I. SYNTHESIS, CHARACTERIZATION, AND BASE CATALYSIS OF NOVEL ZEOLITE SUPPORTED SUPER—BASIC MATERIALS

II.OXIDATIVE DEHYDROGENATION OF ETHANE OVER REDUCED HETEROPOLYANION CATALYSTS

Thesis by

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In Partial Fulfillment of the Requirements

for the degree of

Doctor of Philosophy

CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California

2005

(Defended May 27, 2005)

You make a living by what you earn. You make a life by what you give.

- Sir Winston Churchill

To the glory of God

ACKNOWLEDGEMENTS

I feel blessed to have spent five years at Caltech working with, and around, so many talented and unique individuals. The constant stream of discoveries coming from this small campus never fails to astound me. If you have a good idea, you can pursue it here, and you will find many people willing to help out in any way they can. So, as much as I would like to believe that I made it all on my own, there were numerous people supporting and encouraging me throughout my stay here. I will mention some of the more influential relationships I've made while pursuing my degree, but make no claim that this is a comprehensive list.

I feel particularly fortunate to have been able to work with my advisor Mark Davis. The unceasing stream of ideas produced by Mark is an inspiration and has allowed (and sometimes pushed!) me to learn about far more than zeolite supported base catalysis or the oxidative dehydrogenation of ethane. My experience here would not have been nearly as rich as it was without Mark's mentorship.

Another person who has been through all the projects and side-projects is Jay Labinger, also on my thesis committee. Jay is never lacking of a thoughtful question or quick and relevant insight into whatever problem or result is being discussed. Stacey Zones, another member of my committee also brings thoughtful advice and more than occasionally, a good laugh. I would also like to thank Rick Flagan for serving on my thesis committee after a rapid-fire introduction to my research.

John Bercaw served on my candidacy committee and swapped car stories with me. He even made it out to an autocross once to watch me make a fool of myself after adjusting some suspension settings. I must also thank the Bercaw lab for educating me in the use of very clean dry boxes.

If it were not for Brian Santora, a long since departed post-doctoral scholar in the lab, teaching me how to handle solid sodium and potassium I surely would have caught something on fire during my first few syntheses. Sonjong Wang of the solid state NMR lab was always willing to run a sample for me or help me to interpret NMR results.

My colleagues in the Davis lab have also been good friends, especially my officemate of the last two years Hyunjoo Lee who will go on to be great scientist wherever she ends up. I'll miss our conversations about life, relationships, and God during our ritualistic morning journey to the C-store for diet Coke or the Red Door for a cup of coffee. Alex Blanc, our recently departed French post-doctoral scholar, was extremely helpful in the synthesis of catalytic materials and a great pleasure to work with. Alex, Hyunjoo, and I found ourselves discussing topics from French music to the creation of the universe as a result of one of Alex's questions or remarks. I shared numerous discussions with Andrea Wight, now a proud mother or two working for Exxon-Mobil in Louisiana. John Murphy and his wife Kate swapped dinner parties and recipes with me and my wife, Niki. John always seemed to find that amusing website or article to share with the lab. No one has been able to fill the gap since his departure to Harvard for law school, although Steve Popielarski, Swaroop Mishra, and I have all tried. Jeremy Heidel, Derek Bartlett, and Dr. Siwen Hu were my chaperones to the mouse lab. Joe Holles and Chris Dillon introduced

me to the joy of taking data at a synchrotron and provided friendly banter while sharing an office with me in the first two years of my stay here.

Outside of the lab, it was always nice to visit Mike Roy in the machine shop and trade suspension tuning secrets and be tempted by the latest road racing time trial event. If it weren't for Mike, Rick Gerhart in the glass shop, and Tom Dunn in the electronics shop, none of my equipment would ever have continued working long enough for me to graduate. Mike even helped me fix and fabricate some car parts in the off-hours.

I gratefully acknowledge the sponsors of my research. The National Science Foundation Fellowship provided me support for the first three years of my work. A grant from BP-Amoco funded my research for the remaining two years.

I thank my parents, who have always believed in me and provided the best education they could have while I was young. I thank my wife Niki, who possesses an inspiring passion for life and who has stood by my side during all the best and the worst of times, all while pursuing her own PhD. Degree in the Asthagiri lab. Finally, I thank God, for without his blessings, none of this would have been possible.

ABSTRACT

This thesis is composed of two separate and unrelated projects. The first part of this thesis outlines an investigation into the synthesis and characterization of a novel zeolite supported super-base capable of carbon-carbon olefin addition to alkyl aromatics. A zeolite supported basic material capable of such reactions would benefit many fine chemical syntheses, as well as vastly improve the economics associated with production of the high performance thermoplastic polyester polyethylene naphthalate.

The thermal decomposition of alkali—metal azides impregnated in zeolite X is investigated as a novel route to the synthesis of a zeolite supported super-base. Impregnation of the alkali—metal azide precursor is shown to result in azide species occluded within the pores of the zeolite support by using high speed, solid-state ^{23}Na MAS and 2D MQMAS NMR, FTIR, and TGA characterization methods. Addition of alkali—metal azides to the zeolite results in redistribution of the extra-lattice cations in the zeolite framework. Thermal decomposition of impregnated azide species produces further cation redistribution, but no neutral metallic clusters are detected by high speed, solid-state ^{23}Na MAS NMR following thermal activation of the materials. Instead, it is possible that inactive ionic clusters are formed. The thermally activated materials do not promote base catalysis for the isomerization of 1-butene, the ethylation of toluene and *o*-xylene, and the alkenylation of *o*-xylene with 1,3-butadiene to produce 5-ortho-tolyl-pent-2-ene (5-OTP). The lack of catalytic activity in the materials is attributed to failure of the materials to form neutral metallic clusters during thermal treatment, possibly due to preferential formation of NMR silent ionic clusters. The formation of neutral metallic clusters is found to be

insensitive to synthesis technique and activation procedure. It is concluded that the impregnation of alkali—metal azides in zeolite X does not provide a reliable precursor for the formation of zeolite supported super-basic materials.

