STUDIES ON THE HETEROGENISATION OF SULPHONIC ACID AND GUANIDINES ON SILICA AND THEIR CATALYTIC ACTIVITY

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By

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TABLE OF CONTENTS

Page

CHAPTER 1 –INTRODUCTION

CHAPTER 2 –EXPERIMENTAL

CHAPTER 3 – THE SYNTHESIS AND CHARACTERISATION OF RHAPrSO$_3$H, RHAPrTMG AND RHAPrTBD

CHAPTER 4 –ACETALISATION OF GLYCEROL WITH BENZALDEHYDE OVER RHAPrSO$_3$H

CHAPTER 5 –CYCLOADDITION OF CARBON DIOXIDE TO PROPYLENE OXIDE OVER GUANIDINE CATALYSTS

CHAPTER 6 –THE CHEMICAL FIXATION OF CO_2 WITH HOMOGENEOUS TMG AND TBD CATALYSTS

CHAPTER 7- CONCLUSION AND RECOMMENDATIONS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

LIST OF APPENDICES

Appendix A: The FT IR spectra of fresh and reused catalysts **Page**

Appendix B: The Energy dispersive X-ray (EDX)

Appendix C: The GC and GC-MS spectra

Appendix D: Crystal Structure Report

LIST OF SYMBOLS AND ABBREBIATIONS

APTS	(3-aminopropyl)trimethoxysilane
BJH	Barrett, Joyner and Halenda
BET	Branauer Emmet Tyler
CCDC	Cambridge crystallographic data centre
CHN	Carbon, Hydrogen and Nitrogen elemental analysis
CEC	Cation exchange capacity
CO_2	Carbon dioxide
CP	Cross polarisation
CPTES	3-(Chloroprophyl)triethoxy silane
DABCO	1,4-diazabicyclo[2.2.2]octane
DMF	Dimethylformamide
DCM	Dichloromethane
DTA	Differential thermal analysis
ECHC	Epichlorohydrin carbonate
ECH	Epichlorohydrin
EH	Epoxy hexane
EDS	Energy dispersion spectroscopy
E_a	Activation energy
Et_3N	Triethyl amine
Fig.	Figure
FID	Flame ionisation detector
FT-IR	Fourier Transformed Infra-Red
GC	Gas chromatography

GC-MS	Gas chromatography-mass spectrometry
h	hour
H	Hysterisis loop
IUPAC	International Union of Pure and Applied Chemistry
IR	Infrared
k_a	Rate constant
kJ	Kilo joule
M	Molar amount of grafted material
MAS NMR	Magic Angle Spininig-Nuclear Magnetic Resonance
MCM	Mobil Composition of Matter
mg	milligram
m^2g^{-1}	meter square per gram
min	minute
MPTMS	3-Mercaptopropyltrimethoxysilane
MPa	Millipascal
MTBD	Methyltriazabicyclodec-5-ene
NaOH	Sodium hydroxide
N	Surface coverage
nm	nanometer
μgL^{-1}	microgram per litre
PC	Propylene carbonate
PO	Propylene oxide
pH	hydrogen ion function
P/P_o	Relative pressure
P_w	Weight percent

RH	Rice husk
RHA	Rice husk ash
RHACCl	chloro-propyl silica support
Rpm	rotations per minute
SBA	Santa Barbara amorphous
S_{BET}	BET surface area
SC	Styrene carbonate
SDA	Structure directing agents
SEM	Scan Electron Microscopy
TBD	1,5,7-triazabicyclo[4.4.0]dec-5-ene
TEM	Transmission electron microscopy
THF	Tetrahydrofuran
TMG	1,1,3,3-Tetramethylguanidine
TEOS	Tetraethyl orthosilicate
TGA	Thermogravimetric analysis
TOF	Turnover frequency
TMSCN	trimethylsilyl cyanide
XRD	X-ray diffraction

KAJIAN MENGENAI PENGHETEROGENAN ASID SULFONIK DAN GUANIDINA KE ATAS SILIKA DAN AKTIVITI PEMANGKINAN MEREKA

ABSTRAK

Tiga pemangkin homogen iaitu sulfonik asid, 1,1,3,3-tetrametil guanidina dan 1,5,7-triazabisiklo guanidina telah diimobilisasikan ke atas silika daripada abu sekam padi. Sodium silikat daripada abu sekam padi telah terimobilkan dengan 3-(merkaptopropil)trimetoksilana. Ini seterusnya dioksidakan kepada asid sulfonik dalam satu langkah yang mudah. Pemangkin asid pepejal telah dilabelkan sebagai $RHAPrSO_3H$. Analisis pemangkin oleh penjerapan-penyahjerapan nitrogen menggunakan kaedah Brunauer, Emmet dan Teller (BET) telah menunjukkan bahawa luas permukaan pemangkin adalah 340 m^2g^{-1} dengan purata isipadu liang 0.24 cc g^{-1} dan diameter liang 2.9 nm. Ujian keasidan menggunakan kapasiti pertukaran kation dan penjerapan piridina FT-IR mennujukkan kehadiran tapak asid pada permukaan pemangkin. Hasil kajian MAS NMR ^{29}Si $RHAPrSO_3H$ mendedahkan kehadiran Q^4, Q^3, pusat silikon T^3, T^2 dan T^1, manakala hanya Q^4 dan pusat silikon Q^3 dilemui pada $RHASiO_2$. Mangkin ini telah digunakan dalam tindak balas pengasetalan gliserol dengan benzaldehid. pada keadaan tindak balas tubaih, iaitu suhu 120 °C, nisbah molar 2:1 gliserol:benzaldehid, jisim mangkin 0.15 g dan 8 jam tindak balas penghasilan dengan pemilihan yang tinggi terhadap isomer gelang lima ahli telah diperolehi. Pemisahan campuran tindak balas selanjutnya membolehkan pengasingan tunggal yang telah dianalisis dengan kristalografi sinar-X. Kristal tunggal telah di kenalpasti kristal sebagi isomer cis- gelang enam ahli (*cis-5-hydroxy-2-phenyl-1,3-dioxan*). Mangkin telah dikitar semula beberapa kali dan tidak menunjukkan sebarang perubahan ketara dalam aktivitinya. Sodium silikat dari abu sekam padi (RHA) telah juga digabungkan dengan 1,1,3,3-tetrametilguanidina (TMG) dan 1,5,7-triazabisiklo[4.4.0]dek-5-ena (TBD), melalui 3-kloropropiltrietoksilina (CPTES) sebagai ejen pengsililatan untuk membentuk RHAPrTMG dan RHAPrTBD sebagai pemangkin pepejal. Analisis BET kedua-dua pemangkin menunjukkan bahawa, RHAPrTMG mempunyai luas permukaan 527 m^2g^{-1} dan diameter liang 3.7 nm, manakala RHAPrTBD mempunyai luas permukaan yang lebih rendah aitu 326 m^2g^{-1} dan diameter liang 3.6 nm. Analisis CHN kedua-dua pemangkin menunjukkan kehadiran nitrogen, yang menggantikan klorin pada RHACCl. RHAPrTMG telah digunakan dalam tindak balas penambahan siklik karbon dioksida dengan epoksida, didalam autoklaf 500 mL tekanan tinggi dengan pengacau magnet (Roth Model IV). pada keadaan tindak balas terbaik 130 °C, 50 bar tekanan CO_2, 0.2 g jisim mangkin dan 8 jam tindak balas penghasilan dan pemilihan untuk karbonat bersiklo telah diperolehi. Begitu juga, mangkin RHAPrTBD digunakan dalam tindak balas siklo karbon dioksida dengan epoksida, dalam autoklaf 100 mL tekanan tinggi (Amar Equipments PVT). Di bawah keadaan tindak balas terbaik 130 °C, 50 bar tekanan CO_2, 0.2 g jisim pemangkin dan 10 jam tindak balas penghasilan dan pemilihan untuk karbonat bersiklo telah diperolehi. Kedua-dua mangkin juga telah dikitar semula sekurang-kurangnya tiga kali tanpa kehilangan aktiviti yang ketara.

