

LIQUID-GAS BOUNDARY CATALYSIS BY GOLD/POLYSTYRENE-COATED
HOLLOW TITANIA AND THE EFFECTIVE LOCATION OF ACTIVE SITES
IN LIQUID-LIQUID PHASE-BOUNDARY CATALYST

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To my beloved
Husband
Mother and Father
Mother and Father in law

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ABSTRACT

The research described in this thesis is an attempt to synthesize floating catalyst to be used in phase-boundary catalysis for liquid-gas reaction. It is also an attempt to determine the effective location of catalytic active sites in phase-boundary catalyst for immiscible liquid-liquid reaction. Phase-boundary catalysis (PBC) is a heterogeneous catalytic reaction in which the catalyst particles are located at the interphase of either immiscible liquid-liquid or liquid-gas phases. In this research, gold/polystyrene-coated hollow titania was successfully synthesized. The synthesis steps involved hydrothermal synthesis of carbon sphere from sucrose as the template, coating of the carbon sphere with titania, removal of the carbon sphere to produce hollow titania, followed by coating of polystyrene on the surface of hollow titania and the attachment of gold nanoparticles. The results showed that the size of the carbon spheres increased when the concentration of the sucrose increased. The hollow titania obtained by carbon sphere template was found to have smaller diameter than its template and was in the anatase phase. Polystyrene was coated on hollow titania by *in-situ* polymerization of styrene with aqueous H_2O_2 , while gold was deposited by sputtering deposition technique on the surface of polystyrene-coated hollow titania. It has been demonstrated that gold/polystyrene-coated hollow titania can float on water due to its low density and it is a potential catalyst for liquid-gas boundary catalysis in the oxidation of benzyl alcohol by using molecular oxygen. In this study, some aspects in the determination of the effective location of active sites of PBC in immiscible liquid-liquid system were also studied using NaY, HZSM-5 and TS-1 zeolites as the catalysts in the oxidation of 1-octene and hydroxylation of cyclohexene using aqueous H_2O_2 . Based on experimental results, it is concluded that the effective location of active sites is located on the external surface of zeolites.

ABSTRAK

Penyelidikan yang dinyatakan di dalam tesis ini adalah suatu percubaan untuk mensintesis mangkin terapung untuk digunakan dalam pemangkinan sempadan fasa tindak balas cecair-gas. Penyelidikan ini juga adalah suatu percubaan untuk menentukan lokasi tapak aktif mangkin yang efektif dalam mangkin sempadan fasa bagi tindak balas cecair-cecair yang tak larut campur. Pemangkinan sempadan fasa (PBC) merupakan satu tindak balas pemangkinan heterogen yang mana zarah mangkin terletak di antara fasa cecair-cecair yang tak larut campur atau fasa cecair-gas. Dalam kajian ini, titania berongga bersalut emas/polistirena telah berjaya disintesis. Langkah-langkah sintesis melibatkan sintesis hidroterma sfera karbon daripada sukrosa sebagai templat, penyalutan sfera karbon dengan titania, penyingkiran sfera karbon untuk menghasilkan titania berongga, diikuti dengan penyalutan permukaan titania berongga dengan polistirena dan pengendapan zarah nano emas. Hasil kajian menunjukkan bahawa saiz sfera karbon meningkat apabila kepekatan sukrosa meningkat. Titania berongga yang diperolehi melalui templat sfera karbon didapati mempunyai diameter yang lebih kecil daripada templatnya dan wujud dalam fasa anatas. Titania berongga kemudian disaluti dengan polistirena melalui pempolimeran *in-situ* stirena dengan H₂O₂ akueus. Manakala, emas diendapkan di permukaan titania berongga bersalut polistirena melalui teknik pengendapan percikan. Didapati bahawa titania berongga bersalut emas/polistirena boleh terapung di atas air kerana ketumpatannya yang rendah dan ia merupakan mangkin yang berpotensi bagi pemangkinan sempadan cecair-gas dalam pengoksidaan benzil alkohol dengan menggunakan molekul oksigen. Dalam kajian ini, beberapa aspek dalam penentuan lokasi tapak aktif mangkin yang efektif di dalam sistem cecair-cecair yang tak larut campur juga telah dikaji menggunakan zeolit NaY, HZSM-5 dan TS-1 dalam pengoksidaan 1-oktena dan penghidroksilan sikloheksena menggunakan H₂O₂ akueus. Berdasarkan keputusan eksperimen, kesimpulan yang boleh dibuat adalah lokasi tapak aktif yang efektif terletak di permukaan luar zeolit.

