BASE CATALYTIC PROPERTIES OF ORGANOAMINO-SILICA HYBRIDS PREPARED USING CASHEW NUT SHELL LIQUID COMPONENTS AS TEMPLATES

By

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A Dissertation Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science (Chemistry) of the University of Dar es Salaam

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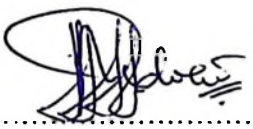
CERTIFICATION

The undersigned certify that he has read and hereby recommend for acceptance by the University of Dar es Salaam a dissertation entitled ***Base Catalytic Properties of Organoamino-silica Hybrids Prepared Using Cashew nut Shell Liquid Components as Templates***, in partial fulfillment of the requirements for the degree of Master of Sciencc (chemistry) of the University of Dar es Salaam.



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Dr. J. E. G. Mdoe

(Supervisor)

11th March 2011

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DECLARATION

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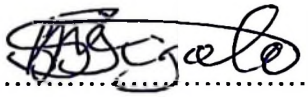
I, **Sijaona Cassian Msigala,** declare that this dissertation is my own original work and that it has not been presented to any other University for a similar or any other degree award.

Signature  .....

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DEDICATION

My lovely wife **Hekima Titus Maketa** for her encouragement, love, care and humble prayers and for a keen handling of our family during my studies and to my lovely daughters **Faith** and **Edith** for being merciful and being patient in my long absence at home.

ABSTRACT

This work was aimed at finding the catalytic efficiency of organoamino-silica hybrids prepared over some components of cashew nut shell liquid (CNSL) as templates. Cardanol and anacardic acid as major components of CNSL, were screened for their efficiency as templates in synthesizing the hybrids. The hybrids were prepared by one-pot co-condensation of three classes of organoaminesilanes and tetraethoxysilane at two different loading ratios, namely 1:4 and 1:9. The results showed that anacardic acid and cardanol formed about 9.2% and 66.3% yields, respectively. Consequently most hybrids were therefore prepared using cardanol. A few hybrids were also prepared using a mixture of cardanol and dodecylamine, the later being a previously established template. The prepared hybrids were characterized by using HCl acid titration technique, Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and Atomic Force Microscopy (AFM). Results indicated that the organic group loading ranged between 0.5 to 2.3 mmol per gram of silica, depending on the loading ratio, type of template and nature of the organoaminesilane. On the other hand, DRIFTS results revealed that the organoaminesilyl groups were successfully incorporated in the silica matrix for each category of the template used. Furthermore, by using AFM the grain size average for cardanol templated hybrids were found to be about 0.25 μm wide and those of the co-templated hybrids were about 0.4 μm wide with irregular shapes. The hybrids were tested for catalytic activity in a model Henry reaction, in particular a reaction between benzaldehyde and excess nitroethane. Results showed that 81% to 98% of benzaldahyde could be converted into product within 3 h showing that the prepared hybrids are suitable catalysts for the model reaction.

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LIST OF ABBREVIATIONS

AFM – Atomic Force Microscopy

BA – Benzaldehyde

CNSL – Cashew nut shell liquid

CTAB - Cetyltrimethylammonium bromide

DCA – Diamino-silica hybrids formed by using cardanol as a template

DCO – Diamino-silica hybrids formed using a co-template

DDO – Diamino-silica hybrids formed by using dodecylamine as a template

DO – *n*- Dodecylamine

DRIFTS- Diffuse Reflectance Infrared Fourier Transform Spectroscopy

FID – Flame Ionization Detector

GC – Gas Chromatography

ID- Dodecane as internal standard

MCA – Monoamino-silica hybrids formed by using cardanol as a template

MCO – Monoamino-silica hybrids formed using a co-template

MDO – Monoamino-silica hybrids formed by using dodecylamine as a template

OASH – Organoamino-silica hybrids

TCA – Triamino-silica hybrids formed by using cardanol as a template

TCO – Triamino-silica hybrids formed using a co-template

TDO – Triamino-silica hybrids formed by using dodecylamine as a template

TEOS – Tetraethoxysilane

CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

1.1 General Introduction

A catalyst is a substance that notably affects the rate of a chemical reaction without itself being consumed or altered chemically. A catalyst can make a reaction go faster and in a more selective manner, because of its ability to speed up some reactions and not others (Lawrence 2005). In most cases, in order for a chemical reaction to occur, energy known as activation energy is required. Without the help of a catalyst the amount of energy needed to spark a particular reaction is high. When the catalyst is present the activation energy is lowered making the reaction happen more efficiently. The catalyst generally works by either changing the structure of a molecule or by bonding to reactant molecules causing them to combine, react and release a product or energy. Therefore, a catalyst enables a chemical process to work more efficiently and often with less waste (Anon 2009).

Catalysts can be either heterogeneous or homogeneous. Homogeneous catalysts are those that are in the same phase as reaction mixtures while heterogeneous catalysts are those that are in different phases to those of reaction mixtures. Essentially, heterogeneous catalysts are solids that act on substrates in liquid or gaseous reaction mixtures.

Heterogeneous catalysts always offer many advantages over their homogeneous counterparts. Such advantages include being environmentally benign owing to non-corrosiveness and having fewer disposal problems. Their reuse is also possible and

separation from liquid products is much easier. Furthermore, they can be designed to give higher activity, selectivity and longer catalyst life hence less waste and possible enhancement of reaction speed under mild conditions (Smith 1992). In addition, one of their attractive features is that many of these heterogeneous catalysts are robust at high temperatures and therefore make available a wide range of operating conditions (Shriver and Alkins 1996).

The field of heterogeneous acid catalysis has received a lot of attention for the past 50 years owing to the fact that the catalysts have wide applications in the petroleum and petrochemical industries. On the other hand, the field of heterogeneous base catalysis has received relatively little attention (Wight 2004). However, there is an upsurge of interest currently in the use of heterogeneous base catalysts for organic synthesis both at laboratory and industrial level. This is due to the increasing social and environmental pressure on industry to substitute traditional homogeneous catalysts by heterogeneous catalysts, which are environmentally friendly (Zhijian 2005).

Heterogeneous catalysts are typically "supported", which means the catalyst is dispersed on a second material that enhances the effectiveness or minimizes their cost. The support may be inert or can participate in the catalytic reactions. For instance, organoaminesilanes which are organic bases can be supported on silica which is a solid, to form organoamine-silica hybrids (Clark 1994). More often the support and the catalyst interact, affecting the catalytic reaction. When a basic group is adsorbed on, dispersed over or intercalated in a solid support, the resulting material becomes a solid base (Clark 1994). However, a support material itself can also be

basic if its surface contains basic hydroxyl groups or oxide ions. If a solid base is able to catalyse a chemical reaction it can be referred to as a solid base catalyst or a heterogeneous basic catalyst.

Organic-silica hybrid nanostructures (*i.e.*, nanoparticles such as hollow spheres, rods, fibers or tubes) are widely applicable for catalysis, adsorption, separation, sensing and medical usage, ecology and nanotechnology (Vinu *et al.* 2006). In catalysis, for instance Mdoe *et al.* (2003 a) synthesized polyamine- silica hybrids that were used effectively as catalysts for epoxidation of enones. On the other hand, Macquarrie *et al.* (1997) found that γ-aminopropyl-silica were effective catalysts for the Knoevenagel condensation of a wide range of carbonyl compounds. Furthermore, Mdoe *et al.* (2003 b) prepared organoamine-silica hybrids on neutral commercial templates, materials that showed good to excellent activities and selectivity in model Michael addition reactions in a range of substrates.

Furthermore, Hilonga (2007) and Hilonga *et al.* (2009) managed to prepare polyamine-silica hybrids using cashew nut shell liquid (CNSL) as a template. The prepared polyamine-silica hybrids over CNSL had desirable properties similar to those prepared over commercial templates. The hybrids were successfully applied in immobilization of invertase enzyme (Kinunda 2009) as well as supporting copper Schiff base catalyst (Hamad 2008). The immobilized invertase showed higher activity than the ones prepared over commercial templates whereas the supported copper Schiff base catalysts were active and reusable in the epoxidation of higher alkenes at room temperature and in oxidation of maleic acid. With the exception of the study on the ability of the CNSL-templated materials to support copper Schiff

base catalyst, their potential as base catalysts has never been demonstrated. In addition, the specific component(s) of the CNSL responsible for the templating process has never been established.

This study therefore seeks to establish the specific components of CNSL that are responsible for templating as well as establishing the base catalytic properties of the resultant organoamino-silica hybrids.

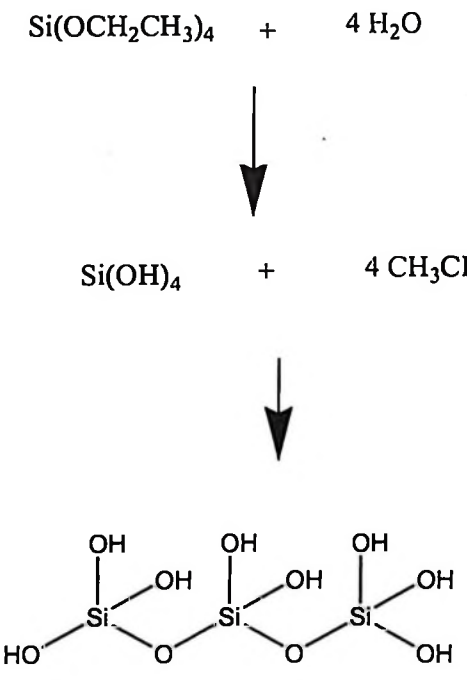
1.2 Literature Review

1.2.1 Silica as a Catalyst Support

A support material is a compound that has a large surface area onto which particles of active phase such as catalyst can become anchored. It has been shown that the type of support material used is a critical factor in the performance of the final product (Clark *et al.* 1992). The effectiveness of solids as supports for catalysts or reagents varies depending on the chemical nature of both the support and the reagent. A match between the support and the reagent has to be achieved by a careful selection based on a thorough knowledge of their physico-chemical properties. Basically there are two main factors to be considered in choosing a material as a support. Firstly, thermal and chemical stability; the material should be thermally and chemically stable during the reaction processes. Secondly, structure of the support material; the active sites have to be well dispersed on its surface and the sites should be easily accessible hence the material must have reasonably high surface area (typically > 100 $m^2 g^{-1}$) (Clark *et al.* 1992).

There is a huge range of materials that can be used as catalyst supports. The chemical nature of the support material ranges from inorganic oxides to organic polymers.

Some of the materials, as reviewed by MacKillop and Young (1979) include celite, silica, alumina, graphite, carbon, montimorillonite K10 clay, Girdler KSF clay, molecular sieves (zeolites) and kieselguhr. Silica is one of the most effective materials that have high thermal and chemical stability hence used widely as a catalyst support. Silica is a term that describes the various polymeric forms of silicon (IV) oxide, SiO_2. Its various forms include hydrated and anhydrous crystalline, microcrystalline and amorphous silica (Vansant *et al.* 1995). Amorphous silica is more interesting for physical and chemical applications than crystalline counterparts as their porosity introduce a large surface area inside the silica particles. Silica is obtained through hydrolytic condensation of its precursor, typically a tetraalkylorthosilicate (scheme 1.1). The silica surface consists of two types of functional groups namely siloxane (Si-O-Si) and silanol (Si-OH).



Scheme1.1: Hydrolytic condensation of silica precursor to form silica

1.2.2 Surface Chemical Modification of Silica

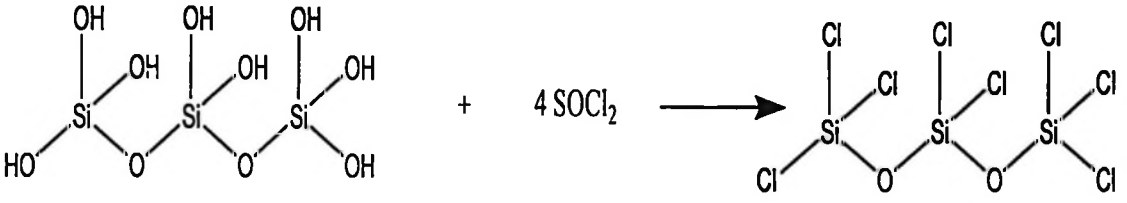
Modification of a silica surface can occur via the reaction of a particular molecule with either the siloxane (nucleophilic substitution at Si) or silanol (direct reaction with the hydoxyl group) functional groups. It is generally accepted that the reaction with silanol functional group constitute the main modification path way (Price *et al.* 2000). The modification of silica materials can either be done via physical treatment (thermal or hydrothermal) that changes a ratio of silanol and siloxane concentration of the silica surface or by chemical treatment that changes the chemical characteristic of the silica surface. A range of possible methodologies exist for attaching organic functionality to the surface of a support. Some methods are pure electrostatic while others are covalent attachment to silica surface. Several routes exist for the covalent attachment of organic functional to the surface of silica; these include grafting of functional organosilanes, surface chlorination and subsequent displacement and direct sol-gel preparation of organomodified silica (Clark and Macquarrie 1998).

1.2.2.1 Grafting Technique

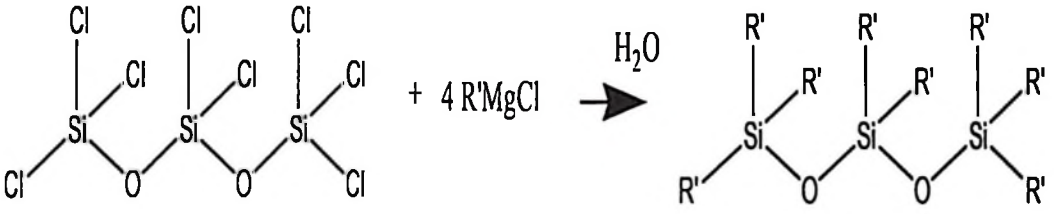
In grafting the silica is reacted with an appropriate organosilane in a suitable solvent, typically toluene at reflux, although ethanol at room temperature is also effective in some cases (Clark and Macquarrie 1998). Essentially, organosilane reacts with surface silanol groups to form a layer of covalently coupled surface functional groups. For example, aminoalkoxysilanes have two functionalities that are capable of reacting with the surface; the amine group is capable of forming a hydrogen bond to the surface of silica or ionic bond (after abstraction of proton from silanol) or formation of siloxane bond after hydrolysis of the alkoxy group. The advantages of

grafting method are good preservation of the mesostructure after post-modification as well as versatility of the method. However, grafting has several shortcomings. Firstly, attachment of a layer of the functional groups on the pore surface results in a reduced pore size and pore volume, which is undesirable in many cases. Secondly, there is little control over loading as well as lack of stability (Vansant *et al.*1995). Thirdly, a limited amount of the functional groups can be grafted because of the limited density of the reactive surface silanol. Finally, grafted functional groups are sometimes ineffective due to partial cross-linking of the functional groups (Burkett *et al.* 1996).

