

TITANIA-POLYSTYRENE TEXTILE AS PHASE BOUNDARY CATALYSIS

RASIDAH BINTI RAZALI

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DEDICATION

*'Praise to Allah who created the heavens and the earth, and made the darkness
and light' (al-An'am 1)*

Specially dedicated to my beloved

Husband

(Mohd Shahir Yaman)

Children

(Muhammad Ali Sufi Mohd Shahir)

Mother and Father

(Suleka Raghavan & Razali Samin)

Mother in law

(Halimah Abd Manap)

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ABSTRACT

In the lights of the trending necessity towards clean and economical technology in chemical industry, heterogeneous catalysts are widely used due to their convenience of effortless separation methodology of catalysts from the products. Thus, this research proposes the establishment of a novel heterogeneous catalytic concept named “Phase-Boundary Catalysis System (PBC)”, utilizing textile as the support of titania active sites and H_2O_2 as the oxidizing agent. The previous catalyst of PBC was in particulate form, indicating existence of challenges to evenly disperse and immobilize at the liquid-liquid interface for 1-octene oxidation reaction. Therefore, the aim in this study is to design layered catalysts that can immobilize steadily at the interface of liquid-liquid layers and hence, applying the PBC catalyst for potential applications. The layered catalyst was designed using cotton textile as the support and polystyrene (PS) as the binder between titania and cotton textile. It is worth noting that the hydrophobic environment is the main character imposed by layered catalyst, which assists the layered catalyst to be floating and located exactly at the interface of liquid-liquid boundary. The titanium propoxide was chosen as titanium precursor due to the aspect of susceptibility towards cotton textile. The six layered catalysts were prepared by styrene polymerization with varied time (minutes) and denoted as T30, T60, T90, T120, T150 and T180. It was discovered that the cotton textiles bearing titania were gradually covered by PS with time. A series of layered catalysts were investigated in application of oxidation reaction using H_2O_2 as oxidizing agent. In the oxidation reaction, the conversion of 1-octene increased by approximately 5%, 10% and 25%, for reaction temperatures of 30°C, 60°C and 90°C, respectively. Reaction temperature 90°C showed the highest conversion to products, but the catalysts were low in the selectivity towards 1,2-epoxyoctane. The high selectivity of the oxidation reaction is towards 2-octanone products. It was possibly due to the concentration of H_2O_2 used (30 mmol) was much higher compared to previous studies (10 mmol), resulting in the process of accelerating 1,2-epoxyoctane to open its oxirane ring, then forming 2-octanone. Amongst all the layered catalyst, layered catalyst T90 gave the highest catalytic activity. It was due to the catalytic active site of layered catalyst T90 that has the optimum condition where the catalytic active site was not surrounded by large amount of polystyrene while attaining the sufficient attachment of titania towards cotton textile. Thus, less energy was needed for the substance to reach the catalyst active site for the reaction. As a comparison from previous study which used particulate catalyst involving variable temperature reaction, layered catalyst improved the catalyst selectivity by giving no side product besides 1,2-epoxyoctane and 2-octanone. However, the conversion activity still remains below 25% as previous study. Despite some limitations, the aim was successfully achieved. Thus, further modification should be carried out to improve the integrity of layered catalyst for potential applications.

