

**THE HETEROGENIZATION OF SULFANILIC AND SULFONIC
ACIDS AND THEIR CATALYTIC ACTIVITY IN THE LIQUID-
PHASE ALKYLATION OF PHENOL**

By

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Praise belongs to God,

The First, without a first before Him, the Last, without a last behind Him.

Beholders' eyes fall short of seeing Him,

Describers' imaginations are unable to depict Him.

He originated the creatures through His power with an origination;

He devised them in accordance with His will with a devising.

He made them walk on the path of His desire,

He sent them out on the way of His love.

Nothing can go against God's willing.

He assigned from His provision to every human A

spirit nourishment known and apportioned. No

decrease decreases those whom He increases;

No increaser increases those of them whom He decreases.

Each spirit He strikes a fixed term in life, for each He sets up a determined end;

When I walk through the days of life and research embracing the reckoning of time,

God seizes me the abundant reward,

His Grace, His Mercy and His Greatest Love..

Worth of Praise above all!

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LIST OF SYMBOLS AND ABBREVIATIONS

RH	–	Rice husk
RHA	–	Rice husk ash
SiO ₂	–	Silica
Si-O-Si	–	Siloxane
Si-OH	–	Silanol
TMOS	–	Tetramethoxysilane
TEOS	–	Tetraethoxysilane
CPTES	–	3-(chloropropyl)triethoxysilane
EWG	–	Electron withdraw group
IUPAC	–	The International Union of Pure and Applied Chemistry
BET	–	Brunauer, Emmett and Teller
RHABzSO ₃ H	–	Sulfanilic acid supported on silica from RHA
RHAPrSO ₃ H	–	Sulfonic acid group supported on silica from RHA
FT-IR	–	Fourier transform infra-red SEM
	–	Scanning electron microscopy TEM
	–	Transmission electron microscopy
EDX	–	Energy dispersive X-ray spectroscopy
XRD	–	X-ray Diffractometry
TGA	–	Thermogravimetric Analysis
BJH	–	Barret, Joyner and Halenda

CEC	–	Cation exchange capacity
TBA	–	<i>Tert</i> -butanol
DTBP	–	Di- <i>tert</i> -butylphenol
TTBP	–	Tri- <i>tert</i> -butylphenol
TBPE	–	<i>Tert</i> -butylphenolether
IPP	–	Isoprpylphenol
TBOC	–	<i>Tert</i> -butylorthocresol
DTBOC	–	Di- <i>tert</i> -butylorthocresol
TTBOC	–	Tri- <i>tert</i> -butylorthocresol
TBOCE	–	<i>Tert</i> -butylorthocresolether
TBMC	–	<i>Tert</i> -butylmetacresol
DTBMC	–	Di- <i>tert</i> -butylmetacresol
TTBMC	–	Tri- <i>tert</i> -butylmetacresol
TBMCE	–	<i>Tert</i> -butylmetacresolether
TBPC	–	<i>Tert</i> -butylparacresol
DTBPC	–	Di- <i>tert</i> -butylparacresol
TTBPC	–	Tri- <i>tert</i> -butylparacresol
TBPCE	–	<i>Tert</i> -butylparacresolether
RHACCI	–	3-(chloropropyl)triethoxysilane supported on silica from RHA
MPTMS	–	3-(mercabto)trimethoxysilane
TBC	–	<i>Tert</i> -butylcresol
DTBC	–	Di- <i>Tert</i> -butylcresol
CTBE	–	<i>Tert</i> -butylcresol ether

LIST OF SYMBOLS

$^{\circ}\text{C}$	–	Celcius (degree temperature unit)
k	–	Reaction rate constant
P_0	–	Absolute pressure inside sample chamber (mm Hg)
P/P_0	–	Relative pressure
S_{BET}	–	BET specific surface area ($\text{m}^2 \text{ g}^{-1}$)
E_a	–	Energy of activation
R	–	Universal gas constant, $8.314 \text{ J}/(\text{mol K})$
T	–	Temperature
A	–	Frequency factor or Arrhenius constant
M	–	Molarity
\AA	–	Angstrom ($= 10^{-10} \text{ m}$)
nm	–	Nanometer ($= 10^{-9} \text{ m}$)

The heterogenization of sulfanilic and sulfonic acids and their catalytic activity in the liquid-phase alkylation of phenol

Abstract:

The new mesoporous silica modified with sulfanilic and sulfonic acids was synthesized by using rice husk ash (RHA) as the silica source. The solid catalysts were denoted as RHABzSO₃H and RHAPrSO₃H. The as-synthesized solid catalysts showed good textural and structural properties. The high-angle XRD diffraction pattern exhibited diffraction at 2 θ which corresponds to amorphous silica. The absence of sharp peaks suggests the material is not crystalline. The ²⁹Si MAS NMR showed the presence of T², T³, Q³ and Q⁴ silicon centres. The ¹³C MAS NMR confirmed that RHABzSO₃H had three chemical shifts consistent with the three carbon atoms of the propyl group and a series of chemical shifts consistent with the presence of the aromatic ring. The activity of the catalysts for the *tert*-butylation of phenol and some substituted phenols and derivatives of alcohol were observed to be positively influenced with increasing reaction temperature. However, it was negatively affected with increasing TBA: phenol molar ratio. The highest catalytic conversion (98 %) was observed over RHAPrSO₃H whereas highest selectivity was for 2-*tert*-butylphenol followed by 4-*tert*-butylphenol. The activity of the catalyst decreased in the order: phenol > *o*-cresol > *m*-cresol > *p*-cresol > 2-propanol > benzyl alcohol. The homogenous sulfanilic acid (un-supported) was less active compared to the heterogeneous catalyst. The catalysts were reused three times in the *tert*-butylation of phenol at the optimum conditions without significant loss in the activity.

Pengheterogenan asid sulfanilik dan sulfonik serta kebolehan memangkin tindak balas pengalkilan fenol dalam fasa cecair

Abstrak:

Silika berliang meso baru telah terkini disintesis dengan mengubahsuai silika yang diperoleh daripada abu sekam padi (RHA) menggunakan asid sulfanilik dan asid sulfonik. Mangkin yang terhasil dilabel sebagai RHABzSO₃H dan RHAPrSO₃H. Mangkin yang disediakan mempunyai kualiti tekstur dan struktur yang baik. Pembelauan XRD sudut tinggi menunjukkan pembelauan pada 2θ 22° yang menunjukkan sifat silika amorfus. Ketiadaan puncak tajam menunjukkan bahan bukan amorfus. Analisis ²⁹Si MAS NMR menunjukkan kehadiran atom silika berpusat T², T³, Q³ dan Q⁴. Analisis ¹³C MAS NMR mengesahkan bahawa RHABzSO₃H mempunyai tiga anjakan kimia konsisten dengan tiga atom karbon kumpulan propil dan beberapa lagi anjakan kimia yang menunjukkan kehadiran gelang aromatik. Peningkatan suhu tindak balas mempunyai pengaruh yang positif keatas aktiviti mangkin dalam tindak balas *tert*-pembutilanfenol dan beberapa kumpulan fenol tertukar ganti serta derivatif alkohol. Walau bagaimanapun, peningkatan nisbah antara TBA:fenol memberi impak negatif terhadap tindak balas tersebut. Penggunaan mangkin RHAPrSO₃H memberikan penukaran substrat tertinggi (98 %) manakala keselektifan yang tertinggi adalah untuk 2-*tert*-butilfenol diikuti oleh 4-*tert*-butilfenol. Aktiviti mangkin berkurangan mengikut urutan berikut: fenol > *o*-kresol > *m*-kresol > *p*-kresol > 2-propanol > benzil alkohol. Asid sulfanilik yang tidak disokong (mangkin *homogen*) adalah kurang aktif berbanding asid sulfanilik yang disokong (mangkin *heterogen*). Mangkin tersebut diguna semula sebanyak tiga kali dalam keadaan optimum tanpa mengalami sebarang kemerosotan dalam kereaktifannya.