STUDIES ON THE HETEROGENISATION OF SULFONIC ACID AND GUANIDINES ON SILICA AND THEIR CATALYTIC ACTIVITY

ABSTRACT

The immobilization of three homogeneous catalysts namely; sulfonic acid, 1,1,3,3-tetramethyl guanidine and 1,5,7-triazabicyclo[4.4.0]dec-5-ene guanidine was carried out on silica from rice husk ash. Sodium silicate from the rice husk ash was immobilised with 3-(mercaptopropyl)trimethoxysilane. This was further oxidised to sulfonic acid in a simple one pot method. The solid acid catalyst was denoted as $RHAPrSO_3H$. Analysis of the catalyst by nitrogen adsorption-desorption using Brunauer, Emmet and Teller (BET) method showed its surface area to be 340 m^2g^{-1} with average pore volume of 0.24 cc g^{-1} and pore diameter of 2.9 nm. Acidity tests by cation exchange capacity and pyridine FT-IR adsorption, revealed the presence of acid sites on the catalyst surface. Similarly, the ^{29}Si MAS NMR of $RHAPrSO_3H$ revealed the presence of Q^4, Q^3, T^3, T^2 and T^1 silicon centres, while only Q^4 and Q^3 silicon centres were present in $RHASiO_2$. The catalyst was used in the acetalization reaction of glycerol with benzaldehyde. Under the best reaction conditions of 120 °C temperature, 2:1 molar ratio of glycerol: benzaldehyde, 0.15g mass of catalyst and 8 h reaction time, significant conversion was achieved with high selectivity towards five member ring isomer. Further separation of the reaction mixture enabled the isolation and X-ray crystallography analysis of a single crystal. The crystal was cis-isomer of the six-membered ring (*cis-5-hydroxy-2-phenyl-1,3-dioxane)* compound. The catalyst was recycled few more times and showed no significant change in its catalytic activity. Similarly, sodium silicate from rice husk ash (RHA) was also functionalised with 1,1,3,3-tetramethylguanidine (TMG) and 1,5,7-

triazabicyclo[4.4.0]dec-5-ne (TBD) via 3-(chloropropyl)triethoxysilane (CPTES) as silylating agent to form RHAPrTMG and RHAPrTBD as solid catalysts respectively. The nitrogen adsorption-desorption using BET method showed that, RHAPrTMG had a surface area of 527 m^2g^{-1} and average pore diameter of 3.7 nm, while RHAPrTBD, had a lower surface area of 326 m^2g^{-1} and average pore diameter of 3.6 nm. The CHN analysis on both catalysts indicated the presence of nitrogen, which substituted the chlorine from RHACCl. RHAPrTMG catalyst was used in the cyclo addition reaction of carbon dioxide with epoxides, in a 500 mL high pressure bottom stirred laboratory autoclave (Roth Model IV). Under the best reaction conditions of 130 °C temperature, 50 bar of CO_2 pressure, 0.2 g mass of catalyst and 8 h reaction time, a significant conversion and selectivity to cyclic carbonates was achieved. Similarly, the catalyst, RHAPrTBD was also used in the cyclo addition reaction of carbon dioxide with epoxides, in a 100 mL high pressure bottom stirred reactor (Amar Equipments, PVT). Under the best reaction conditions of 130 °C temperature, 50 bar of CO_2 pressure, 0.2 g mass of catalyst and 10 h reaction time, a significant conversion and selectivity to cyclic carbonates was achieved. Both catalysts were also recycled at least three more times without significant loss of activity.

CHAPTER 1

INTRODUCTION

1.0 Catalysis

The 2005 Nobel Prize in Chemistry was awarded to Chauvin, Grubbs, and Schrock for their research on olefin metathesis catalysis. Their work specifically highlighted the potential of their research to provide access to ‘‘greener’’ synthetic routes (Anastas and Beach, 2007). In other words, their research stressed the importance of catalysis to green chemistry.

Catalysts are species that are capable of accelerating thermodynamically feasible reactions, while they remain unaltered at the end of the reaction. Catalysts increase the rate of the reaction by providing an alternative route with lower activation energy for the reaction. The performance of a catalyst is largely measured in terms of its effect on the reaction kinetics (Clark, 2002).

