

SYNTHESIS, CHARACTERIZATION AND CATALYTIC
PROPERTIES OF TITANIUM CONTAINING SILICA AEROGEL

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SYNTHESIS, CHARACTERIZATION AND CATALYTIC PROPERTIES OF
TITANIUM CONTAINING SILICA AEROGEL

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*Dedicated to
My Parents*

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ABSTRACT

Silica aerogel and titania silica aerogel were synthesized by chemical means. The effect of titanium source, sulphuric acid and titanium loading were studied. The structure and properties of the aerogels were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), nitrogen adsorption (BET), energy dispersive X-ray analysis (EDX), Fourier transform infrared (FTIR), and ultra violet-visible diffuse reflectance spectroscopy (UV-Vis DRS). Both silica aerogel and titania silica aerogel are amorphous. The surface area of the resulting titania silica aerogel was significantly affected by the quantity of the acid used during synthesis. The physicochemical properties were found could be engineered by the change of acid loading and titanium loading. Isolated titanium in tetrahedral framework position, well dispersed titania particle or crystalline titania (anatase) were formed in-situ during the aerogel synthesis process. Catalytic reaction of cyclohexene and hydrogen peroxide was carried out at 70 °C in a fixed batch reactor. The effects of physicochemical properties of the catalyst, solvent, reaction temperature, oxidant content and alkene to the reaction have been investigated. Both allylic and non-allylic oxidation process have occurred in the reaction. 1,2-cyclohexanediol was formed as major compound in the reaction.

ABSTRAK

Aerogel silika dan aerogel titania-silika telah disintesis melalui pendekatan kimia. Pengaruh daripada sumber titanium, asid sulfurik dan kepekatan titanium telah dikaji. Struktur dan sifat aerogel telah dikaji menggunakan pembelauan sinar-X (XRD), mikroskop imbasan elektron (SEM), penjerapan nitrogen, analisis penyerakan tenaga sinar-X (EDX), Fourier transform infra merah (FTIR), and spektroskopi pemantulan bauran ultra lembayung-nampak (UV-Vis DRS). Kedua-dua aerogel silika dan aerogel titania-silika bersifat amorfus. Luas permukaan aerogel titania silika didapati amat dipengaruhi oleh kuantiti asid yang digunakan semasa sintesis. Sifat fizikokimia didapati dapat dikawal dengan mengubah penggunaan asid dan penggunaan titanium. Titanium terpengkil dalam keadaan rangka tetrahedral, partikel titania dalam penaburan sempurna and hablur titania (anatase) didapati terbentuk *in-situ* dalam proses sintesis aerogel. Tindakbalas pemangkinan bagi sikloheksena dengan hidrogen peroksida telah dijalankan dalam reaktor pukal. Pengaruh daripada sifat fizikokimia mangkin, pelarut, suhu tindakbalas, kuantiti pengoksida dan alkena terhadap keaktifan mangkin telah dikaji. Kedua-dua proses pengoksidaan alilik and bukan-alilik didapati telah berlangsung dalam tindakbalas. 1,2-sikloheksanadiol didapati terbentuk sebagai hasil utama dalam tindakbalas.

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LIST OF ABBREVIATIONS

λ	Wavelength
2θ	Bragg angle
BET	Brunauer, Emmet, Teller
Cu K_α	X-ray diffraction from copper K energy level
EDX	Energy dispersive X-ray analysis
etc	Etcetera
FTIR	Fourier Transform Infrared
GC-FID	Gas Chromatography – Flame Ionisation Detector
iep	Isoelectric point
IUPAC	International Union of Pure and Applied Chemistry
KBr	Potassium bromide
MCM	Mobil Crystalline Material
MS	Mass Spectroscopy
m/z	Mass-to-charge ratio
NMR	Nuclear Magnetic resonance
ppm	Part per million
RHA	Rice husk ash
Si:Ti	Silicon to titanium molar ratio of starting material
TMOS	Tetramethylortosilicate
TOF	Turnover frequency
UV-Vis DRS	Ultra Violet-Visible diffuse reflectance spectroscopy
XRD	X-ray diffraction

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Aerogel is a gel in which the liquid phase has been replaced by air without damaging the solid phase. Aerogel is a novel space-age super material. It is inert, non-toxic, and environmental friendly new material. It has been used as a catcher's mitt in spacecraft to capture dust from a comet [1].

Silica aerogel is a very interesting material. It is extremely light (specific gravity as low as 0.025 g/cm^3), with the lowest thermal conductivity known to solid material, high surface area and high porosity. This makes it suitable for many applications. It has been applied as heat storage systems, catalysts and catalyst supports. Silica aerogel is dielectric with air filled pores (can be as small as 10 nanometers in diameter) offers a better way to keep the interconnecting wires from shorting across the narrow dividing space between transistors [2].

Many physical and chemical properties of a metal oxide can be modified by interaction with a second oxide. Silica–alumina, for example, has stronger acidity than both silica and alumina [3]. A screening study of silica-supported catalysts was conducted by Hisao Yoshida et al. and they found that silica supported Ti system was the most effective catalyst for epoxidation of propene [4]. It strongly suggests that silica-titania mixed oxide might be the best combination to become the best catalyst for the oxidation reaction compared to other oxides.

1.2 Research Background and Problem Statement

Titania (TiO_2) is a technologically important material as catalyst and as support. With its special properties, TiO_2 attracts more attention recently, especially for hydrodesulphurisation (HDS) or hydrodenitrogenation (HDN) in the petroleum refining process [5, 6, 7]. The character of the catalyst with TiO_2 carrier is superior to that with $\gamma\text{-Al}_2\text{O}_3$ carrier. However, TiO_2 is seldom used as a catalyst carrier in commercial process due to two disadvantages. TiO_2 has a small specific surface area (usually $10 \text{ m}^2/\text{g}$) and the mechanical strength is five times less than $\gamma\text{-Al}_2\text{O}_3$. In addition, TiO_2 in high surface area form has low mechanical strength, limited extrudability and low thermal stability. Therefore, effort has been devoted in recent years to coat titania onto high surface area supports such as silica and alumina to improve the thermal stability and the surface area of TiO_2 [8].