The technique of surface chlorination and subsequent displacement is another type of surface chemical modification of silica. Although it has an advantage of forming a direct Si-C bond at surface and precludes the formation of surface bound oligomers and variable modes of attachment, is much less used. Groups are robustly bound and are typically less prone to leaching than those attached via direct grafting (Clark and Macquarrie 1998). This technique involves a reaction of the silica with the chlorinating agent. The reaction converts surface hydroxyls to Si-Cl bonds (Scheme 1.2). Then reacts with a solution of Grignard reagent or an organo lithium species leading to displacement of the Cl and thus formation of a Si-C surface bond (scheme1.3). The main drawback in this technique is that the requirement for strongly nucleophilic reagents limits the functionality which can be successfully attached (Clark and Macquarrie 1998).



Scheme 1.2: Surface chlorination of silica



Scheme 1.3: Reaction of chlorinated silica with Grignard reagent

1.2.2.2 One-Pot Co-condensation Technique

Surface chemical modification by a sol-gel technique is essentially the co-polymerisation of a silica precursor (typically a tetraalkylorthosilicate) with an organosilicate precursor (typically a trialkoxyorganosilane) (Macquarrie 1996). The polymerization occurs in the presence of a templating agent through the hydrolysis condensation reaction (Fig. 1.1).

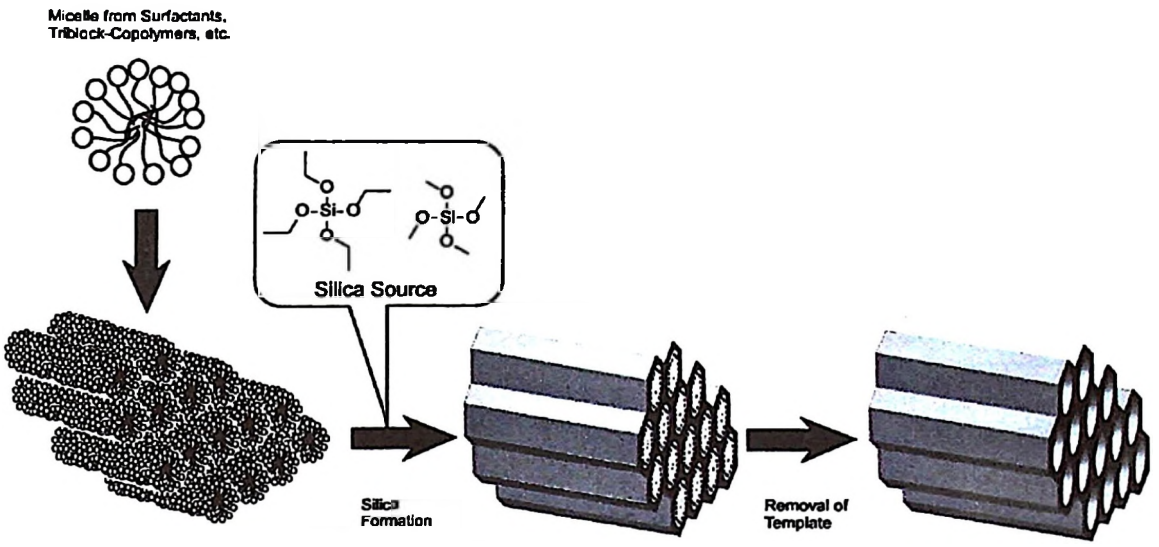


Fig. 1.1: General concept for synthesis of mesoporous silica from micelle template (Vinu *et al.* 2006).

The sol-gel technique is believed to be a good alternative to grafting owing to its advantages such as incorporation of the organic group during the condensation of the silica framework. Thus, it is likely to be fully integrated into the final material (Burkett *et al.* 1996). This technique involves a simple procedure compared to the grafting technique and complete recovery of the templates using one of the reaction solvents makes the process simple, mild and atom efficient. Other advantages of the sol-gel technique are that the materials produced are thermally stable and the loading can be high (Macquarrie 1999).For instance, materials with a loading of 3.0 mmol g^{-1} have been prepared by this technique, a loading much higher than those obtained by grafting (Clark and Macquarrie 1998). The surface areas of the material obtained through sol-gel technique are also very high ranging from 700 to *ca.* 1600 $m^2 g^{-1}$. Typically silica supported reagents have surface area of *ca.* 75- 300 $m^2 g^{-1}$. However, the main disadvantage of the sol-gel based materials is the potential sensitivity of the

sol-gel process to the functional group R (Clark 2001). This can be a problem if relatively well ordered materials with narrow (meso) pore size distribution are required.

1.2.3 Surfactant as a Source of Template

Surfactants are materials which consist of molecules containing both polar and non-polar parts. Surfactants are classified as anionic, cationic, non-ionic or ampholytic according to the charge carried by the surface-active part of the molecules (Shaw 1980). At critical micelle concentration, micelles formation is appreciable, that is formation of aggregates of surfactants' molecules of which the polar part points toward the aqueous medium and the non-polar points away from the aqueous medium. Under certain conditions, the micelle can adopt a spherical shape, a rod-like shape or a cylindrical shape. However, the most common favourable form is the spherical shape owing to the lower energy, hence the most stable form. Micelles are particularly the templates for formation of silica.

1.2.3.1 Template-directed Synthesis and the Role of a Template

A template-directed approach to preparing nanomaterials has been pioneered by Martin and his co-workers since early 1990s (Bae *et al.* 2008). It is generally accepted that template-directed synthesis provides a simple high throughput and cost effective procedure (Xia *et al.* 2003). It provides a straightforward morphology control, allows for scale up of the synthesis and is used for a broad spectrum of composition. After the reaction has taken place the template may remain in place, be forcibly removed or may be automatically decomplexed.

Various researchers have successfully employed template-directed approach in synthesis of mesoporous-silica hybrids. For example, Macquarrie *et al.* (1999) prepared organically modified silicates with tightly controlled porosity by using dodecylamine as a template, On the other hand, Kruk *et al.* (2002) synthesized ordered mesoporous silicas with high loading of organic groups using cetyltrimethylammonium surfactant as a template. Furthermore, Mdoe (2002) prepared polyamine-silica hybrids, an efficient catalyst for epoxidation of unsaturated olefins using dodecylamine as a template.

A template can either be an organic species particularly a surfactant, or an alkali or metal ion, and so-called mineralizing agent (Derouane 2006). A template can serve different purposes. For instance, formation of nanomaterials with uniform shapes and sizes in a precisely controlled fashion. In this particular case it serves as a scaffold within which the material acquires morphology complementary to that of the template (Xia *et al.* 2003). On the other hand, a template can provide instructions for the formation of a single product from a substrate or substrates which otherwise have the potential to assemble and react in a variety of ways (Anderson e*t al.* 1993). Thus, changing the template should result in a different substrate assembly and consequently a different product.

Furthermore, the pore size of the resulting mesoporous material can be controlled by the choice of a template (Derouane 2006). In most studies, charged (cationic and anionic) and neutral surfactants have been employed as templates to direct the mesophase formation based on the electrostatic and hydrogen bonding interactions, respectively. The charged templates normally produce materials with the most

extensive long-range order and possibly the tightest pore size distribution whereas non-charged materials display lower long-range order and slightly wider pore size distributions (Pinnavaia *et al.* 1995).

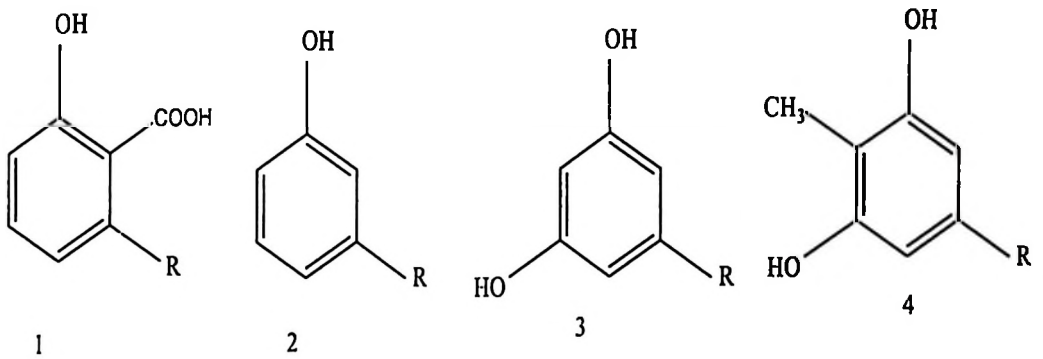
1.2.3.2 Co-templating Technique

Co-templating is a technique of using a mixture of templates in the synthesis of materials. A mixture of templates influences differently the pore size and pore size distribution of the mesoporous material prepared compared to when the templates are used separately. For instance, Yi-Qi Yeh *et al.* (2006) successfully prepared a novel morphology of the mesoporous silica hollow spheres over ternary-surfactant mixtures as a template and a highly dilute sodium silicate solution as silica source under ambient conditions. The mesoporous material had large pore sizes, high adsorption capacity and different nanochannels. On the other hand, Liu *et al.* 2010 synthesized structurally stable MCM-48 mesoporous silica using a mixture of cationic surfactants namely cetyltrimethylammonium (CTAB) bromide and nonionic poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer surfactant as a co-template. The MCM-48 obtained via mixed surfactants showed higher adsorption capacity compared with the one obtained using a single cataionic CTAB template.

1.2.4 Cashew Nut Shell Liquid (CNSL)

Cashew (*Anacarduim occidentale L.*) nut shell liquid (CNSL) is a unique natural source for unsaturated long-chain phenols, obtained during the processing of cashew nuts (Kumar *et al.* 2002). In Tanzania CNSL is a major industrial by-product of the cashew nut processing plants. On the basis of the mode of CNSL extraction from

cashew nut shells, CNSL can be classified into two types; solvent extracted and technical CNSL which is obtained by roasting the cashew nut shells. Solvent-extracted CNSL contains anacardic acid (**1**) (60-65%), cardanol (**2**) (10%), cardol (**3**) (15-20%), and traces of methyl-cardol (**4**). On the other hand, technical CNSL contains mainly cardanol (60-65%), cardol (15-20%), polymeric material (10%) and traces of methyl-cardol (Kumar *et al.* 2002). The heat supplied during thermal extraction causes decarboxylation of the anacardic acid to form cardanol. As a result the major components of technical CNSL are cardanol and cardol. The CNSL components have saturated and unsaturated hydrocarbons with fifteen carbons side chains (R). Qualitative analysis of R has been carried out and established that cardanol and cardol have saturated and unsaturated (*i.e.*, monoene, diene and triene) alkyl side chain (scheme 1.4).



$R = C_{15}H_{31-n}$ n = 0, 2, 4, or 6

Scheme 1.4: Structures of the major phenolic constitutes of CNSL (Tyman 1975)

Hilonga (2007) and Hilonga *et al.* 2009 successfully synthesized polyamine-silica hybrids using technical cashew nut shell liquid as a template. The hybrids had desirable properties similar to those prepared over commercial template. These hybrids were successfully used by Kinunda (2009) to immobilize invertase enzyme as explained earlier. The immobilized invertase showed higher activity than the ones prepared over commercial template. Likewise, Hamad (2008) used the same hybrids for supporting copper (II) Schiff- base catalysts, materials that were active and reusable in the epoxidation of higher alkenes as well as in oxidation of maleic acid.

1.2.5 Characterization of Heterogeneous Catalysts

Various techniques are available for characterization of heterogeneous catalysts. The techniques are either based on the physical structure like surface area, pore volume and pore size or on the chemical nature such as the amount and structure of the active species. The techniques include nitrogen physisorption studies, scanning electron microscopy, atomic force microscopy, diffuse reflectance infrared fourier transform spectroscopy and acid titration.

1.2.5.1 Acid Titration

Acid titration gives information about the amount of surface bound basic species, i.e., loading. A silane reagent may attach to a support material by one, two or three sites. In that case the amount of basic functional group for example amino group in the sample is equivalent to the amount of HCl consumed during the titration (Mdoe 2000).

1.2.5.2 Diffuse Reflectance Infrared Fourier Transform Spectroscopy Studies

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) technique is widely used in the studies of supported reagents and catalysts. It provides specific information about chemical bonding and molecular structures. For instance, Hamad (2008) used it to confirm the coordination of azomethine nitrogen with copper of a supported copper (II) Schiff base catalyst. Mdoe (2002) and Hilonga *et al.* 2009 applied the DRIFTS technique to verify the incorporation of organic N-H groups onto silica for the polyamine-silica hybrids.

1.2.5.3 Atomic Force Microscopy (AFM)

Macroscopic features such as grain size, texture, and porosity are important for determining mechanical strength and material performance (Hunks and Ozin 2005). Therefore, several researchers have used AFM to determine surface characteristics of materials such as grain size and texture. For instance, Hilonga (2007) and Hilonga *et al.* 2009 used this technique to determine grain size and morphology of polyamine-silica hybrids prepared using CNSL as a template. Also Kinunda (2009) successfully used AFM to determine the roughness of the Micelle Templated Silica Material (MTS). In addition, Hamad (2008) used AFM to determine the grain size and morphology of copper (II) Schiff base catalysts.

1.2.6 Measurement of Catalytic Efficiency

The suitability of a catalyst depends mainly on its activity, selectivity and stability in the reaction of interest (Hagen 2006). The higher the catalysts' activity the more suitable it becomes. However, its suitability is more superior if it has both higher selectivity and higher stability both chemically and mechanically.

1.2.6.1 The Catalyst Activity

Catalytic activity is a measure of how fast one or more reactions proceed in the presence of a catalyst (Hagen 2006). The absolute measure for catalytic activity is the reaction rate.

Catalytic activity can be determined by kinetic techniques. In a formal kinetic treatment, it is appropriate to measure reaction rates in the temperature and concentration ranges that will be present in the reactor. The kinetic activities are derived from the fundamental rate laws. For example, eq. 1.1 is rate for a simple irrervisible reaction: R → P,

$$\frac{dr}{d\tau} = k[R]^* \quad \text{.....Eq. 1.1}$$

Where k is a rate constant and $[R]^*$ is a concentration term that can exhibit a first or higher order depending on the adsorption equilibria, $d\tau$ denotes the time consumed and dr denote the change of the amount of a reactant.

The reaction rate r is calculated as the rate of change of the amount of substance n_A of reactant A with time relative to the reaction volume or the mass of catalyst (eq. 1.2)

$$r = \frac{\text{converted amount of substance of a reactant}}{\text{volume or catalyst mass} \cdot \text{time}} \quad ; \text{mol} \cdot L^{-1} \quad \text{Eq. 1.2}$$

Another measure of catalyst activity is the turnover number (TON), which originates from the field of enzymatic catalysis. The turnover number is defined as the product of turnover frequency with the lifetime of the catalyst i.e. TON = TOF * lifetime of the catalyst (Hagen 2006). Turnover frequency (TOF) means number of molecules produced per one active center per second (eq. 1.3) (Hagen 2006).

$$TOF = \frac{nR\ in - nR\ out}{\tau \cdot n_{cat}} \quad [s^{-1}] \qquad \text{Eq. 1.3}$$

Where $n_{cat.}$ denotes number of active centers in a catalyst, *nR, in* denotes number of moles of reactant before reaction, *nR, out* denotes number of moles of reactant after reaction has taken place and τ denotes time consumed.