In addition to increasing the rate of reaction, the presence of catalysts in reactions offers the advantages of: (i) increase in the productivity (ii) formation of new products (iii) economisation of raw materials and energy consumption (iv), minimise of waste products and hence, protecting the environment (Barrault, et al., 2002). Catalysis has played a central role in the chemical industry from its beginning in the late eighteenth century.

Today, catalytic processes are used to make gasoline, to synthesize most pharmaceuticals, chemicals, polymers, and to reduce pollution from cars and power plants (Smith, 2003). By the 20th century, the estimated total contribution of catalysts in World Gross National Product (GNP) reached ~20% (Clark, 2002). The word catalysis was coined by Berzelius in 1836, specifically referring to a growing body of experimental data. Half a century later, Wilhelm Ostwald linked catalysis to chemical thermodynamics and kinetics and therefore refined the definition of catalysis as substances that alter the velocity of chemical reactions without appearing in the end products. Homogeneous catalytic processes have been used by mankind for some thousands of years, for example in fermentation (Robertson, 1975).

The immobilization of homogeneous catalysts onto a solid support is a promising strategy to simplify the separation of catalysts from the reaction mixture and provide means of recycling the catalyst. This will also reduce waste and minimise pollution of the environment. However, heterogenization of homogeneous catalysts often sacrifices catalytic performance, which includes activity and/or selectivity (Takenaka, et al., 2012).

1.1.1 Heterogeneous catalysts

Generally, there are three types of catalysts, i.e. heterogeneous, homogeneous and biological. However, among these catalysts, heterogeneous catalyst has several advantages over the others. These include:

- Easy and cheap recovery after use
- Generally considered as non toxic (depending on the support material)
- Easy to handle without posing any danger
- Recyclable for subsequent application
- Tolerate a wide range of temperatures
- Easy and safe disposal method

The most important physical properties of heterogeneous catalysts are surface area, pore volume and pore size distribution. The importance of surface area on a solid catalyst is to provide adequate space for the substrate to adsorb or react on.

Thus, other related properties such as surface roughness, the functional group present, hydrophilicity and hydrophobicity are also important in catalysis. The presence of wide pores in a catalyst, usually leads to small surface area in a given volume of catalyst, which results in poor catalytic activity (Brunauer, 1976). On the other hand, too narrow pores result in diffusion restriction, which could lead to poor catalyst also. According to IUPAC notation, catalytic materials are classified with respect to their sizes in to three groups: microporous, mesoporous and macroporous materials (Pierotti and Rouquerol, 1985). Microporous materials have diameters less < 2 nm, mesoporous materials have pore diameters between 2 and 50 nm, and macroporous materials have pore diameters > 50 nm.

1.1.2 Types of support for heterogeneous catalysts

Catalytic support in a heterogeneous system refers to the substance, usually solid, with high surface area, to which the active phase of the catalyst is, affixed (Brunauer, 1976). Such a solid could be catalytically inert, but it may contribute in the overall catalytic activity of the reaction system. Good support material possesses the quality of high dispersion and high degree of thermal stability for the catalytic component (Campanati, et al. 2003).

Depending on the internal architecture of the catalyst, there are several kinds of support for heterogeneous systems, which include:

ü Armorphous support: example, metal oxides, silica, carbon etc.
ü Layard support: example, Clay.
ü Microporous supported material: These include zeolites, which are crystalline aluminosilicates having microporous channels or cages within their structure.

1.2 Rice Husk

Rice husk is the hard outer covering of the rice grain. It is an agricultural waste abundantly available in rice-producing countries. It constitutes about 20% of the weight of rice, and contains about 50 % cellulose, 25–30 % lignin, and 15–20 % silica (Riveros and Garza, 1986; Chandrasekhar et al., 2003; Adam; Chua 2004; and Abubakar et al., 2010). When rice husk is burnt, rice husk ash (RHA) is generated. The burning of rice husk can be controlled to produce better quality rice husk ash, whose specific particle size and surface area are dependent on burning conditions (Nizam, 1993; and Watari, et al., 2006). Sun and Gong (2001) reported that, the combustion of RHA below 800 °C produces amorphous silica. However, some researchers are of the view that, in addition to variation of composition due to burning conditions, the composition of the ash also depends upon soil type and the farming environment (Nizam, 1993; Souza, 2000). It has been estimated that, out of every 1000 kg of paddy rice milled, about 200 kg (20%) of husk is produced, which when burnt, also produces about 50 kg (25%) of rice husk ash (Abubakar, et al., 2010). It accounts for about one-fifth of the annual gross rice production of 545 million metric tons, of the world (Srivastava, et al., 2006).

Due to its high silicon content, rice husk has become one of the major sources for elementary silicon (Hunt, et al., 1984, Banerjee et al., 1982) and a number of silicon compounds (Karera et al, 1986). Many studies have reported the chemical composition of rice husk in different parts of the world; however, most of these studies reported the organic content in rice husk as 72% by weight, with variation in the different constituents (Chandrasekhar et al., 2003). Govindarao, (1980) has analysed some reported data on the chemical composition of rice husk from various countries and gave an average composition on dry basis as: ash 20%, lignin 22%, cellulose 38%, pentose's 18% and other organic matter 2%. Due to its high calorific power (approximately 16720 kJ/kg), there is an increase in the application of rice husk as a source of fuel for heat generation, particularly, for drying rice (Della, et al., 2002). However, after burning of rice husk, approximately 20 wt % of ash is left as a waste, and this constitutes a pollution hazard (Souza, et al., 2000) if it is left in the open.

Rice husk ash contains high proportions of silica. Many authors have reported different proportions of silica in rice husk ash, depending upon the burning conditions and the extraction process. Table 1.1 shows the chemical composition of rice husk ash from different authors. It can be observed from the table that, the ash produced from the rice husk burning contains a great amount of silica and small amounts of other elements which are considered as impurities. The most common trace elements in RHA are sodium, potassium, calcium, magnesium, iron, copper, manganese and zinc (Foletto et al., 2006). Differences in composition may occur due to geographical factors, type of ground, and year of harvest, sample preparation and analysis methods.

The chemical composition of silica in the rice husk ash ranges between 84.30–94.95 %, with some trace amount of metal oxides such as Al_2O_3 Fe_2O_3, CaO. etc.

