

TUNGSTEN-PHOSPHATE SUPPORTED ON TITANIA-SILICA AS
OXIDATIVE-ACIDIC BIFUNCTIONAL CATALYST FOR DIOL SYNTHESIS

SALASIAH BINTI CHE ME

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*I dedicated this thesis to my beloved mother AZIZAN BINTI IDRIS and my husband
MD KHUDRI BIN ABD RAHIM,
To all my brothers, sisters and friends
Thank you very much*

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ABSTRACT

Diols are important as raw materials and intermediates for different processes in a wide variety of chemical industries. The preparation of diols is commonly carried out in two steps involving the epoxidation of olefin and continued by hydrolysis of the epoxides; the reactions are carried out using different catalysts in two separate chambers. Therefore, development of a bifunctional catalyst for production of diol in a single step reaction is highly desirable. In this research, a new oxidative-acidic bifunctional catalyst of tungsten-phosphate supported on $\text{TiO}_2\text{-SiO}_2$ has been synthesized. $\text{TiO}_2\text{-SiO}_2$ support was prepared via sol-gel method, followed by impregnation of WO_3 and PO_4^{3-} . The amounts of WO_3 and PO_4^{3-} in the materials were varied in order to investigate the role of tungsten oxide and phosphoric acid in generating oxidative and acidity active sites. X-ray diffraction analysis showed the $\text{TiO}_2\text{-SiO}_2$ support remained amorphous even after loading of WO_3 and PO_4^{3-} , indicating that WO_3 and PO_4^{3-} were highly dispersed on the surface of SiO_2 , while TiO_2 was fused into the SiO_2 framework. The relatively higher tungsten loading seemed to increase the amount of octahedrally coordinated Ti species which acted as oxidative active site. Although titania-silica impregnated with 5 wt% tungsten possessed high surface area ($473 \text{ m}^2/\text{g}$), the addition of both WO_3 and PO_4^{3-} resulted in a dramatic decrease in the surface area ($15 \text{ m}^2/\text{g}$). FTIR results of tungsten-phosphate supported titania-silica implied the attachment of the phosphate to the hydroxyl groups. Increment in acidity of $\text{TiO}_2\text{-SiO}_2$ after the modification with WO_3 and PO_4^{3-} was confirmed by TPD- NH_3 analysis. Pyridine adsorption analysis monitored by FTIR spectroscopy showed the $10\text{WO}_3/\text{TiO}_2\text{-SiO}_2$ had the highest amount of Lewis and Brønsted acid sites. However, the Brønsted acid sites formation within 0.2 M $\text{PO}_4^{3-}/10\text{WO}_3/\text{TiO}_2\text{-SiO}_2$ might be obstructed by the competition between WO_3 and PO_4^{3-} to react with $\text{TiO}_2\text{-SiO}_2$. The catalytic activities of $\text{TiO}_2\text{-SiO}_2$ and $x\text{W}/\text{TiO}_2\text{-SiO}_2$, ($x = 1, 5, 10, 15 \text{ wt}\%$) were evaluated through 1,2-octanediol formation in the conversion of 1-octene to 1,2-epoxyoctane using aqueous H_2O_2 as oxidant. Only samples with more than 5 wt% tungsten loading were found to act as oxidative-acidic bifunctional catalysts to produce 1,2-epoxyoctane and 1,2-octanediol. In the series of bifunctional catalysts, $10\text{W}/\text{TiO}_2\text{-SiO}_2$ showed the best performance with the highest formation of 1,2-epoxyoctane ($754 \mu\text{mol}$) and 1,2-octanediol ($51 \mu\text{mol}$). Further modification with H_3PO_4 demonstrated that 0.2 M $\text{PO}_4^{3-}/10\text{WO}_3/\text{TiO}_2\text{-SiO}_2$ was the best bifunctional oxidative-acidic catalyst which produced $679 \mu\text{mol}$ 1,2-epoxyoctane and $436 \mu\text{mol}$ 1,2-octanediol from 1-octene after 24 h. As a conclusion, more active sites were generated via the tungsten-phosphate modification, thus accelerating the production of epoxide for diol formation in the one step reaction. The resulting bifunctional oxidative-acidic catalysts are potentially useful for the chemical production industry.

