# STUDY ON STRUCTURAL TRANSFORMATION OF MOLYBDENUM OXIDE CATALYST FOR PROPANE OXYDEHYDROGENATION (ODH) REACTION

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# STUDY ON STRUCTURAL TRANSFORMATION OF MOLYBDENUM OXIDE CATALYST FOR PROPANE OXYDEHYDROGENATION (ODH) REACTION

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**DISSERTATION SUBMITTED IN FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE
OF MASTERS OF SCIENCE**

**DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
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KUALA LUMPUR**

**2012**

# ABSTRACT

Catalytic oxidative dehydrogenation (ODH) of propane is recognized as an attractive alternative process as compared to propane dehydrogenation which the latter requires higher reaction temperature. For ODH of propane, key points in synthesizing an active catalyst are the preparation method, surface reducibility, and acid-base properties. However, existing ODH catalysts gives low activity and poor selectivity. Combination of optimal activation thermal analysis and structural control can help to guide and gain insight into the structure-activity relationship of the nanostructured catalyst system**.** Molybdenum and vanadium oxide based catalyst has been identified as one of the most suitable catalyst for the reaction. However it is difficult to control the key properties such as crystal size, structure, particle shape and surface area that influence the catalysts performances. In these studies, molybdenum oxides based catalysts (MoOx and MoVOx) were synthesized using controlled precipitation method. Parameters varied were pH, concentration, temperature and also rate of addition. For MoOx based catalysts, the phase obtained were 'supramolecular' phase ($Mo_{36}O_{112}$) and hexagonal phase (h-$MoO_3$). Protonation encourages the growth of the catalytic structure where $Mo_7O_{24}$ acts as a nucleus creating the polyoxomolybdates. Both phases have bulk structural corner sharing pentagonal channels as structural motif which is catalytically active. For MoVOx based catalyst, amorphous phase was observed for all spray dried precursors. Highly crystalline hexagonal phase ($MoV_2O_8$) and tetragonal phase [$(MoV)_5O_{14}$] were obtained after activation under static air and inert respectively when vanadyl was used as the vanadium source. Dispersion of vanadium creates the 'site isolation' effect which is important to avoid olefins transforming to neighboring oxidized sites. When vanadates were used as the vanadium source, different phases were observed at varying of vanadium loading. Orthorhombic phase was observed at low vanadium loading whilst mixed phase of monoclinic and triclinic were obtained at higher vanadium loading. Temperature programmed activation using *in-situ* XRD was used to study the dynamics of structural transformation of selected synthesized molybdenum oxide-based precursor. The structural evolution for MoOx precursor takes place from ‘supramolecular’ to metastable hexagonal phase at 300 ºC. The structural changed finally to the stable orthorhombic phase at 450 ºC. For MoVOx precursor, the structural transformation takes place from amorphous to nanocrystalline phase at 400 ºC. At 500 ºC, the catalyst morphology transforms finally to thermodynamically stable crystallized tetragonal phase. By correlating *in-situ* XRD reactivity studies with temperature programmed *in-situ* DSC, catalytic activity in MoOx catalyst was not observed whilst for reaction using MoVOx catalyst, catalytic activity was observed at the nanocrystalline phase.

