



**UNIVERSITI PUTRA MALAYSIA**

***CATALYTIC OXIDATIVE DEHYDROGENATION OF PROPANE BY  
AMoVNbO<sub>x</sub> (A = Ni, Co, Pt) SYNTHESISED VIA IMPREGNATION  
METHOD***

**WONG MEI SAM**

**FS 2013 93**



**UPM**  
UNIVERSITI PUTRA MALAYSIA  
BERILMU BERBAKTI

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AMoVNbO<sub>x</sub> (A = Ni, Co, Pt) SYNTHESISED VIA IMPREGNATION METHOD**

By

**WONG MEI SAM**

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

**July 2013**



**UPM**  
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**WONG MEI SAM**

**MASTER OF SCIENCE  
UNIVERSITI PUTRA MALAYSIA**

**2013**

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

**CATALYTIC OXIDATIVE DEHYDROGENATION OF PROPANE BY  
AMoVNbO<sub>x</sub> (A = Ni, Co, Pt) SYNTHESISED VIA IMPREGNATION METHOD**

By

**WONG MEI SAM**

July 2013

**Chairman : Associate Professor Irmawati Ramli, PhD**

**Faculty : Science**

Propane is a natural gas that is found abundant and low cost material in petroleum industry. In order to upgrade the value of propane, catalytic oxidative dehydrogenation of propane has been carried out to form propylene which is widely used as chemical intermediate in manufacturing process. Thus, Ni, Co and Pt-doped MoVNbO<sub>x</sub> catalysts were prepared by using impregnation method. These catalysts were used for oxidative dehydrogenation reaction of propane to propylene. The catalysts prepared were characterized by X-ray diffraction (XRD), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), Brunauer-Emmett-Teller (BET) Surface Area Measurement,  $S_{BET}$ , Scanning Electron Microscopy (SEM), and Temperature Programmed Reduction in Hydrogen (H<sub>2</sub>-TPR). From the XRD data, it has been found that all doped catalysts showed the presence of tetragonal Mo<sub>5</sub>O<sub>14</sub>-like phases with a much

better crystallite formation as compared to the undoped MoVNbOx. The particle crystallinity increases as the amount of dopant loaded increases. ICP-OES analysis displayed that the atomic ratio of Mo/V/Nb was 1/0.24/0.13, agreeing well with the theoretical ones. However, the amount of dopant was a bit less especially for Pt doped catalysts. Doping of Ni, Co and Pt lowered the surface area value as compared to undoped MoVNbOx catalysts (8.8 m<sup>2</sup>/g). This confirmed the incorporation of dopants occur in the catalytic system. Furthermore SEM images supported this claim by showing the particles developed into c-direction which supported high crystallinity of doped catalysts and the role of dopants as structural promoter. Therefore, the reputed active site (i.e. Mo<sub>5</sub>O<sub>14</sub>-like phase) improved when dopants were added, eventually affecting the catalytic performance. H<sub>2</sub>-TPR showed the reducibility of the catalyst confirming the existence of lattice oxygen of high reaction temperature. Catalytic test of Pt-MoVNbOx catalysts gave the highest activity (13.4 % for aPtMoVNbOx and 23.4 % for bPtMoVNbOx) in propane conversion but 0 % selectivity towards propylene due to the poisoning of Pt site by CO<sub>x</sub>. Meanwhile Ni-MoVNbOx catalysts have relatively lower activity (7.5 % for aNiMoVNbOx) than Pt-MoVNbOx catalysts but higher selectivity for propylene production (44.0 % for aNiMoVNbOx). For Co-MoVNbOx catalysts, the higher activity for propane conversion is found for lower loading of dopants, while high selectivity for propylene is observed for high loading of dopants.

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

**PENYAHIDROGENAN OKSIDATIF PROPANA DENGAN MENGGUNAKAN MANGKIN  $AMoVNbO_x$  (A = Ni, Co, Pt) YANG DISINTESIS MELALUI KAEDAH IMPREGNASI**

Oleh  
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Propana merupakan gas asli yang terdapat banyak dan murah dalam industri petroleum. Demi meningkatkan nilai propana, proses oksidatif penyahhidrogenan propana telah dijalankan untuk membentuk propena yang digunakan secara luas sebagai bahan kimia perantaraan dalam proses pembuatan. Oleh itu, mangkin  $MoVNbO_x$  yang didopkan Ni, Co, dan Pt yang disediakan melalui kaedah impregnasi dan diguna untuk menghasilkan propena daripada propana dengan tindak balas oksidatif penyahhidrogenan. Semua mangkin dikaji dengan menggunakan belauan sinaran X (XRD), spektroskopi pancaran optik dengan sumber plasma berganding secara aruhan (ICP-OES), Brunauer-Emmett-Teller (BET) ukuran luas permukaan,  $S_{BET}$ , mikroskop imbasan elektron (SEM), dan penurunan hidrogen dengan suhu kawalan ( $H_2$ -TPR). Data hasil daripada analisis XRD menunjukkan mangkin yang didopkan Ni, Co dan Pt menunjukkan kewujudan fasa tetragonal yang menyerupai  $Mo_5O_{14}$  dengan

