Selective catalysis utilizing bifunctionalized MCM-41 mesoporous materials.

by

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For the Major Program

Dedicated to...

Scott, Marsha, Ben, Ken, and Vickie
for all of your love and support.

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CHAPTER 1. GENERAL INTRODUCTION

MCM-41 Properties and Applications

Selective catalysis is a field that has been under intense investigation for the last 100 years. The most widely used method involves catalysts with stereochemical selectivity. In this type of catalysis, the catalyst controls which reactants will be transformed into the desired product. The secret to employing this type of catalysis, though, is to design the proper catalyst, which can be difficult. One may spend as much time developing the catalyst as spent separating the various products achieved. Another method of selective catalysis is now being explored. The method involves utilizing a multifunctional mesoporous silica catalyst with a gate-keeping capability.

Properly functionalized mesoporous materials with well-defined pore morphology and surface properties can provide an ideal three-dimensional environment for anchoring various homogeneous catalysts. These materials can circumvent the multi-sited two-dimensional nature most heterogeneous systems have without adversely impacting the reactant diffusivity. These single-site nanostructured catalysts with ordered geometrical structure are advantageous in achieving high selectivity and reactivity. Mesoporous materials can be prepared to include pores lined homogeneously with tethered catalysts via co-condensation. Additionally, these materials can be reacted with another $(\text{RO})_3\text{Si}^{\sim}\text{Z}$ group by using the traditional grafting method; this group is anchored predominately at the entrances to the pores rather than inside the pores. Thus, if these $^{\sim}\text{Z}$ groups are chosen properly, they can select certain molecules to enter the pores and be converted to products (Scheme 1). In such multifunctional catalysts, the selectivity depends on the discrimination of the gatekeeper. Gate-keeping MCM-41 materials are at the forefront of catalytic substances.

Scheme 1. Gatekeeper groups allow only reactant A to enter the catalyst-functionalized mesopores to selectively yield product A.

Mesoporous materials are defined as having pores in the range of 2 to 50 nm.¹ Many varieties of mesoporous catalysts are now available (MCM-41, MCM-48, SBA-15, etc.); however, the focus herein will be on MCM-41. Mobil Oil Corporation scientists created the siliceous ordered mesoporous material in 1992. MCM-41, Mobil Composition of Matter No. 41, displays a highly ordered hexagonal array of pores with a very narrow pore size distribution.²

One of the enormous benefits of MCM-41 over other mesoporous materials is its well-defined pore diameter and channel-like pore structure with hexagonal symmetry. The pore diameter ranges from 15 Å to more than 100 Å.² This size, much larger than zeolites, is of much greater utility in catalysis. The periodic mesopores allow for easier diffusion of substrates through the pores. Another immense advantage is the tunability of the pores. The size of the pores can be altered based upon the surfactant utilized in the synthesis. The longer the carbon chain utilized, the greater the pore size; therefore, one can modify the pore diameter in order to fit with the application of the material.² The larger pore sizes allow for easier diffusion of reactants into and products out of the pores; however, the pores must be small enough as to provide the desired type of environment.

The surface area offers another immense benefit of the mesoporous materials. The surface area of MCM-41 can range from $\sim 500 \text{ m}^2/\text{g}$ to $\sim 1,000 \text{ m}^2/\text{g}$.^{2,3} When used for catalytic purposes, the large surface area imparts a considerable number of catalytic sites in a small amount of material. This implies that one does not have to consume as much of the solid support when performing heterogeneous catalytic reactions.

It is also possible to modify the particle shape of MCM-41. One can prepare different particle morphologies by varying the pH,⁴ utilizing base catalysts,⁵ using co-solvents,⁶ and introducing multiple organic functional groups, which will be discussed in further detail later in this chapter.⁷ The shape appears to play a role in the effectiveness of the catalyst; however, it is not yet clear as to whether this is because of the actual morphology or because of the number of defects in various mesoporous materials.⁸ Most MCM-41 utilized for catalysis seems to be particulate (spherical) rather than tubular.

The stability of MCM-41 may be a concern for some applications. The thermal stability depends upon the wall thickness and the silica precursor used in the synthesis.⁸ The average wall thickness of MCM-41 is $\sim 1 \text{ nm}$, which is comparable to MCM-48 but much lower than SBA-15 having a wall thickness of $\sim 3 \text{ nm}$.⁸ One can conclude from this that MCM-41 is not the most stable mesoporous material; however, it is stable at $\leq 550^\circ \text{C}$. The hydrothermal stability is also determined by the wall thickness, but the extent of silica polymerization is another major factor.⁸ Hydrothermal stability is necessary for most applications, so this is an area that is under investigation for possible improvements.⁹ The mechanical stability does not seem to be an issue for most applications of MCM-41.⁸

The possibilities for using MCM-41 are nearly endless. As mentioned previously, catalysis is at the forefront of uses for MCM-41. It can be used in acid/base reactions, redox

reactions, and in metal-catalyzed reactions. There are, however, numerous other applications of the mesoporous silica material. Some of these other uses include adsorbents,¹⁰ sensors,¹¹ carrier systems for controlled release of various compounds,¹² etc. As research progresses, there will likely be even more possible applications of this remarkable material.

MCM-41 Synthesis

The basic idea behind MCM-41 synthesis is to form surfactant micelles, which then form micellar rods. These rods aggregate to create hexagonal arrays. By adding a silica source to this, the rods are coated with silica. Following this, the surfactant can be removed leaving silica particles with empty pores.³ As mentioned earlier, the pore size and surface area of the materials can vary greatly by altering the synthesis procedure. By controlling the particle morphology of and introducing functionalities to these mesoporous silica materials, their utility increases tremendously.

Controlling the particle morphology is essential for determining catalysis kinetics. The regularity of the particle morphology must be regulated, as well as fine-tuning the actual particle shapes. A series of new MCM-41s containing different organic functional groups, such as a primary amine, secondary amine, urea, isocyanate, vinyl group, and nitrile, have been synthesized with high reproducibility.^{7,13} The particle morphology of the resulting materials can be directed to form different particle shapes and sizes, such as spheres, tubes, and rods, simply by introducing different organoalkoxysilane precursors into our co-condensation reactions. For example, mesoporous silicas functionalized with 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (AEPTMS) and cyanopropyltriethoxysilane (CPTES) groups exhibit very different particle shapes and sizes, i.e., spheres with an average particle diameter = 3 μm and rods with an average particle size: $L \times W = 1 \times 0.2 \mu\text{m}$, respectively.

