UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERISATION OF BISMUTH OXIDE POWDERS

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By

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Especially Dedicated To

My Dearest Mama & Abah	*Noorsiah Morat* *Mhamat Nasudin Ismail*
My Dear Sisters & Brother	*Noordianiwati Nasriah* *Noorhidayati Nasriah* *Noorhafiza Nasriah* *Mohd Ismadi Nasri*
My Dear Brother-in-law	*Khairul Anwar Ismail*
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Without whose love and continued support, this thesis would not have been possible.

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Chairman: Associate Professor Irmawati Ramli, PhD
Faculty : Science

Bismuth oxide has found application in various areas including medicine, material synthesis, organic synthesis and catalysis. In catalysis, this single oxide found important role in providing oxygen for the α-hydrogen abstraction of propene to produce acrolein and acrylonitrile via oxidation and ammoxidation process. This study investigates the influence of multitude of synthesis parameters (precipitating agent, concentration and aging process) on the formation of bismuth oxide powders. The samples microstructural properties were determined using a variety of techniques such as X-Ray Diffraction (XRD), BET Surface Area Measurement, Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) Spectroscopy. Extend of reduction of the oxide was also investigated by employing Temperature Programmed Reduction (TPR) technique. Finally, a Temperature Programmed Reaction (TPRn) was conducted on selected samples to determine the surface intermediates.

On the influence of precipitating agent, α-Bi_2O_3 that were produced via NaOH as a precipitating agent and calcined in air were discerned to exhibit higher surface areas and higher intrinsic activity as compared to β-Bi_2O_3 which is produced by using NH_4OH as a precipitating agent. However, increment in NaOH concentration has induced the formation of low surface area material.

Investigation on the influence of bismuth concentration on the formation of final products gave high surface area powders with high oxide reducibility when using low concentration of bismuth. The sample high surface area property with its corresponding small particle size has been evidenced to be an induction factor to enhance the oxygen reducibility of the samples. Study on the effect of aging process showed that the parameters controlled the powders particle size.

Temperature programmed reaction studies of propane oxidation showed that α-Bi_2O_3 gave the higher percentage of selectivity to propene and acrolein when compared to β-Bi_2O_3. The reaction was found to be in step-wise mechanism through the formation of propene intermediate. On the other hand, β-Bi_2O_3 revealed a direct propane conversion into acrolein without having to go through propene route.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SINTESIS DAN PENCIRIAN SERBUK BISMUT OKSIDA

Oleh

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Bismut oksida mempunyai aplikasi dalam pelbagai bidang termasuk perubatan, sintesis bahan, sintesis organik dan pemangkinan. Di dalam pemangkinan, oksida tunggal ini di dapati mempunyai peranan penting di dalam menyediakan oksigen untuk penyingkiran hidrogen α propena bagi menghasilkan akrolin atau akrilonitril. Pembelajaran ini mengkaji kesan daripada pelbagai parameter melalui proses sintesis (agen pemendakan, kepekatan dan proses penglewatan) ke atas pembentukan serbuk bismut oksida. Ciri-ciri struktur mikro sampel-sampel telah ditentukan menggunakan pelbagai teknik seperti Pembelauan X-Ray (XRD), Pengukuran Luas Permukaan dengan kaedah BET, Mikroskopi Pengimbas Elektron (SEM) dan Spektroskopi Inframerah (FTIR). Pemanjangan penurunan oksida telah dikaji dengan menggunakan teknik Penurunan Berprogram Suhu (TPR). Akhirnya, Tindakbalas Berprogram Suhu (TPRn) telah dijalankan ke atas sampel-sampel terpilih untuk menentukan perantara permukaan.

Berdasarkan kesan oleh agen pemendakan, α-Bi_2O_3 yang terhasil melalui NaOH sebagai agen pemendakan dan dikalsin dalam udara jelas menunjukkan luas permukaan dan aktiviti intrinsik yang lebih tinggi berbanding β-Bi_2O_3 yang terhasil dengan menggunakan NH_4OH sebagai agen pemendakan. Walau bagaimanapun, peningkatan dalam kepekatan NaOH telah menggalakkan pembentukan bahan berluas permukaan yang rendah.

