SYNTHESIS AND CHARACTERISATION OF BISMUTH OXIDE POWDERS

By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of Requirements for the Degree of Master of Science

JUNE 2005
Especially Dedicated To

My Dearest Mama & Abah

Noorsiah Morat
Mhamat Nasudin Ismail

My Dear Sisters & Brother

Noordianiwati Nasriah
Noorhidayati Nasriah
Noorhafliza Nasriah
Mohd Ismadi Nasri

My Dear Brother-in-law

Khairul Anwar Ismail

My Beloved Nephew & Niece

Nurina Maisara
Muhammad Nazril Hadani

Without whose love and continued support, this thesis would not have been possible.
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 $\alpha$-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, $\alpha$-$\text{Bi}_2\text{O}_3$ 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 $\beta$-$\text{Bi}_2\text{O}_3$ which is produced by using $\text{NH}_4\text{OH}$ 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 $\alpha$-$\text{Bi}_2\text{O}_3$ gave the higher percentage of selectivity to propene and acrolein when compared to $\beta$-$\text{Bi}_2\text{O}_3$. The reaction was found to be in step-wise mechanism through the formation of propene intermediate. On the other hand, $\beta$-$\text{Bi}_2\text{O}_3$ 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

**NOORFARIZAN NASRIAH BINTI MHAMAT NASUDIN**

*June 2005*

Pengerusi: Professor Madya Irmawati Ramli, PhD

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Berdasarkan kesan oleh agen pemendakan, \( \alpha\)-Bi\(_2\)O\(_3\) yang terhasil melalui NaOH sebagai agen pemendakan dan dikalsin dalam udara jelas menunjukkan luas permukaan dan aktiviti intrinsik yang lebih tinggi berbanding \( \beta\)-Bi\(_2\)O\(_3\) yang terhasil dengan menggunakan NH\(_4\)OH sebagai agen pemendakan. Walau bagaimanapun, peningkatan dalam kepekatan NaOH telah menggalakkan pembentukan bahan berluas permukaan yang rendah.


Kajian Tindakbalas Berprogram Suhu bagi pengoksidaan propana menunjukkan bahawa \( \alpha\)-Bi\(_2\)O\(_3\) memberikan peratus lebih tinggi bagi pemilihan kepada propena dan akrolin jika dibandingkan dengan \( \beta\)-Bi\(_2\)O\(_3\). Tindakbalas di dapati merupakan mekanisma langkah tersusun melalui pembentukan perantara propena. Sebaliknya, \( \beta\)-Bi\(_2\)O\(_3\) menunjukkan penukaran penukaran propana secara menerus kepada akrolin tanpa perlu melalui laluan propena.
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I certify that an Examination Committee met on 17th June 2005 to conduct the final examination of Norfarizan Nasirah Mhamat Nasudin on her Master of Science thesis entitled “Synthesis and Characterisation of Bismuth Oxide Powders” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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Date: 08 SEP 2005
DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

NOORFARIZAN NASRIAH MHAMAT NASUDIN

Date: 16/6/2015
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6.12 H₂-TPR spectra of (a) 1BH0J, (b) 1BH3J, (c) 1BH24J, (d) 1BH96J and (e) 1BH168J samples

7.1 TPRn profile of α-Bi₂O₃
7.2 TPRn profile of β-Bi₂O₃
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>BET</td>
<td>Brunauer-Emmer-Teller</td>
</tr>
<tr>
<td>Bi</td>
<td>Bismuth</td>
</tr>
<tr>
<td>Bi$_2$O$_3$</td>
<td>Bismuth Trioxide</td>
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<tr>
<td>CO</td>
<td>Carbon Monoxide</td>
</tr>
<tr>
<td>Dy$_2$O$_3$</td>
<td>Dysprosium Trioxide</td>
</tr>
<tr>
<td>fcc</td>
<td>Face Centered Cubic</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full-Width at Half Maximum</td>
</tr>
<tr>
<td>HPC</td>
<td>Heteropoly Acids and Salts</td>
</tr>
<tr>
<td>JCPDS</td>
<td>Joint Committee on Powder Diffraction Standards</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>Molybdenum Trioxide</td>
</tr>
<tr>
<td>NO</td>
<td>Nitrogen Monoxide</td>
</tr>
<tr>
<td>O</td>
<td>Oxygen</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SOHIO</td>
<td>Standard Oil Company of Ohio</td>
</tr>
<tr>
<td>T$_{\text{max}}$</td>
<td>Temperature at peak maximum</td>
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<tr>
<td>TCD</td>
<td>Thermal Conductivity Detector</td>
</tr>
<tr>
<td>TPR</td>
<td>Temperature Programmed Reduction</td>
</tr>
<tr>
<td>VPO</td>
<td>Vanadium Phosphorus Oxide</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>Tungsten Trioxide</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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</table>
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.

![Energy diagram in the presence of a catalyst](image1.png)

**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

<table>
<thead>
<tr>
<th>Industry</th>
<th>Catalyst</th>
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<tbody>
<tr>
<td>Petroleum Refining Process</td>
<td>Catalytic reforming/ naphta</td>
</tr>
<tr>
<td></td>
<td>Hydrodesulphurization/ petroleum fraction</td>
</tr>
<tr>
<td></td>
<td>Catalytic cracking large petroleum molecules</td>
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<tr>
<td>Petrochemical Process</td>
<td>Ethylene, O₂</td>
</tr>
<tr>
<td></td>
<td>H₂C=CH₂, HCl</td>
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<tr>
<td></td>
<td>Benzene, O₂</td>
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<tr>
<td>Inorganic Chemical Process</td>
<td>N₂, H₂</td>
</tr>
<tr>
<td></td>
<td>SO₂, O₂</td>
</tr>
<tr>
<td></td>
<td>NH₃, O₂</td>
</tr>
<tr>
<td></td>
<td>CO, H₂</td>
</tr>
<tr>
<td>Pollution-controlled Industries</td>
<td>Reduction of NOx with ammonia from stationary emissions</td>
</tr>
<tr>
<td></td>
<td>Oxidation of Volatile Organic Compounds</td>
</tr>
<tr>
<td></td>
<td>Catalytic combustion of methane</td>
</tr>
<tr>
<td>Food Industry</td>
<td>Hydrogenation of vegetable oil</td>
</tr>
</tbody>
</table>

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.