Table1.1: Comparative analysis on the chemical composition of rice husk ash (RHA).

S/N	Constituents	% Composition			
		Nizam, (1993)	Della et al., (2002)	Rodríguez (2006)	Foletto, et, al., (2006)
1.	SiO_2	92.01	94.95	87.20	94.4
2.	Al_2O_3	1.48	0.39	0.15	0.61
3.	Fe_2O_3	0.40	0.26	0.16	0.03
4.	TiO_2	Traces	0.02	-	NR
5.	P_2O_5	Traces	0.74	-	NR
6.	CaO	1.52	0.54	0.55	0.83
7.	MgO	0.41	0.90	0.35	1.21
8.	Na_2O	0.63	0.25	1.12	0.77
9.	K_2O	1.53	0.94	3.60	1.06
10.	Loss on ignition	2.01	0.85	6.55	-

1.2.1 Extraction of silica from Rice Husk Ash (RHA)

Silica is the major constituent of rice husk ash (RHA) as seen in the Table 1.1 above. The extracted silica could be utilised for several applications such as adsorbents and catalyst support. Due to its high thermal and chemical stability, high surface area, porosity and accessibility, many organic functional groups can be immobilised on the silica surface, to produce multitude of heterogeneous catalysts (Gupta, et al, 2007). The common way of extracting silica from RHA is by acid-leaching and pyrolysis (Conrad et al., 1992; Real et al., 1996; Yalcin and Sevinc, 2001; Della et al., 2002; Liou, 2006). At acidic pH, gelation of silica is slower and hence sodium ions may diffuse out of the gel matrix and can be washed out easily to produce high purity silica (Kalapathy, 2002).

The effect of H_2SO_4, HCl and HNO_3 on the extraction of silica from RHA was reported by Matori, *et al.,* (2009). The study found that, HCl was the most effective among the acids used, particularly in removing metal impurities.

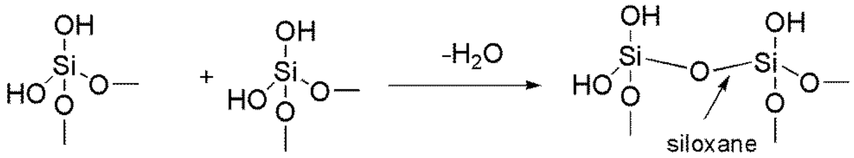
A simple method based on alkaline extraction followed by acid precipitation was used to produce pure silica from RHA (Kalaphathy 2000, 2002). The method involved dissolving the silica with alkaline solution at 100°C to form sodium silicate solution and subsequently converted to silica gel by the addition of HCl to lower the pH to 7.

Similarly, Adam et al., (2009) reported an eco- friendly sol-gel method of extracting silica from RHA. The sodium silicate solution was converted to silica gel by the gradual addition of HNO_3 at room temperature to lower the pH to 3.

Due to its amorphous nature, the silica from RHA is best extracted using sol-gel process at lower temperature. This is because the solubility of amorphous silica is very low at a lower pH, and therefore, enables the silica to be extracted in pure form by solubilisation under alkaline condition and subsequently precipitate at lower pH. (Kamath and Proctor,1998).

1.2.2 Modification of silica surface

The general purpose of supporting active sites of a homogeneous catalyst on an insoluble solid is to make a heterogeneous catalyts. There are many ways to make a heterogeneous system, this ranges from mere physisorption (adsorption by physical forces) onto the solid surface, to covalent anchoring. Covalent anchoring on silica surfaces is based on the presence of silanol groups. These silanol groups are of two types: Isolated, which are those with single hydroxyl group attached to the silicon atom ($\equiv$SiOH), and the germinal, which are those with two hydroxyl groups attached to the same silicon atom ($=Si(OH)_2$). The silica samples obtained by sol-gel synthesis have a considerably higher population of silanol groups, due to incomplete condensation of the molecular precursors (Coma and Garcia, 2006). When silica is treated at a temperature of about 900 °C, the neighbouring surface silanol groups condense together to form a siloxane bond [≡Si−O−Si≡]. The formation of siloxane bond is shown in Scheme 1.1



Scheme 1.1: The formation of siloxane bond by condensation of silanols

The most common methodology used to anchor other molecules on silica surfaces is the reaction of surface silanol groups with silylating reagents (Coma and Garcia, 2006). These silylating agents are chemically reactive towards the free silanol groups on the silica surface (Cestari, et al., 2001). The silylating agents are usually alkoxysilanes with general formula $(RO)^3Si - R^*$ where *R* is methyl or ethyl groups and *R** is an *n*–propylic carbon chain containing end functional groups such as: amine, halogen or sulfur, or a combination of them (Cestari & Airoldi, 1997).

One of the advantages of immobilisation of functional groups on the silica surface through the silylating agents is to make the functional group resistant to elimination by the use of water and other organic solvents (Arakaki and Airoldi, 2000).

1.3 Solid sulfonic acid catalyst

Acid-catalyzed reactions are among the most extensive areas for the application of heterogeneous catalysis (Sheldon and Downing, 1999). A solid acid catalyst is a solid porous support (rigid or non-rigid) upon which active acid groups are grafted or otherwise incorporated. In the past, traditional homogeneous acid catalysts such as $AlCl_3$, HF, BF_3, H_2SO_4 etc, were mainly used for liquid phase reactions, but due to some drawbacks such as production of large volume of toxic waste during catalyst separation, and corrosiveness, it makes the process economically unacceptable and environmentally hazardous (Margolese et al., 2000).

Al-MCM-41 was among the earliest solid acid catalysts synthesised, but due to its low acid strength (Armengol et al., 1995), it has been replaced with more efficient organic-inorganic supported materials such as alkyl and aryl sulfonic acid groups (Nakajima, 2005; Diaz, et al., 2000; Lim, et al., 1998; Van Rhijn, et al., 1998).