Chapter One

Introduction

1.1 Rice Husk

Rice husk (RH) is an agricultural waste, obtained from rice mills after the separation of the rice from paddy. Rice husks produce high ash content, varying from 13 to 29 wt.% depending on the variety, climate, and geographic location. The rice husk ash (RHA) is largely composed of silica (87–97 %) with small amounts of inorganic salts (Lanning 1963). Though the ash of RH is rich in silica, the raw RH contains mainly organic matter (≈ 85 %) composed of cellulose, lignin, D-xylose, small quantities of methyl glucuronic acid and D-galactose. The elemental analysis of the organic matter as calculated by Sharma *et al.*, (1984) is 51 wt.% carbon, 7 wt.% hydrogen and 42 wt.% oxygen.

The presence of silica in rice husk has been known since 1938 (Martin, 1938). Many researchers have concluded that rice husk is an excellent source of high-grade amorphous silica. Due to its high silica content RH has become a source for preparation of a number of silicon compounds such as silicon carbide, (Krishnarao, *et al.*, 1991; 1998), silicon nitride (Hanna, *et al.*, 1985). RHA has good adsorptive properties and has been used for the removal of various dyes Rahman *et al.*, (2005) and Mane *et al.*, (2007), heavy metals Nakbanpote *et al.*, (2000), Khalid *et al.*, (2000), Kumar and Bandyopadhyay, (2006). Fixed bed column study was reported for Cd(II) removal from wastewater using treated rice husk, (Kumar and Bandyopadhyay, 2006; Srivastava *et al.*, 2006; Srivastava *et al.*, 2007) and other

compounds like chlorinated hydrocarbons (Imagawa *et al.*, 2000), palmytic acid (Adam and Chua, 2004), etc. The burning of RH in air always leads to the formation of rice husk ash varying in colour from grey to black and with inorganic impurities along with unburned carbon (Krishnarao *et al.*, 2001). RHA has fine particle size and high reactivity and has been used in the production of activated silica, sodium silicate, potassium silicate and solar grade silicon Banerjee *et al.* (1982). Figure 1.1 shows the physical colour and texture of RHA burnt at different temperature.



Fig. 1.1: The appearance of RHA obtained after calcining at different temperatures [Adapted from Krishnarao *et al.*, 2001].

1.2 Amorphous silica

Amorphous silica, i.e., silicon dioxide (SiO_2), does not have a crystalline structure as defined by X-ray diffraction measurements. Amorphous silica, which can be naturally occurring or synthetic, can be either surface-hydrated or anhydrous.

Microamorphous silica includes silica sols, gels, powders, and porous glasses. These consist of ultimate particles of the inorganic polymer $(\text{SiO}_2)_n$, where a silicon atom is covalently bonded in a tetrahedral arrangement to four oxygen atoms. Each of the four oxygen atoms is covalently bonded to at least one silicon atom to form a siloxane, Si-O-Si , or a silanol, Si-O-H , functionality. The bond distances and bond angles in amorphous silica are similar to those of cristobalite. Si-O bond distances are ~ 0.16 nm, and Si-O-Si bond angles are $\sim 148^\circ$. Surface silanol groups can be isolated from one another, so that intramolecular hydrogen bonding does not occur (Fig.1.2a); vicinal to one another, thus promoting the formation of intramolecular hydrogen bonding (Fig. 1.2b); or geminal to one another, whereby two silanol groups are bonded to the same silicon atom (Fig.1.2c). Initially formed low molecular weight species condense to form ring structures so as to maximize siloxane and minimize silanol bonds (Fig. 1.3) (Kirk-othmer, 2006).

A random arrangement of rings leads to the formation of complex structures of generally spherical particles less than ~ 100 nm in diameter (Fig. 1.4). These particles have high surface area values, generally greater than $\sim 3 \text{ m}^2\text{g}^{-1}$ (Kirk-othmer, 2006).

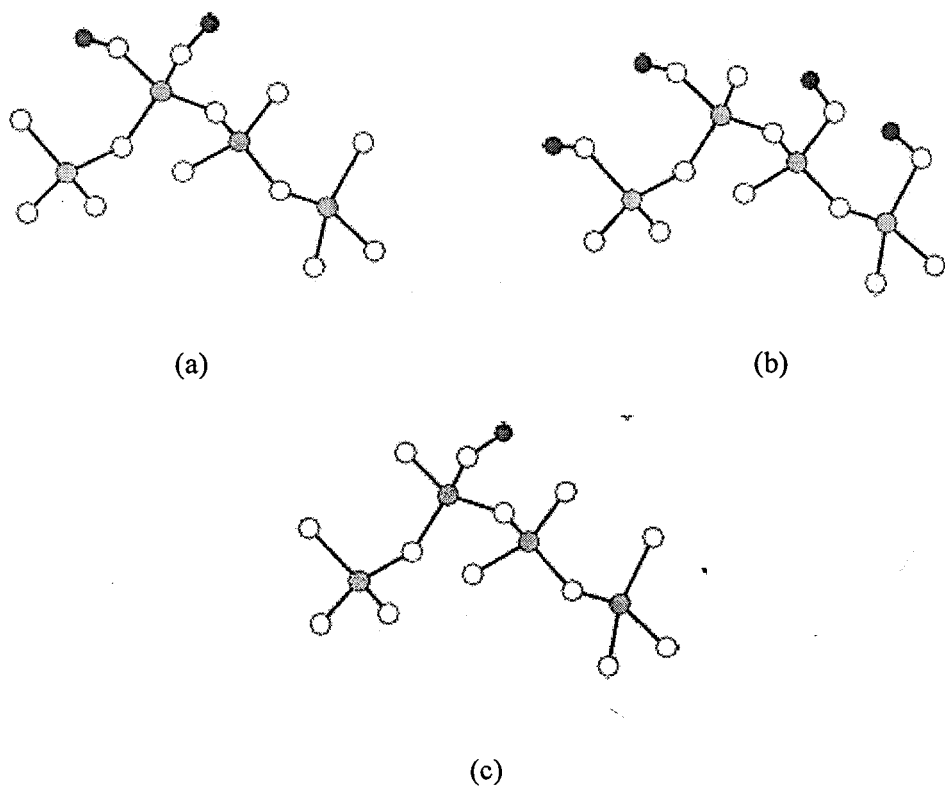


Fig. 1.2: Silanol groups of amorphous silica surface, where \bullet Silicon; \circ Oxygen; and \bullet Hydrogen: (a) isolated, (b) vicinal, and (c) geminal.

