SILICA SUPPORTED INDIUM HETEROGENEOUS CATALYST IN BENZYLATION AND BENZOYLATION OF TOLUENE

SEK KEI LIN

UNIVERSITI SAINS MALAYSIA

2013

SILICA SUPPORTED INDIUM HETEROGENEOUS CATALYST IN BENZYLATION AND BENZOYLATION OF TOLUENE

By

SEK KEI LIN

Thesis submitted in fulfillment of requirements for the degree of master

June 2013

ACKNOWLEDGEMENTS

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LIST OF ABBREVIATIONS

AAS	- Atomic Absorption Spectroscopy
BET	- Brunauer-Emmett–Teller theory
BMS	- Bimodal mesoporous silica
BoC	- Benzoyl chloride
BzC	- benzyl chloride
DR UV-Vis	- Diffuse Reflectance Ultra-Violet Visible
F	- Response factor
FC	- Friedel-Crafts
FT-IR	- Fourier Transform Infra-Red spectroscopy
GC	- Gas chromatograph
GC-MS	- Gas chromatograph equipped with mass spectroscopy
i.e	- That is
MCM	- Mesoporous molecular sieve
MBP	- Methylbenzonephenone
MDM	- Methyldiphenylmethane
$-OCH_3$	- Methoxy
RH	- Rice husk
SEM/EDX	- Scanning Electron Microscopy combined with Energy Dispersive Spectrometry
Si-OH	- Silanol group
Si-O-Si	- Siloxane group
SiO_2	- Silicon dioxide
SiO_4	- Silicon Tetraoxide
TEM	- Transmission Electron Microscopy
wt	- Weight
XRD	- Powder X-Ray Diffractometry

LIST OF SYMBOLS

%	- Percentage
K	- Kelvin
h	- Hour
g	- Gram
M	- Molarity
mL	- milliliter

LIST OF PUBLICATION

1. Heterogenization of Indium for the Friedel-Craft Benzoylation of Toluene F,.Adam, K. L. Sek, Chin. J. Catal., (2012), 33: 1802–1808 [doi:10.1016/S1872-2067(11)60453-1]

MANGKIN HETEROGEN INDIUM DISOKONG OLEH SILIKA DALAM TINDAK BALAS PEMBENZILAN DAN PEMBENZOILAN TOLUENA

ABSTRAK

Indium disokong oleh silika dengan kandungan indium yang berbeza disintesis dengan menggunakan kaedah sol-gel tanpa templat. Silika yang diguna adalah diekstrak daripada sekam padi (RH) dan mangkin yang diperolehi dilabel sebagai RH-xIn (x = 5, 10, 15 dan 20).

Mangkin yang disintesis telah dicirikan dengan teknik fizik-kimia seperti FTIR, penjerapan N_2 (BET), serbuk XRD, UV-Vis, SEM, EDX, TEM dan AAS. RH-blank (tanpa indium) disintesis sebagai kawalan. Tiada indium dikesan dalam RH-blank dan kandungan peratus indium meningkat dari RH-5In hingga RH-20In. Penjerapan N_2 menunjukkan isoterma jenis IV bagi RH-blank dan RH-xIn. Ini membuktikan mangkin yang disediakan adalah berliang meso. XRD merekod jalur lebar pada $2\theta = 25°$, menunjukkan ciri-ciri amorfus RH-blank dan RH-xIn tidak berubah walaupun selepas indium ditambah. Mikrograf TEM mendedahkan mangkin tersebut adalah terdiri daripada nanopartikel.

Pembenzilan dan pembenzoilan Friedel-Crafts toluena telah dilakukan dengan benzil klorida (BC) dan benzoil klorida (BOZ) dimangkin oleh RH-xIn (x= 5, 10, 15 dan 20). Pembenzilan toluena menghasilkan 4-metildifenilmetana (4-MDM) and 2-metildifenilmetana (2-MDM) sebagai produk utama, manakala penukargantian-dwi dikesan sebagai produk sampingan. Pembenzoilan toluena menghasilkan 4-metilbenzofenon (4-MBP) dan 2-metilbenzofenon (2-MBP) sebagai produk utama, dan 3-metilbenzofenon (3MBP) sebagai produk sampingan.

Kedua-dua tindak balas menunjukkan kenaikan dalam peratusan penukaran yang dipengaruhi oleh kenaikan suhu, jisim mangkin dan peratusan muatan logam. RH-20In didapati merupakan mangkin heterogen yang baik dalam fasa cecair untuk pembenzilan toluena. Ia mencapai penukargantian 100 % dan kira-kira 70 % kepilihan bagi produk *para* (4-MDM). Keadaan optimum bagi pembenzoilan toluena pula menunjukkan mangkin RH-10In manghasilkan penukargantian 100 % dan kepilihan 89 % bagi produk *para* (4-MBP).

SILICA SUPPORTED INDIUM HETEROGENEOUS CATALYST IN BENZYLATION AND BENZOYLATION OF TOLUENE

ABSTRACT

Indium incorporated silica with different indium content were synthesized via a template free sol-gel method. The silica used was extracted from rice husk (RH) and the resulting catalyst was labeled as RH-xIn (x = 5, 10, 15 and 20).

