

MESOSTRUCTURED TECHNISCHE UNIVERSITEIT DELFT-1 AND  
TECHNISCHE UNIVERSITEIT DELFT-CRYSTALLINE SUPPORTED METAL  
OXIDE DOPED TITANIA AS PHOTOCATALYST AND OXIDATIVE  
CATALYST

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This thesis is gratefully dedicated to my parents, for without their love, patience and perpetual support, none of this would have happened.

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## ABSTRACT

This research focused on the development of new Technische Universiteit Delft (TUD)-supported catalysts that are applicable for the photodegradation of organic pollutants and for the epoxidation of various olefins. In this study, the feasibility of relatively new mesoporous materials namely Technische Universiteit Delft-1 (TUD-1), amorphous silica material and Technische Universiteit Delft-Crystalline (TUD-C), hierarchical zeolitic material with MFI framework as the support for transition metal oxide doped titania was investigated. Two series of samples TUD-1 supported Cr doped  $\text{TiO}_2$  ( $\text{Cr-TiO}_2/\text{TUD-1}(x)$ ) and TUD-C supported Mo doped  $\text{TiO}_2$  ( $\text{Mo-TiO}_2/\text{TUD-C}(y)$ ) were synthesized via a single soft-templating approach involving the combination of sol-gel and hydrothermal treatment. The synthesized materials were characterized using X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Diffused Reflectance Ultraviolet-visible Spectroscopy (DRUV-Vis), Nitrogen adsorption-desorption surface analysis, Temperature Programmed Desorption of Ammonia analysis ( $\text{NH}_3$ -TPD), X-ray Photoelectron Spectroscopy (XPS), Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM). Optimization was carried out by varying the Si/Ti molar ratio in TUD-1 ( $x = 10 - 50$ ) and Si/Al molar ratio in TUD-C ( $y = 10 - 50$ ). For the photocatalytic reactions, results demonstrated that all the TUD-1 supported  $\text{Cr-TiO}_2$  materials were better photocatalysts compared to that of unsupported  $\text{Cr-TiO}_2$ .  $\text{Cr-TiO}_2/\text{TUD-1}(30)$  achieved the highest photodegradation percentage for Malachite Green (75.6%), Congo Red (50.8%) and phenol (82.0%) under visible light irradiation. The adsorption of phenol followed the Langmuir adsorption isotherm, while the photodegradation of phenol obeyed the first order kinetics. As for the oxidative reactions,  $\text{Mo-TiO}_2$  supported on TUD-C, with Si/Al molar ratio = 10 exhibited the highest epoxide yield for various types of olefins at ambient conditions. As compared to the unsupported  $\text{Mo-TiO}_2$ , TUD-C supported  $\text{Mo-TiO}_2$  samples showed significantly higher conversion with 100% selectivity towards formation of epoxides. All the epoxidation reactions followed the first order kinetics. The increment of catalytic activities for both series of materials is attributed to the high surface area ( $496 - 1034 \text{ m}^2/\text{g}$ ) and tunable porosity ( $2.83 - 5.84 \text{ nm}$ ), which provides better adsorption and diffusivity. The excellent oxidative capabilities of TUD-C supported materials were also accounted for the increased acidity originated from the aluminosilicate framework. Effect of reaction parameters including initial concentration (100 - 500 ppm), pH (2 - 11), catalyst amount (0.05 - 0.5 g), and reaction duration (6 - 72 h) in both photocatalytic and oxidative reactions were studied. TUD-1 and TUD-C are promising catalyst supports and have significantly improved the photocatalytic and catalytic performance of the transition metal oxides doped  $\text{TiO}_2$ .