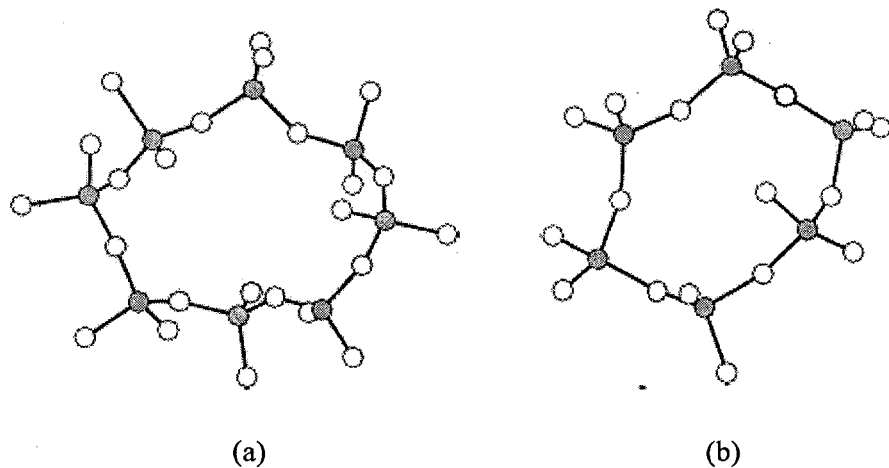


Fig. 1.3: Silica ring structures, where \bullet Si; \circ O: (a) 12-membered SiO_2 hexamer, and (b) 16-membered SiO_2 octamer.

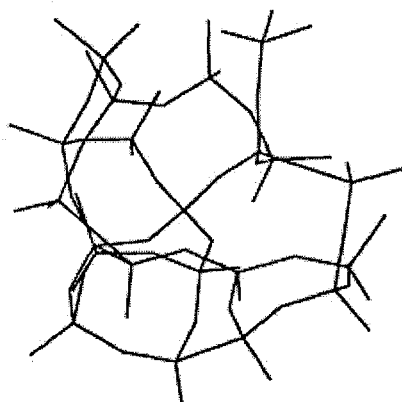


Fig. 1.4: Complex ring structures in SiO_2 polymer.

1.3 Applications of silica

In 2002, more than 83,000 metric tons of colloidal silica were typically used for making silica gels having uniform pore sizes and pore volumes to be used as binders in molds for precision casting of superalloys, for increasing the friction properties of surfaces, such as paper, floors, fibers, and films, as antisoiling finishes on paper, textiles, and painted surfaces, for hydrophobizing surfaces and polishing silicon wafers used in electronics industry, for improving performance of agents used for wetting and dispersing, as photographic emulsions, and for clarifying wines, beers and gelatin (Kirk-othmer, 2006).

1.4 Surface modification

Surface modification means a heterogeneous chemical reaction which takes place at a solid–gas or a solid–liquid interface to yield an immobile chemically bonded surface layer. When the reaction is limited to the formation of a monolayer, it can be viewed as chemisorption (Hayward and Trapnd 1964). Porosity of the support creates additional problems in surface modification owing to the difficulty in the

diffusion of the reactant from the exterior of particles into the pores to the active surface sites. Diffusion can be activated or non-activated depending on the reaction system and on the conditions. Furthermore, owing to the surface heterogeneity of silica some surface sites that are favourably positioned will react rapidly while others may require considerable activation energy. Thus, a quantitative treatment of the surface modification of porous silica is extremely difficult and only limited evaluations can be made. In order to understand the type of reaction and its mechanism the different reactants should be considered.

Incompletely dehydrated silica surface is usually covered with a multilayer of physisorbed water. On addition of an organochlorosilane the water produces an organosilanol by means of hydrolysis, which rapidly undergoes condensation to an organosiloxanol and an organosiloxane. When the amount of physically adsorbed water becomes negligibly small, isolated, geminal and vicinal hydroxyl groups comprise the active surface sites. It seems each of these types possess different, reactivity depending on its structure and accessibility.

Annealing of silica at temperatures up to 773 K causes partial surface dehydroxylation, yielding strained and hence highly reactive siloxane groups (Stahlin 1976). The role of such siloxane groups in addition to hydroxyl groups in surface interactions is not clear. When trace amount of water are present in the reactant the siloxane groups readily give hydroxyl groups. In the presence of alcohols, however, ester bonds are formed. In conclusion, the pre-treatment conditions of silica predominantly govern the type and reactivity of surface species that are involved in the reaction.

1.5 Sol-gel

Sol-gel science and technology continues to attract the attention of researcher's decades after its discovery. Although first discovered in the late 1800s and extensively studied since the early 1930s, it met a renewed interest (Gaishun *et al.* 2008) in the early 1970s, when mono-lithic inorganic gels were formed at low temperatures and converted to glasses without high temperature melting process (Brinker and Scherer 1990). Using this approach, homogeneous inorganic oxide materials with properties of hardness, optical transparency, chemical durability, tailored porosity, and thermal resistance, can be produced at room temperature, in contrast to much higher melting temperatures required in the production of conventional inorganic glasses (Brinker and Scherer 1985; Keefer 1990). The specific use of these sol-gel produced glasses and ceramics is derived from different material shapes generated in the gel state, i.e. monoliths, films, fibers, and nano sized powders.

The sol-gel process, as the name implies, involves development of inorganic net-works through formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel) (Brinker and Scherer 1990). The precursors for synthesis of these colloids consist of a complex of metal or metalloid element with different reactive ligands. Metal alkoxides are most popular because they react readily with water. The most widely used metalloid alkoxides are the alkoxysilanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS). However, other metal alkoxides such as alkyl aluminates, titanates, or metalloid alkoxides such as alkyl borates are also commonly used in the sol-gel process, often mixed with TEOS (Gaishun *et al.*, 2008).

Sol-gel method is most often applied for the synthesis of polysiloxane mesoporous materials that contain complexing groups in its surface layer (Zub and Parish 1996). Introduction of water and catalyst (e.g. H^+ , OH^- , F^-) in the primary system leads to hydrolysis of alkoxysilanes with formation of silanol groups, $\equiv Si-OH$. These groups interact with each other (or with alkoxysilyl groups, $RO-Si\equiv$) immediately, which leads to a creation of siloxane bonds ($\equiv Si-O-Si\equiv$), causing formation of oligomers. Further condensations of these oligomers are responsible for polymers of different structures. The growth of polymers results in the formation of colloidal particles which consequently lead to sol. The further integration of these particles and creation of aggregates causes transition of sol into gel. The appropriate treatment of formed gel (ageing, washing, drying, etc.) results in a polysiloxane xerogel with functional groups in its surface layer (Zub, 2009).