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LIST OF ABBREVIATIONS

CS	-	Carbon sphere
ODS	-	<i>n</i> -octadecyltrichlorosilane
MPTS	-	3-mercaptopropyl trimethoxysilane
w-Ti-NaY	-	Unmodified Ti-NaY
w/o-Ti-NaY	-	Partly modified Ti-NaY
o-Ti-NaY	-	Fully modified Ti-NaY
w-HZSM-5	-	Unmodified HZSM-5
w/o-HZSM-5	-	Partly modified HZSM-5
o-HZSM-5	-	Fully modified HZSM-5
w-TS-1	-	Unmodified TS-1
w/o-TS-1	-	Partly modified TS-1
o-TS-1	-	Fully modified TS-1
w-SO ₃ H-Ti-NaY	-	Unmodified sulfonyl Ti-NaY
w/o- SO ₃ H-Ti-NaY	-	Partly modified sulfonyl Ti-NaY
o- SO ₃ H-Ti-NaY	-	Fully modified sulfonyl Ti-NaY
TEA	-	Trimethylammonium chloride
HTAB	-	Hexadecyltriammonium bromide
TIP	-	Titanium(IV) isopropoxide
CS-T	-	Carbon sphere with TEA
CS-H	-	Carbon sphere with HTAB
HT	-	Hollow titania
HT CS	-	Hollow titania using CS as template
HT CS-T	-	Hollow titania using CS-T as template
HT CS-H	-	Hollow titania using CS-H as template
PBC	-	Phase-boundary catalysis
PS-HT	-	Polystyrene-coated hollow titania
Gold/PS-HT	-	Gold nanoparticle deposited on PS-HT

LIST OF SYMBOLS

Å	-	Armstrong (1×10^{-10} m)
g	-	gram
M	-	Molar
mM	-	miliMolar (1×10^{-3} mol/volume)
mg	-	miligram (1×10^{-3} g)
mL	-	millilitre (1×10^{-3} L)
nm	-	nanometre
ppm	-	part per million
µm	-	micrometre (1×10^{-6} m)

CHAPTER 1

GENERAL INTRODUCTION

1.1 Background of the Research

For faster economic growth, a huge amount of energy is needed for different purposes in industrial facilities worldwide. Energy is a vital factor to allow competitiveness and employment. It has been reported that the consumption of energy worldwide in the industrial sectors, including energy from chemicals by major energy-intensive industry, was statistically 29 % in 2006 [1]. Since the global population and energy needs are increasing yearly, it is necessary to establish an economical way for chemical processes.

Recently, a novel concept of phase-boundary catalysis (PBC) was proposed in order to utilize the immiscible liquid-liquid reaction system with solid catalysts [2]. Without stirring and heating, the amphiphilic zeolite particle was demonstrated to have excellent catalytic properties in the epoxidation reaction with the catalyst located between aqueous and organic phases. The location of the active sites at the phase boundary (Figure 1.1) makes stirring no longer required because in PBC, mass transfer is not the rate determining step. However, in conventional catalytic reaction, mixing is an essential prerequisite to ensure the occurrence of mass transfer between the phases of organic substrate and aqueous oxidant. There are seven steps involved in conventional catalytic system (Figure 1.1), which are: step 1 is the transfer of aqueous phase to the external surface of the solid catalyst. Step 2 is the transfer of

aqueous phase to the inside of the pore volume of the solid catalyst followed by step 3 which is the transfer of the substrate from the organic phase to the interphase.

