

**SYNTHESIS AND CHARACTERISATION OF
HYDROPHOBIC CATALYST –
Cs SALT OF 12-PHOSPHOTUNGSTIC ACID
FUNCTIONALISED DEALUMINATED USY
FOR THE ESTERIFICATION OF
ACRYLIC ACID WITH BUTANOL**

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ABSTRACT

Research and development work of acrylic acid (AA) recovery from petrochemicals industries effluent has been extensively carried out to minimize the production cost as well as to save the environment from any impacts of its high COD level. Esterification in reactive distillation column is one of the promising methods to recover the AA from the effluent. A hydrophobic heterogeneous catalyst is required to treat the dilute AA in RD column. In this work, heterogeneous hydrophobic catalyst -the Cesium (Cs) Salt of Phosphotungstic Acid (PW) Functionalised Dealuminated Ultra-Stable Y Zeolite (DUSY) with various loadings and amount of Cs was synthesised through impregnation method for the esterification reaction of AA with butanol. The catalyst was characterised using X-Ray Diffraction and X-Ray Fluorescence analysis method. The DUSY supported Cs salt of PW with 0.5 mole of Cs/mole of salt showed highest activity at 50% AA dilute system (23% yield & 27% conversion). It was found that the highest yield of 26% and conversion of 32% can be attained in the esterification reaction catalysed by the catalyst with 40% loading of Cs salt of PW (0.5 mole of Cs/1 mole of salt). Leaching test which performed using UV-Vis Spectrophotometer showed that the water tolerance ability decreased with increasing loading of % Cs_{0.5}PW. The developed catalyst is potential to be employed in the esterification of dilute AA with butanol, aiming to recover the AA from the petrochemical waste effluent.

ABSTRAK

Penyelidikan dan pembangunan kerja asid akrilik (AA) pemulihan daripada petrokimia industri efluen telah banyak dijalankan untuk mengurangkan kos pengeluaran dan juga untuk menyelamatkan alam sekitar daripada apa-apa kesan daripada tahap COD yang tinggi. Pengesteran dalam turus penyulingan reaktif adalah salah satu kaedah yang menjanjikan untuk mendapatkan semula AA dari efluen. A pemangkin heterogen hidrofobik diperlukan untuk merawat AA cair dalam ruangan RD. Dalam karya ini, pemangkin hidrofobik heterogen -The Cesium (Cs) Garam Asid Phosphotungstic (PW) Functionalised Dealuminated Ultra-Stabil Y Zeolite (DUSY) dengan pelbagai beban dan jumlah Cs telah disintesis melalui kaedah pengisitepuan untuk tindak balas pengesteran AA dengan butanol . Pemangkin dicirikan menggunakan Nitrogen Adsorption, X-Ray Belauan dan kaedah analisis X-Ray pendarfluor. The DUSY disokong Cs garam PW dengan 0.5 mol Cs / mol garam menunjukkan aktiviti tertinggi pada 50% sistem AA cair (23% hasil dan 27% penukaran). Ia telah mendapati bahawa hasil yang paling tinggi sebanyak 26% and penukaran 32% boleh dicapai dalam tindak balas pengesteran dilincirkan pula oleh pemangkin dengan muatan 40% daripada Cs garam PW (0.5 mol Cs / 1 mol garam). Larut lesap ujian yang dilakukan dengan menggunakan UV-Vis Spectrophotometer menunjukkan bahawa keupayaan toleransi air menurun dengan muatan meningkat% Cs_{0.5}PW. Pemangkin dibangunkan potensi untuk digunakan dalam pengesteran cair AA dengan butanol, yang bertujuan untuk mendapatkan semula AA dari efluen sisa petrokimia.