Sulfonic acid resins such as Amberlyst-15 suffer from low surface area and thermal stability (Shimizu et al., 2004), while zeolites provide some reaction products with high conversion and selectivity. However, these catalysts also suffer from diffusion restrictions, due to small pore diameter (Hermida et al., 2008). These makes them unsuitable for liquid phase reactions, especially with bulky molecules such as 1,3-dioxane and 1,3-dioxolanes. To overcome this drawback, a number of silica supported catalysts such as SBA-15 sulfonic acid (Margolese et al., 2000), MCM-41 sulfonic acid (Van Rhijn et al., 1998), and even polymer supported sulfonic acids (Xing, et al., 2007; Siril, et al., 2007) have been employed in acetalization, esterification, ketalization, and other related processes. This is partly because these catalysts are non-volatile, recoverable, and easy-to-synthesize. These types of catalysts are also generally regarded as “green catalysts”, because of their eco-friendly nature.

The tedious work-up procedure such as several hours of refluxing and use of hazardous chemicals such as tetraethoxysilane (TEOS) as silica source or poly(ethyleneglycol), and cetyltrimethylammonium bromide (CTAB), as template, are considered as the main drawbacks of this types of solid acid catalysts. In the present work, template-free, and one-step process was used to synthesize a silica supported sulfonic acid catalyst, using rice husk ash (RHA) as a cheap source of silica, under ambient conditions.

1.4 Guanidines

Guanidines are regarded as organic super bases (Costa, et al., 1998). This is due to the resonance stability of their conjugated acids (Yamamoto, and Kojima, 1991). Guanidinium salts are well known for their denaturing action on proteins; for example, in a 6.0 M solution of guanidinium chloride, almost all proteins lose their ordered secondary structure.

In addition to the electron donating ability of the C=N bond, guanidines also possess a lone pair of electrons which can act as Lewis base. This is why they are used in several base catalysed reactions.

As strong organic bases, guanidines catalyse various types of organic reactions. Among the guanidine compounds; 1,1,3,3-tetramethylguanidine(or N,N,N-tetramethylguanidine, (TMG) is regarded as a typical and fundamental guanidine compound, and it has been utilised in many kinds of base-catalysed reactions. Another example, is the preparation of pentaalkylguanidines by Barton et al., (1982) and their application in organic synthesis as sterically-hindered organic bases, which are called ‘Barton’s bases’. Similarly, bicyclic guanidines, such as, 1,5,7-triazabicycle(4.4.0)dec-5-ene (TBD) and its *N-methyl* analogue (MTBD) were introduced by Schwesinger, (1985). One of the derivatives of guanidine, which is refered to as arginine, is found in the side-chain of the amino acid, and plays an important role in the interaction with enzymes or receptors through hydrogen bonding and/or electrostatic interactions, largely because of its strong basic character (de Assuncao, et al., 2010).

Guanidines have been used both as homogeneous and heterogeneous catalysts in several base catalyzed organic reactions, such as Michael addition (Ye, et al., 2005; Ma and Cheng,1999), transesterification of vegetable oils (Schuchardt, et al., 1998; Serchelli, et al.,1999; Faria, et al, 2008; Meloni, et al., 2011), methylation of phenol (Bercelo, et al., 1990), Aldol and Knoevenagel condensation reactions (Serchelli, et al., 1997), esterification of glycerol (Jerome, 2004) and in cyclo addition of carbon dioxide to cyclic carbonates (Zhang, et al., 2006; Barbarini, et al., 2003; Dai, et al., 2009).

1.4.1 Functionalisation of silica with guanidine

The silica material can be functionalised with an organic moiety using a silylating agent. These silylating agents can be functionalised on the silica either by one-pot process or post synthesis-grafting method. While the later involves high refluxing temperature and use of toxic chemicals, on the other hand, the former is an eco-friendly method and less time consuming. So far, most of the works published indicated the use of post synthesis grafting method for the covalent attachment of organic moieties on to the silica surface. In addition to the variation in the methods adopted to functionalise silica, other types of alkyl silane linkers have also been used to functionalise silica with several types of guanidines. For example, trimethoxysilylpropoxymethyloxirane was used as a linker in Michael addition reactions (Rao, et al., 2003), and in transesterification reactions (Sercheli et al., 1999).

1.4.2 1,1,3,3-Tetramethyl guanidine (TMG)

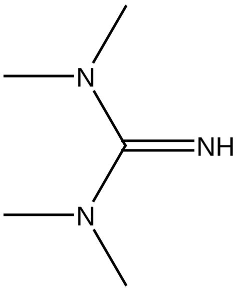


Fig. 1.1: The structure of 1,1,3,3-tetramethylguanidine

Tetramethylguanidine is among the different types of guanidines with the molecular formula $HNC(N(CH_3)_2)_2$. It is a colourless liquid with strong basic character comparable to that of NaOH. Few literature reports have shown that, tetramethylguanidine can be immobilised on solid support and be used as a heterogeneous catalyst as detailed out below.

Faria, et al, (2008) has reported the immobilisation of tetramethylguanidine on silica gel and applied it as a catalyst on transesterification of vegetable oil to produce biodiesel. The catalyst was effective in the transesterification of soya bean with methanol. Using 0.5 g amount of catalyst and reaction temperature of 80 °C, 86 % yield was achieved in three hours reaction time. It was also found to be recoverable and reusable nine times, thus satisfying many principles of green chemistry.

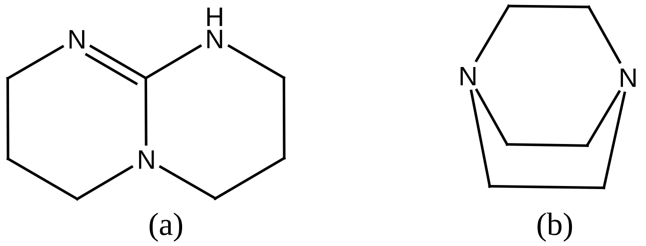
De Oliveira, et al., (2006) has reported a methodology for the attachment of tetramethylguanidine to silica gel by co-condensation process and used the catalyst in the Michael addition reaction between nitro methane and cyclopentenone. Under mild reaction conditions, the result presented an excellent yield of 98 % after 3 h.

Studies on the preparation and use of silica supported tetramethylguanidine and triazabicyclodecene guanidine as catalysts in the epoxidation reaction of alkenones was reported by Blanc et al., (2000). Results show that, the conversion and selectivity depends on the type of catalyst employed. The same catalysts were also found to be effective in the Aldol condensation of malonic acid with heptanal. However, the reusability studies for this reaction proved to be poor, possibly due to adsorption of some by products, such as diols at the active site.