ABSTRAK

Dalam memacu keperluan ke arah corak teknologi yang bersih dan ekonomik dalam industri kimia, mangkin heterogen telah digunakan secara meluas kerana ia memberi kemudahan kaedah pemisahan mangkin dari produk. Dengan itu, kajian ini mencadangkan penubuhan konsep pemangkinan heterogen baharu yang dinamakan “Sistem Pemangkinan Sempadan Fasa (PBC)” menggunakan tekstil kapas sebagai penyokong tapak aktif titania dan H_2O_2 sebagai agen pengoksidaan. Pemangkin PBC yang sebelumnya adalah dalam bentuk zarah yang menunjukkan ia mempunyai kekurangan untuk tersebar dengan seragam dan tidak bergerak di antara fasa cecair-cecair untuk tindak balas pengoksidaan 1-oktena. Oleh itu, matlamat kajian ini ialah untuk mereka bentuk mangkin berlapis yang tidak bergerak di antara muka lapisan cecair-cecair dan seterusnya boleh dipraktikkan dalam applikasi yang berpotensi. Mangkin berlapis telah direka bentuk menggunakan tekstil kapas sebagai penyokong dan polistirena (PS) sebagai pengikat di antara titania dan tekstil kapas. Harus ditekankan bahawa sifat persekitaran hidrofobik merupakan sifat utama mangkin berlapis yang membantu mangkin berlapis untuk terapung dan berada betul-betul di antara muka sempadan cecair-cecair. Titanium peroksida telah dipilih sebagai bahan pelopor titanium disebabkan aspek kepekaan terhadap tekstil kapas. Enam sampel mangkin berlapis telah disediakan melalui pempolimeran stirena dengan perbezaan masa pempolimeran yang dilabel T30, T60, T90, T120, T150 dan T180. Didapati, tekstil kapas yang mengandungi titania semakin dilitupi PS dengan pertambahan masa. Satu siri mangkin berlapis telah dikaji untuk applikasi tindak balas pengoksidaan menggunakan H_2O_2 sebagai agen pengoksidaan. Dalam tindak balas pengoksidaan, penukaran 1-oktena didapati meningkat masing-masing sebanyak 5%, 10% dan 25% bagi suhu tindak balas $30^\circ C$, $60^\circ C$ dan $90^\circ C$. Suhu tindak balas $90^\circ C$ menunjukkan hasil penukaran tertinggi, tetapi mangkin berkepilihan rendah terhadap 1,2-epoksioktana. Kepilihan tinggi tindak balas pengoksidaan adalah terhadap produk 2-oktanon. Ini berkemungkinan kerana kepekatan H_2O_2 yang digunakan (30 mmol) adalah lebih tinggi berbanding kajian sebelum ini (10 mmol) yang mendorong 1,2-epoksioktana untuk membuka gegelang oksirana lalu membentuk 2-oktanon. Dari kesemua mangkin berlapis, mangkin berlapis T90 telah memberikan aktiviti pemangkinan tertinggi. Ini disebabkan tapak aktif mangkin berlapis T90 memiliki keadaan yang optimum di mana tapak aktif mangkin tidak dikelilingi oleh jumlah polistirena yang banyak sementara mencapai ikatan yang mencukupi antara titania dengan tekstil kapas. Dengan itu, kurang tenaga diperlukan untuk bahan mencapai tapak aktif mangkin untuk tindak balas. Sebagai perbandingan dengan kajian terdahulu yang menggunakan mangkin zarah yang melibatkan tindak balas suhu berubah, mangkin berlapis telah meningkatkan kepilihan mangkin dengan tidak memberikan sebarang produk sampingan selain 1,2-epoksioktana dan 2-oktanon. Walau bagaimanapun, aktiviti penukaran masih di bawah 25% seperti kajian terdahulu. Walaupun terdapat kekangan, namun matlamat kajian telah berjaya dicapai. Dengan itu, pengubahsuaian pada masa hadapan perlu dilaksanakan untuk memperbaiki integriti mangkin berlapis untuk applikasi yang berpotensi.

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LIST OF ABBREVIATIONS

APTS	-	Aminopropyltriethoxysilane
DRUV	-	Diffuse reflectance ultraviolet
EDX	-	Energy dispersive X-ray
FTIR-ATR	-	Fourier transform infrared with attenuated total reflection
GC	-	Gas chromatography
H ₂ O ₂	-	Hydrogen peroxide
H ₂ O	-	Water
OTS	-	Octadecyltrichlorosilane
PBC	-	Phase boundary catalysis
PTC	-	Phase transfer catalysis
PS	-	Polystyrene
SEM	-	Scanning electron microscopy
TGA	-	Thermogravimetric analysis
Ti	-	Titanium
TS-1	-	Titanium silicate 1
XPS	-	X-ray photoelectron spectroscopy

LIST OF SYMBOLS

%	-	Percentage
▼	-	Negative gradient
●	-	Radical
°	-	Degree
e ⁻	-	Negative electron
g	-	Gram
g/L	-	Gram per liter
g/mol	-	Gram per mol
kV	-	Kilo volt
M	-	Molar
mg	-	Milligram
mL	-	Millimeter
mm	-	Millimeter
mM	-	Milimolar
mmol	-	Milimol
nA	-	Nano ampere
nm	-	Nanometer
rpm	-	Rotation per minute
s	-	Second
t	-	Time
wt	-	Weight

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CHAPTER 1

INTRODUCTION

1.1 Research Background

In the 21st century, the chemical industrial processes look forward in two major shifts: a continuing shift in reaction that produces little waste (Yamabe, 2005) and an easy way in handling which results in time and energy consumption. Energy and time are the dynamic factors to allow competitiveness and employment for industries. The faster economic growth pursues the research to be ventured into green chemistry, thus leading to the studies in the field of environmentally benign catalysts (Nur, 2006).

