SYNTHESIS AND CHARACTERIZATION OF TIN-MODIFIED MESOPOROUS SILICA MCM-48 FOR SELECTIVE OXIDATION OF ALCOHOL TO ALDEHYDE

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Amitabha

To my beloved parents

Lam Ah Lin and Wong Heng Hoong

for their love that made me firm and resolute

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PREFACE

This thesis is the result of my work carried out in the Department of Chemistry; Universiti Teknologi Malaysia between November 2004 to September 2006 under supervision of Assoc. Prof. Dr. Salasiah Endud. Part of my work described in this thesis has been reported in the following publications or presentations:

1. Wong, K.-L. and Endud, S. Synthesis, Characterization, and Catalytic Properties of Tin Containing MCM-48 in Oxidation of Alcohols. *Proceedings of Annual Fundamental Science Seminar 2005*. July 4-5, 2005. Johor, Malaysia: Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia. 2005. 87-95.

2. Wong, K-L. and Endud, S. Tin-containing Mesoporous MCM-48 in Oxidation of Benzyl Alcohol to Benzaldehyde. Poster presentation at the *18th Simposium Kimia Analisis Malaysia (SKAM-18)*. Universiti Teknologi Malaysia, Skudai, Johor, Malaysia. September 12-14, 2005. P-90.

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5. Endud, S. and Wong, K-L. Mesoporous Silica MCM-48 Molecular Sieve Modified with $SnCl_2$ in Alkaline Medium for Selective Oxidation of Alcohol. *Micropor. Mesopor. Mater*., 2007. 101: 256-263.

ABSTRACT

Tin-modified mesoporous silica MCM-48 with various Si/Sn ratios has been prepared by post synthesis modification in alkaline medium. Local rice husk ash (RHA) has been used as Si precursor in the synthesis of Si-MCM-48 samples while $SnCl_2$ was used as the tin source in the modification. The tin-modified MCM-48 samples were characterized by using powder X-ray diffraction (XRD) analysis, Fourier transform infrared (FTIR) spectroscopy, ultraviolet-visible diffuse reflectance (UV-Vis DR) spectroscopy, nitrogen physisorption measurement, field emission scanning electron microscopy (FESEM) and temperature-programmed reduction (TPR) analysis. Surface acidity of the prepared samples was determined by using pyridine adsorption-desorption measurement followed by FTIR spectroscopy. In addition, thermal and hydrothermal stability testing for the tin-modified samples were carried out. The FTIR, UV-Vis DR and XRD results show that tetrahedral tin species can be introduced into the mesoporous material without destroying the framework structure of the molecular sieves. Surface acidity studies confirm that Lewis acid sites had been generated on the mesoporous silica MCM-48 by post-synthesis modification. The generation of Lewis acid sites could be due to the introduction of tin species and/or because of defect sites that had been created during post-synthesis modification. Tin-modified sample SnM60 (Si/Sn = 60) possessed highest amount of Lewis acidity. In oxidation of benzyl alcohol, all the tin-modified samples gave 100% selectivity to benzaldehyde in reaction time under 22 hours. The catalytic activity can be correlated with the Lewis acid sites generated by post-synthesis modification. Purely siliceous MCM-48 and physically mixed tin-containing MCM-48 samples that possesses no Lewis acidity gave poor performance in the catalytic reaction. With the increase in the amount of oxidant in the reaction mixtures, the conversion of benzyl alcohol increased significantly but the selectivity for benzaldehyde was reduced. For reusability test, the catalytic performance of the re-used samples was maintained within 5-10% after two cycles of reuse without significant loss of activity. Comparison of the catalytic performance of SnM60 in the oxidation of unsaturated primary alcohols and saturated aliphatic primary alcohol towards the corresponding aldehydes showed higher % conversion of the unsaturated primary alcohols than that of the saturated aliphatic primary alcohol.