ABSTRAK

Diol adalah penting sebagai bahan mentah dan perantara untuk proses berlainan dalam pelbagai industri bahan kimia. Penyediaan diol biasanya dilakukan dalam dua langkah yang melibatkan pengoksidaan olefin dan diteruskan dengan hidrolisis epoksida; tindak balas ini dilakukan menggunakan mangkin yang berbeza dalam dua bekas berasingan. Oleh itu, pembangunan mangkin dwifungsi untuk penghasilan diol dalam satu langkah tindak balas sangatlah diinginkan. Dalam penyelidikan ini, mangkin dwifungsi oksidatif-berasid baharu yang merupakan tungsten-fosfat disokong pada $\text{TiO}_2\text{-SiO}_2$ telah disintesis. Penyokong $\text{TiO}_2\text{-SiO}_2$ telah disediakan melalui kaedah sol-gel, diikuti dengan penambahan WO_3 dan PO_4^{3-} . Namun WO_3 dan PO_4^{3-} dalam bahan telah diubah-ubah untuk mengkaji peranan oksida tungsten dan asid fosforik dalam penjanaan tapak aktif oksidatif dan keasidan. Analisis pembelauan sinar-X menunjukkan penyokong $\text{TiO}_2\text{-SiO}_2$ kekal amorfus bahkan selepas WO_3 dan PO_4^{3-} dimuatkan, menunjukkan bahawa WO_3 dan PO_4^{3-} tersebar secara meluas di permukaan SiO_2 , manakala TiO_2 terlakur dalam bingkai SiO_2 . Muatan tungsten yang relatif lebih tinggi dalam sampel kelihatan meningkatkan amaun spesies Ti oktahedral yang bertindak sebagai tapak aktif oksidatif. Walaupun titania-silika terisitepu dengan 5 wt% tungsten memiliki luas permukaan yang tinggi ($473 \text{ m}^2/\text{g}$), penambahan kedua-dua WO_3 dan PO_4^{3-} mengakibatkan luas permukaan berkurangan secara mendadak ($15 \text{ m}^2/\text{g}$). Hasil FTIR untuk tungsten-fosfat berpenyokong titania-silika mencadangkan pengikatan kumpulan fosfat pada kumpulan hidroksil. Peningkatan keasidan $\text{TiO}_2\text{-SiO}_2$ selepas pengubahsuaian dengan WO_3 dan PO_4^{3-} disahkan oleh analisis TPD- NH_3 . Analisis penjerapan piridina yang dipantau menggunakan spektroskopi FTIR menunjukkan sampel $10\text{WO}_3/\text{TiO}_2\text{-SiO}_2$ mempunyai amaun tertinggi untuk tapak asid Lewis dan Brønsted. Namun demikian, pembentukan tapak asid Brønsted dalam $0.2 \text{ M PO}_4^{3-}/10\text{WO}_3/\text{TiO}_2\text{-SiO}_2$ mungkin terhalang disebabkan persaingan antara WO_3 dan PO_4^{3-} untuk bertindak balas dengan $\text{TiO}_2\text{-SiO}_2$. Aktiviti pemangkinan $\text{TiO}_2\text{-SiO}_2$ dan $x\text{W}/\text{TiO}_2\text{-SiO}_2$, ($x = 1, 5, 10, 15 \text{ wt}\%$) telah dinilai melalui penghasilan 1,2-oktanadiol dalam penukaran 1-oktena kepada 1,2-epoksioktana menggunakan H_2O_2 akueus sebagai oksidan. Hanya sampel yang dimuati tungsten melebihi 5 wt% didapati bertindak sebagai mangkin dwifungsi oksidatif-berasid untuk menghasilkan 1,2-epoksioktana dan 1,2-oktanadiol. Dalam siri mangkin dwifungsi, $10\text{W}/\text{TiO}_2\text{-SiO}_2$ menunjukkan prestasi terbaik dengan pembentukan tertinggi 1,2-epoksioktana ($754 \mu\text{mol}$) dan 1,2-oktanadiol ($51 \mu\text{mol}$). Pengubahsuaian lanjut menggunakan H_3PO_4 mempamerkan bahawa $0.2 \text{ M PO}_4^{3-}/10\text{WO}_3/\text{TiO}_2\text{-SiO}_2$ adalah mangkin dwifungsi oksidatif-berasid yang terbaik yang menghasilkan $679 \mu\text{mol}$ 1,2-epoksioktana dan $436 \mu\text{mol}$ 1,2-oktanadiol daripada 1-oktena selepas 24 jam. Kesimpulannya, lebih banyak tapak aktif terjana melalui pengubahsuaian tungsten-fosfat, dengan ini mempercepatkan penghasilan epoksida untuk pembentukan diol dalam tindak balas satu langkah. Mangkin dwifungsi oksidatif berasid yang terhasil berpotensi digunakan untuk industri pengeluaran bahan kimia.

