MODIFIED MANGANESE OXIDE OCTAHEDRAL MOLECULAR SIEVES FOR OXIDATION AND CONSECUTIVE OXIDATION-ACID REACTIONS

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To my husband, Dr. Hendriyawan
To my mother, Raidas
To my father, Darmalis
To my sons: Faizan Munawwar Alfindri and Muhammad Husein Murtaza
For my Brothers: Yon Elfi, Joni Indra, Yalmasri and Khairul Arif

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ABSTRACT

The research was focused on improvement of the catalytic activity of octahedral manganese oxide molecular sieve (OMS-2) in oxidation and consecutive oxidation-acid reactions. For oxidation reaction, OMS-2 was modified through incorporation of metals and ion-exchange. Sulphation was applied in order to create the acid sites on Ti-OMS-2 sample which was proven to have the highest oxidative properties and tested for consecutive oxidation-acidic reaction. Ti, Fe, Co and Cu were incorporated into the OMS-2 framework by isomorphous substitution to form Ti-OMS-2, Fe-OMS-2, Co-OMS-2 and Cu-OMS-2, respectively. A new method to synthesize Ti-OMS-2 with high Ti/Mn ratio was applied. Titanium incorporated OMS-2 was successfully synthesized without addition of manganese (II) solution which was normally necessary to synthesize metal substituted OMS-2. Ion-exchange was carried out in order to replace K^+ ion in the tunnel structure of OMS-2 framework by H^+ ions using concentrated HNO_3. Sulphation was done by impregnation of certain amount of H_2SO_4 in different solvent. The characterization results show that Ti-OMS-2 exhibited a significantly higher Lewis acidity compared to the un-incorporated one. The physicochemical properties-catalytic activity of the modified OMS-2 catalyst was studied in the oxidation of cyclohexane, cylohexene and styrene, and also in consecutive transformation of 1-octene to 1,2-octanediol. Oxidation of cyclohexane with TBHP as oxidant on transition metal substituted OMS-2 showed that Ti-OMS-2 with high titanium content gave the highest conversion, which may be due to the presence Ti sites in the framework and non-framework. For metal incorporated in the framework, there is a correlation of ionic radii of metal substituted with conversion of cyclohexane. An increase in ionic radii of metal substituted OMS-2 increased the conversion of cyclohexane. This correlation may be due to the increase in the Lewis acidity in the metal incorporated OMS-2. The study on the catalytic activity of H-exchanged catalysts in oxidation of cyclohexane showed an increase in conversion of cyclohexane after ion-exchange. For further investigation, Ti-OMS-2 with high Ti/Mn ratio was used in oxidation of cyclohexene and styrene using TBHP as oxidant. The results showed that both titanium sites in framework and non-framework increased the activity of OMS-2 in the oxidation of cyclohexene. However, it was observed that only non-framework titanium species induced a synergetic effect that enhanced the oxidation of styrene. There is a correlation between Ti site location in Ti-OMS-2 catalyst with activation of C-H and C=C bonds. Ti sites in the framework only played role in C-H bond activation whereas Ti site non-framework enhanced the catalytic activity for both types of bond activation. SO_4^{2-}/Ti-OMS-2 was proven to be active for consecutive transformation of 1-octene to 1,2-octanediol. However, it was confirmed that Brönsted acid sites did not exist in the sample. The success of the consecutive reactions may be due to the generation of Brönsted acid from hydrolysis of water on the Lewis acid sites of SO_4^{2-}/Ti-OMS-2 sample.