In the case of homogeneous catalysis, in which well defined catalyst molecules are generally present in solution, the TON can be directly determined. For heterogeneous catalysts, this is generally difficult because the activity depends on the size of the catalyst surface which unfortunately does not have a uniform structure. For example the activity of a supported metal catalyst is due to active metal atoms dispersed over the surface. The number of the active centers per unit mass or volume of catalyst can be determined indirectly by means of chemisorption experiments, but such experiments require great care and the results are often not applicable to process conditions.

In practice, readily determined measures of the activity are often sufficient. The following activity measures can be used; conversion under constant reaction

conditions, space velocity for a given constant conversion, space-time yield and temperature required for a given conversion (Hagen 2006).

In order to collect rate data relevant to a given catalyst and reaction, a reactor type and its operating conditions must be selected. Moreover, an analytical technique capable of collecting and analyzing reactants in the inlet reactor and products in the outlet reactor should be designed (Ciambelli *et al.* 2003). The commonly employed techniques in rate measurement are; gas chromatography, high performance liquid chromatography, mass spectrometry and flame ionization.

Through using a selected analytical technique, catalytic activity can be computed using a more convenient formula and can be expressed in terms of either percentage conversion or percentage yield or in terms of turnover number. Various researchers use percentage conversion or percentage yield of product to express catalytic activity. For instance, Mdoe (2002) used percentage conversion of reactant to express catalytic activity of polyamine-silica hybrids on epoxidation of electron deficient olefins. Likewise Anan *et al.* (2008) used percentage conversion of reactant for catalytic activity of aminopropyl mesoporous material on Henry reaction. Furthermore, Krishna *et al.* (2010) expressed catalytic activity of secondary amine-functionalized hybrids in terms of percentage yield of product. Some researchers use turnover number to express catalytic activity. For instance, Xie *et al.* (2009) used turnover number to express catalytic activity of organoamine mesoporous silica hybrids on aldol condensation. This work adopted percentage conversion of limiting reactant to express the catalytic activity of the organoamino-silica hybrids, in which the reaction was easily monitored using gas chromatography.

1.2.6.2 The Catalyst Selectivity

The selectivity of a reaction is the percentage of the starting material that is converted to the desired product. It is expressed by a ratio of the amount of desired product to the reacted quantity of a reaction partner and therefore, gives information about the course of the reaction. The selectivity can be calculated using the eq. 1.4 (Hagen 2006).

$$S_{P_i} = \frac{\cdot}{V_r} \frac{n_{P_i,out}}{nR,in - nR,out} \cdot 100\,[\%] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots Eq.1.4$$

Where S_{Pi} denotes the selectivity of a reaction, $n_{Pi,\,out}$ denotes the number of moles of desired product P_i , V_l denotes the volume of reaction mixture, nR,in denotes number of moles of reactants before reaction start and nR, out denotes number of moles of reactant after reaction has taken place in a given time.

1.2.6.3 The Catalyst Stability

The chemical, thermal and mechanical stability of a catalyst determines its lifetime in a chemical reaction. The catalyst reusability expresses its stability. If a catalyst is reused and maintains its catalytic activity and selectivity, then it is very stable. A catalyst may be deactivated over time and the general causes of this include poisoning, fouling or sintering. Poisoning is the process of catalyst deactivation due to impurities introduced in the feed stream. As a result the catalyst activity or selectivity is reduced. Whereas, fouling is a physical blocking of the active sites of the catalyst by a solid material, sintering is the use of elevated temperatures resulting in reduced surface area of the active component.

1.2.7 Overview of Reactions Catalysed by Base Catalysts

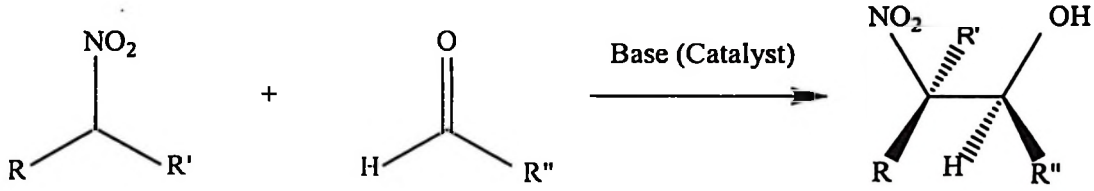
Reactions that are catalysed by bases are numerous. In such reactions reactants act as acids toward catalysts which act as bases. Some well documented organic reactions catalysed by solid bases are Henry reaction, Michael reaction, epoxidation of enone, Knoevenagel condensation reaction, and aldol condensation. The base catalysed condensation and addition reactions are some of the important reaction steps for building large and complex molecules. The molecules characterize many of the fine chemicals and pharmaceutical products (Zhang *et al.* 2004).

1.2.7.1 Henry Reaction

Henry reaction is a base-catalysed carbon-carbon forming reaction between nitroalkanes and aldehydes or ketones (scheme 1.5). It is similar to aldol addition and is also referred to as the nitro aldol reaction. The most commonly applied protocols to perform the Henry reactions require the use of base catalysts under both homogeneous and heterogeneous conditions (Ono 2001). If acidic protons are available *i.e.*, when R = H the products tend to eliminate water to give nitroalkenes (scheme 1.5). Therefore, only small amounts of a base should be used if isolation of the β-hydroxyl nitro-compounds is desired. Wang and Shantz (2010) found that high selectivity to the nitroalcohol product was achieved by introducing secondary and tertiary amino groups on MCM-41 surface while nitroalkene was dominant product for primary amines. Likewise, Anan *et al.* (2008) controlled synthesis of the Henry reaction products; nitroalcohol versus nitrostyrene by a simple change of amino- groups of amino-functionalized nanoporous catalyst. In such case the primary amine gave nitrostyrene product while the secondary and tertiary amines produced

nitroalcohol. In addition Krishna *et al.* (2010) reported on the substituent and catalyst dependent selectivity to aldol or nitrostyrene products. They found that secondary amine-functionalized catalysts were the most efficient and selective, followed by tertiary amine, but primary amine-functionalized gave exclusively the nitrostyrene product regardless of the identity of the substituent groups on the aromatic aldehyde substrate.

The Henry reaction has several applications in pharmaceutical industries, synthesis of natural products, polyamine alcohols and polyhydroxylated amides (Zhou *et al.* 2003). The reaction is catalysed by both strong and mild bases.

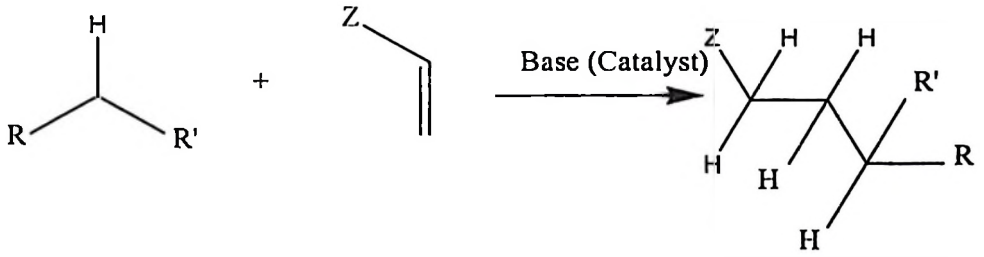


Scheme 1.5: General scheme for Henry reaction

1.2.7.2 Michael Reactions

A Michael reaction is a nucleophilic addition of carbanion or another nucleophile to α,β-unsaturated carbonyl compound (scheme 1.6). This reaction involves a nucleophilic species (Michael donor) and an unsaturated acceptor (Michael acceptor) of the general form –C=C-Z where Z= CHO, COR, COOR, CN, NO_2 etc. This is one of the most important carbon-carbon bond forming reactions in synthetic Chemistry. It is catalysed by mild bases such as primary, secondary and tertiary amines. Mdoe *et al.* (2003b) prepared dimethylaminopropyl-silica hybrids which were effective

catalysts for Michael addition using a range of substrates. On the other hand, Motokura *et al.* (2009) deduced that catalytic activity of tertiary alkylamines for Michael reactions increased dramatically by the immobilization on silica-alumina whereas a homogeneous tertiary amine scarcely promoted the reaction.

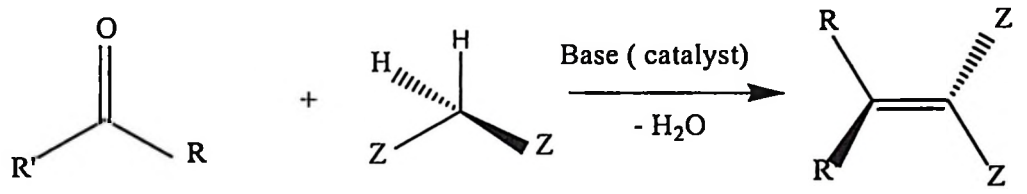


Scheme1.6: General scheme for Michael addition reaction

1.2.7.3 Knoevenagel Condensation Reaction

Knoevenagel condensation is a nucleophilic addition of active hydrogen compound to a carbonyl group followed by a dehydration reaction, in which a molecule of water is eliminated, hence condensation (Scheme 1.7). The product is often α, β-conjugated enone. This reaction is commonly catalysed by weakly basic supported amines. γ-Aminopropylsilica has been found to be effective catalyst for this reaction for a wide range of carbonyl compounds (Macqurrie *et al.* 1997). In addition, Zhang *et al.* (2004) found that new basic zeolite catalysts obtained by grafting amino groups onto NaX and CsNaX, exhibited excellent catalytic activities for the Knoevenagel condensation, particularly a reaction between benzaldehyde and ethylcyanoacetate. Furthermore, Xin *et al.* (2007) reported that cyclic guanidium lactate ionic liquid catalysed Knoevenagel condensation of aromatic aldehydes with active methylene

compounds at room temperature. The yield in that reaction was over 90% within just 1 to 7 minutes. Moreover, Shang *et al.* (2010) demonstrated that bifunctional mesoporous MCM-41 silica materials containing amine and sulfonic acid groups displayed excellent catalytic activity to Knoevenagel condensation reaction.

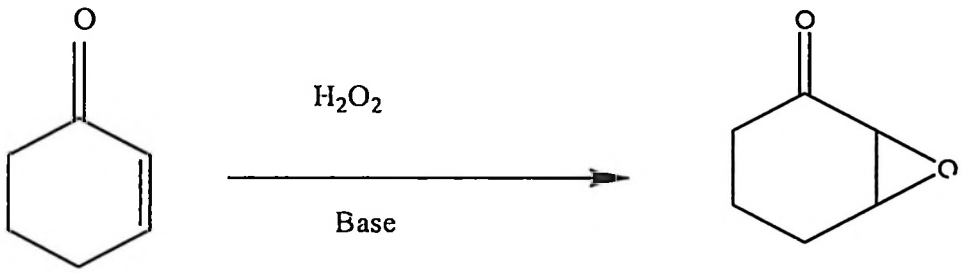


Scheme 1.7: General scheme for Knoevenagel condensation reaction

1.2.7.4 Epoxidation of Electron Deficient Olefins

Epoxidation of olefins is a chemical reaction in which an oxygen atom is joined to an olefinically unsaturated molecule to form cyclic, three-membered ether (scheme 1.8). The products of epoxidation are known as oxirane compounds or epoxides. Epoxides are highly useful intermediates for the manufacture of a range of important commercial products. Olefins epoxidation is one of the main routes which lead to the production of epoxides on both a laboratory and industrial scale (Sienel *et al.* 1999). This reaction can be catalysed by either chiral ligand-metal peroxide system or polyamino or organocatalyst (Diez *et al.* 2008). For instance, epoxidation of electron-deficient olefins with hydrogen peroxide can be catalysed by Mn in cyclic triamine ligand and oxalate as co-catalyst (De Vos *et al.* 1998). In addition, chiral amines have recently been used as organocatalyst for asymmetric epoxidation of α,β-unsaturated aldehyde and ketone (Diez *et al.* 2008).

Furthermore, Mdoe *et al.* (2003a) found that polyamine-silica hybrids showed excellent selectivity and moderate to good activity in the epoxidation of electron deficient olefins.



Scheme 1.8: Epoxidation of cyclohex-2-ene-1-one under basic conditions

1.3 The Present work

CNSL has been proved to be a suitable template for the synthesis of organoamino-silica hybrids (Hilonga *et al.* 2009). Unfortunately it is not known which particular component of CNSL is responsible for the templating. In addition, the catalytic efficiency of the hybrids prepared over CNSL has never been established. Therefore, in this study the templating efficiency of the major components of CNSL, namely anarcardic acid and cardanol and catalytic efficiency of the resultant hybrids are assessed. Hence, organoamino-silica hybrids have been synthesized using the named CNSL components as well as a mixture of cardanol and dodecylamine as templates. Dodecylamine as a template has also been used for comparison purposes. A thorough study on the suitability of the hybrids as base catalysts has also been made by using a model Henry reaction.

The general objective of this study is therefore to assess the suitability of organoamino-silica hybrids templated using CNSL components as base catalysts.

The specific objectives are;

(i) To assess the suitability of CNSL components in templating organoamino-silica hybrids

(ii) To determine the catalytic efficiency of organoamino-silica hybrids prepared over CNSL components as templates in a model base catalysed reaction.

Generally, the dissertation is divided into five chapters; chapter one is for general introduction and literature review, chapter two explains the experimental work whereas chapter three and four gives information on the results and discussion respectively. The basic findings of the research and the recommendations are summarized in chapter five.

CHAPTER TWO

EXPERIMENTAL

2.1 Materials and Reagents

Cashew nut shells were collected from Mtwara cashew nut processing factory, in Tanzania. The shells were processed in Chemistry Department at the University of Dar-es-Salaam to obtain Cashew Nut Shell liquid (CNSL). The list of chemicals used were as follows, petroleum ether and dichloromethane (99.8%) were purchased from Carlo Erba Reagent-SA, 3-[2(2-amino)ethylamino]propyltrimethoxysilane (assay 97%), 3-aminopropyltrimethoxysilane (assay 97%), N-(3-(trimethoxysily)propyl)-ethylene diamine (assay 97%) and nitroethane were purchased from Aldrich-Chemie GmbH & Co KG-D-89555-Steinheim-Germany. Other chemicals including tetraethoxysilane (assay 98%), *n*-dodecane, *n*-dodecylamine (assay 98%), calcium hydroxide, benzaldehyde, methanol and ethanol were purchased from Fluka Chemie GmbH CH-4971 Buchs-Germany. All chemicals were used as purchased without further purification.

2.2 Extraction of CNSL

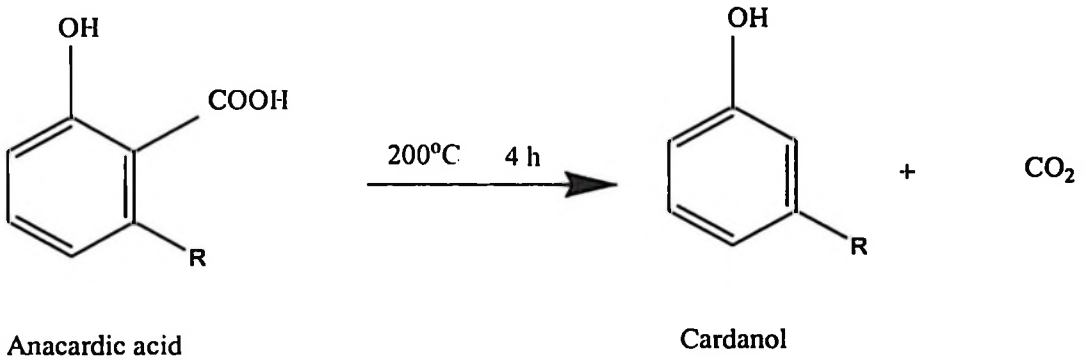
The CNSL was extracted by soaking cashew nut shells in petroleum ether for three days. A dark brownish oil was obtained. The oil was then poured to a round bottomed flask then fitted to a rotavapour machine (model Buchi R-205) in order to concentrate the oil at about 40°C of water bath.