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LIST OF ABBREVIATIONS

2θ	- Bragg angle
BET	- Brunauer Emmett Teller
BJH	- Baret, Joyner and Halenda
DR UV-Vis	- Diffuse Reflectance Ultraviolet-Visible
EDX	- Energy dispersive X-ray
EtOH	- Ethanol
FESEM	- Field Emission scanning electron microscopy
FTIR	- Fourier transform infrared spectroscopy
g	- gram
GC	- Gas chromatography
h	- Hour
K	- Kelvin
μ	- Micro (10^{-6})
mg	- Milligram
mL	- Milliliter
min	- minute
M	- Molar
nm	- Nanometer
TiO ₂ -SiO ₂	- Titania-silica
s	- Second
TEM	- Transmission electron microscopy
TEOS	- Tetraethylorthosilicate
TS-1	- Titanium silicate-1
TTIP	- Titanium(IV) isopropoxide
TPD	- Temperature Programmed Desorption
UV-Vis DR	- Ultraviolet-visible diffuse reflectant

- xW/TiO₂-SiO₂ - WO₃ are impregnated separately onto TiO₂-SiO₂ support, where x = 1, 5, 10 & 15 wt%
- XRD - X-ray diffraction
- yM PO₄³⁻/10WO₃/TiO₂-SiO₂ - PO₄³⁻ treated on 10WO₃/TiO₂-SiO₂ support, where y = 0.05, 0.1, 0.2 & 0.3 M
- λ - Wavelength
- wt% - Weight percent

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Acid catalysis is one of fundamental industrial importance, where it plays an important role in organic synthesis for example, alkylation, saturated hydrocarbon isomerization, esterification, cracking, condensation and so on (Jiang *et al.*, 2008; Zhao *et al.*, 2008). Solid acid heterogenous catalysts contain both Brønsted and Lewis acid sites which normally enhance their functionalities superior to those of the conventional inorganic acids. On the other hand, solid acid catalysts with nanosized metal oxides have some known difficulties such as acidity adjustment and small surface area that limits their catalytic performance (Jiang *et al.*, 2008). Therefore, a major focus is to support the nanosized catalytic active materials through embedding them on a high surface area material in order to retain their catalytic activities and in order to increase their acidity, whilst the functional group were attached on the surface of metal oxide (Shao *et al.*, 2013).

An epoxide is an organic compound and important raw material for a broad range of products, from pharmaceuticals and plastics to paint and adhesives (Mohammed *et al.* 2015). However, production of epoxides can be expensive, especially on a large scale, as well as damaging to the environment. The conventional epoxidation methods in the fine chemicals industries employ either stoichiometric peracids as a catalyst which produces acid waste, or chlorohydrin. This results in chlorinated by-products and calcium chloride waste. Therefore, an oxidative-acidic

bifunctional catalyst was believed to improve the production of epoxide and diols consequently gave advantages to the chemical industry. Besides, it could also be further modified to enhance stability and catalytic performance so it could be used in the synthesis of other valuable diols (Mohammed *et al.*, 2015).

Diols are chemical compounds which contains two hydroxyl groups. They are important raw materials for a wide variety of chemicals industry such as polyester, surfactant, pharmaceutical and etc (Beller *et al.*, 2004). Diols have a good reaction with many organic compounds such as linear and aliphatic carbon chain due to their high water solubility and reactivity. Linear diol consists of two primary hydroxyl groups for example in 1,2-octanediol, which are beneficial as an emollient, preservative, humectant and wetting agent in cosmetics and skin care products (Brown *et al.*, 2003; Mildbradt *et al.*, 2005). The preparation of diols is mostly carried out by two steps series which are epoxidation of olefin continued by the hydrolysis of the epoxides. It has been notified that the formation of diols from epoxides is catalyzed by Brønsted acid sites (Lee *et al.*, 2010; Prasetyoko *et al.*, 2005a). In other words, in order to manufacture diols successively in the manufacturing industry, two reactors have to be build which give rise to the time and cost for production process (Ekhsan *et al.*, 2014). Therefore, it is highly desired to develop the beneficial bifunctional catalyst for consecutive reaction of diol.