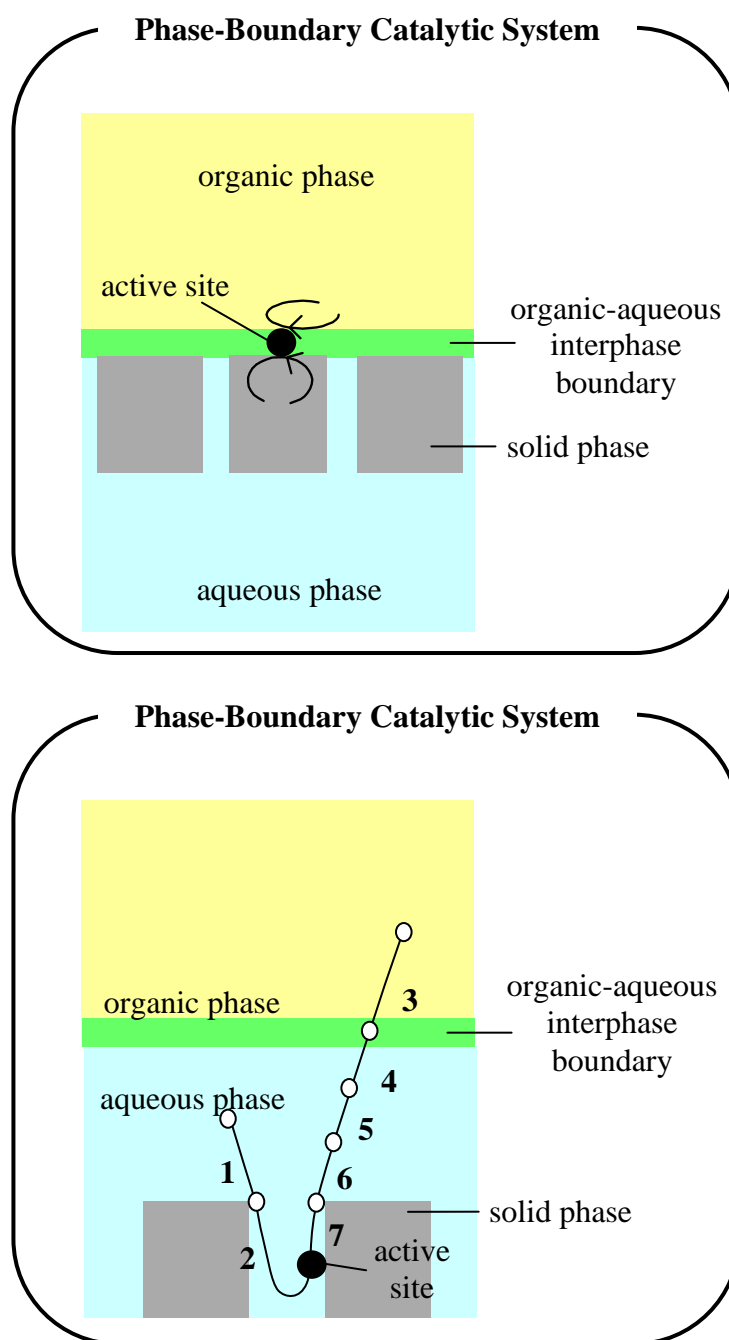


Figure 1.1: Schematic diagrams of catalytic action between the conventional and phase-boundary catalytic systems [3].

The next step is the transfer of the substrate from the interphase to the aqueous phase and step 5 is the mixing and diffusion of the substrate in the aqueous phase. Step 6 is

the transfer of the substrate from the aqueous phase to the external surface of the solid catalyst and step 7 is the transfer of the substrate to the inside of the pores of the solid catalyst. The last step is the catalytic reaction of adsorption, chemical reaction and desorption.