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LIST OF ABBREVIATIONS

Cs	Cesium
PW	Phosphotungstic Acid
DUSY	Dealuminated ultra-stable Y zeolite
AA	Acrylic Acid
BA	Butyl Acrylate
XRD	X-ray Powder Diffraction
XRF	X-ray Fluorescence
GC	Gas Chromatography
FID	Flame Ionization Detector
CsxPW	$CsxH_3-xPW_{12}O_{40}$

1 INTRODUCTION

1.1 Background of Study

Acrylic acid is a commonly used, yet extremely valuable chemical intermediate. However, it is corrosive, toxic and hazardous. For certain known sites of super absorber polymers production and wet polymerisation, regular effluent concentrations up to 100 mg/L acrylic acid and significantly more was produced in the acrylic acid production plant. This indicates that high acrylic acid effluent concentration is unavoidable, even if certain types of process engineering are applied ("Acrylic Acid summary risk assessment report," 2002). The industrial effluent consists of acrylic acid with the concentration of 4-15 wt% is difficult to be handled or biodegraded due to its high chemical oxygen demand (COD) level. The industrial effluents of the toxic acrylic acid and its affiliate compounds are usually concentrated and termed as high strength waste water which is refractory to be treated.

It was reported that this waste water can be treated mainly through wet oxidation, adsorption, biological treatment, incineration and etc. Wet oxidation and adsorption methods are not economic feasible, biological treatment requires long residence time and incineration is neither economical nor environmental friendly (Silva et al., 2004). It has been discovered that esterification of waste water containing carboxylic acid with alcohol could be a promising method to recover the acrylic acid while treating this type of waste water (Ahmad et al., 2014).

1.2 Motivation and statement of problem

Due to the shortcoming of existing acrylic acid treatment methods such as adsorption (not economic feasible and long contact time), biological treatment (long residence time and inhibited by contaminants), incineration (neither economical nor environmental friendly) and wet oxidation (not economic feasible, unstable for prolong reactions, severe salt deposition and corrosion). It has been revealed by studies before that the esterification of waste water containing carboxylic acid such as acetic acid with alcohol in a reactive distillation column could be a promising method to treat the waste water (Arpornwichanop et al., 2009; Saha et al., 2000; Singh et al., 2006; Tian et al., 2012).

Esterification of the acrylic acid with alcohol is commonly catalysed by the homogeneous catalysts such as sulfuric acid, hydrofluoric acid and para-toluenesulfonic acid. However, the homogeneous catalyst has caused corrosion problems and it is difficult to be separated from the product (Altiokka & Ödeş, 2009)

Heterogeneous catalysts such as sulphated metal oxide have been developed as an alternative to overcome the shortcomings of the homogeneous catalyst (Kiss et al., 2006). Nevertheless, most of these heterogeneous catalysts are non-water tolerant and leaching would happen in the presence of water. Therefore, it is vital to develop the less toxic yet hydrophobic solid acid catalyst for the esterification of the dilute carboxylic acid with alcohol.

The heteropoly acids (HPA) kind of heterogeneous catalyst have been fame of their benignity and strong acidity (Yuan et al., 2005). The HPA has been found with increased acidic properties when functionalised dealuminated zeolite Y (Olejniczak et al., 2000). However for supported pure HPAs, there existed separation problem when applied in polar reaction system such as water, which caused mainly by their low specific area and high solubility (Sani et al., 2014). In other words, they have considerable level of leaching problem in medium such as water. To solve this problem, the H^+ ions in HPA can be partially substituted by several kind of large alkaline monovalent cations such as NH_4^+ , Rb^+ , K^+ and Cs^+ . By doing this, there would be a changing in pore structure, surface area which has a minimum amount of $100m^2/g$ and consequently more resistant to deactivation by any polar substances such as water (Santos et al., 2011; Shiju et al., 2009).

The DUSY zeolite supported cesium salt of phosphotungstic acid was claimed to be hydrophobic in the esterification reaction (Zhang et al., 2006). The present study aims to synthesis and examine the hydrophobicity of the DUSY supported cesium salt of 12-phosphotungstic acid catalyst for the esterification of dilute acrylic acid with butanol.

1.3 Objective

The objectives of this study are to synthesis and characterize the dealuminated ultra-stable Y zeolite supported cesium salt of phosphotungstic acid for the esterification of dilute acrylic acid with butanol.