Over the past decades, the development of bifunctional catalysts has drawn researchers' attention for their potential application in consecutive reactions. A bifunctional catalyst consists of two active sites (Lee *et al.*, 2008) which are oxidative and acidic sites in a single material (Lee *et al.*, 2010). It is also known as dual function catalyst where a catalytic substance possesses two active sites and it capables of catalyzing two different types of reaction. The whole process is more practical and economical than the two-step process using two different catalysts. As the process is time-consuming and requires a high cost (Ekhsan *et al.*, 2014), an oxidative-acidic bifunctional catalyst is highly demanded to especially ensure rapid production of diols. The proposed of consecutive reaction of diol formation by using an oxidative-acidic bifunctional catalyst is shown in Figure 1.1.

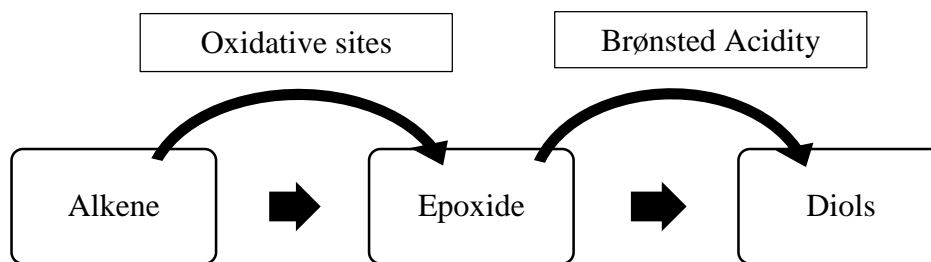


Figure 1.1 Oxidative-acidic bifunctional catalyst for diol production in a consecutive reaction

In the past few years, various oxidative-acidic bifunctional catalysts have been reported. These include zirconium sulphate loaded TS-1 (Prasetyoko *et al.*, 2005b), titanium ion (Ti^{4+}) together in the framework of zeolites (Lee *et al.*, 2008) sulphate-vanadium treated titania-silica aerogel (Lee *et al.*, 2010), niobium-phosphate impregnated titania-silica (Ekhsan *et al.*, 2014) and HZSM-5 supported Mo and combination of trivalent metal ions (Al^{3+} , B^{3+} , Fe^{3+} , Ga^{3+}) (Trong On *et al.*, 2003). It was declared that the presence of metal oxides such as V, Mo, Zr and Nb acted as redox centers had influenced formation of both Lewis and Brønsted acidity sites. Besides, it was also claimed that V and Nb acted as oxidative active sites for epoxidation (Ekhsan *et al.*, 2014; Lee *et al.*, 2010). Owing to the similar chemical properties of tungsten to Mo and Nb, it is worthy to explore the possibility usage of tungsten in a bifunctional catalyst's design.

It was reported that tungsten oxide species dispersed on zirconia supports ($\text{WO}_x\text{-ZrO}_2$) by impregnation with a solution of tungstate anions show strong acidity (Barton *et al.*, 1998). Acid properties of tungsten/zirconia were characterized using adsorption microcalorimetry showing that the acid site strength of the tungsten/zirconia materials was similar to or slightly higher than that found in zeolites or sulphated zirconia and was comparable to sulphuric acid (Vartulli *et al.*, 1999). Increasing tungsten loadings in tungstated titania, with and without platinum, rose acidity of catalyst and favored isomerization of *n*-pentane and of *n*-butane (Eibl *et al.*, 2000). The dispersion of the supported tungsten oxide phase and their surface acidity was varied depending on metal precursor and atmosphere of pretreatments (Perez-

Cadenas *et al.*, 2003). For many of these catalytic applications, the solid acidity of the supported tungsten oxide phase played a crucial role in their overall catalytic performance (Wachs *et al.*, 2006).

It is known that the formation of diols from epoxides catalyzed only by Brønsted acid sites (Lee *et al.*, 2008). However, titania-silica aerogel consists of only Lewis acidity (Hu *et al.*, 2003). In some research, the Brønsted acid sites can be created by adding the metal oxide on the surface of titania-silica (Ekhsan *et al.*, 2014; Lee *et al.*, 2010). It was also reported that Brønsted acid sites and Lewis acid sites are present at tungsten oxide surface coverage (Wachs *et al.*, 2006).