ABSTRAK

Silika berliang meso MCM-48 yang terubahsuai dengan timah dalam pelbagai nisbah Si/Sn telah disediakan melalui pengubahsuaian pasca-sintesis dalam medium alkali. Abu sekam padi tempatan telah digunakan sebagai sumber Si dalam sintesis sampel Si-MCM-48, manakala $SnCl_2$ telah digunakan sebagai sumber timah dalam pengubahsuaian tersebut. Sampel MCM-48 yang mengandungi timah telah dicirikan dengan kaedah pembelauan sinar-X (XRD), spektroskopi inframerah transformasi Fourier (FTIR), spektroskopi pemantulan difusi ultralembayung-nampak (UV–Vis DR), penjerapan nitrogen, mikroskopi elektron pengimbasan pancaran medan (FESEM) dan analisis penurunan dengan suhu teraturcara (TPR). Keasidan permukaan bagi sampel yang telah disediakan telah diperolehi melalui penjerapan-penyahjerapan piridina diikuti dengan spektroskopi inframerah. Ujian kestabilan termal dan hidrotermal juga telah dijalankan ke atas sampel. Hasil XRD, FTIR and UV-Vis DR menunjukkan bahawa spesis timah dapat diselitkan dalam bahan berliang meso tanpa memusnahkan struktur kerangka penapis molekul tersebut. Kajian keasidan permukaan mengesahkan bahawa tapak asid Lewis telah dapat dihasilkan pada silika berliang meso MCM-48 dengan pengubahsuaian pasca-sintesis. Penghasilan tapak asid Lewis tersebut mungkin disebabkan oleh penyelitan sepsis timah atau tapak kecelaan yang terbentuk semasa pengubahsuaian pasca-sintesis. Sampel terubahsuai dengan timah SnM60 (Si/Sn = 60) mempunyai keasidan Lewis yang tertinggi. Dalam ujian pemangkinan, semua sampel terubahsuai dengan timah memberikan kepilihan 100% terhadap benzaldehid dalam masa tindak balas bawah 22 jam. Aktiviti pemangkinan dapat dikaitkan dengan tapak asid Lewis yang terhasil dengan pengubahsuaian pasca-sintesis. MCM-48 bersilika tulen dan sampel MCM-48 terkandung timah yang disediakan secara campuran fizikal memberikan prestasi yang rendah dalam tindak balas pemangkinan. Dengan peningkatan kandungan ejen pengoksidaan dalam campuran tindak balas, nyata sekali bahawa penukaran benzil alkohol juga meningkat, tetapi kepilihannya terhadap benzaldehid telah menurun. Dalam ujian penggunaan semula, prestasi pemangkinan bagi sampel terpakai masih dapat dikekalkan setelah dipakai semula sebanyak dua kali dengan hanya perbezaan aktiviti sebanyak 5-10% berbanding dengan yang asal. Perbandingan aktiviti pemangkinan SnM60 dalam penukaran alkohol primer tak tepu dan alkohol primer alifatik tepu kepada aldehid sepadan menunjukkan % penukaran alkohol primer tak tepu lebih tinggi daripada alkohol primer alifatik tepu.

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LIST OF ABBREVIATIONS

%	-	Percentage
°	-	Degree
AAS	-	Atomic Absorption Spectroscopy
a_o	-	Unit cell parameter
Au	-	Aurum (gold)
BET	-	Brunauer-Emmett-Teller
BJH	-	Barrett, Joyner and Halenda
cm	-	centimeter
CO_2	-	Carbon dioxide
CTABr	-	Cetyltrimetylammonium bromide
Cu-K_α	-	X-Ray diffraction from copper K energy levels
d	-	*d*-spacing
EDL		Electrodeless discharge lamp
FESEM	-	Field emission scanning electron microscopy
FTIR	-	Fourier Transform Infrared
g	-	Gram
GC	-	Gas chromatography
GC-MS	-	Gas chromatography with mass spectroscopy
H_2O	-	Water
IUPAC	-	International Union of Pure and Applied Chemistry
K	-	Kelvin
KBr	-	Potassium bromide
L	-	Liter

M41S	-	Family name given to mesoporous materials that were synthesized by researchers from ExxonMobil
MCM-41	-	Mobil Composition of Matter No. 41
MCM-48	-	Mobil Composition of Matter No. 48
MCM-50	-	Mobil Composition of Matter No. 50
mL	-	milliliter
MPVO	-	Meerwein-Ponndorf-Verley reduction of aldehydes and Oppenauer's oxidation of alcohols
NCS	-	*N*-chlorosuccinimide
nm	-	Nanometer
NO_x	-	Nitrogen oxide
p/p_o	-	Relative pressure
P_o	-	Saturated pressure
ppm	-	Part per million
RHA	-	Rice husk ash
SBA-15	-	Santa Barbara No. 15
S_{BET}	-	BET surface area
Si-MCM-48	-	Purely siliceous MCM-48
SiO_2	-	Silica
TBHP	-	*tert*-butyl hydroperoxide
TCD		Thermal conductivity detector
TPR	-	Temperature-programmed reduction
TX-100	-	Triton X-100
USD	-	Currency of United State of America, *Dollar*
UV-Vis DR	-	Ultraviolet-visible diffuse reflectance spectroscopy
% wt.	-	Percentage of weight
XRD	-	X-Ray diffraction
θ	-	Theta (Bragg angle)