The catalysts were characterized by physico-chemical techniques such as FTIR, N_2 adsorption (BET), powder XRD, UV-Vis, SEM, EDX, TEM and AAS for the elemental analysis. RH-blank (without indium) was synthesized as the control for the reaction. No indium was detected in the RH-blank and the percentage of indium was found increase from RH-5In to RH-20In. The N_2 adsorption analysis showed the presence of type IV isotherm in RH-blank and RH-xIn, indicating the mesoporous nature of the catalysts. The XRD recorded a broad band at $2\theta = 25°$, which showed their amorphous character. TEM micrographs revealed the catalysts to be composed of nanoparticles.

Friedel-Craft benzylation and benzoylation of toluene with benzyl chloride (BC) and benzoyl chloride (BOZ) were carried out by using RH-xIn (x= 5, 10, 15 and 20) as the catalyst. Benzylation of toluene resulted in 4-methyldiphenylmethane (4-MDM) and 2-methyldiphenylmethane (2-MDM) as the major products while di-substituted products were detected as minor product. Benzoylation of toluene gave 4-methylbenzophenone (4-MBP) and 2-methylbenzophenone (2-MBP) as major products, and 3-methylbenzophenone (3-MBP) as the minor product.

Both reactions were observed to be increasing in conversion with the increase of reaction temperature, mass of catalyst and percentage of metal loading.RH-20In was found to be a good heterogeneous catalyst in the liquid phase benzylation of toluene. It achieved 100 % conversion and about 70 % of the selectivity toward *para* product (4-MDM). The optimum conditions for the benzoylation of toluene were determined to be RH-10In as the catalyst which gave 100 % conversion and 89 % selectivity toward *para* product (4-MBP).

Chapter 1

INTRODUCTION

1.1   Rice husk

Rice is the most important staple food for more than half the world's human population especially in East and South Asia (Chandrasekhar *et al.* 2003). Rice is the only food that is suitable to be planted in rainy seasons in waterlogged tropical areas (Amuthu *et al.* 2010). Husk is the outer shell that surrounds the rice kernel. Every ton of rice produces 0.23 ton of rice husk (RH) (Chandrasekhar *et al.* 2003) and the world annually produces about 120 million ton of rice. This means that about 20 % RH will be produced. An increase in rice consumption has given rise to disposal problem of RH which is the by-product from rice milling industry (Acharya *et al.* 1980; Adam *et al.* 2006; Nakbanpote *et al.* 2007).

1.1.1   Utilization of rice husk

Commercial utilization of RH is still not widely being investigated. Generally, RH was utilized as animal feeds, fertilizer, and additive compound in bricks-making and reinforcing material in cement. Also as raw material in making fuel briquettes, biomass fuel for heat and electricity generation (Chiarakorn *et al.* 2007; Yaacob, *et al.* 2009). Other than that, the disposal of RH mostly is carried out by burning which produce toxic gases and fine ash that cause side effects to the environment and living organisms (Adam and Iqbal 2010; Chiarakorn *et al.* 2007). Therefore, conversion of RH into useful material to overcome the problematic waste is very important.

1.1.2   RH as silica source

The beneficial advancement of mesoporous and macroporous materials in biotechnology, polymerization, and heterogeneous catalysis has prompted a wide investigation in inorganic silica (He *et al.* 2010; Ho *et al.* 2007; Witoon *et al.* 2008). Generally, the silicon source is obtained from sodium silicate which is produced by smelting quartz sand and sodium carbonate at a high temperature of 1300 °C (Adam and Andas 2007; Liou and Yang 2011). This process requires high energy resource to obtain the sodium silicate. Commercial silica such as tertraethoxysilane (TEOS) (Jafarzadeh *et al.* 2009; Menon *et al.* 1998) and tetramethoxysilane (TMOS) (Baccile *et al.* 2009) were used to synthesize these porous materials. According to Nakashima *et al.* (1994), these commercialized silica are costly, environmental unfriendly, toxic and harmful to human health. Therefore, RH will be an excellent silica source to replace these existing silica sources.

On the average 20 % of the rice paddy is husk which amounts to 120 million tons annually (Shelke *et al*. 2010). The presence of silica in RH has been known since 1938 and many researchers have concluded that RH is a good silica source. As RH has high silica content and has a protective function. The silicon is taken up from the soil as the plant grows. The silicon will deposit in the leaves and stems membrane or form a layer between epidermis and cuticles to prevent the evaporation of moisture to the surrounding (Zakharov *et al*. 1993).

According to Chiarakorn *et al*. (2007), silicon dioxide in rice husk is purer than rice husk ash (RHA) as RHA can be contaminated with some inorganic compounds during the calcination process. Therefore, the high temperature calcinations of RHA

should be avoided to prevent pollution. Silica extracted from RH was in the hydrated amorphous form, i.e. either opal or silica gel (Chandrasekhar *et al*. 2003; Zakharov *et al*. 1993).

Recently many researchers published their work regarding the extraction of silica from RH to produce new catalyst such as mesoporous molecular sieve (MCM-41) (Chiarakorn *et al.* 2007), bimodal mesoporous silica (BMS) (Jullaphan *et al.* 2009) silicon carbide, silicon-nitride, pure silicon and silicon tetrachloride (Amuthu *et al*. 2010; Della *et al*. 2002). Mostly, the extraction method was a template which is expensive and environmentaly harmful (Witoon *et al.* 2008).

1.2 Silica

1.2.1 Appearance of silica

Silicon is one of the most abundant elements in the earth's crust. It was discovered by Berzelius, a Swedish chemist in 1824. Silicon is a semi-metal with a melting point of 1687 K and boiling point at 3538 K, and is present in solid phase at room temperature (Jefferson 2012). Naturally, silica exists in the form of silicon dioxide, SiO_2, or with several metals in the silicate form. Silica is a polymer of silicic acid which consists of inter-linked SiO_4 units in a tetrahedral configuration with a general formula SiO_2 (Jal *et al*. 2004). The use of silica is attractive due to its special properties, such as stability to heat, non-toxicity and chemical inertness (Nakbanpote *et al*. 2007).