## ABSTRAK

Kajian ini tertumpu kepada pembangunan mangkin tersokong Technische Universiteit Delft (TUD) baharu yang boleh digunakan untuk fotodegradasi pencemar organik dan pengepoksidaan pelbagai olefina. Dalam kajian ini, kesesuaian bahan liang meso relatif baharu iaitu Technische Universiteit Delft-1 (TUD-1), bahan silika amorfus dan Technische Universiteit Delft-Berhablur (TUD-C), bahan zeolit berhiraki dengan rangka kerja MFI sebagai penyokong untuk logam peralihan oksida terdopkan titania telah dikaji. Dua siri sampel TUD-1 disokong Cr terdopkan  $\text{TiO}_2$  ( $\text{Cr-TiO}_2/\text{TUD-1}(x)$ ) dan TUD-C disokong Mo terdopkan  $\text{TiO}_2$  ( $\text{Mo-TiO}_2/\text{TUD-C}(y)$ ) telah disintesis menggunakan pendekatan templat lembut tunggal yang melibatkan gabungan rawatan sol-gel dan hidroterma. Bahan yang disintesis dicirikan menggunakan belauan sinar-X (XRD), spektroskopi infra merah transformasi Fourier (FTIR), spektroskopi pantulan terbaur ultralembayung-nampak (DRUV-Vis), analisis permukaan penjerapan-nyaherapan nitrogen, penyaherapan suhu teraturcara analisis ammonia ( $\text{NH}_3$ -TPD), spektroskopi fotoelektron sinar-X (XPS), mikroskopi imbasan elektron pancaran medan (FESEM) dan mikroskopi penghantaran elektron (TEM). Pengoptimuman telah dijalankan dengan mengubah nisbah molar Si/Ti dalam TUD-1 ( $x = 10 - 50$ ) dan nisbah molar Si/Al dalam TUD-C ( $y = 10 - 50$ ). Untuk tindak balas fotopemangkinan, keputusan menunjukkan bahawa semua TUD-1 disokong bahan Cr- $\text{TiO}_2$  adalah fotomangkin yang lebih baik berbanding dengan Cr- $\text{TiO}_2$  yang tiada penyokong. Cr- $\text{TiO}_2/\text{TUD-1}(30)$  mencapai peratus fotodegradasi tertinggi bagi Malakit Hijau (75.6%), Kongo Merah (50.8%) dan fenol (82.0%) di bawah penyinaran cahaya nampak. Penjerapan fenol menurut isoterma penjerapan Langmuir, manakala fotodegradasi fenol mematuhi kinetik tertib pertama. Untuk tindak balas pengoksidaan, Mo- $\text{TiO}_2$  tersokong pada TUD-C, dengan nisbah molar Si/Al = 10 menunjukkan hasil epoksida tertinggi untuk pelbagai jenis olefina pada keadaan ambien. Berbanding dengan Mo- $\text{TiO}_2$  tidak disokong, sampel Mo- $\text{TiO}_2$  disokong TUD-C menunjukkan penukaran yang lebih tinggi dengan 100% kepilahan ke arah penghasilan epoksida. Kesemua tindak balas pengepoksidaan mengikut kinetik tertib pertama. Peningkatan aktiviti bermangkin untuk kedua-dua siri bahan disebabkan oleh luas permukaan yang tinggi ( $496\text{-}1034 \text{ m}^2/\text{g}$ ) dan keliangan tertala ( $2.83\text{-}5.84 \text{ nm}$ ), yang memberikan penjerapan dan kerosapan yang lebih baik. Keupayaan oksidaan cemerlang bahan TUD-C berpenyokong juga menyumbang kepada peningkatan keasidan yang berasal daripada kerangka kerja aluminosilikat. Kesan parameter tindak balas termasuk kepekatan asal (100 - 500 ppm), pH (2 - 11), amaun mangkin (0.05 - 0.5 g), dan tempoh tindak balas (6 - 72 j) dalam kedua-dua tindak balas pemfotomangkinan dan oksidaan telah dikaji. TUD-1 dan TUD-C adalah penyokong mangkin yang berpotensi dan telah menambahbaik prestasi pemfotomangkinan dan pemangkinan logam oksida peralihan terdopkan  $\text{TiO}_2$  dengan ketara.

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## LIST OF ABBREVIATIONS

TiO <sub>2</sub>	-	Titanium dioxide/Titania
VB	-	Valence band
CB	-	Conduction band
$E_g$	-	Band-gap energy
TUD-1	-	Technische Universiteit Delft-1
TUD-C	-	Technische Universiteit Delft-Crystalline
ZSM-5	-	Zeolite Socony Mobil-5
MFI	-	Mordenite Framework Inverted
TEA	-	Triethanolamine
TEAOH	-	Tetraethylammonium hydroxide
XRD	-	X-ray Diffraction
BET	-	Brunauer-Emmett-Teller
BJH	-	Barrett-Joyner-Halenda
FTIR	-	Fourier Transformed Infrared Spectroscopy
DRUV-Vis	-	Diffused Reflectance Ultraviolet-Visible Spectroscopy
NH <sub>3</sub> -TPD	-	Ammonia Temperature Programmed Desorption
FESEM	-	Field Emission Scanning Electron Microscopy
EDX	-	Energy Dispersive X-ray
TEM	-	Transmission Electron Microscopy
XPS	-	X-ray Photoelectron Spectroscopy
GC-FID	-	Gas Chromatography-Flame Ionization Detector
a.u.	-	Arbitrary unit
eV	-	Electronvolt