Liquid-liquid PBC are well-established and has been successfully tested in several reactions [2, 4-8]. However, the location of the effective active site remains unidentified. The purpose of this research is to identify the effective location of active site in liquid-liquid PBC by using several types of model catalysts, in which the location of the active sites is located at the internal and external, internal or external surface of zeolite. In order to prove the effect of mass transfer of substrates to the active sites, reaction of 1-octene with gradual addition of aqueous H_2O_2 was carried out.

Besides the determination of the effective location of active site in phase-boundary catalyst, the research was extended to a liquid-gas catalytic system. From an industrial point of view, continuous processes which are carried out in gas phase are preferred. In large production, they offer advantages to the field of economy process, plant security, process control and heat recovery [9]. For reactions in gas and liquid phases, such as hydroprocessing operations and oxidation of organic substances in liquid phase [10-13], the mass transfer is brought into contact to carry out chemical reactions [14]. Gas and liquid phases have various mixing patterns, such as plug flow, well-stirred and plug-flowed with axial dispersion. These mixing patterns have been considered as the conventional way to carry out chemical reactions. The conventional system for liquid-gas reaction uses stirring to increase the solubility of gas in the liquid phase. In the conventional system, the process is generally executed under stirred condition in a batch reservoir reactor. Consequently, the catalysts must be in the form of delicate powder to ensure easy dispersion in the substrate medium [15].

The fast-growing insight into the functional materials has led researches to be more focused on the synthesis of materials with specific properties. The preparation of hollow materials with low density is one of the targets of many researchers [16-

18]. For photocatalysis application, floatable low density materials, such as polystyrene [19], vermiculite [20] and polypropylene [21], have been used as catalyst support for titania. Besides that, it has been reported that hollow titania can also float on water [17]. This is because the tight aggregation of titania particles give buoyancy by preventing water from penetrating into the titania network.

In this thesis, a ball-like microparticle material of gold/polystyrene-coated hollow titania (gold/PS-HT) has been synthesized for catalytic reaction in liquid-gas PBC system. The gold/PS-HT, which floats on water, is able to carry out the reaction without stirring and heating. The precursors used to prepare gold/PS-HT were sucrose, titanium(IV) isopropoxide (TIP) and styrene. In order to synthesize a low density polystyrene-coated hollow titania (PS-HT), a relatively big space inside the hollow structure is required. Carbon microsphere was preferred as the template because its size can be easily tuned. Larger size of template will decrease the density of the hollow material, hence allowing its floatability in water. Figure 1.2 shows the schematic diagram of the structure of the floating catalyst, which consists of a void in its structure. It is expected that the density of gold/PS-HT is lower than the density of organic solution. Void in the catalyst will result in the floatability of the catalyst on the surface of liquid, thus allowing the reaction between gas and liquid substrates to take place without stirring. This concept can potentially save a lot of energy since stirring is not required.

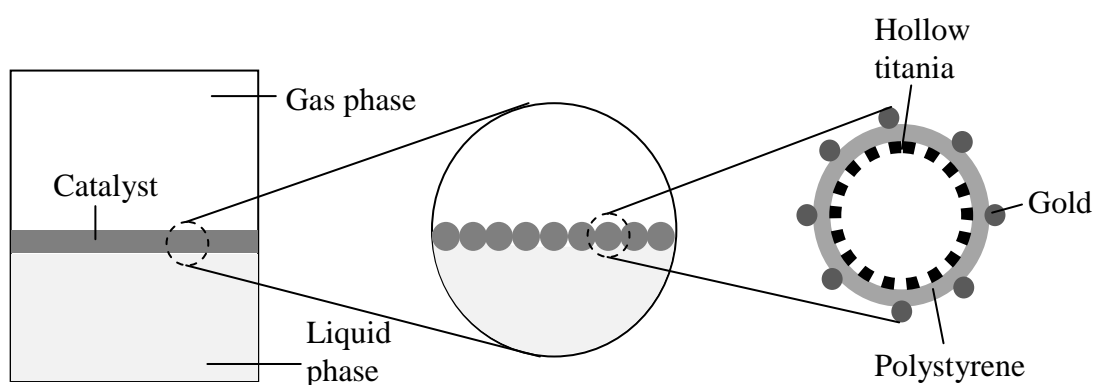


Figure 1.2: Schematic diagram of phase-boundary catalyst for liquid-gas system.