formasi hablur yang lebih baik berbanding mangkin MoVNbOx tanpa dop. Tahap penghabluran mangkin juga didapati meningkat apabila jumlah dop meningkat. Analisis ICP-OES menunjukkan nisbah atom Mo/V/Nb juga didapati menuruti nisbah yang dikira secara teori, 1/0.24/0.13. Walau bagaimanapun, logam dopan didapati kurang daripada nilai teori terutamanya bagi mangkin yang didopkan Pt. Mangkin yang didopkan Ni, Co, dan Pt menunjukkan jumlah luas permukaan yang lebih rendah berbanding mangkin tanpa dop (8.8 m<sup>2</sup>/g). Dengan ini, bahan dopan mangkin dapat disahkan terdapat dalam mangkin dikaji. Imej SEM juga digunakan untuk mengesahkan pendopan mangkin dengan menunjukkan zarah yang membentuk pada arah c, menyebabkan penghabluran yang tinggi pada mangkin yang didop dan membantu peranannya sebagai penyokong struktur. Oleh itu, tapak aktif (fasa tetragona meyerupai Mo<sub>5</sub>O<sub>14</sub>) bertambah baik apabila mangkin didop seterusnya mempengaruhi prestasi mangkinan. Analisis menggunakan H<sub>2</sub>-TPR menunjukkan penurunan aktiviti mangkin, mengesahkan kewujudan kekisi oksigen dengan suhu tindak balas yang tinggi. Ujian mangkinan menunjukkan mangkin Pt-MoVNbOx mempunyai aktiviti paling tinggi (13.4 % bagi aPtMoVNbOx dan 23.4 % bagi bPtMoVNbOx) dengan 0.0 % kadar keterpilihan terhadap propena. Ini adalah kerana tapak Pt dipengaruhi oleh kehadiran CO<sub>x</sub>. Mangkin Ni-MoVNbOx (7.5 % bagi aNiMoVNbOx) pula mempunyai aktiviti yang lebih rendah berbanding dengan Pt-MoVNbOx dengan kadar keterpilihan terhadap propena yang lebih tinggi (44.0 % bagi aNiMoVNbOx). Mangkin Co-MoVNbOx menunjukkan aktiviti yang lebih



tinggi bagi mangkin yang mempunyai amaun Co yang rendah manakala kadar keterpilihan terhadap propena yang tinggi bagi mangkin yang mempunyai amaun Co yang tinggi.



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I certify that an Examination Committee has met on 2nd July 2013 to conduct the final examination of Wong Mei Sam on her degree thesis entitled "CATALYTIC OXIDATIVE DEHYDROGENATION OF PROPANE BY AMoVNbOx (A = Ni, Co, Pt) SYNTHESISED VIA IMPREGNATION METHOD" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Degree of Master.

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## DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.



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WONG MEI SAM

Date:

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## LIST OF ABBREVIATIONS

ODH	Oxidative dehydrogenation
MCM	Multicomponent molybdates
HPC	Heteropolycompounds
XRD	X-ray Diffraction
JCPDS	Joint Committee of Powder Diffraction Standards
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
BET	Brunauer-Emmett-Teller surface area measurements
SEM	Scanning Electron Microscopy
H <sub>2</sub> -TPR	Temperature Programmed Reduction in Hydrogen
MS	Mass Spectrometer
TCD	Thermal Conductivity Detector
FID	Flame Ionization Detector
GC	Gas Chromatography
MFC	Mass Flow Controllers
PC	Personal Computer
Ref	Reference
Meas	Measurement
T <sub>max</sub>	Maximum Reduction Temperature
FWHM	Full Width of Half Maximum