Majority of silica exists in crystalline form and there are three types of crystalline silica, i.e. quartz, cristobalite and tridymite (Unger 1979). The most common is the quartz which can be found in granite and sand. It can be used in electrical industry as piezoelectric to stabilize the amplifier circuit and measure high electrical potentials or pressure. Cristobalite and tridymite can only be found in volcanic rock and do not have any application (Silicon occurrence 2012).

Amorphous silica was found in the form of opal or silica gel existing in nature. It is divided into three types of vitreous silica made by fusing quartz, silica M which irradiated with high speed of neutrons and microamorphous silica which included sols, gels, powders and porous glasses. Amorphous silica was very useful in several applications such as thin-films, transistors, colour sensors and photovoltaic cells (Sava 2007).

1.2.2 Metal supported of silica

Metal incorporation into silica, for example, zirconium (Sun *et al.* 2006), iron (Adam *et al.* 2006; Chen *et al.* 2010), nickel (Chang *et al.* 1997), vanadium (Renu *et al.* 2008), and aluminum (Tsai and Wu 2005), have been widely studied to produce catalysts. These catalysts were applied in industrial reactions such as esterification (Sun *et al.* 2006), benzylation (Adam *et al.* 2006), and oxidation (Renu *et al.* 2008). The metal-supported silica caused a change in properties of the catalysts which can improve the catalytic effects such as selectivity and conversion (Jehng *et al.* 1996).

1.3 Sol-gel method

One of the simple and economical methods to extract silica from RH was carried out by sol-gel. Since 40 years ago, sol-gel method has been developed in the preparation of glass and ceramics at a low temperature (Dimitriev *et al.* 2008). Sol-gel is a wet chemical technique which involves colloidal suspension in the gel form. Sol-gel method can produce various morphological materials such as bulks, fiber sheets, coating films, and particles at low temperature (Dimitriev *et al.* 2008). Sol-gel technique is very useful as it allows the formation of silica particles in aerogel or xerogel at low temperature (Muñoz and Acuña 2010). Therefore, this simple method is widely used to prepare mesoporous material.

$$\equiv\text{Si-OR} + \text{H}_2\text{O} \rightarrow \equiv\text{Si-OH} + \text{ROH} \qquad (1.1)$$

$$\equiv\text{Si-OH} + \text{RO-Si}\equiv \rightarrow \equiv\text{Si-O-Si}\equiv + \text{ROH} \qquad (1.2)$$

$$\equiv\text{Si-OH} + \text{HO-Si} \rightarrow \equiv\text{Si-O-Si}\equiv + \text{H}_2\text{O} \qquad (1.3)$$
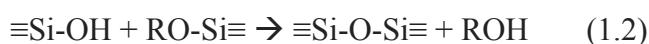
Scheme 1   Hydrolysis of alcohol and water condensation in sol-gel process.

Sol-gel involves hydrolysis and condensation reactions. In this process the sodium silicate or alkoxysilane is converted to a polymeric network gel (Jal *et al.* 2004). These reactions give rise to the formation of Si-O-Si, siloxane bonds. Scheme 1 shows the hydrolysis of alcohol and water condensation in the sol-gel process. Equation 1.1 shows the formation of Si-OH, silanol group and alcohol will be eliminated after the hydrolysis of alkoxysilane and water. Equations 1.2 and 1.3 shows the formation of Si-O-Si group with the elimination of alcohol or water after the reaction between the silanol groups with alkoxysilane or others silanol groups (Buckley *et al.* 1997; Muñoz and Acuña 2010). These reactions continue to build the

large silicon containing siloxane groups to form a large inorganic polymer which on dehydration porous silica.

This simple method gives many advantages especially for environment as it is not toxic nor does it release poisonous material. It can be carried out at low temperature and the products are also very pure.

1.4 Indium

Indium was first discovered in 1863 by Reich and Richter from Germany. They found it as an unknown blue color coating on the spectrograph while studying zinc ores from a local polymetallic vein deposit while looking for thallium (Jorgenson and George 2005). Indium is a byproduct of the electrolytic refining of zinc. Indium is element number 49 in the periodic table, with an atomic weight of 114.82 g mol^{-1}. Indium is a post transition metal which is silvery white and very soft.

Indium is normally used in making alloys and is known as "metal vitamin" in alloy industries, because it gives a large change in properties in an alloy with a small amount of its addition. Indium when added to solder will reduce the melting point, increase strengthen and prevent the solder from breaking down easily. For electronic industries, indium is mostly used in making electroluminescent panels and semiconductors (Hasan 2009).

Indium was selected as the metal to be incorporated in silica due to its specific properties such as its stability in air and oxygen and its low toxicity (Jang *et al.* 2006). Indium does not react with water but dissolves in mineral acid (Du *et al.* 2010). It has been reported that indium will give a high selectivity at low metal loading in

catalytic reactions such as Friedel-Crafts (FC) alkylation, acylation, Wagner-Meerwein rearrangement and Diels-Alder reaction (Ahmed and Adam 2007; Miyai *et al.* 1998; Wildermann *et al.* 2007).