In this research, gold was used as the catalytic active site. Gold catalysts have been found to be active in the oxidation of benzyl alcohol in water at ambient temperature and pressure [22]. Gold supported PS-HT can be easily prepared by sputter deposition techniques. Previous study on the interaction between the active sites and the support is not only dependent on the nature of the system, but also on the preparation method [23]. This fact has a significant effect in the resulting metal dispersion on the catalysts.

Heterogeneous catalysts have been widely investigated and employed since they are easily recovered and regenerated compared to homogeneous catalysts [4, 24]. Supported catalysts are of particular interest since it enables better dispersion and stabilization of small metal particles [15]. This is due to its ability to provide greater access to the catalytic active sites than its bulky form. Recovery, refining and recycling of precious metal catalysts make supported catalysts important in the economic sense [15]. The technology is also ecologically-safe since it does not produce large amounts of solid waste that needs to be disposed off in land fills.

1.2 Statement of the Problems

In this study, there are two main problems to be addressed. First, the location of effective catalytic active sites in phase-boundary catalyst in liquid-liquid system and second, developing a new catalyst for liquid-gas PBC system. Figure 1.3 shows the research strategy in the development of liquid-liquid and liquid-gas PBC.

In liquid-liquid system, the strategy is to synthesize amphiphilic structured catalyst, where the hydrophobic part interacts with the organic phase (substrate) and the hydrophilic part interacts with the aqueous phase (oxidant). The catalyst is made by NaY zeolite impregnated with titania (TiO_2) as the active site and modified with alkylsilyl group to make half of its structure hydrophobic. It was demonstrated that the amphiphilic catalyst has been successfully synthesized and work efficiently in PBC system for oxidation and hydration reactions [4, 6]. However, basic fact on the

location of the effective active sites remains unclear. The active sites may be attached to the external surface of the catalyst or in their pores, which needs to be clarified in the present work.