ABSTRAK

Penyelidikan difokuskan pada peningkatan aktiviti pemangkinan daripada penapis molekul oksida mangan oktahedral (OMS-2) sebagai mangkin dalam tindak balas pengoksidaan dan juga tindak balas berturutan pengoksidaan dan keasidan. Untuk tindak balas pengoksidaan, OMS-2 diubah suai melalui pemasukan logam dan pertukaran ion. Pensulfatan telah dilakukan untuk membina tapak asid pada mangkin Ti-OMS-2 yang terbukti mempunyai aktiviti pemangkinan paling tinggi dalam tindak balas pengoksidaan dan seterusnya diuji pada tindakbalas berturutan pengoksidaan dan keasidan. Ti, Fe, Co dan Cu dimasukkan ke dalam bingkaian OMS-2 melalui penukargantian isomorfus untuk membentuk Ti-OMS-2, Fe-OMS-2, Co-OMS-2 dan Cu-OMS-2. Satu kaedah baru telah digunakan untuk mensintesis Ti-OMS-2 pada nisbah Ti:Mn yang tinggi. Titanium yang digabungkan dengan OMS-2 telah berjaya disintesis tanpa penambahan larutan mangan(II) yang biasanya diperlukan untuk mensintesis penukargantian logam pada OMS-2 seperti yang dilaporkan sebelum ini. Penukaran ion telah dilakukan untuk menggantikan ion K^+ didalam struktur terowong dengan ion H^+ menggunakan HNO_3 pekat. Pensulfatan telah dilakukan dengan pengisitepuan jumlah tertentu H_2SO_4 dalam pelarut yang berbeza. Hasil kaedah pencirian didapati bahawa penggabungan titanium kepada OMS-2 telah meningkatkan keasidan Lewis jika dibandingkan dengan OMS-2 sahaja. Pengoksidaan terhadap sikloheksana dengan TBHP sebagai agen pengoksidaan pada OMS-2 yang telah ditukarkan dengan logam peralihan memperlihatkan bahawa Ti-OMS-2 yang mempunyai kandungan titanium yang tinggi menghasilkan peratus penukaran yang paling tinggi, mungkin disebabkan oleh wujudnya tapak titanium dalam dan luar bingkaian. Untuk penggabungan logam di dalam bingkai, ada hubungkait antara jejari ion logam yang menukarganti dengan peratus penukaran sikloheksana. Peningkatan jejari ionik daripada logam yang menukarganti meningkatkan peratus penukaran sikloheksana. Hubungkait ini mungkin disebabkan oleh peningkatan tapak asid Lewis pada logam yang digabungkan dengan OMS-2. Kajian terhadap aktiviti pemangkinan ke atas mangkin tertukarganti H di dalam pengoksidaan menunjukkan peningkatan peratusan penukaran daripada sikloheksana setelah penukaran ion. Untuk kajian selanjutnya, Ti-OMS-2 dengan nisbah Ti:Mn yang lebih tinggi telah digunakan dalam pengoksidaan sikloheksena dan stirena dengan TBHP sebagai agen pengoksida. Didapati bahawa kedua-dua tapak titanium dalam dan luar bingkai meningkatkan aktiviti OMS-2 dalam pengoksidaan sikloheksena. Walau bagaimanapun, telah dibuktikan bahawa hanya spesies titanium bukan-bingkai sahaja menghasilkan kesan sinergi yang meningkatkan pengoksidaan stirena. Didapati bahawa wujud hubungkait antara lokasi tapak titanium pada mangkin Ti-OMS-2 dengan pengaktifan ikatan C-H dan C=C. Tapak titanium dalam bingkai memainkan peranan hanya untuk pengaktifan ikatan C-H sahaja sedangkan tapak titanium luar bingkai meningkatkan aktiviti pemangkinan pada kedua-dua jenis pengaktifan ikatan. Sampel SO_4^{2-}/Ti-OMS-2 aktif untuk pertukaran berterusan 1-oktena kepada 1,2 oktanadiol. Bagaimanapun, telah dipastikan bahawa tidak ada tapak asid Brönsted pada sampel SO_4^{2-}/Ti-OMS-2. Kejayaan daripada tindak balas berterusan tersebut mungkin disebabkan oleh pembentukan asid Brönsted daripada hidrolisis air yang terjadi pada tapak asid Lewis yang terdapat pada sampel SO_4^{2-}/Ti-OMS-2.

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LIST OF SYMBOLS/ABBREVIATIONS

%	-	percent
~	-	approximately
μ	-	micron (10^{-6})
2Ө	-	Bragg angle
Å	-	angstrom (10^{-10})
a.u.	-	arbitrary unit
BET	-	Brunnauer, Emmett and Teller
c.a.	-	about (Latin:*circa*)
cm^{-1}	-	per centimeter
Co^{2+}	-	Cobalt ion
Co-OMS-2	-	Cobalt substituted OMS-2
Cu Kα	-	X-ray diffraction from copper Kα energy levels
Cu^{2+}	-	Copper ion
Cu-OMS-2	-	Copper substituted OMS-2
d	-	distance
DTG	-	Differential thermogravimetry
e.g.	-	example (Latin*: exempli gratia*)
EDAX	-	Energy dispersive analysis by X-ray
		equilibrium pressure and vapour pressure Po of the adsorbate at the temperature where the isotherm is measured
et al.	-	and others (Latin: *et alia*)
eV	-	electrovolt
Fe^{3+}	-	Iron ion
Fe-OMS-2	-	Iron substituted OMS-2
FESEM	-	Field Emission Scanning Electron Microscope
FID	-	Flame ionisation detector
FTIR	-	Fourier transform infrared

g	-	grams
h	-	hour
H_2O_2	-	Hydrogen peroxide
HF	-	Hydrofluoric acid
i.e.	-	that is (Latin : *id est*)
IUPAC	-	International Union of Pure and Applied Chemistry
K	-	degree Kelvin
KBr	-	Potassium bromide
M	-	Molar
m^2g^{-1}	-	meter square per gram
mA	-	milliampere
min	-	minute
mL	-	millilitre
mol	-	mole
M-OMS-2	-	Metal substituted OMS-2
N_2	-	Molecular nitrogen
nm	-	nanometer (10^{-9})
^oC	-	degree celcius
OL-1	-	OL-1 is manganese oxide Octahedral layered with interlayer spacing of ~7 Å.
OMS-1	-	Manganese oxide octahedral molecular sieve with 3 x 3 tunnel structure.
OMS-2	-	Manganese oxide octahedral molecular sieve with 2 x 2 tunnel structure.
OMS-5	-	Manganese oxide octahedral molecular sieve with 2 x 4 tunnel structure.
OMS-6	-	Manganese oxide octahedral molecular sieve with 2 x 3 tunnel structure.
OMS-7	-	Manganese oxide octahedral molecular sieve with 1 x 1 tunnel structure.
OTS	-	Octadecyltrichlorosilane
P/Po	-	relative pressure; obtained by forming the ratio of the equilibrium pressure and vapour pressure p^o of the adsorbate at the temperature where the isotherm is measured
$SO_4^{2-}/Ti\text{-}OMS\text{-}2$	-	Sulphated Ti-OMS-2
ST150-Ti-OMS-2	-	Sulphated Ti-OMS-2 with 150 μL concentrated H_2SO_4 using toluene as solvent