The sol-gel process is a low temperature synthetic path for the preparation of inorganic oxides. Scheme 1.1 illustrates the two reactions that best summarize the sol-gel process. The synthesis employs a metal alkoxide (e.g. $Si(OCH_3)_4$, TMOS, $Si(OCH_2CH_3)_4$, TEOS) as a starting material (Brinker and Scherer 1989). In Scheme 1.1, TMOS is first hydrolyzed into silanol, which then undergoes condensation to produce a highly porous and disorganized three-dimensional network of silicon oxide. The stochastic nature of solution chemistry leaves many unreacted alkoxyl and hydroxyl terminal groups randomly distributed throughout the silica framework and produces an amorphous material that is both structurally and chemically heterogeneous. Unreacted alkoxyl and hydroxyl groups also leave behind silica pores of dimension ranging from a few nanometers to hundreds of nanometers. The porous nature of silica sol-gel not only supplies a

viable platform to immobilize active biomolecules, but it also permits small molecules to diffuse inside and interact with the encapsulated biomolecules. The room-temperature sol-gel silica formation process is also suitable for the encapsulation of biomolecules that are prone to denaturation at high temperatures (Yip *et al.*, 2009) .

Hydrolysis



Condensation



Scheme 1.1: The sol-gel process.

During hydrolysis, addition of water results in the replacement of [OR] group with [OH] group. Hydrolysis can be accelerated by adding a catalyst such as HCl and NH₃. Hydrolysis continues until all alkoxy groups are replaced by hydroxyl groups. Subsequent condensation involving silanol group (Si-OH) produced siloxane bonds (Si-O-Si) and alcohol and water.

Polymerization to form siloxane bond occurs by either a water or alcohol release. The condensation leads to formation of monomer, dimer, cyclic tetramer, and high order rings. The rate of hydrolysis is affected by pH, reagent concentration and H₂O/Si molar ratio (in case of silica gels). Also ageing and drying are important. By control of these factors, it is possible to vary the structure and properties of sol-gel derived inorganic networks.

As the number of siloxane bonds increases, the molecules aggregate in solution, where they form a network, a gel that can be reinforced by drying. The water and alcohol are driven off and the network shrinks. There are three pH domains in the polymerization process. At pH above 2 the formation and aggregation of primary particles occur together. However, in this region Ostwald ripening contributes little to growth after particles exceed 2 nm in diameter, thus developing gel network are composed of exceedingly small primary particles (Brinker and Scherer 1990). At pH 2 the isoelectric point is reached and above the point the condensation preferentially occurs between more highly condensed species and those less highly condensed and somewhat neutral species. Cyclization occurs and particle growth stops when the particles reach 2–4 nm in diameter (Keefer 1990). At pH of greater than 7, and $\text{H}_2\text{O}/\text{Si}$ ratio ranging from 7 to 5, spherical nano-particles are formed. Polymerization to form siloxane bonds by either an alcohol or water elimination occurs.

Above pH 7, silica is more soluble and silica particles grow in size. Growth stops when the difference in solubility between the smallest and largest particles becomes indistinguishable.

1.6 Silica Modification

The modification of the silica surface has received a great deal of attention (Brunel, 1999; Airoidi & Arakaki, 2001). This process can lead to control and change in the chemical properties and technological characteristics of the composite material. It is a preparation which is essential for the synthesis of materials with many specific properties. These could be for the preparation of selective

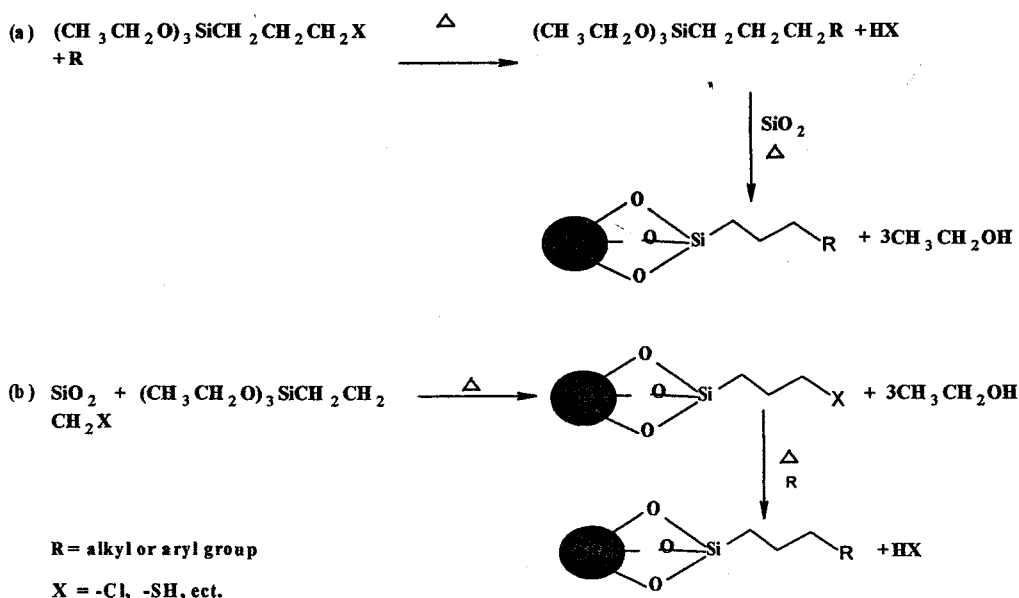
heterogeneous catalysts, nanostructured silica materials, liquid crystals (Tertykh & Belyakova, 1996) ect.

Organic functionalized silica represented a new class of materials for the design of catalyst, because their high surface areas, controllable pore structures and tailored pore surface chemistry allowed the binding of a large number of surface chemical moieties (Kuroki *et al.*, 2002). Generally, these mesoporous materials could be synthesized either by a post-modification or by a co-condensation method (Kuroki, *et al.*, 2002; Liu, *et al.*, 2002; Darmstadt, *et al.*, 2003; Ding, *et al.*, 2004).

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_3Si-R^* , where R is methyl or ethyl groups and R^* is an n -propylic carbon chain containing end functional groups, e.g. amine, halogen or sulfur group, or a combination of them (Cestari & Airoidi, 1997).

Silica modified with silylating agent is one of the best choices to introduce basic groups through an anchored pendant chain (Prado & Airoidi, 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 & Airoidi, 2001). It also offers good thermal and hydrolytic stability with accessibility to the reactive centres (Prado & Airoid, 2001b).

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 1.2a. The second strategy is to treat the post-polysiloxane with the complex group as in Scheme 1.2b.



