THE HETEROGENATION OF SACCHARIN, MELAMINE AND SULFONIC ACID ONTO RICE HUSK ASH SILICA AND THEIR CATALYTIC ACTIVITY IN ESTERIFICATION REACTION

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by

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LIST OF SYMBOLS AND ABBREVIATIONS

APTES	3–(aminopropyl)triethoxysilane
AR	Room Temperature
CHN	Carbon, Hydrogen, and Nitrogen Elemental Analysis
ca.	Calculated
CP	Cross Polarisation
CPTES	3–(chloropropyl)triethoxysilane
DMF	Di–methylformamide
DCM	Di–chloromethane
E_a	Activation Energy
EDX	Energy Dispersive X–ray
Fig	Figure
FT-IR	Fourier Transform Infra–Red spectroscopy
Et_3N	Tri–ethylamine
GC	Gas Chromatography
GC–MS	Gas Chromatography Mass Spectroscopy
IUPAC	The International Union of Pure and Applied Chemistry
R	Alkyl group
RHA	Rice husk ash
MPTMS	3–(mercaptopropyl)trimethoxysilane
N	Surface Coverage
Sac	Saccharine
SEM	Scanning Electron Microscopy

Si–OH	Silanol
Si–O–Si	Siloxane
k_a	The Apparent Rate Constant
kJ	Kilo joule (The unit of energy)
M	Molar Amount of Grafted
Mela	Melamine
MAS NMR	Magic angle–spinning Nuclear Magnetic Resonance
pp	Page
P/P_o	Relative Pressure
pH	The Hydrogen Function
P_W	Weight Percentage
T	Tesla (Unit For Measuring Magnetic Induction)
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analyses
XRD	X–ray Diffraction

PENGHETEROGENAN SAKARINA, MELAMINA DAN ASID SULFONIK KE ATAS SILIKA ABU SEKAM PADI DAN AKTIVITI PEMANGKINAN DI DALAM TINDAK BALAS PENGESTERAN

ABSTRAK

Natrium silikat daripada abu sekam padi (RHA) telah dimodifikasikan dengan 3–(kloropropil)trietoksisilan (CPTES), 3–(merkaptopropil)trimetoksisilan (MPTMS) dan 3–(aminopropil)trietoksisilan (APTES) untuk menghasilkan RHACCl, RHAPrSH dan $RHAPrNH_2$ melalui kaedah sintesis one–pot. Analisis ^{29}Si MAS NMR pada RHACCl menunjukkan kewujudan pusat silikon T^2, T^3, Q^3 dan Q^4 manakala pusat silikon T^1, T^2, T^3, Q^2, Q^3 dan Q^4 wujud pada RHAPrSH dan RHAPrNH. Spektrum ^{13}C MAS NMR menunjukkan RHACCl mempunyai 3 anjakan kimia pada 10.37, 26.70 dan 47.69 ppm yang merujuk kepada 3 atom karbon moiti CPTES. RHAPrSH mempunyai anjakan kimia pada 16.59, 32.73 dan 14.58 manakala $RHAPrNH_2$ menunjukkan hanya dua daripada tiga jalur yang dijangkakan pada 26.13 dan 47.87 ppm disebabkan oleh pertindihan kedua jalur antara satu sama lain. Kombinasi analisis CHN dan EDX telah menunjukkan kewujudan unsur klorin di dalam RHACCl, sulfur di dalam RHAPrSH, nitrogen di dalam $RHAPrNH_2$ dan seterusnya kewujudan karbon dan silikon yang membuktikan silylating agents bergabung dengan silika RHA. Sakarin (Sac) dan Melamina (Mel) immobilized dengan silika untuk membentek RHAC-Sac dan RHAPrMela. Kedua spektrum ^{29}Si MAS NMR, RHAC-Sac dan RHAPrMela menunjukkan anjakan kimia yang sama dengan RHACCl. Spektrum ^{13}C MAS NMR menunjukan RHAC-Sac mempunyai siri anjakan kimia yang konsisten dengan kehadiran gelang aromatik dan laktam. Dua anjakan kimia pada 161.52 dan 169.67 ppm dengan jalur sisi putaran dubel pada ^{13}C MAS NMR RHAPrMela, menunjukkan tiga atom karbon di dalam gelang

melamina tidak ekuivalen dalam RHAPrMela. Kumpulan berfungsi $–CH_2–SH$ dalam RHAPrSH telah dioksidakan ke asid sulfonik, $–CH_2–SO_3H$ dengan hidrogen peroksida pada suhu bilik. ^{29}Si MAS NMR menunjukkan anjakan kimia yang serupa dengan RHAPrSH. Tiada pertindihan anjakan kimia C3 dan C2 dalam ^{13}C MAS NMR diperhatikan selepas tranformasi kepada $RHAPrSO_3H$. RHAC-Sac, RHAPrMela, $RHAPrSO_3H$ dan RHA–Blank (kawalan) berserta dengan Sac dan Mela homogen digunakan sebagai mangkin dalam tindak balas esterifikasi. Aktiviti mangkin keatas ester didapati mengikut urutan berikut:

$RHAPrSO_3H$ > RHAPrMela > Sac homogen > RHAC-Sac > Mela homogen > RHA–Blank.

Mangkin diaktifkan semula dengan pemanasan untuk mengeluarkan air dan boleh digunakan semula beberapa kali tanpa kehilangan sifat mangkinnya.

