation method with APTMS functional group as a representative.

1.3 Metal Adsorption

These tailored molecular sieves can now be used as adsorbents. Previous metal adsorption studies have utilized an amine functionalized zeolite for the removal of heavy metals.⁵ This research focuses on copper removal. It is of vital importance to remove such heavy metals from drinking water systems due to contamination leading to health problems. The key here is to remove copper contaminants and have more effective and economical wastewater treatments by utilizing the fairly large and accessible surface area.^{5,16} With a large surface area there are more active sites for functionalization which then leads to more copper adsorption sites.

1.4 Thesis Overview

In this thesis, porous ordered structures, such as nanocrystalline Silicalite-1 and MCM-41, were synthesized and functionalized with organic moieties that contain one, two, or three amino functional groups to create an adsorbent tailored for copper adsorption. The first part of this research focuses on synthesis and functionalization of both Silicalite-1 (Chapter 2) and MCM-41 (Chapter 3). The materials were extensively characterized to verify crystallinity and to quantify the functional group loading. The functionalization of both molecular sieves can be categorized by method of functionalization and by nitrogen content in the functional group. The modified samples are then further used in Cu(II) metal adsorption experiments as described in Chapter 4. Conclusions and possible future work will be discussed in Chapter 5.

CHAPTER 2: SYNTHESIS, CHARACTERIZATION AND FUNCTIONALIZATION OF SILICALITE-1

2.1 Introduction

Silicalite-1 is a siliceous zeolite with an MFI framework consisting of pentasil chains of tetrahedrally coordinated silicon linked by oxygen bridges shown in Figure 2.1. Silicalite-1 has a unit cell volume of 5.21 nm^3 , a formula ratio of 96 Silicon: 192 Oxygen, a formula weight of 5856 g/mol, and molecular dimensions of 5.5 \AA . The elliptical pore openings of $5.1\text{-}5.6 \text{ \AA}$ are shown in Figure 2.2.

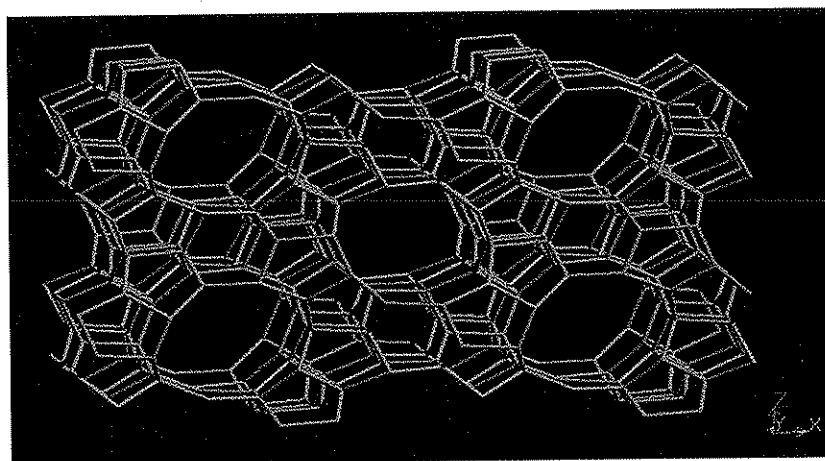


Figure 2.1 MFI framework with 10-membered ring formation.

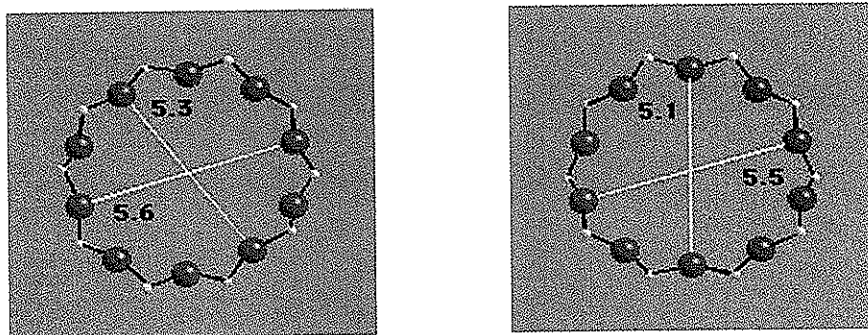


Figure 2.2 MFI Pore openings.

Nanocrystalline Silicalite-1 will be synthesized with crystal sizes of 30 nm using a procedure previously developed in our group.¹⁷ Silicalite-1 was functionalized with APTMS (1N), AAPTMS (2N), and AEPTMS (3N). The functionalized samples were extensively characterized by Nitrogen adsorption isotherms (BET method), powder X-Ray Diffraction (pXRD), and ThermoGravimetric Analysis (TGA).

2.2 Experimental Section

2.2.1 Synthesis

Nanocrystalline Silicalite-1 samples were synthesized according to previously described methods.⁶ In a round bottom flask, a gel composition of 9 TPAOH: 0.16 NaOH: 25 TEOS: 495 H₂O: 100 EtOH was stirred at 60°C for 10 days; Tetrapropylammonium hydroxide (TPAOH, Sigma-Aldrich), Sodium Hydroxide (NaOH, Fisher), Tetraethylorthosilicate (TEOS, Sigma-Aldrich). The samples were calcined at 600°C under air flow for 6 hours for template removal from the zeolite pores.