Modification via acid treatment is one of the approaches used to enhance the Brønsted acidity in a catalyst. Generation of Brønsted acidity in phosphorus-containing MCM-41, sulphated Al-MCM-41, and sulphuric acid and phosphoric acid modified titania-silica aerogel have been reported (Kawi *et al.*, 2002; Ng *et al.*, 2006; Lee *et al.*, 2011). Increasing amount of phosphoric acid amount has increased the Brønsted acid sites for the isomerization of *n*-butene (Tada *et al.*, 1995). In addition, loading both sulphate and vanadium onto the material has improved the Brønsted acidity in titania-silica aerogel (Lee *et al.*, 2010). Thus, it is an opportunity to enhance the catalytic activity of diol formation by the addition of acid into the tungsten oxide supported titania-silica.

In this research, a new bifunctional catalyst of tungsten-phosphate supported on titania-silica was synthesized via sol-gel and impregnation methods. A study was carried out to study the function of tungsten oxide in creating both oxidative and acidity active sites. Besides, the interaction among tungsten oxide, silica support and phosphoric acid was investigated to achieve the high catalytic activity.

1.2 Problem statement

In industry, diols production is carried out by two steps order which is epoxidation of olefin, continued by the hydrolysis of the epoxides. However, the process is time-consuming and costly. Currently, the organic synthesis of diols production uses the conventional liquid acids such as H_2SO_4 , HF, HCl and H_3PO_4 . Due to their toxicity and corrosive nature of these acids, their usage has generated great risks in handling, containment and disposal. Moreover, waste disposal has increased the environmental cost and increased the chemical waste poisonous towards public (Jiang *et al.*, 2008). Thus, it is important to develop a new functional material to replace the liquid acids.

In the previous study, titania-silica have been found as a good catalyst for epoxidation affected by the highly dispersion of Ti^{4+} species in the catalyst (Muller *et al.*, 2000). Nevertheless, this material only consisted of Lewis acidity but did not consist of Brønsted acidity which important for transformation of diols from epoxides. Therefore, titania-silica itself was unable to transform epoxide to diols due to lack Brønsted acid site in the materials (Lee *et al.*, 2008). Another bifunctional catalyst has been synthesized through impregnation technique by the incorporation of titanium ion and sulphated zirconia together in silica. It was stated that the existence of octahedral titanium and sulphated zirconia, activate this catalyst in both oxidation reactions and acid catalyzed reactions. However, the insufficient Brønsted acidity in the catalyst has been identified resulted in low production of diols (Prasetyoko *et al.*, 2005b).

Recently, Ekhsan *et al.* (2014) has proved that both phosphate-vanadium impregnated titania-silica aerogel and sulphate-vanadium impregnated titania-silica aerogel were excellent bifunctional oxidative and acidic catalysts (Lee *et al.*, 2009; Lee *et al.*, 2010). The addition of acid groups to vanadium was crucial for formation of Brønsted acid sites. Most lately, it has been demonstrated that co-existence of niobium and phosphate were crucial for Brønsted acidity formation in niobium-phosphate impregnated titania-silica (Ekhsan *et al.*, 2014). However, the competition between titanium and niobium seemed to hinder generation of more acidity.

Tungsten oxide materials possessing high Brønsted acidity have been investigated for their excellent catalytic activity in dehydration of isopropanol (Perez-Cadenas *et al.*, 2003). Due to similar properties of transition metals in Group 5 and 6, tungsten oxide is selected as modifier for TiO₂ to enhance the formation of both oxidative and acidic sites on catalysts. Besides, it was found that the Brønsted acid site density increased with increasing of tungsten loading in various materials, reflecting tungsten could act as an important part in the generation of Brønsted acidity sites (Pedrosa *et al.*, 2008). However, the performance is less satisfactory in terms of amount of Lewis and Brønsted acidity created, selectivity as well as catalytic yield. Another effective way to improve the catalytic activity and increase Brønsted acidity is treatment with acid. In consideration of generating oxidative and Brønsted acidity within the sample, the tungsten-catalyst was proposed to be treated with phosphoric acid, H₃PO₄ particularly to enhance the acidity of the resulting catalyst. Thus, the role of tungsten and phosphate in generation of both oxidative and Brønsted acidity in a single materials were worthy for exploration.

1.3 Objectives

The objectives of the study were:

1. To synthesize and characterize tungsten-phosphate supported on titania-silica as bifunctional catalysts;
2. To investigate the role of tungsten oxide (WO₃) and phosphate (PO₄³⁻) in acidity formation by examining type and amount of acidity formed;
3. To evaluate the catalytic performance of titania-silica supported tungsten-phosphate as oxidative-acidic bifunctional catalyst in single step diol formation.