ST200-Ti-OMS-2	-	Sulphated Ti-OMS-2 with 200 μL concentrated H_2SO_4 using toluene as solvent
SW150-Ti-OMS-2	-	Sulphated Ti-OMS-2 with 150 μL concentrated H_2SO_4 using water as solvent
SW200-Ti-OMS-2	-	Sulphated Ti-OMS-2 with 200 μL concentrated H_2SO_4 using toluene as solvent
t	-	crystallite size
TBHP	-	*tert*-butyl hydroperoxide
TGA	-	Thermogravimetry analysis
Ti^{3+}	-	Titanium ion
TiO_2	-	Titanium dioxide
TiO_2-OMS-2 (imp)	-	Impregnation of TiO_2 on OMS-2 surface
TiO_2-OMS-2 (mix)	-	Physical mixture of rutile TiO_2 and OMS-2
Ti-OMS-2	-	Titanium substituted OMS-2
TS-1	-	Titanium Silicate-1
wt %	-	weight percentage
λ	-	wavelength

LIST OF PUBLICATIONS AND PRESENTATIONS

1. H. Nur, F. Hayati, H. Hamdan, "On the location of different titanium sites in Ti-OMS-2 and their catalytic role in oxidation of styrene", Catalysis Communications, 8 (2007) 2007-2011.

2. F. Hayati, H. Nur, H. Hamdan, "Titanium Doped Octahedral Manganese Oxide Hybrid Catalyst in the Oxidation of Cyclohexene", Buletin Kimia, 21 (2005) 49-54.

3. F. Hayati, H. Hamdan, H. Nur, "Synergetic effect of titanium and OMS-2 as Ti-OMS-2 hybrid catalyst in oxidation of cyclohexene", Book abstract of Annual Fundamental Science Seminar 2005, 4-1 July 2005, Johor Bahru, Malaysia. p. 67.

4. F. Hayati, H. Nur and H. Hamdan, "Synthesis and characterization of octahedral molecular sieves (OMS-2)", Book of abstract of Annual Fundamental Science Seminar 2004, 14-15 June 2004, Johor Bahru, Malaysia. p. 73.

CHAPTER 1

INTRODUCTION

A catalyst is a substance which accelerates a chemical reaction. The basic principle of how a catalyst works for a chemical reaction is shown by the example in Figure 1.1. It does so by forming bonds with the reacting molecules (*i.e.* adsorption), followed by breaking and weakening of the intramolecular bonds. Next, the adsorbed species react on the surface to a particular product, often in several consecutive steps. Finally, it detaches itself from the catalyst (*i.e.* desorption) and leaves the catalyst unaltered so that it is ready to interact with the next set of molecules. A catalyst cannot alter the chemical equilibrium of a given reaction; it only creates a favourable reaction pathway. This is done by decreasing the activation barrier ($E_{a,cat}$) compared to non catalytic reaction ($E_{a,non}$) and thus increasing the reaction rate. In general, a successful catalyst increases the yield of the desired product while decreasing that of other products, which has advantages for both economic and environmental reasons [1].

The first introduction of the word 'catalysis' was by Berzelius in 1836, while Ostwald presented the first correct definition of a catalyst in 1895 [2]. He described a catalyst as a substance that changes the rate of a chemical reaction without itself appearing in the products. Today, catalysis lies at the heart of our quality of life: the reduced emissions of modern cars, the abundance of fresh food at our stores, and the new pharmaceuticals that improve our health are made possible by chemical reactions controlled by catalysts [3]. It covers multidisciplinary science that serves a broad range of chemical industries covering specialty, fine, intermediate, commodity,

and life science chemicals [4]. It played a major role in establishing the economic strength of the chemical and related industries in the first half of the 20th century and an estimated 90% of all of the chemical processes introduced since 1930 depend on catalysis [5]. According to a report from Freedonia [6] the world catalyst demand will rise by 3.6% per year to $12.3 billion in 2010.
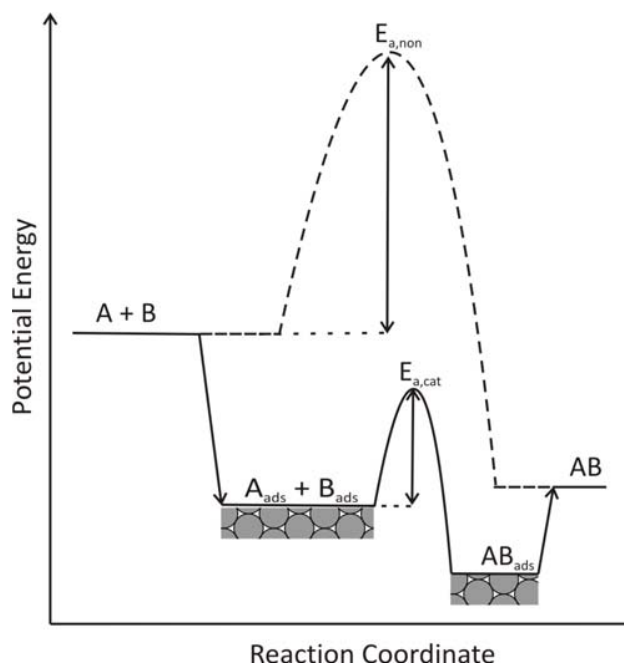
Figure 1.1: Potential energy diagram for a catalytic reaction (solid line), *i.e.* reaction of A and B to form AB, compared with the non-catalytic reaction (dashed line). The presence of a catalyst lowers the activation energy (E_a) considerably [7].