2.2.2 Functionalized of Silicalite-1

Silicalite-1 samples were functionalized by post synthesis grafting by adding toluene and functional group (APTMS, AAPTMS, AEPTMS) to the sample in a round bottom flask followed by refluxing for 5 hours at 120 °C. Toluene (Fisher), 3-aminopropyltrimethoxysilane, N-[3-(trimethoxysily)propyl] ethylenediamine, and N-[3-(trimethoxysilyl)propyl] diethylenetriamine, (APTMS, AAPTMS, AEPTMS, Sigma-Aldrich) were used. The solids were collected, washed, and dried overnight in preparation for characterization. Figure 1.3 depicts a scheme of how functionalization is occurring on the Silicalite-1 surface. Samples were labeled according to type of

molecular sieve, functionalization method, and functional group. For example S-1N for Silicalite-1 functionalized with APTMS, S-2N for AAPTMS, and S-3N for AEPTMS.

2.2.3. Characterization

Samples were characterized by the following instruments and methods: Nitrogen adsorption isotherms were collected on a Quantachrome Nova 4200e multipoint apparatus (BET method) to determine surface area. Powder X-Ray Diffraction (pXRD) patterns were obtained using a Siemens D5000 diffractometer with Cu K α target and nickel filter to verify crystallinity. ThermoGravimetric Analysis (TGA) was performed on a TA Instruments Q500 TGA by heating from room temperature and increasing by 5°C/min to 800°C while under N₂ to measure organic loading.

2.3 Results and Discussion

The specific surface area measured is reported in Table 2.1 (BET method), approximately 0.15 g of each sample was degassed under vacuum at 120 °C overnight prior to the N₂ adsorption measurement.¹⁸ The BET method is then used to measure the surface area after calcination providing information on the total surface area. After calcination the sample is now ready for functionalization. ~30% of the total surface area is on the external surface providing an additional reactive surface. The crystal size of Silicalite-1 was calculated to be 30 nm from the external surface area (103 m²/g) measured by nitrogen adsorption via the BET method according to Equation 2.1:⁴

$$S_{ext} = 3214/x \text{ (m}^2\text{/g)} \quad (2.1)$$

where S_{ext} is the external surface area in m^2/g and x is the Silicalite-1 crystal size in nm. The surface area was also measured for each of the functionalized Silicalite-1 samples and is reported in Table 2.1. The surface area decreases when the surface is functionalized suggesting that functionalization restricts access of molecule to the pores.

The characteristic Silicalite-1 framework, before and after functionalization, was identified and verified by pXRD patterns collected between $2\Theta = 5^\circ$ and 35° , the spectra in Figure 2.3 shows intense reflection peaks in the 8-10 and 23-25 (2Θ) regions. The MFI structure is verified using pXRD. The collected spectrum is compared to a standard MFI powder pattern. After functionalization the relative peak intensities did not change indicating that the structure was not affected.

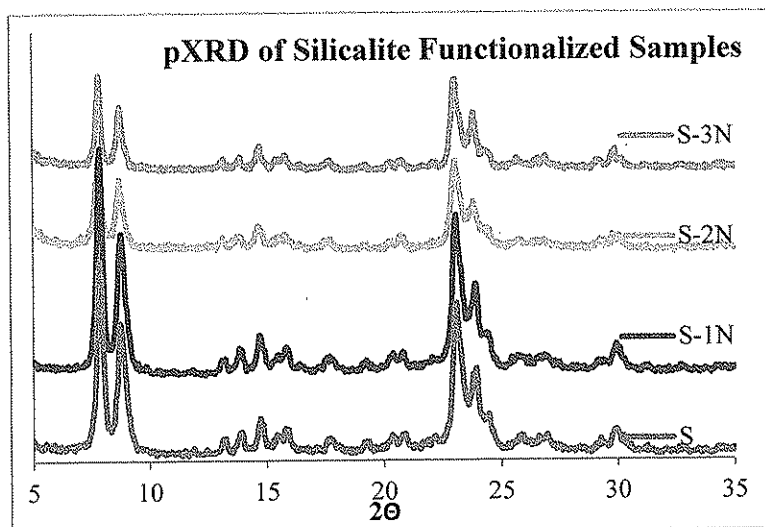


Figure 2.3 Representative pXRD of functionalized Silicalite-1

TGA was used to measure the extent of functionalization Figure 2.4 shows a representative example of TGA of Silicalite-1 and amine functional Silicalite-1. For functionalized Silicalite-1 a significant weight change is seen when the temperature

reaches 200 °C. The amount of functional group coming off can be calculated by this measurement and is listed in Table 2.1. A decrease in functional group loading is observed comparing 1N, 2N, and 3N respectively. This is attributed to the size of the functional group and possible blocking of Si-OH groups needed for functionalization.