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CHAPTER 1

INTRODUCTION

1.1 Catalyst

Catalyst is defined as a substance that increases the rate of approach to equilibrium of a chemical reaction without being substantially consumed [1]. Normally, a catalyst offers an alternative path for a reaction, which is energetically more favourable. The activation energy of the catalyst added reaction is significantly smaller than that of the similar reaction but without catalyst; hence, the rate of the former is much higher. The action of a catalyst in acceleration of such chemical reaction is called catalysis.

Catalysts accelerate reactions and thus enable industrially important reactions to be carried out efficiently under practically attainable conditions. Much of the food we eat and the medicines we take, many of the fabrics and building materials that keep us warm and almost all the fuels that transport us by road, sea or air are produced with the aid of catalysts [2]. Nowadays, the chemical industry is largely based upon catalysis. In 2001, global top 50 chemical sales exceeded USD 404.4 billion. Roughly 85-90% of these chemicals were produced throughout the world in chemical manufacturing processes that involved catalysis [3]. In the same year, the world merchant market for catalysts (i.e., excluding catalysts manufactured and consumed internally by industrial companies) was worth about USD 10 billion [4].

1.2 Heterogeneous Catalysts

Catalysts are generally divided into two basic types, heterogeneous and homogeneous, depending on their state relative to the reaction medium [5]. Heterogeneous catalysts are present in different phase to the reaction medium. In most cases the catalyst is a solid with the reactants being either in the gas or liquid phase. On the other hand, homogeneous catalysts are present in the same phase (the gas phase or most often the liquid phase) as the reactants. The most widely used homogeneous catalysts are acids (e.g. sulfuric acid), bases (e.g. sodium hydroxide) and (organo)metallic complexes. Overview comparisons between these two types of catalysts are summarized in Table 1.1.

Table 1.1: Comparison of heterogeneous and homogeneous catalysts [5].

Heterogeneous	Homogeneous
Usually distinct solid phase	Same phase as reaction medium
Readily separated	Often difficult to separate
Readily regenerated and recycled	Expensive/difficult to recycle
Rates not usually as fast as homogeneous	Often very high rates
May be diffusion limited	Not diffusion controlled
Quite sensitive to poisons	Usually robust to poisons
Long service life	Short service life
Poor mechanistic understanding	Often mechanism well understood

Majority of the fine, speciality, and pharmaceutical chemicals manufacturing processes rely on homogeneous catalysts, with solid heterogeneous catalysts used in little beyond hydrogenation processes [6]. Many of these homogeneous catalysis processes generate huge amount of inorganic waste and toxic by-products. Since the early 1990s, the issues concerning the environmental impact of the hazardous waste and by-products from chemicals manufacturing processes have alarmed the public and environmentalists. Public concern is a potent influence; industry sectors are now

looking towards innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture and use of chemical products. In this respect, there is no doubt that heterogeneous catalysts with their advantages such as ready separability, recyclable, reduction of waste can play a key role in replacing the conventional homogeneous catalysis route towards environmentally benign processes. Consequently, developing heterogeneous catalysts for various kinds of chemical reactions that are involved in the industrial processes become a new challenge to scientists and researchers.

1.3 Research Background and Problem

In the past few years, various oxidation reactions in the gas or liquid phases have been studied to synthesize valuable intermediate products or fine chemicals [7]. Among the reactions, the catalytic oxidation of primary and secondary alcohols into their corresponding aldehydes and ketones are essential reactions in organic synthesis [8,9]. Primary alcohols usually are oxidized to aldehydes or acids, while secondary alcohols are oxidized to ketones. Tertiary alcohols are normally resistant to oxidation.