# CHAPTER 1

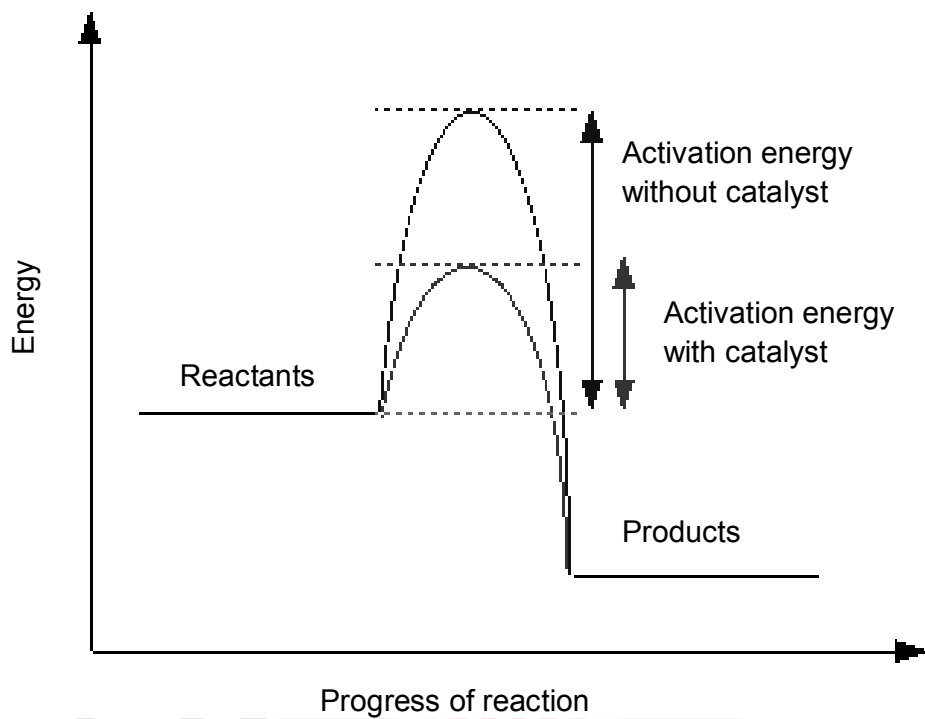
## INTRODUCTION

### 1.1 Catalysis and Catalysts

Catalysis is a process of changing the rate of a chemical reaction by using a substance called catalyst. Majority of catalysis process involves multiple steps in the reaction with rate determining step (RDS) is the slowest step in a chemical reaction which involves multiple steps. Reaction which contains several steps is always has a single step that is slower than the other steps, and this step will determine the overall rate of the reaction. To increase the rate reaction, catalyst plays an important role. A catalyst will participate in the slowest step and will provide another pathway which has lower rate determining free energy of activation. So, with the assistance of catalyst, the overall rate of reaction will increase.

A catalyst can speed up a chemical reaction by providing an alternative reaction pathway which has lower activation energy as shown in Figure 1 (Brady *et al.*, 2000). Although catalyst may involves in multiple chemical transformations, it does not be consumed and can be regenerated after undergoes a chemical reaction. The amount of a catalyst needed during the chemical reaction is small. For a solid catalyst the reaction only takes place on the surface of the catalyst. The understanding of catalyst's surface and its structure is very important and helpful in order to produce highly efficient

catalyst. As stipulated by Periana and co-workers (2004), a useful and effective catalyst must attain minimum performance in its stability, rate and selectivity. The strategy to develop a catalyst which fulfil the above mentioned requirements is depended on the modification and amelioration of molecular structure, the composition of the catalyst and the synthesize condition of catalyst (Periana *et al.*, 2004).



**Figure 1: Comparison of activation energy between reaction with and without catalyst.**

## 1.2 Heterogeneous Catalysis

Catalytic reaction can be divided into two main groups which are homogeneous and heterogeneous catalysis. Homogeneous catalysis is a catalytic reaction where the reactants are in the same phase with the catalyst. The phase involved in homogeneous catalysis is mainly in liquid form where the catalyst is co-dissolved in a solvent with the reactants, whereas, heterogeneous catalysis involves two different phases between catalyst and reactant. The catalyst is usually in liquid or solid form, while the reactant is in liquid or gas form. Heterogeneous catalyst works in stages as described below (Viswanathan *et al.*, 2002):

- a) Diffusion of reactant molecules onto to the surface of catalyst.
- b) Reactant molecules are adsorbed on the active sites of catalyst surface.
- c) On the catalyst surface, the chemical reaction happens between the reactant molecules. Molecules rearrangement happened.
- d) The formed products desorbed from the surface of the catalyst.
- e) Diffusion of products from catalyst surface.
- f) The active sites now are available for new reactant molecules to attach and ready for next reaction.

Since heterogeneous catalysis it involves adsorption of reactant(s) on the surface of a catalyst, therefore the strength of adsorption is very important. It can be considered as a good catalyst if the adsorption of reactants is strong

enough for the reaction to begin and not so strong for product to leave. The amount of adsorbed reactants may also depend on the surface area of the catalyst. In other words, high surface area of catalysts is favourable in a catalytic reaction.