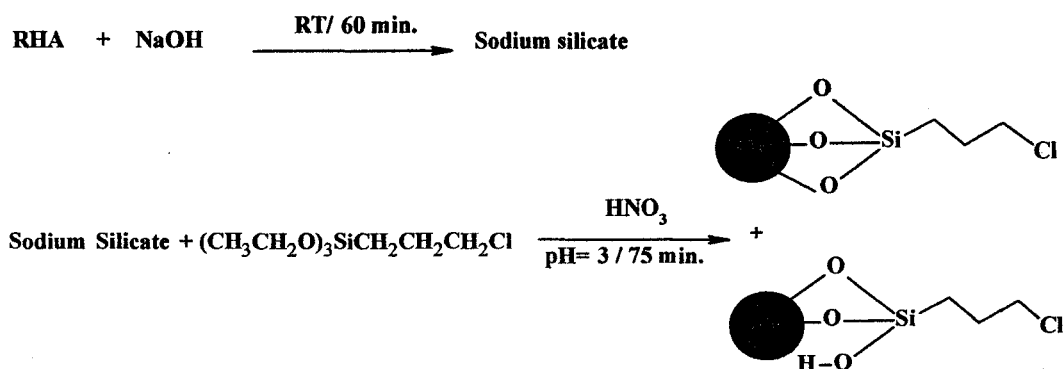
Scheme 1.2: (a) The reaction of silylating agent with the ligand complex followed by immobilization of the resulting ligand onto silica. (b) The immobilization of of silylating agent onto silica followed by immobilization of the ligand complex (Vansant, *et al.*, 1995).

Both strategies have been studied widely by many researchers (Vansant, *et al.*, 1995; Brunel, 1999; Airoidi & Arakaki, 2001). It was observed that these two reported preparation methods involved long preparation times and the use of hazardous chemicals leading to inefficient preparation techniques. This results in low yield, employ harsh reaction conditions, multiple steps, long reaction time, use of high energy, and costly chemicals. Therefore, there is a need to design a new method which is easy, cost-effective, environment-friendly, and time saving, minimal

energy loss, high yield and can be used especially in the heterogenation of homogeneous catalysts.

1.7 Direct immobilized halide systems

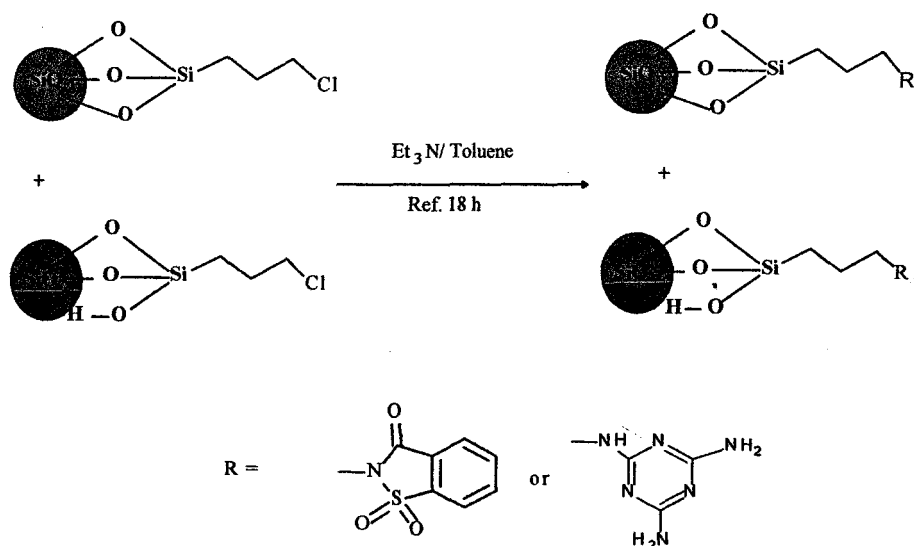
Silica modified with 3-(chloropropyl)triethoxysilane (CPTES) is usually carried out in a solid-liquid mixed phase reaction (heterogeneous reaction). However, Adam et al., (2009) had described the simple and fast technique to immobilize the halide system onto silica extracted from rice husk ash. This method described the functionalization of sodium silicate from RHA with CPTES to produced silica with $\text{CH}_2\text{-Cl}$ end group in 75 min via a simple one-pot synthesis at room temperature and pressure. The product was labelled as RHACCl, and the reaction sequence is shown Scheme 1.3.



Scheme 1.3: The reaction sequence and the possible structures for RHACCl [Adam, *et al.*, (2009)].

The product RHACCl had been used successfully to heterogenize different organic molecules, i.e. saccharine and melamine as in Scheme 1.4 (Adam, *et al.*,

2009) to produce heterogeneous catalysts. The immobilization of saccharine and melamine was carried out under reflux condition in toluene for 24 h. These catalysts were successfully used for esterification of different alcohols with acetic acid.



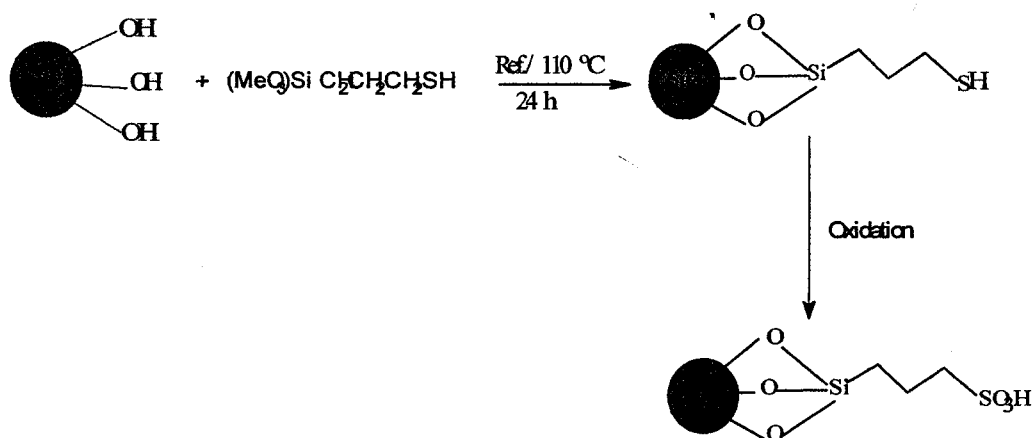
Scheme 1.4: The reaction sequence and the possible structures for immobilization of saccharine and melamine onto RHACCl. The approximate times taken for the completion of the experimental processes are also shown [adapted from Adam *et al.*, 2009, 2010].

1.8 Immobilized thiol ligand systems

Silica functionalized with thiol or sulphonic acid has broad application in the binding metal ions (Wilson *et al.* 2002). Elimination of sulphuric acid is possible in the presence of alkyl sulphuric acids (ROSO_3H) by using (auto-catalysed) hydrolysis. In contrast, alkyl sulphonic acids (RSO_3H) combine strong acidity with good hydrolytic stability. According to Djis *et al.*, (2002) to form silica functionalized alkyl sulphonic acids material, the silica surface undergoes derivation with alkyl thiols or alkyl thioacetic ester and later the thiol and thioacetic ester groups were oxidized with H_2O_2 .