THE HETEROGENATION OF SACCHARIN, MELAMINE AND SULFONIC ACID ONTO RICE HUSK ASH SILICA AND THEIR CATALYTIC ACTIVITY IN ESTERIFICATION REACTION

ABSTRACT

Sodium silicate from rice husk ash (RHA) was functionalized with 3–(chloropropyl)triethoxysilane (CPTES), 3–(mercaptopropyl)trimethoxysilane and 3–(aminopropyl)triethoxysilane to give RHACCl, RHAPrSH and $RHAPrNH_2$ via a simple one–pot synthesis. The ^{29}Si MAS NMR of RHACCl showed the presence of T^2, T^3, Q^3 and Q^4 silicon centres, while the T^1, T^2, T^3, Q^2, Q^3 and Q^4 silicon centres were present in both RHAPrSH and $RHAPrNH_2$. The ^{13}C MAS NMR showed that RHACCl had three chemical shifts at 10.37, 26.70 and 47.69 ppm, which was attributed to the three carbon atoms of the CPTES moiety. $RHAPrNH_2$ had chemical shifts at 16.59, 32.73 and 14.58, while RHAPrSH showed only two signals at 26.13 and 47.87 ppm instead of the expected three signals. This was due to the superimposition of two signals on each other. The combination of elemental and EDX analysis showed the presence of chlorine in RHACCl, sulfur was found in RHAPrSH and nitrogen was found in $RHAPrNH_2$ as well as the presence of carbon and silicon in the samples confirmed that the silylating agents were incorporated onto RHA silica. Saccharine (Sac) and Melamine (Mela) were immobilized onto RHACCl to form RHAC-Sac and RHAPrMela. Both ^{29}Si MAS NMR spectra of RHAC-Sac and RHAPrMela showed similar chemical shifts to the RHACCl. The ^{13}C MAS NMR showed that RHAC-Sac had a series of chemical shifts consistent with the presence of the aromatic and lactam ring. Two chemical shifts at 161.52 and 169.67 ppm with double spinning side bands were seen in the ^{13}C MAS NMR of RHAPrMela, indicating that the three carbon atoms in the melamine ring were not

equivalent. The functionalized –CH_2–SH group in RHAPrSH was oxidized to sulfonic acid, –CH_2–SO_3H with hydrogen peroxide at room temperature. The ^{29}Si MAS NMR showed similar chemical shifts to the RHAPrSH. No overlapping of the C3 and C2 chemical shifts in the ^{13}C MAS NMR was observed after the transformation to RHAPrSO_3H. RHAC-Sac, RHAPrMela, RHAPrSO_3H, RHA–Blank (as control) as well as homogenous Sac and homogenous Mela were used as catalysts in the esterification reaction. The catalytic activity of the catalysts toward the respective esters was found to follow the sequence below.

RHAPrSO_3H > RHAPrMela > homogenous Sac > RHAC-Sac > homogenous Mela > RHA–Blank.

The catalysts were easily regenerated by heating to remove water and could be reused several times without loss of catalytic activity.

Chapter One

Introduction

1.0 Overview

Zhuravlev (2000) and Vansant, et al. (1995) stated that studies on silica started in the1930s when a number of scholars such as Endell, Wilm, Carman and Rideal studied the condensation processes of silicic acids which led to the discovery of surface silanol groups, ≡Si–OH. After that, by using an infrared spectroscopy method, Yaroslavsky and Terenin had proved the presence of hydroxyl groups on the silica surface (porous glass) (Zhuravlev, 2000). Because of numerous spectral and chemical data, it has become well known that silica has two types of functional groups, i.e. the siloxane (≡Si–O–Si≡) in the bulk and several forms of silanol groups (≡Si–OH) on its surface.

There are two surface silanol groups found experimentally on the silica surface: the isolated (a single hydroxyl group attached to the silicon atom, ≡SiOH) and the geminal (two hydroxyls group attached to the same silicon atom, $=Si(OH)_2$) as shown in Fig 1.1. Hydrogen bonds can be formed between the two vicinal silanol groups (Yang, et al., 2006). On the other hand, silica shows three types of siloxane groups (≡Si–O–Si≡). According to NMR study, these siloxane groups (≡Si–O–Si≡) are represented as Q^n, where *n* indicates the number of bridging bonds (–O–Si) tied to the central Si atom, i.e.: Q^4 – four siloxane bonds to the silicon atom; Q^3 – three siloxane bonds to the silicon atom; and Q^2 – two siloxane bonds to the silicon atom

as shown in Fig 1.1. Generally, the number of siloxane groups can be determined from the following equation: $Q^n = Si\ (OSi)_n(OH)_{4-n}$ (Zhang, et al., 2006).

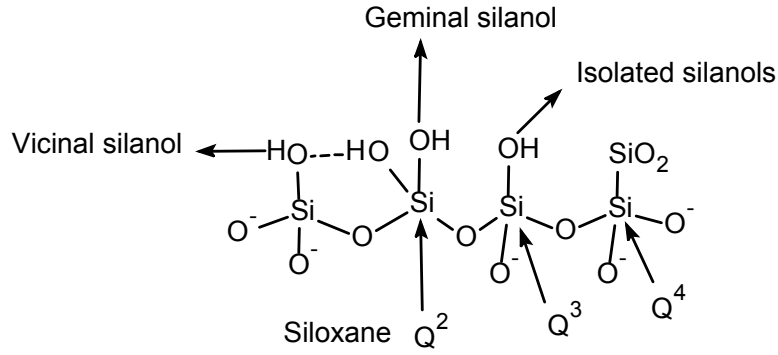


Fig. 1.1: Types of silanol groups and siloxane bridges on the surface of silica [adopted from Zhuravlev, 2000].

1.1 Silica Modification

The modification of the silica surface has received a great deal of attention (Brunel, 1999; Bae, et al., 2000; Airoldi & Arakaki, 2001; Al–Nahhal, et al., 2007; Gübbük, et al., 2008). This process can empower the researchers to control and change the chemical properties and technological characteristics of the composite material. The modification of the silica surface is important for the preparation of essential for the synthesis of materials with many specific properties; these could be for the preparation of selective heterogeneous catalysts, nanostructured silica materials and liquid crystals (Tertykh & Belyakova, 1996).