Two methods exist for introducing functionality into the MCM-41: post-synthesis grafting and co-condensation.¹⁴ Post-synthesis grafting was the first method developed for functionalizing mesoporous materials. Grafting entails introducing an organosiloxane after the siliceous mesoporous material has been synthesized. The grafting method has one very major drawback, lack of functionality control. The functional groups tend to aggregate around the pore mouths and on the exterior surface.¹⁵ Many times the functional groups block the pore openings because of the aggregation, negating the purpose of the mesoporous materials, which is to exploit the pore interiors. Functional groups on the surface exterior also defeat the purpose of the pores.

Co-condensation is a fairly new development and appears to be the superior method. Co-condensation involves introducing an organosiloxane in addition to the siloxane in the material synthesis.¹⁶ Co-condensation yields a mesoporous material with organic functionalities distributed fairly evenly within the pores. During co-condensation synthesis, the functional groups introduced are electrostatically or hydrophobically attracted to the ammonium surfactant head groups. The functional groups then position themselves inside the surfactant micelle, ensuring that they are primarily present only on the interior of the mesopores. Since they compete with the silicate anions, the functional groups are randomly distributed upon the pore surface.¹³

Multifunctionalization has also been achieved using the co-condensation method. This approach allows for many more options in the usefulness of MCM-41. One functional group can be used as the catalyst while the other group permits one to select which compounds are able to enter the pores. This selectivity is usually the result of hydrophobic/hydrophilic

interactions of the functional group with the entering compounds. This type of interaction is the key to creating a selective mesoporous catalyst.

Essentially, the secondary functional group in the multifunctionalized MCM-41 acts as a gatekeeper; this is how the selective mesoporous catalyst evolved. The gatekeeper permits the desired reactants to diffuse into the material's pores but excludes those that do not fit the requirements. This type of catalyst is much easier to prepare than the chiral catalyst used in previous selective catalysis reactions.

Surface Characterization

The MCM-41 was characterized by several methods: x-ray diffraction (XRD), transmission electron microscopy (TEM), N₂ sorption analysis, and electron spectroscopy for chemical analysis (ESCA). Powder XRD is a useful tool in determining the order and symmetry of the mesopores. The sample, comprised of many randomly oriented powder particles, is exposed to the monochromatic x-rays. Each powder particle has a particular crystal structure so a large number of them oriented randomly guarantees the probability of every possible set of crystallographic planes being available for diffraction. The diffractometer contains an x-ray source and a counter. The counter rotates at an angle of 2θ while the sample rotates through an angle of θ , so the incident and reflection angles remain equal to one another. A recorder then plots the diffracted beam intensity as a function of 2θ . High intensity peaks result when the Bragg diffraction condition is met by some set of crystallographic planes.¹⁷ The peak patterns can be interpreted to determine the mesoporous material's symmetry (i.e. cubic, hexagonal) and the distance between pores.

N₂ sorption analysis is a valuable tool in determining the specific surface area, pore volume, and pore size distribution, as well as the surface properties. The adsorption isotherm

provides an enormous amount of information about the surface properties. There are six types of isotherms possible, but only five apply to materials like those discussed herein. Type I isotherms (substantial adsorption at low relative pressures then leveling off with no hysteresis loop) indicate micropores. Neither type II nor type III isotherms contain hysteresis loops. These designate macroporous solids. Type IV and V isotherms possess hysteresis loops and are indicative of mesoporous solids. The hysteresis loops are the result of capillary condensation and evaporation taking place at different pressures. The hysteresis loops can also be very helpful in determining particle shape. Two of the most important are types H1 and H3. Type H1 loops usually signify agglomerated materials, spherical particles compacted in a reasonably uniform manner, and materials with cylindrical pores and a high degree of pore size homogeneity. H3 loops exist for materials with aggregates of plate-shaped particles forming slit-like pores.¹⁸

The Brunauer-Emmett-Teller (BET) method¹⁹ is the standard for determining the specific surface area. This equation assumes many properties, including a flat surface, and determines the surface area based upon an evaluation of the monolayer capacity on the material's surface. The specific surface area is another indication of the degree of porosity of a material. The higher the surface area, the greater the number of pores there are and the fewer blockages of pores. The pore volume is calculated using the amount of gas adsorbed at a relative pressure close to the saturation vapor pressure. This amount of gas is then converted to the analogous volume of liquid adsorbate at that temperature to give the pore volume. The pore diameter of a material with uniform cylindrical pores is simply determined using the surface area and pore volume. The pore size distribution of a material is usually determined via the Barrett, Joyner, and Halenda (BJH) method. The BJH method utilizes an algorithm²⁰ that depends on the accuracy of the relation between pore size and capillary

condensation/evaporation pressure, the correct t-curve(s), and the aptness of the adsorption/desorption curves.¹⁸ All of the information collected during N₂ sorption analysis supplies a tremendous amount of information about the mesoporous material, but it still does not supply an actual image of the material.

TEM is an indispensable tool in visualizing mesoporous materials. The bright-field images collected using a TEM, similar to those of the light microscope, reveal the internal components of the sample. Because electrons generate the sample image, TEM images are only available in black and white. In order to obtain a high-quality image, the sample must also be thin enough for the electron beam to pass through; therefore, sample preparation is a key step in acquiring high-quality TEMs. TEM, operating under high-vacuum conditions, has a greater resolving power and a higher magnification range than the light microscope. The TEM's resolving power is related to the wavelength and numerical aperture of a lens. It typically produces a 1,000-fold increase in resolving power over the light microscope. In contrast to the light microscope, diffraction can be a very useful tool in TEM because it differentiates between "holes" and solid surfaces. Also, unlike SEM, a sizeable portion of the TEM sample is illuminated with the electron beam because it operates in a flood-beam manner. One can then visualize the mesopore structures, confirming XRD measurements.²¹