### 1.3 Propylene

Propylene also known as propene, methylethene or methylethylene with molecular formula  $C_3H_6$ , is an unsaturated hydrocarbon with one carbon-carbon double bond. Propylene appears as gas at room temperature and atmospheric pressure. It is a colourless, odourless, low boiling point (225 K) and flammable gas. According to DOW Chemical Corporate, there are three grades of commercial propylene available in the market which are:

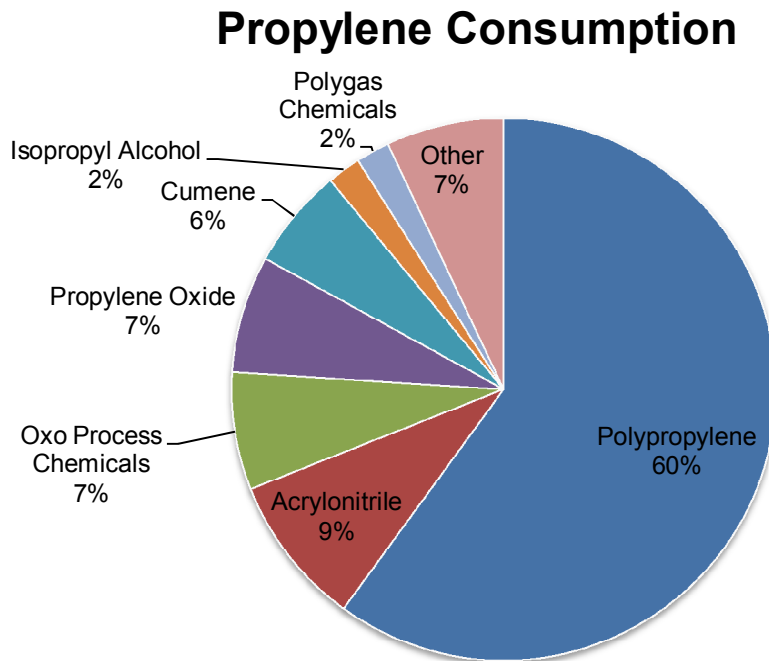
- a) 95 – 100 % polymer grade
- b) 90 – 99.8 % chemical grade
- c) 50 – 70 % refinery grade

The different between polymer grade, chemical grade and refinery grade is on the purity of propylene. For example, propylene gas with polymer grade has 95 – 100 % propylene purity with limited addition of ethylene and butylene and the rest is contaminant such as sulphur, arsine and dienes.

Propylene is mainly can be produced via two routes which are as a by-product either from ethylene production by steam cracking process or fluid catalytic

cracking process. Steam cracking is a petrochemical process by using heat without the presence of oxygen to break down saturated hydrocarbon to lighter olefin such as ethylene and propylene while fluid catalytic cracking is a process by using fluidized powdered catalyst to break down high molecular weight hydrocarbon into lighter molecules such as gasoline and olefin at high temperature and moderate pressure. Then, the lighter molecules are separated by distillation.

Propylene is used to form chemical intermediates in manufacturing processes. The following pie chart (Figure 2) shows the global propylene consumption and its application (Table 1) as provided by DOW Chemical Corporate (2003).



**Figure 2: Global propylene consumption (DOW Chemical Corporate, 2003).**



**Table 1: List of propylene application**

<b>Product</b>	<b>Application</b>
Polypropylene	Polypropylene is flexible, light, cracking resistant and corrosion resistant, it is used to produce plastic products, prosthetics and orthopaedic appliances.
Acrylonitrile	Acrylonitrile always involve in polymer production to produce resins and carbon fibres. Besides, it also is consumed for water treatment and paper manufacturing.
Oxo process chemicals	Propylene is used to make <i>n</i> -butanol and 2-ethyl hexanol which will then use to produce PVC plasticisers and coatings.
Propylene oxide	Propylene oxide acts as chemical intermediate to form polyurethane polyols and propylene glycols. Polyurethane polyols involve in industry coatings and adhesive, while propylene glycol are used to manufacture resins, antifreeze, cosmetics, drugs and pet foods.
Cumene	Cumene can be produced by alkylation of benzene with propylene. Cumene mainly used in the production of phenol to produce phenolic resins.
Isopropyl alcohol	Isopropyl alcohol mainly involved in solvent application such as surface coatings, shellac, gums, personal care (after-shaves), and antiseptic (rubbing alcohol).
Polygas chemicals	Polygas chemicals included nonene, dodecene and heptene. Polygas involves in the field of surfactants, lubricant, plasticize PVC and phosphite antioxidants.

## 1.4 Problem Statement

Propane is a natural gas that is found abundant in petroleum industry. It is widely used for the generation of heat for industrial and domestic applications. This commodity can be further upgraded by converting it into propylene which has more commercial value as starting chemicals for many usages. Propylene is an important commodity which is only derived as side product from steam cracking of ethylene production and from catalytic cracking process of gasoline production. In order to increase the value of propane and yield of propylene, catalytic reaction especially oxidative dehydrogenation (ODH) can be carried out. It is a preferred method as compared to direct dehydrogenation of propane because the latter is an endothermic process that would incur high manufacturing cost due to it requires high reaction temperature during the reaction. It will induce some side reactions such as thermal cracking and deactivate the catalysts by coke formation. Thus, ODH has offered an alternate route for propylene production. ODH is an exothermic process so it does not require high reaction temperature which will help in reduce the manufacturing cost and it will not induce the formation of coke. In order to increase the rate of ODH, Ni, Co and Pt had been impregnated onto MoVNbO<sub>x</sub> since they are good dehydrogenating agents. In oxidative dehydrogenation, the presence of the dopants is used to assist the process abstraction of methylene hydrogen (rate determining step) from propane to form propylene. Effect of the type of dopant and the amount of dopant on the properties of catalyst and oxidative dehydrogenation process

will be studied to improve the understanding in development active and selective catalysts.