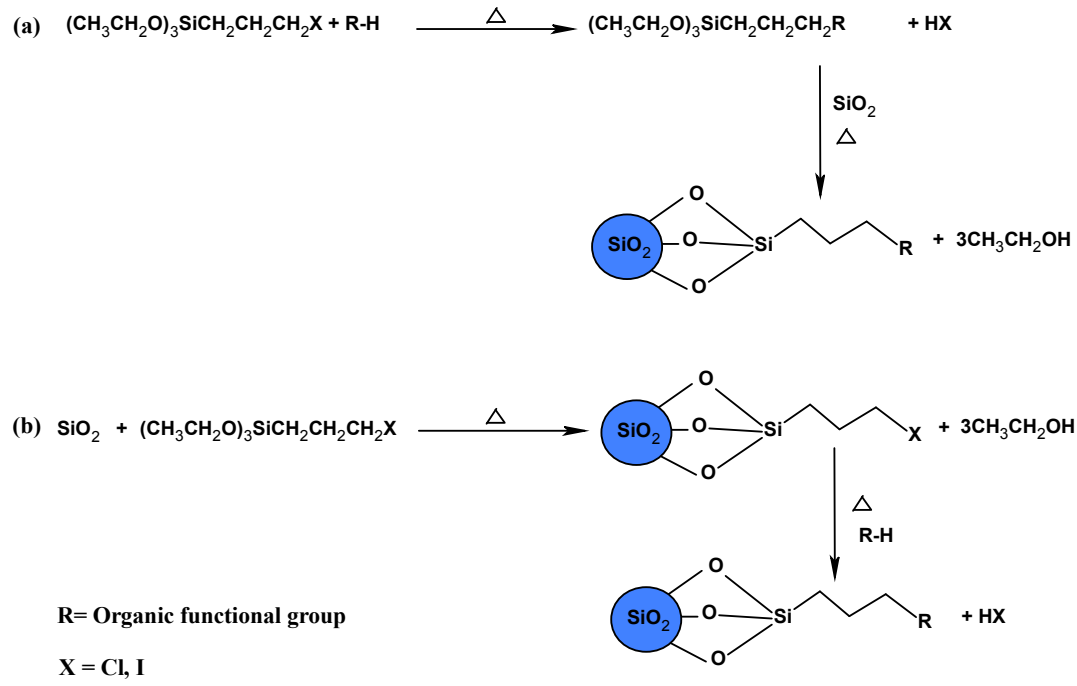
The silanol groups on the silica surface play a significant role during modification of the surface with alkyl silanes (Dash, et al., 2008). As the temperature increases, the silanol groups on the silica surface are dehydrated. The continuous

increase in temperature leads to the dehydration of silanol groups (Peng, et al., 2009) resulting in the formation of siloxane bond.

The modification of silica is mostly carried out by using organic molecules in order to functionalize its surface. 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 $(RO)_3$Si–*R**, where *R* is methyl or ethyl groups and *R** is an *n*–propylic carbon chain containing an end functional groups, e.g.: amine, halogen or sulfur group, or a combination of them (Cestari & Airoldi, 1997).

Silica modified with silylating agent is one of the best choices to introduce basic groups through an anchored pendant chain (Prado & Airoldi, 2001a). One of the important advantages of the immobilization of functional groups on silica via this route is to make the organic functional group resistant to removal from the surface by different organic solvent or water (Arakaki & Airoldi, 2000). It also offers good thermal and hydrolytic stability with accessibility to the reactive centres (Prado & Airold, 2001b; Filha, et al., 2006).

There are two strategies for the immobilization of the silylating agents. The first strategy is to react the silylating agents with the ligand complex, and then to immobilize the resulting ligand with the pre–formed silica in a heterogeneous reaction as in Scheme 1a. The second strategy is to treat the post–polysiloxane with the complex group as in Scheme 1b.



Scheme 1.1: (a) The reaction of silylating agent with the ligand complex followed by immobilizes the resulting ligand onto silica. (b) The immobilized of silylating agent onto silica followed by immobilized the ligand complex.

Both strategies have been studied widely by many researchers (Vrancken, et al., 1995; Brunel, 1999; Bae, et al., 2000; Hoegaerts, et al., 2000; Airoldi & Arakaki, 2001; Al–Nahhal, et al., 2007; El–Ashgar, et al., 2007; Gübbük, et al., 2008; Shi & Wei, 2008). It was observed that these two reported preparation methods involved long preparation times and they utilized hazardous chemicals leading to inefficient preparation techniques as discused in the sub–section below.

1.1.1 Immobilized halide systems

Silica modified with 3–(chloropropyl)triethoxysilane (CPTES) is usually carried out in a solid–liquid mixed phase reaction (heterogeneous reaction). Bae, et al. (2000), Hoegaerts, et al. (2000), Shi and Wei (2008) had reported that the reaction needs to be refluxed in toluene for 12–24 h. This is followed by soxhlet extraction

with different organic solvents such as toluene and dichloromethane. Brunel (1999) had reported the functionalization of silica (which was pre–dried at 150 °C at 10^{-1} Torr for 12 h) by refluxing it with CPTES in toluene at 120 °C with total time of approximately 14 h. Alcântara, et al. (2007) showed that 3–(chloropropyl)trime–thoxysilane (CPTMS) can also be used to functionalize silica to produce the same product. However, the reaction needs to be refluxed for 72 h at 150 °C. The same reaction was carried out by Soundiressane, et al. (2007) by refluxing CPTMS with silica for 24 h, followed by soxhlet extraction with dichloromethane (DCM) for 12 h. Kovalchuk, et al. (2006) had reported that amorphous silica needs to be refluxed in aqueous HNO_3 (2 M) for 6–10 h, followed by washing with distilled water and dried at 150 °C for 4 h. Finally, the post–synthetic treatment was performed to graft the silica with CPTES, by heating at 130–150 °C in air or at 200 °C under vacuum.

1.1.2 Immobilized amine ligand systems

The condition for functionalization of 3–(aminopropyl)triethoxysilane (APTES) is almost similar to CPTES. Hoegaerts, et al. (2000) took 31 h, using toluene, diethyl ether and dichloromethane as solvents during various stages of the transformation. While Macquarrie and Jackson (1997) and Macquarrie (1996) took 21 h to functionalize APTMS onto silica, employing different techniques such as reflux and extraction. Brunel (1999) also needed 27 h to fabricate APTES onto silica. However, the temperature used was quite high, i.e. 120 °C and 150 °C for the fabrication reaction. Brunel used toluene, diethyl ether and DCM as solvents during the reaction and the extraction procedures. Wu, et al. (2008) had reported the functionalization of silica by refluxing it with APTES in toluene, followed by soxhlet extraction with total time of approximately 48 h. The method used by

Vejayakumaran, et al. (2008) needed 36 h to fabricate APTES onto silica. Multiple technique, higher temperature and different organic solvents were used during these fabrication process.