Presently, catalysts in the immiscible liquid-liquid reaction applied in most of the industries becomes a dime a dozen. Rational design of the conventional catalytic system requires vigorous stirring to remove the diffusion boundary layer and additional cosolvent to enhance mass transfer. Both of these approaches are to obtain homogeneous solution for reactions to take place. To minimize energy consumption in the process, a novel concept of phase boundary catalytic (PBC) system using solid catalysts has been proposed recently to solve the problem in immiscible liquid-liquid reaction (Nur *et al.*, 2000). With no stirring and cosolvent in the reaction, the solid catalyst was proven to have an outstanding catalytic activity in epoxidation reaction.

The location of the solid catalyst placed between aqueous and organic phase plays the main role towards the simplicity of reaction methodology since the mass transfer is not the rate determining step in PBC system. Conventional catalytic reaction requires seven steps for the catalytic reaction to take places. On the contrary, PBC reaction does not require any steps since the reaction take places at the boundary of the immiscible liquid-liquid phase. It is clearly elucidated that organic

phase, aqueous phase and catalyst are contacted at a point, without involving multiple routes travelled by organic substrates to reach inner pore of solid catalysts.

The novel concept of PBC for liquid-liquid reaction has been well established since PBC concept was successfully tested in several reactions in previous studies (Nur *et al.*, 2004a; Nur *et al.*, 2004b; Nur *et al.*, 2004c; Nur *et al.*, 2012). A preliminary study of PBC concept was started by using NaY zeolite catalyst which has been modified to be partly alkylsilane-covered titanium dioxide. The primary stage of this study aimed to place the bifunctional particles acquiring features of hydrophobic and hydrophilic regions to function as a role of catalyst in epoxidation reaction for PBC system. A discovery has shown that partial modification of alkylsilyl-Ti-NaY led to significant epoxide yield in the PBC system compared to the conventional system. This finding has been published previously (Nur *et al.*, 2000).

Despite of the PBC is endowed with the aforementioned advantages, some flaws are discovered though. The previous catalyst of phase boundary was in form of particulates. Particle form of solid catalyst leads to tedious methodology, which centrifugation for several times with high speed is required after the reaction. Unequivocally, it is less practical to be applied for the industries. To resolve the separation process of catalyst from liquid-liquid immiscible separation, hence emerging of this research to design and synthesize new catalyst for PBC system using layered concept. This layered catalyst immobilized in the system which could assist the PBC system to be practically applied in industries for huge batch of processes since the methodology of separating the catalyst from the reaction has been simplified. As illustrated in Figure 1.1, design of the layered catalyst involving choosing cotton textile as the layered platform while titanium(IV)-based materials as the solid active sites.

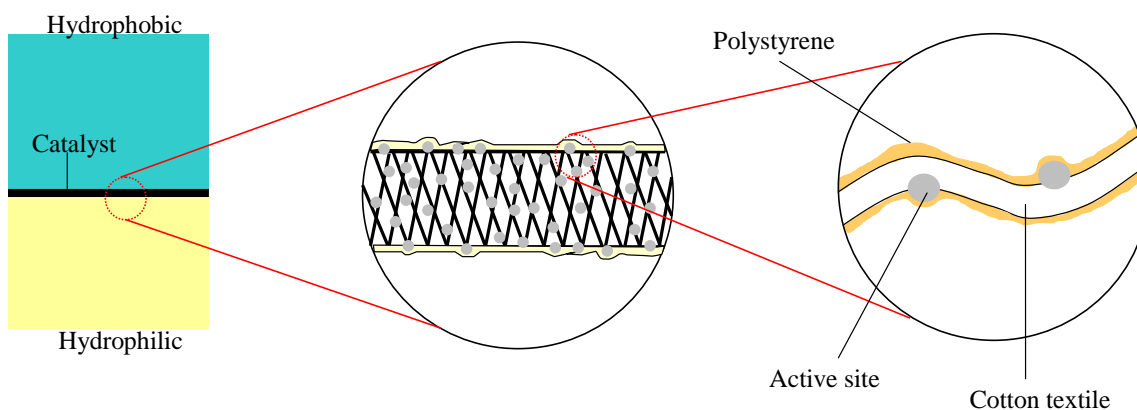


Figure 1.1 Schematic diagram of layered catalyst for PBC of liquid-liquid system.