The immobilisation of ionic liquid, 1,1,3,3-tetramethylguanidinium lactate on two kinds of support, SBA-15 and bentonite were studied by Liang, et al., (2010). The catalysts were proved to be excellent for the reaction of methanol with propylene oxide to form propylene glycol methyl ether (PGME). At the optimised reaction conditions, the yield of (PGME) and selectivity towards 1-methoxy-2-propanol over the TMG-bentonite catalyst was as high as 89 and 93 % respectively.

1.4.3 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD)

Bicyclic guanidine bases such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 1,4-diazabicyclo[2.2.2]octane (DABCO) are among the class of guanidines with strong basic character.



(a) (b)

Fig. 1.2: The structures of (a) 1,5,7-triazabicyclo[4.4.0]dec-5-ene and (b) 1,4-diazabicyclo[2.2.2]octane.

Among these bases, triazabicyclodec-5-ene has been shown to promote various organic transformations, such as Wittig reaction (Simoni, et al., 2000). The reaction was carried out in the presence of polymer supported bicyclicguanidine catalyst. Results show that, between 80-95 % conversion was achieved in 1 h at 0 °C. However, the catalyst was not active for aliphatic ketones and acetophenone. Similar catalyst has also been used in the nitro Aldol condensation reaction. Under mild reaction conditions, high conversion was achieved within few minutes (Simoni et al., 2000).

A mild, catalytic and efficient methodology for the Micheal-type reactions, using homogeneous TBD as catalyst was reported by Ye, et al., (2005). Their study showed that, TBD catalysed the reaction much faster compared to other organic bases.

The cyanosilylation of aldehydes and ketones with trimethylsilyl cyanide (TMSCN) was studied by Matsukawa, (2012). The reaction was carried out in the presence of 1 mol % polymer supported TBD catalyst. High yield was achieved, but the reaction was carried out in presence of CH_3CN solvent, and the polymer supported catalysts usually suffer from swelling when in contact with the solvent.

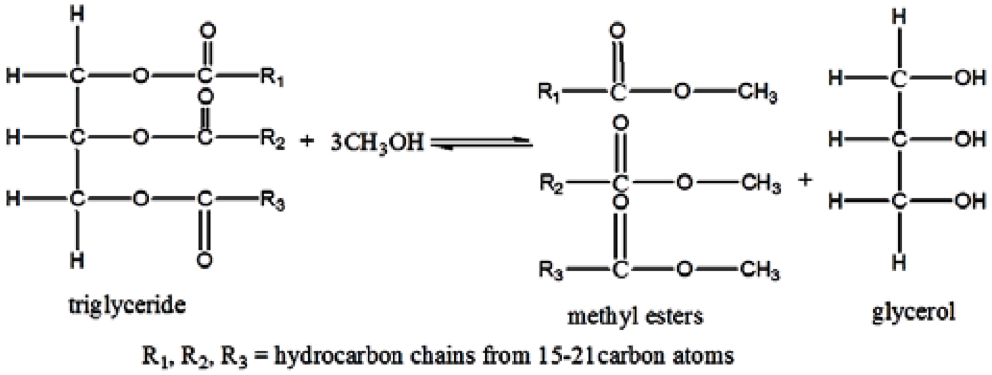
The chemical fixation of CO_2 to propylene carbonate over various amine-functionalised silica catalysts was investigated by Zhang, et al. (2006), their study indicated that, among the amine-functionalised catalysts, TBD/SiO_2 showed the highest catalytic activity, showing 100 % conversion in 20 h using 20 bar CO_2 pressure.

The design of a suitable catalyst to activate CO_2 into more useful products must consider energy input, eco-friendly process and simple work-up procedure. In this context therefore, the use of toxic chemicals, complicated methodology, or the application of higher temperatures during catalyst preparations are obvious limitations.

While a large body of work has been devoted to the study of the chemistry of ionic bases, and their utility in organic synthesis is well established (Simoni et al., 2000), non-ionic nitrogen bases such as guanidines have not been fully utilised for similar organic transformations. In addition to their simplicity in handling, non-ionic bases such as guanidines are also environmentally friendly and commercially available. This is why these types of organocatalysts offer the practical alternatives for several catalytic transformations, such as cycloaddition of CO_2 to epoxides.

1.5 Glycerol production

Environmental pollution has been a source of concern for the growing population. Efforts must be made to minimise the presence of these pollutants, otherwise, the effect could be catastrophic. As a result of increasing demand for renewable energy, biodiesel production has been on the increase and by extension to glycerol as well. However, one of the challenges in the production of biodiesel is disposal of the glycerol which is a by-product. Every three molecules of biodiesel results in the production of one molecule of glycerol (Scheme 1.2)



Scheme 1.2: The transesterification reaction of triglyceride with methanol showing the formation of glycerol as by-product. The equation shows that, every three molecules of biodiesel produced, one molecule of glycerol is formed as by-product.

Biodiesel production has created a large influx of glycerol into the market. The great challenge here is what to do with the glycerol that is produced as by-product. Reports have shown that, every one metric ton of biodiesel produced is accompanied by 100 kg of glycerol as by product (Behr, et al., 2008). As of 2008, it has been estimated that, the world biodiesel production had reached 12.24 million metric tonnes (Lines, 2009; Zhou, 2008). By extension this means that, 1.224 million metric tonnes of crude glycerol was produced from the biodiesel conversion process. With the increased expansion of biodiesel and the sharp decrease in the glycerol prices, the excess crude glycerol produced must be utilised in the best way possible. Some of the excess glycerol is utilised for pharmaceutical and food applications. However, the rest end up as a waste and is largely disposed by incineration (Liang, 2011). The burning of glycerol in power station results in poor energy conversion and inefficient combustion, thereby creating pollution.