Catalysis plays an important role in the green chemical processes, which is to minimize environmental impact and to reduce costs of the process. It is crucial to achieve the "ideal synthesis" which would be atom efficient, safe, one step, involving no wasted reagents, based on renewable resources, and environmentally acceptable to overcome some of the biggest problem areas in synthetic methodology such as in oxidation and acid-catalyze reactions [8].

In catalytic process, for example catalytic oxidation, there are some options to consider, *i.e.* phase (gas or liquid) and catalytic system as shown in Figure 1.2. Firstly, the selection of either a gas or liquid phase depends largely on the boiling

point and thermal stability of the reactants, especially of a desired fine chemical intermediate. However, catalytic gas phase is limited to relatively simple molecules. More complicated molecules cannot be brought easily into the gas phase and many of these molecules are unstable at elevated temperatures. In addition, the gas phase needs special reactor and costly. Therefore, working in liquid phase is relatively easier than in gas phase, as simpler equipments are required which can be performed for more complicated molecules.
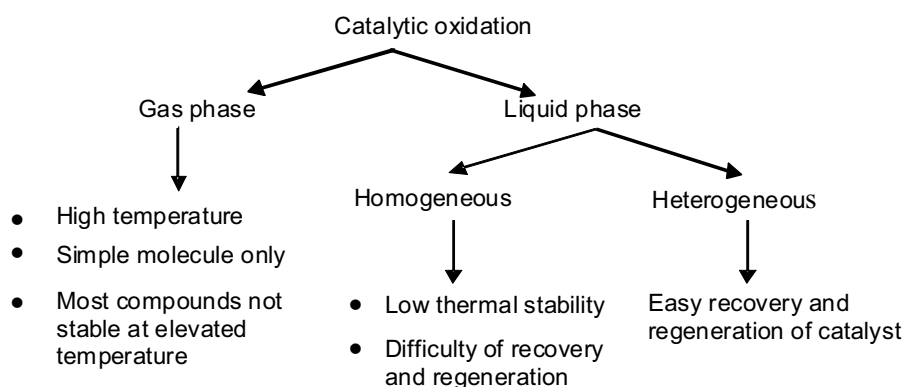
Figure 1.2: Process options in catalytic oxidation and some of their disadvantages.

As also shown in Figure 1.2, another important choice to consider is whether the oxidation should be performed using homogeneous or heterogeneous catalyst. In homogeneous catalysis, the reaction mixture and the catalysts are all in the same phase, usually the liquid phase. The catalyst may be a metal complex, which is dissolved in a solvent together with the reagents. Homogeneous catalysts are characterized by high activity and selectivity. The main advantage of homogeneous catalysts is the ease of accessibility of the active site, resulting in a high activity, no mass transfer limitations and generally low temperature and pressure requirements. The main disadvantages of this type of catalysts are low thermal stability, difficulty of recovery and regeneration. In combination with high cost of catalyst, this makes homogeneous catalysis less popular in industry. Homogeneous catalysts are mostly found in batch processes where volumes are small and the added value is high, *e.g.*, in pharmaceuticals.

The problems faced by homogeneous catalyst can be solved by using heterogeneous catalyst [1, 2, 5]. In heterogeneous catalysis, the catalyst is in a different phase than the reaction mixture. Usually, the catalyst is a solid substance (*e.g.*, a metal or a metal oxide) and the reaction mixture can be a gas or a liquid. Heterogeneous catalyst may be easily recovered by filtration and recycle. The success of this type of catalyst is due to the ease at which it can be applied in all types of reactions, carried out in both continuous and batch mode. It is relatively easy to separate the catalyst from the reaction mixture and reuse it. The solid, heterogeneous phase, however, may introduce mass transfer limitations, presumably resulting in a lower activity or selectivity. Therefore, the selection of suitable active site for heterogeneous catalyst is a challenge in academic and industry.

Many heterogeneous or solid catalysts are based on porous inorganic solids [5]. The important physical properties of these materials are surface area (often very large and measured in hundreds of m^2/g), pore volume, pore size distribution (which can be very narrow or very broad), the size and shape of the particles and their strength. The solid catalyst provides a surface, usually large internal, for the substrates to adsorb and react on. Thus the surface characteristics (roughness, functional groups, organophilicity, hydrophobicity, *etc*.) are also vital to performance.

Following the definition accepted by the International Union of Pure and Applied Chemistry (IUPAC), porous materials can be grouped into three classes based on their pore diameter (d): microporous, d < 2.0 nm; mesoporous, 2.0 < d < 50 nm; macroporous, d > 50 nm. In the class of microporous materials, zeolites and related materials such as aluminophosphates have found for a long time applications outside the traditional areas of acid and bifunctional catalysis [9-14]. With the introduction of the ordered micelle-templated inorganic materials, the choice of available supports has been considerably extended into the mesoporous domain. Examples are M41S groups materials such as MCM-41, MCM-48, MSU, HMS, FSM-16, and various SBA type materials [9, 10]. Macroporous metal oxides such as titania, zirconia and alumina are example for macroporous material. However, all of the above materials in general are insulating materials. In addition they are often

synthesized with charge compensation in mind. For example, Al^{3+} substituted for Si^{4+} in zeolites lead to an inherent cation-exchanged capacity.

Another way to approach the generation of microporous material is to generate element with mixed valencies in a structure which should also lead to cation exchange capacity [11]. Porous manganese oxides with mixed valencies could be a challenge due to wider application over aluminosilicate materials *e.g.* redox catalysis, battery and sensor [12].