2.3 Isolation of Anacardic Acid from CNSL

The isolation of anacardic acid from CNSL was done using a procedure reported by Paramashivappa *et al.* (2001). Anacardic acid was selectively isolated as calcium anacardate by dissolving the solvent extracted CNSL in 5% aqueous methanol (600 mL) followed by addition of calcium hydroxide (50 g) in portions under stirring. After a complete addition of calcium hydroxide the reaction was left at room temperature for 24 hours. Thereafter, calcium anacardate precipitates were filtered and washed thoroughly with methanol (200 mL). The filtrate collected contained other phenolic constituents but no anacardic acid. The calcium anacardate cake was then suspended in distilled water (440 mL) followed by addition of 60 mL of 11 M HCl. The mixture was stirred for 1 hour. The resultant solution was then extracted with ethyl acetate (2 x 150 mL). The combined organic layer was washed with distilled water (2 x 100 mL), dried over anhydrous sodium sulphate and concentrated under reduced pressure using a rotavapour machine to yield anacardic acid.

2.4 Decarboxylation of Anacardic Acid

Anacardic acid can decarboxylate on heating to form cardanol. Essentially the decarboxylation of anacardic acid occurs when heated between 170°C and 200°C. In this case the decarboxylation was achieved by heating anacardic acid in a furnace model Nabertherm Controller P 320, at a maximum temperature of 200°C for 4 hours (scheme 2.1).



Anacardic acid Cardanol

Scheme 2.1: Decarboxylation of anacardic acid

2.5 Synthesis of Organoamino-silica Hybrids through a Sol-gel Method

Synthesis of organoamine-silica hybrids was carried through a one-pot co-condensation technique *i.e.*, direct sol-gel preparation owing to its advantages compared to other techniques.

2.5.1 Experimental Procedures

The synthesis of the organoamine-silica hybrids (OASH) was done following a procedure by Hilonga *et al.* 2009. The organoamine-silane and TEOS were added at molar ratio of 1:4 and 1:9. A typical preparation of a OASH was as follows: to a stirred solution of cardanol (2.5 g) in aqueous ethanol (46 ml of absolute ethanol and 53 ml of distilled water) at ambient conditions of temperature and pressure was added separately, but simultaneously and rapidly, TEOS (18.8 g, 0.09 mol) and 3-aminopropyltrimethoxysilane (2.2 g, 0.01 mol). The solution was stirred for 18 hours. After 18 hours, the thick solution was vacuum filtered, and the brownish solid

washed with ethanol. The template was removed by using a Soxhlet apparatus for 10 hours using ethanol as a solvent. The final solid obtained after the template removal was dried in an oven at 100°C for 8 hours and then stored in desiccators ready for characterization and application as base catalysts. The same procedure was also used for different organoaminesilanes (namely, diamine and triamine).

Other organoamino-silica hybrids were prepared through co-templating (*i.e.*, using a mixture of cardanol and dodecylamine). In this case, 2.5 g of dodecylamine was mixed with 1.5 g of cardanol. Other hybrid materials were also prepared using 5.08 g of dodecylamine as a template for comparison purposes.

An unmodified silica was also prepared using TEOS alone as a control sample to elucidate the role of silica as a support for catalyst. The synthesis was carried out through the one-pot co-condensation technique using dodecylamine as a template (Macquarrie *et al.* 1999). The template was extracted for 30 hours using ethanol as a solvent to ensure complete removal of the template.

2.6 Characterization of the Prepared Materials

Characterization of the materials was achieved through acid titration, Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT) and Atomic Force Microscopy (AFM).

2.6.1 Determination of Loading

Determination of the amount of the surface bound species (*i.e.*, loading) was done by HCl acid titration. The amount of surface bound species is equivalent to the amount of HCl acid consumed.

2.6.1.1 Experimental Procedures

A 0.1 g amount of an OASH sample was stirred for varying amounts of time in contact with dilute (50 cm^3, 0.012 M) solution of HCl acid. Then it was filtered and the acid solution was back-titrated with 0.028 M NaOH. Titrations after 1, 2 and 24 h contact times all led to the same loadings of the basic sites in each case.

2.6.2 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

Diffusion Reflectance Infrared Fourier Transform Spectroscopy was used to identify the functional groups and their dispersion in the organoamino-silica hybrids that were synthesized. The experimental work was carried out using a Perkin-Elmer 2000 FTIR spectrophotometer at the Physics Department, University of Dar es Salaam.

The advantages of DRIFTS technique are; sampling is fast and easy because little or no sample preparation is required. It is a perfect tool for organic analysis since it has extensive libraries of reference spectra available to match with unknowns. In addition, it is a non-destructive technique (Reche 2004). Furthermore, it is a versatile technique, thus widely used in nanotechnology because of its ability to assess molecular arrangement in small domains (Doucourse 2000). However, the technique has some limitations, as it does not provide elemental information. Neither has it had exhaustive library for inorganic compounds. It also operates mainly in transparent or reflective mode.

2.6.2.1 The Principles of DRIFTS

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is a technique which analyzes the interaction of scattered infrared radiation (IR) with the

sample (Fig. 2.1). The technique measures the frequencies at which the sample absorbs IR as well as the intensities of these absorptions. Determining these frequencies allows identification of the sample's chemical makeup, since chemical functional groups are known to absorb radiations at specific frequencies. The intensity of the absorption is related to the concentration of the component. Intensity and frequencies of sample absorption are depicted in a two- dimensional plot called a spectrum (Doucoure 2000). For a pure compound, this plot is like a molecular fingerprint because of its unique characteristics. Like a fingerprint no two unique molecular structures produce the same infrared spectrum (Nicolet 2001). Intensity is generally reported in terms of absorbance *i.e.*, light absorbed by a sample or percent transmittance (light that passes through it). Frequency is usually reported in terms of wavenumbers or in length unit.

The DRIFTS technique provides specific information about chemical bonding and molecular structures. Hence, it is useful for analyzing organic materials and certain inorganic materials. It is particularly used for measurement of fine particles and powders, as well as rough surface for instance the interaction of a surfactant with the inner particle, the adsorption of molecules on the particle surface *e.t.c* (NUANCE 2009).

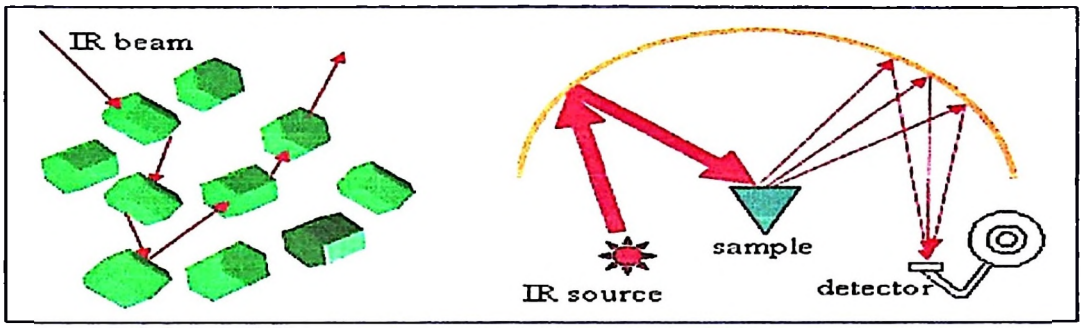


Fig. 2.1: Schematic diagram of DRIFTS technique (NUANCE 2009)

2.6.2.2 Experimental Procedures

Before the analysis, the samples were first dried overnight in a vacuum oven at 100°C. Spectra were collected in the mid-IR region (4000 cm^{-1} to 600 cm^{-1}) at 4 cm^{-1} resolution (2 cm^{-1} step) with 8 scans. The spectra of the samples were obtained by subtracting the KBr background spectrum from the sample spectra. In all the DRIFT analysis, samples were prepared by diluting the sample to about 10% in KBr followed by grinding with a pestle and mortar.

2.6.3 Atomic Force Microscopy (AFM)

Atomic force microscopy was used to determine the grain size and morphology of the organoamino-silica hybrids that were synthesized. The experimental work was carried out using AFM Version 3.0 Digital Instruments, Veeco Metrology Group at the Department of Physics, University of Dar es Salaam.

Atomic Force Microscopy has several advantages over conversional microscopy. Some of the advantages are higher lateral resolution, it allows imaging and measurement of features in the order of a few nanometers, the vertical resolution is less than 1 Å, the image of AFM can be computer-rendered with tilt or rotational

angle and it provides accurate measurements in all three dimensions on features of interest. It is also a non-destructive technique. Furthermore, AFM can characterize several material properties such as surface topography, adhesion, viscoelasticity, hardness, friction and other properties revealed with nanometer resolution (Serry 2004). Nevertheless, AFM has some limitations. The physical probe used in AFM imaging is not ideally sharp; consequently, an image does not reflect the true sample topography but rather represents the interaction of the probe with the sample.

2.6.3.1 The Principles of AFM

Atomic Force Microscopy provides a three dimensional profile of the surface on a nanoscale by measuring forces between a sharp probe and a surface at a very short distance (0.2-10 nm) probe-sample separation (Wilson and Bullen 2006). The probe is supported on a flexible cantilever. The probe tip gently touches the surface and the small force between the probe and surface is recorded. The AFM has got a contact, non-contact and a tapping mode of operation. The tapping mode is the one used in this work. It is a method of achieving high resolution without inducing destructive frictional forces both in air and fluid. The very soft and fragile samples can be imaged successfully. In tapping mode imaging is implemented in ambient air by oscillating the cantilever assembly at or near the cantilevers resonant frequency using a piezoelectric crystal. The piezo motion causes the cantilever to oscillate with high amplitude when the tip is not in contact with the surface. The oscillating tip is then moved toward the surface until it begins to lightly touch or tap the surface. During scanning the vertically oscillating tip alternately contacts the surface and light off.

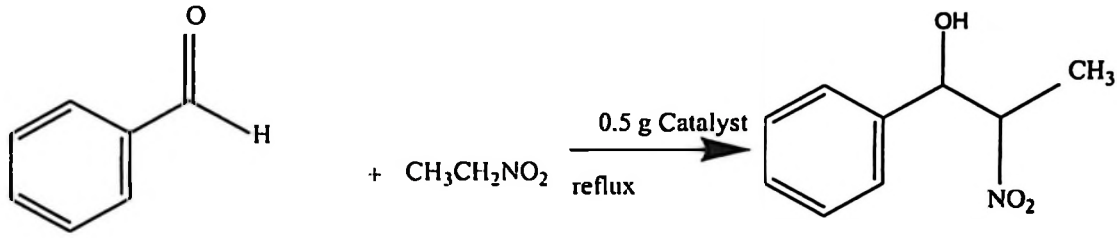
The identification and measurements of surface features are done through the use of reduced energy oscillation occurring when the tip contacts the sample surface.

2.6.3.2 Experimental Procedures

A powder sample of organoamine-silica hybrids was fixed on a glass surface (about 1 cm^2) by using a transparent paper glue adhesive (the product of Dollar Industries (PVT) LTD). Then the glass with the sample was placed on the substrate holder of the AFM. The tapping tip was set and then engaged while the laser beam is on, following a guided technical outline. Proper software was employed to observe real time images; also saving them as off line version for further analysis.

2.7 Application of the Materials as Base Catalysts in the Henry Reaction

The model Henry reaction in this research was the reaction between benzaldehyde and excess nitroethane (scheme 2.2).



Scheme 2.2: A reaction between benzaldehyde and nitroethane

2.7.1 Experimental Procedures

The model Henry reaction was carried as follows; 15 ml (0.22 mol) nitroethane was mixed with 3 ml (0.03 mol) benzaldehyde in the presence of 0.5 g organoamino-

silica hybrid as a base catalyst and 0.5 ml *n*-dodecane as a GC internal standard. The reaction was carried out by refluxing for three hours. A 1 ml of reaction mixture was drawn immediately after mixing the reaction components, then after every ten minutes for the first hour and again after every twenty minutes for the second and third hour. The drawn reaction mixture was diluted by 4 ml of dichloromethane for analysis using gas chromatography model Varian 3400.

The same procedures were repeated but using 0.5 g of silica instead of the organoamino-silica catalyst. The experiment was aimed at verifying the role of the catalyst in the model Henry reaction.

2.8 Monitoring the Henry Reaction through Gas Chromatography Analysis

A gas chromatography is widely used for quantitative and qualitative analysis of mixtures and for purification of organic compounds. In this work the technique was used to quantify the limiting reactant particularly benzaldehyde relative to GC internal standard. The experiment was carried using GC model Varian 3400, attached with FID detector, at the Department of Chemistry.

The gas chromatography technique is commonly used owing to its advantages; such as very good separation of components of a mixture is achieved, analysis takes short time, a small sample is needed and good detection system. Nevertheless, the drawback for this technique is that the materials to be analysed have to be volatilized at 250°C without decomposition.

2.8.1 Principles of Gas Chromatography

A gas chromatography is a chemical analysis instrument for separating chemicals in a complex sample. The instrument uses a flow-through narrow tube known as the column, through which different chemical constituents of the sample pass in a gas stream (carrier gas, mobile phase) at different rates depending on their various chemical and physical properties and their interaction with a specific column filling, called the stationary phase. As the carrier gas sweeps the analytes molecules through the column, this motion is inhibited by the adsorption of the analyte molecules either onto the column walls or onto packing materials in the column. The rate at which the molecules progress along the column depends on the strength of adsorption, which in turn depends on the type of molecule and on the stationary phase materials. Other parameters that can be used to alter the order or time of retention are the carrier gas flow rate, and the temperature. Since each type of molecule has a different rate of progression, the various components of the analyte mixture are separated as they progress along the column and reach the end of the column at different times (retention time). A detector is used to monitor the outlet stream from the column. The chemical constituents in the mixture are finally detected in the detector, which sends signals proportional to the amount of the compound to the recorder. Consequently each compound is registered as a peak. Generally, substances are identified (qualitatively) by the order in which they emerge (elute) from the column and by the retention time of the analyte in the column (Pavia *et al.* 2006).

2.8.2 Flame ionization detector (FID)

Flame ionization detector is a type of gas detector used in gas chromatography. The detection of organic compounds is most effectively done with flame ionization. Biochemical compounds such as proteins, nucleotides and pharmaceuticals can be studied with flame ionization as well as other detectors like thermal conductivity, thermionic or electric conductivity due to the presence of nitrogen, phosphorus or surfur atoms or because of the universality of the thermal conductivity detector. However, typically the biochemical compounds have a greater amount of carbon present than other elements. This means that a particular compound may be more easily detected using flame ionization over the other methods because of higher carbon concentration and also flame ionization's sensitivity (Anon 2010).