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Research Background

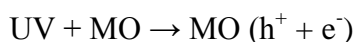
Catalysis is circumscribed as the incremental rate of chemical reaction due to the involvement of a surplus matter entitled catalyst. A catalyst works via a surrogate labile pathway to acquire the output. The reaction rate is escalated as the alternative pathway features lower energy of activation compared to the primary reaction route that is not ameliorated exploiting the catalyst. Reactions become quicker and expend comparably lesser energy with the employment of catalyst. Since catalysts are not consumed hence the catalysts could be recycled. Furthermore, only infinitesimal quantities of catalyst are required during a reaction. The manufacture of industrially essential chemicals generally copes with catalysis. Concurrently, almost all biochemically pivotal activities are catalyzed utilizing enzyme as the catalyst likewise (Friedrich & Hahn, 2015). Research of catalysis is a prime acquisition discipline in applied sciences and regards broad arrays of chemistry, specifically in organometallic catalysis and engineering science. Catalysis is also colligated to numerous attributes of environmental chemistry, e.g. the greenhouse gas catalytic convertor for automotive vehicles and the kinetics of ozone disparity (Botas *et al.*, 2001). Catalytic practices incurred much attention in green chemistry which is environmentally benignant due to the diminutive amount of waste matter created; contradicted to stoichiometric applications where every last reactants are consumed entirely with the production of unsought by-products. The by-large applied catalyst is normally the hydrogen ion,  $H^+$ . Assorted transition metals and transition metal complexes are as well highly applied in catalysis. The chemical attributes of catalysts

are as contrasting as the catalysis itself, even though several inductive reasoning can be inculcated. Protonated acids are perhaps the highest amply employed catalysts, particularly for various applications that concern water, hydrolysis reactions and its inverse (Dassie, 2014). Multifunctional catalysts e.g. zeolites, alumina, higher-oxidation state oxides, graphitic carbon, nanoparticles, quantum dots, and characteristics of sizeable materials are commonly catalytically activated (Ozekmekci *et al.*, 2015; Dong *et al.*, 2014). Transition metals are ordinarily applied to catalyze reduction-oxidation reactions for example oxidation, epoxidation and hydrogenation. In industry, Raney nickel is used for hydrogenation reaction; while vanadium(V) oxide is applied for oxidation of sulfur dioxide to make sulfur trioxide via the renowned contact process (Wang *et al.*, 2012; Sakurai *et al.*, 2000). Numerous catalytic practices, especially those are utilized in organic synthesis demand transition metals, for example chromium, vanadium, cobalt, molybdenum, rhodium, or iridium (Huber *et al.*, 2014). Chemical species which heighten the catalytic activeness are titled co-catalysts or boosters in synergetic catalysis.

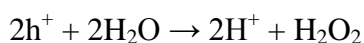
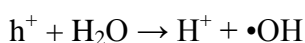
According to chemistry definition, photocatalysis is ascertained as the speedup of a photoreaction within the existence of a catalyst. In the catalytic photoreaction, photon is assimilated by the photocatalyst. In photo-generation catalysis, the photocatalytic activity (PCA) reckoned on the potency occurrence of the photocatalyst to generate electron-hole, that produces emancipated radicals e.g. hydroxyl radical,  $\bullet\text{OH}$  which is employed to go through progressive reactions. Its pragmatically employment was made accomplishable due to the insight in water electrolysis via application of titanium dioxide ( $\text{TiO}_2$ ) (Chatterjee, 2010). The specialized utilized overture is called the advanced oxidation process (AOP) which is cardinal for abjection of environmentally pestilent organic waste matter such as synthetic dyes and phenolic substances (Gasull *et al.*, 2015). There are numerous impartment the AOP can be implemented, nevertheless it perchance may not even feature  $\text{TiO}_2$  or the irradiation of UV light. In general, the determinant component is the creation and employment of the hydroxyl radical. Heterogeneous catalysis is defined as the catalyst which is in a discrete phase different to the reactants. Heterogeneous photocatalysis is a discipline that pertain a broad assemblage of intermediate or absolute oxidation procedures, e.g. dehydrogenation, hydrogen