1.1   Research Background

1.1.1   Porous Manganese Oxide Materials

Porous manganese oxide is one of the largest families of porous materials. These are two major structures of porous manganese oxides, tunneled and layered materials with pore size from ultra-micropores to mesopores [13]. Natural manganese oxides are found abundant as manganese nodules which exist in a wide variety of locations such as the ocean floor, the beds of many fresh-water lakes, rocks, and soil. Manganese oxide minerals have been used for thousands of years as pigments and to clarify glass, and more recently as ores of Mn metal, catalysts and battery material [14].

Porous manganese oxide materials have been described as useful catalysts in the oxidation of carbon monoxide, methane and butane, the reduction of nitric oxide with ammonia and demetallation of topped crude in the presence of hydrogen [15]. However, the structures and properties of the natural source are usually not uniform and its activity is not reproducible.

The porous manganese oxides have been extensively investigated for their economic value and their potential applications. Due to their excellent cation-exchange and molecule adsorptive properties, like the aluminosilicates, these

manganese oxides can be used as ion-sieves, molecular-sieves, and catalysts similar to the aluminosilicates. In contrast to aluminosilicate based zeolite, these manganese oxides are mixed valencies materials (mainly, 4+, 3+, or 2+). The mixed valency materials are important in biology, chemistry, and physics which occur in manganese redox enzymes, in natural manganese oxide nodules, chemiluminescence systems, electron transfer and electrocatalysis, electrochromism, secondary nonaqueous rechargeable batteries, magnetics, ceramics, and biological systems. In chemistry, mixed valency in mixed metal oxides is important for electron transport. For example, the effectiveness of metal oxides as catalysts for redox reactions, as electrode materials for electrochemical processes, and as chemical sensors for reductive gases are usually governed by their ability and tendency to cycle between different valence states of relevant cations and the mobility of oxygen ions. From this standpoint, manganese oxide materials have distinct advantages over aluminosilicate molecular sieve materials for applications in redox catalysis, batteries, and chemical sensors [12].

The synthetic manganese oxides have been intensively studied by Suib and his group since 1990's[16-18]. The synthetic names, the natural minerals and unit structures are listed in Table 1.1. In general manganese oxide materials can be classified into two kinds *i.e.* tunnel and layered structures. The term of octahedral molecular sieves (OMS) and octahedral layered (OL) materials are referred to the synthetic manganese oxides with tunnel and layered structure, respectively [19]. OMS materials comprise infinite 3-D crystalline frameworks with molecule-sized tunnels similar to the naturally occurring zeolites. The structural frameworks of the manganese oxides consists of MnO_6 octahedral units shared by corners and/or edges in comparison with, in general, SiO_4-AlO_6 frameworks of the porous aluminosilicates. OMS-1 and OMS-2 are two types of OMS materials which are built of 3x3 and 2x2 MnO_6 octahedral units, respectively. The other types are pyrolusite-, ramsdellite-, and romanechite-type manganese oxides which have one-dimensional (1×1), (1×2) and (2×3) tunnel structures, respectively. OL materials have interlayer spacings that are similar to clay-type materials. OL-1 is synthetic name of birnessite which has the interlayer spacing of ~7 Å and it contains exchangeable cations and water molecules.

Table 1.1: The synthetic manganese oxides, their natural counterpart and structures as reported by Suib [12, 20-22].

Synthetic Name	Natural counterpart	MnO_6 octahedral units
OMS-1	todorokite	3x3
OMS-2	cryptomelane	2x2
OMS-5	-	2x4
OMS-6	romanechite	2x3
OMS-7	pyrolusite	1x1
OL-1	birnessite	2x~

Among most of the OMS and OL materials, OMS-1 and OMS-2 materials have been used widely as catalysts, chemical sensors and batteries due to their mixed-valency, high porosity, thermal stability, surface areas, and inexpensive manufacturing cost. However, OMS-2 materials have been used as catalyst even more widely than OMS-1 materials since they are more active and selective in catalytic oxidation [20].

1.1.2   Manganese Oxide Octahedral Molecular Sieves (OMS-2)

As mentioned before OMS-2 materials are synthetic manganese oxide which is built of 2x2 MnO_6 octahedral and also known as synthetic cryptomelane [11]. The tunnel size of this material is 4.6 Å x 4.6 Å and potassium ion exists in the tunnel to balance the charge of the structure as shown in Figure 1.3. General composition of OMS-2 materials is $K_{0.8-1.5}Mn_8O_{16}$. These materials are not expensive and easy to prepare compared to other manganese oxide type materials.

For its application in catalytic reaction, OMS-2 materials were reported to be selective in oxidation of benzyl alcohol [23, 24]. Besides, OMS-2 materials are potential electrocatalysts for the oxidation of methanol, for fuel cell applications