### 1.5 Objectives

The objectives of this study are:

1. To synthesize doped-AMoVNbO<sub>x</sub> catalysts where A = Ni, Co and Pt by impregnation method.
2. To investigate the influence of different amount of loading and type of metal dopants on the catalyst characteristics of MoVNbO<sub>x</sub> by XRD, ICP-OES BET, SEM, and H<sub>2</sub>-TPR.
3. To evaluate catalytic performance of the doped MoVNbO<sub>x</sub> catalysts.

## REFERENCES

Product Safety Assessment (PSA): Propylene, DOW Chemical Corporate, <http://www.dow.com/productsafety/finder/pro.htm>, viewed on 19 October 2012.

Abello, M. C., Gomez, M. F., and Ferretti, O., (2001) Mo/gamma-Al<sub>2</sub>O<sub>3</sub> catalysts for the oxidative dehydrogenation of propane. - Effect of Mo loading, Applied Catalysis A: General 207, 421-431.

Aitani, A., Encyclopedia of Chemical Processing: Propylene Production, 2006, Taylor & Francis, New York, pp. 2461-2466.

Allison, J. D., Ramani, S., Chen, Z., Charmicheal, M., Chen, S. Y., McDonald, S. R., and Gaffney, A., (2004) Oxidative Dehydrogenation of Hydrocarbons Using Catalysts With Trace Promoter Metal Loading., US 2004/0068148 A1.

Atkins, P., and de Paula, J., (2009) Physical Chemistry, W. H. Freeman.

Ballarini, N., Cavani, F., Di Memmo, S., Zappoli, F., and Marion, P., (2009) The role of Sb and Nb in rutile-type Sn/V/Nb/Sb mixed oxides, catalysts for propane ammoxidation to acrylonitrile, Catalysis Today 141, 264-270.

Barbero, B. P., Prada Silvy, R., and Cadús, L. E. U., (2005) Oxidative dehydrogenation of propane over (Mo)-Sm-V-O catalytic system: Role of the different phases, Latin American applied research 35, 273-280.

Beck, B., Harth, M., Hamilton, N. G., Carrero, C., Uhlrich, J. J., Trunschke, A., Shaikhutdinov, S., Schubert, H., Freund, H.-J., Schlögl, R., Sauer, J., and Schomäcker, R., (2012) Partial oxidation of ethanol on vanadia catalysts on supporting oxides with different redox properties compared to propane, Journal of Catalysis 296, 120-131.

Bobaru, Ş. C., (1975). High-Pressure STM Studies of Oxidation Catalysis. Chapter 2 : Introduction to the theory concerning CO oxidation over platinum group metals, pp: 11 - 17, Leiden University, Netherlands.

Botella, P., Solsona, B., Martinez-Arias, A., and López Nieto, J. M., (2001) Selective Oxidation of Propane to Acrylic Acid on MoVNbTe Mixed

Oxides Catalysts Prepared by Hydrothermal Synthesis, *Catalysis Letters* 74, 149-154.

Botella, P., López Nieto, J. M., Dejoz, A., Vázquez, M. I., and Martínez-Arias, A., (2003) Mo-V-Nb mixed oxides as catalysts in the selective oxidation of ethane, *Catalysis Today* 78, 507-512.

Botella, P., García-González, E., Dejoz, A., López Nieto, J. M., Vázquez, M. I., and González-Calbet, J., (2004) Selective oxidative dehydrogenation of ethane on MoVTeNbO mixed metal oxide catalysts, *Journal of Catalysis* 225, 428-438.

Bradley, C. A., McMurdo, M. J., and Tilley, T. D., (2007) Selective Catalytic Cyclohexene Oxidation Using Titanium-Functionalized Silicone Nanospheres, *The Journal of Physical Chemistry C* 111, 17570-17579.

Brady, J. E., Russell, J. W., and Holum, J. R., *Chemistry Matters and It Changes. In the Study of Rate Reaction*, 2000, New York:Wiley, pp. 610-613.

Burch, R., Crittle, D. J., and Hayes, M. J., (1999) C-H bond activation in hydrocarbon oxidation on heterogeneous catalysts, *Catalysis Today* 47, 229-234.

Cadus, L., and Ferretti, O., (2000) Highly effective molybdena-manganese catalyst for propane oxidative dehydrogenation, *Catalysis Letters* 69, 199-202.