1.5   Friedel-Crafts (FC) Reaction

Encyclopedia Britannica defines FC as "a reaction that involves a process of uniting two or more organic molecules through the formation of carbon to carbon bonds under the catalyzed activity of a strongly acidic metal halide such as aluminium chloride, boron trifluoride, ferric chloride or zinc chloride" (Anand *et al.* 1995; Wimsatt 1963). FC reactions were first published in 1877 by Charles Friedel and James Mason Crafts (Wimsatt 1963). There are two types of FC reaction, alkylation and acylation.

The reaction can involve isomerization, elimination, cracking, polymerization or addition reactions under the catalytic effect of Lewis acid (Gracia *et al.* 2008). FC alkylation and acylation are the reactions which involve the substitution of electrophile on to aromatic compounds. The electrophile is a carbocation. The reaction involves the formation of carbon-carbon bond and the substitution of alkyl or acyl group into aromatic derivatives.

The substituent on the benzene ring can influence the placement of additional substituent on the benzene ring during FC reaction. Generally, there are three positions for substitution on the benzene ring, i.e. *ortho*, *para* and *meta*. The substituent with electron donating groups such as $-CH_3$, $-OCH_3$, $-OH$ or $-NH_2$, having a lone pair electron on the atom directly bonded to the ring, will result in

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subtituition at the *ortho* or *para* position on the benzene ring (Murry 2011).

Toluene is one of the activated benzene derivatives which will give *ortho* and *para* products when it undergoes FC benzylation and benzoylation reactions.
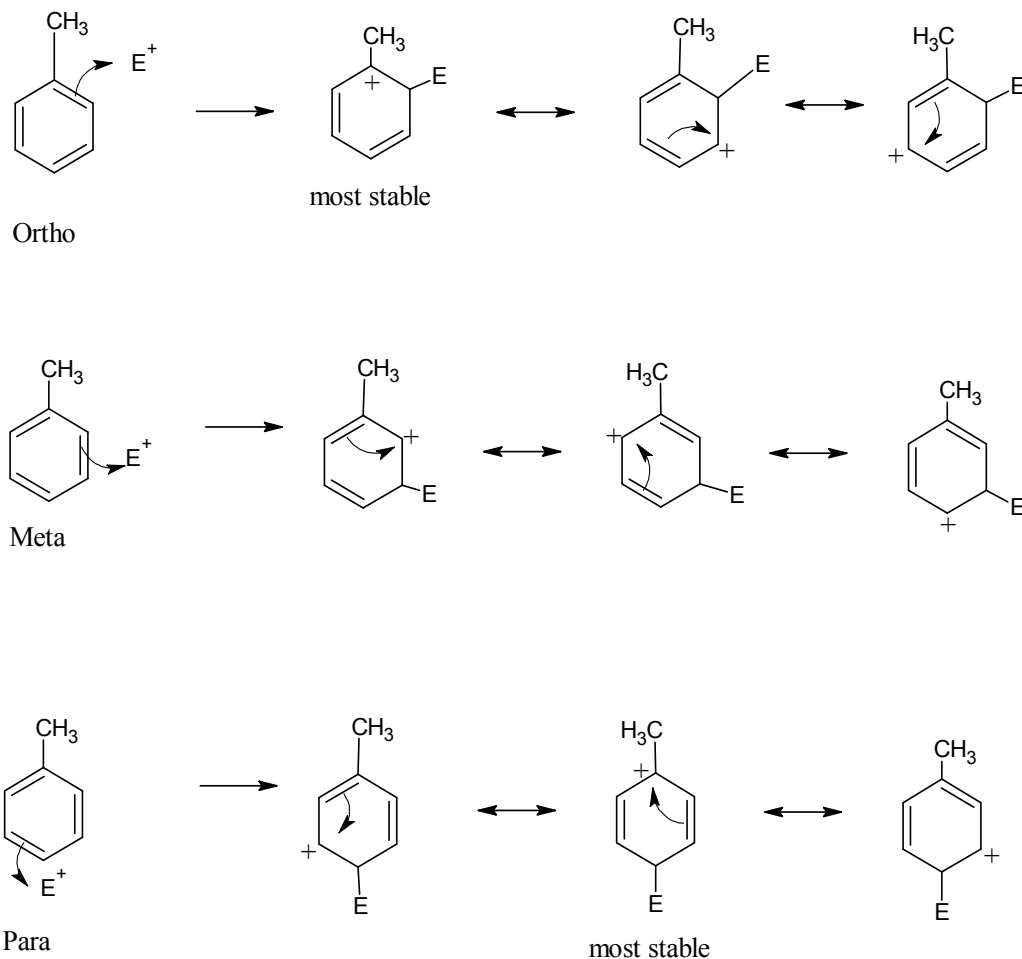
Scheme 2   The resonance structures when toluene is attacked by electrophile.

These electron-donating groups cause the second substituent to favor bonding to *ortho* and *para* positions due to the stability of carbocation resonance structures. Scheme 2 shows the resonance structures when toluene is attacked by an electrophile. When the electrophile attacks the *para* or *ortho* position, there are three carbocation resonance structures formed and one of them is the most stable tertiary carbocation. However, when the electrophile attacks at the *meta* position, it results in a secondary resonance carbocation which is less stable (Murry 2011).

Benzylation of toluene is one of the alkylation reaction which substitutes benzyl halide group as alkylating reagent into toluene (aromatic) to form methyldiphenyl. Benzoylation of toluene is the reaction between benzoyl halide with toluene to produce methyl benzophenone (MBP). Their products are useful as intermediates for the synthesis of pharmaceutical, fine chemical industries, petroleum and as fixative in perfumery industries (Bordoloi *et al.* 2006; Gracia *et al.* 2008; Vinu *et al.* 2005).