Kajian ke atas kesan kepekatan bismut ke atas pembentukan produk-produk terakhir memberikan serbuk berluas permukaan tinggi dan pembebasan oksigen yang tinggi apabila menggunakan kepekatan bismut yang rendah. Ciri-ciri sampel berluas permukaan tinggi dan saiz partikel kecil telah dibuktikan menjadi satu faktor dorongan untuk meningkatkan pembebasan oksigen sesuatu sampel. Kajian ke atas kesan proses penglewatan menunjukkan bahawa parameter ini mengawal saiz partikel serbuk.

Kajian Tindakbalas Berprogram Suhu bagi pengoksidaan propana menunjukkan bahawa α-Bi_2O_3 memberikan peratus lebih tinggi bagi pemilihan kepada propena dan akrolin jika dibandingkan dengan β-Bi_2O_3. Tindakbalas di dapati merupakan mekanisma langkah tersusun melalui pembentukan perantara propena. Sebaliknya, β-Bi_2O_3 menunjukkan penukaran propana secara menerus kepada akrolin tanpa perlu melalui laluan propena.

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmer-Teller
Bi	Bismuth
Bi_2O_3	Bismuth Trioxide
CO	Carbon Monoxide
Dy_2O_3	Dysprosium Trioxide
fcc	Face Centered Cubic
FWHM	Full-Width at Half Maximum
HPC	Heteropoly Acids and Salts
JCPDS	Joint Committee on Powder Diffraction Standards
MoO_3	Molybdenum Trioxide
NO	Nitrogen Monoxide
O	Oxygen
SEM	Scanning Electron Microscopy
SOHIO	Standard Oil Company of Ohio
T max	Temperature at peak maximum
TCD	Thermal Conductivity Detector
TPR	Temperature Programmed Reduction
VPO	Vanadium Phosphorus Oxide
WO_3	Tungsten Trioxide
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 General Introduction to Catalysis and Catalyst

Catalysis is an extremely important phenomenon for our modern industrial economy. Generally, catalysis is a process whereby a reaction occurs faster than the uncatalysed reaction, with the presence of a catalyst (Bowker, 1998) [1]. The term "catalysis" was coined by Berzelius in 1835 in his renowned appraisal of the researches by Edmund Davy (1820), J.W. Döbereiner (1822) and others (Thomas and Thomas, 1967) [2]. The word catalysis comes from two Greek words, the prefix *cata-*, meaning down and the verb *lysein*, meaning to split or break.

Later, in 1895, William Ostwald was the first to write down a definition of a catalyst: 'a catalyst is a substance that changes the rate of a chemical reaction without itself appearing in the products'. A catalyst enters into the reaction process, accelerating the rate of a reaction, without going through any permanent chemical change itself (Burton, 1996) [3]. A catalyst does not appear in the stoichiometric equation for an overall reaction, but it is nevertheless directly involved in the conversion and appears both in individual mechanistic steps, and in the kinetic rate law (Bowker, 1998) [1]. The catalyst remains, in general, unaltered at the end of the catalytic process.

`1.2 The Catalytic Cycle

From a molecular point of view, the catalyst provides a surface for the reactant molecules to position themselves with one another so that when they do collide they will do so much more effectively. Figure 1.1 shows the crucial part of a supported metal catalyst, where all the chemical action takes place on the surface.