Conventional methods for performing such transformations generally involve the use of stoichiometric or more than stoichiometric quantities of inorganic oxidants, such as chromium (VI) reagents, dimethyl sulfoxide, ceric ammonium nitrate, permanganates, periodates, or *N*-chlorosuccinimide (NCS) [10]. In many instances, these homogeneous catalysts provide powerful solutions, but on an industrial scale the problems related to corrosion and plating out on the reactor wall, handling, recovery, and reuse of the catalyst set up the limitations of these processes [11]. Besides, safety hazards associated with these oxidants and their toxic by-products and waste are also the major problems of such processes. Furthermore, these methods are usually carried out in halogenated organic solvents, typically chlorinated hydrocarbons which are environmentally undesirable and often require one or more equivalents of these relatively expensive

oxidizing agents. Consequently, there is a marked trend towards the use of catalytic alternatives that do not generate aqueous effluents containing large quantities of inorganic salts. Much effort has been made to develop homogeneous catalytic systems to solve these problems [12-17]. However, most systems still required the inert atmosphere condition, addition of toxic additives and hazardous solvent.

A liquid phase catalytic oxidations for alcohols employing heterogeneous catalysts has the maximum potential to solve most of the problems faced by homogeneous catalysts in both economic and environmental aspects. A liquid phase reaction allows better control of heat and mass transfer limitation, thus making the operation safer and also economical energy-wise. Effective liquid phase alcohol oxidation reactions can be carried out over heterogeneous catalyst in combination with clean and inexpensive oxidants such as *tert*-butyl hydroperoxide (TBHP) [18,19]. As shown in Figure 1.1, oxidation of alcohols by TBHP will only give water and tertiary alcohol as the only by-products.

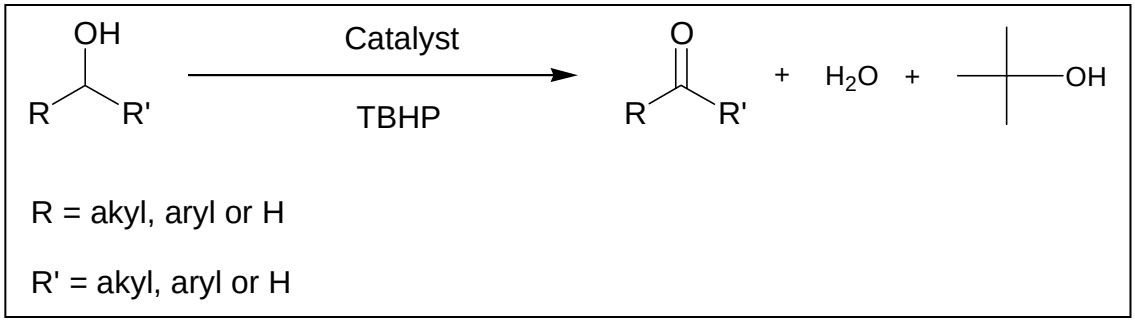

Figure 1.1 Scheme of the catalytic oxidation of alcohol by TBHP.

Study on the oxidation of alcohols over heterogeneous catalysts is gaining interest from researchers since few years ago. Many of the catalysts developed were based on noble and rare metals, such as ruthenium (Ru), palladium (Pd), platinum (Pt) and gold (Au) [20-27]. These catalysts are expensive and some of them require inert atmosphere during the preparation of the catalyst. Sometimes they even need other promoter ions to achieve good catalytic activities. There are also heterogeneous catalytic oxidations of alcohols based on molecular sieves such as zeolites [28-32].

Most of the catalysts are prepared by incorporating or supporting transitional metal species on the microporous materials (pore size < 2nm). Even though the reaction rates are slower and the product yields were lower compared to their conventional homogeneous counterparts, heterogeneous catalysts based on molecular sieves is a more acceptable pathway due to the ease in separation, recovery, recycling, and amenability for continuous processing. Therefore, further studies on developing heterogeneous catalysts based on molecular sieves with better catalytic performance should be carried out.

In the synthesis of naturally occurring compounds, one usually faces the manipulation of compounds containing several types of hydroxyl functional groups, and it is necessary to selectively oxidize a single hydroxyl group (primary or secondary alcohol) within the same molecule [33]. The difficulties are multiplied when more complexes structures, such as polyfuntionalized and thermo-labile alcohols, which a lot of them are precursors or chemical intermediates for fine chemicals and pharmaceuticals, have to be oxidized. Thus, selective transformation of hydroxyl groups have been a challenging target since it offers an alternative to synthesis via selective protection and deprotection.