2.8.2.1 FID Operating Principles

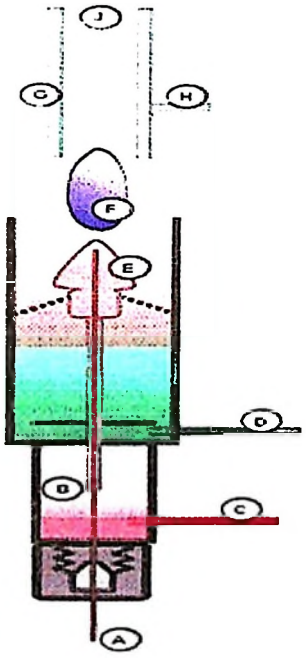


Fig.2.2: Schematic diagram of FID (Anon 2010)

Fig. 2.2 shows a schematic diagram of flame ionization detector (FID). The parts of FID and description are as follows; the eluent exits the GC column and enters the FID detetor's oven (B). The oven is needed to make sure that as soon as the eluent exits the column, it does not come out of the gaseous phase and deposit on the interface between the column and FID. This deposition would result in loss of effluent and errors in detection. As the eluent travels up the FID (Fig. 2.2), it is first mixed with hydrogen fuel (C) and then with an oxidant (D). The effluent/fuel/oxidation mixture continues to travel up to nozzle head where a positive bias voltage exists (E). This positive bias helps to repel the reduced carbon ions created by the flame (F) pyrolyzing the eluent. The ions are repelled up toward the collector plates (G) which are connected to a very sensitive ammeter, which detects the ions hitting the plates, then feeds that signal to an amplifier, integrator, and display system. The products of the flame are finally vented out of the detector or through the exhaust port (I).

2.8.3 Experimental Procedure

The GC conditions were as follows: the column was heated from 80°C to 180°C at rate of 5°C, Injector at 250°C and detector at 300°C. Carrier gas used was nitrogen and the type of column used was semi polar column OV1701. Firstly, each of the reaction components was analysed separately in order to determine the retention time. A 1 ml of each *i.e.*, nitroethane, benzadehyde and dodecane (GC internal standard) was diluted by 4 ml of dichloromethane and then 2 µl of each was injected separately into the column. A chromatogram for each reactant and dodecane were obtained.

The sampled reaction mixtures were run in the GC so as to quantify the limiting reactant particularly benzaldehyde relative to GC internal standard. A 2 µl of the reaction mixture was injected. Since each type of molecule had a different rate of progression, the various components of the reaction mixture were separated as they progressed along the column and reached the end of the column at different times (retention time).

The rate of reaction was monitored by calculating the percentage conversion of benzaldahyde to product using eq. 2.1.

$$\%\text{Conversion of } BA = \frac{\frac{P_{Ba}}{P_{D}}_{(time=t)} - \frac{P_{Ba}}{P_{D}}_{(time=0)}}{\frac{P_{Ba}}{P_{D}}_{(time=0)}} \times 100\% \quad \text{...eq. 2.1}$$

(Where by P_{Ba} denotes peak area for benzaldehyde and P_D denotes peak area for *n*-dodecane, BA denotes benzaldehyde)

CHAPTER THREE

RESULTS

3.1 Screening of the Major Components of CNSL as Templates

Cardanol and anacardic acid, being the major components of the technical and solvent extracted CNSL, respectively, were screened as templates in the synthesis of organoamino-silica hybrids. A one-pot condensation technique was employed for the synthesis. Results show that cardanol is more effective as a template than anacardic acid. High yield of organoamino-silica hybrids was obtained when cardanol was used as a template as justified in Fig. 3.1, in which the whole mixture turned into a brownish thick mass of a material. The dried material after template removal was found to be 66.3% relative to the theoretical yield. When anacardic acid was used as a template a very low yield (9.2%) of organoamino-silica hybrids was obtained (Fig. 3.2).

Having seen the effectiveness of cardanol as a template, it was therefore used for the preparation of the rest of the materials. Dodecylamine, which was used before for synthesis of organoamino-silica hybrids (Mdoe 2000), was also used in this work for comparison purposes. Furthermore, a mixture of dodecylamine and cardanol was also tested as a co-template.

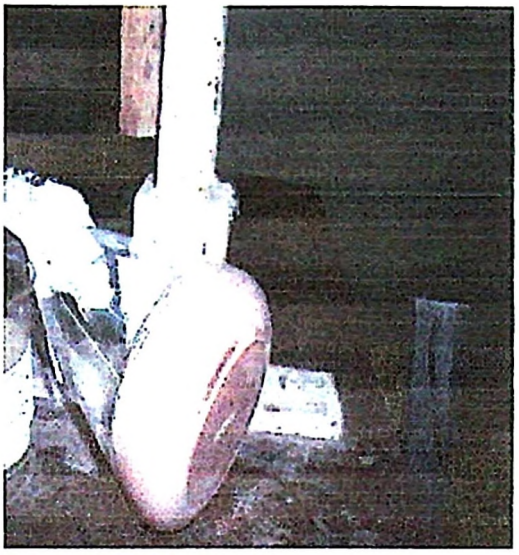


Fig.3.1: Organoamino-silica hybrids synthesized using cardanol as a template at 1:9 organoamine to TEOS ratio.

(as-synthesized)

Fig. 3.2: Organoamino-silica hybrids synthesized using anacardic acid as a template at 1:9 organoamine to TEOS ratio. (as-synthesized)

3.2 Characterization of the Prepared Materials

3.2.1 Determination of Loading by HCl Acid Titration

An acid titration technique was employed for determining the amino groups loading onto silica because the materials were basic in nature. The results obtained are shown in Fig.3.3. The results show that the organic groups for the prepared materials ranged from 0.5 to 2.9 mmol g^{-1} of organoamine per gram of silica. When cardanol was used as a template, the loading ranged from 0.5 - 0.8 mmol g^{-1} and 0.9 - 1.9 mmol g^{-1} at an organoaminesilane to TEOS ratios of 1:9 and 1:4, respectively. On the other hand, dodecylamine produced materials with a loading ranging from 0.8 - 1.2 mmol g^{-1} and 1.5 - 2.9 mmol g^{-1} at 1:9 and 1:4, ratios respectively. On mixing dodecylamine and cardanol as a co-template the loading ranged from 0.7 - 1.8 mmol g^{-1} and 1.2 - 2.3 mmol g^{-1} at 1:9 and 1:4, ratios respectively. The results also show

that for monoamine-silica hybrids the loadings ranged from 0.8 – 1.8 mmol g^{-1} and from 1.9 – 2.9 mmo g^{-1} at 1:9 and 1:4 ratios, respectively. The loadings for diamine-silica hybrids ranged from 0.6 - 0.8 mmol g^{-1} and from 0.8 – 1.9 mmol g^{-1} at 1:9 and 1:4 ratios, respectively. Furthermore, triamine-silica hybrids loading ranged from 0.5 – 0.8 mmol g^{-1} and from 0.9 – 1.5 mmol g^{-1} at 1:9 and 1:4 ratios, respectively.

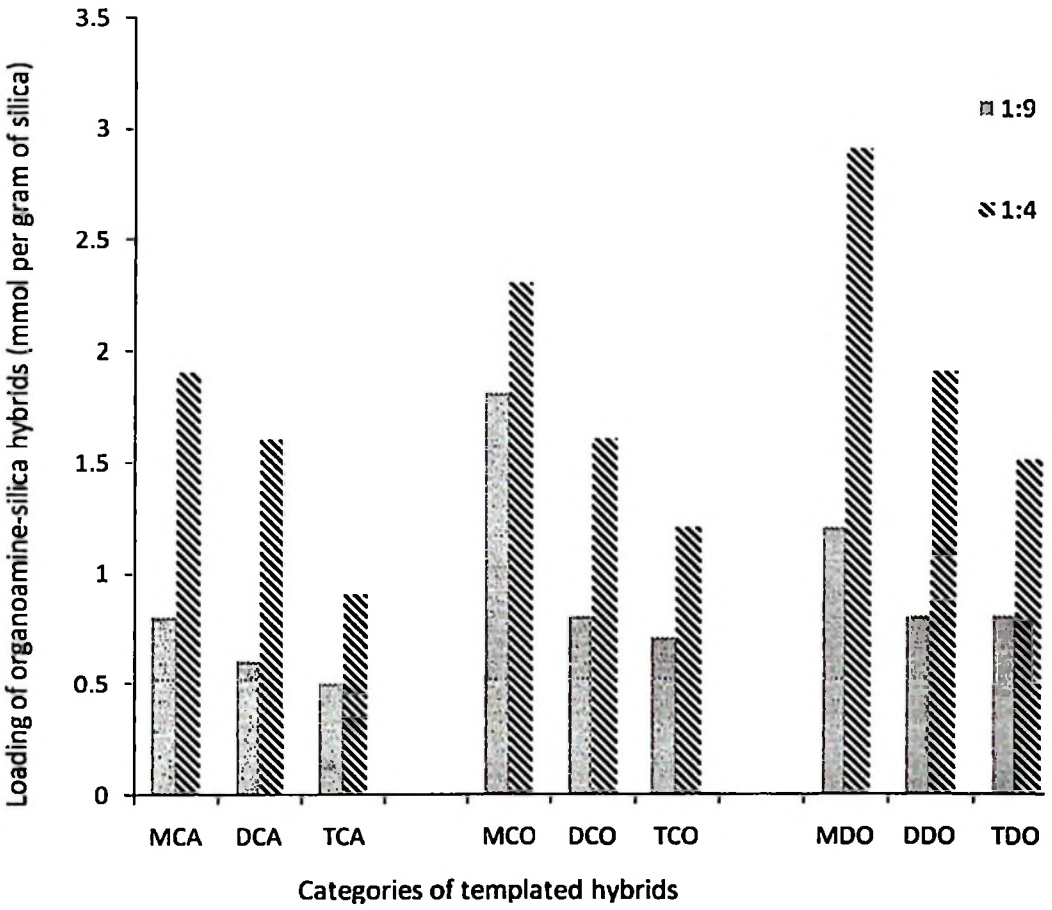


Fig. 3.3: The loadings of the organoamino-Silica hybrids at 1:4 and 1:9 ratios of organoaminesilane to TEOS.

Generally the loading results show that monoamine always had the highest loading regardless of the template. As expected 1:4 ratio gave higher loading than 1:9 ratio for all materials. Furthermore, the co-templated materials had loading that were comparable to those of dodecylamine-templated materials with a few exceptions.

3.3.2 DRIFTS Results

The DRIFTS technique was used to verify whether the amino groups have being successfully incorporated into silica or not. The results showed that indeed the amino groups were successfully incorporated in all hybrids as exemplified by Figs. 3.4 to 3.6 and tables 3.1 to 3.3. This was evidenced by the N-H bending mode at *ca* 1500 ± 30 cm^{-1} as well as the aliphatic C-H stretching modes at 2900 ± 50 cm^{-1} , respectively. In addition to the vibrations attributable to the supported organic groups, vibrations associated with the silica framework were also present. These were observed at 1800 ± 50 cm^{-1} and 1050 ± 50 cm^{-1} due to the Si-O-Si bond. All spectra showed a hydrogen bonded Si-OH stretching band at 3200 - 3650 cm^{-1}. The N-H stretching band appears in a similar region but is masked by the Si-OH band. Most spectra constituted a peak for adsorbed water molecules at around 1600 ± 50. All others (not shown) were similar regardless of the type of template used. A spectrum for unmodified silica (Fig. 3.7) was also included to show the lack of NH-bending at around 1500 ± 30 cm^{-1}, as well as lack of aliphatic C-H stretching modes at 2900 ± 50 cm^{-1}.

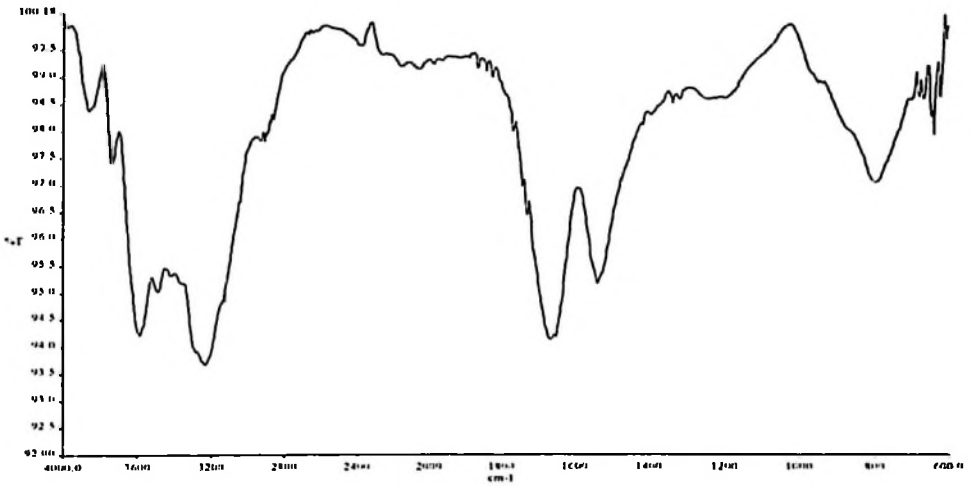


Fig. 3.4: FTIR Spectrum for triamine-silica hybrids prepared using a co-template

Table 3.1: Interpretation for FTIR spectrum of triamine-silica hybrids-co-templating

Wavenumber cm^{-1}	Assignment for Triamine-silica hybrids prepared using co-template
3200-3600	H-bonded Si-OH stretching vibration
2800-3000	Alkyl CH stretching vibration
1600-1650	Molecular H_2O bending
1530	NH bending
900-1150	Si-O-Si symmetric and asymmetric stretching vibrations

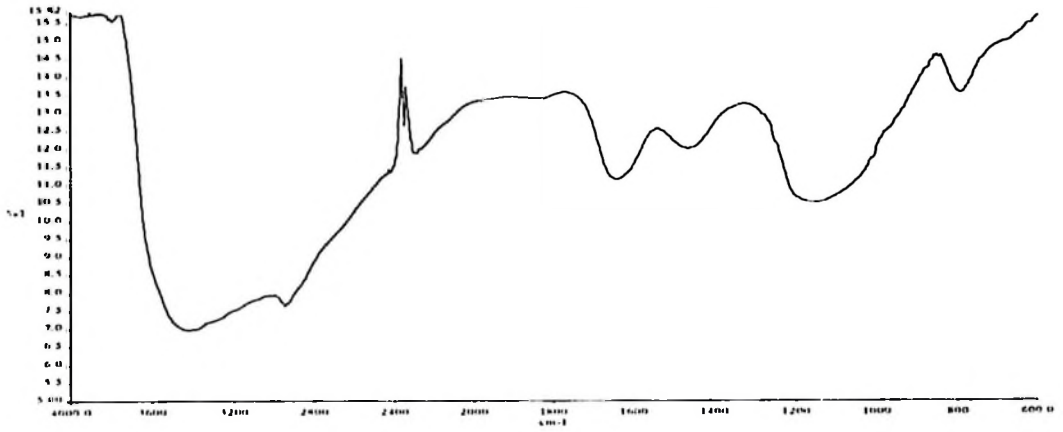


Fig. 3.5: FTIR Spectrum for triamine-silica hybrids prepared using cardanol as a Template