1.1.3 Immobilized thiol ligand systems

Silica gel modified with 3–(trimethoxysilyl)propane–1–thiol (MPTMS) has been studied by Eunice, et al. (1997) and Simoni, et al. (2000). Functionalized polysiloxane containing thiol ligand was prepared by hydrolytic polycondensation of silica with $(MeO)_3Si(CH_2)_3SH$. The anchored thiol groups can be oxidized to provide sulfonic acid functionality for the applications in solid acid catalysts (Yang, et al., 2005). The potential use of these derivatives as well as other organo functional derivatives critically depends on the loading of accessible functional groups into the framework (Prado & Arakaki, 2001c).

To graft MPTMS onto silica, Yang, et al. (2005) took 5 days to immobilize it onto silica using different hazardous organic solvents. Shylesh, et al. (2004) modified the silica with MPTMS in 61 h, and used toluene and methanol during the process under a nitrogen atmosphere. The method used by Bossaert, et al. (1999) needed 54 h to fabricate MPTMS onto silica. They used multiple techniques and different organic solvents during the fabrication process. Karimi and Khalkhali (2005) and Gupta, et al. (2007) had tried to activate the silica by refluxing in concentrated hydrochloric acid for 24 h; and then they proceeded with another reflux with MPTMS in dry toluene for 18 h. They also used soxhlet extraction for 36 h. The total time required for the whole process was 78 h.

The brief review above shows that the present methods to functionalize silica with CPTES, APTES and MPTMS resulted in low yield, employing harsh reaction conditions, multiple steps, long reaction time, using non–environmental friendly organic solvents, use of high energy, and costly chemicals. Therefore, there is a need to design a new method which is easy, cost–effective, environment–friendly, time saving, minimal energy loss, high yield and can be used especially in the heterogenation of homogeneous catalysts. Such a method could have a wide impact.

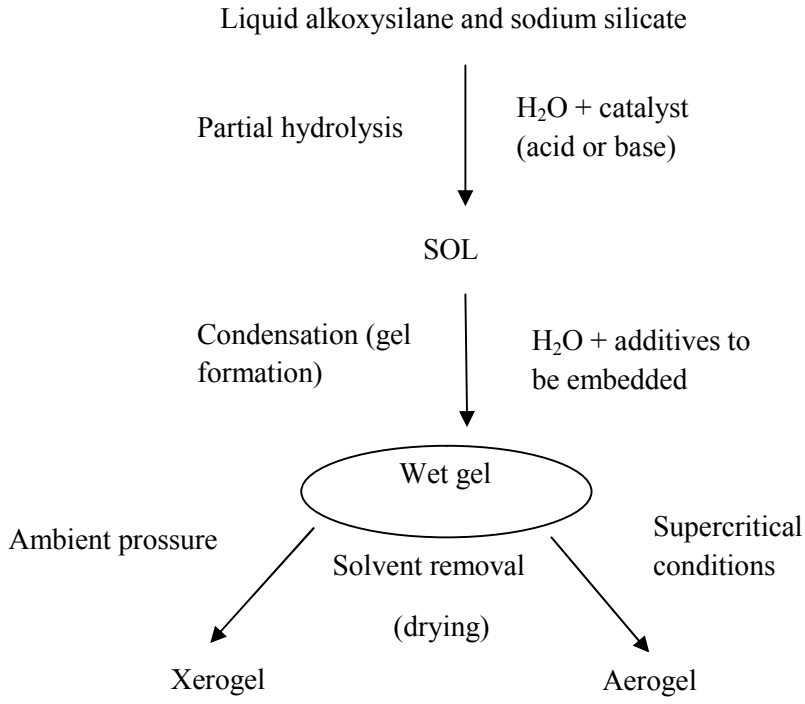
1.2 Sol–gel process

Sol–gel method is one of the well known wet chemical methods. It is a transitional process between a liquid phase "sol" to the solid phase "gel" (Ahmed, 2008); or it can be seen as a hydrolysis and condensation of silicon (or any other metal alkoxides) and organoalkoxysilanes (Hofacker, et al., 2002).

The recent great interest in organic–inorganic hybrid materials prepared by sol–gel chemistry along with the growing interest in functionalization of inorganic matrices may be due to the ease in which it can be used to design unique materials with controllable pore size, structural rigidity, thermal stability, and enhanced recognition properties (Airoldi and Arakaki, 2001; Arrachart, et al., 2009).

According to Prokopowicz, et al. (1998), more than 89 % of the literature describing the application of materials to chemically modify surfaces deals with sol–gel. The sol–gel process comprises several steps in general. When the silicate precursor mixes with silylating agent in the presence of the solvent (water or alcohol) and a catalyst (acid or base), which was stirred for several hours, leads to

partial hydrolysis of the Si–O–R (R = methyl or ethyl group) bonds in the silylating agent. When alcohol is used as a solvent, the hydrogel structure will be formed. There are some parameters that control the hydrogel structure. These parameters include temperature, pH of the medium, nature of the solvent, nature of the added electrolyte and the type of the starting salt or alkoxide. The xerogel is formed by aging and drying the gel. If the gel has a very large pore volume (up to 98 % of the total volume), it is named as aerogel (Vansant, et al**.**, 1995). Scheme 1.2 shows the details of these (Teoli, et al., 2006).



Scheme 1.2: The usual steps of a sol–gel process [adapted from Teoli, et al., (2006)].

Scheme 1.3 shows some equations of reaction proposed by Chen and Lin (2003). This is to explain the hydrolysis and polymerization which may take place in the sol–gel processes. As shown in the reaction equations below, hydrolysis of the

precursor produces a sol of soluble hydroxylated monomer (equation 1.1), followed by polymerization and phase separation to form a hydrated oxide hydrogel (equation 1.2). Controlled removal of water from the wet gel by extraction or drying produces the dry, porous xerogel (equation 1.3).