ESCA, also known as x-ray photoelectron spectroscopy (XPS), is a technique based on the photoelectric effect that is used to explore surface compositions. ESCA, therefore, provides information about the elemental composition of a material's surface, not just the physical properties. During analysis, the x-ray source excites an area of 1 cm² and to a depth of approximately 1 μm. Electrons are emitted from this entire volume. The kinetic energy of the ejected electrons is then measured. Utilizing the equation $BE = h\nu - KE - \Phi_{spec}$ where $h\nu$ is the

known energy of the x-ray source, KE is the kinetic energy collected during analysis, and Φ_{spec} is the spectrometer work function; one can determine the binding energy, BE , which is the standard method of reporting ESCA results. Binding energies are different for each energy level the electrons are ejected from and are fairly specific for each element. The binding energies can shift slightly because of nucleus-electron attractions and electronegativity. Spin-orbit coupling results in multiple peaks a specified distance apart. There can also be multiplet splitting as a result of unpaired ions in the same atom coupling.²²

Thesis Organization

The following research utilizes the fact that one can utilize these mesoporous materials to catalyze reactions not only by typical means (i.e. metal centers) but also by introducing a secondary functional group that can drive the reaction by physically isolating the reactant. This isolation could occur by simply forcing the reactant into the material's pores or by constraining the reactant into the necessary conformation for the reaction.

Chapter 2 will focus on merely driving the reactants into the pores. This particular research utilizes MCM-41 as a selective catalyst for 1,2,3-triazole formation. The type of reaction is "click chemistry" between an organic azide and an acetylene. The reaction is very fast (complete in 6 to 36 hours at room temperature), can be performed in H_2O at a pH from 4 to 10, and the products can usually be removed by filtration.²³ It is typically catalyzed by copper(I) in solution. Copper always produces 1,4-disubstituted-1,2,3-triazoles; however, tin, germanium, silicon, sodium, lithium, and magnesium generate 1,5-disubstituted-1,2,3-triazoles.²⁴ The multifunctional MCM-41 utilized herein contains a copper-complexed diamine as well as a pentafluorophenyl (PFP) group. The PFP group, the gatekeeper, enhances the hydrophobic environment naturally created by the mesoporous silica nanospheres. The hydrophobicity of

the pores promotes diffusion of the hydrophobic reactants into the pores, which creates the close contact of the reactants with copper complexed in the pores. These interactions are proven by employing two very different solvents: water and benzene. The benzene's nonpolar environment is not unlike that of the mesoporous material's pore interior; however, the water's polar environment presents a stark contrast to that of the pore interior. The results demonstrate the dramatic difference in how the reaction proceeds.

Chapter 3 is an introduction to work that attempts to power a reaction by imposing a specific conformation upon a reactant molecule. The reaction discussed is a syn elimination to form a cis olefin. This type of reaction is very rare—nearly impossible—in acyclic systems, so an easily synthesized catalyst for this application would be ground-breaking. The catalyst, again a mesoporous material, utilizes hydrophobicity/hydrophilicity as the driving force for the regioselective conformational catalyst.

Chapter 4 will summarize the idea behind utilizing secondary groups as a driving force in the heterogeneous MCM-41 catalysis as well as the importance of surface dilution. Primary groups are used as the actual catalyst; however, the secondary groups are the essential parts of the catalyst. Without the secondary groups, the catalytic effect would certainly be reduced. These secondary groups, used as gatekeepers of the mesopores, control the diffusion of reactants into the pores. This control is the crucial ingredient for successful selective catalysis.

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CHAPTER 2. SELECTIVE CATALYSIS OF HYDROPHOBIC 1,2,3-TRIAZOLES UTILIZING Cu/PFP MCM-41

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Abstract

A 1,2,3-triazole formation reaction from benzyl azide and phenyl acetylene was catalyzed by Cu/PFP MCM-41 in two solvents: benzene and water. The water system produced yields of 23% for the grafted Cu/PFP MCM-41 and 59% for co-condensed Cu/PFP MCM-41. The reactions in benzene produced yields of only 4% and 5% for grafted and co-condensed Cu/PFP MCM-41, respectively.

Introduction

MCM-type materials have been the focus of much research since their discovery in 1992.¹ Catalysis employing mesoporous materials has grown in interest because of recent advances in functionalization of these MCM-type materials. Several previous studies² involved immobilization of single-site catalysts, such as transition metal complexes and Lewis or Bronsted acids and bases, onto the mesopore surfaces. However, in contrast to zeolite-based catalysts, which utilize the “shape/size selective cavity effect”,³ the selectivity of mesoporous silica-based systems was mainly controlled by the intrinsic coordination environment of the heterogenized catalytic group. The mesoporous silica itself served only as an inert supporting matrix with a large surface area, whose chemical and geometric properties were often not utilized.^{2a,c,4}

As recently reported, co-condensation of organic functional groups allows more possibilities for the pore interiors. The functional groups themselves may contain the catalytic

group; however, one can utilize various noncovalent interactions to assist in the catalysis. Herein a bifunctionalized MCM-41 material is employed to catalyze the formation of a 1,2,3-triazole using a Cu(I) catalyst. The bifunctionalized MCM-41 material contains a hydrophobic pentafluorophenyl group and a copper-complexed diamine ligand. Grafting and co-condensation were utilized to synthesize two varieties of the copper-complexed *N*-(2-aminoethyl)-3-aminopropyl/pentafluorophenylpropyl (PFP) MCM-41. The grafting method involved co-condensing the *N*-((2-aminoethyl)-3-aminopropyl)trimethoxysilane and 3-(pentafluorophenyl)propyltrimethoxysilane during the MCM-41 synthesis, followed by subsequent complexation of the Cu^{2+} moiety to the diamine ligands of the material. The co-condensation method required complexing Cu^{2+} to the *N*-((2-aminoethyl)-3-aminopropyl)trimethoxysilane prior to the co-condensation synthesis of the MCM-41 material. Hydrophobic interactions in the MCM-41 pore interiors were then utilized as the driving force of the copper-catalyzed “click chemistry” reaction between an acetylene and an azide to form a 1,4-disubstituted-1,2,3-triazole (Scheme 2).

Scheme 2. Schematic representation of the synthesis of the 1,2,3-triazole using Cu/PFP MCM-41 as the catalyst.