Traditionally, these reactions are carried out using homogeneous Lewis acid catalyst such as AlCl$_3$, FeCl$_3$, BF$_3$ and ZnCl$_2$ (Arata *et al.* 2000; Gracia *et al.* 2008; Morais *et al.* 1996; Singh *et al.* 1995). However, these catalysts are difficult to separate from their products, posses high toxicity, corrosive and not environmentally friendly (Bordoloi *et al.* 2006; Gawande *et al.* 2005; Phan *et al.* 2010). To overcome these problems, a combination of green technology has been used to replace the hazardous Lewis acid catalysts with heterogeneous catalysts. The new catalysts must be environmentally friendly, low cost and highly reusable to avoid generation of waste.

1.5.1   Friedel- Crafts Benzylation

FC alkylation is a typical electrophilic (carbocation) substitution reaction. The first FC alkylation reaction published was the reaction between benzene and amyl chloride catalyzed by aluminum(III) chloride (AlCl$_3$) to form amylbenzene by Charles Friedel and James Mason Crafts in 1877 (Roberts and Khalaf 1984). Equation 2 shows the general equation of FC alkylation. Two types of intermediate complexes can be formed in alkylation reaction i.e. π-complexes or σ-complexes are

formed between the alkyl halide and the metal halide catalyst.

$$RCH \; + \; R'Cl \; \xrightarrow{AlCl_3} \; RCR' \; + \; HCl \qquad (2)$$

Mostly alkyl halide, alkyl sulfonate, alkene, alcohol and alkene oxide were used as alkylating agents (Phan *et al.* 2010). The reactivity was influenced by the alkylating agent. The reactivity was found to increase in order of primary > secondary > tertiary> allylic ~ benzylic (Smith and March 2001).

There are several limitation in FC alkylation reaction. One of them is that it only takes place with alkyl halides, it does not react with vinyl or aryl halides due to their unstable intermediate carbocations. Only benzene or activated benzene derivatives which are more reactive than the mono-halobenzene will undergo alkylation reaction with Lewis acid catalyst. A mixture of products will be obtained as the reaction will undergo carbocation rearrangement to the most stable products. Over alkylation will occur also since the product was more reactive than the reactant but this can be overcome by using an excess of reactant to the alkylating reagent (Kalsi 2000).

Friedel-Crafts benzylation of toluene by benzyl chloride will form the monosubstituted methyldiphenylmethane (MDM) as product. The 4-methyldiphenylmethane (4-MDM) and 2-methyldiphenylmethane (2-MDM) will be the major products, while the di-substituted product will be the minor products as shown in Scheme 3.
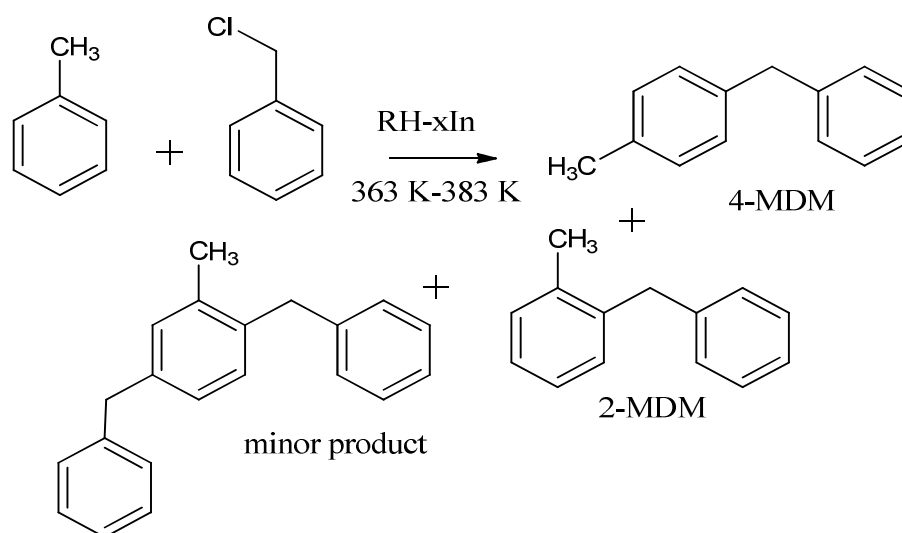
Scheme 3 The benzylation of toluene with benzyl chloride.

MDM is useful in several applications such as in the preparation of intermediate for pharmaceutical, petroleum and fine chemical industries (Gracia *et al.* 2008; Morais *et al.* 2008). These liquid phase reactions are usually catalyzed by homogenous Lewis acids as described earlier (Phan *et al.* 2010; Yang *et al.* 2005). Since these catalysts are difficult to recover, and separate from the products, hence the replacement of these homogeneous catalysts is important and has many advantages.

The Friedel-Crafts benzylation of benzene and other aromatics was reported by Anand *et al.*, (2010). The reaction was catalyzed by mesoporous gallosilicate nonacage (GaSBA) with different gallium contents. GaSBA-1 (Anand *et al.*, 2010) was found to be the best catalyst as it gave 99-100 % conversion for the benzylation of toluene and benzene in 75 min at 353 K.