$$\equiv Si–OR + H_2O \longrightarrow \equiv Si–OH + ROH \quad (1.1)$$

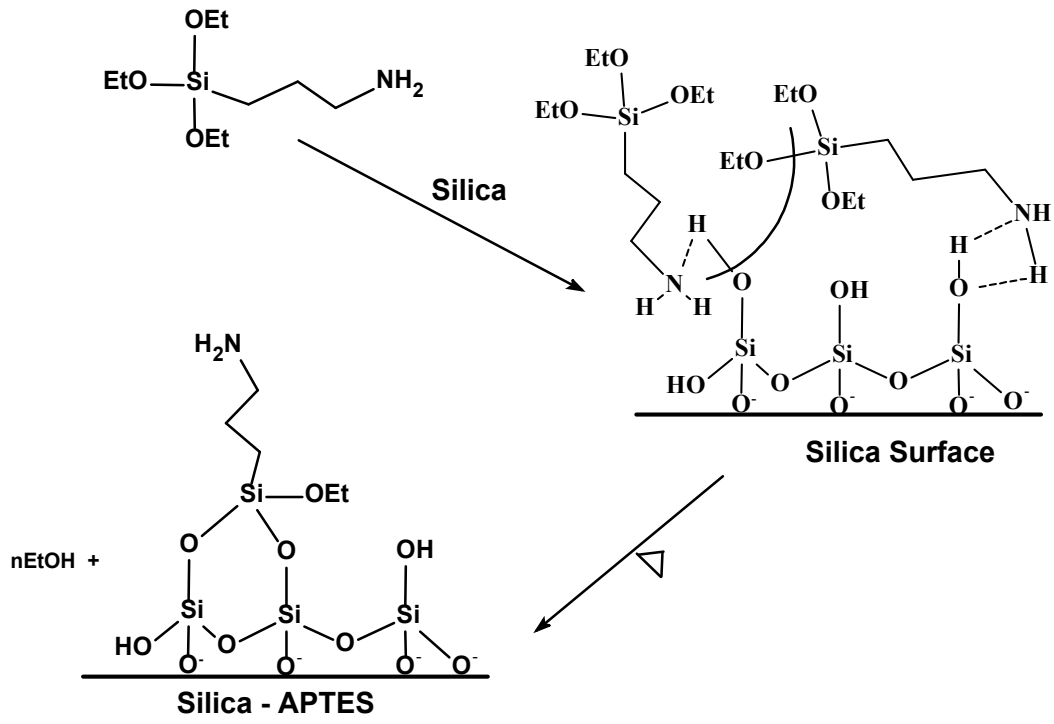
$$\equiv Si–OH + RO–Si\equiv \longrightarrow \equiv Si–O–Si\equiv + ROH \quad (1.2)$$

$$\equiv Si–OH + HO–Si\equiv \longrightarrow \equiv Si–O–Si\equiv + H_2O \quad (1.3)$$

Scheme 1.3: The probable reaction during the hydrolysis of alcohol and water condensation in the sol–gel processes.

1.3 Proposed mechanism of silica gel modified with silylating agent

The reaction mechanism between silylating agent and silica gel could be a type of condensation reaction. The general sequence for the condensation of APTES is given in Scheme 1.4. In this type of mechanism, small molecules will be liberated as a result of the condensation. According to Vansant, et al. (1995), and Vrancken, et al. (1995) the initial step of silica modification includes physical adsorption. This physisorption depends on the availability of silanol groups on the silica surface and the hydrogen bond between silanol groups and the silylating agent. The hydrolysis of ethoxy silane group leads to form silanol group. The formed silanol group will be condensed to form siloxane bonds at the surface.



Scheme 1.4: The reaction mechanism for the condensation of silylating agent onto silica.

1.4 Rice Husk

Rice husk (RH) is a cellulose–based fibre which is suitable for recycling (Ndazi, et al., 2007). Rice is grown in over 75 countries (Huang, et al., 2001). The annual world rice production amounts to 400 – 545 million metric tons, of which more than 10 % is husk (Conradt, et al., 1992; Mansaray and Ghaly, 1998; Feng, et al., 2004). Due to the high silica content in the husk (Yalçin, et al., 2000), it makes economic sense to utilize this free raw material. RH contains about 20 % silica which can be extracted and used in many areas where commercial silica is being used (Della, et al., 2002).

Rice husk is composed of 20 % ash, 38 % cellulose, 22 % lignin, 18 % pentose, and 2 % other organic components and water (Adam & Chua, 2004). Burning the rice husk causes environmental pollution. Therefore, efforts have been

made to burn the husks under moderate temperature and pressure (Feng, et al., 2004). When burning the rice husk, a white ash which is porous silica with high specific surface area can be obtained (Watari, et al., 2006). This ash (RHA) contains more than 95 % silica. Table 1.1 below shows a typical analysis of RHA obtained at 700 °C (Della, et al., 2002). It can be seen that ca. 95 % of the ash in the composed of silica, SiO_2.

Table 1.1: Chemical composition of RHA after burning out at 700 °C for 6 h [adapted from Della, et al., (2002)].

Oxides	Component expressed as RHA %
SiO_2	94.95
Al_2O_3	0.39
Fe_2O_3	0.26
CaO	0.54
Na_2O	0.25
K_2O	0.94
MnO	0.16
TiO_2	0.02
MgO	0.90
P_2O_5	0.74
Loss on ignition at 700 $^{\circ}C$	0.85

1.5 The applications of silica from rice husk ash (RHA)

The existence of silica in RHA was known since in 1938. The acid leaching, pyrolysis, and carbon–removing processes from rice husk can give amorphous silica (Radhika & Sugunan, 2006). The purity of silica in RHA can reach as high as 99.9 % (Chang, et al., 2003). The silica extracted from rice husk has many advantageous properties, such as high chemical and thermal stability, high specific surface area, high porosity, good accessibility (Gupta, et al., 2007), and functionalization of organic groups can be robustly anchored to the surface.

Chang, et al. (2003) was the first to describe the use of RHA as a support for heterogeneous catalyst. He used RHA as a support for nickel catalyst which exhibited a very high activity in the hydrogenation of CO_2. Adam, et al. (1990, 2004, 2006, 2007, and 2008) have described the use of RHA silica as a support for different metals, such as, Al, Gl, In, Fe, and Ru and used them as heterogeneous catalysts for different purposes.

1.6 Saccharine

Saccharine (Sac) or *o*–sulfobenzimide was discovered accidentally by Fahlberg in 1878 during his PhD research, and published it a year later (Remsen & Fahlberg, 1879). A short time after this discovery, Sac was produced on an industrial scale as the first sweetening agent which does not contain carbohydrate, with a sweetening power of about 550 times that of sucrose (Ellis, 1995; Baran, et al., 2006).

Sac can be synthesized by the oxidation of *o*–toluenesulfonamide using $KMnO_4$ in a base medium to produce sodium *o*–sulfonamidobenzoate which can give Sac by acidifying the latter, using HCl (Vogel, 1973).