Silica gel modified with 3-(trimethoxysilyl)propane-1-thiol (MPTMS) had been studied by Eunice, *et al.* (1997) and Simoni, *et al.* (2000). Functionalized

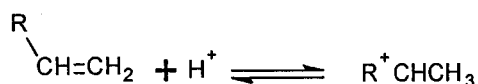
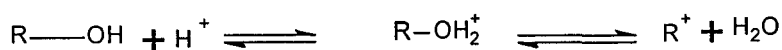
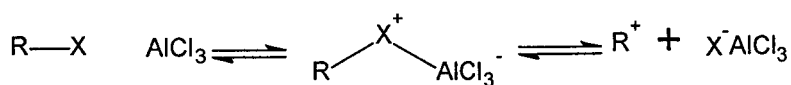
polysiloxane containing thiol ligand was prepared by hydrolytic polycondensation of silica with $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{SH}$. The anchored thiol groups can be oxidized to provide sulfonic acid functionality for the applications as solid acid catalysts (Yang, *et al.*, 2005) as shown in Scheme 1.5. The potential use of these derivatives as well as other organo functional derivatives critically depends on the loading of accessible functional groups onto the framework (Prado & Arakaki, 2001).



Scheme 1.5: The reaction sequence, the possible structures and the oxidize of RHACSH (thiol group) to sulfonic acid (RHACSO_3H). [Adapted from Shylesh *et al.*, 2004]

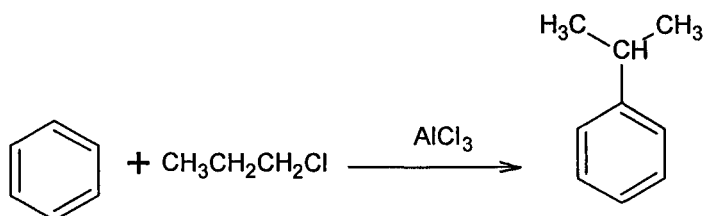
1.9 Friedel–Crafts Alkylation

Friedel–Crafts alkylation reactions are an important method for introducing carbon substituents on aromatic rings. The reactive electrophiles can be either discrete carbocations or polarized complexes that contain a reactive leaving group. Various combinations of reagents can be used to generate alkylating species. Alkylations usually involve the reaction of alkyl halides and alcohols or alkenes with strong acids with aromatic system and catalyzed by acid as shown in Scheme 1.6. below:



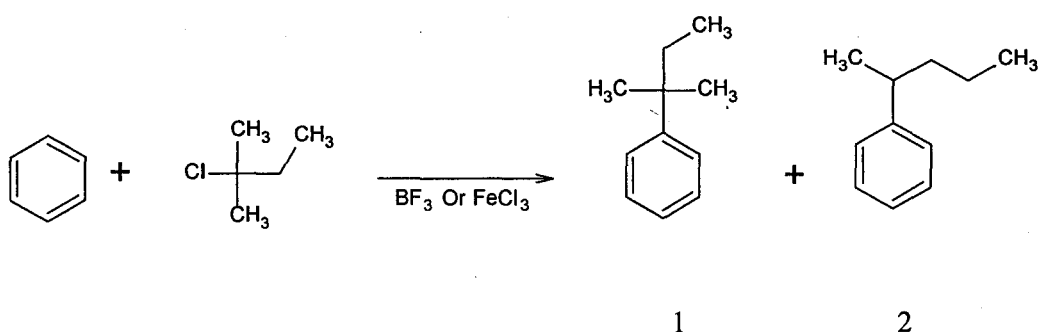
Scheme 1.6: The alkylation of different starting material with aromatic system and catalyzed by acid.

Owing to the involvement of carbocations, Friedel–Crafts alkylation can be accompanied by rearrangement of the reaction carbocation. For example, isopropyl groups are often introduced when n-propyl reactants are used as the reactant in Scheme 1.7 (Carey and Sundberg 2007). These rearrangements are well known in carbocation chemistry.



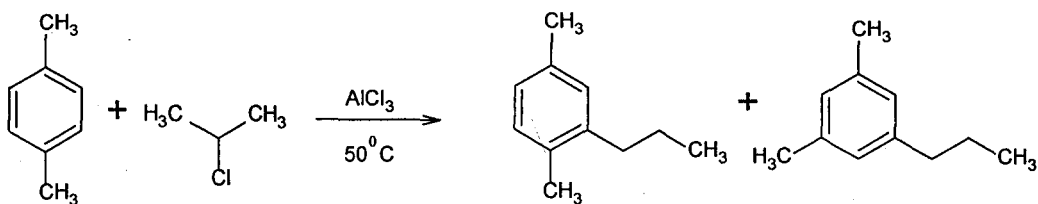
Scheme 1.7: The rearrangements occur during the alkylation reaction.

Similarly, under a variety of reaction conditions, alkylation of benzene with either 2-chloro or 3-chloropentane gives a mixture of both 2-pentyl- and 3-pentylbenzene (Roberts, *et al.*, 1976). Rearrangement can also occur after the initial alkylation. The reaction of 2-chloro-2-methylbutane with benzene is an example of this behavior (Khalaf and Roberts 1970). With relatively mild Friedel-Crafts catalysts such as BF_3 or FeCl_3 , the main products are shown in Scheme 1.8. With AlCl_3 , equilibration of 1 and 2 occurs and the equilibrium favors 2. The rearrangement is the result of product equilibration via reversibly formed carbocations.



Scheme 1.8: The reaction of benzene with 2-chloro-2-methyl-buthane using mild catalysts like BF_3 or FeCl_3 .

Alkyl groups can also migrate from one position to another on the ring (Carey and Sundberg 2007). Such migrations are also thermodynamically controlled and proceed in the direction of minimizing steric interactions between substituents as in Scheme 1.9.



Scheme 1.9: The immigration of methyl group during the alkylation of p-xylene.

The relative reactivity of Friedel–Crafts catalysts has not been described in a quantitative way, but comparative studies using a series of benzyl halides has resulted in the qualitative groupings shown in Table 1.1. Proper choice of catalyst can minimize subsequent product equilibrations.

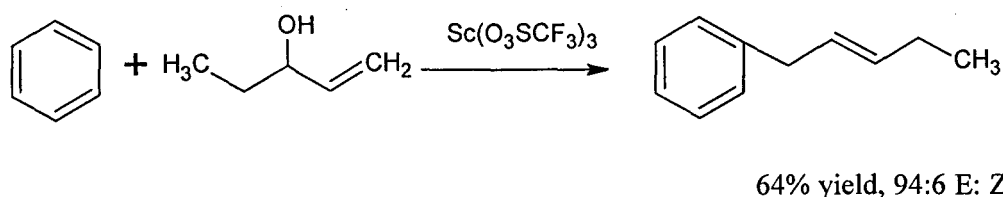
The Friedel–Crafts alkylation reaction does not proceed successfully with aromatic reactants having EWG (electron withdraw group) substituents. Another limitation is that each alkyl group that is introduced increases the reactivity of the ring toward further substitution, so polyalkylation can be a problem. Polyalkylation can be minimized by using the aromatic reactant in excess.