Chaston, J. C., (1964) Reaction of Oxygen with the Platinum Metals: I - The Oxidation of Platinum, *Platinum Metals Review* 8, 50-54.

Christensen, C. H., and Norskov, J. K., (2008) A molecular view of heterogeneous catalysis, *The Journal of chemical physics* 128, 182503.

Claude Gagnadre, A. C., Hervé Guézénoc, Yves Grohens, (2009) Electron microscopy pictures, mathematical model and approximate solution of the surface potential, *Kybernetes* Vol. 38, pp.780 - 788.

Crabtree, R. H., (2004) Organometallic alkane CH activation, *Journal of Organometallic Chemistry* 689, 4083-4091.

- Dieterle, M., Mestl, G., Jäger, J., Uchida, Y., Hibst, H., and Schlögl, R., (2001) Mixed molybdenum oxide based partial oxidation catalyst: 2. Combined X-ray diffraction, electron microscopy and Raman investigation of the phase stability of (MoVW)<sub>5</sub>O<sub>14</sub>-type oxides, *Journal of Molecular Catalysis A: Chemical* 174, 169-185.
- Doornkamp, C., and Ponc, V., (2000) The universal character of the Mars and Van Krevelen mechanism, *Journal of Molecular Catalysis A: Chemical* 162, 19-32.
- Fadoni, M., and Lucarelli, L. 1999. Temperature programmed desorption, reduction, oxidation and flow chemisorption for the characterisation of heterogeneous catalysts. Theoretical aspects, instrumentation and applications. Pages 177-225 in Dąbrowski, A, ed. *Studies in Surface Science and Catalysis*, vol. Volume 120, Part A Elsevier.
- Gooch, J. 2011. Active Site. Pages 17-17 in Gooch, J, ed. *Encyclopedic Dictionary of Polymers*, Springer New York.
- Grasselli, R. K., (2001) Genesis of site isolation and phase cooperation in selective oxidation catalysis, *Topics in Catalysis* 15, 93-101.
- Grasselli, R. K., (2002) Fundamental Principles of Selective Heterogeneous Oxidation Catalysis, *Topics in Catalysis* 21, 79-88.
- Guan, J., Song, K., Xu, H., Wang, Z., Ma, Y., Shang, F., and Kan, Q., (2009) Oxidation of isobutane and isobutene to methacrolein over hydrothermally synthesized Mo-V-Te-O mixed oxide catalysts, *Catalysis Communications* 10, 528-532.
- Herrmann, J.-M., Vernoux, P., Béré, K. E., and Abon, M., (1997) In Situ Study of Redox and of p-Type Semiconducting Properties of Vanadyl Pyrophosphate and of V-P-O Catalysts during the Partial Oxidation of n-Butane to Maleic Anhydride, *Journal of Catalysis* 167, 106-117.
- Irmawati, R., Noorfarizan Nasriah, M. N., Taufiq-Yap, Y. H., and Abdul Hamid, S. B., (2004) Characterization of bismuth oxide catalysts prepared from bismuth trinitrate pentahydrate: influence of bismuth concentration, *Catalysis Today* 93-95, 701-709.

- Jiang, H. C., Lu, W. M., and Wan, H. L., (2004) The effect of MoV<sub>0.3</sub>Te<sub>0.23</sub>PxO<sub>n</sub> catalysts with different phosphorus content for selective oxidation of propane to acrolein, *Journal of Molecular Catalysis a-Chemical* 208, 213-217.
- Jibril, B. Y., (2005) Effects of Feed Compositions on Oxidative Dehydrogenation of Propane over Mn–P–O Catalyst, *Industrial & Engineering Chemistry Research* 44, 702-706.
- Jibril, B. Y., and Ahmed, S., (2006) Oxidative dehydrogenation of propane over Co, Ni and Mo mixed oxides/MCM-41 catalysts: Effects of intra- and extra-framework locations of metals on product distributions, *Catalysis Communications* 7, 990-996.
- Kardash, T. Y., Plyasova, L. M., Bondareva, V. M., Andrushkevich, T. V., Dovlitova, L. S., Ischenko, A. I., Nizovskii, A. I., and Kalinkin, A. V., (2010) M5O14-like V–Mo–Nb oxide catalysts: Structure and catalytic performance, *Applied Catalysis A: General* 375, 26-36.
- Keulks, G. M., Krenzke, L. D., and Notermann, T. M., (1978) *Adv. Catal.* 27, 183.
- Koc, S. N., Gurdag, G., Geissler, S., and Muhler, M., (2004) Effect of Nickel, Lanthanum, and Yttrium Addition to Magnesium Molybdate Catalyst on the Catalytic Activity for Oxidative Dehydrogenation of Propane, *Industrial & Engineering Chemistry Research* 43, 2376-2381.
- Kubo, J., Watanabe, N., and Ueda, W., (2008) Propane ammoxidation with lattice oxygen of Mo-V-O-based complex metal oxide catalysts, *Chemical Engineering Science* 63, 1648-1653.
- Kum, S. S., Jo, B. Y., and Moon, S. H., (2009) Performance of Pd-promoted Mo-V-Te-Nb-O catalysts in the partial oxidation of propane to acrylic acid, *Applied Catalysis A: General* 365, 79-87.
- Lemonidou, A. A., Nalbandian, L., and Vasalos, I. A., (2000) Oxidative dehydrogenation of propane over vanadium oxide based catalysts: Effect of support and alkali promoter, *Catalysis Today* 61, 333-341.
- Levin, D., and Ying, J. Y. 1997. Oxidative dehydrogenation of propane by non-stoichiometric nickel molybdates. Pages 367-373 in R.K. Grasselli,