[25], are also active catalyst for the total oxidation of benzene and ethanol [26] and epoxidation of olefins [27, 28]. The mild oxidants i.e. molecular oxygen and *ter*-butyl hydrogen peroxide (TBHP) used as oxidizing agents on OMS-2 materials have let to these materials being promising catalysts in fulfilling the environmental concern and regulations for clean environment.
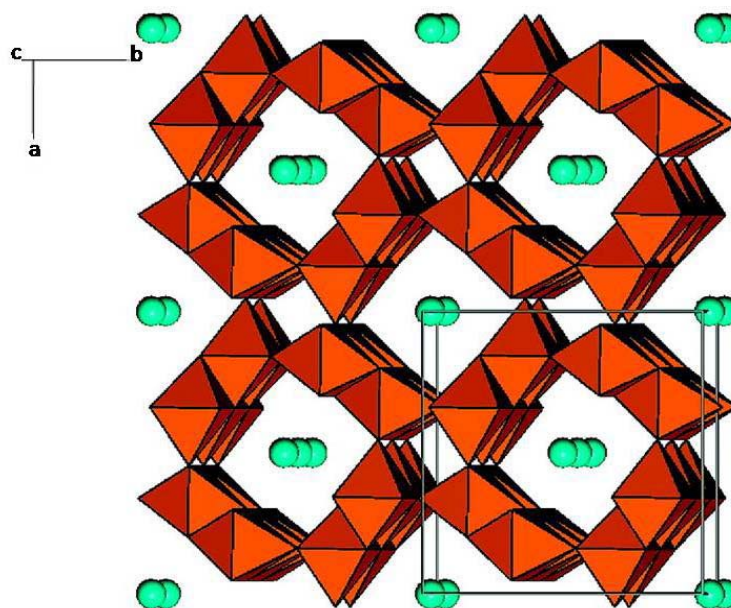
Figure 1.3: Crystal structure of cryptomelane-type OMS-2: potassium atoms are shown as green spheres; MnO_6 octahedra are shown in brown.

The high oxidation ability of OMS-2 materials has mainly been related to two factors: the presence of Mn^{2+}/Mn^{4+} or Mn^{3+}/Mn^{4+} redox couples and the ability of active participation of the lattice oxygen in these systems in oxidation process leading to a Mars van Krevelen type of oxidation mechanism [23, 24]. The mechanism involves two steps as illustrated in Figure 1.4. Firstly, the lattice oxygen oxidizes the substrate molecule, followed by a reoxidation of the partially reduced catalyst by molecular oxygen in order to regenerate the catalyst.

To date, however, the report on liquid phase oxidation *via* Mars-van Krevelen-type mechanism is limited, *i.e.*, homogeneous catalysis by phosphovanadomolybdate [29] and heterogeneous catalysis by OMS-2 catalyst [23,

24]. The high selectivity of product makes this mechanism interesting and worthwhile for intensive study.
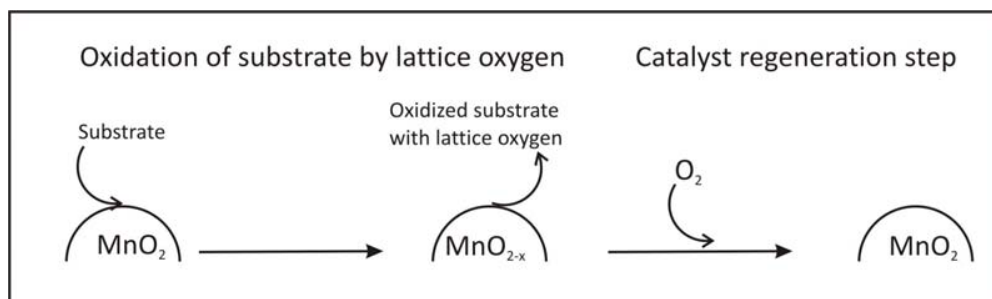
Figure 1.4: Mars van Krevelen mechanism.

1.1.3 Modification of OMS-2 Materials

In order to alter their structures and properties and generate better electronic and catalytic performance, the modification was done by doping cation into OMS-2 materials. The cations doped into OMS-2 materials are listed in Table 1.2. These cations can substitute potassium and/or manganese ions which exist in the tunnel and framework structure, respectively [30]. Doping of alkali metals or NH_4^+ or H^+ was reported to substitute some potassium ions which exist in the tunnel structure of OMS-2 materials. Transition metal oxides were incorporated in the framework and/or exist in the tunnel structure. The existence of metal oxides in the framework indicated that those metal oxides were substituted for manganese. When metals exist in a tunnel structure, it suggests that the metals have replaced potassium. The location of doped metal depends on the preparation method [31]. The transition metal cations are mostly situated in the framework positions of the OMS-2 structure with a priori incorporation. In a posteriori incorporation, the cations are situated in either the tunnel positions (if prepared by ion-exchange) or in extraframework positions (if prepared by homogeneous precipitation).

Table 1.2: The cations were doped OMS-2 and their location in OMS-2 material.

Doping cations	Location	References
H^+/NH_4^+	In tunnel structure	[23, 24, 32]
Alkali metals	In tunnel structure	[32-34]
Transition metals	In framework and/or tunnel structure	[27, 30, 31, 35-46]

The summary on incorporation of transition metals into OMS-2 materials is shown in Figure 1.5. Among these transition metals, titanium incorporated OMS-2 has not been reported and therefore is appropriate to be explored.

Figure 1.5: Partial periodic table showing transition metals that have been incorporated into OMS-2 materials.

The physical and chemical properties of doped OMS-2 are greatly influenced by the type, amount and location of the doping ions, where the properties of doped materials are significantly different from those of the undoped ones [12]. In the tunnel cations position, H^+ doped OMS-2 exhibits the surprising activity in oxidation of alcohols and acid-catalyze condensation of phenylhydroxylamine with aniline to 2-aminodiphenylamine. Among the transition metal doped OMS-2 materials, Fe-OMS-2 seems to be the best catalyst in some catalytic reactions such as oxidative dehydrogenation of 1-butene [40], oxidation of toluene [41], decomposition of the cyanine dye and pinacyanol chloride [44], and oxidative dehydrogenation of ethanol [46]. However the activity of Fe-OMS-2 is lower than Co-OMS-2 in oxidation of styrene [27]. It suggests that the activity of metal doped OMS-2 also depends on the type of substrates involved in the reactions.