transferral, metal accretion, water treatment, and gasified pollutant removal (Wang *et al.*, 2015). Usually, the employed heterogeneous photocatalysts are oxides of transition metal and semiconducting materials, which comprise circumstantial features. Incommensurable to metals which possess an incessant electronic band; semiconductors have a nullity energy region where none of the energy bands are accessible to encourage the recombining of electron-hole consequence via excitement of electron because of trapped photon within the photocatalyst. The vacant void that protracts inside the upper berth of the filled valence band (VB) until the lower berth of the empty conduction band (CB) is defined as the band gap. When single photon with correspondent to or higher energy comparative to the photocatalyst band gap is assimilated, an excited electron is produced and followed by the promotion from the VB to the CB, constituting a positively charged hole situated within the valence band (Hamad *et al.*, 2015). The excited electron ( $e^-$ ) within the conduction band and hole ( $h^+$ ) are able to recombine and the emancipated energy will be incurred as discharged heat from the recombination process. An ineffective photocatalyst always directs to speedup of electron-hole recombination thus it is unenviable. The eventual objective of this process is to incur a response between the reaction of photoexcited electrons with an oxidant to create ablated and elementary matters, and also a reduction process of the positively charged vacant holes to generate an oxidized matter. Via the constitution of vacant holes and photoexcited electrons, occurrence of redox reactions will locate at the boundary of photocatalysts. For the oxidation reaction, the positively charged holes respond with the surface moisture to generate hydroxyl radicals.

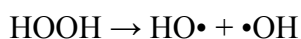
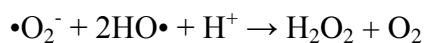
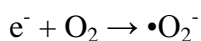
Oxidation procedures described from the photocatalytic effect (Mills & Le Hunte, 1997) are expressed below:



Where MO is denoted as metal oxide



Meanwhile, reduction procedures described from the photocatalytic effect are shown below:



Eventually, the oxidation-reduction process creates hydroxyl radicals which perform as the essential reactants for the photodegradation of the organic pollutant. Generated hydroxyl radicals are extremely oxidative with negligible selectivity and possess a reduction potential equal to  $E_0 = +3.06$  V (Yang *et al.*, 2015). Figure 1.1 shows the generic delegacy for the production of hydroxyl radical generated from the AOPs within the photocatalysis procedures.

Photocatalysis is pivotal for the amelioration of environmental difficulties especially in the photodegradation of organic waste matters for instance synthetic dyes and phenolic compounds. Dyes are ordinarily separated into acidic and basic dyes, based on the chemical features. Synthetic dyes are produced industrially by large quantity; approximately  $7 \times 10^5$  tons are synthesized per year ((Ning *et al.*, 2015). Dyes manufacturers have high interest with dyes that possess strong durability and high consistency. Consequently, the synthetic dyes produced are unremarkably much too stronghold for the degradation via the wastewater treatment. Most synthetic dyes are ignorantly discarded, thus their carcinogenic and mutagenic natures could result in caustic deformation towards living organisms and environment health. Presently, numerous physicochemical and biological handling manners for instance coagulation, flocculation, oxidation, chemical treatments and adsorption have been copiously utilized for the intent of dyes elimination (Suresh *et al.*, 2015). Still, these handling methods do poses their hold back such as formation of toxic sludge as undesired side products, expensive operational cost, mechanical restrictions, reliability on waste concentration, environmentally malignancy and inefficiency in getting rid of dye color as reported (Gautam *et al.*, 2015). Phenol is a broadly utilized compound that performed as a crucial commercial commodity. Phenol also performs as a starting material for the production of numerous materials and utile merchandise. Besides, phenol and its chemical derivatives is chief constructing unit for polycarbonates, epoxies, Bakelite, nylon, detergents, herbicides, and various pharmaceutical drugs. Hence, phenol has been produced in an immense

quantity, which is estimated to be 7 billion kg per annum (Kumaran & Paruchuri, 1997). Nonetheless, due to vast scale synthesis, inordinate output, and crude handling, phenol has induced environmental phenomenon in the pattern of water resources contamination. Phenol possesses superior water solubility yet human physique permissiveness towards phenol is only 311 mg/kg (Chen *et al.*, 2010), hence it is exceedingly hazardous to human health as phenol can ensue systemic poisoning and deterioration to the eyes, skin and respiratory tract. Thus, photocatalysis is recommended as a suitable candidate for phenol degradation via conversion of phenol into lesser extent harmful components through total mineralization approach employing AOPs.