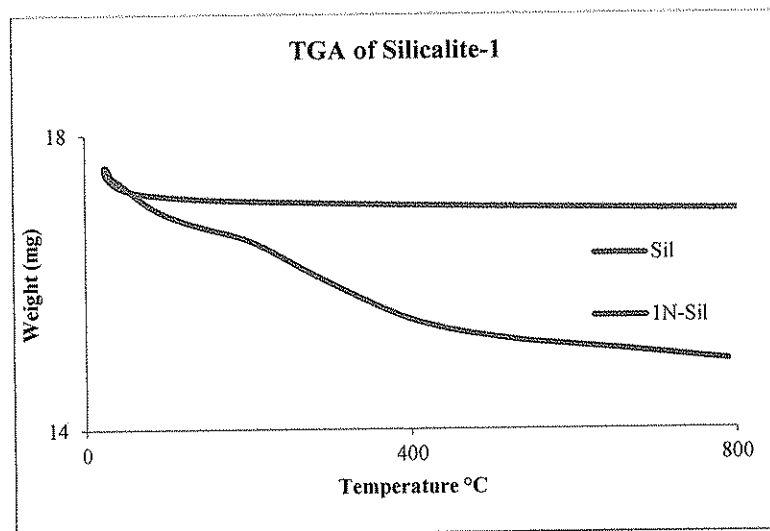


Figure 2.4 Representative TGA of functionalized Silicalite-1

Table 2.1 Surface Area and Functional Group loading of Silicalite-1.

Sample	Surface Area (m ² /g)	TGA Loading (mmol/g)
Silicalite-1 (as prepared)	103 ^a	-
Silicalite-1 (after calcination)	357 ^b	-
1N-Silicalite-1	296 (3) ^b	0.67
2N-Silicalite-1	262 (3) ^b	0.24
3N-Silicalite-1	279 (1) ^b	0.19

^a is the External Surface Area and ^b is the Total Surface Area.

2.4 Conclusions

Nanocrystalline Silicalite-1 with a crystal size of ~30 nm was functionalized with aminopropylsilanes and the results have been reported in this chapter. The pXRD shows no change in the powder pattern after functionalization which indicates that the MFI structure stayed intact after functionalization. The functional group loading decreased with increasing nitrogen content in the functional group. The decrease may be caused by the variation in size of functional group. The 3N samples are larger than the 2N and much larger than the 1N. The functional group itself may be blocking access to active Si-OH groups on the external Silicalite-1 surface. The prepared and characterized samples will be evaluated copper adsorption studies which will be discussed in Chapter 4.

CHAPTER 3: SYNTHESIS, CHARACTERIZATION AND FUNCTIONALIZATION OF MCM-41

3.1 Introduction

In 1992, researchers at Mobil Corporation discovered the M41S family of mesoporous structures. From this family MCM-41 has been used extensively. MCM-41 is a mesoporous silica with very high surface area $\sim 1000 \text{ m}^2/\text{g}$ and large pores with diameters of 15 to 100 Å. MCM-41 possesses a regular hexagonal array of uniform pore openings controlled by the templating agent used in the synthesis. MCM-41 was synthesized and functionalized with amine functional groups. Two methods for functionalization were used and compared: co-condensation and post synthesis grafting.

3.2 Experimental Section

3.2.1 Synthesis

MCM-41 samples were synthesized according to previously described methods.¹⁹ In a round bottom flask, a composition of 1 CTAB: 2.55 NaOH: 4857 H₂O was stirred at 80 °C for 30 minutes before 8.16 of TEOS was added to the mixture and stirred for 2 hours; Cetly Trimethylammonium Bromide (CTAB, Sigma-Aldrich). An acid extraction was performed on MCM-41 samples with 1.0 mL of 12 M HCl and 100 mL Methanol at 60 °C for 6 hours. Solid products were filtered and washed with water and methanol then dried at 100 °C overnight and labeled MCM-41.^{20,21}

3.2.2 Functionalization of MCM-41

3.2.2.1 Post Synthesis Grafting

MCM-41 samples were functionalized with APTMS, AAPTMS, and AEPTMS by post synthesis grafting as previously described in Chapter 2. Samples were labeled

according to type of molecular sieve, functionalization method, and functional group. For example G-1N –MCM-41 for MCM-41 functionalized with APTMS by post synthesis grafting.

3.2.2.2 Co-Condensation

Functionalization of MCM-41 by co-condensation was performed during synthesis by adding an appropriate amount of functional group after the addition of TEOS to the mixture.²² Samples were labeled according to type of molecular sieve, functionalization method and functional group. For example Co-C-1N-MCM-41 for MCM-41 functionalization with APTMS by co-condensation, Co-C-2N-MCM-41 for AAPTMS, and Co-C-3N-MCM-41 for AEPTMS.

3.2.3 Characterization

Samples were characterized by the following instruments and methods: Nitrogen adsorptions isotherms were collected on a Quantachrome Nova 4200e multipoint apparatus (BET method), powder X-Ray Diffraction (pXRD) patterns were obtained using a Siemens D5000 diffractometer with Cu K α target and nickel filter, ThermoGravimetric Analysis (TGA) was performed on a TA Instruments Q500 TGA by heating from room temperature and increasing by 5°C/min to 800°C while under N₂ flow.

3.3 Results and Discussion

Direct synthesis of amine functionalized MCM-41 by co-condensation was performed so that the aminopropyl groups would be integrated in the mesoporous structure with the expectation that more functional group would be attached as compared to post synthesis grafting. Samples prepared by both methods will be characterized and compared. The characteristic MCM-41 framework was identified and verified by pXRD. The spectra of

the MCM-41 materials feature an intense reflection peak (100) near 2 (2θ) and two broad peaks between 3 to 6 (2θ) for (110) and (200) shown in Figure 3.1.⁷ The intense reflection peak (100) near 2 (2θ) shifts due to structural change in the amorphous MCM-41 caused by the functional group loading.