Materials and Methods

Materials

Benzyl chloride (PhCH_2Cl), copper(II) bromide (CuBr_2), *n*-cetyltrimethylammonium bromide (CTAB), sodium azide (NaN_3), and triethylamine (NEt_3) were all obtained from Sigma-Aldrich, Inc. and used without further purification. *N*-((2-aminoethyl)-3-aminopropyl)trimethoxysilane (AAPTS), 3-(pentafluorophenyl)propyltrimethoxysilane, and tetraethylorthosilicate (TEOS) were purchased from Gelest, Inc. and used without further purification. Benzene, hydrochloric acid (37.3%), methanol, and *N,N*-dimethylformamide were acquired from Fisher Scientific. Nanopure water was obtained using a Barnstead E-pure water purification system.

Co-condensed Cu/PFP MCM-41 Synthesis

Cetyltrimethylammonium bromide (CTAB, 1.0 g, 2.74×10^{-3} mol) was dissolved in 480 mL of nanopure water at room temperature. An aqueous solution of NaOH (2 M, 3.5 mL) was added to the CTAB solution. The temperature of the solution was then increased to 80 °C. TEOS (5.0 mL, 2.24×10^{-2} mol) was added via a fast addition, followed by simultaneous introduction of 3-(pentafluoro)propyltrimethoxysilane (0.34 mL, 1.31×10^{-3} mol) and a $\text{Cu}(\text{AAPTS})_2^{2+}$ complex solution. The $\text{Cu}(\text{AAPTS})_2^{2+}$ complex solution was prepared previously by combining 7.5 mL of methanol, CuBr_2 (137.3 mg, 6.1×10^{-4} mol), and AAPTS (0.272 mL, 1.2×10^{-3} mol). The solution immediately turned blue upon addition of the AAPTS. The CTAB, TEOS, 3-(pentafluoro)propyltrimethoxysilane, and $\text{Cu}(\text{AAPTS})_2^{2+}$ precursor were stirred for 2 h. The resultant blue solid was isolated by filtration, washed with methanol, and dried under vacuum. The as-synthesized material (500 mg) was washed to remove the CTAB surfactant by Soxhlet extraction using 200 mL of methanol and 6.0 mL of HCl for 18 h. The

washed MCM-41 was filtered, rinsed with methanol, and dried under vacuum.

Grafted Cu/PFP MCM-41 Synthesis

Cetyltrimethylammonium bromide (CTAB, 1.0g, 2.74×10^{-3} mol) was dissolved in 480 mL of nanopure water at room temperature. An aqueous solution of NaOH (2 M, 3.5 mL) was added to the CTAB solution. The temperature of the solution was then increased to 80 °C. TEOS (5.0 mL, 2.24×10^{-2} mol) was added via a fast addition, followed by simultaneous introduction of 3-(pentafluorophenyl)propyltrimethoxysilane (0.216 mL, 0.83×10^{-4} mol) and AAPTS (0.374 mL, 1.67×10^{-3} mol). The CTAB, TEOS, 3-(pentafluorophenyl)propyltrimethoxysilane, and AAPTS were stirred for 2 h. The solid was isolated by filtration, washed with methanol, and dried under vacuum. The as-synthesized material (500 mg) was washed to remove the CTAB surfactant by Soxhlet extraction using 200 mL of methanol and 6.0 mL of HCl for 18 h. The washed MCM-41 was filtered, rinsed with methanol, and dried under vacuum. The washed material (150 mg) was suspended in 20 mL of methanol, which was stirred for 1 h. CuBr₂ (100 mg, 4.48×10^{-4} mol) was added, followed by stirring for 24 h. The resulting green solid was filtered, washed with methanol, and dried under vacuum.

Benzyl Azide Synthesis

Benzyl chloride (5.76 mL, 5.0×10^{-2} mol) was suspended in *N,N*-dimethylformamide (200 mL). NaN₃ (6.50 g, 1.0×10^{-1} mol) was added to the solution, which was then refluxed for 24 h. 200 ML of H₂O were introduced to the reaction mixture after cooling to room temperature. The solution was extracted with toluene (3 x 100 mL). The combined toluene layers were washed with brine (100 mL), followed by H₂O (100 mL). The toluene layers were

dried with MgSO_4 and nearly all of the solvent was removed under vacuum. Some DMF remained (3 mol benzyl azide: 1 mol DMF) to ensure the chemical stability of the azide.

1,2,3-Triazole Formation Reactions Using Cu/PFP MCM-41

Two solvent systems were used, benzene and H_2O . Aside from the different solvents, all conditions were identical for the grafted and co-condensed Cu/PFP MCM-41 reactions. Reaction vials contained 12 mL of solvent, benzyl azide (2.3×10^{-3} mol plus minimal DMF), phenylacetylene (0.33 mL, 3.0×10^{-3} mol), triethylamine (0.42 mL, 3.0×10^{-3} mol), and ~ 20 mg Cu MCM-41 catalyst. The contents of the vials were stirred at room temperature for the indicated number of hours. The contents of the benzene-containing vials were filtered to remove the MCM-41 and the filtrate was placed under a vacuum to isolate the product. Toluene (30 mL) was added to the H_2O -containing vials to extract the product. The toluene was filtered to remove any MCM-41. The toluene was removed under vacuum.

Homogeneous 1,2,3-Triazole Formation Reaction

All reaction vials contained 12 mL solvent (benzene or H_2O), benzyl azide (2.3×10^{-3} mol plus minimal DMF), and phenylacetylene (0.33 mL, 3.0×10^{-3} mol). CuBr_2 (8.5 mg, 3.8×10^{-5} mol) and triethylamine (0.42 mL, 3.0×10^{-3} mmol) were introduced as indicated in Table 3. For the reaction vials containing ethylenediamine, the Cu content remained constant, but the diamine amount was varied. The vials were stirred at room temperature for the indicated number of hours. The benzene-containing vials were extracted using 25 mL of H_2O and 10 mL of toluene. The organic layers were combined and the solvent removed under vacuum. The contents of the H_2O -containing vials were extracted using 40 mL toluene. The toluene was removed under vacuum.

XRD

Low angle powder x-ray diffraction (XRD) data was collected on a Scintag XRD 2000 X-Ray Diffractometer using Cu K α radiation.

TEM

For transmission electron microscopy (TEM) measurements, a small aliquot was ground with methanol in an agate mortar and pestle. A single drop of this suspension was placed on a lacey carbon-coated copper TEM grid and air dried. The TEM examination was completed on a Philips model CM-30 operated at 300 kV.