Oxidation reactions perform as a decisive role in chemical industry for the synthesis of various pivotal compounds. Numerous principal chemicals and intermediates such as alcohols, epoxides, aldehydes, ketones and organic acids are produced via selective oxidation processes in the latter-day chemical industry (Thompson *et al.*, 2015; Witt *et al.*, 2015). For instance, the selective oxidation of alkyl-exchanged benzene produces alcoholic components and ketones which dominate considerable involvement in biochemically and mechanically contemporary organic synthesis. Phenylethane is an emblematic component in the synthesis of various straight-chain and phenyl-replaced alkanes. It was abundantly used as a representative reactant to scrutinize the oxidation processes of alkanes. The oxidation resultants of phenylethane forms phenylethanone and phenylmethylethanol which have been broadly utilized as starting blocks for the synthesis of a huge variance of pharmaceutical drugs, for instance hydrogel, chiral alcohols, hydrazones, benzylideneacetophenone, resins and numerous scents (Gan *et al.*, 2015; Asati *et al.*, 2015). The selective oxidation of propene to produce propenal (acrolein), ammoxidation of propene to generate 2-propenenitrile via Standard Oil of Ohio (SOHIO) process, selective oxidation of butane to form 2,5-furandione, epoxidation of ethene to form ethanal (acetaldehyde) and selective oxidation of methanol to produce methanal (formaldehyde) are the notably ideal exemplars (Cespi *et al.*, 2014; Dias *et al.*, 2015)



Oxidation is the succeeding most prominent process subsequent of polymerization. The oxidation processes substantiate approximately 30% of total manufactory of commercial chemicals (Charles *et al.*, 2014). Selective oxidative catalysis is also pivotal for the corroboration of green chemistry and substantial chemical processes. Particular representation is the selective oxidation of hydrocarbons; the selectivity in the occurring chemical industry has to be farther improvised to relegate the production of non-selective side products, particularly CO<sub>2</sub> (Zhai *et al.*, 2015). This demands optimization of precocious catalysis and the industrial operations employed in the existing chemical synthesis. Secondly, there is a substantial inducement to design unprecedented oxidation processes which accomplish the generalization of green chemistry. Specifically, it is needy sought after to come up with novice catalytic oxidation methods for the amelioration of current energetically inefficient and environmentally malignance multi-stepwise processes. Oxidative catalysis has been a pivotal procedure in various industrial employments especially in the synthesis of epoxides. Numerous epoxides acquired from different olefins are crucial by acting as starting materials and intermediates in the production of various advantageous end outputs for instance plastics, polymers, and pharmaceutical drugs (Zhang *et al.*, 2015). The epoxides are mostly applied in fine chemical synthesis, polymer production, cosmetics and pharmaceutical applications. Nonetheless, even though catalysis has been utilized in the industrial synthesis for production of epoxides, the yield of product and selectivity remain unfavorable. Moreover, harsh experimental condition, application of hazardous solvents and oxidants are not exactly environmental benignant as presented in previous researches. Hence, an environmentally friendly catalyst which possesses high compatibility with numerous olefins is a requisite in order to produce high product yield and selectivity towards the formation of epoxides.