Pal *et al.*, (2011) reported the benzylation of aromatics catalyzed by mesoporous perovskite $ZnTiO_3$ materials. The benzylation of toluene resulted in 90.2 % conversion with 65 % of selectivity toward 4-MDM. The benzylation of toluene by

benzyl bromide catalyzed by metal-organic framework (MOF-5) was reported by Phan *et al*., (2010). The reaction was carried out at 333 K for 6 h. The highest conversion obtained was 100 % with 60 % of selectivity towards 4-MDM.

These catalysts have their disadvantages, as they need longer time to achieve higher conversion, to obtain higher selectivity of 4-MDM, preparation process involving high calcinations and preparation material was very costly. Therefore, better, cheaper and much more selective catalyst is required.

The benzylation of toluene by benzyl chloride catalyzed by iron incorporated silica (RHA-Fe) and modified with benzoic acid iron incorporated silica (RH-Fe (5 % amino)) were studied by Adam *et al*. (2006) and Adam *et al*. (2007). For RHA-Fe, 100 % conversion was obtained at 373 K within 60 min, with about 45 % selectivity of 4-MDM. While for RH-Fe, 98 % conversion and 95 % of the mono-product (4-MDM and 2-MDM) was obtained within 120 min.

1.5.2 Friedel-Crafts benzoylation

FC acylation is a reaction between the acyl halide and aromatic compound to produce an acyl group substituted aromatic ring compound catalyzed by Lewis acid. Equation 3 shows the general equation of acylation reaction catalyzed by aluminium(III) chloride (Lewis acid).

$$RCH \;+\; R'OCl \;\xrightarrow{AlCl_3}\; RCOR' \;+\; HCl \qquad (3)$$

Acylation is a common reaction which gives carbon-carbon coupling (Karthik *et al.* 2008).   Its limitation is slightly different from alkylation reaction. Limitation in the FC acylation reaction includes the fact that only ketone compounds will be formed. For acyl halide, only acylium ion will be formed as alkylating agent. Over acylation does not happen as the product formed during the first acylation is less reactive than the starting material. The other limitation is similar to the alkylation, i.e. only the benzene or activated benzene derivatives will undergoes this reaction as the deactivated benzene derivatives are not reactive (Kalsi 2000).

Aromatic ketones are very widely used in several industries such as in the synthesis of fine chemicals, pharmaceutical industries, agro chemical and perfumery chemicals (Gawande *et al.* 2005; Laidlawa *et al.* 2001). Formations of aromatic ketones are mostly obtained from Friedel-Crafts acylation of aromatic compounds. Benzoylation of aromatic compounds by benzoyl chloride was one of the important reactions in the formation of benzophenone. This reaction will produce three types of isomers, i.e. *para, ortho* and *meta*.
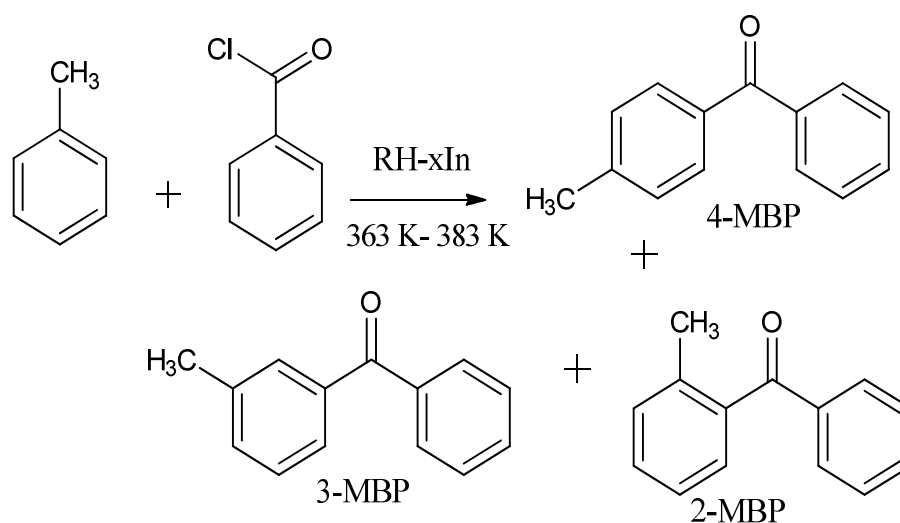
Scheme 4   The benzoylation of toulene with benzoyl chloride

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Scheme 4 shows the general reaction between toluene and benzoyl chloride. The major products that formed were 4-methylbenzophenone (4-MBP) and 2-methylbenzophenone (2-MBP), while 3-methylbenzophenone (3-MBP) was the minor product.

Generally these reactions were catalyzed by homogenous Lewis acid catalysts that results in large amount of hazardous waste. To minimize these problems, heterogeneous catalysts is a good alternative. Singh *et al.* (1995) carried out the benzoylation of toluene with benzoyl chloride over zeolite catalysts at 383 K. They found that H-beta zeolite gave the highest conversion of 83.4 % with 95 % selectivity towards 4-MBP in 18 h.

Arata *et al.* (2000) studied the acylation of toluene with benzoic acid and benzoyl chloride catalyzed by solid superacid (sulfated zirconia and alumina) and the reaction was carried out at 373 K for 3 h. It resulted in 92 % conversion with 73 % selectivity for 4-MBP using benzoic anhydride, while benzoyl chloride gave a conversion of 60 % and 68 % selectivity toward 4-MBP.

Gawande *et al.* (2005) studied the benzoylation of arenes by benzoyl chloride catalyzed by PIZP (potassium iron zirconium phosphate). The benzoylation was carried out at 373 K with 0.1 mol of toluene to 0.02 mol of benzoyl chloride for 3 h. It resulted in a conversion of 90 % with 80 % selectivity towards 4-MBP.