1.5.1 Applications of glycerol

The first industrial application of glycerol was discovered in 1860 by Alfred Nobel, during the production of nitroglycerin, which later gave access to production of dynamite (Sudarsanam, 2013). Since then, various reaction methodologies have been evolved for the transformation of glycerol to valuable chemicals, such as, etherification, esterification, acetalisation, oligomerisation, polymerisation, pyrolysis, hydrogenolysis and many other applications (Behr et al., 2008). Below are some important applications of glycerol.

1.5.1.1 Food industry

In the 21st century, the increasing world population faced two major problems, these are; the supply of food and energy. In order to meet the demand of food, the commercial production of fats and oils has increased rapidly. In 1970 the total production of fats and oils was in the range of 40 million tons (MT).This value increased to about 144 MT in 2005. A further rise to about 200 MT can be foreseen by the year 2015. In many such processes, the natural fats and oils are used in food applications to obtain chemical products some of which can lead to glycerol as a by-product (Behr, 2008).

Glycerol is used as an artificial sweetener, which is a substitute to sugar; it is also used as a softening agent in candy and cakes, as a solvent for certain flavours, and as a substitute ingredient in animal feed (Lines, 2009).

1.5.1.2 Pharmaceuticals Industry

Glycerol is used as an additive in cough syrup, toothpaste, skin and hair care products and in soap manufacturing (New world Encyclopaedia, 2008).

1.5.1.3 Chemicals Industry

Explosives - Nitroglycerin is a compound made from glycerol, this compound is commonly used in all types of explosives (Lines, 2009).

1.5.1.4 Acetalisation of glycerol

One of the important applications of glycerol is the condensation reaction with aldehydes or ketones to form cyclic acetals. These acetals are useful in cosmetics (Bauer, 1990), pharmaceuticals (Bruns, 1979), food and beverage industries (Behr, 2008; Climent, 2002) as fuel additives (Mota, et al., 2010), surfactants, flavours, disinfectants and so on (Silva et al., 2010).

Until recently, most catalysts employed for the acetalization and ketalisation reactions are generally, Lewis acids (Umbarkar, et al., 2009) and several types of transition metal complexes such as Rh, Pd and Pt (Cataldo, 1999). Although the use of these types of catalyst may yield good results, however, the separation of the catalyst from the reaction mixture and products may be a strong draw-back, in addition to the expensive nature of these noble metals. Recently, a series of heterogeneous catalytic processes of converting glycerol to acetals has been reported in the literature. For instance, Deutsch et al. (2007) reported the use of zeolite, amberlyst-36 and perfluoroalkane sulfonic acid polymer catalysts, for the condensation of glycerol with aldehydes and ketones. Results of their study showed that, when formaldehyde was used in place of benzaldehyde, high selectivity towards 6-membered cyclic acetal was obtained. However, when the reaction was carried out in presence of acetone, instead of formaldehyde, higher selectivity towards 5-membered cyclic acetal was achieved.

The formation of heterocyclic acetals from the reaction of glycerol and acetaldehyde (in a port wine condition) was investigated by Antonio (2002). During the oxidative aging, the concentrations of the *cis- and trans-5-hydroxy-2-methyl-1,3dioxane and cis- and trans-4-hydroxymethyl-2-methyl-1,3-dioxolane* isomers increased with time.

The valorisation of glycerol with acetone over silica-immobilised heteropoly cids, i.e. molybdophosphoric (PMo), tungstosilisic (SiW) and molybdosilisic (SiMo) acids were investigated by Ferreira, et al., (2010). Their report showed about 98% selectivity towards solketal ((2,2-dimethyl-1,3-dioxolan-4-yl)methanol).

A comparative study on the acetalisation of glycerol with formaldehyde employing homogeneous Bronsted and Lewis acids was performed by Ruiz, et al., (2010). Results of their study indicated that, the valorization of pure glycerol and glycerol in water was achieved by reaction with aldehydes to form valuable acetals. It was also discovered that, homogeneous para-toluenesulfonic acid was more active than solid Brønsted acids such as zeolites and resins.

In general, the reaction of glycerol with carbonyl compounds give acetals as the major product; however, the selectivity of the acetal is usually a function of the type of carbonyl compound employed and sometimes the nature of the catalyst used.

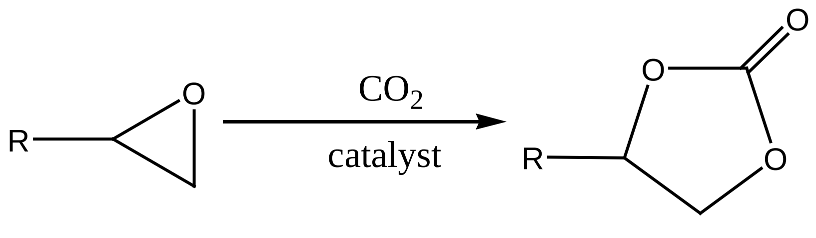
1.6 Transformation of CO_2 into cyclic carbonate

Despite its environmental impact, carbon dioxide remains an economical C1 source for organic synthesis- it being an inexpensive reagent, non-toxic and renewable. Its utilisation to generate valuable chemicals has attracted much attention (Omae, 2006; Sakakura, 2007; Sakakura, 2009). In 1800, before the industrial era, the atmospheric level of CO_2 was about 280 ppm (Neftel, 1988; Barnola, 1987).

However, its level continues to rise reaching 367 ppm in 1999. The rate of increase is unprecedented, reaching 391.57 ppm in 2011 (Neftel, 2011). Most of the increasing level of CO_2 is associated with anthrapogenic activities, such as emissions from vehicles and industries. About three-quater of these emissions are due to burning of fossil fuel (Odenberger and Johnsson, 2010).

The increasing level of CO_2 in the atmosphere is of greater concern, especially to the survival of our planet Earth. However, besides trying to implement regulations to reduce CO_2 emission, one of the best ways is to utilise CO_2 to transform it to important compounds such as cyclic carbonates. These carbonates are classified into cyclic and linear, which include; propylene carbonate (PC), styrene carbonate (SC), dimethyl carbonates (DMC), and ethylene carbonates (EC). Cyclic carbonates are colorless, odorless, and biodegradable chemicals that have many applications such as, polar aprotic solvents, electrolytic and engineered polymeric materials as well as precursors for the synthesis of many pharmaceutically important and fine chemicals (Tu and Davis, 2001; Babarini, et al., 2003; Gosh et al., 2010).