Sac has different hetero atoms within its molecule, one N, one O (carbonylic) and two S=O (sulfonic) atoms. Using these donor atoms, the anion can generate either N– or O–monodentate or bidentate (N, O) coordination, and also more complex polymeric species with the participation of all possible donor atoms. These atoms have lone pair electrons which combine with the strained ring of the Sac molecule. This could in essence act as catalytic sites imparting a certain degree of selectivity. These hetero atoms can also be used to form coordination bonds with transition metals that can be utilized further for catalysis. In this regard, Adam, et al. (2007) had reported the synthesis of a Sac–Cu coordination complex, $Cu(Sac)_2 – 2H_2O$ which has a square planar configuration at the copper centre. It is believed that these complexes could be more useful if they were immobilized onto solids.

Several Sac derivatives were synthesized by Yablonsky, et al. (2001); they have found applications for the monomers of polycondensation, bioactive substances, and additives improving the nickel plating process and others. Their study also proved that Sac molecules can associate with carbonyl groups due to H–bonds and it can also form eight member ring dimmers (see Fig. 1.2).

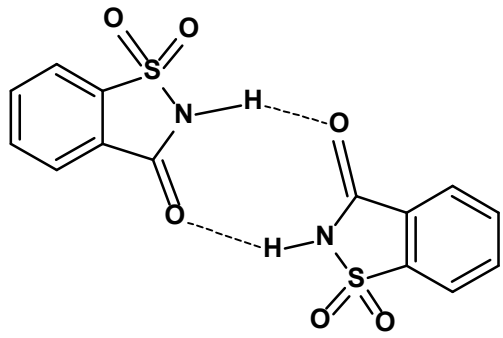


Fig. 1.2: The dimerization of two molecules of Sac via H–bonds giving rise to the eight member ring structure.

1.7 Melamine

Melamine (Mela) (1,3,5–triazine–2,4,6–triamine) with a chemical formula of $C_3H_6N_6$ is an organic compound that consists of 66 % nitrogen (Wu, et al., 2009). It has several industrial uses such as in the manufacture of amino resins and plastics (Cook, et al., 2005; Buu, et al., 2008).

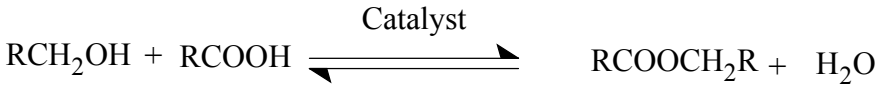
Mela was first synthesized by Justus von Liebig in 1834 by heating dicyandiamide above its melting temperature (Bozzi, et al., 2004). Mela is commercially available and it has been used in a wide range of products. For example, it is combined with formaldehyde to produce melamine resin as durable thermosetting plastic, and melamine foam as a polymeric cleaning product (Rima, et al., 2008). However, it must be acknowledged that the recent misuse of Mela in tainted infant milk powder raised awareness worldwide. It also raised our curiosity and interest due to the presence of a large number of heteroatoms in the Mela molecule.

Mela can directly react with reducing sugars (specifically with lactose and Strecker aldehydes) to consequently interfere with Maillard reactions in chemical

model systems. It was found that Mela influences the levels of different kinds of volatile products and colour development in Maillard[1] models. The presence of melamine in foods can therefore have a significant impact on various organoleptic properties (Ma, et al., 2010).

1.8 Esterification

The condensation of organic acids and alcohols produce esters, (see Scheme 1.5). The esters with small molecular weight are industrially important intermediate class of substances in the synthesis of fine chemicals, polyesters, drugs, plasticisers, food preservatives, pharmaceuticals, solvents (for cellulose, oils, gums, and resins), perfumes, cosmetics, pesticides and chiral auxiliaries (Haslam, 1980; Lilja, et al., 2002; Bhagiyalakshmi, et al., 2004; Palani & Pandurangan, 2005).



R = alkyl or aryl group

Scheme 1.5: The reaction of alcohol with organic acid to produce ester.

[1]*Maillard reactions:* the reaction of active carbonyl group of the reducing sugars (such as glucose, fructose and lactose) with the nucleophilic amino groups of amino acids, peptides or proteins, and subsequently produces a large number of poorly characterised compounds, contributing to the colour and flavour of foods.

Esterification reaction is a liquid–phase process and can take place without adding catalysts due to the weak acidity of carboxylic acids. However, the reaction requires several days to attain equilibrium in the absence of catalysts (Liu, et al., 2006a). Therefore, adding a catalyst for the liquid–phase process is necessary (Ajaikumar & Pandurangan, 2007). There are two types of catalysts for the esterification reactions, either homogenous, by strong mineral acids or heterogeneous. The mineral acid used for the esterification reaction involves the use of H_2SO_4, HCl, HF, H_3PO_4 and $ClSO_2OH$. These acids suffer from drawbacks such as high toxicity and corrosion. The excess acid has to be neutralized after the reaction and left behind considerable amounts of salts to be disposed off into the environment. Since all these substances are miscible with the reaction medium it is very difficult to separate them, and reusability of the catalyst is usually not possible (Lu, 1995; Liu & Tan, 2001; Harmer & Sun, 2001; Lilja, et al., 2002).

Hence, the catalyst for this process should be replaced by a heterogeneous process; therefore, there is a need to design a heterogeneous catalyst (Sheldon, 1997). The design of new heterogeneous catalysts requires some conditions. One of these conditions is the availability and simplicity of the preparation procedures. It must be also cost–effective, and reduce the waste to minimize environmental pollution which is a crucial factor for developing environmentally friendly catalysts. The recoverable and reusability is also one of the important conditions and advantages of heterogeneous catalysts (Liu & Tan, 2001; Harmer & Sun, 2001; Dash & Parida, 2007).

In this regard, several types of heterogeneous catalysts have been reported in the literature for esterification. These include iodine (Ramalinga, et al., 2002), copper (Inui, et al., 2002), lipase (Novak, et al., 2003), MCM–41 (Díaz, et al., 2001; Koster, et al., 2001), zeolites beta (da Silva–Machado, et al., 2000), ion exchange resin (Gimenez, et al., 1987), supported acids (Yang, et al., 2005), and acidic ionic liquids (Gui, et al., 2004). There are two types of heterogeneous catalysts for the esterification reaction, i.e. acid catalysts and base catalysts. Both catalysts are discussed in detail below.