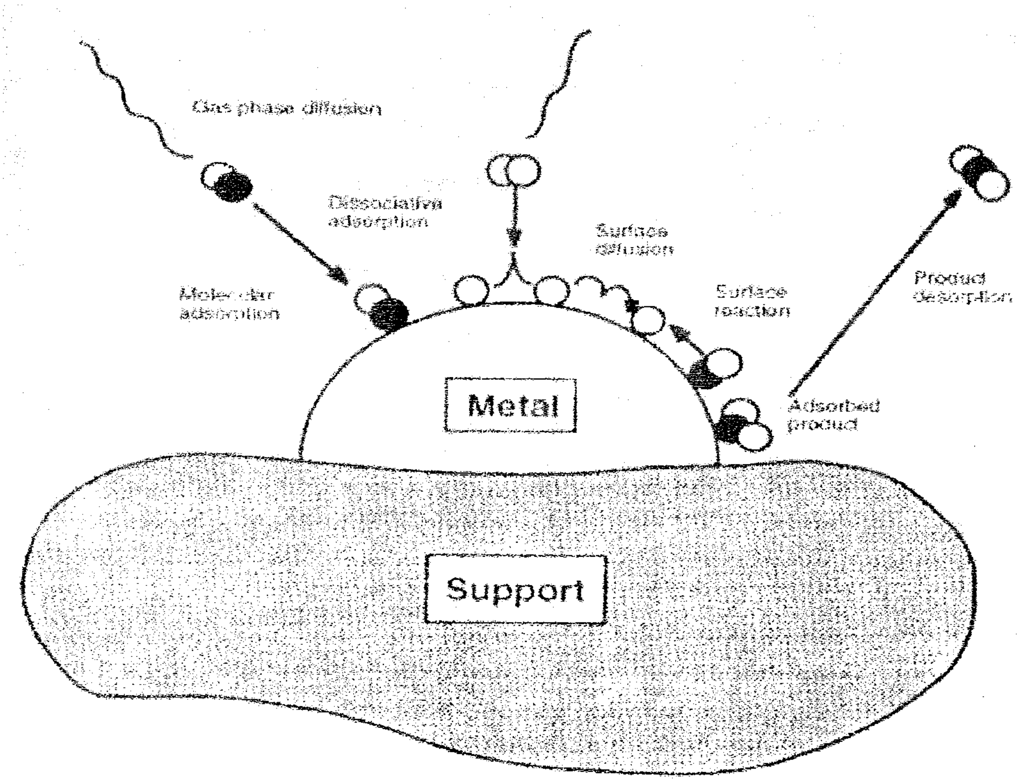

Figure 1.1 Molecular and atomic events during a catalytic reaction [1]

The first step is diffusion of the molecules through the gas phase to the metal surface where the molecules may bond (adsorption) in a molecular form. Surface diffusion may then occur and the molecule may dissociate into atoms. The next step is a surface reaction whereby the adsorbed product was formed. The surface reaction step is often the rate-determining step in a catalytic reaction. Finally, product desorption occurs, where the adsorbed product enters the gas phase and diffuses down the catalyst pores to emerge finally at the end of the reactor.

Catalysts provide a different pathway for the reaction, which has lower activation energy than before (Logan, 1997) [4]. Figure 1.2 shows the energy diagram in the presence of a catalyst. Because the energy barrier is now lower, the reaction proceeds with greater speed. Catalysts generally reduce the energy of activation so that product might be formed at a lower temperature.

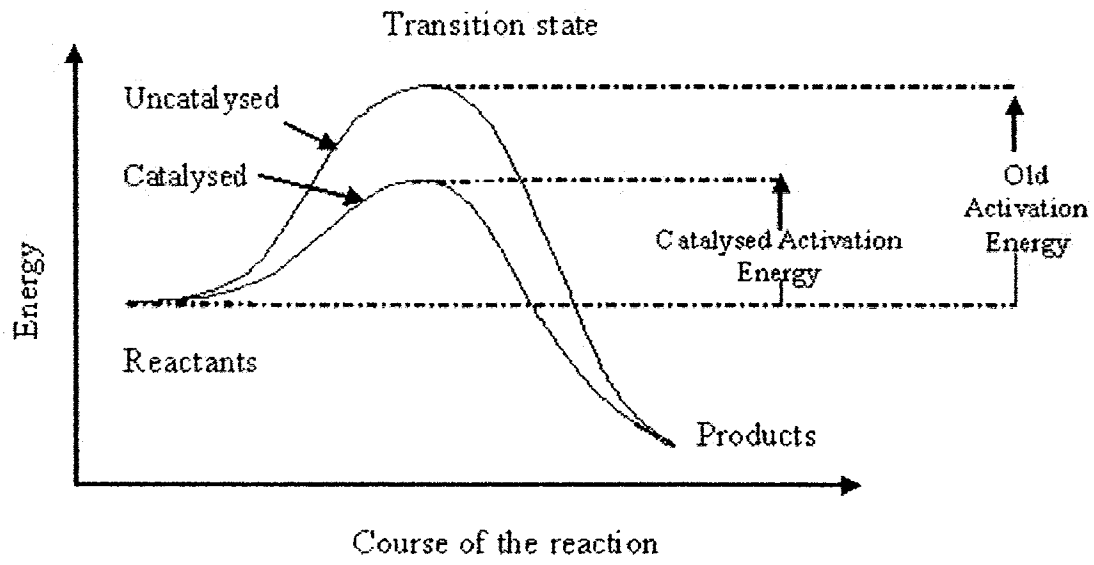

Figure 1.2 Energy diagram in the presence of a catalyst [1]