In particular, the cotton textile consists of cellulose which is the molecular ribbon shape structure of the cellulose allows the cellulose to be twisted and bent in any directions and makes the molecular moderately flexible (Agrawal, Nierstrasz, Klug-Santner, Gübitz, Lenting and Warmoeskerken, 2007). in any circumstances for designing layered catalyst. Titanium-based materials are utilized as active sites for the layered catalyst. In order to determine titanium(IV) precursor that are compatible with the cotton textile, various types of titanium(IV) precursors are tested including Ti(IV) sulphate, Ti(IV) chloride, Ti(IV) isopropoxide and Ti(IV) propoxide.

Subsequently, the polystyrene are strategically added to enhance binding of Ti(IV)-based materials onto the textile layered. This step also creates hydrophobic environment for the catalyst and simultaneously protect the catalyst from catalyst poisoning caused by water and hydrogen peroxide (H_2O_2). In order to observe the degree of success in designing and synthesizing new layered catalyst, the physicochemical properties of the new layered catalyst is studied in this thesis. Consequently, the layered catalyst is undergone an oxidation reaction of 1-octene with H_2O_2 which the reaction is carried out with varied temperatures starting from 30, 60 and 90°C.

1.2 Problem Statement

Emerging of PBC in particulate concept has been ventured for almost two decades. It is preponderance with its no stirring and no-co-solvent added into reaction system because of its reactivity is comparable to the conventional catalytic system. In spite of PBC system is on the horizon, a research is working on to overshadow the particulate concept of PBC. To meet the requirements of low energy consumption and easy separation of chemical processes in industries, it comes to a light with a newly designed PBC layered catalyst with titanium(IV)-based materials as active sites and light weight textile as floating material. The PBC layered catalyst can standalone in immiscible liquid-liquid system with immediate removal after the reaction is complete. The research question is listed in Figure 1.3.

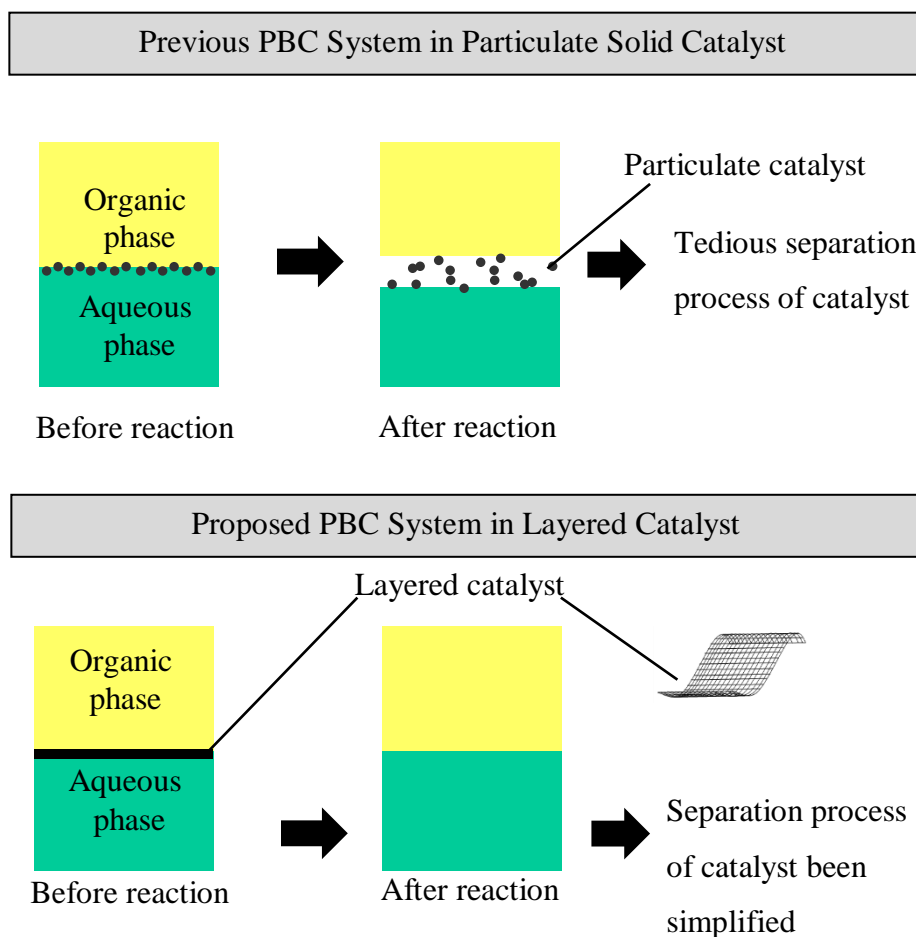


Figure 1.2 Schematic diagram of comparison between previous particulate solid catalyst and proposed new layered catalyst.