On the other hand, the element tin or *Stannum* (Sn) in Latin has played an increasingly important role in organic and organometallic chemistry. In fact, tin is one of the elements that has been used extensively in the petrochemical industry to improve the selectivity of the bimetallic catalyst systems [34-36]. Study on introduction of tin species into molecular sieves to enhance catalytic property of the latter has gained great interest. Tin can exist as tin (IV) species in the tin-containing molecular sieves, in which they form tetrahedral coordination [37-41]. This tin (IV) species can either be substituted into the silica framework of molecular sieves or just simply grafted onto the surface of the molecular sieves. Besides, tin can also exist as hexacoordinated mono- and/or polymeric tin species. Methods reported for introducing tin species into porous materials usually used $SnCl_4$ as tin source under acidic conditions. These methods

sometimes are inconvenient when the chemical compositions in the porous materials are sensitive to acidic conditions.

Recently, tin-containing molecular sieves have been reported to be an efficient catalyst for the Baeyer-Villiger oxidation with hydrogen peroxide in aqueous solution with a very high selectivity to targeted products [42-44]. Baeyer-Villiger oxidation is the oxidation of a ketone to an ester or lactone by a hydroperoxide and it is a prominent reaction in synthetic organic chemistry due to its versatility and highly predictable regioselectivity and stereoselectivity [45]. An additional beneficial property of this chemoselective oxidation system is that isolated double bonds are not epoxidized. Besides, tin-containing molecular sieves also showed good conversion and selectivity in the Meerwein-Ponndorf-Verley (MPV) reduction of aldehydes and Oppenauer's (O) oxidation of alcohols reactions (together denoted as MPVO reactions) [46,47]. In MPV reduction, a secondary alcohol is the reductant whereas in Oppenauer oxidations a ketone is the oxidant. The tin-containing catalyst has been proposed to act as a Lewis acid. The activation of the carbonyl group through its coordination to the metal center was proposed to be the origin of the catalytic activity in Baeyer-Villiger and MPVO reactions [42,45].

By considering their excellent catalytic activity in Baeyer-Villiger and MPVO reactions, tin-containing molecular sieves seem to have the potential as highly selective catalyst in oxidation of alcohol. Therefore the study and development of tin-containing molecular sieves as highly selective catalyst in oxidation of alcohol to their corresponding carbonyl compounds by using clean oxidants should be carried out. To avoid the pore diffusion limitations involving large substrates, tin-containing mesoporous molecular sieves (pore size in 2–50 nm) such as MCM-48 should be developed rather than microporous molecular sieves.

1.4 Research Objectives

The objectives of this research are:

i. To synthesize tin-containing mesoporous MCM-48 materials by post synthesis modification.

ii. To characterize the tin-containing mesoporous MCM-48 materials by physicochemical characterization techniques such as powder X-ray diffraction (XRD) analysis, ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DR), nitrogen (N_2) physisorption measurement and so on.

iii. To investigate the catalytic properties of tin-containing mesoporous MCM-48 materials in the oxidation of benzyl alcohol to benzaldehyde as model reaction.

1.5 Scope of the Study

In this research, the correlation between the structural and physicochemical properties of various tin-containing mesoporous MCM-48 materials and catalytic properties of the materials in oxidation of various alcohols are to be studied. For that reason, the research is divided into three main areas.

First, is the synthesis of tin-containing mesoporous silica MCM-48 with different tin loadings by post-synthesis modification. The modification on purely siliceous MCM-48 (or referred as mesoporous silica) was carried out under alkaline medium by using $SnCl_2$ as tin source. Samples prepared by this method are hereafter referred as tin-modified samples. The synthesis procedure of mesoporous silica MCM-48 in this research is similar to that of the mixed cationic-neutral surfactant templating route that was first introduced by Ryoo et al. [48] and then modified by Lau [49]. Rice husk ash (RHA) obtained from the pilot plant of Zeolite and Porous Materials Group (ZPMG), Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia was used as silica source. As a comparison to post-synthesis modification method, tin-

containing mesoporous silica MCM-48 samples were also prepared by physical-mixing method, in which purely siliceous MCM-48 was physically mixed with tin (IV) oxide, SnO_2.

Second, is the characterization of the prepared tin-modified mesoporous silica MCM-48 samples. To understand the physicochemical properties; appropriate techniques were used in the characterization, including powder X-ray diffraction (XRD) analysis, Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DR), nitrogen (N_2) physisorption measurement, field emission scanning electron microscopy (FESEM), and temperature-programmed reduction (TPR). Surface acidity of the prepared materials had been carried out by using pyridine adsorption-desorption measurement followed by FTIR spectroscopy. In addition, thermal and hydrothermal stability testing for the tin-modified samples were carried out.