N₂ Sorption Analysis

The nitrogen adsorption and desorption isotherms, surface area, and average pore diameter were measured using a Micromeritics ASAP 2000 sorptometer. Sample preparation included degassing at 90 °C for 1 h. Nitrogen adsorption and desorption isotherms were taken at -196 °C. Specific surface areas and pore size distributions were calculated using the Brunauer-Emmett-Teller (BET) and the Barrett-Joyner-Halenda (BJH) methods, respectively.

ESCA

Electron spectroscopy for chemical analysis (ESCA) was performed on a Physical Electronics, Inc. 5500 MultiTechnique system using Al K α (1486.6 eV) X-ray for excitation and a spherical section analyzer. The instrument has 16 element multichannel detection. The analyzer was run in a constant pass energy mode with a width of 1 mm x 0.8 mm. The incident angle of the X-ray beam was 45°, as was the emission angle. The collected data were referenced to an energy scale with binding energies for Si_{2p} in SiO₂ at 103.4 eV. The elements were quantified using the sensitivity factors taken from the "PHI Sensitivity Factors Reference Table" of the Physical Electronics standard software. The peak areas are the areas of the fitted

curves above the Shirley background. The atomic concentration for an element X is calculated as: $AC(X) = [I_x/S_x]/[\sum I_y/S_y]$, with S_x as the sensitivity factor for element X and the I_x as the area of the fitted Lorentzian-Gaussian curve for the corresponding photopeak of element X.

Results and Discussion

The differing physical appearance, on the macro scale, of the two types of Cu/PFP MCM-41 is apparent. Upon synthesis, the co-condensed Cu/PFP MCM-41 displays a bright blue color. The grafted Cu/PFP MCM-41, however, forms a green material after the CuBr_2 addition. Both Cu/PFP MCM-41 materials exhibit a spherical particle shape as the TEMs demonstrates in Figures 2(a) and 2(b).

Figure 1. Transmission electron micrographs (TEMs) of the (a) grafted and (b) co-condensed Cu/PFP MCM-41 materials.

Powder X-ray diffraction (XRD) measurements of the two materials demonstrate another physical difference between the two materials the pore structures (Figure 2). The XRD measurement of the grafted Cu/PFP MCM-41 shows the typical diffraction pattern of an MCM-41 type mesoporous silica with hexagonal symmetry. This result is also confirmed by the TEM [Figure 1(a)], which illustrates the closely-packed hexagonal, linear pores. The co-

condensed Cu/PFP MCM-41 exhibits a diffraction pattern of an MCM-41 material with no apparent hexagonal symmetry. The pattern reveals that the co-condensed material contains pores but with no obvious structure. The TEM confirms the wormhole-type structure as seen in Figure 1(b).

Figure 2. XRD of the grafted (green) and co-condensed (blue) Cu/PFP MCM-41.

The N₂ surface sorption analyses of the Cu/PFP MCM-41 materials express typical type IV BET isotherms and H1 hysteresis loops [Figure 3(a)]. The measured BET surface areas of the grafted and co-condensed Cu/PFP MCM-41 materials are 854.6 and 610.1 m²/g, respectively. The BJH pore distributions of grafted and co-condensed materials exhibit pore diameters of 25.8 and 22.5 Å, respectively, as seen in Figure 3(b).

Figure 3. (a) BET and (b) BJH adsorption data for grafted (green) and co-condensed (blue) Cu/PFP MCM-41.

Electron spectroscopy for chemical analysis (ESCA) was performed on the two Cu/PFP MCM-41 materials. The results of the Cu and Br ESCA are presented in Figure 4. The Cu spectrum demonstrates that both materials contain the same copper species, copper(II), because of their identical binding energies and the satellite peaks proportional to the major peaks. The presence of bromine in the grafted Cu/PFP MCM-41, but a lack thereof in the co-

condensed Cu/PFP MCM-41, results from the CuBr_2 used during the post-synthesis grafting. ESCA spectra for all elements present in the two Cu/PFP MCM-41 materials are given in Figure 5. Other than varying intensities, the ESCA spectra are nearly identical. Table 1 supplies the atomic concentrations of the two materials. From this information, one can speculate that the differing appearances of the Cu/PFP MCM-41 materials result from the differing coordination environments. The co-condensed Cu/PFP MCM-41 nitrogen to copper ratio is 6:1, whereas the ratio of nitrogen plus bromine to copper in the grafted material was only found to be 3:1. The copper concentration is also 2.2 times greater in the grafted Cu/PFP MCM-41 than in the co-condensed material. This disparity presumably results from the grafting procedure in that the copper aggregates at the pore mouths instead of diffusing into the pore interiors, similar to the post-synthesis functionalization grafting.

Figure 4. ESCA spectra of (a) copper and (b) bromine of the grafted (red) and co-condensed (blue) Cu/PFP MCM-41.

Figure 5. ESCA data of grafted (red) and co-condensed (blue) Cu/PFP MCM-41 data.

Table 1. Atomic concentrations (% of total composition) of grafted and co-condensed Cu/PFP MCM-41 collected via ESCA.

	C _{1s}	N _{1s}	O _{1s}	F _{1s}	Si _{2p}	Cu _{2p}	Br _{3d}
Grafted	14.35	1.58	58.08	3.27	21.60	0.67	0.45
Co-condensed	24.91	1.83	50.18	4.64	18.14	0.30	0.00

The grafted and co-condensed Cu/PFP MCM-41 materials were utilized in the 1,2,3-triazole formation reactions as described earlier. ¹H NMR spectra were run to determine the amount of product in the resulting solutions/solids of these reactions. The percent yields of the 1-benzyl-4-phenyl-1,2,3-triazole product were determined from these spectra. A histogram of the yields is presented in Figure 6. Table 2 also contains the average yields for each reaction type.