Sulfated fibrous ZrO_2/Al_2O_3 core and shell nanocomposites as strong acid catalyst were studied by Liu *et al.* (2012). The highest conversion of toluene was reported as 75 % in 6 h under reflux catalyzed by S-Zr-50 (50 % of ZrO_2 in Al_2O_3).

Benzoylation of aromatic compounds catalyzed using Indium(III) oxide impregnating on Si-MCM-41 was studied by Choudhary *et al.* (2002). The benzoylation of toluene was carried out at 383 K for 2.5 h and the result obtained was 85 % conversion when 20 % In(III) impregnated Si-MCM-41 was used as the catalyst.

1.6   Objectives of study

From the literature review, it is evident that there is a need for new catalysts for FC reactions. Therefore, the synthesis of new catalyst by using RH (waste), as a material to produce amorphous silica incorporated with indium was undertaken in this study. The objectives of this study are:

- To synthesize the indium incorporated silica supported heterogeneous catalyst by a simple template free sol-gel method.

- To fully characterize these catalysts using the techniques of FTIR, SEM/EDX, TEM, XRD, BET and AAS.

- To study the Friedel Crafts benzylation and benzoylation of toluene using the prepared heterogeneous catalysts.

- To compare the catalytic activity of the homogeneous indium nitrate salt and the synthesized RH-xIn catalyst.

Chapter 2

EXPERIMENTAL

2.0   Raw Materials

Rice husk (RH) was collected from a rice mill in Penang, Malaysia. Indium nitrate (Alfa Aesar, 99 %) was used as the source for indium. Other materials included sodium hydroxide (Systerm, 99 %), nitric acid (Systerm, 99 %), dodecane (Merck, 99 %), toluene (QReC), benzyl chloride (Fluka) and benzoyl chloride (Acros, 99.5 %). All these chemicals were used directly without further purification.

2.1   Extraction of silica from rice husk (RH).

Rice husk (RH) was washed with plenty of tap water to remove the dust, and then rinsed with distilled water and dried at room temperature for 24 h. 30 g of RH was stirred in 500 mL of 1.0 M nitric acid for 24 h at room temperature. The treated RH was washed with plenty of distilled water to remove the acid and dried in oven at 373 K for 24 h. The mass of the dried treated RH was recorded as (a). The treated RH was stirred with 0.1 M sodium hydroxide (500 mL) at room temperature for 24 h, to extract the silica from the RH in the form of sodium silicate. The resulting mixture was filtered and washed. Both residue and the filtrate were collected. The filtrate was used as the sodium silicate. The residue RH was dried at 373 K in an oven for 24 h and the mass was recorded as (b).

The mass of extracted silica was computed as [(a) − (b)] g.

2.2   Preparation of RH-xIn (x = 5, 10, 15 and 20)

For the preparation of RH-xIn (x = 5, 10, 15 and 20), the sodium silicate that extracted from RH will titrated with nitric acid which added with indium salt (indium(III) nitrate). The metal loading used was 5%, 10%, 15% and 20%. The amount of indium was calculated using the following method.

Mass of indium = % of indium loading x [(a) − (b)] g

The mass of indium salt was added into the 3.0 M of nitric acid and titrated with the sodium silicate until it reached pH 9 and the brownish gel was formed. The brownish gel was aged for 48 h. The gel was filtered and washed with plenty of hot distilled water to remove the sodium hydroxide. The white gel was dried at 373 K for 24 h and ground into the fine powder form. The catalysts were labeled as RH-5In, RH-10In, RH-15In and RH-20In. RH blank was prepared as the same method but without adding any metal.

2.3   Physico-chemical characterization

The catalysts were characterized by several analytical techniques such as, Fourier Transform Infra-Red spectroscopy (FT-IR), Scanning Electron Microscopy combined with Energy Dispersive Spectrometry (SEM/EDX), Transmission Electron Microscopy (TEM), Nitrogen Adsorption-desorption Isotherms (BET), Powder X-Ray Diffractometry (XRD), Atomic Absorption Spectroscopy (AAS) and Diffuse Reflectance Ultra-Violet Visible (DR UV-Vis). For catalytic activities, products from Friedel-Craft catalytic activities were detected by a gas chromatograph (GC) and were then identified by gas chromatograph equipped with mass spectroscopy

(GC-MS).

2.3.1   Fourier Transform Infra-Red Spectroscopy (FT-IR) analysis

Fourier Transform Infra-Red spectroscopy (FT-IR) data were obtained by using Perkin Elmer 2000 FT-IR Spectrometer in wavenumber range of 400-4000 cm^{-1} with 4 cm^{-1} resolution. Potassium bromide (KBr) pellet for silica samples consisted of RH-blank and RH-In. The ratios of KBr (spectral grade) to catalysts were in 10:1 and the solid samples were pressed into pellets using a hydraulic press ($\sim$ 8 ton $inch^{-2}$).

2.3.2   Scanning Electron Microscopy and Energy Dispersive X-Ray (SEM/EDX) analysis.

The silica samples were first ground into fine powder form, and then mounted onto SEM specimens stub with double tape. The specimens were covered with a layer of gold and this coating process was needed about 15-20 min. Then, the samples were scanned with electronic microscope. Leo Supra 50 VP Field Emission Scanning Electron Microscope equipped with Oxford INCA 400 Energy Dispersive X-ray Microanalysis System (Carl-Ziess SMT, Oberkochen, Germany; Oxford Instruments Analytical, Bucks.U.K.) was used to carry out SEM imaging and EDX elemental analysis.