1.4 Scope of this Research

1. The catalyst will be synthesised:
 - (a) by varying the molar ratio of cesium salt (Cs) to 12-phosphotungstic acid group (PW)
 - (b) by varying the loading level of salts of heteropoly acid to dealuminated ultra-stable Y zeolite

2. The catalyst will be characterized for its
 - a) crystal structure by using X-ray powder diffraction (XRD)
 - b) catalyst components' surface area and pore size by using Brunauer, Emmett and Teller (BET) method analysis
 - c) Catalyst components' constituted portions by using X-ray fluorescence (XRF) analysis.

3. The catalyst activity and hydrophobicity will be examined in a batch wise esterification of dilute acrylic acid and butanol

1.5 Main Contribution of this work

The following are the contributions:

1. Synthesis of a more hydrophobic catalyst which could help to enhance the performance of esterification process in a dilute environment.
2. Assist in overcome the separation and corrosion problems caused by homogeneous catalyst as well as the leaching problem of heterogeneous catalyst in esterification process.

1.6 Organisation of this thesis

The structure of the remainder of this thesis is outlined as follow:

Chapter 2 provides a description of the existing treatment methods for the waste water containing acrylic acid. The advantages and disadvantages of each method are presented. This chapter justifies the proposed acrylic acid recovery method through esterification of

dilute acrylic acid with alcohol. The performances of the homogeneous catalyst and heterogeneous catalyst are compared.

Chapter 3 gives an overview of the chemical materials and methods used in the experimental studies.

Chapter 4 is devoted to the results and discussion of the preliminary study. The esterification of dilute acrylic acid with butanol catalysed by different molar ratios of cesium salt to 12-phosphotungstic acid and loading levels of the heteropoly acid upon DUSY zeolite is carried out in a batch reaction. The conversion profile obtained is elucidated with the support of proper references and logical explanation.

2 LITERATURE REVIEW

2.1 Treatment Methods of the Waste Water Containing Acrylic Acid

Acrylic acid (AA) is a commonly used, yet extremely valuable chemical intermediate applied in the areas of polymers, textiles, painting, adhesive, detergent, paper and numerous other industrial and consumer products. However, acrylic acid is corrosive, toxic and hazardous. The effluent containing acrylic acid with the concentration of 4-15 wt% is difficult to be handled or biodegraded due to its high chemical oxygen demand (COD) level (Ahmad et al., 2014).

Previous studies indicated that several recovery methods being performed widely particularly wet oxidation, adsorption, biological treatment, incineration and etc. Acrylic acid is a refractory compound for the non-catalytic wet oxidation (WO) process. According to the study of catalytic wet air oxidation (CWAO) of acrylic acid, catalytic activity of heterogeneous catalyst Mn: Ce (1:1) was the best to reduce 86% COD of the solution with 5g/l AA (Kumar et al., 2006). Catalytic wet oxidation (CWO) is efficient for the acrylic acid wastewater treatment, however the catalyst itself does bring pollution issue yet can't be stable for prolong reactions. Notwithstanding the high stability of catalyst Mn/Ce in terms of metal leaching, its economic feasibility depends on further research (Silva et al., 2004). Likewise, supercritical water oxidation (SCWO) using H₂O₂ is another method proposed to overcome the same hazardous stream. Nevertheless, severe salt deposition and corrosion still exist even the Transpiring Wall Reactor (TWR) reactor was used to anti-corrosion (Gong et al., 2007).

The agriculture waste residue, palm ash has been discovered for its suitability as an adsorbent to remove Acrylic Acid (AA). Palm ash was treated by reflux with sulfuric acid before the adsorption. Isotherm data were fitted well with Freundlich model. The maximum adsorption capacity of AA onto palm ash was obtained as $q_m = 1.8 \text{ mg g}^{-1}$ with an initial AA concentration of 100ppm. This method appeared to be more suitable for wastewater containing less AA concentration as the adsorption capacity reduced to 0.4 when the initial AA concentration being 500ppm. The highest % removal of AA achieved was 90% with optimum palm ash dosage, w being 200 g L^{-1} and initial AA concentration, $C_0 = 100 \text{ mg L}^{-1}$ after 6 h at 30°C. The results indicated that palm ash suitable to be used