1.8.1 Esterification by using base catalyst

Esterification by base catalysts has not received much attention because it is usual to use acids to catalyse this reaction. A reaction between a carbon–halogen functional group and an organic base or ligand such as amine groups is a nucleophilic substitution reaction (Cauvel, et al., 1997; Lasperas, et al., 1997). These organic amines and ammonium salts have been used as base heterogeneous catalysts for esterification reactions (Barcelo, et al., 1990; Gui, et al., 2004).

In this regard, Brunel (1999) had functionalized some organic amines onto silica such as piperidine, 1,5,7–triazabicyclo[4.4.0]dec–5–ene and (1*R*,2*S*)–ephedrine. These compounds proved to be efficient base catalysts for transesterification reaction and Knoevenagel[1] condensation. These catalysts are shown in Fig. 1.3.

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[1] *A Knoevenagel condensation* is a nucleophilic addition of an active hydrogen compound to a carbonyl group followed by a dehydration reaction in which a molecule of water is eliminated. The product is often an alpha, beta conjugated enone.

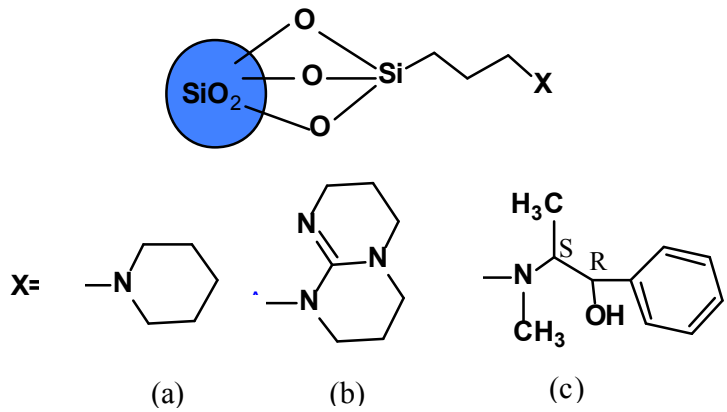

Fig. 1.3: Some examples of base functionalized silica. (a) piperidine, (b) 1,5,7–triazabicyclo[4.4.0]dec–5–ene, (c) (1*R*,2*S*)–ephedrine.

Several pentaalkylguanidines have been prepared and found to be superior catalysts for the preparation of aryl and aryl alkyl ethers from carbonates and for the methylation of phenols with dimethylcarbonate. They also act as effective catalysts for esterification of acids with alkyl chloroformates (Barcelo, et al., 1990).

Kobayashi and Okamoto (2006) investigated the catalytic potential of some organic compounds for acylation of 1–phenylethylalcohol with acetic anhydride (Ac_2O) at room temperature. The investigation showed the catalytic activity of the catalysts followed the sequence as shown in Fig. 1.4. In these studies, these organic molecules were used as homogeneous catalysts.

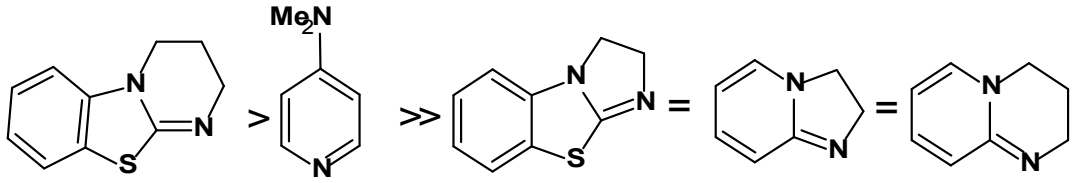

Fig. 1.4: The relative catalytic activity of various organic molecules in the acylation reaction. [adopted from Kobayashi & Okamoto, 2006].

Schuchardt, et al. (1995) explained the use of eight homogenous substituted cyclic and acyclic guanidines on transesterification of rapeseed oil with methanol. The conversion was 90 % yield of methyl esters with in 1 h of reaction. They stated that alkylguanidines can easily be heterogenized on chloromethylated polystyrenes (Schuchardt, et al., 1996). The catalysts that they used showed a good activity towards transesterification.

Kovalchuk et al, (2009) had described the immobilization of heteropolyacids on functionalized silica with (3–propyl–N–pyridinium, 3–propyl–N–methyl and 3–propyl–N–butyl–imidazolium) salts. These catalysts had been used to catalyse the reaction of acetic acid with ethanol. The conversion of acetic acid was measured after 20 h and found to be in the range of 15.5 to 68 %. However, they used multiple techniques for the catalysts preparation and the time used for esterification was quite long with poor yield.

Mercs et al., (2007) had tested ammonium triflates as direct catalysts for esterification reaction using toluene as a solvent in 7 h reaction time at 80 °C. The catalyst had shown good catalytic activity and was easily recovered by simple phase separation.

Rad et al, (2008) had used *N*-(*p*-toluenesulfonyl)imidazole (TsIm) as a catalyst for esterification reaction. In their experiments, the alcohols were refluxed with a mixture of RCO_2Na (R: alkyl and aryl), TsIm, and triethylamine in the presence of catalytic amounts of tetra-*n*-butylammonium iodide (TBAI) in DMF to afford the corresponding esters. Different solvent had been tested and the conversion

of ester was in the range of 0 to 94 % at different reaction times. The maximum conversion of ester was 94 % when DMF was used as the solvent. However, different organic solvents were used during the fabrication process with poor yield of ester.

1.8.2 Esterification by using acid catalyst

Heterocids are widely used in a variety of acid–catalyzed reactions as in esterification. It has been observed that solid acids such as modified forms of zeolites and oxides are very efficient for esterification (Nagaraju & Mehboob,1996). The esterification of glycerol with lauric acid to produce monolaurin using zeolites, sulfonic resins, and sulfonic mesoporous materials as catalysts has been investigated by Bossaert, et al. (1999).

Jackson, et al. (2006) functionalized organosulfonic acid on to mesoporous silica and tested them to see their catalytic performance in the esterification of oleic acid with methanol under supercritical carbon dioxide flow. The study found the activation energy was about 42 kJ mol^{-1} and the activity of the catalyst was shown to be independent of pore size. The catalyst showed higher activity than that of Novozym[1] 435.