Despite the disadvantages, titania has the ability to modify catalytic properties of the metal, thus attracts the studies of the interaction between titania-metal interfaces [9]. Since, it is very difficult to obtain high surface area titania ($>100 \text{ m}^2/\text{g}$); its use has been limited.

It is now established that nanoscale engineering of sol-gel $\text{TiO}_2\text{-SiO}_2$ mixed oxides provides excellent epoxidation catalysts. The area of titanasilicate-catalyzed epoxidation of olefins with hydrogen peroxides is largely because of the discovery of TS-1 where Ti has been substituted for Si in the MFI framework by Shell in 1971 [10]. This molecular sieve was reported to be active in the following oxidation reactions [11]: (i) oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones, (ii) hydroxylation of aromatics to phenol derivatives, (iii) epoxidation of alkenes to epoxides, (iv) oxyfunctionalization of alkanes to alcohol and ketones, (v) ammoximation of carbonyl compounds aldoximes or ketoximes, (vi) oxidation of thioethers to sulfoxides and sulfones, and (vii) oxidation of primary and secondary amines to oximes or azoxy compounds and hydroxylamines. TS-1 is the most prominent representative of epoxidation catalyst [12]. However, the use of TS-1 is limited by inherently small pore size and only relatively few substrates can be oxidized. Moreover, an obstacle in the commercialisation of TS-1 is that it is not possible to be moulded.

The search for large pore analogues of TS-1 has led to the study of Ti substituted into the framework or grafted onto the channels of zeolite beta or MCM type silicalites. A series of new preparation methods of materials containing highly dispersed titanium centres in a silica matrix were developed [13, 14, 15].

Smaller particles of metal oxide can be obtained when two oxide gel are mixed at the same time. However, phase separation may occur due to different rates of hydrolysis (sol-gel process) of silicon and titanium alkoxide, which results in formation of larger TiO_2 particles and prevents the homolytic substitution of titanium in silica framework. Thus, Ti-MCM, Ti-aerogel or Ti-zeolite in several researches are fail to be engineered the Ti-O-Si bonding as in TS-1 [3, 13, 15]. However, high catalytic activity has been achieved by the use of organic based peroxide as oxidant if the TiO_2 particle was small enough. Thus, most studies avoid the use of hydrogen peroxide in their catalytic oxidation. In addition, Dusi [16] has synthesized 20% TiO_2 –80 wt% SiO_2 aerogel from alkoxide sources and found that highly dispersed titania in the silica matrix was obtained, showed outstanding performance in the epoxidation of cyclic olefins with alkylhydroperoxides but inactive with hydrogen peroxide. This was due to the formation of TiO_2 particles inside the silica matrixes.

Therefore, it is a challenge to synthesize titania-silica aerogel to produce homogeneous or well-dispersed mixed oxide by using aqueous solution. In recent publications, there were several synthesis routes for the production of titania-silica mixed oxide but alkoxide precursors are used. As the alkoxide is commonly more expensive starting material, it will directly increase the cost of the final material and limit its commercial value. Recently, Chan [17] have successfully synthesized silica aerogel using organic waste precursor. Their innovation has resulted in a more economical production of silica aerogel. Therefore it is feasible to find a better path to synthesize well-dispersed titania-silica mixed oxide prepared from an organic waste.

In addition, crystalline titanium oxide has great potentials in other various applications, such as in photocatalysis [18], making the study of the titania-silica aerogel more desirable.

Titania oxide is of interest as catalyst or support. A disadvantage of titania as support is its low surface area. Therefore, inert oxide like silica aerogel is selected as a support in order to obtain higher surface area dispersed titania.

1.3 Research Objectives and Scope

The objectives of this research are:

- 1) To synthesize titanium containing silica aerogel.
- 2) To investigate and characterize the physical and chemical properties of titanium containing aerogel.
- 3) To identify the catalytic properties of the titanium containing silica aerogel in the oxidation of cyclohexene by using hydrogen peroxide as oxidant.
- 4) To identify the influence of reaction conditions in the oxidation of cyclohexene by titanium containing silica aerogel.

1.4 Hypothesis

To overcome these problems, inert oxides like silica have been used as support to obtain high surface area dispersed titania. In this research work, direct synthesis, precipitation and grafting of titania were implemented on the silica aerogel as support. This approach not only increases the surface area of the titanium oxide but also strengthens the silica aerogel.

Deposition or anchoring of Ti sites on silica circumvents the steric problem by avoiding narrow channels. Sol-gel process provides an attractive route to the preparation of multi-component oxide materials that show homogeneity in the distribution of heterometal oxide bonds [19]. Catalysts prepared by sol-gel contain accessible immobilized Ti within the silica framework. Since high specific surface area is obtained and the resulting porous structure is very open, larger substrates can

access the active sites. Better accessibility may be obtained by having the active component on the surface.

5.2 Suggestions

Some suggestions for future work:

1. Incorporation of third oxide to the titania silica aerogel either during the sol-gel synthesis or via post synthesis. The properties of the physical and chemical properties of the ternary oxide system formed may be varied.
2. Application of titania silica aerogel in photocatalytic reaction. The advantage of in-situ formation of the crystalline anatase during aerogel synthesis, in addition to immobilization of anatase in the silica matrix may overcome the anatase powder lost during the application.

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