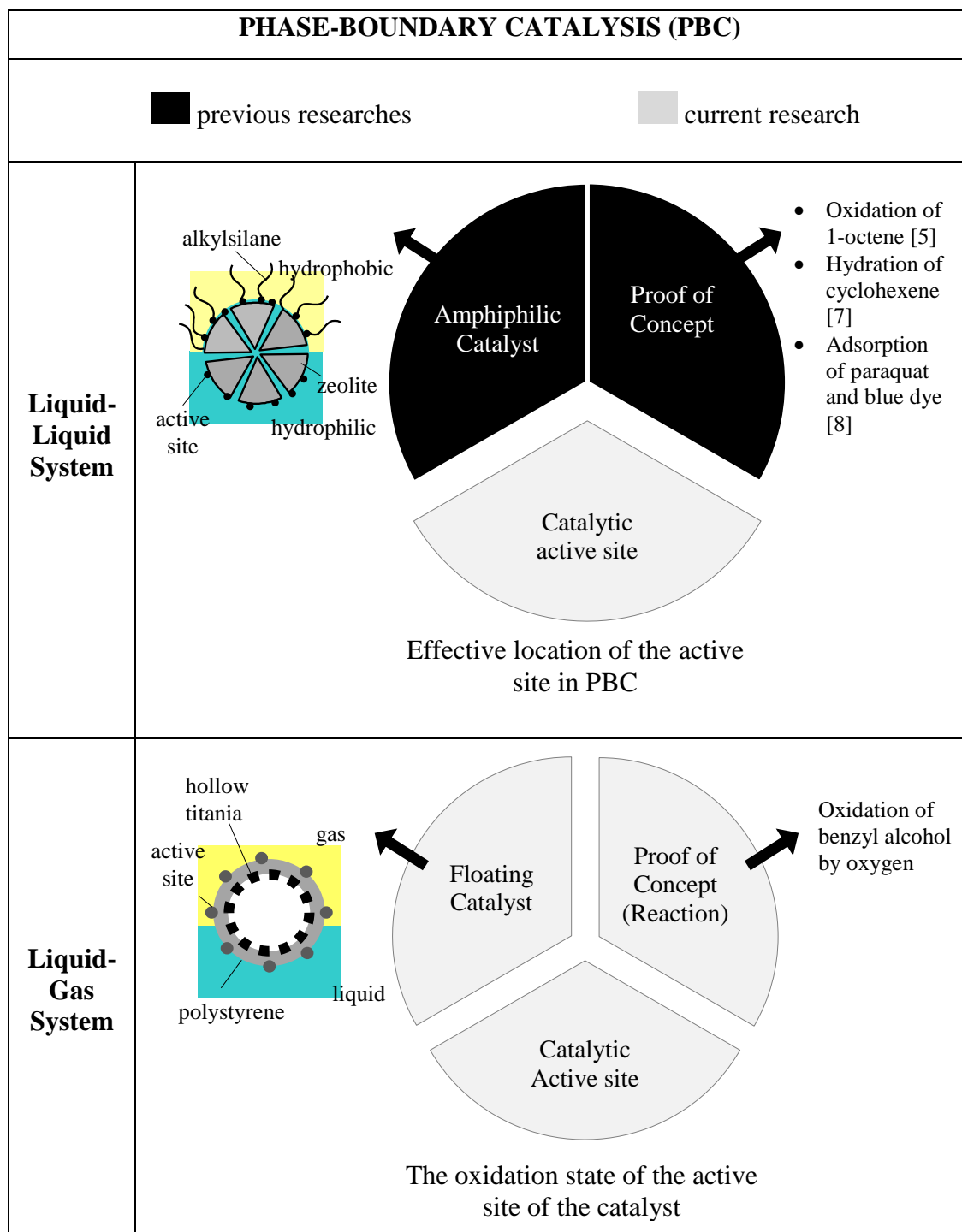


Figure 1.3: Research strategy in the development of liquid-liquid and liquid-gas phase-boundary catalysts.

It is of interest to extend the concept of PBC to liquid-gas system by using floating catalyst. Four consecutive steps are involved in developing a floating catalyst; (1) preparation of CS template hydrothermally by using sucrose as the precursor, (2) synthesis of HT by using sol-gel method and the removal of the carbon template by calcination, (3) polystyrene coating of HT particles and (4) gold sputtering of PS-HT. So far, most CSs were synthesized with various carbon precursors, such as polystyrene [25], corn starch [26], acetylene [27], glucose and furfuryl alcohol [28]. Sucrose is an important carbon source that is available at a low cost. It can easily react with other materials due to its high amount of free hydroxyl group. Besides that, the excess sucrose after reaction can be effortlessly removed due to its good solubility in water, and the byproducts are environmentally benign [23]. Many studies have been done by controlling the duration, temperature and concentration of the precursor in order to control the size of the carbon [23, 26, 29, 30]. There are limited researches regarding the effect of surfactant toward the size of the carbon particles. Therefore, deeper understanding of the mechanism of sucrose transformation to CSs with various particles size needs to be investigated. The physicochemical properties of the CSs should also be analyzed.

Syntheses of HT by the one-pot approach such as Layer-by-Layer technique, Kinkerdall effect and Ostwald ripening were proven to be successful [31, 32]. However, drawbacks such as lack of control over the size and shape, poorly understood mechanisms and the difficulties in developing a general strategy for the synthesis substantially limits their application [33]. Templating method is reproducible and facile to fabricate the hollow structure. It also easily adjusts the hollow sphere's diameter and the shell thickness. It is interesting to explore energy-saving and cost-effective routes to fabricate HT. The effects of size and wall thickness of HT also need to be studied.