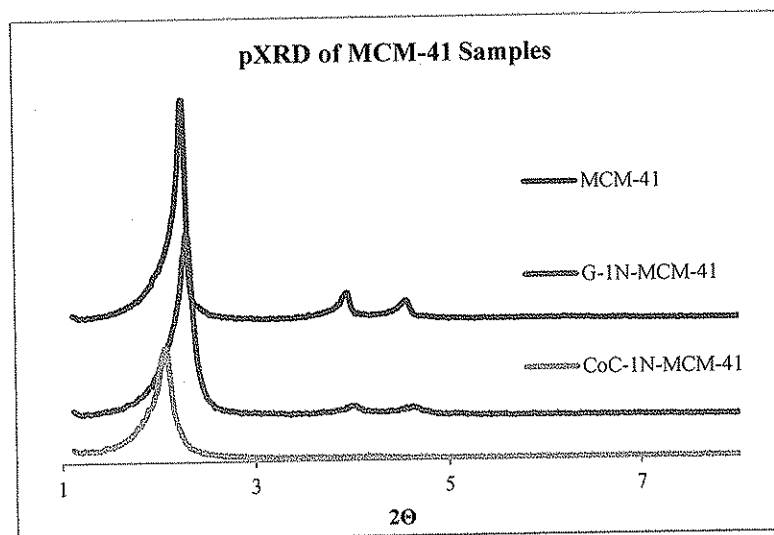


Figure 3.1 Representative pXRD of functionalized MCM-41.

Nitrogen adsorption isotherms were measured by the BET method and the data is shown in Table 3.1. The parent MCM-41 material has a surface area of 1021 m²/g. After functionalization by either method, the surface area decreases, indicating that the functional groups restrict access to the pores. The surface area decrease for samples prepared by grafting is much larger, suggesting that more functional group is on the surface. The low surface area for 1N, 2N, and 3N functionalization correlates to the high

functional group loading. Figure 3.2 shows a representative TGA of amine functionalized G-1N-MCM-41 and Co-C-1N-MCM-41 samples by TGA.

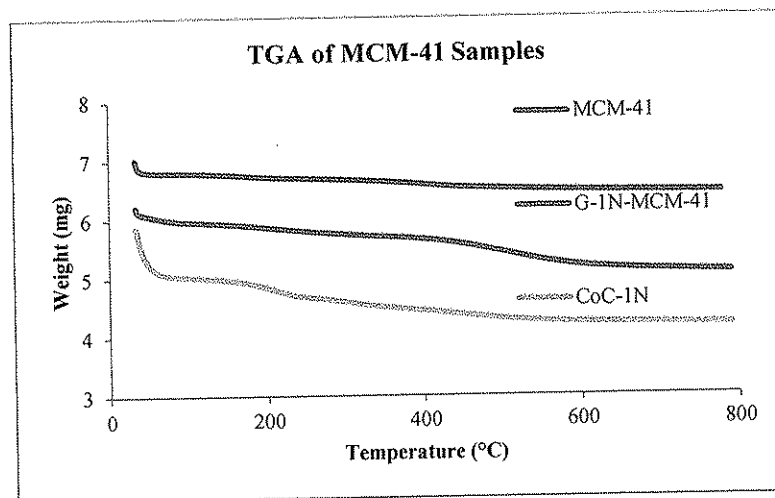


Figure 3.2 Representative TGA of functionalized MCM-41.

The amount of functional group loading is calculated in mmol functional groups/g MCM-41 and is reported in Table 3.1. In comparison to the post synthesis grafting, there are two distinct weight changes in the overall curve. This can be attributed to the presence of functional groups incorporated inside and outside the MCM-41 framework via co-condensation. The functional group loading from the post synthesis grafting method seemed to be consistent no matter which functional group was used. The functional group loading from the co-condensation method varied and no specific trend was observed.

Table 3.1 Surface Area and Functional Group loading of MCM-41

Sample	Surface Area (m ² /g)	TGA Loading (mmol/g)
MCM-41	1021 (2)	-
G-1N-MCM-41	85 (1)	0.90
G-2N-MCM-41	106 (0)	0.85
G-3N-MCM-41	111 (1)	0.93
Co-C-1N-MCM-41	663 (3)	0.67
Co-C-2N-MCM-41	702 (2)	1.48
Co-C-3N-MCM-41	725 (1)	1.06

3.4 Conclusions

MCM-41 samples were functionalized with aminopropylsilanes according to the amount of nitrogen content and results have been reported in this chapter. The pXRD shows a shift in peak position which may be due to the incorporation of the functional groups. Since MCM-41 is not crystalline, the functional groups can in fact slightly disturb the overall structure. The functional group loading seems to be approximately the same for the post synthesis grafting method for (0.90) 1N, (0.85) 2N, and (0.93) 3N mmol/g. However, for the co-condensation functionalization method, the loading does not seem to follow a systematic order. This may be due to incorporation of functional groups in the pore walls or uneven distribution of functional groups. Next, the prepared

and characterized samples will be evaluated for copper adsorption which will be discussed in Chapter 4.