Strategies	Research questions
Design and synthesis layered catalyst	<ul style="list-style-type: none"> • How to design and synthesize the new layered catalyst for PBC system in immiscible reaction? • What are the physicochemical properties of new layered PBC catalyst?
Proofs of the concept	<ul style="list-style-type: none"> • Are the new layered catalysts can be located at the phase boundary of immiscible liquid-liquid system and active as catalyst?
Outcomes of the concept	<ul style="list-style-type: none"> • How are the performance of the catalytic activity and selectivity of layered catalyst compared to solid particulate catalyst? <p>(a)</p>

Figure 1.3 Schematic representation of strategies and research questions of the PBC system in immiscible liquid-liquid reaction.

1.3 Objectives of Study

The aims of this study are to provide a comprehensive study on preliminary design of new PBC layered catalyst, the effect of polymerization time on the changes in the properties of new PBC layered catalyst and the correlation between the series of layered catalyst to its catalytic activities and selectivity in order to identify the optimum condition to design enhanced layered catalyst. With the issues mentioned above, this research is conducted based on the following objectives;

- To design and synthesize layered catalyst with titanium(IV)-based materials.
- To investigate the physicochemical properties of new PBC layered catalyst
- To investigate the catalytic activity and selectivity of the layered catalyst in 1-octene oxidation reaction.

1.4 Scope of Study

This study is focused on the selection of titanium(IV) precursor that are compatible with the environment of cotton textile as a based of layered catalysts. The motivation is to study the enhancement of the attachment integrity on the new layered catalyst with different time of polymerization. This is also a study to understanding the changes in the physical and chemical properties of the cellulose-derived polystyrene-TiO₂ layered catalyst with the catalytic activity and selectivity relationship of the layered catalyst. In order to accomplish the research's objective, the scope of the study is divided into three parts, which are the designation and synthesizes of the new layered catalyst, the characterization of layered catalyst and the application of the layered catalyst in catalytic reaction.

The design and synthesize of new layered catalyst was done with the selection of cotton textile as the based for the layered of catalyst support. The cotton textile was first scoured in order to remove impurities. The scoured cotton textile was impregnated with compatible selection of titanium(IV) precursor that can adapt cotton textile environment. The selected titanium(IV) precursor was then been improved the integrity of attachment with cotton textile is assisted by styrene polymerization that been varied by time of polymerization of 30, 60, 90, 120, 150 and 180 minutes in order to study the effect of polymerization on the properties of layered catalyst.

The characterization of layered catalyst was conducted to study surface, physical and chemical properties of the layered catalyst. The properties of layered

catalyst were the correlated to the catalytic activity and selectivity of the layered catalyst. The catalytic performance of layered catalyst was done by oxidation reaction of 1-octene with the hydrogen peroxide as the oxidant in the reaction with three different reaction temperature 30, 60 and 90°C.was investigated.

1.5 Significance of Study

The results from this study provide useful information of the new perspective of catalyst that can be used for PBC in immiscible liquid-liquid system. This study explores a new design of catalyst which is more practical to be applied either in small or huge batch processes. The simplicity of the methodology would benefit the industries in term of low consumption of energy and time which are favoured by the industries nowadays.

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LIST OF CONFERENCES RELATED TO THIS RESEARCH

1. Razali, R., Yuan, L. S., Nur, H. & Buang, N. A. "Strategy of Attachment Catalyst Active Site on Cotton Textile by Layering Technique", poster presentation at The International Postgraduate Conference on Science and Mathematics (IPCSM), 5-6 October 2013, e-Leraning Building Universiti Pendidikan Sultan Idris, Tanjung Malim, Perak, Malaysia.
2. Razali, R., Yuan, L. S., Nur, H. & Buang, N. A. "Preparation of Gold-Loaded Textile as Catalyst in Phase-Boundary Catalytic System", poster presentation at Technology, Education and Science International Conference (TESIC), 20-21 November 2013, Universiti Teknologi Malaysia, Skudai, Johor, Malaysia.
3. Razali, R., Yuan, L. S., Nur, H. & Buang, N. A." New Layer Catalyst for Application of Phase Boundary Catalysis System" poster presentation at 8th Southeast Asean Technical University Consortium Symposium (SEATUC), 3-5 March 2014, M-Suites Hotel, Johor Bahru , Malaysia.
4. Razali, R., Yuan, L. S., Chandren, S., Nur, H. & Buang, N. A. "Layer Catalyst As New Catalyst For Phase Boundary Catalysis System" poster presentation at Twelfth Regional Annual Fundamental Sciences Symposium (RAFSS), 8-10 September 2014, Persada Johor International Convention Centre, Johor Bahru, Malaysia.