TiO<sub>2</sub> is an efficacious substance aptly acting as both photocatalyst and oxidative catalyst. Its high efficiency and non-toxicity successfully made it a desirable nominee for numerous catalytic reactions. Nevertheless, the low surface area, aggregation/agglomeration and incapability to execute under visible light irradiation have been the fundamental drawbacks of TiO<sub>2</sub> (Wickramaratne & Jaroniec, 2015). Umpteen modifications have since been researched in order to

promote the surface area and efficiency of TiO<sub>2</sub> via usage of templates as structure directing agents. Many alterations have been implemented such as transition metal oxide doping using Mo, V, Cr, Pd, Co, Pt, Ag, Au etc., surface functionalization via numerous organic chelating ligands, spatial templating modification (hollow, nanorod, nanosphere, nanotube etc) and employment of catalytic support (Ou & Lo, 2007; Devi & Kavitha, 2013). Silica matrixes for example Mobil Composition Matter-41 (MCM-41), Santa Barbara Amorphous-15 (SBA-15), Folded Sheet Mechanism-16 (FSM-16), zeolites and metal oxides have been intensively reported as catalyst support (Nomura *et al.*, 2015; Salis *et al.*, 2015). In this research, transition metal doping and catalyst support were designated as the modification methods. Transition metal doping enabled TiO<sub>2</sub> to perform at visible light region via modification of the extended wavelength response range. The doped transition metal oxides could also act as active sites. On the other hand, employment of catalytic support has rendered a high surface area, high porosity with homogeneous distribution of catalytic active sites for promoted catalytic activity.

Utilization of silica and zeolites as catalytic support has been a well-documented modification method. Nonetheless, silica supports for instance MCM-41, SBA-15, FSM-16 and silica aerogel are catalytically latent with repressing selectivity, low compatibility, aggregates/agglomerates formation and involves high cost with time consuming synthesis procedures (Yeung & Han, 2014). Application of templates in the synthesis of these silica supports has also acquainted impurities. Zeolites have been employed in numerous catalytic processes, for instance in catalytic cracking and hydroxygenation. Even so, the microporosity of zeolite has been the firsthand constraining cause, resulted in permanent adsorption, steric blockage, formation of coke and travail in shape selectivity exploitation (Galadima & Muraza, 2015). Thus, in order to meliorate this susceptibility, mesoporous zeolite with various frameworks for instance Faujasite (FAU), Zeolite Socony Mobil-5 (ZSM-5), Potassium exchanged Zeolite A (KA), Linde Type N (LTN) etc. has been presented in recent exploitation of catalytic support which demonstrated huge potentiality and curiosities (Johnson & Arshad, 2014). In this study, comparatively novice catalytic support of Technische Universiteit Delft (TUD) was used. Its members of Technische Universiteit Delft-1 (TUD-1) and Technische Universiteit

Delft-Crystalline (TUD-C) were employed as catalytic support for TiO<sub>2</sub>-based photocatalyst and oxidative catalyst, respectively. In fact, TUD-1 is mesoporous silica; while TUD-C is a hierarchical mesoporous zeolitic material that could be easily obtained from the modification of TUD-1. Thus, TUD-C possessed both the assets of mesoporosity from silica and catalytic reactivity from zeolites (Wang *et al.*, 2009). It was reported that, by loading transition metal doped TiO<sub>2</sub> onto TUD-1, the catalytic activities in oxidation reactions was increased substantially. However, there are still numerous features and characteristics of TUD-1 that remain unexplored. Similarly, usage of TUD-C as catalyst support is limited. Hence, further studies are required to apprehend a thorough discernment of how this novel catalyst performs as well as the interactive phenomenon between the catalyst and catalytic support. Furthermore, feasibility of TUD-1 and TUD-C performing as catalytic support demands much vindication.

## 1.2 Problem Statement

Transition metal oxide doping has been reasoned to be a competent alteration mean to promote the photocatalytic and oxidative catalytic capabilities of the TiO<sub>2</sub>. Nonetheless, transition metal oxide doped TiO<sub>2</sub> experienced quite several drawbacks for example low surface area and porosity. Likewise, the agglomeration/aggregation of TiO<sub>2</sub> active sites has diminished its efficacy as photocatalyst and oxidative catalyst. Moreover, higher content of transition metal oxides might also perform as recombination centers for the photon excited charge carriers hence, reducing the quantum efficiency. Transition metal oxides have also been exposed to induce thermal instability to the anatase phase of TiO<sub>2</sub>. Another disadvantage is photocorrosion and encouraged charge recombination at dopant centers. In order to curb these liabilities, application of high surface area and porous materials has been highly recommended. Among the materials studied, zeolite, MCM-41 and SBA-15 were always preceded to be prime selection. Zeolite is a well reported material featuring surface active sites that are capable of forming good interaction with various organic pollutants and olefins. Still, microporous zeolite suffered from pore blockade and limited diffusivity due to diminutive pore diameter, while mesoporous

silica that features bigger pore diameter lacked of appropriate active centers for the interaction with olefins for epoxidation reaction. Thus, the design of novice multifunctional catalytic supports with tailored pore diameter and active sites was carried through in this study.