Table 3.2: Interpretation for FTIR spectrum of triamine-silica hybrids-cardanol template

Wavenumber cm^{-1}	Assignment for Triamine-silica hybrids prepared using cardanol as a template
3200-3600	H-bonded Si-OH stretching vibration
2800-3000	Alky CH stretching vibration
1600-1650	Molecular H_2O bending
1500	NH bending
1000-1200	Si-O-Si symmetric and asymmetric stretching vibrations

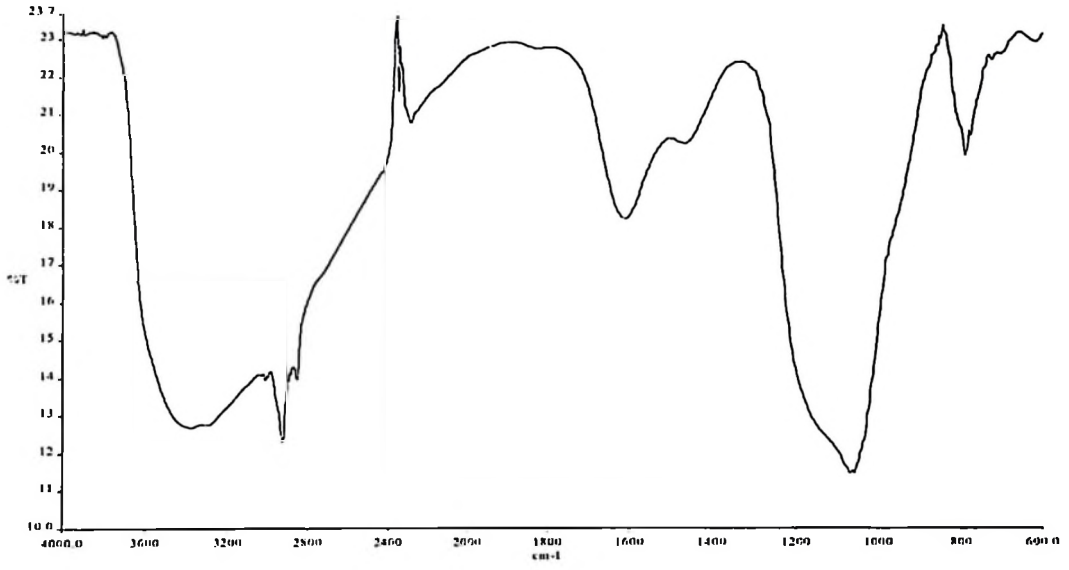


Fig.3.6: FTIR spectrum for diamine-silica hybrids prepared using cardanol as a template

Table 3.3: Interpretation for FTIR spectrum of diamine-silica hybrids-cardanol template

Wavenumber cm^{-1}	Assignment for diamine-silica hybrids prepared using cardanol as a template
3200-3600	H-bonded Si-OH stretching vibration
2800-3000	Alky CH stretching vibration
1600-1650	Molecular H_2O bending
1500	NH bending
1000-1200	Si-O-Si symmetric and asymmetric stretching vibrations

Fig. 3.7: FTIR Spectrum for unmodified silica

Table 3.4: Interpretation of FTIR spectrum of unmodified silica

Wavenumber cm^{-1}	Assignment for unmodified silica
3200-3600	Hydrogen-bonded Si-OH stretching vibration
1800-1900	Si-O-Si vibration
1600-1650	Molecular H_2O bending
1050-1200	Si-O-Si symmetric and asymmetric stretching vibration

3.3.3 Atomic Force Microscopy Data

The representative typical AFM micrographs of the organomino-silica hybrids are presented in Figs. 3.8 and 3.9. The grain size of the materials was calculated manually using the AFM software for grain size average analysis. The micrographs show that the hybrids prepared using cardanol had smaller grain size average about 0.25 μm wide and had an irregular shape. Whereas those prepared using co-template had bigger grain size average of about 0.4 μm wide, also with irregular shapes.

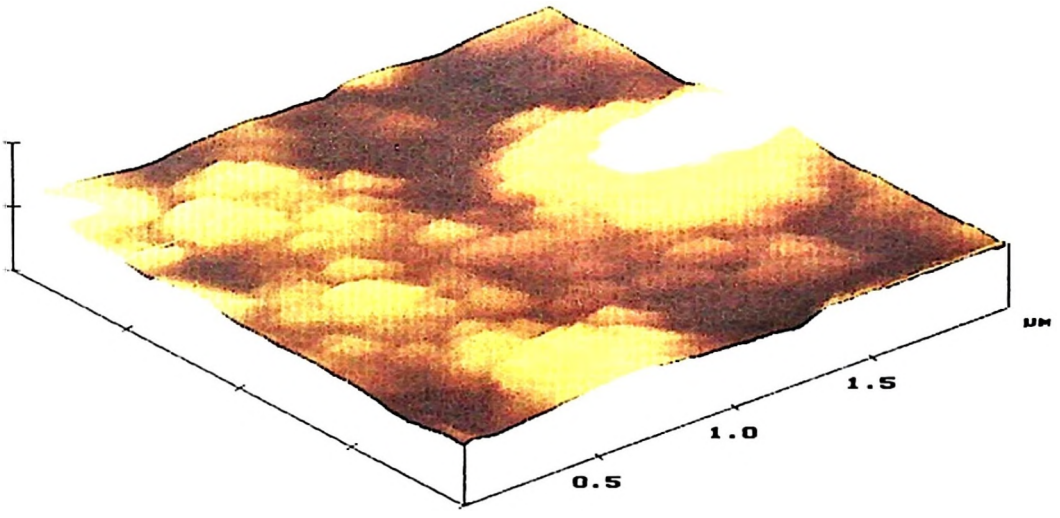


Fig. 3.8: A three dimensional AFM micrograph for TCO

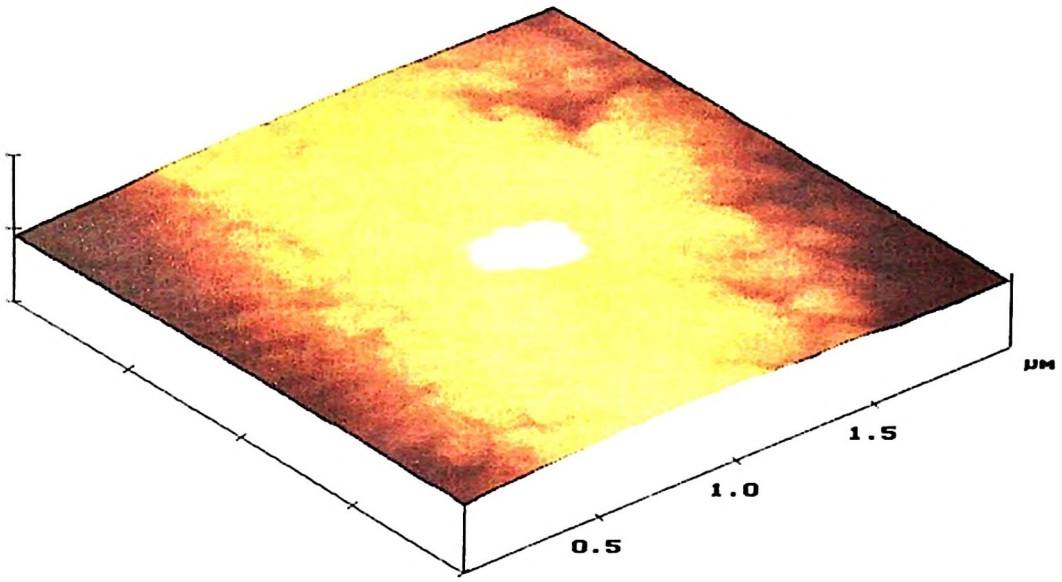


Fig.3.9: A three dimensional AFM micrograph for MCA

3.4 Application of the Material as Catalysts in a Model Henry Reaction

3.4.1 Monitoring the Progress of the Model Henry reaction

Monitoring of the model Henry reaction was achieved by using a GC. The percentage conversion of benzaldehyde, a limiting reactant to product was calculated using eq. 2.1. Firstly, samples from control experiments were run in the GC. Two sets of control experiments were run. In first set in which reactants, internal standard and unmodified silica were mixed and refluxed for three hours, only 1.8% of benzaldehyde was converted into product in three hours (Fig.1 in appendix). For the second set in which reactants and internal standard were mixed and refluxed for three hours, the percentage conversion of benzaldehyde to the product after three hours

was 1.4% (Fig. 2 in appendix). Practically therefore there was no conversion of the benzaldehyde to product in the absence of a catalyst.

Each of the materials prepared was used separately in a reaction between excess nitroethane and benzaldehyde in the presence of dodecane as a GC internal standard under reflux conditions. A ratio of the peak area of benzaldehyde to that of *n*-dodecane as internal standard was computed and then used to calculate the percentage conversion of benzaldehyde as described before. Representative chromatograms are given in Figs. 3 – 5 in appendix, whereas Figs. 3.10 - 3.17 show the progress of the reaction under different conditions.

A Comparison of the catalytic activities of monoamine-silica hybrids prepared by using cardanol, dodecylamine as templates and through co-templating is displayed in Fig.3.10. The results show that the catalytic activity of the monoamine-silica hybrids prepared using dodecylamine (MDO) and through co-templating (MCO) had the same catalytic activity. Both gave approximately 98% conversion of benzaldehyde to product after 180 minutes. On the other hand, hybrids prepared using cardanol as a template gave 81% conversion in 180 minutes. Likewise, Fig. 3.11 compares the catalytic activities of diamine-silica hybrids prepared using the three templates. As seen from the figure, the hybrids prepared using dodecylamine as a template led to the completion of the reaction after 120 minutes, whereas the co-templated and cardanol-templated hybrids achieved the reaction completion after 160 and 180 minutes, respectively. Furthermore, a comparison for catalytic activities of triamine-silica hybrids prepared using the three categories of templates (Fig. 3.12) showed that the hybrids prepared through co-templating and using dodecylamine had similar

catalytic activities. They both gave about 98% conversion after 100 minutes. On the other hand, the hybrid prepared using cardanol gave about 98% conversions after 180 minutes.

The comparison of the catalytic activities of the different organoamino-silica hybrids prepared at 1:4 and 1:9 ratios are given in Figs. 3.13 to 3.16. In all cases the catalytic activities of organoamino-silica hybrids prepared at 1:4 ratio were higher than those for 1:9 ratio, regardless of the type of template used. Furthermore, a comparison of the catalytic activities of the three classes of organoamino-silica hybrids prepared on different templates show that triamine had always the highest catalytic activity followed by diamine and monoamine in that order. This is exemplified by materials prepared on cardanol as a template (Fig. 3.17). In the said example the conversions after 180 minutes were 81 %, 92% and 97 % for monoamine, diamine and triamine-silica hybrids in that order (Table 3.5).

Table 3.5 also summarizes the loading and catalytic activities of the organoamino-silica hybrids. Despite the type of template used triamino-silica hybrids had the lowest loading, followed by diamino-silica hybrids and monoamine-silica hybrids in that order. Even though triamino-silica hybrids had lowest loading, it showed the highest catalytic activity followed by the diamino-silica hybrids, the monoamine-silica hybrids had the least activity. An exception is the monoamino-silica hybrids (MCO) prepared through co-templating which seemed to have the highest activity compared to the rest. Moreover, organoamino-silica hybrids prepared using cardanol as a template had the lowest catalytic activity followed by those prepared through co-templating. Those of dodecylamine had the highest activity.

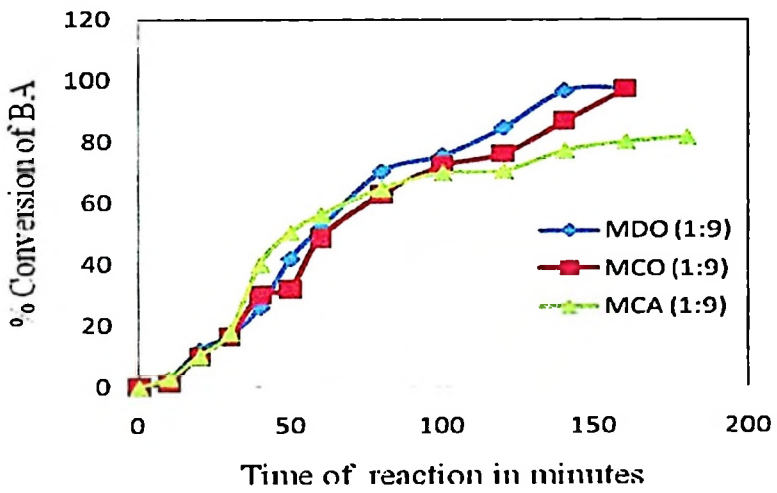


Fig. 3.10: Rate curves for the reaction between benzaldehyde and excess nitroethane using MDO (1:9), MCA (1:9) and MCO (1:9) as catalysts.

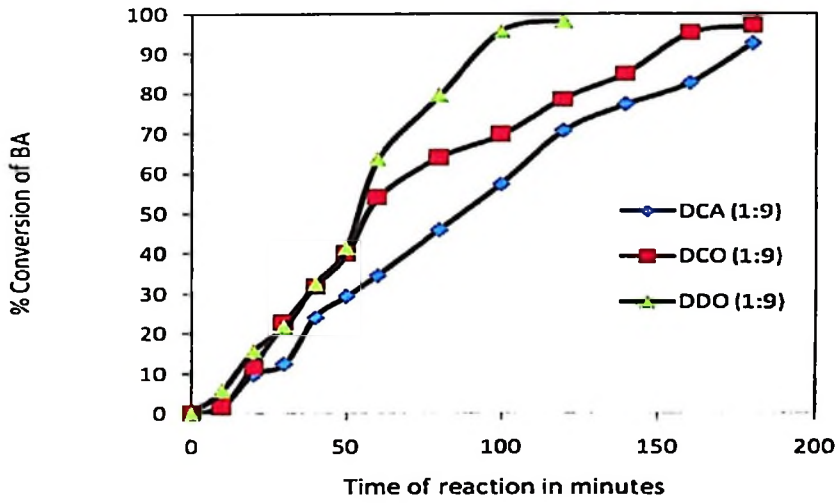


Fig. 3.11: Rate curves for the reaction between benzaldehyde and excess nitroethane using DCA (1:9), DDO (1:9) and DCO (1:9) as catalysts

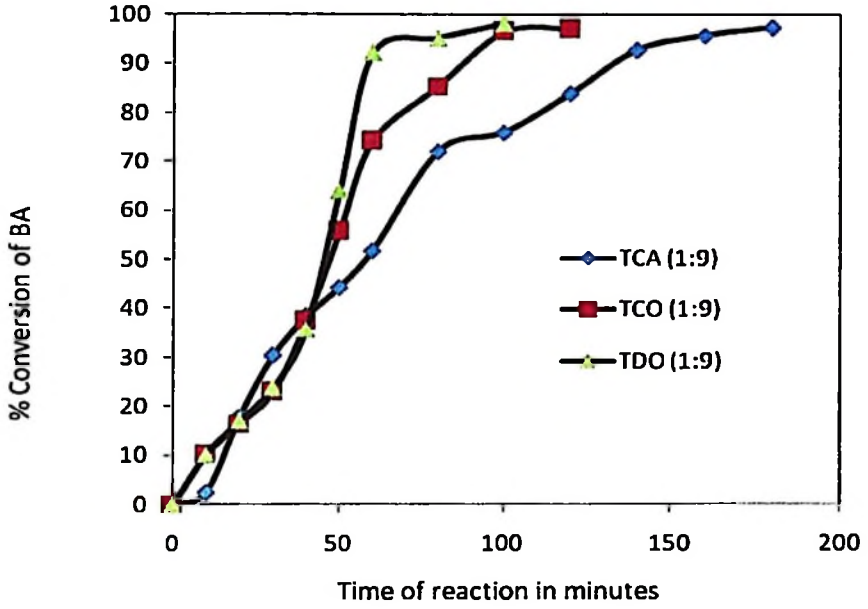


Fig. 3.12: Rate curves for the reaction between benzaldehyde and excess nitroethane using TCA (1:9), TDO (1:9) and TCO (1:9) as catalysts.