Table 1.1: Relative Activity of Friedel–Crafts Catalyst (Olah, *et al.*, 1972).

Very active	Moderately active	Mild
AlCl ₃ , AlBr ₃ ,	InCl ₃ , InBr ₃ , SbCl ₄ , FeCl ₃ ,	BCl ₃ , SnCl ₄ ,
GaCl ₃ , GaCl ₂ ,	AlCl ₃ –CH ₃ NO ₂ ,	TiCl ₄ , TiBr ₄ ,
SbF ₅ , MoCl ₅ ,	SbF ₅ –CH ₃ NO ₂	FeCl ₂

Apart from the alkyl halide–Lewis acid combination, two other sources of carbocations are often used in Friedel–Crafts reactions. Alcohols can serve as carbocation precursors in strong acids such as sulfuric or phosphoric acid. Alkylation can also be effected by alcohols in combination with BF₃ or AlCl₃ (Schriesheim 1964). Alkenes can serve as alkylating agents when a protic acid, especially H₂SO₄, H₃PO₄, and HF, or a Lewis acid, such as BF₃ and AlCl₃, is used as a catalyst (Patinkin and Friedman, 1964). Stabilized carbocations can be generated from allylic

and benzylic alcohols by reaction with $\text{Sc}(\text{O}_3\text{SCF}_3)_3$ and results in the formation of alkylation products from benzene and activated derivatives as in Scheme 1.10 (Fukuzawa *et al.*, 1997; Carey and Sundberg, 2007).



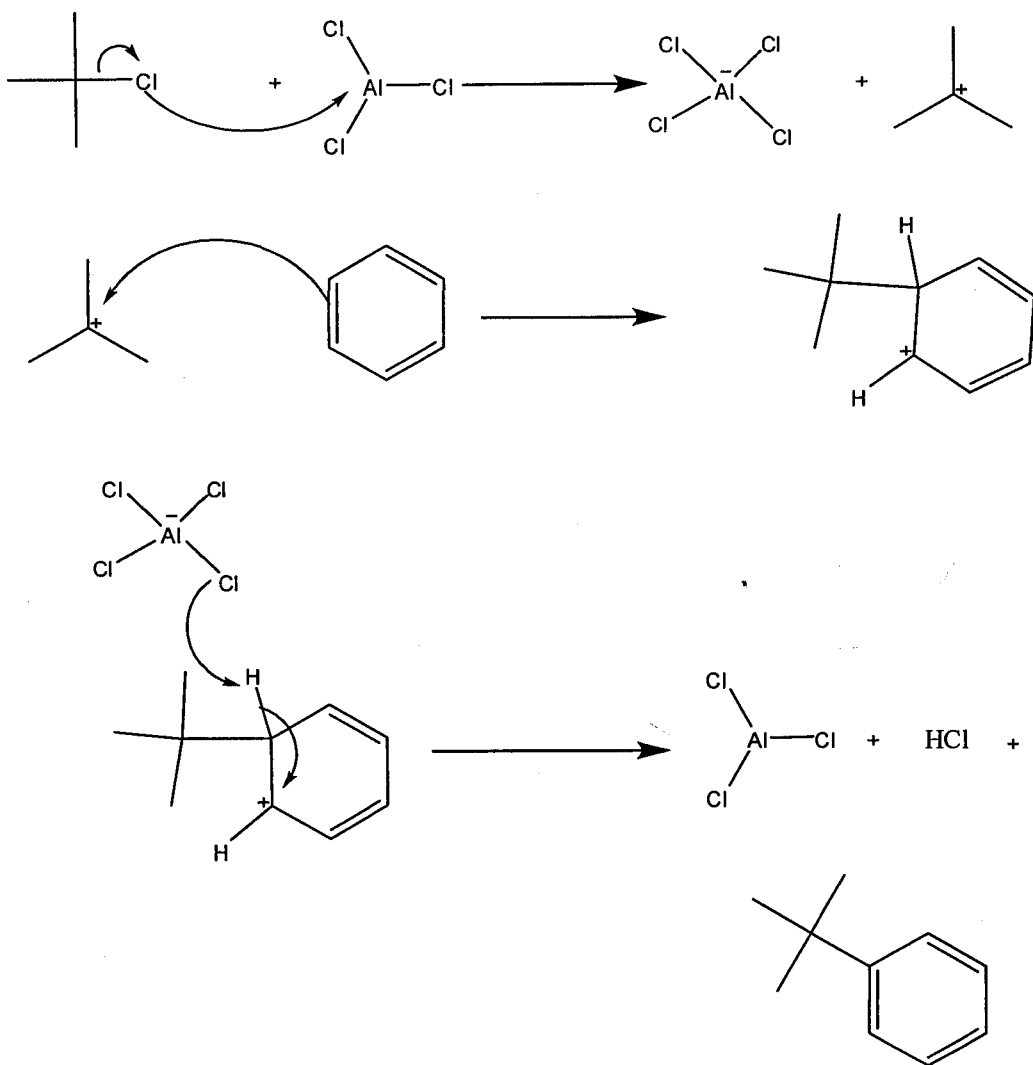
Scheme 1.10: The reaction of benzene with pent-1-en-3-ol using $\text{Sc}(\text{O}_3\text{SCF}_3)_3$ as the catalyst.

1.10 Mechanism of Friedel–Crafts

The Friedel–Crafts alkylation reactions are a set of reactions developed by Charles Friedel and James Crafts in 1877 (Carey and Sundberg 2007). There are two main types of Friedel–Crafts reactions: alkylation and acylation reactions. The alkylation reaction is a type of electrophilic aromatic substitution. Alkylations are not limited to alkyl halides. Friedel–Crafts reactions are possible with any carbocationic intermediate such as those derived from alkenes and a protic acid, alcohol, Lewis acid, enones and epoxides.

Since the reaction has a carbocation intermediate, the intermediate may undergo a hydride or methyl shift to form a more stable cation. If the chlorine, hydroxyl or carbocation are not on a tertiary carbon, carbocation rearrangement reaction will occur. This is due to the relative stability of the tertiary carbocation over the secondary and primary carbocations (Smith and Sella. 1963).

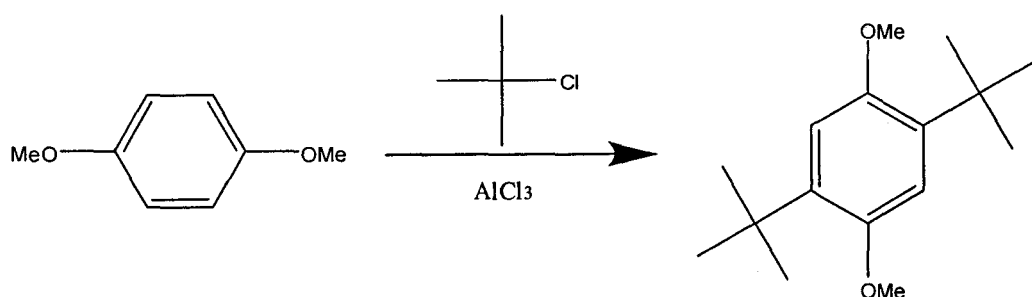
The reaction mechanism of Friedel–Craft reaction is presented in Scheme 1.11 below:



Scheme 1.11: The mechanism of Friedel–Crafts alkylation over AlCl_3 as a catalyst.