Finally, investigation of the catalytic activity of the tin-modified samples were conducted with oxidation of primary alcohol to aldehyde in liquid-phase system. Oxidation of benzyl alcohol to benzaldehyde using *tert*-butyl hydroperoxide, TBHP as oxidant was performed at 353 K as a model reaction. For comparison proposes, commercially available bulk tin (IV) oxide, SnO_2 and purely siliceous MCM-48 were used in the catalytic tests. Reusability and the effect of substrate to oxidant ratio on activity of tin-modified samples were studied. Oxidation of unsaturated primary alcohols (cinnamyl alcohol and geraniol) and primary aliphatic alcohol have been carried out as well. The research design is illustrated in Figure 1.2.

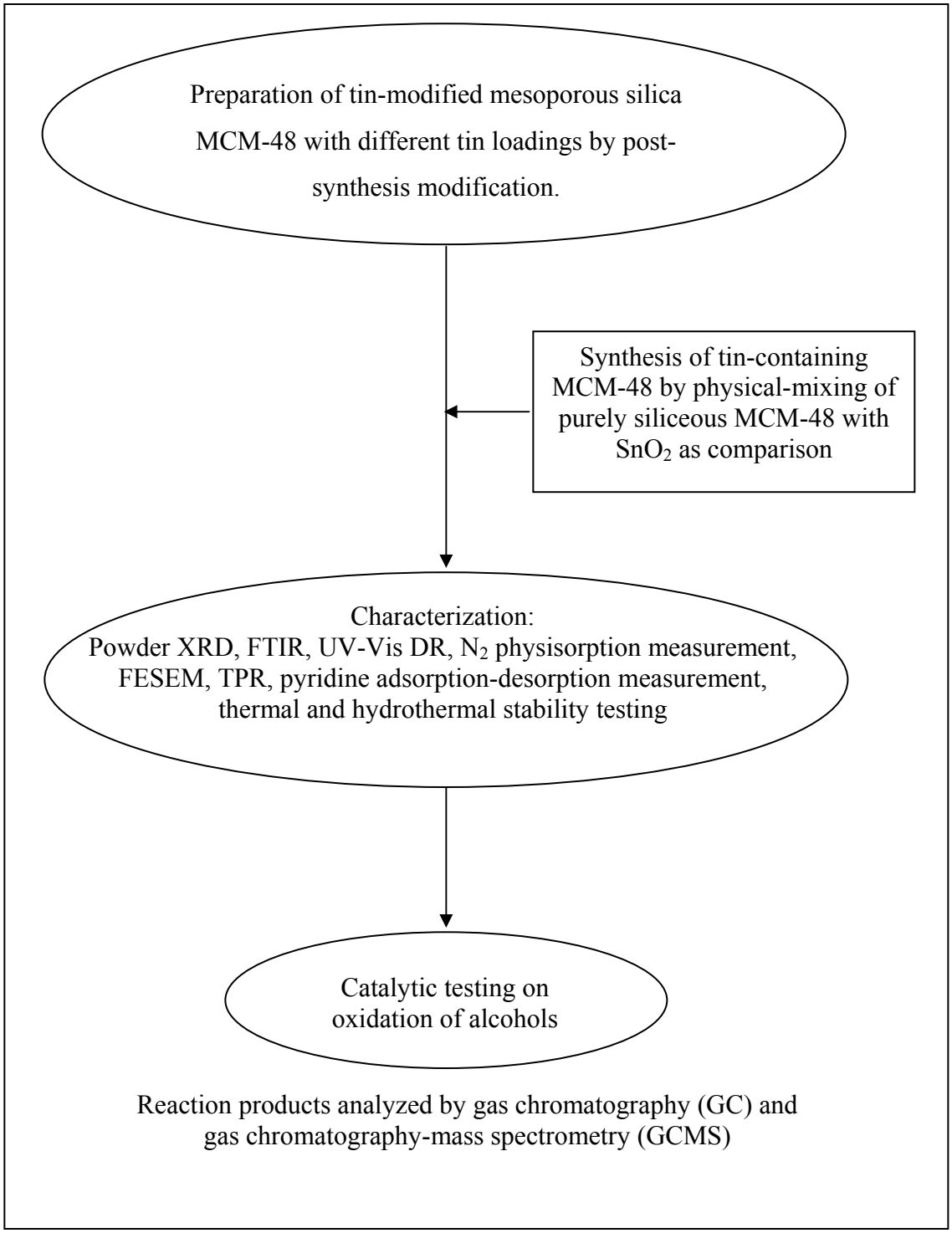

Figure 1.2 Flowchart of the research design.

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