With the rising demand for these organic carbonates, the use of CO_2 as a raw material in these transformations has been extensively studied.



Scheme 1.3: Equation of synthesis of cyclic carbonate from CO_2 and epoxide.

A particularly studied reaction involving CO_2 is the synthesis of five-membered cyclic carbonate via the coupling of CO_2 epoxide, as shown in scheme

1.3. Many organic and inorganic compounds, including metals (Kihara, et al., 1993), ammonium salts, (Nishikubo, et al.,2003), metal oxides (Yano, et al., 1997; Yamaguchi, et al., 1999, Tu and Davis, 2001) and most recently ionic liquids (Peng and Deng, 2001; Yang, et al., 2002; Kim, et al., 2002; Kim, et al, 2005; Xiao, et al., 2006), have reported to catalyse the reaction of CO_2 with epoxides. However, problems with the separation process, poor reusability and sensitivity to air are some of the draw backs of these types of catalysts. The immobilisation of homogeneous catalysts to transform them into heterogeneous catalysts has become the pursuit of researchers in recent times (Corma and Garcia, 2006). In sections 1.4.2 and 1.4.3 of this thesis, some literature review is described in the use of heterogeneous base catalysts for the synthesis of cyclic carbonates.

In the past, the conventional methods for the synthesis of cyclic carbonate involved the use of phosgene, which is a very toxic chemical (Darensbourg, 1996, Fujita, et al., 2002; Aresta and Didenedetto, 2002). However, the present idea of CO_2 insertion to cyclic ethers to produce cyclic carbonates using immobilised base catalysts is regarded as one of the safest and ecofriendly methods.

1.7 Problem Statement

Rice Husk is an agricultural biomas produced during rice milling. Except for the small fraction of rice husk that is utilised for heating and other purposes, the rest of it constitutes a huge waste which demands proper disposal. The use of rice husk for the synthesis of green catalyst is therefore, an important step towards resource utilisation and pollution control. Similarly, both glycerol and carbon dioxide are industrial waste products which contribute to environmental pollution and global warming respectively. Effective utilisation of these waste products for the synthesis of important compounds is also another step towards recycling and a hazard free society. In this context therefore, the development of solid acid and base catalysts for the purpose of converting these environmental contaminants is very essential.

1.8 Scope of the study

The research focused on the synthesis of three heterogeneous catalysts, namely; RHAPrSO$_3$H, RHAPrTMG and RHAPrTBD, using rice husk ash as source of silica. A simple and eco-friendly sol-gel method was employed in the preparation of the catalysts.

The catalysts were characterised using various physico-chemical techniques, such as Fourier Transformed-Infrared (FT-IR) spectroscopy, to study the functional groups present, Microscopy analysis such as, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM), to study the surface morphology of the samples. The Thermo gravimetric Analysis (TGA) was also performed to study the stability of the prepared catalysts. The textural properties such as specific surface area, pore volume and pore diameter were measured using nitrogen gas adsorption desorption analysis. The silicon-29 and carbon-13 CP/MAS NMR study was also performed to determine the ^{29}Si and ^{13}C environments on the solid catalysts.

The solid acid catalyst was tested using the reaction of glycerol with benzaldehyde, while the base catalysts were tested using the reaction of CO$_2$ with cyclic ethers. The reaction conversion was determined using gas chromatography (GC) and the products were identified using gas chromatography mass spectrometer (GC-MS).

1.9 Objectives of the study

The main objectives of this work are to:

1. To extract silica from rice husk ash and modify its surface with propyl sulfonic acid; 1,1,3,3-tetramethylguanidine and 1,5,7-triazabicyclo[4.4.0]dec-5-ene as catalysts using 3-(Mercaptopropyl)trimethoxysilane and 3-(chloropropyl) triethoxysilane as silylating agents.
2. To characterise the catalysts using various techniques such as CHN, TGA/DTA, XRD, nitrogen adsorption-desorption, FT-IR, solid state NMR, SEM/EDX and TEM.
3. To study the catalytic activity of silica-propyl sulfonic acid using acetalisation of glycerol with benzaldehyde.
4. To study the catalytic activities of silica-tetramethylguanidine and silica-triazabicyclo decene in the cyclo addition of carbon dioxide to epoxides.

1.10 Thesis outline

This thesis consists of seven chapters, as briefly described in the following section.

Chapter 1 describes the concept of catalysis and catalysts classification. It also discusses about rice husk as a source of silica and the various methods of its extraction, based on literature review. The chapter also describes the important applications of glycerol as a by-product of biodiesel synthesis. Similarly, the role of carbon dioxide as a green house gas and its utilisation as a raw material in the synthesis of cyclic carbonate has been discussed.

Chapter 2 gives an account of the extraction of silica from rice husk ash and its subsequent use in the synthesis of the catalysts. It provides an overview of the various physico-chemical characterisation methods used in the study. The chapter also discusses the detailed experimental procedure used in the study.

Chapter 3 discusses in details about the characterisation and the surface properties of the catalysts.

Chapter 4 describes the catalytic study on RHAPrSO_3H catalyst. Acetalisation of glycerol with benzaldehyde was used as a model reaction. The effect of various reaction parameters, such as; time, temperature, catalyst amount, molar ratio of the reactants and type of solvents have been evaluated. Reusability study on the catalyst was performed to determine its stability. The isolation and single crystal study on one of the reaction products was also carried out.

Chapter 5 discusses the catalytic study of RHAPrTMG and RHAPrTBD as solid base-catalysts. The cyclo addition of carbon dioxide to epoxides was used as the model reaction. The effect of various reaction parameters, such as; time, temperature, catalyst amount and CO_2 pressure, have been investigated. Reusability study on the catalyst was performed to determine its stability.

Chapter 6 describes the chemical fixation of CO_2 with unsupported TMG and TBD catalysts. The chapter discusses the study of the reaction of CO_2 with the catalysts at room temperature and atmospheric pressure. Both ^{13}C and ^{15}N MAS NMR study was carried out on the reaction products. Interesting results showed that, CO_2 can be activated by the guanidine at ambient conditions.

Chapter 7 is the conclusion and possible recommendation for future studies on the research.