CHAPTER 4: COPPER ADSORPTION ON AMINE FUNCTIONALIZED SILICALITE-1 AND MCM-41

4.1 Introduction

Heavy metal contamination in drinking water systems can cause health problems and removal from aqueous solutions can be troublesome. Previously studied methods include ion-exchange membranes and magnetic sorbents.^{15,16} Copper is not only a drinking-water contaminant, but in small amounts (1 mM) an essential nutrient that plays a role in myelin, collagen and melanin production. It can also act as an antioxidant damaging free radicals accumulated in the body. The World Health Organization (WHO) has established a ≤ 0.005 to > 2 mM threshold of copper in wastewater discharge. A large accumulation in the body can cause skin, brain, pancreatic, and heart diseases. Amine functionalized Silicalite-1 and MCM-41 will be evaluated for copper adsorption from aqueous solutions.

4.2 Experimental Section

Copper adsorption isotherm experiments for Silicalite-1, G- and C- MCM-41 functionalized samples (APTMS, AAPTMS, and AEPTMS) were conducted by stirring 10 mg of sample with 10 mL of CuSO_4 aqueous solutions (0.5 to 8 mM) for 24 hours at pH 4-5. The supernatant was collected by centrifugation for further analysis using by Inductively Coupled Plasma/Optical Emission Spectrometer (ICP/OES) Varian 720-ES.

4.3 Results and Discussion

Copper adsorption studies were conducted with the functionalized samples. The literature precedent shows that very little metal adsorption occurs on the non-functionalized samples, in case of mesoporous silica and zeolite, despite the fact that

these samples have a high surface area. This is evidence that adsorption occurs through the interaction between the nitrogen of the functional group and metal species as shown in Figure 4.1.²³

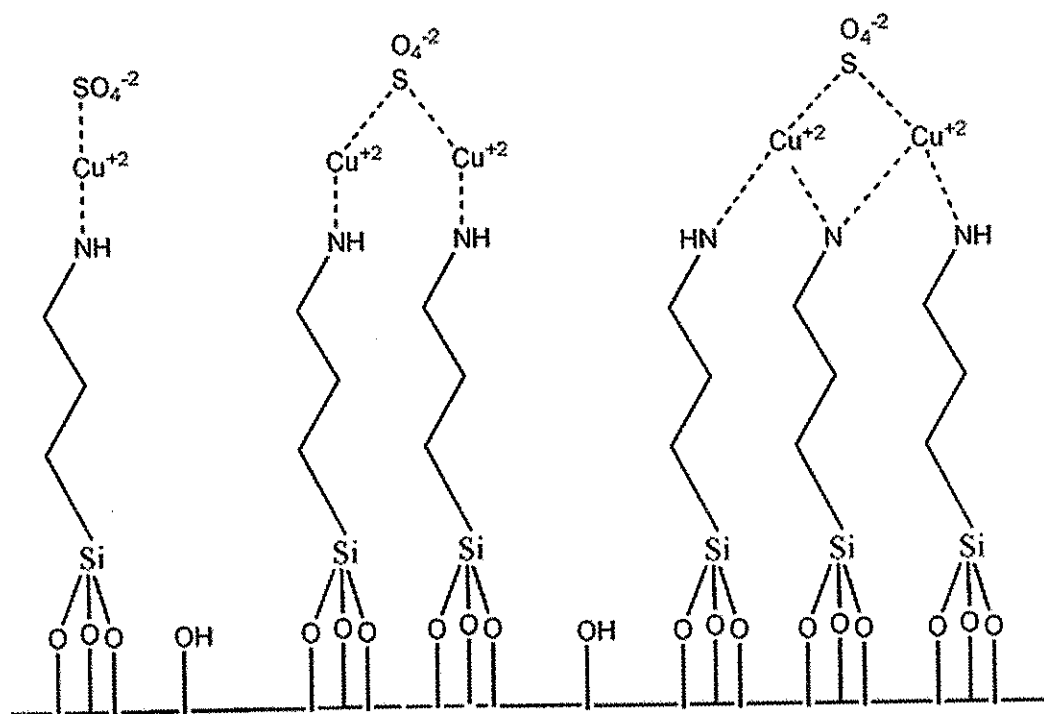


Figure 4.1 Adsorption of CuSO_4 scheme.²⁴

The amount of Cu(II) adsorbed on the functionalized samples was determined using ICP/OES. Figures 4.2, 4.3, and 4.4 illustrate Langmuir Isotherms of Cu(II) adsorption on the functionalized Silicalite-1, MCM-41 via post synthesis grafting and co-condensation samples. The equilibrium adsorption capacity was calculated from the following equation.

$$q_e = \frac{(C_o - C_e) * V}{m}$$

where q_e (mmol/g) is the adsorption capacity, C_o (mM) and C_e (mM) are respectively the initial and equilibrium metal concentrations, V (L) is the solution volume, and m (g) is the weight of aminopropylsilane functionalized sample.²⁴