The reactions containing the grafted and co-condensed Cu/PFP MCM-41 run in benzene demonstrated very little catalytic ability with maximum yields of 5.3% and 6.4%, respectively. The hydrophobic solvent in combination with the hydrophobic pore interiors impart strikingly similar interiors. This similarity establishes little incentive for the reactants and products to diffuse into and out of the pores, removing the driving force for the catalytic reaction. The reactions in benzene are controlled only by how fast the copper can catalyze the reaction. The reactions performed in water, however, show a significant catalytic ability. There is a discrepancy in the catalytic capacity between the grafted and co-condensed Cu/PFP MCM-41 materials. The co-condensed Cu/PFP MCM-41 material generates an average percent yield (based on three runs) of 78% after 72 h. Despite its larger average pore volume, the grafted Cu/PFP MCM-41 exhibits a lower catalytic ability with only a 36% average yield. The difference between the grafted and co-condensed Cu/PFP MCM-41 presumably arises from the fact that the copper is more “dilute” in the co-condensed material and is spread more evenly

over the interior of the pores. The grafted material appears to have copper localized at the pore mouths, which accounts for the lower yield. The surface dilution effect, well proven in other heterogeneous catalytic systems, presumably creates the considerable catalytic difference. Overall, the amount of conversion of the reactants to 1,2,3-triazole in water is regulated by how fast the reactants, triethylamine, and products diffuse into and out of the pores in addition to the copper coverage.

Figure 6. Percent yield histogram of the Cu/PFP MCM-41 catalyzed 1,2,3-triazole reactions.

Table 2. Average percent yield results of selective 1,2,3-triazole formation using grafted and co-condensed Cu/PFP MCM-41 (based on three independent runs).

	Benzene Grafted	H ₂ O Grafted	Benzene Co-cond	H ₂ O Co-cond
24 h	3.3% ± 0.9%	20% ± 10%	2.3% ± 1.0%	24% ± 3%
48 h	4.8% ± 1.1%	14% ± 5%	4.3% ± 2.0%	52% ± 20%
72 h	5.3% ± 0.4%	36% ± 2%	6.4% ± 1.3%	78% ± 20%

Homogeneously catalyzed reactions were also performed with CuBr_2 , triethylamine, and ethylenediamine. The percent yields for these reactions are presented in Table 3. The reaction containing only benzene, reactants, CuBr_2 , and triethylamine afforded a 100% yield of triazole. Copper generally has very poor solubility in benzene, but the addition of triethylamine increases copper's solubility via complexation. This increase in solubility accounts for the high yield. The copper/triethylamine reaction in water, however, afforded only a moderate yield of 33%. The reactions in benzene, where various ratios of ethylenediamine were added, produce lower amounts of products than that of the triethylamine only but ranged from 17% to 59%. The yields obtained in the same aqueous reactions were also in the moderate range, ranging from 49% to 73%. These yields were all higher than those attained using only triethylamine. This result presumably arises from the greater amount of amine for the copper to complex with and more amine to reduce the copper from Cu(II) to Cu(I) .

Table 3. Percent yield of 1,2,3-triazole formation by homogeneous catalysis using CuBr_2 .

	72 h
Benzene, CuBr_2 , triethylamine	100%
H_2O , CuBr_2 , triethylamine	33%
Benzene, 1 CuBr_2 : 1 ethylenediamine, triethylamine	59%
H_2O , 1 CuBr_2 : 1 ethylenediamine, triethylamine	57%
Benzene, 1 CuBr_2 : 2 ethylenediamine, triethylamine	28%
H_2O , 1 CuBr_2 : 2 ethylenediamine, triethylamine	73%
Benzene, 2 CuBr_2 : 1 ethylenediamine, triethylamine	17%
H_2O , 2 CuBr_2 : 1 ethylenediamine, triethylamine	49%

Conclusions

The Cu/PFP MCM-41 effectively catalyzes the 1,2,3-triazole formation from an organic azide and an acetylene. The aqueous solvent provides a polar environment for the hydrophobic reactants to be driven out of, forcing them into the mesoporous material. Nonpolar solvents, such as benzene, do not force the reactants into the pores of the MCM-41 material because there is essentially no difference between the solvent and the hydrophobic pore interior. These solvents, therefore, do not produce the same catalytic effect. The homogeneous catalytic reaction had the opposite effect with a quantitative yield in benzene and only a moderate (33% yield) in water. One can, therefore, assume that the Cu/PFP MCM-41 produces the proper surroundings for differentiation between the solvent systems.

The two methods of Cu/PFP MCM-41 synthesis do produce mesoporous materials with different properties. The grafted Cu/PFP MCM-41 has the more ordered, hexagonal pore structure, but the catalytic properties are only approximately equal to that of the homogeneous catalytic reaction. The co-condensed MCM-41 with the less ordered, wormhole structure has a much greater catalytic ability (approximately 42% greater) than the homogeneously catalyzed reaction. The difference between the two catalytic abilities is found to be a surface dilution effect, not a consequence of the structure. The grafted material contains more Cu at the pore mouths; however, the copper is well distributed throughout the pores of the co-condensed material. The co-condensed Cu/PFP MCM-41 incorporates less copper and is spread over the entire pore interior. This "dilute" copper coverage is extremely beneficial, as demonstrated in other heterogeneous catalysis research efforts.

The benefits of the MCM-41 reaction catalyst may be applied in many other types of catalytic applications. The MCM-41 can effectively control the catalysis utilizing solvent. One may soon be able to control the catalytic reactions utilizing other noncovalent interactions.

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CHAPTER 3. CONFORMATIONAL CATALYSIS OF A SYN ELIMINATION TO FORM A CIS OLEFIN

Introduction

There are four types of elimination reactions: anti elimination to a trans alkene, anti to cis, syn to trans, and syn to cis^{1,2} (Figure 7). The most difficult of these reactions is by far the last—syn elimination to a cis alkene. The reactant must go through a sterically and torsionally hindered eclipsed conformation for the reaction to occur,³ which precludes the reaction from taking place in most cases. The energy difference between transforming the reactants to the syn elimination cis product and the anti elimination trans product, respectively, is approximately 5 kcal/mol.⁴ This large energy gap indicates the difficulty in performing the syn elimination to the cis product. In fact, there is only one known case of a syn elimination to a cis olefin taking place in an acyclic system^{1,3,4}; moreover, the syn elimination to a trans alkene is even rare in acyclic systems despite the theoretically easier transformation.

Figure 7. Diagram of the four types of elimination reactions: syn elimination to cis and trans alkenes, anti elimination to cis and trans alkenes.