Among the preliminary test, gold (Au) on carbon showed it to be a good alternative with respect to the classical system. It has been found that monometallic catalysts can operate several times without deactivation and very selective when polyhydroxylated molecule was used as the substrate [34]. It is very facile to anchor the gold active site on the support by sputter deposition technique. However, the

effects on the catalytic activity need to be confirmed. The effects of the amount of gold used also need to be thoroughly investigated.

The synthesis of high catalytic active gold/PS-HT materials in liquid-gas system remains a challenge. To the best of our knowledge, this is the first example of phase-boundary catalyst in liquid-gas system. This research is important in contributing to the understanding of floating gold/PS-HT catalysts in liquid-gas reaction. It is necessary to fabricate polystyrene-coated hollow titania with low density for floatation to increase the selectivity and catalytic activity for the active site.

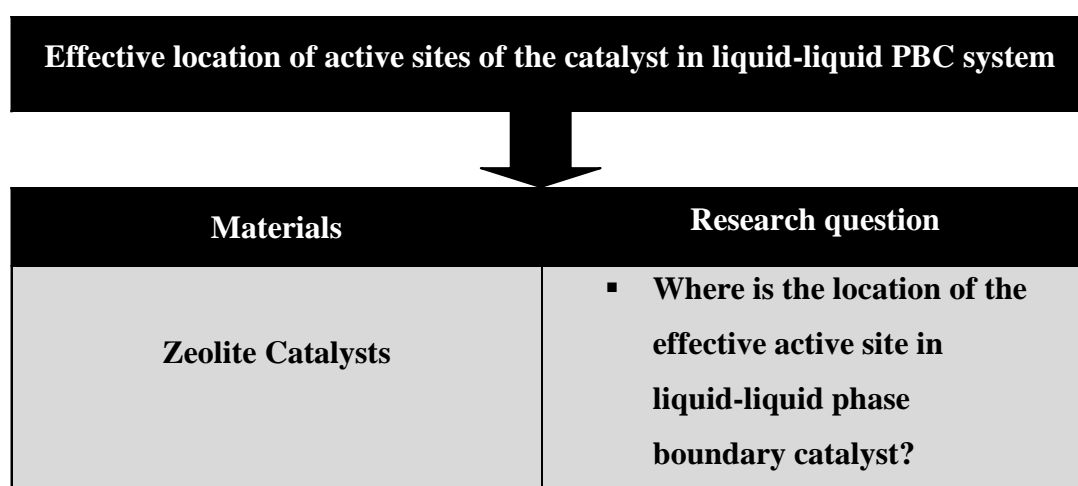


Figure 1.4: Schematic representation of the research question and statement of the problem for liquid-liquid PBC system.

Figures 1.4 and 1.5 show the schematic representation of the research questions for liquid-liquid and liquid-gas phase boundary catalysis, respectively.

Design and catalytic activity of floating catalyst in liquid-gas PBC system	
Materials	Research questions
Carbon spheres (CS)	<ul style="list-style-type: none"> ▪ What are the criteria to control the size of carbon sphere? ▪ What are the physicochemical properties of carbon sphere?
Hollow titania (HT)	<ul style="list-style-type: none"> ▪ What are the physicochemical properties of HT?
Gold/polystyrene-coated hollow titania (gold/PS-HT)	<ul style="list-style-type: none"> ▪ What are the physicochemical properties and catalytic activity of gold/PS-HT in liquid-gas boundary catalysis?

Figure 1.5: Schematic representation of the research question and statement of the problem for liquid-gas PBC system.

1.3 Objectives of the Research

The objectives of the research are:

- To determine the location of the effective active sites in liquid-liquid PBC system.
- To synthesize and characterize CS, HT and gold/PS-HT.
- To investigate the physicochemical properties of CSs, HT and gold/PS-HT.
- To investigate the catalytic properties of the gold/PS-HT in the oxidation of benzyl alcohol with molecular oxygen.