as adsorbent to remove AA from aqueous solutions. Nevertheless, it required a relatively long contact time for the AA molecules adsorb onto the interior surfaces when the exterior surface of the palm ash is saturated (Nuradibah et al., 2013). The study of (Kumar et al., 2010) revealed the potential of powdered activated carbon (PAC) for the adsorption of acrylic acid (AA) from aqueous solution which was studied at the initial concentration ($C(0)$) in the range of 50-500 mg/l AA over the temperature range of 303-348 K. The maximum adsorption capacity of AA onto PAC was obtained as $q(m)=36.23$ mg/g with an optimum PAC dosage $w=20$ g/l at 303 K for $C(0)=100$ mg/l. However, this method also still in immature stage and its commercialisation need for further research (Ahmad & Kumar, 2010). In addition, the concerned wastewater concentration of 4-15wt% or 4×10^4 - 15×10^4 ppm in the current study is much higher in quantity. Hence, adsorption method is not a proper way for the high carboxylic acid content recovery from wastewater through esterification.

Moreover, biological treatment of wastewater can be inhibited by contaminants. The process is temperature dependent as the micro-organisms do not work at extreme temperatures, either too low or too high. Besides, it leads to the generation of sludge that has to be disposed of. Biological treatment method is generally time consuming (Henze, 2008). Hence, it is unsuitable for high concentration of AA wastewater.

Incineration is widely applied to burn off the waste water containing acrylic acid with concentration higher than 4wt%. This method is neither environmental nor economical friendly. Disposal method of the incinerated acrylic waste oil, waste water, and waste gas altogether induced the environmental problem and rendered the acrylic acid within to recovery from no way. Since acrylic acid has high viscosity, the disposed waste oil by the combustion tends to clog the piping of the combustion furnace. It is further at a disadvantage in inducing the incinerator to form a deposit on the inner wall (Matsumoto et al., 2007).

It has been revealed by the previous studies about the esterification of waste water containing carboxylic acid such as acetic acid with alcohol could be a promising method to treat the waste water (Yagyu et al., 2013). In addition, the recovery of acrylic acid from industrial waste water via esterification with 2-ethyl hexanol in RD column was found to be potential. By using constant water removal set up with Amberlyst 15 as catalyst at

373K (limiting temperature of water), the yield of ester has been observed to be 28% and 2% for the reaction with the aqueous solutions containing 10% and 50% AA respectively. However, with under total reflux set up, the dilute AA system has been found to result a yield of less than 5% for both the aqueous solutions containing 10% and 50% AA (Ahmad et al., 2014). The higher ester yield obtained by continuous water removal set up compared with total reflux set up for same initial AA concentration can be explained by Le Chatelier's principle. The equilibrium will constantly shift towards the ester product side when the water being constantly removed. However, the catalyst activity of CsxPW/DUSY will be first examined under total reflux in this research study.

Due to the demand for wastewater treatment, the interest in the development of efficient and environmentally benign water tolerance catalysts for esters synthesis has been increased drastically. The esterification reaction is a liquid-phase process, where the limiting conversion of the reactants is determined by equilibrium. Typically esterification reactions are extremely slow; it requires several days to attain the equilibrium. Therefore, the reaction is enhanced with an added catalyst. Introduction of a catalyst to the carboxylic acid recovery through esterification significantly increase not only the speed but also the yield, took an extremely important role to raise up further the efficiency.

Esterification in reactive distillation column is one of the promising methods to recover the AA from the effluent (Bock et al., 1997; Choi & Hong, 1999; Mahajan et al., 2008; Orjuela et al., 2012). The reactive distillation (RD) operates by the method in which the chemical reaction and distillation are integrated into one unit and therefore decreases the amount of equipment and operating costs required for the process (Bolun et al., 2006). The equilibrium of the esterification reaction of the pure and dilute carboxylic acid could be shifted to the product sides in the RD column. The recovery of AA from industrial waste water via esterification with 2-ethyl hexanol in RD column was found to be potential as the yield of the butyl acrylate (BA) was significantly increased when the esterification of dilute AA was carried out in an experimental set up (Ahmad et al., 2014). The reaction was catalysed by Amberlyst 15 at 373K. Nevertheless, acrylic acid is highly reactive and polymerizes easily, as such a polymerization inhibitor conventional stabiliser such as hydroquinone, hydroquinone monomethyl ether, methylene blue and/or phenothiazine must be added in the process for the recovery purpose. The acrylic acid can be recovered from the butyl acrylate formed through the esterification process in a