STOAMG, and Lyons, J.E., eds. *Studies in Surface Science and Catalysis*, vol. Volume 110 Elsevier.

Liang, H., Zhang, Y., and Liu, Y., (2008) Three-dimensionally ordered macroporous Pt/TiO<sub>2</sub> catalyst used for water-gas shift reaction, *Journal of Natural Gas Chemistry* 17, 403-408.

Lin, M. M., (2001) Selective oxidation of propane to acrylic acid with molecular oxygen, *Applied Catalysis A: General* 207, 1-16.

Lin, M. M., (2003) Complex metal-oxide catalysts for selective oxidation of propane and derivatives - I. Catalysts preparation and application in propane selective oxidation to acrylic acid, *Applied Catalysis a-General* 250, 305-318.

Liu, Q., Wang, L.-C., Chen, M., Cao, Y., He, H.-Y., and Fan, K.-N., (2009) Dry citrate-precursor synthesized nanocrystalline cobalt oxide as highly active catalyst for total oxidation of propane, *Journal of Catalysis* 263, 104-113.

Liu, Y.-M., Feng, W.-L., Li, T.-C., He, H.-Y., Dai, W.-L., Huang, W., Cao, Y., and Fan, K.-N., (2006) Structure and catalytic properties of vanadium oxide supported on mesocellulose silica foams (MCF) for the oxidative dehydrogenation of propane to propylene, *Journal of Catalysis* 239, 125-136.

López-Medina, R., Fierro, J. L. G., Guerrero-Pérez, M. O., and Bañares, M. A., (2010) Nanoscaled rutile active phase in Mo-V-Nb-O supported catalysts for the oxidation of propane to acrylic acid, *Applied Catalysis A: General* 375, 55-62.

Mazzocchia, C., Aboumradi, C., Diagne, C., Tempesti, E., Herrmann, J. M., and Thomas, G., (1991) On the NiMoO<sub>4</sub> oxidative dehydrogenation of propane to propene: some physical correlations with the catalytic activity, *Catalysis Letters* 10, 181-191.

Meunier, F. C., Yasmeen, A., and Ross, J. R. H., (1997) Oxidative dehydrogenation of propane over molybdenum-containing catalysts, *Catalysis Today* 37, 33-42.



- Mishakov, I. V., Vedyagin, A. A., Bedilo, A. F., Zaikovskii, V. I., and Klabunde, K. J., (2009) Aerogel VOx/MgO catalysts for oxidative dehydrogenation of propane, *Catalysis Today* 144, 278-284.
- Naraschewski, F. N., Praveen Kumar, C., Jentys, A., and Lercher, J. A., (2011) Phase formation and selective oxidation of propane over MoVTeNbOx catalysts with varying compositions, *Applied Catalysis A: General* 391, 63-69.
- Oshihara, K., Hisano, T., and Ueda, W., (2001) Catalytic oxidative activation of light alkanes over Mo–V-based oxides having controlled surface, *Topics in Catalysis* 15, 153-160.
- Panov, G. I., Dubkov, K. A., and Starokon, E. V., (2006) Active oxygen in selective oxidation catalysis, *Catalysis Today* 117, 148-155.
- Pereira, E. B., Pereira, M. M., Lam, Y. L., Perez, C. A. C., and Schmal, M., (2000) Synthesis and characterization of niobium oxide layers on silica and the interaction with nickel, *Applied Catalysis A: General* 197, 99-106.
- Periana, R. A., Bhalla, G., Tenn, W. J., Young, K. J. H., Liu, X. Y., Mironov, O., Jones, C. J., and Ziatdinov, V. R., (2004) Perspectives on some challenges and approaches for developing the next generation of selective, low temperature, oxidation catalysts for alkane hydroxylation based on the CH activation reaction, *Journal of Molecular Catalysis A: Chemical* 220, 7-25.
- Petkovic, L. M., Ginosar, D. M., Rollins, H. W., Burch, K. C., Pinhero, P. J., and Farrell, H. H., (2008) Pt/TiO<sub>2</sub> (rutile) catalysts for sulfuric acid decomposition in sulfur-based thermochemical water-splitting cycles, *Applied Catalysis A: General* 338, 27-36.
- Pless, J. D., Bardin, B. B., Kim, H.-S., Ko, D., Smith, M. T., Hammond, R. R., Stair, P. C., and Poepelmeier, K. R., (2004) Catalytic oxidative dehydrogenation of propane over Mg–V/Mo oxides, *Journal of Catalysis* 223, 419-431.
- Redhead, P. A., (1961) Chemisorption on polycrystalline tungsten. Part 1.- Carbon monoxide, *Transactions of the Faraday Society* 57, 641-656.