Richard Lerner's group at the Scripps Research Institute developed a scheme to perform the disfavored syn elimination to a cis olefin.⁴ Their method involves an antibody as the conformational catalyst. A specific molecule was designed to elicit antibodies that would bind to and lock the substrate into the desired position for reaction. Of the 26 antibodies they found to be specific to their designed molecule, only one performed the syn elimination to the cis olefin of the substrate. This is the most energetically-demanding reaction to have been catalyzed by an antibody to date. Despite the success of this reaction, the amount of work and time finding the antibody is tremendous considering that each antibody is specific to only one substrate; therefore, the idea arose to utilize MCM-41 as a conformational catalyst for the syn elimination to a cis olefin.

In the previous chapter, the hydrophobicity of the molecule as a whole was utilized to develop a selective catalyst. The hydrophobic pores possessed the environment necessary to force the entire hydrophobic molecule into the pore to interact with the catalytic copper complexes. This next endeavor takes this idea one step further in attempting to control the regioselectivity of a catalytic reaction. A bifunctionalized mesoporous material designed to exploit the hydrophobicity inside the pores could influence the conformation of the substrate. A substrate with both hydrophobic and hydrophilic sections, in the presence of an aqueous suspension of a hydrophobically-functionalized mesoporous material, should orient itself with the substrate's hydrophobic ends in the MCM-41 material and the substrate's hydrophilic ends in the aqueous solution. With the substrate in the correct conformation, the bifunctionalized mesoporous material with an acid primary functional group has the ability to catalyze the elimination reaction. The following scheme employs an MCM-41 material functionalized with

sulfonic acid groups as the chemical catalyst and pentafluorophenyl groups to drive portions of the substrate into the mesopores.

Scheme 3. Selective catalysis of the elimination reaction. Only the hydrophobic side of the reactant molecule diffuses into pores to interact with the acid catalyst immobilized inside hydrophobic mesopores.

The correct type of substrate must also be obtained in order to perform this reaction successfully. The substrate, as previously mentioned, must have both hydrophobic and hydrophilic groups in addition to the leaving group. Attempting to synthesize these materials is where this research concludes.

Methods and Materials

Sulfonic acid/pentafluorophenyl MCM-41 Synthesis

Cetyltrimethylammonium bromide (CTAB, 1.0 g, 2.74×10^{-3} mol) was dissolved in 480 mL of nanopure water at room temperature. An aqueous solution of NaOH (2 M, 3.5 mL) was added to the CTAB solution. The temperature of the solution was then increased to 80 °C. TEOS (5.0 mL, 2.24×10^{-2} mol) was added via a fast addition, followed by simultaneous

introduction of 3-(pentafluorophenyl)propyltrimethoxysilane (0.29 mL, 1.1×10^{-3} mol) and 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (50% in CH_2Cl_2 , 0.60 mL). The CTAB, TEOS, (PFP)propyltrimethoxysilane, and 2-(4-Chlorosulfonylphenyl)ethyltrimethoxysilane were stirred for 2 h. The resultant solid was isolated by filtration, washed with methanol, and dried under vacuum. The as-synthesized material (500 mg) was washed to remove the CTAB surfactant by refluxing in a solution of 160 mL of methanol and 5.0 mL of HCl for 24 h. The surfactant-free MCM-41 was filtered, washed with methanol, and dried under vacuum. The final product is a sulfonic acid/pentafluorophenyl mesoporous material.

Substrate Synthesis

Figure 8. Proposed synthesis schemes for two substrates (a) and (b) that could be used in the syn elimination to a cis olefin utilizing MCM-41 as a conformational catalyst.

The substrates were not synthesized; however, a synthesis proposal is depicted in Figure 8 for two different substrates desired for this project. The dashed lined indicates the last product reached in this research. The first substrate, 3, was prepared in the following manner. The first reaction is an aldol condensation between ethyl benzoylacetate and benzaldehyde. A solution of ethyl benzoylacetate (8.6 mL, 5.0×10^{-2} mol) in benzene (150 mL) containing molecular sieves was heated to 80 °C. To this solution, glacial acetic acid (0.14 mL, 2.5×10^{-3} mol), piperidine (0.25 mL, 2.5×10^{-3} mol), and benzaldehyde (5.1 mL, 5.0×10^{-2} mol) were

Figure 9. NMR spectra of (a) 1, (b) 2, and (c) 4.

added. The mixture was refluxed for 4 h. The solution was extracted with 100 mL of ethyl ether and 50 mL of nanopure H_2O . The organic layer was washed with 50 mL of H_2O , 100 mL of 1M HCl , 100 mL of NaHCO_3 , and 100 mL of H_2O . It was dried over MgSO_4 . The solvent was removed under vacuum. The reaction yield was 69%. An NMR spectrum of the product, 1, is presented in Figure 9(a).

The second reaction in the synthesis of the first substrate is a hydrobromination of 1, the alkene produced in the previous step. A solution of 1 (5.0 g, 1.8×10^{-2} mol) in CH_2Cl_2 (20 mL) was added dropwise to 33% HBr in acetic acid (9.73 mL, 5.4×10^{-2} mol) at 0°C . The mixture was stirred for 40 min. H_2O (20 mL) were then added, and the organic layer was separated. The organic layer was washed with two 20 mL portions of a saturated NaHCO_3 solution and one 20 mL portion of H_2O . MgSO_4 was used to dry the organic layer, which was then removed under vacuum. The percent yield of 2 was 84% and the NMR spectrum is shown in Figure 9(b). The spectrum shows that two stereoisomers of the product were achieved. A separation of the two products must be performed. The (*S*) conformation of this product, 2, could be used as a possible substrate for the syn elimination; however, this product is not soluble in water. The molecule must be altered slightly to make it more water-soluble. A suggested method of doing this is by substituting the ester group for another more hydrophilic ester as depicted in Figure 8.

The synthesis of second substrate, 6, was also not completed; however, a scheme to prepare this compound is depicted in Figure 8(b). The first reaction was run as follows. Phenylacetic acid (8.7 g, 6.4×10^{-2}) was dissolved in 2-methoxyethanol (96 mL, 1.2 mol). Conc. H_2SO_4 (3.2 mL) were added, followed by sonication for 6 h. H_2O (175 mL) was added. The solution was extracted three times with CH_2Cl_2 , totaling 500 mL. The organic layer was then

washed with two 100 mL portions of 10% NaHCO_3 (aq) and two 100 mL portions of H_2O . The organic layer was dried with MgSO_4 and removed under vacuum to isolate 4. The percent yield of 4 was 80% and the NMR spectrum is presented in Figure 9(c).