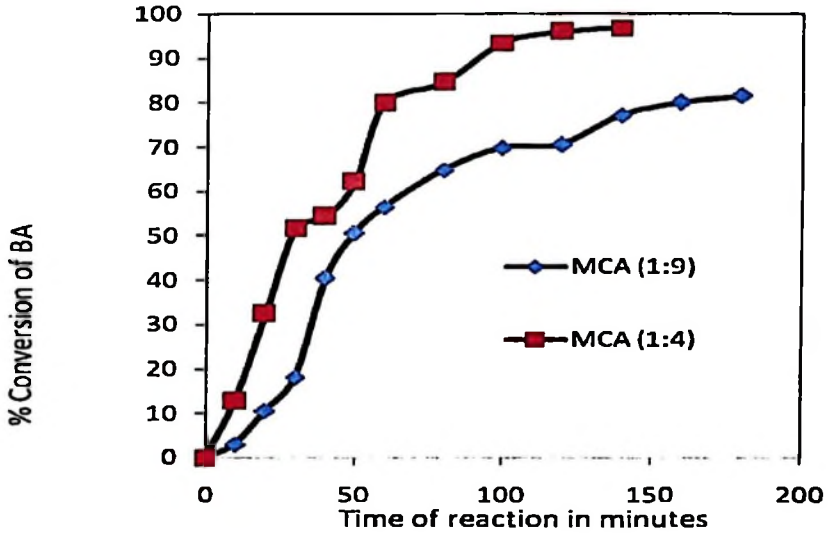


Fig. 3.13: Rate curves for the reaction between benzaldehyde and excess nitroethane using MCA (1:4) and MCA (1:9) as catalysts.

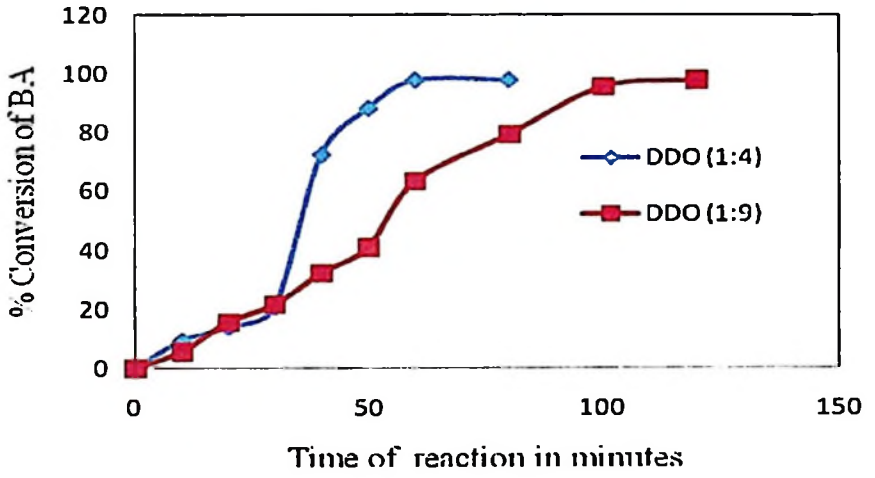


Fig. 3.14: Rate curves for the reaction between benzaldehyde and excess nitroethane using DDO (1:4) and DDO (1:9) as catalysts.

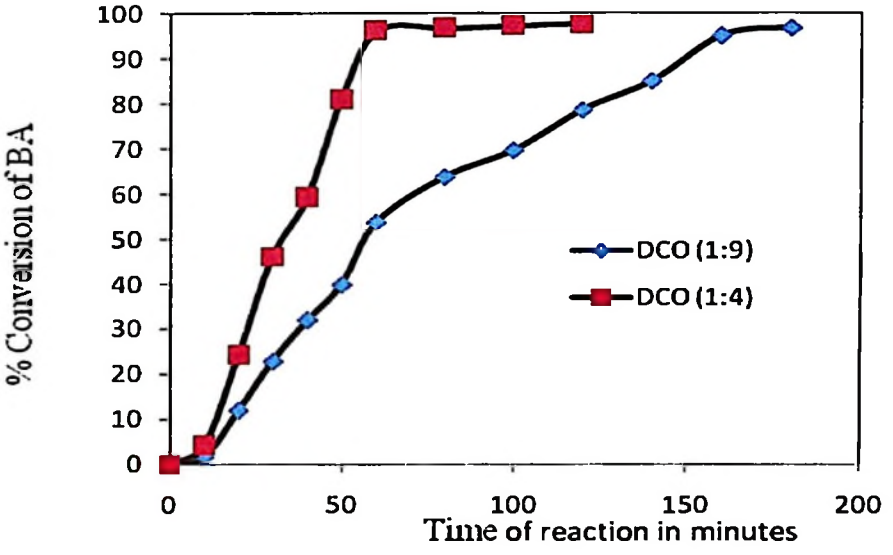


Fig. 3.15: Rate curves for the reaction between benzaldehyde and excess nitroethane using DCO (1:4) and DCO (1:9) as catalysts.

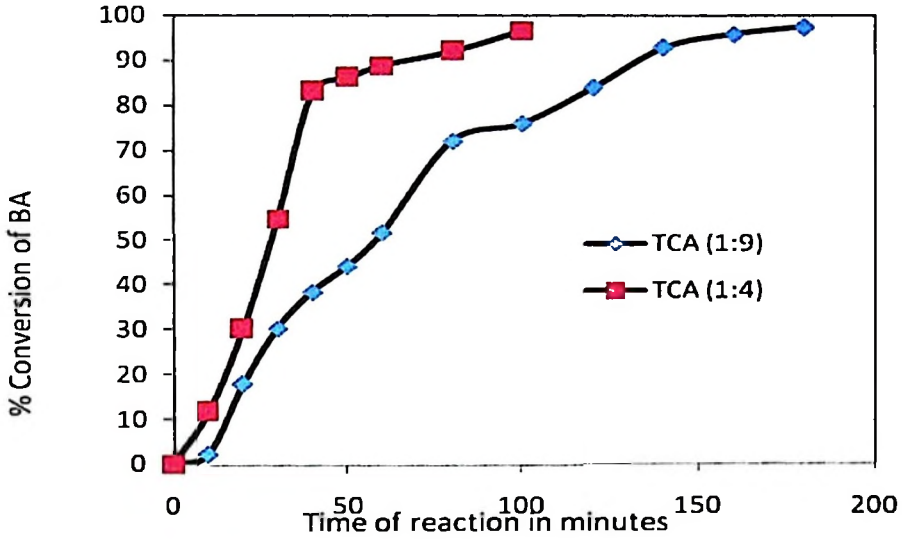


Fig. 3.16: Rate curves for the reaction between benzaldehyde and excess nitroethane using TCA (1:4) and TCA (1:9) as catalysts.

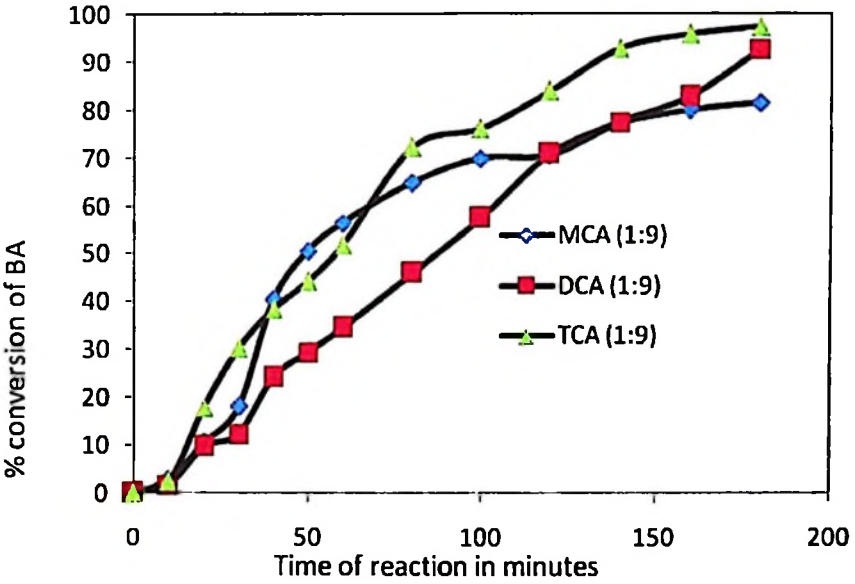


Fig. 3.17: Rate curves for the reaction between benzaldehyde and excess nitroethane using MCA (1:9), DCA (1:9) and TCA (1:9) as catalysts

Table 3.5: Loading and catalytic activity of the organoamino-silica hybrids

Hybrid Material	Ratio of organoaminesilane to TEOS	Loading (mmol g^{-1})	Reaction time (min.)	% Conversion
MCA	1:4	1.9	140	96
	1:9	0.8	180	81
DCA	1:4	1.6	100	98
	1:9	0.6	180	92
TCA	1:4	0.9	120	99
	1:9	0.5	180	97
MCO	1:4	2.3	100	98
	1:9	1.8	160	97
DCO	1:4	1.6	120	98
	1:9	0.8	180	98
TCO	1:4	1.2	140	98
	1:9	0.7	180	97
MDO	1:4	2.9	100	98
	1:9	1.2	140	97
DDO	1:4	1.9	60	98
	1:9	0.8	120	98
TDO	1:4	1.5	100	97
	1:9	0.8	100	98

CHAPTER FOUR

DISCUSSION

4.1 Preparation of the Organoamino-silica Hybrids

Two major components of CNSL, namely, cardanol and anacardic acid were used separately to determine their effectiveness as templates in the synthesis of organoamino-silica hybrids. Cardanol has a phenyl group with a fifteen carbon side chain which constitutes a non-polar portion of the molecule. It has thus a potential of forming micelles. On the other hand, anacardic acid has both a phenyl and a carboxyl group, which form a polar end whereas the fifteen carbon chain forms a non-polar portion of the molecule. Thus anacardic acid has also a potential of forming micelles. Unfortunately cardanol and anacardic acid as templates led to a formation of quite different amounts of the organoamino-silica hybrids. Whereas cardanol gave a high yield of about 66.3%, anacardic acid gave only about 9.2% yield. The chemical difference between cardanol and anacardic acid could be responsible for the difference in the yields. However, this calls for further investigation.

When cardanol was used as a template the loading for monoamino-silica hybrids was 0.8 and 1.9 mmol g^{-1} at 1:9 and 1:4 of organoaminesilane to TEOS ratios, respectively. Over the same template, diamino-silica hybrids loading was 0.6 and 1.6 mmol g^{-1} at 1:9 and 1:4 ratios, respectively. On the other hand, for triamino-silica hybrids the loading was 0.5 and 0.9 mmol g^{-1} at 1:9 and 1:4 ratios, respectively. The loadings for cardanol-based hybrids are lower than those reported by Hilonga *et al.* (2009) in which technical cashew nut shell liquid was used as a

template. In the later case the loading ranged from 1.4 to 2.5 mmol g^{-1} and from 1.4 to 2.1 mmol g^{-1} at 1:4 and 1:9 ratios, respectively. The results suggest that there was a synergistic effect of the components of technical cashew nut shell liquid leading to higher loadings. When dodecylamine was used as a template the loadings of monoamino-silica hybrids were 1.2 and 2.9 mmol g^{-1} at 1:9 and 1:4 ratios, respectively. For diamino-silica hybrids the loadings were 0.8 and 1.9 mmol g^{-1} at 1:9 and 1:4 ratios, respectively, whereas for the triamino-silica hybrids the loadings were 0.8 and 1.5 mmol g^{-1} at 1:9 and 1:4 ratios, respectively. Thus, cardanol templated organoamino-silica hybrids have lower loadings than those of dodecylamine templated hybrids. The presence of amines groups in dodecylamine is responsible for the difference in loading. The amines act as catalysts in the condensation of silanol groups, hence lead to higher loadings. When a mixture of cardanol and dodecylamine was used as a co-template, the loadings for monoamino-silica hybrids were 1.8 and 2.3 mmol g^{-1} at 1:9 and 1:4 ratios, respectively; for diamino-silica hybrids the loadings were 0.8 and 1.6 mmol g^{-1} at 1:9 and 1:4 ratios, respectively; and for triamino-silica hybrids the loadings were 0.7 and 1.2 mmol g^{-1} at 1:9 and 1:4 ratios, respectively. Generally, these loadings are intermediate between those observed for cardanol and dodecylamine when used separately.

The type of organoaminesilane incorporated into silica, affected the loading as well. Triamines had the least loading, followed by diamines and monoamines in that order. The trend concurs with the already reported work by Mdoe *et al.* (2003 b). This observation is attributed to steric effects. Triamine being the largest molecule is most sterically hindered, therefore only a few molecules are anchored onto silica surface

whereas for the monoamines many molecules are anchored owing to their smaller sizes.

Loadings at a ratio of 1:4 are higher than at 1:9. As expected greater organoaminosilane to TEOS ratio leads to higher loadings as seen for the case of 1:4 and 1:9 ratios (table 3.5). The same observation is reported by Macqurrie *et al.* (1999) and Hilonga *et al.* (2009). At a 1:9 ratio most silanol functional groups are left unmodified owing to a much higher amount of silica precursor relative to amount of organoaminesilane.

Generally, the amount of organoaminesilyl groups incorporated onto silica, was found to be affected by three factors. These are the type of template, type of organoaminesilane incorporated, and the ratio of organoaminesilane to TEOS.

4.2 Identity of Functional Groups on the Organoamino-silica Hybrids

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was used in the qualitative determination of the functional groups in the prepared organoamino-silica hybrids. The results showed that amino groups were successfully incorporated. This was evidenced by the N-H bending mode at ca 1500 ± 30 cm^{-1} as well as the aliphatic C-H stretching modes at 2900 ± 50 cm^{-1}. These results concur with already published work by Wang *et al.* (2005).