- Ribeiro, C., Vila, C., Milton Elias de Matos, J., Bettini, J., Longo, E., and Leite, E. R., (2007) Role of the Oriented Attachment Mechanism in the Phase Transformation of Oxide Nanocrystals, *Chemistry – A European Journal* 13, 5798-5803.
- Saadi, A., Merabti, R., Rassoul, Z., and Bettahar, M. M., (2006) Benzaldehyde hydrogenation over supported nickel catalysts, *Journal of Molecular Catalysis A: Chemical* 253, 79-85.
- Scherrer, P., (1918) Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen, *Göttinger Nachrichten Gesell* 26, 98-100.
- Sokolovskii, V. D., (1990) Principles of Oxidative Catalysis on Solid Oxides, *Catalysis Reviews* 32, 1-49.
- Stern, D. L., and Grasselli, R. K. 1997. Mechanistic aspects of propane oxidation over Ni-Co-molybdate catalysts. Pages 357-365 in R.K. Grasselli, STOAMG, and Lyons, JE, eds. *Studies in Surface Science and Catalysis*, vol. Volume 110 Elsevier.
- Stern, D. L., and Grasselli, R. K., (1997) Propane Oxydehydrogenation over Molybdate-Based Catalysts, *Journal of Catalysis* 167, 550-559.
- Sugiyama, S., Osaka, T., Ueno, Y., and Sotowa, K.-I., Oxidative Dehydrogenation of Propane over Vanadate Catalysts Supported on Calcium and Strontium Hydroxyapatites 2008 *Journal of the Japan Petroleum Institute*, pp. 50-57.
- Ueda, W., Vitry, D., Kato, T., Watanabe, N., and Endo, Y., (2006) Key aspects of crystalline Mo-V-O-based catalysts active in the selective oxidation of propane, *Research on Chemical Intermediates* 32, 217-233.
- Viparelli, P., Ciambelli, P., Lisi, L., Ruoppolo, G., Russo, G., and Volta, J. C., (1999) Oxidative dehydrogenation of propane over vanadium and niobium oxides supported catalysts, *Applied Catalysis A: General* 184, 291-301.
- Viswanathan, B., Sivasanker, S., and Ramaswamy, A. V., (2002) *Catalysis Principles and Applications*, Narosa Publishing House, India, pp. 207 - 217.

Yi, X. D., Sun, X. D., Zhang, X. B., Huang, C. J., Weng, W. Z., and Wan, H. L., (2009) Highly dispersed MoVTeNbO/SiO<sub>2</sub> catalysts prepared by the sol-gel method for selective oxidation of propane to acrolein, *Catalysis Communications* 10, 1591-1594.

Yoon, Y. S., Ueda, W., and Moro-oka, Y., (1995) Oxidative dehydrogenation of propane over magnesium molybdate catalysts, *Catalysis Letters* 35, 57-64.

Zhaorigetu, B., Li, W., Xu, H., and Kieffer, R., (2004) Correlation Between the Characteristics and Catalytic Performance of Ni-V-O Catalysts in Oxidative Dehydrogenation of Propane, *Catalysis Letters* 94, 125-129.

Zhu, B., Li, H., Yang, W., and Lin, L., (2004) Effects of reaction conditions on the selective oxidation of propane to acrylic acid on Mo-V-Te-Nb oxides, *Catalysis Today* 93-95, 229-234.

## PUBLICATION

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## SEMINARS / CONFERENCES ATTENDED

1. Feb 2012 - Young Catalysis Scientist Meeting at UPM.
2. November 2011, Oral presentation - The 24th Regional Symposium of Malaysian Analytical Sciences (SKAM-24) at One Helang Hotel, Kedah.
3. Aug 2011 - Envisioning the Research Enterprise-Random Thoughts of an Itinerant Chemist at UPM.
4. Mac 2011 - Step-by-Step Approach to Manuscript Writing and Publishing at UPM.
5. Mac 2011 - Elements of thesis writing at UPM.
6. June 2010 - Seminar on Bimetallic Catalysts for the Hydrogenation of Aromatics at UPM.
7. May 2010 - Energy issues and renewable from biomass/ wastes at UPM.
8. Apr 2010 - Chemical handling & safety in the lab with Merck at UPM.