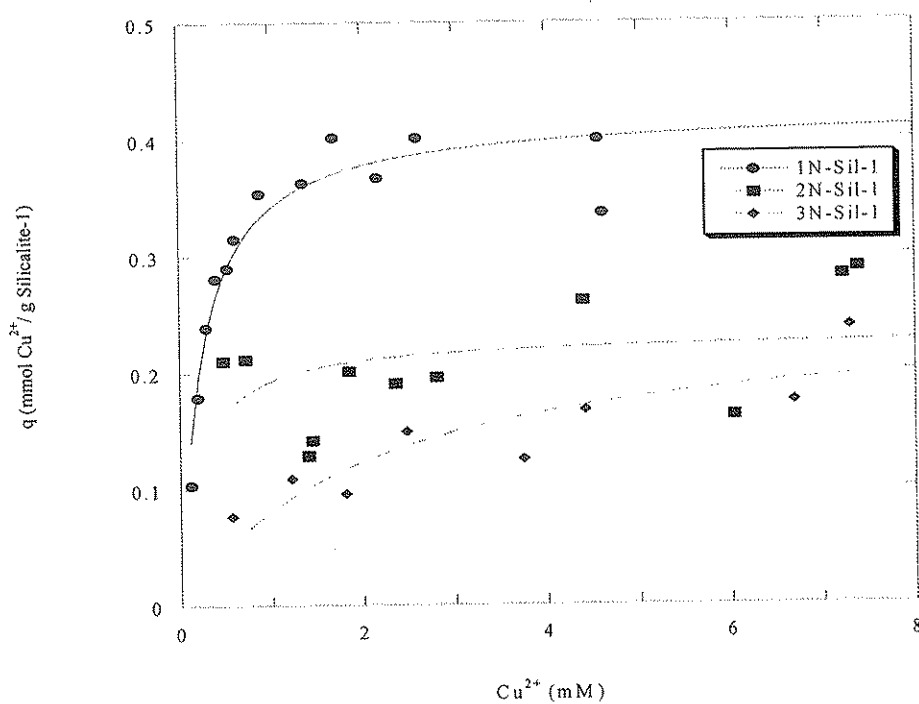


Figure 4.2 Langmuir copper adsorption with 1N-, 2N-, and 3N- Silicalite-1 functionalized samples. The lines show the best fit to a Langmuir Isotherm.

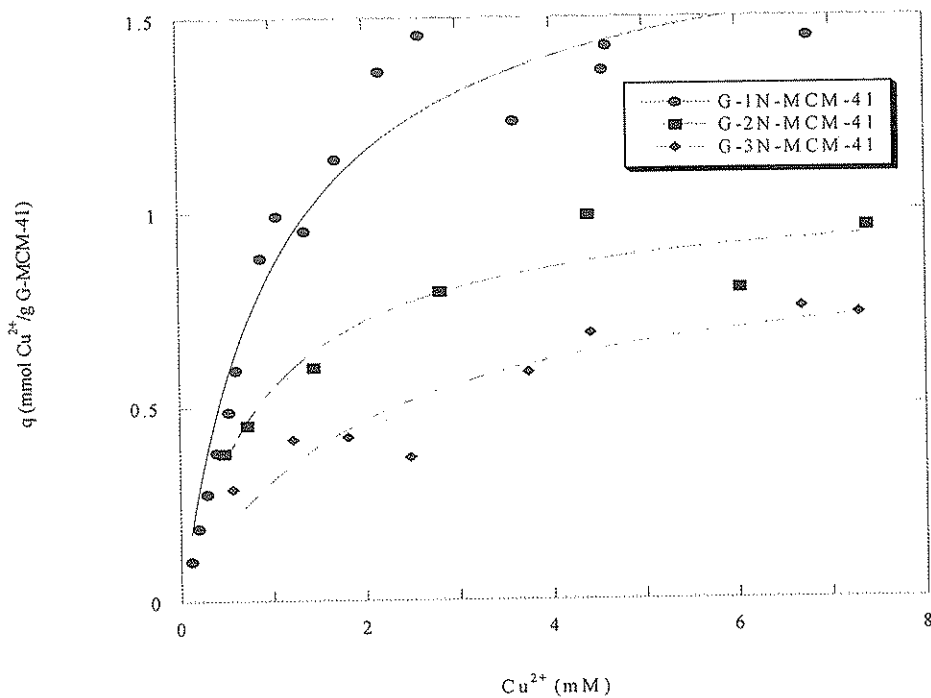


Figure 4.3 Langmuir copper adsorption with 1N-, 2N-, and 3N- MCM-41 functionalized samples by post synthesis grafting. The lines show the best fit to a Langmuir Isotherm.