RD column. Butyl acrylate which is formed through esterification from wastewater can be used to produce poly-acrylic acid or cross-linked poly-acrylic acid compounds in the manufacture of super absorbent polymers. These polymers have wide range of applications in hygienic products, detergents, and waste water treatment chemicals. Several studies showed that reactive distillation column generally gives high recovery conversion of diluted carboxylic acid from wastewater by esterification process. (Gangadwala et al., 2008) revealed nearly 100% conversion can be obtained for esterification reaction of 30wt% initial concentration of acetic acid with n-butanol by using sulphuric acid as catalyst. Moreover, (Aaromi et al., 2014) has been obtained 82.95% conversion for esterification reaction of 30wt% initial concentration of acetic acid with ethanol by using Amberlyst-35 as catalyst. In addition, (Yogesh et al., 2008) also declared a 58% conversion for esterification reaction of 5wt% initial concentration of trifluoroacetic acid with 2-propanol without catalyst.

Therefore, the recovery of acrylic acid from the aqueous effluent of AA through esterification with butanol appears to be a promising method, doubtlessly presence of a compatible catalyst is vital for the efficiency. The following sections within this chapter justify the importance of synthesising a hydrophobic catalyst in the study for the diluted acrylic acid esterification.

2.2 Homogeneous Catalyst for Esterification

Conventionally, the esterification reaction is catalysed by homogeneous catalysts such as sulphuric acid, hydrofluoric acid, para-toluene sulfonic acid and strong mineral acids (Liu et al., 2006; Sert et al., 2013). Literature has shown that the homogeneous esterification of acrylic acid has scarcely been studied. (Liu et al., 2006) studied both the heterogeneous and homogeneous esterification of acetic acid with methanol and found that the catalytic activity of H₂SO₄ was greater than that of SAC-13 by only a factor of 3 per acid site basis. (Rönback et al., 1997) studied the kinetic model of the homogeneous esterification of acetic acid with methanol catalysed by hydrogen iodide and revealed the side reaction appeared in which the catalyst, hydrogen iodide, was esterified by methanol to methyl iodide.

Generally, the homogeneous catalysts are toxic, caused corrosion problems and it requires additional separation step to remove it from the reaction medium. Besides, the residues

also built up during separation and catalyst neutralization after the reaction. Therefore, the interest to the development of efficient and environmentally benign catalysts, particularly heterogeneous catalysts for esters synthesis has increased tremendously.

2.3 Heterogeneous Catalyst for Esterification

Heterogeneous catalysts are declared to be able to overcome the shortcomings of homogeneous catalyst. In addition, it enables a catalyst-free product easily obtained by filtration (Caetano et al., 2013). The use of supported catalyst is desirable in terms of its recovery, environmental friendly, better selectivity and cost effectiveness. In addition, they allow continuous operation in column reactors, high product purity and side reactions can be suppressed or eliminated. The main types of heterogeneous catalysts include ion exchange resin catalyst, metal based catalyst and supported heteropoly acid catalyst.

Ion exchange catalyst such as Amberlyst is known to catalyse organic reactions. It consists of the interchange of ions between two phases. With ion-exchange resins, the resin - a crosslinked polymer network-is the insoluble phase to which an ion is electrostatically bound; when contacted with a solution containing ions of same charge, an exchange can occur. Ion-exchange resins are useful because of the insolubility of the resin phase (Alexandratos, 2008). Typical ion-exchange resin catalysts such as sulphonic acids fixed to polymer carriers in solid state can be separated from the reaction product, enable continuous operation in column reactors, high product purity, side reactions can be suppressed or eliminated, reaction intermediates can be isolated and, ion-exchange resins can discriminate between small and large molecules. In the study of (Sert et al., 2013), the esterification of acrylic acid and n-butanol was catalyzed by three different ion exchange resins, Amberlyst 15, Amberlyst 131 and Dowex 50Wx-400. Amberlyst 131 was found to be more efficient by giving the maximum conversion of 40%.