Figure 10. Attempted methyldiphenylsilylation reaction of 4 to 5 in the synthesis of the second substrate, 6.

The second reaction in the formation of substrate two has not been performed. A reaction involving methyldiphenylsilylation (Figure 10) was attempted; however, it did not produce the correct product, presumably from the silylation on the carbonyl oxygen atom. The final step should be the same as the second reaction, 1 to 2, in the formation of the first substrate [Figure 8(a)].

Work to Be Completed

The major step in completing this proposal is the synthesis of the substrates. Many other substrates may be utilized in this type of syn elimination given they have the proper hydrophobic/hydrophilic groups as well as a good leaving group. Another phase in the project is the characterization of the sulfonic acid/pentafluorophenyl MCM-41. The XRD, N_2 sorption analysis, and TEM must be completed in order to determine the properties of this material. A solid-state NMR spectrum could also be run.

Following the synthesis of the substrates and the characterization of the sulfonic acid/pentafluorophenyl MCM-41, the reaction (Figure 11) must be tested in order to determine

if it can overcome the 5 kcal/mol energy difference between anti elimination to the E (trans) olefins and the syn elimination to the Z (cis) olefins.

Figure 11. Syn eliminations to the Z (cis) alkenes, 7 and 8, from the two proposed substrates, 3 and 6.

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CHAPTER 4. GENERAL CONCLUSIONS

Research Summary

MCM-41 has emerged as a very valuable tool in many fields, including the described application, catalysis. The MCM-41 pore diameter controls the quantity of reactants that are allowed to diffuse into and out of the pores. The expansive surface area permits more molecules to be present on the surface.

Advances in MCM-41 synthesis have played an enormous role in advancing the utility of the materials. Creating a regular particle shape ensures a better dispersion for catalytic purposes. Monodispersed particle shapes eliminate the complex reaction kinetics imparted by polydispersed MCM-41 materials. Functionalization allows for even greater catalytic value. Introducing an organic functional group gives one the ability to provide catalytic sites for various reactions. The functional group may just be an acid or base, but metal centers can also be complexed inside the mesopores. The addition of another functional group, a secondary group, affords an opportunity to manipulate noncovalent interactions between the mesoporous material and the reactants/substrate. Hydrophobicity is the foremost example of this and has been employed throughout the preceding research.

The mesoporous material discussed in Chapter 2, Cu/PFP MCM-41, is a prime example of a bifunctionalized material that can be utilized as a catalyst. This particular material was used as a catalyst for a 1,2,3-triazole formation using an organic azide and a terminal acetylene. The copper complexed to the ligand on the pore interiors acts as a typical reaction catalyst; however, the pentafluorophenyl groups provide the driving force for the reaction. The pentafluorophenyl groups increase the hydrophobicity of the pores. This is in great contrast to the aqueous solvent the mesoporous material is suspended in. The dissimilarity between the

two environments compels the hydrophobic reactants to diffuse into the pores. This inward diffusion permits the necessary interaction between the reactants and the copper complexes for the reaction to take place. From the experimental results comparing benzene and H_2O , the reactivity difference becomes obvious. The hydrophobicity of the pores allows for significant yields in the aqueous solutions because of the very dissimilar environment between the pores and the solvent; however, the yields are considerably lower in the benzene-containing reactions. The benzene is too similar to the pore interior's pentafluorophenyl groups to encourage the reactants to diffuse into the pores.

The other major effect exhibited in that study was the pore dilution effect. The two types of Cu/PFP MCM-41, created by co-condensing the copper complexes and by grafting the copper onto the surface subsequent to the MCM-41 synthesis, afford very different yields. The grafted Cu/PFP MCM-41 provided 36% less product than did the co-condensed Cu/PFP MCM-41. The ESCA revealed 2.2 times more copper in the grafted Cu/PFP MCM-41 than in the co-condensed material. Since ESCA measures only the surface composition, this additional copper must be located at the pore mouths of the grafted material. The co-condensed Cu/PFP MCM-41, however, has copper distributed randomly along the pore interior. This accounts for a more dilute copper-containing surface, which almost certainly accounts for the greater yields in the co-condensed material. Surface dilution is a well-known phenomenon in other heterogeneous catalytic systems, so this system merely reinforces the model.

The catalytic scheme suggested in Chapter 3 involves making use of a sulfonic acid/pentafluorophenyl MCM-41 as a regioselective, conformational catalyst. The reaction involves a highly disfavored syn elimination to a cis olefin in an acyclic system. The pentafluorophenyl groups act to create the same type of hydrophobic environment as discussed

in Chapter 2. Placed in an aqueous solution of sulfonic acid/PFP MCM-41, the substrate (containing both hydrophobic and hydrophilic groups) should orient itself with the hydrophobic tails inside the mesopores and the hydrophilic tails in the water. Once in this position, the sulfonic acid groups could then catalyze the elimination. The MCM-41, therefore, acts as a regioselective conformational catalyst for the syn elimination. The complete synthesis of the substrates must first be accomplished in order to determine the effectiveness of this proposed reaction scheme.

In conclusion, the hydrophobicity created inside the MCM-41 mesopores can be a valuable tool in selectively catalyzing reactions. The hydrophobic groups essentially produce a gate-keeping effect. They restrict the type of molecules that can enter the mesopores via their electronic properties. The gate-keeping strategy appears to be the best new strategy for selective diffusion, reactions, and catalysis. As this type of research continues, the MCM-41 gatekeepers may find many more applications in chemical and biological fields.

Suggestions for Future Research

In the future, one could extend the catalytic concept even further. This thesis has focused on selective catalysis based on the electronic properties of the reactants and the MCM-41 particles as well as on regioselective, conformational MCM-41 catalysts; however, a selective catalyst that has the ability to control stereoselectivity is the next logical phase. The bifunctionalized MCM-41's gatekeepers should restrict which reactant molecules are capable of diffusing into the mesopores; the use of chiral catalysts should then stereoselectively catalyze the reaction. This kind of regulation would present an extremely powerful catalytic tool. Being able to control both the chemical properties of the reactants and the stereochemical selectivity would be a huge advance in this field.