Titanium oxide attracts much attention in catalysis as well as photocatalysis and it has been used in the synthesis of many chemical compounds. Titanium incorporated material shows outstanding catalytic properties, particularly in liquid phase oxidation process [47-49]. Shell catalyst (Ti(IV)/SiO$_2$) is the basis of the commercial process for the epoxidation of propene with ethylbenzene hydroperoxide. Thus, the discovery of titanium silicate-1 (TS-1) by Taramasso *et al.* [50] exhibited the remarkable catalytic activity, selective epoxidations with 30% aqueous hydrogen peroxide under very mild conditions, constituted a milestone in oxidation catalysis. The discovery of TS-1 led to the study on incorporation of titanium into porous materials: microporous material such as silicoaluminophosphate (SAPO-5) and aluminophosphates (AlPO-5, AlPO-11 and AlPO$_4$-36) and mesoporous materials such as MCM-41 and MCM-48.

The incorporation of titanium into manganese oxide molecular sieve frameworks is feasible because of similar sizes, charges, and coordination tendencies of manganese and titanium cations. Ionic radii of octahedral Mn^{3+}, Mn^{4+}, and Ti^{4+} of 0.65 Å, 0.53 Å and 0.61 Å, respectively [54-55] in crystals are close to one another, hence Ti^{4+} can easily substitute either Mn^{3+} or Mn^{4+} without causing much structural disorder and serious charge imbalance. Due to the mixed-valence character of manganese in OMS-2, this material has distinct advantages over silicate, aluminosilicate and aluminophosphate molecular sieve materials in catalytic applications [12, 30]. The incorporation of titanium into OMS-2 is expected to give excellent performance in oxidation reaction.

The previous sections have demonstrated that OMS-2 and metal doped OMS-2 materials are potential catalysts in oxidation reactions. The catalytic activity of metal doped OMS-2 varies depending on the substrate. Further study of the metal doped OMS-2 is required in order to understand the physicochemical properties-catalytic activity of the catalysts. Besides that, the effect of titanium incorporated OMS-2 has not been reported. Therefore, the study on the effect of titanium incorporated OMS-2 to the physicochemical properties and catalytic activity of OMS-2 material in oxidation reaction is needed. Further investigation in the potential application of Ti incorporated OMS-2 in consecutive oxidation and acid

reaction should be done. The next section describes how Ti incorporated OMS-2 is modified to bifunctional oxidative and acidic catalyst.

1.1.4 Design of Sulphated Ti-OMS-2 as Bifunctional Oxidative and Acidic Catalyst

A bifunctional or multifunctional catalyst is the catalyst which has two or more active sites. The catalysts have active sites which can catalyze two or more transformations which are carried out as a "one-pot" process. They offer a number of advantages to the organic chemist: in particular, they result in a reduced number of operations, giving significant time-cost benefits, but they also often allow "difficult" intermediate compounds (*i.e.*, those that are volatile, toxic, or otherwise noxious) to be prepared and elaborated in situ, thus preventing problems associated with their isolation and handling [51].

A bifunctional oxidative and acidic catalyst catalyzes for oxidation and acid-reaction, respectively. The catalyst effectively directs transformation of alkenes to alcohols. The oxidative sites catalyze the oxidation of alkenes to epoxide followed by transformation of epoxide to diols in the presence of Brönsted acid site in the catalyst. At present, 1,2-diols are manufactured industrially by a two-step sequence consisting of epoxidation of an olefin with a peracid followed by hydrolysis of the resulting epoxide as shown in Figure 1.6.
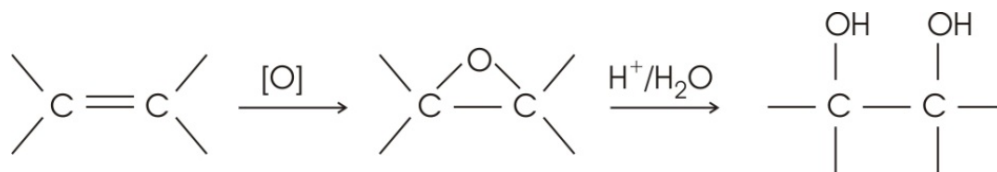
Figure 1.6: Transformation of alkenes to diols *via* two step reaction.

Recently, Prasetyoko *et al.* [52-54] reported that titanium silicalite (TS-1) loaded with sulphated zirconia or niobium oxide demonstrated bifunctional oxidative and acidic properties. However, TS-1 is expensive and difficult to prepare. The

purpose of this research is to design a novel bifunctional oxidative and acidic catalyst. Combining oxidative OMS-2 and acidity, one can come up with the bifunctional catalyst for consecutive liquid phase oxidation and acid reactions. Sulphated titanium oxide is a solid superacid which exhibits both Lewis and Brönsted acidity [55] which are considered as acid sites. The solid acid is used to overcome the problems of using homogeneous acid.

One approach is to create acidity *via* incorporation of acidic sites in the framework of OMS-2. It is expected that bifunctional oxidative and acidic catalyst can be created by sulphation of TiO_2 phase in titanium supported OMS-2 (Ti-OMS-2) to form SO_4^{2-}-TiO_2 superacid active site. Based on this consideration, a catalytic model of consecutive oxidation and acid catalyst (sulphated Ti-OMS-2) to catalyze consecutive reactions of alkenes to alcohols *e.g.* 1-octene to 1,2-octanediol could be synthesized. MnO_6 octahedra as a basic of OMS-2 unit acts as an oxidative site for epoxidation of 1-octene to 1,2 epoxyoctane and SO_4^{2-}-TiO_2 superacid acts as an acidic site for transformation of 1,2 epoxyoctane to 1,2 octanediol. Hence the use of OMS-2 materials which are relatively cheap and easily prepared and use a mild oxidant for oxidation process and sulphated TiO_2 environmentally friendly as acid sites is expected to be the best solutions to overcome the related problems.