Nevertheless, the previous studies showed that heterogeneous ion-exchange catalysts such as Amberlyst 15, sulphated zirconia and Nafion-H which applied in the acrylic acid esterification were deactivated with aqueous acrylic acid environment (Essayem et al., 2007). The commercial solid acid Amberlyst catalyst, when immersed in aqueous

processes, would have leaching problems and swelling which interferes the mass transfer in water.

Metal based catalyst such as Ti-Nb mixed oxide nanosheets (HTiNbO₅ and HTiNbO₇ nanosheets) are found to be water tolerant solid acid catalyst for esterification of acetic acid. They have strong Brønsted acid sites, attributed to bridging OH groups. The acid strength is strongly dependent on the metal composition of these nanosheets (Wilson & Lee, 2012). Meanwhile, metal based catalyst are experienced leaching problem whenever utilised in watery system (Ramos et al., 2005). Besides, it is relatively expensive compared with other types of catalyst.

Keggin heteropoly acids (HPAs), in particular the most typical one such as H₃PW₁₂O₄₀, H₄SiW₁₂O₄₀, H₃PMo₁₂O₄₀ and H₄SiMo₁₂O₄₀, have been reported to be the potential catalysts for esterification process. HPAs possess very strong Brønsted acidity, being stronger than conventional acids such as H₂SO₄, Al₂O₃-AO₂, zeolites, acidic resins, etc. Hence HPAs frequently exhibit superior catalytic activity in acid-catalysed reactions, including (trans) esterification, in homogeneous and heterogeneous systems (Alsalmeh et al., 2008). However, pure HPAs are having drawbacks such as low thermal stability, low surface area and separation problem (Akbay et al., 2007). Table 2.2 shows the significant findings of the researches about the heterogeneously catalysed AA esterification reactions. Besides, there are also some studies done on heterogeneously catalysed carboxylic acid esterification as shown in Table 2.3.

Table 2.1: Previous researches done on heterogeneously catalysed AA esterification process

Researchers	Reactants /Type of Catalyst	Operating Condition	Performance
(Chin & Kumaruzaman, 2013)	Acrylic Acid with butanol /Zirconium Phosphate (metal based catalyst)	373K	Yield 50% conversion after 12 hours , can be reused
(Chen et al., 1999)	Acrylic acid with 1-butanol /Variety of solid acids including an acidic	353 K	Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ and H ₃ PW ₁₂ O ₄₀ gave 40.7% and 14.5% conversions

	salt of $H_3PW_{12}O_{40}$, $C_{82.5}H_{0.5}PW_{12}O_{40}$ (supported heteropoly acid catalyst)		respectively.
(Ahmad et al., 2014; Chen et al., 1999; Fremy et al., 1998)	Acrylic acid with 2-ethyl hexanol/Amberlyst-15	373K	45% yield after 5h under continuous water removal set up.
(Essayem et al., 2007)	Acrylic acid with but-1- ene/ sulphated Fe and Mn promoted Zirconia	343K	62% conversion after 4h
(Komoń et al., 2013)	Acrylic acid with 2- ethylhexan-1- ol/ Amberlyst 39, Amberlyst 46, Amberlyst 70, and Amberlyst 131	353 to 393 K	76% conversion for Amberlyst70
(Sert et al., 2013)	Acrylic acid and n- butanol/ Amberlyst 131	358K	50% conversion with 3 alcohol/acid ratio at 10g/L catalyst loading
(Altıokka & Ödeş, 2009)	Acrylic acid with propylene glycol/Amberlyst-15	353K	45% conversion with 0.7 selectivity
(Ströhlein et al., 2006)	Acrylic acid with methanol/Amberlyst-15	333K	98% conversion
(Iizuka et al., 1986)	Acrylic acid with methanol/Niobic acid	-	90% for 6h
(Dupont et al., 1995)	Acrylic acid with butanol/Activated carbon supported HPA	-	43% conversion
(Sert & Atalay, 2014)	Acrylic acid and n- butanol/ Amberlyst 131	358K	90% conversion