4.3 Grain Size and Morphology of the Organoamino-silica Hybrids

The average grain sizes for the hybrids prepared using cardanol was about 0.25 μm wide, a size that is smaller than for CNSL-templated materials (Hilonga 2007). In the later, the average grain size of polyamine-silica hybrids prepared using technical

cashew nut shell liquid was about 0.5 μm wide. This suggests that synergistic effect of the phenolic components of technical cashew nut shell liquid is responsible for the bigger grain sizes. The average grain size for the organoamino-silica hybrids prepared using a co-template had bigger size than those prepared using cardanol alone. This signifies the additive effect of the dodecylamine and cardanol as templates in determining the grain size. A grain of a material is usually a complex entity composed of a porous solid, serving as the support for one or more catalytically active phase(s), inturn influencing catalytic activity. Therefore, provided other factors are kept constant the loadings of the prepared hybrids using a co-template were higher than those based on cardanol.

4.4 Catalytic Efficiency of the Templated Organoamino-silica Hybrids

The catalytic efficiencies (catalytic activity) of the hybrids were evaluated using a model Henry reaction. The reaction requires a catalyst in order to obtain a significant amount of product. In the control experiments that were conducted in this study, the reaction was carried out for three hours using unmodified silica instead of the hybrids, only 1.8% of benzaldehyde was converted into product. When the reactants were mixed and refluxed for three hours, only 1.4% of benzaldehyde was converted into product. The results prove that without a catalyst the reaction does not produce a significant amount of product.

In the course of adding the hybrids to the reaction, about 81% to 98% conversion of benzaldahyde to product was afforded within three hours (table 3.5) and (Figs. 3.10 to 3.17). However, the percentage conversions observed in this work were attained at a much longer duration compared to the work by Anan *et al.* (2008). In the later

work, Anan *et al.* (2008) reported approximately 100% conversion of benzaldehyde within 15 to 30 minutes using solid-base nanoporous catalysts. In a different work Krishna *et al.* (2007) reported that bifunctional nanocatalysts afforded a 99.4% yield for the Henry reaction within 15 minutes. In addition, polyamine-silica materials prepared over dodecylamine as a template were applied successfully as base catalysts in epoxidation of electron deficiency olefins (Mdoe 2002). In the later study triamine-based hybrids afforded 76% conversion in 10 hours, whereas diamine-based material gave 52% in 12 hours.

The catalytic efficiency of the prepared materials was influenced by the following factors, namely, type of template, ratio of organoaminesilane to TEOS, loading of the organoamine-silica hybrids and the nature of the organoaminesilane incorporated on silica.

As seen in Figs. 3.10 - 3.12 the type of template used in preparing the hybrids had some influence on the catalytic efficiency. Whereas cardanol templated hybrids afforded a percentage conversion to product of 81% to 99% within 100 to 180 minutes, dodecylamine templated hybrids afforded about 98% conversions within 60 to 140 minutes. On the other hand, the co-templated hybrids gave about 98% product within 100 to 180 minutes. Therefore, cardanol templated hybrids ranked lowest in catalytic efficiencies of all three categories of templates. As explained earlier a template determines the arrangement of the active groups and the surface area of the hybrids (Anderson *et al.* 1993), which in turn influence the catalytic efficiency. Cardanol as a template allowed relatively the smallest amount of organoaminesilane to be incorporated onto the silica surface compared to dodecylamine and a mixture of

dodecylamine and cardanol. This assertion is justified by the loadings displayed in table 3.5, where cardanol templated hybrids have the lowest loading compared to others.

The ratio of organoaminesilane to TEOS is another factor that influenced catalytic efficiency. A greater ratio leads to higher loading and hence higher catalytic activity. Consequently the ratio of 1:4 led to a higher catalytic activity compared to 1:9 ratio regardless of the type of template used. The results concur well with other reports by Mdoe (2002) and Mdoe *et al.* (2003a).

The presence of densely populated organic groups reduces the surface areas and pore volume of the materials (Krishna *et al.* 2007). Densely populated organoamine catalysts are typically accompanied by loss of catalytic efficiency. However, results in table 3.5 show that increase in loading led to an increase in activity. For higher loaded hybrids most active groups are embedded within the bulk structure and hence do not take part in catalysis. For instance, Mdoe *et al.* (2003b) observed that organoamino-silica hybrids with loading of 2.9 mmol per g gave 95% conversion of Michael product in 1.5 hours whereas a 2.2 mmol per gram material afforded 94% in 1.2 hours. For materials in this study, this observation was not very apparent.

The type of organoaminesilane incorporated onto silica surface also influenced the catalytic efficiency of the prepared materials. The triamines based hybrids had the highest catalytic efficiency compared to diamines and monoamines (Fig. 3.17). A triamine molecule has three amino groups, thus has the greatest number of active sites of the three. Hence, if all parameters are held constant, the order of catalytic efficiency in the increasing order is monoamine, diamine and triamine-based hybrids.

This trend is clearly demonstrated in table 3.5. A different study by Mdoe (2002) also showed triamine-based hybrids to be more active than their diamine counterparts.

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 Summary

Cardanol and anacardic acid, the major components of CNSL, were evaluated for their suitability as templates in the synthesis of organoamino-silica hybrids. When cardanol was used as a template it gave 66.3% yield of the hybrids, whereas anacardic acid gave only 9.2% yield. This implies that anacardic acid was less suitable for the synthesis of organoamino-silica hybrids when compared to cardanol. In that case, the rest of the hybrids were prepared using cardanol as a template. Dodecylamine was also used for comparison purposes. In addition, a mixture of dodecylamine and cardanol was also used as a co-template.

The organoamino-silica hybrids were synthesized through a one-pot co-condensation of organoaminesilane and TEOS. Three categories of organoaminesilanes namely, monoamine, diamine and triamine were separately incorporated onto silica using the earlier mentioned templates. The hybrids were prepared at organoaminesilane to TEOS ratios of 1:4 and 1:9. Thereafter, the hybrids were characterized using HCl acid titration technique, Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and Atomic Force Microscopy.

DRIFT studies demonstrated that the organoaminesilanes were successfully incorporated onto silica by using the different templates. This was evidenced by the N-H bending mode at *ca* 1500 ± 30 cm^{-1} as well as CH stretching modes at 2900 ± 50 cm^{-1}.

Loadings of organoamines onto silica were assessed by using HCl acid-titration technique. The cardanol templated hybrids had the least loading of the three templates. The loadings for cardanol templated monoamino-silica hybrids were 0.8 and 1.9 mmol per gram at 1:9 and 1:4 ratios of organoaminesilane to TEOS, respectively. For cardanol templated diamino-silica hybrids the loadings were 0.6 and 1.6 mmol g^{-1} at 1:9 and 1:4 ratios, respectively. In the case of triamino-silica hybrids loadings were 0.5 and 0.9 mmol g^{-1} at 1:9 and 1:4 ratios, respectively. The loadings were significant enough for the hybrids to be applied as base catalysts. On the other hand, when a mixture of cardanol and dodecylamine was used as a co-template, the loadings for monoamino-silica hybrids were 1.8 and 2.3 mmol g^{-1} at 1:9 and 1:4 ratios respectively. Loadings for the diamino-silica hybrids were 0.8 and 1.6 mmol g^{-1} at 1:9 and 1:4 ratios, respectively, whereas, the loadings for triamino-silica hybrids were 0.7 and 1.2 mmol g^{-1} at 1:9 and 1:4 ratios, respectively. Triamines-based hybrids had the lowest loading followed by the diamines and monoamines in increasing order, an observation attributed to steric effects. Generally, the loadings were influenced by the type of template, the nature of organoaminesilane and the ratio between organoaminesilane to TEOS.

The grain size of the material was calculated using the AFM software for grain size average analysis. The AFM micrographs show that the hybrids prepared using cardanol had smaller average grain size of about 0.25 μm wide, whereas those prepared using a co-template had bigger average grain size of about 0.4 μm wide. Both grains were irregular in shape.

The prepared materials were effective as base catalysts in a model Henry reaction. The increasing order of the activity was cardanol-based hybrids, co-templated hybrids and dodecylamine-based hybrids. The triamines- based hybrids had the highest catalytic efficiency followed by diamine and monoamines-based hybrids in a decreasing order. Furthermore, materials prepared at a ratio of 1:4 had higher catalytic efficiency than those prepared at 1:9 ratio.

5.2 CONCLUSION

Cardanol as a template gave higher yields of organoamino-silica hybrids than when anacardic acid was used. Hence it was used for the prepation of the materials used in this study. The materials were found to be effective as base catalysts in a model Henry reaction. Materials based on triamines had the highest catalytic efficiency followed by diamine and monoamines-based hybrids in that order. Furthermore, the organoamino-silica hybrids prepared at a ratio of 1:4 of organoaminesilane to TEOS had higher catalytic efficiency than those prepared at 1:9 ratio. Thus, the catalytic efficiency of the hybrids was dependent on four factors, namely, type of template, loading, type of organoaminesilane incorporated onto silica and the ratio of organoaminesilane to TEOS.

5.3 RECOMMENDATIONS

The development of new catalysts with even better characteristics in terms of activity, selectivity and stability is an on-going challenge. Tailoring of microscopic properties such as pore size, shape and surface reactivity will continue to improve the

properties of organocatalysts (Hunks and Ozin 2005). The cardanol templated hybrids have proved to be effective base catalysts, particularly in the Henry reaction. However, further studies need to be carried out to improve their catalytic efficiency, so as to afford the highest percentage conversions in a shortest time possible. It is also recommended that the reuse of the organoamino-silica hybrids prepared using cardanol be studied in order to elucidate their stability and recyclability. In addition, it will be very useful if the surface areas, pore sizes and pore size distributions are established and compared to materials prepared using conventional templates.

Further research on base catalytic suitability of the cardanol templated organoamino-silica hybrids in other base catalysed organic reactions is also necessary. Reactions such as Michael addition, Knoevenagel condensation, epoxidation of enones and aldol condensation could be good candidates. It would also be worthwhile to characterize the hybrids developed on anacardic acid as a template. This also applies to screening of other CNSL minor components such as cardol and methyl cardol as templates. Furthermore, studies on the effect of solvents on the Henry reaction catalysed by cardanol templated hybrids are important since solvents tend to affect rates of reactions.

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APPENDIX

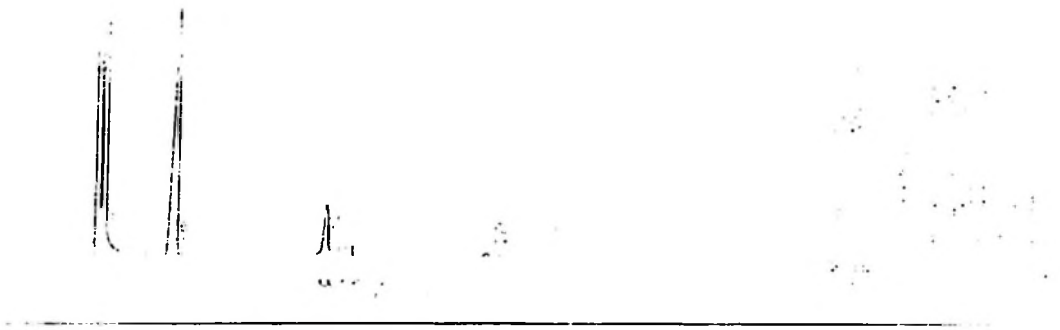

Fig. 1: A chromatogram for the reaction mixture drawn after three hours, when unmodified silica was used instead of organoamino-silica hybrid.

Fig. 2: A chromatogram for the reaction mixture drawn after three hours, when neither unmodified silica nor organoamino-silica hybrids were added.

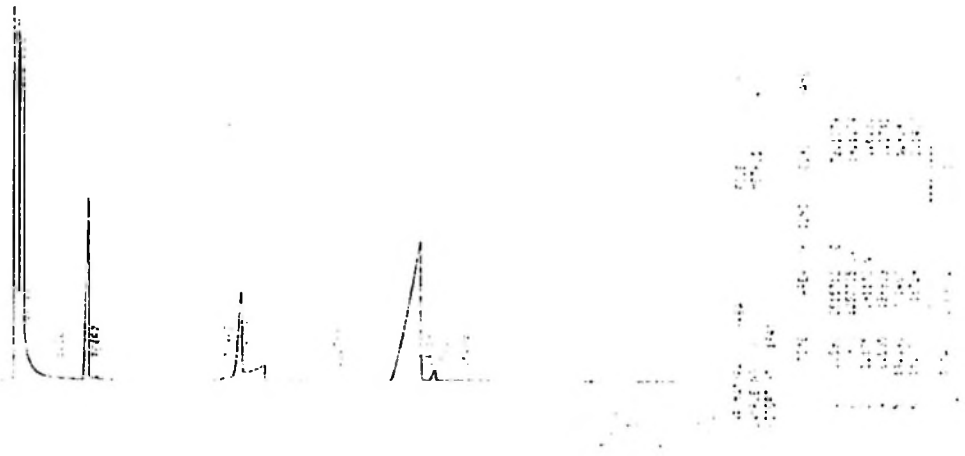

Fig. 3: A chromatogram for the reaction mixture drawn after 180 minutes, for reaction catalysed by MCA (1:9)

Fig. 4: A chromatogram for the reaction mixture drawn after 160 minutes, for reaction catalysed by DCA (1:9)

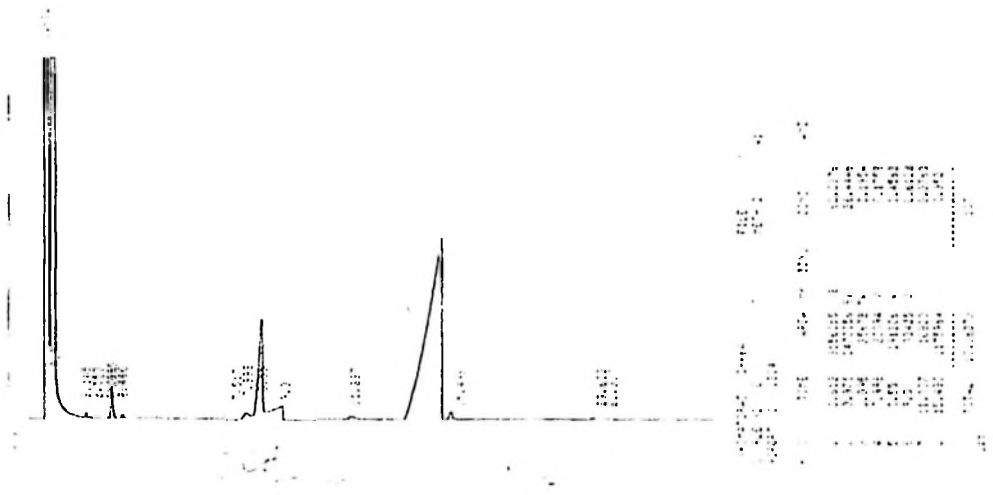

Fig. 5: A chromatogram for the reaction mixture drawn after 120 minutes, for reaction catalysed by TCA (1:4)