# ABSTRAK

Propylene adalah bahan mentah yang digunakan secara meluas dalam industri petrokimia. Permintaan yang tinggi dan kepelbagaian dalam pengunaan propylene merangsang pembangunan teknologi pengeluaran terkini. Oksidatif pengdehidrogenan propana yang menggunakan mangkin merupakan alternatif yang menarik berbanding pengdehidrogenan propana yang memerlukan suhu yang tinggi meyebabkan kos yang mahal. Dalam ODH propana, perkara utama yang perlu diberikan perhatian untuk mensintesis mangkin yang sempurna adalah kaedah penyediaan, aspek penurunan permukaan dan sifat asid-bes. Walau bagaimanapun, Mangkin ODH yang ada pada masa kini masih mempunyai aktiviti dan pemilihan yang rendah. Pemilihan produk sintesis adalah berdasarkan struktur mangkin. Gabungan analisis terma dan kajian struktur boleh membantu dalam membimbing dan mendapat pemahaman atas hubungan struktur-aktiviti sistem pemangkin nanostruktur. Mangkin Molibdenum dan Vanadium oksida telah dikenal pasti sebagai salah satu mangkin yang sesuai untuk tindak balas ini. Walau bagaimanpun, adalah sukar untuk mengawal sifat-sifat utama seperti saiz dan struktur kristal, bentuk dan luas permukaan zarah yang menentukan prestasi mangkin tersebut. Dalam kajian ini, mangkin berasaskan Molibdenum oksida (MoOx dan MoVOx) telah disintesis mengunakan kaedah pemendapan terkawal. Parameter seperti pH, kepekatan, suhu dan kadar penambahan telah diubah-ubah. Untuk mangkin $MoO_x$, fasa yang telah diperolehi adalah fasa ‘supramolekular’ ($Mo_{36}O_{112}$) dan fasa heksagon (h-$MoO_3$). Protonasi menggalakkan pembesaran struktur mangkin dimana $Mo_7O_{24}$ selaku nukleus membentuk polioxymolibdates. Kedua-dua fasa mempunyai sudut berstruktur pukal dan berkongsi saluran pentagonal sebagai motif stuktur mangkin yang aktif. Untuk mangkin berasaskan $MoVO_x$, fasa amorfus didapati untuk semua prekursor yang diperolehi melalui semburan kering. Fasa hexagon ($MoV_2O_8$) dengan kehabluran yang tinggi dan fasa tetragon [$(MoV)_5O_{14}$] telah diperoleh selepas pengaktifan masing-masing di bawah udara statik dan gas lengai apabila vanadil telah digunakan sebagai sumber vanadium. Oksida $Mo_5O_{14}$ struktur dengan fasa tetragon juga mempunyai saluran pentagon dan herotan fasa dioksida meningkat dengan kandungan vanadium. Penyebaran vanadium mewujudkan kesan 'tapak terasing' yang penting untuk mengelakkan olefin berubah ke tapak teroksida bersebelahan. Apabila vanadate digunakan sebagai sumber vanadium, fasa berbeza diperolehi pada muatan vanadium yang berbagai. Fasa ortorombik diperhatikan pada peratus muatan vanadium rendah manakala fasa campuran monoklinik dan triklinik didapati pada peratus muatan vanadium yang lebih tinggi. Pengaktifan dengan suhu terprogram menggunakan XRD *in-situ* telah digunakan untuk mengkaji transformasi dinamik struktur prekursor mangkin molibdenum oksida. Evolusi struktur untuk prekursor MoOx berlaku dari fasa ‘supramolekular’ ke fasa heksagon metastabil pada suhu 300 ºC. Struktur tersebut akhirnya berubah ke fasa ortorombik yang stabil dari segi termodinamik pada suhu 450 ºC**.** Bagi prekursor MoVOx, transformasi adalah dari amorfus ke fasa nanokristal pada 400 ºC. Pada 500 ºC, morfologi mangkin berubah ke tetragon iaitu fasa yang stabil dari segi termodinamik. Dengan menghubungkaitkan kajian reaktiviti XRD *in-situ* bersama dengan DSC *in-situ* dengan program suhu, aktiviti pemangkinan pada mangkin MoOx tidak diperhatikan manakala untuk mangkin MoVOx, aktiviti pemangkinan telah diperhatikan pada fasa nanokristal.

# ACKNOWLEDGEMENT

First and foremost I would like to thank God for guiding me in completing this dissertation successfully. I would also like to give great thanks to my supervisor, Prof. Dr. Sharifah Bee Abd Hamid for all the advice, knowledge and helpful support in completing this project. I am also very grateful to Dr. Muralithran Kutty, Dr. Looi Ming Hong and Fazliana Abd Hamid for all their encouragement, assistance and suggestions in helping me to complete my MSc studies. Not to forget, the COMBICAT technical service team for all their contributions in samples characterization. I would also want to expresses sincere gratitude to the National Science Foundation (NSF) for financially supporting me and my MSc program and PPP Grant (PS374/2010B) for providing financial support for this project. Finally I am very grateful to my parents and friends for all their understanding and support throughout my MSc program.

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| | |
|---|---|
| **2θ** | Two theta |
| **ABS** | Acrylonitrile-butadiene-styrene |
| **AHM** | Ammonium HeptaMolybdate |
| **$C_3$** | Propane |
| **$C_4$** | Butane |
| **$C_5$** | Pentane |
| ***d* value** | Interplanar spacing |
| **DSC** | Differential Scanning Calorimetry |
| **DTG** | Differential Thermogravimetric |
| **EDX** | Energy Dispersive X-ray |
| **FCC** | Fluid Catalytic Cracking |
| **FWHM** | Full Width Half Maximum |
| **LPG** | Liquefied Petroleum Gas |
| **m/e** | Mass/charge ratio |
| **MoOx** | Molybdenum based Oxides |
| **MoVOx** | Molybdenum Vanadium based Oxides |
| **MS** | Mass Spectroscopy |
| **ODH** | Oxidative Dehydrogenation |
| **PDF** | Powder Diffraction File |
| **PDH** | Propane Dehydrogenation |
| **PP** | Polypropylene |
| **SAN** | Styrene acrylonitrile |
| **SAXS** | Small-Angle X-ray Scattering |

| | |
|---|---|
| **SEM** | Scanning Electron Microscope |
| **Tcf** | Trillion cubic feet |
| **TG** | Thermogravimetric |
| **Ts** | Sample Temperature |
| **WAXS** | Wide-Angle X-ray Scattering |
| **XRD** | X-Ray Diffraction |
| **XRF** | X-Ray Fluorescence |

# List of Appendices