1.4 Significance of Research

This research is important to enhance the production of diols by synthesizing the tungsten oxide and phosphoric acid impregnated titania-silica as oxidative and acidic bifunctional catalyst. It is also to understand the role of tungsten oxide in creating acidity in the catalyst. Besides, the bifunctional oxidative-acidic catalyst for diol production was design. This research aims to investigate the role of tungsten oxide in generation of both oxidative and acidity active sites and Brønsted acid sites in a newly designed bifunctional catalyst.

1.5 Scope and Limitation of Study

The bifunctional catalytic activity of the tungsten-phosphate supported on titania-silica promoted generation of Brønsted acidity, leading to sufficient production of diols. The physicochemical properties of the synthesize catalyst were explored. It is also important to study the interaction among WO_3 , PO_4^{3-} , TiO_2 and SiO_2 support to their catalytic performance.

A bifunctional catalyst tungsten-phosphate supported on titania-silica was synthesized using sol-gel and impregnation methods. Tetraethylorthosilicate (TEOS) was hydrolyzed to form $\text{Si}(\text{OH})_4$ and continued by condensation to form Si-O-Ti bonds, which Titanium(IV) isopropoxide (TTIP) was used as a precursor of Ti. The titania-silica was impregnated with tungsten oxide and had been treated with phosphoric acid.

Physical and chemical properties of catalyst were characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), diffuse reflectance ultraviolet-visible (DR UV-Visible) spectroscopy, temperature programmed desorption/reduction/oxidation (TPD/R/O), and fourier transform infrared (FTIR) spectroscopy. Besides, samples'

surface area was measured by means of N_2 adsorption surface area analysis. Type and amount of acidity were examined via FTIR using pyridine as a probe molecule.

Catalytic performance of tungsten-phosphate supported titania-silica as oxidative-acidic bifunctional catalyst was examined in consecutive transformation of 1-octene to 1,2-octanediol through generation of 1,2-epoxyoctane at 343 K in the presence of aqueous H_2O_2 as oxidant. The yields of the reaction were evaluated on a HP Agilent 6890N gas chromatograph. Figure 1.2 shows the flowchart of the research.

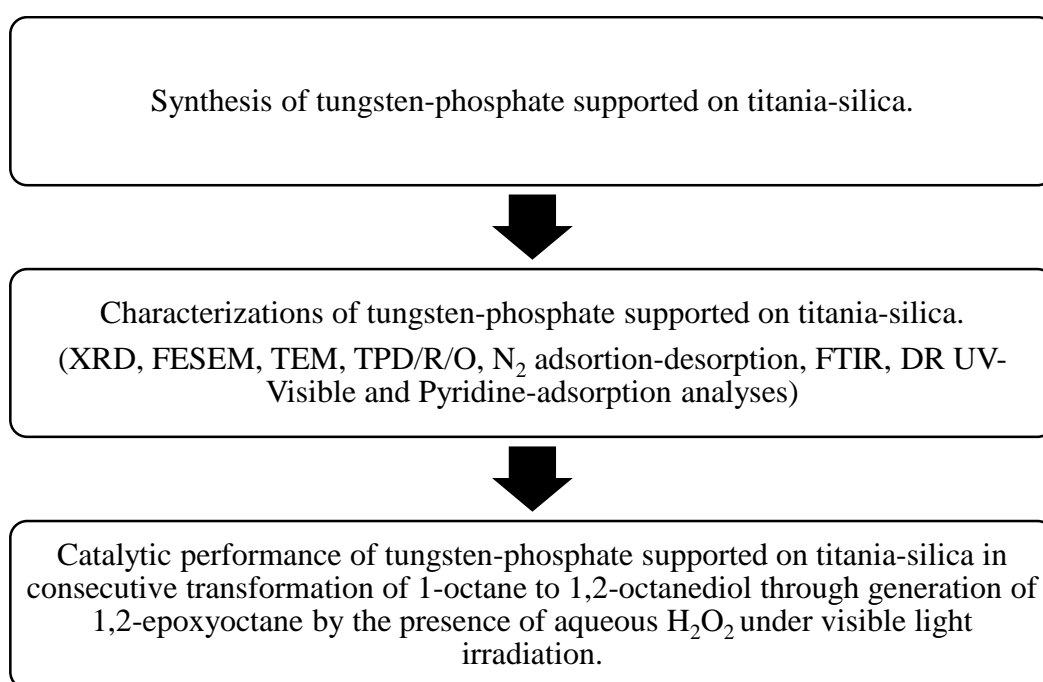


Figure 1.2 Flow chart of research

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