2.3.3 Transmission Electron Microscopy (TEM) analysis

Fine powder of catalysts was first suspended in distilled water in the small sample bottle. One droplet of the sample was dropped onto a carbon film coated with 400 mesh copper grid and allowed to stand for 1-3 min. TEM images were taken using Philips CM12 instrument (Eindhoven, Netherlands) equipped with Analysis Docu Version 3.2 image processing software (Munster, Germany).

2.3.4 Nitrogen adsorption-desorption analysis (BET) analysis

The catalysts were out degassed for 12 h at 473 K under nitrogen gas flow and then evacuated to 1 μm Hg in degassing port of adsorption analyzer. Nitrogen adsorption-desorption isotherms were measured at 77 K by Quantachrome NovaWin2. Nitrogen was used as an adsorbate. The specific surface area was calculated using the BET model. The pore diameter and pore size distribution of the samples could be obtained using Barrett-Joyner-Halenda (BJH) method.

2.3.5 Powder X-ray Diffraction (XRD) analysis

The powder XRD patterns of the catalysts were collected from Siemens Diffractometer D5000, Kristlloflex with 40 kV Voltage and 30 mA current using CuKα. (λ= 0.154 nm) radiation. Angle of diffraction was scanned at 2θ range, $10^{°}$ to $80^{°}$ for 2 h, at rate of $6.0^{°}$/min. XRD is used to identify the structure, phase purity, degree of crystallinity, unit cell parameters and crystallite size.

2.3.6   Atomic Absorption Spectroscopy (AAS) analysis

Atomic Absorption Spectroscopy (AAS) analysis was used to determine the actual metal content loaded into the silica catalysts. The samples were prepared as follows or using the method below:- 0.05 g of the RH-xIn was dissolved into a mixture of 0.5 mL aqua regia (HNO_3: HCl = 1:3 v/v) and 3 mL HF in the polytetrafluoroethylene (PTFE) bottle, and heated at 373 K for 45 min. Cool the mixture at room temperature. Then, 10 mL of the deionised water and 0.5 g of boric acid (H_3BO_3) were added into the mixture. The mixture was diluted to 100 mL by using volumetric flasks. The standard solution of the indium ions was used to do the calibration and to ensure the reproducibility of the results, the samples were analyzed duplicated.

2.3.7   Diffuse Reflectance Ultra-Violet Visible (DR UV-Vis) analysis

The DR UV-Vis spectra of the catalyst were obtained by using Perkin Elmer Lambda 35 UV-Vis spectrometer equipped with a diffuse reflected attachment with solid sample holder. The spectra were recorded in the range of 200-1000 nm and the KBr was used as the reference for the base line correction.

2.4   Catalytic Reactions

2.4.1   Friedel-Craft benzylation and benzoylation of toluene

Liquid phase Friedel-Craft benzylation and benzoylation of toluene were performed in the presence of catalyst (RH-xIn) using two necked round bottom flask and the solution was magnetically stirred under refluxed method. The temperature was maintained at constant by using an oil bath. Argon gas flow was used to avoid the moisture effect. Benzylation of toluene involved the reaction between benzyl chloride (BzC) with toluene. On the other hand, benzoylation involved the reaction between benzoyl chloride (BoC) with toluene. Both reactions were studied using the same set of molar ratios which are 5:1, 10:1, 15:1 and 20:1. Others parameters such as temperature (363 K, 373 K and 383 K), mass of catalyst (0.05 g, 0.10g, 0.15 g and 0.20 g), time and percentage of metal loading were also observed. The products from Friedel-Craft catalytic activities were detected by gas chromatograph (GC) and were then identified by gas chromatograph equipped with mass spectrometer (GC-MS).

2.4.2   GC and GC-MS

Gas chromatograph (Clarus 500, Perkin Elmer) equipped with 30 m length and 0.32 mm inner diameter VB-1 capillary column and FID detector was used to monitor the catalytic activities. To confirm the product, GC-MS (Trace GC 2000, Thermo Finnigan) with MS (Trace MS, Thermo Finnigan) detector was used. Both GC and GC-MS were performed under the same conditions.

Table 2.1: GC and GC-MS conditions for separation and identification of benzylation and benzoylation products.

Condition	Benzylation	Benzoylation
Initial temperature, K	353	353
Initial time, min	0.00	0.00
Ramp	10.0	10.0
Final temperature, K	503	503
Injector temperature, K	513	513
Detector temp., K	523	523
Carrier (GC)	Nitrogen gas	Nitrogen gas
Carrier (GC-MS)	Helium gas	Helium gas
Hold time	3 min	1 min

2.4.3 Response factor (F)

BzC, toluene and dodecane were mixed with ratio of 1:1:1 (mol/mol) for benzylation of toluene. For benzoylation of toluene, BzC was replaced with BoC. Both mixtures were detected by GC. Response factor was calculated as below:-

$$\frac{Area_x}{Area_y} = \frac{k_x \ x \ M_x \ x \ V_x}{k_y \ x \ M_y \ x \ V_y}$$

$$F = \frac{k_x}{k_y} = \frac{\frac{Area_x}{M_x}}{\frac{Area_y}{M_y}}$$

x represented the reactants used such as toluene, benzyl chloride (BzC) and benzoyl

chloride (BoZ). Dodecane is represented as y and k as constants. M is molarity of the

solvent, V is the volume of the solvent.