Diffusion restrictions are a stellar drawback of proliferous catalysts. It is specifically epochal for applications regarding huge reactants, for instance the fluid catalytic cracking (FCC) process in petroleum refinery. The reinforced functioning of porous catalysts can be visualized upon increased availability to the active centers in the micropores and diminution of pore obstruction. Minuscule zeolite crystals, for instance, possess truncated diffusion distance; hence, the availableness of the active centers is accrued. To lessen the pore impediment, an accomplishable way is to enclose interlinked bigger pores inside the array constitution. These pores can also facilitate the conveyance of huge reactants. Prompted by nature constructions, for example human lungs and foliage, it is anticipated that umpteen catalytic applications could have higher selectivity and efficacies if the catalysts featured tailored hierarchical porous network architecture. Construction of pores at various length measurements (e.g. micro-, meso-, and macro-) in a controlled regulated method, rather than random assemblage, appeared as the direction of such on-going investigation. This study aimed especially on the hierarchically construction of mesopores in the resulted catalysts.

From the forego researches, there are several disfavours encountered in the photodegradation of organic pollutants and epoxidation of olefins. Among the difficulties faced are expensive synthesis cost of the materials utilized, rudimentary mineralization, production of unsought by-products and intermediates with decline product yield and selectivity. In order to counter these shortcomings, low cost novice multipurpose catalysts that are capable to perform as both photocatalyst and oxidative catalyst with high efficacy are much coveted. TUD-1 and TUD-C are silica matrix and hierarchical zeolitic matter with high surface area. However, reports on their usage as catalytic support remain limited. Moreover, reaction parameters that could impact the effectiveness of catalyst on photodegradation of organic pollutants and olefins epoxidation continue to be unclear. Hence, effects of

various experimental states were studied meticulously to present the optimum catalytic achievement of transition metal oxide doped titania.

### 1.3 Objectives

In order to study the feasibility of TUD-1 and TUD-C as catalyst supports, multiple objectives have to be achieved. The objectives of this study were:

- 1) To synthesize the chromium oxide doped titania supported TUD-1 ( $\text{Cr-TiO}_2/\text{TUD-1}(x)$ ,  $x = \text{Si/Ti}$  molar ratio) and molybdenum oxide doped titania supported TUD-C ( $\text{Mo-TiO}_2/\text{TUD-C}(y)$ ,  $y = \text{Si/Al}$  molar ratio) via sol-gel method, followed by hydrothermal treatments with single template approach.
- 2) To characterize the physical and chemical properties of the synthesized  $\text{Cr-TiO}_2/\text{TUD-1}(x)$  and  $\text{Mo-TiO}_2/\text{TUD-C}(y)$  with lower band-gap and higher surface area, porosity and acidity.
- 3) To assess the catalytic performance of  $\text{Cr-TiO}_2/\text{TUD-1}(x)$  and  $\text{Mo-TiO}_2/\text{TUD-C}(y)$  in photodegradation of organic pollutants and epoxidations of various olefins, respectively.

### 1.4 Scope of Study

Transition metal oxide doped titania ( $\text{M-TiO}_2$ ) with Cr and Mo dopants set at 1 mol% was synthesized via sol-gel method. Combining sol-gel, wet impregnation and hydrothermal treatment, TUD-1(x) was prepared. TUD-C(y) was synthesized via the similar process with the addition of aluminium isopropoxide ( $\text{Al(O-i-Pr)}_3$ ) for the formation of zeolitic material where y is denoted as Si/Al molar ratio ( $y = 10, 20, 30, 40, 50$ ). Both synthesis procedures employed triethanolamine (TEA) and tetraethylammonium hydroxide (TEAOH) as structure guiding and scaffolding precursor, respectively.  $\text{Cr-TiO}_2$  was supported onto TUD-1(x) and  $\text{Mo-TiO}_2$  was

supported onto TUD-C(y) via wet impregnation approach in order to obtain chromium oxide doped titania supported TUD-1 (Cr-TiO<sub>2</sub>/TUD-1(x)) and molybdenum oxide doped titania supported TUD-C (Mo-TiO<sub>2</sub>/TUD-C(y)), where x is denoted as the Si/Ti molar ratio (x = 10, 20, 30, 40, 50) and y is denoted as the Si/Al molar ratio (y = 10, 20, 30, 40, 50). For comparison intent, TiO<sub>2</sub> was synthesized.