Friedel–Crafts alkylation is a reversible reaction. In a reversed Friedel–Crafts reaction or Friedel–Crafts dealkylation, alkyl groups can be removed in the presence of protons and a Lewis acid. This reaction has one big disadvantage, namely that the product is more nucleophilic than the reactant due to the electron donating alkyl-chain. Therefore, hydrogen is substituted with an alkyl-chain, which leads to overalkylation of the molecule. Steric hindrance can be exploited to limit the number

of alkylations (Wallace et al. 2005), as in the *tert*-butylation of 1,4-dimethoxybenzene Scheme 1.12.



Scheme 1.12: The alkylation reaction of 1,4-dimethoxybenzene with *tert*-butanol (TBA) over AlCl_3 as a catalyst

1.11 Alkylation of phenol: Literature review

Heterogeneous catalysis looks to be far away from organometallic chemistry and homogeneous catalysis. It is indispensable to introduce this aspect, because it is complementary to homogeneous catalysis, and the majority of industrial processes are carried out with heterogeneous catalysts (Astruc, 2007). Moreover, the molecular approach is now common in heterogeneous catalysis and a continuity of disciplines is being established which runs from monometallic activation to solid-state via organometallic clusters, giant clusters, then to mono- or polymetallic nanoparticles of various sizes. Homogeneous and heterogeneous catalytic processes were discovered at about the same time two centuries ago (Astruc, 2007).

Kumbar *et al.* (2006) was investigated butylation of *p*-cresol with TBA on titania modified with 12-tungstophosphoric acid (TPA/ TiO_2) catalyst under vapor phase conditions. These catalysts showed both Brønsted and Lewis acidity and 20 %

TPA on TiO₂ calcined at 700 °C (20 % TT-700) had the highest Brønsted as well as total acidity. Further, the catalytic activities were examined in *tert*-butylation of *p*-cresol with TBA. The catalytic activity depended on TPA coverage, and the highest activity corresponded to the monolayer of TPA on titania. The most active catalyst was 20 % TT-700 which gave 82 % conversion of *p*-cresol and 89.5 % selectivity towards 2-*tert*-butyl cresol (TBC), 7.5 % 2,6-di-*tert*-butyl cresol (DTBC) and 3 % cresol-*tert*-butyl ether (CTBE) under optimized conditions.

Alkylation of *m*-cresol with cyclopentene in the presence of benzenesulphonic acid was studied statistically with a three-factored experimental design (Alama *et al.* 2008). Factorial design was employed to study the effects of single factors and the effects of their interactions on the yields of alkylation. Reaction temperature, molar ratio of *m*-cresol to cyclopentene and amount of benzenesulphonic acid were considered as the major variables. An optimum yield (about 94 %) of the product was obtained under the reaction conditions of a temperature of 140 °C; a 5:1 molar ratio of *m*-cresol to cyclopentene and 8 % by weight benzenesulphonic acid of *m*-cresol.

Alkylation reaction of phenol with TBA catalyzed by SO₃H-functionalized ionic liquids has been investigated (Gui, *et al.*, 2005). The influences of different ionic liquids, reaction time, reaction temperature, reactant ratio (mole ratio of phenol to that of TBA), the amount and the recycle of ionic liquid were studied. The conversion of phenol and the selectivity of 2,4-DTBP were 80.4 and 60.2 %, respectively, under optimum reaction condition.

Alkylation of phenol with *tert*-butyl alcohol (TBA) at room temperature with ionic liquid, 1-butyl-3-methylimidazoliumhexafluorophosphate ([bmim]PF₆), has been investigated (Shen, *et al.*, 2003). The [bmim]PF₆ ionic liquid was found to catalyze the reaction with high conversion and good selectivity. The optimum reaction conditions for this reaction were: molar ratio of 1:2 of phenol to TBA, 0.5 mmol ionic liquid per 10 mmol phenol, 60 °C for 4 h. This study showed that ionic liquid has a potential application in the production of *tert*-butyl phenols with high activity and selectivity to 2,4-DTBP.

The efficacies of several novel solid superacids designated as UDCaT-4,-5 and -6 of sulphated zirconia in liquid phase alkylation of phenol with *tert*-amyl alcohol Yadav and Pathre (2006) showed. The conversion of *tert*-amyl alcohol and the selectivity for C-alkylated products were 96 and 85 %, respectively.

A heterogeneous or a homogenous catalyst can be used for the alkylation of phenol. The major drawbacks of homogenous catalysts are its hazardous nature and difficulty in separation of the catalyst from the reaction mixture. The cationic exchange resins are inefficient due to its lower activity and selectivity as well as lower stability at high temperature (Krithiga 2005). It is therefore preferable to use heterogeneous catalyst due to the inherent advantages of its ease of separation from reaction mixture, environmental friendliness, chemical stability, reusability and absence of corrosion problems (Krithiga 2005).

tert-Butylation of phenol is an alkylation reaction and is usually carried out using isobutylene, di-isobutylene, TBA and *tert*-butyl halides as alkylating agent

(Kumar *et al.* 2007). Alkylation of TBA with phenol is an industrially important reaction because many alkylated phenols are important intermediates in industrial processes. *P*-TBP is used as a raw material for resins, modifiers for polymers, stabilizers for polymers, surface coating, varnishes, wire enamels, printing ink, and so forth (Krishnan *et al.* 2002). The applications for surface active agents include rubber chemicals, antioxidants, fungicides and petroleum additives.

A survey of the literature shows that during *tert*-butylation of phenol with TBA over zeolite H β , strong acid sites are advantageous to the formation of 2,4-DTBP and medium acid sites are helpful for the production of *P*-TBP, while weak acid sites are effective in producing the *O*-TBP.

Vinu *et al.* (2005 a) had synthesized mesoporous molecular sieve AISBA-15 with n_{Si}/n_{Al} ratio between 7 and 215. The catalytic activity of the AISBA-15 was tested in the acid-catalyzed vapor phase *tert*-butylation of phenol employing TBA as the alkylating agent. Among all catalyst used, AISBA-15(45) was found to be the most active. A high phenol conversion of 86.3 % was observed for this catalyst at a reaction temperature of 150 °C over AISBA-15(45). The 4-TBP yield was found to be 40.5 % and the 2,4-DTBP yield was reported to be 37.9 %.

Mathew *et al.* (2004) reported a comparative study of various phenol alkylation reactions over the catalyst system of $Cu_{1-x}Co_xFe_2O_4$ with five alkylating agents, i.e. methanol DMC, ethanol, isopropanol and isobutene under a variety of reaction conditions. The trimetallic oxide, $Cu_{0.5}Co_{0.5}Fe_2O_4$ was found to be the best giving a high yield of ortho-alkylated phenol. With regard to the alkylating ability of the