[1]Novozym 435 is a lipase (lipase B) from *Candida antarctica* produced by submerged fermentation of a genetically modified *Aspergillus* microorganism and adsorbed on a macroporous resin [adapted from Novozym® 435, 2010].

Miao and Shanks (2009) functionalized mesoporous silica with different loadings of propylsulfonic acid groups by using a one–step co–condensation procedure. The resulting materials were effective in the esterification of acetic acid with methanol. They used this as a model reaction for stabilization of bio–oil. The catalyst showed multiple cycle stability without significant loss of activity.

Yang, et al. (2005) described the synthesis of sulfonic acid–functionalized hydrophobic mesoporous benzene–silica with lamellar pore wall structure. They found that the mesoporous benzene–silica was attached to propylsulfonic groups to the crystal–like periodic pore walls. The catalyst showed higher conversion compared to the commercial Nafion–H (sulfonated tetrafloroethylene, $C_7HF_{13}O_5S.C_2F_4$).

1.9 Esterification of long–alkyl chain fatty acid

Esterification of long–alkyl chain fatty acids with alcohols represents a well–known category of liquid–phase reactions of considerable industrial interest due to the enormous practical importance of organic ester products (Altıokka & Çıtak, 2003). Recently, the esterification of long–alkyl chain fatty acids has spurred a great deal of interest due to their important and multiple applications. For example, long–alkyl chain fatty acid esters can be used as a biofuel. The esters produced from long–alkyl chain fatty acids (12–20 carbon atoms) and short–alkyl chain alcohols (three to eight carbon atoms) have been used increasingly in the food, detergent, cosmetic and pharmaceutical industries (Bauer, et al., 1990). Esters prepared from the reaction of long–alkyl chain acids with long–chain alcohols (12–20 carbon atoms) also have important applications as plasticisers and lubricants (Gandhi, et al., 1995). It is

economically important to develop catalysts for the production of such esters from cheaper and more broadly available raw materials.

1.10 Objectives of the study

As mentioned earlier, scientists discovered silanol groups on silica surface in 1930. These silanol groups have been used to heterogenize silylating agents through heterogeneous methods. Due to the unfavourable conditions of the current method, this study aims to improve on these conditions. It must be clarify that Sac and Mela have never been used as a homogenous or heterogeneous catalyst in any form based on the literature reviewed. The main objectives of this work are:

1. To modify the silica extracted from RHA with different silylating agents such as CPTES, MPTMS and APTES via a simple one–pot synthesis.
2. To use this new method to synthesize RHAC-Sac, RHAPrMela and RHAPrSO_3H as heterogeneous catalysts.
3. To characterize the catalysts using various spectroscopic and microscopic techniques such as CHN analysis, TGA, Powder X–ray, N_2 adsorption–desorption, FT-IR, ^{29}Si and ^{13}C MAS NMR, SEM/ EDX and TEM.
4. To investigate the catalytic potential of the catalysts on the esterification of different alcohols with acetic acids.
5. To determine the reaction kinetic parameters of each catalyst in the esterification reaction.

1.11 Outline of Thesis

This thesis consists of six chapters. They are briefly outlined below.

Chapter 1 provides an overview on the study and reviews the available literature on silica modification. It describes the synthesis strategies and the mechanism of synthesis. It also discusses some relevant materials such as Sac, Mela, acid and base catalysts for esterification.

Chapter 2 gives an account of the synthesis of silica with silylating agent using a simple strategy and also describes the catalysts synthesis with physicochemical characterization method used in this study. It also describes the experimental procedures used in this study.

Chapter 3 and 4 deals with the physicochemical characterization of the samples synthesized by different methods. The elemental composition was determined using a combination of chemical analysis (CHN) with Energy Dispersive X–ray (EDX). Thermal analysis and N_2–sorption studies are used to calculate the loading of the grafted organic molecule. FT-IR spectroscopy is used to monitor the change in the functional groups. Solid state ^{29}Si and ^{13}C MAS NMR studies were carried out to understand the catalysts structures. X–ray diffraction (XRD), Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) were also used to determine the morphology of the modified silica and the synthesised catalysts.

Chapters 5 describe the catalytic performances of the bases and acid catalyst samples. The esterification of ethanoic acid versus different alcohols were investigated. The effect of reaction time, temperature, molar ratio of the reactants and the amount of the catalyst on esters formation were evaluated to optimize the reaction conditions. The reusability of the catalyst, the temperature effect on the regeneration of the catalyst, the reactions of methanol with different acids (acetic acid (C2), capric acid (C10) and myristic acid (C14)), reaction kinetics and mechanisms are also reported.

Finally, in **Chapter 6** a summary of the results obtained and the conclusions are presented.

Chapter Two

Experimental Methods

2.0 Raw materials

All chemicals are of AR grade or high purity and was used directly without further purification. These include; sodium hydroxide (Systerm, 99%), nitric acid (Systerm, 65%), CPTES (Sigma–Aldrich, 95%), MPTMS (Merck, 95%), APTES (Merck, 98%), toluene (J.T. Baker, 99.8%), Sac (Fluka, 99%), Mela (Acros Organics, 99%), hydrogen peroxide (J.T. Baker, 30%), triethylamine (Et_3N) (R&M chemical, 99%), dimethylformamide (DMF) (Systerm, 99.5%), dichloromethane (DCM) (Merck, 99%), methanol (Systerm, 99.9%), ethanol absolute (HmbG Chemical, 99.74%),1–propanol & 1–butanol (R&M chemical, 99.5%), benzyl alcohol (Unilab, 97%), tertiary–butyl alcohol (Merck, 99%), 2–propanol (Unvasol, 99%), acetic acid (Systerm, 99.5%), capric acid (C10) (Acidchem, 99%), myristic acid (C14) (Acidchem, 98%), and n–decane (Acrös Organics, 99%). The rice husk (RH) was collected from a rice mill in Penang, Malaysia.

2.1 Extraction of silica from rice husk

The rice husk RH was chosen as the source of amorphous silica as it was available in abundance. The silica was extracted from RH according to a reported method Kalapathy, et al. (2000); Ahmed (2008).

The RH was washed with water then rinsed with distilled water and dried at room temperature for 24 h. A 35 g sample of the cleaned RH was stirred with