The characteristics of the synthesized samples were characterized via X-ray diffraction (XRD) analysis, N<sub>2</sub> adsorption-desorption analysis, Fourier-transform infrared (FTIR) spectroscopy, diffuse reflectance ultraviolet-visible (DRUV-Vis) spectroscopy, transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM) and energy dispersive X-ray (EDX) spectroscopy. Ammonia temperature programmed desorption (NH<sub>3</sub>-TPD) and X-ray photoelectron spectroscopy (XPS) analyses were also executed.

For the initial section of the catalytic testing, a series of Cr-TiO<sub>2</sub>/TUD-1(x) samples with 1 mol% dopant and Si/Ti molar ratios were subjected to the photocatalytic degradation of selected organic pollutants, namely synthetic dyes and phenol. The adsorption isotherm models for synthetic dyes and phenol were studied via three propositions, namely Langmuir, Freundlich and Temkin isotherms, severally. Numerous parameters for instance initial concentration of organic pollutants (100 – 500 ppm), reaction duration (3 – 12 h), pH (2 – 11) and amount of photocatalyst used (0.1 – 0.5 g) were studied in order to achieve the principal component influencing the photocatalytic activities. The photocatalytic efficiency of Cr-TiO<sub>2</sub>/TUD-1(x) in photodegradation of synthetic dyes and phenol was measured using UV-Vis spectroscopy. In the secondary section of the catalytic testing, Mo-TiO<sub>2</sub>/TUD-C(y) with various Si/Al molar ratios was subjected to the epoxidation of olefins. Effect of numerous experimental conditions for example reaction duration (6 – 72 h), initial concentration (5 – 25 mmol), and pH (2 – 11) were studied. The catalytic achievement of Mo-TiO<sub>2</sub>/TUD-C(y) was appraised via gas chromatography (GC). Kinetic studies were studied on Mo-TiO<sub>2</sub>/TUD-C(y) for epoxidation of various olefins in order to perceive better apprehension on the rate of reaction and reaction order.

## 1.5 Significance of Study

In the preceding studies, great attempt has been allotted in the studies of discovering appropriate materials and methods for the removal of extremely dangerous organic pollutants and for epoxidation reactions. In this study, Cr-TiO<sub>2</sub>/TUD-1(x) and Mo-TiO<sub>2</sub>/TUD-C(y) are novice catalytic materials used for the photocatalytic degradation of organic pollutants and epoxidation of olefins, severally. Both TUD-1 and TUD-C were able to perform as good catalytic supports because of their high surface area, porosity, and tunable features which can be tailored for various catalytic applications. Initial attempt was carried out in this study to investigate the feasibility of the TUD-1 and TUD-C as catalytic support for transition metal oxide doped titania in both photocatalytic and oxidative catalytic applications.

These novel catalytic materials were found to enhance the adsorption potentiality and photocatalytic/catalytic capability comparative to the unsupported transition metal oxide doped titania. These important discoveries not only broaden the utilization of TUD-based materials, but also profoundly improved the cognition in material science. Additionally, the pivotal features of the multipurpose TUD-based catalysts for the photodegradation of organic pollutants and epoxidation of numerous olefins were elucidated. The knowledge would renders heighten understanding for the constitution of other photocatalysts and oxidative catalysts.

Due to the huge quantity of the synthetic dyes and phenol being discharged per annual, removal of these waste matters is necessary nowadays for the restoration of the environment and human wellbeing. Epoxides are fundamentally utile in the production of useful end products; thus it is perspicacious to design a novel matter which is appropriate for the upscale production with high yield and selectivity at the same time environmentally benignant. Via conduction of this study, novel effective multifunctional catalyst for the removal of organic pollutants and epoxidation of olefins was acquired. The synthesized materials feature an easy and low-cost synthesis approach, which is beneficial for the utilization in environmental science and industrial production.

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