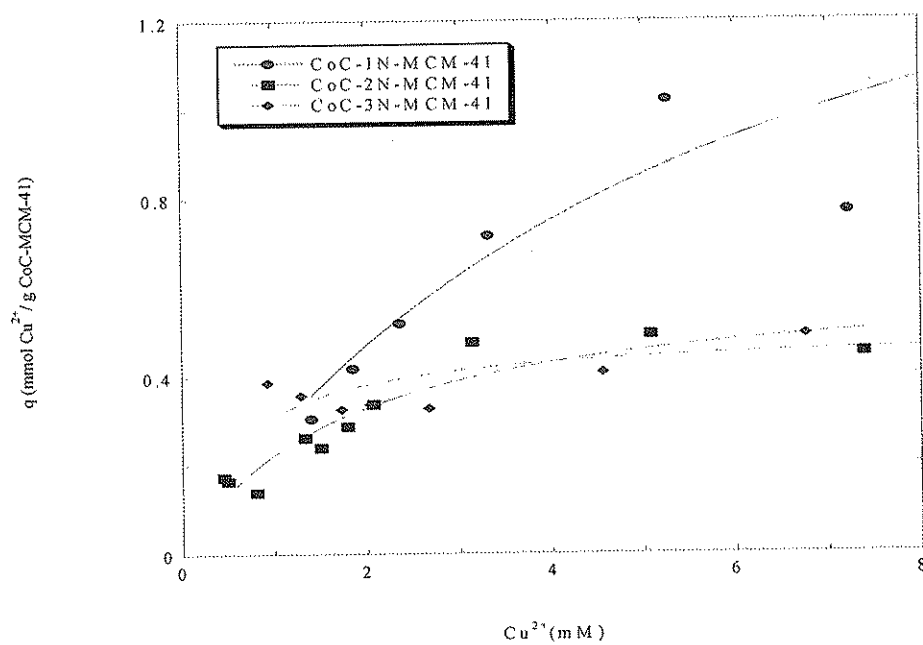


Figure 4.4 Langmuir copper adsorption with 1N-, 2N-, and 3N- MCM-41 functionalized samples by co-condensation synthesis. The lines show the best fit to a Langmuir Isotherm.

The q_{\max} data in Table 4.1 suggest that higher functional group loading in MCM-41 results in more copper adsorption compared to Silicalite-1.

Table 4.1 Analysis from Langmuir data where q_{\max} represents mmol of Cu(II) per gram of sample; ^a shows the standard deviation in parenthesis, ^b is the R value of q_{\max} .

Sample	TGA Loading (mmol/g)	q_{\max} (mmol/g) ^a	R ^b
1N-Silicalite-1	0.67	0.42 (0.02)	0.93
2N-Silicalite-1	0.24	0.23 (0.03)	0.31
3N-Silicalite-1	0.19	0.25 (0.05)	0.86
G-1N-MCM-41	0.90	1.8 (0.1)	0.98
G-2N-MCM-41	0.85	1.06 (0.08)	0.96
G-3N-MCM-41	0.93	0.93 (0.13)	0.92
Co-C-1N-MCM-41	0.67	1.8 (0.6)	0.91
Co-C-2N-MCM-41	1.48	0.62 (0.07)	0.94
Co-C-3N-MCM-41	1.06	0.49 (0.05)	0.65

Previous studies have shown Cu(II) can be more efficiently adsorbed on amine functionalized materials.¹⁴ The use of aminopropylsilane ligands with multiple nitrogen sites was predicted to increase Cu(II) adsorption since there would be more copper binding sites per functional group. Therefore, Silicalite-1 and MCM-41 were each functionalized by 1N, 2N, and 3N aminopropylsilane groups. The results showed 1N functionalized on Silicalite-1, post synthesis grafting MCM-41, and co-condensation

grafting MCM-41 to be 0.42, 1.8, and 1.8 mmol Cu(II)/ g, respectively and 0.25, 0.93, 0.49 mmol Cu(II)/ g for the 3N respectively. The 1N functionalized samples have higher adsorption capacities in comparison to the 3N functionalized samples, contrary to what was originally predicted. The decrease in mmol Cu(II) adsorption for the 3N can be caused by interweaving of the longer chains with each other or on the surface thus hindering the accessibility of active amino sites reducing copper adsorption. A further comparison of functionalization can be made between post synthesis grafting and co-condensation methods on the MCM-41 samples. The amount of functional group per gram of sample appeared consistent throughout the G-MCM-41 materials 0.9, 0.85, and 0.93 mmol/g as compared to the Co-C-MCM-41 0.67, 1.48, and 1.06 mmol/g for 1N, 2N, and 3N, respectively. This behavior shown in the co-condensation samples indicates that the introduction of the functional group in the mesoporous structure during synthesis can be difficult. Despite the larger amounts of the functional group per gram of co-condensation prepared materials, the study shows negligible metal adsorption capacity which can be due to inaccessible nitrogen binding sites.

Table 4.2 shows literature reported Cu(II) adsorption on functionalized MCM-41. Laurence Bois et.al. functionalized MCM-41 by the co-condensation method with APTMS, AAPTMS, and AEPTMS.²⁵ The experiments for Co-C-2N-MCM-41 and Co-C-3N-MCM-41 as compared to the results in this thesis are approximately close, though there is a large difference in comparison of the Co-C-1N-MCM-41 samples. The functional group loading by Bois is much larger than the one reported here in this thesis though the Cu(II) adsorbed is larger for my samples. As functional group loading decreases in Bois' experiments Cu(II) adsorption increases, which is not the case reported

in this thesis. In comparison with the G-1N-MCM-41 reported by Lam et.al. the functional group loading and maximum Cu(II) adsorption is minimal related to the samples reported here.^{24,26}

Table 4.2 Literature Review where loading refers to functional group loading and q_{\max} represents mmol of Cu(II) per gram of sample. Author of article is give with references.

Sample	Loading (mmol/g)	q_{\max} (mmol/g)	Reference
Co-C-1N-MCM-41	1.8	0.1	L. Bois ²⁵
Co-C-2N-MCM-41	1.6	0.5	L. Bois
Co-C-3N-MCM-41	1.1	0.5	L. Bois
G-1N-MCM-41	1.01	0.25	K. Lam ²⁴
G-1N-MCM-41	2.53	0.82	K. Lam ²⁶

4.4 Conclusions

In an overall comparison, the MCM-41 samples surpass Silicalite-1 in the amount of Cu(II) adsorbed. With a larger surface area than the Silicalite-1 samples, MCM-41 had more anchoring sites for functionalization and therefore more copper adsorption. Though it was first predicted that the 3N functionalized samples would have the highest loading, it was observed not to be the case. The 1N functionalized samples had a much higher loading no matter the molecular sieve or functionalization method.