1.2   Research Questions and Scope of Research

Based on the above descriptions, one considers that OMS-2 is the potential heterogeneous catalysts for liquid phase oxidation. Although modification of OMS-2 by doping of transition metal oxides have been reported but Ti incorporated OMS-2 has not been reported yet [30-46]. The effect of the location, amount and synthesis method of titanium incorporated OMS-2 to the catalytic properties of OMS-2 in some oxidation reactions have not been studied yet. The relationship between physicochemical properties and catalytic activity of titanium and other metals incorporated system are not well understood. In addition, design of bifunctional oxidative and acidic catalyst in order to form the more effective and efficient catalyst

for consecutive oxidation and acid reactions is a challenge that has less studied. Modification of OMS-2 by enhancement of the oxidative ability and creation of the acid site may together be beneficial and advantageous to create the bifunctional catalyst for synthesis of diols from alkenes.

Figure 1.7 shows the research approach and questions of the research. The research includes the study on effect of synthesis method and some modifications to physicochemical properties of OMS-2 and their correlation to catalytic activity of the catalysts. Generally, there were two categories of modifications of OMS-2; firstly, metals substituted and H-exchanged, aimed to improve the catalytic oxidation of OMS-2 catalyst. The catalysts were characterized by several characterization methods to find out their physicochemical properties. Thus, those were correlated to the catalytic activity of the catalysts in oxidation of cyclohexane. However, this study emphasized on titanium incorporated OMS-2. The effect of synthesis method, amount and location of the titanium substituted to the physicochemical properties of OMS-2 were evaluated. Characterizations were done by several methods such as structural and acidity analysis, surface area, hydrophobicity-hydrophylicity, *etc.* Thus, their physicochemical properties were correlated to catalytic activity of the catalyst in several oxidation reactions such as cyclohexane, cyclohexene and styrene. The second modification was sulphation of titanium supported OMS-2 aimed to create acid sites on the oxidative catalyst. The catalysts were characterized and tested in consecutive oxidation and acid reactions for direct synthesis of diols from alkene. Briefly, the research attempted to answer some questions as depicted in Figure 1.7.

1.3 Research Objectives

The research proposed is a fundamental study of heterogeneous catalytic system for both oxidation process and consecutive reaction of alkenes to alcohols under mild conditions. Since it is a one step, inexpensive and easy preparation of the

Synthesis

- OMS-2 synthesized in different methods
- Synthesis of metals substituted OMS-2 (M = Ti, Fe, Cu, Co)
- H-exchanged OMS-2
- Sulfation of Ti-OMS-2

Research Questions

Characterization

- Structural analysis
- Acidity analysis
- Surface area
- Hydrophobicity-hydrophilicity

Catalytic activity

- Oxidation reactions
- Consecutive oxidation and acid reactions

1. Which method gives the best performance of OMS-2 in oxidation of benzyl alcohol.

2. What are the effects of metals substituted and H-exchanged to the physicochemical properties of OMS-2 and its correlation to catalytic activity of the catalyst in oxidation reaction?

3. How are the catalytic activities of Ti-OMS-2 compared to the other metals incorporated OMS-2?

4. What are the effects of the synthesis method, amount and location of titanium sites to physicochemical properties of Ti-OMS-2 and its correlation to catalytic activity in oxidation reaction?

5. How is catalytic activity of Ti sites in different substrates in oxidation reaction?

6. Is sulfation of Ti-OMS-2 catalyst successfully designed as a bifunctional oxidative and acidic catalyst for synthesis of diols from alkene?

Figure 1.7: The schematic of the research approach and research questions.

catalyst using mild oxidant as oxidizing agent, these systems are more economical and environmentally friendly (see Figure 1.8).

In light of the issues described previously, the research was conducted with the following objectives:

1. To synthesize manganese oxide octahedral molecular sieve (OMS-2), titanium supported OMS-2 (Ti-OMS-2), metal supported OMS-2 (M-OMS-2) and H doped metal supported OMS-2 (H-M-OMS-2).

2. To modify the surface of Ti-OMS-2 by sulphation as a bifunctional catalyst.

3. To study the physicochemical properties-catalytic activity relationship in model reactions.

Multidisciplinary Science

⬇

Catalysis

⬇

Importance

- Success of the industry in 20th century
- Greener industry in 21th century
- The heart of quality of life
- A healthy economy growth

⬇

Oxidation reaction ⟵ **Biggest problem areas** ⟶ **Acid-catalyze reaction**

⬇ | ⬇

- OMS-2 as a promising heterogeneous catalyst (active with mild oxidant, inexpensive and easy preparation)
- TS-1 as a milestone in oxidation catalysis

Sulfated metal oxide as a strong solid acid catalyst which more environmentally friendly

Catalyst Design

Ti-OMS-2

Catalyst Design

Sulfated Ti-OMS-2

⬇

A new heterogeneous catalyst for oxidation reaction under mild condition

Bifunctional oxidative and acidic catalyst for consecutive reaction of alkene to diols (one pot reaction)

Significant

More economic and environmentally friendly catalysts

Figure 1.8: The significant of the use Ti-OMS-2 in heterogeneous oxidation and acid reactions.