1.3 Classification of Catalytic System

Catalytic system can be divided into two categories: homogeneous catalysis and heterogeneous catalysis. According to Cavani and Trifirò (1997) [5], homogeneous catalysis occurred when the reactants, the products and the catalysts are in the same phase, usually the liquid phase. "Homo" means "same" and "geneous" is derived from a Greek word meaning "descent", so homogeneous means of the "same kind". Examples of homogeneous catalysts are soluble acids, bases, salts and organometallic compounds. The advantages of homogeneous catalysis are the utilization of almost all the molecules of the catalyst in the catalytic act, the higher selectivity obtained in some reactions, especially in the synthesis of optically-active compounds, the easier control of the temperature for highly exothermic reactions and the higher selectivity achieved due to the fact that it is possible to operate at milder conditions (for instance, in oxidation reactions).

The second category of catalytic system is heterogeneous catalyst. Heterogeneous catalyst is widely utilised in the industrial processes. More than 90% of the chemical manufacturing processes in use throughout the world utilise this type of catalysts. These processes include petroleum refining, petrochemical, inorganic chemical processes, etc. Table 1.1 lists some examples of the industrial processes and types of catalysts employed.

Table 1.1 Industrial processes and type of catalyst applied

Industry		**Catalyst**
Petroleum Refining Process	Catalytic reforming/ naphta	Pt/Al_2O_3
	Hydrodesulphurization/ petroleum fraction	$Co\text{-}Mo/Al_2O_3$
	Catalytic cracking large petroleum molecules	Zeolite/silica-alumina
Petrochemical Process	Ethylene, O_2	Supported Ag
	$H_2C{=}CH_2$, HCl	Supported $CuCl_2$
	Benzene, O_2	$V_2O_5\text{-}MoO\text{-}H_3PO_4$
Inorganic Chemical Process	N_2, H_2	$Fe/Al_2O_3/K_2O/CaO$
	SO_2, O_2	V_2O_5
	NH_3, O_2	Pt/Rh
	CO, H_2	$ZnO\text{-}Cr_2O_3$
Pollution-controlled Industries	Reduction of NO*x* with ammonia from stationary emissions	DeNO*x*
	Oxidation of Volatile Organic Compounds	Supported copper oxide
	Catalytic combustion of methane	Aluminate supported oxide
Food Industry	Hydrogenation of vegetable oil	Ni/silica

The term 'heterogen' means that the catalyst and reactant are present in different phases. Sometimes, it was called surface catalysts because they position the reactant molecules on their very surface (Burton, 1996) [3]. An example of this would be using nickel (solid) to catalyze the hydrogenation of vegetable oils to make margarine. The heterogeneous catalysts are either inorganic solids, such as metal oxides, sulfides or chlorides, or organic solids, such as modified polymers (Cavani *et al.*, 1997) [5]. In heterogeneous catalysis, products and catalyst can be separated easily (Kawai *et al.*, 1998) [6] because the catalyst and reactant are present in different phases. It is also able to withstand high temperatures. This is why heterogeneous catalytic reaction systems are suitable for large scale processes for high temperature chemicals and refining industries.

1.4 The Importance of Catalyst

Catalysts are used in all sectors of the chemical industry (Cavani *et al.*, 1997) [5]. For examples in basic chemistry for the synthesis of nitric acid, sulphuric acid, ammonia, methanol and aromatics, in petrochemistry for the synthesis of intermediate chemicals and polymers, in refining essentially in reactions of fluid catalytic cracking and hydrotreatments, in technologies for the abatement of pollutants for removal of NO, CO and hydrocarbons in emissions of stationary and mobile combustors, in the production of fine chemicals for the synthesis of intermediates and active compounds. According to Bowker (1998) [1], our present economy is highly geared to the use of catalysis. The fuel for cars was produced by cracking and reforming oil into petrol and diesel using a variety of catalysts. The ethylene and propylene from the cracking of naphtha is used in large-scale polymer production.