CHAPTER 5: CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

In this study, two types of porous silica materials (MCM-41 and Silicalite-1) were synthesized and functionalized with amine groups. Two different methods of functionalization (co-condensation and post synthesis grafting) and three different functional groups (APTMS, AAPTMS, and AEPTMS) were used in this study. The copper adsorption capacities of all of these materials were compared. MCM-41 APTMS had the highest adsorption capacity for Cu(II) in aqueous solutions at 1.8 mmol functional group/ g MCM-41.

5.2 Future Work

This preliminary work can lead to different and more types of functionalization and adsorption reactions. Future work will focus on mesoporous silica because of its higher surface area and thus adsorption capacity. Functionalization via co-condensation and grafting will be further investigated to better understand the distribution of functional groups. Bifunctional (two functional groups) can be grafted on the surface of molecular sieves for future work in heavy metal adsorption.

REFERENCES

- (1) Lai, C.; Trewyn, B. G.; Jeftinija, D. M.; Jeftinija, K.; Xu, S.; Jeftinija, S.; Lin, V. S. *Journal of the American Chemical Society* **2003**, *125*, 4451-4459.
- (2) Barquist, K.; Larsen, S. C. *Microporous and Mesoporous Materials* **2008**, *116*, 365-369.
- (3) Cheng, C.; Bae, T.; McCool, B. A.; Chance, R. R.; Nair, S.; Jones, C. W. *The Journal of Physical Chemistry C* **2008**, *112*, 3543-3551.
- (4) Song, W.; Grassian, V. H.; Larsen, S. C. *Chem. Commun.* **2005**, 2951-2953.
- (5) Barquist, K.; Larsen, S. C. *Microporous and Mesoporous Materials* **2008**, *116*, 365-369.
- (6) Larsen, S. C. *The Journal of Physical Chemistry C* **2007**, *111*, 18464-18474.
- (7) Zhao, X. S.; Lu, G. Q. (.; Millar, G. J. *Industrial & Engineering Chemistry Research* **1996**, *35*, 2075-2090.
- (8) Chen, N.; Degnan, T.; Lutner, J.; Pelrine, B. In *Catalyst Deactivation 1991, Proceedings of the 5th International Symposium*; Elsevier, 1991; Vol. Volume 68, pp. 773-782.
- (9) Zhan, B.; White, M. A.; Lumsden, M. *Langmuir* **2003**, *19*, 4205-4210.
- (10) Lai, C.; Trewyn, B. G.; Jeftinija, D. M.; Jeftinija, K.; Xu, S.; Jeftinija, S.; Lin, V. S. *Journal of the American Chemical Society* **2003**, *125*, 4451-4459.
- (11) Lin, Y.; Tsai, C.; Huang, H.; Kuo, C.; Hung, Y.; Huang, D.; Chen, Y.; Mou, C. *Chemistry of Materials* **2005**, *17*, 4570-4573.
- (12) Giri, S.; Trewyn, B. G.; Stellmaker, M. P.; Lin, V. S. *Angewandte Chemie International Edition* **2005**, *44*, 5038-5044.
- (13) Salmio, H.; Bruhwiler, D. *The Journal of Physical Chemistry C* **2007**, *111*, 923-929.
- (14) Aguado, J.; Arsuaga, J. M.; Arencibia, A.; Lindo, M.; Gascón, V. *Journal of Hazardous Materials* **2009**, *163*, 213-221.
- (15) Lim, S.; Zheng, Y.; Zou, S.; Chen, J. P. *Chemical Engineering Journal* **2009**, *152*, 509-513.
- (16) Ray, P. *Journal of Applied Polymer Science* **2009**, *113*, 1155-1164.
- (17) Song, W.; Grassian, V. H.; Larsen, S. C. *Langmuir* **2004**, *20*, 4696-4702.
- (18) Song, W.; Justice, R. E.; Jones, C. A.; Grassian, V. H.; Larsen, S. C. *Langmuir* **2004**, *20*,

4696-4702.

- (19) Chen, H.; Huh, S.; Wiench, J. W.; Pruski, M.; Lin, V. S. *Journal of the American Chemical Society* **2005**, *127*, 13305-13311.
- (20) Huh, S.; Wiench, J. W.; Yoo, J.; Pruski, M.; Lin, V. S. *Chemistry of Materials* **2003**, *15*, 4247-4256.
- (21) Slowing, I.; Trewyn, B. G.; Lin, V. S. *Journal of the American Chemical Society* **2006**, *128*, 14792-14793.
- (22) Radu, D. R.; Lai, C.; Huang, J.; Shu, X.; Lin, V. S. *Chem. Commun.* **2005**, 1264-1266.
- (23) Barquist, K.; Larsen, S. C. *Microporous and Mesoporous Materials* **2008**, *116*, 365-369.
- (24) Lam, K. F.; Chen, X.; McKay, G.; Yeung, K. L. *Industrial & Engineering Chemistry Research* **2008**, *47*, 9376-9383.
- (25) Bois, L.; Bonhommé, A.; Ribes, A.; Pais, B.; Raffin, G.; Tessier, F. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2003**, *221*, 221-230.
- (26) Lam, K. F.; Yeung, K. L.; McKay, G. *Microporous and Mesoporous Materials* **2007**, *100*, 191-201.