1.4 Scope of the Research

The focus of this research is to determine the effective location of active sites of Ti-NaY in liquid-liquid PBC. In order to prove the effective locations of active sites in PBC, several catalyst models were used *i.e.* active site located at external and internal, internal or external of zeolite catalysts.

This research was further expanded to study the liquid-gas PBC system. Three types of materials that were synthesized were carbon sphere (CS), hollow titania (HT) and gold/polystyrene-coated hollow titania (gold/PS-HT). In this study, the size of the CSs was controlled by varying the concentration of sucrose with or without addition of surfactant (TMAC or HTAB) using hydrothermal method. HT spheres were obtained by sol-gel process using different sizes of CSs as the template. The reason is to ascertain the effect on wall thickness, hollow sphere's size, crystalline phase and crystallite size of titania. Since HT cannot float in water, an alternative way is to coat it using polystyrene. The gold was deposited on the PS-HT by sputter deposition to obtain gold/PS-HT. The gold loading was controlled by regulating the time taken for gold to be sputtered on the sample.

The gold/PS-HT catalyst was applied for the oxidation of benzyl alcohol in liquid-gas PBC system under static and stirring condition. Comparison of dispersion between the catalyst and other materials were conducted in water. Contact angle test was also conducted to prove that the floatability is caused by low density instead of hydrophobicity.

1.5 Significance of the Study

The results from this study would provide important information for the effective location of the active sites in phase-boundary catalyst in immiscible liquid-liquid system. Besides that, this research provides a new perspective in the use of

floating catalyst in heterogeneous liquid-gas boundary system. It also gives a new approach to control the size of CS, HT and gold/PS-HT. In this study, a new technique to coat polystyrene layer on the surface of HT microsphere has been demonstrated. Gold/PS-HT, with better control of interior spaces and exhibited floating ability, showed good catalytic activity in liquid-gas reaction without stirring. Since the process can be carried out without stirring, this system has the potential to be used in the industrial sector.

Figure 1.6 shows the schematic illustration of the strategy used in the synthesis of floating gold/PS-HT. The value of the materials was increased from CS to the final product as the starting material to synthesize CS is cheap. This is an effective route as each material has its own superiority.

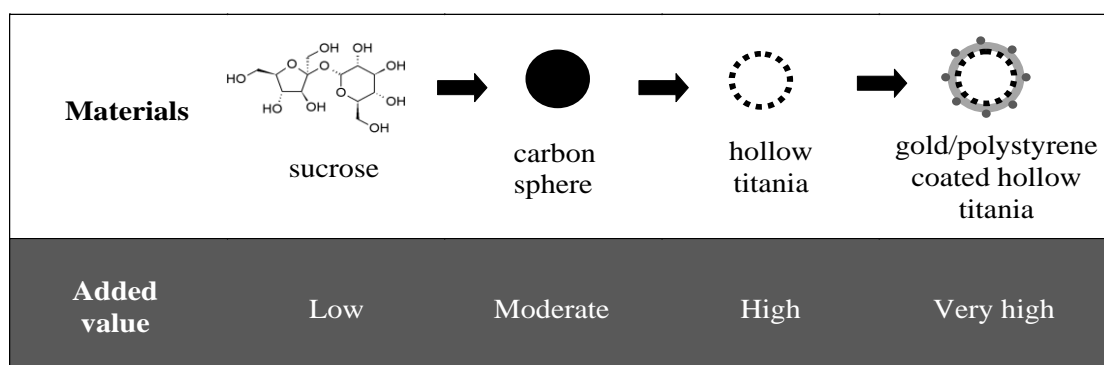


Figure 1.6: Schematic illustration of the added value of CS, HT and floating gold/PS-HT synthesized from sucrose as the precursor.

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