The second part of this thesis describes the oxidative dehydrogenation of ethane over partially reduced heteropolyanions. Niobium and pyridine exchanged salts of phosphomolybdic ($NbPMo_{12}Pyr$) and phosphovanadomolybdic ($NbPMo_{11}VPyr$) acids are investigated as catalyst precursors to prepare materials for catalyzing the oxidative dehydrogenation of ethane to ethylene and acetic acid at atmospheric pressure. The effects of feed composition, steam flow, temperature, and precursor composition on catalytic activity and selectivity are presented for both ethane and ethylene oxidation. Production of ethylene and acetic acid from ethane using the catalytic materials exceeds that reported in the literature for Mo-V-Nb-O_x systems under atmospheric or elevated pressure. Production of acetic acid from ethylene is also greater than that observed for Mo-V-Nb-O_x systems. Addition of vanadium reduces catalytic activity and selectivity to both ethylene and acetic acid while niobium is essential for the formation of acetic acid from ethane. Other metals such as antimony, iron, and gallium do not provide the same beneficial effect as niobium. Molybdenum in close proximity to niobium is the active site for ethane activation while niobium is directly involved in the transformation of ethylene to acetic acid. A balance of niobium and protonated pyridine is required to produce an active catalyst. Water is found to aid in desorption of acetic acid, thereby limiting deep oxidation to carbon oxides. A reaction scheme is proposed for the production of acetic acid from ethane over the catalytic materials.

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CHAPTER 1

INTRODUCTION AND ORGANIZATION OF THESIS PRESENTATION

The work presented in this thesis is the result of two separate and unrelated projects. Part I of this thesis outlines an investigation into the synthesis and characterization of a novel zeolite supported super-base capable of carbon-carbon olefin addition to alkyl aromatics. A zeolite supported basic material capable of such reactions would benefit many fine chemical syntheses, as well as vastly improve the economics associated with production of the high performance thermoplastic polyester polyethylene naphthalate. Although zeolites are well known for their acidic properties, their use as solid bases is much less widespread, despite the obvious advantages associated with solid versus homogenous base catalysis.

Chapter 2 presents a brief introduction to zeolites and their use in base catalysis. The utility of a zeolite supported super-basic material is described in the context of the industrially relevant reaction of *o*-xylene and 1,3-butadiene to produce 5-ortho-tolyl-pent-2-ene. The requirements associated with a super-basic solid catalyst and its synthesis are presented along with prior art supporting the use of alkali—metal azides as precursors to alkali—metal occluded zeolites. Finally, a strategy for the creation of a novel zeolite supported super-basic catalyst is presented.

Chapter 3 explores the experimental methods for occluding alkali—metals within zeolite X using alkali azide precursors. Synthesis conditions such as method of impregnation, activation technique, alkali—metal azide/alkali exchanged zeolite X pairing,

and reactive conditions are described. Characterization showing that the azides are easily occluded within the pores of zeolite X and reactivity results for base catalyzed reactions requiring weakly basic materials to very strongly basic materials are presented.

Chapter 4 provides a discussion of the results presented in Chapter 3. The results of base catalysis are analyzed and conclusions about the use of the alkali—metal azide system as a route to the reliable synthesis of a zeolite supported super-basic materials are made.

Part II of this thesis describes the use of partially reduced heteropolyanions for the oxidative dehydrogenation of ethane to ethylene and acetic acid in high yield at atmospheric pressure and moderate temperature. The syntheses of ethylene and acetic acid are usually performed in separate steps or at high pressures. Acetic acid is traditionally synthesized from partially oxygenated precursors such as ethylene, the supply of which is becoming increasing strained. Ethane, on the other hand, is easily obtainable. Thus, a catalyst capable of producing ethylene and acetic acid directly from ethane is extremely valuable.

Chapter 5 introduces the state of the art in ethane and ethylene oxidation to ethylene and acetic acid, respectively, and describes the utility of the heteropolyanion system for use in direct ethane oxidation to ethylene and acetic acid. A brief survey of heteropolyanions in oxidation catalysis is given, including previous work from this group.

Chapter 6 outlines the synthesis of the heteropolyanion materials and the results of their activity for the oxidation of ethane, ethylene and ethanol. The effects of catalyst composition, reaction temperature, oxygen to hydrocarbon feed ratio, and water on catalytic oxidation of ethane, ethylene, and ethanol are investigated in an effort to determine the nature of the active site on the catalysts.

Chapter 7 discusses the results of the reactivity data presented in Chapter 5. Conclusions and recommendations for further investigation into the active site of the catalyst are also discussed. Catalytic activity of the heteropolyanion system is compared with data presented in the literature for the most active ethane and ethylene oxidation catalysts. The active sites for ethane and ethylene oxidation are discussed and a reaction pathway for the oxidation of ethane to ethylene and acetic acid is presented based on the findings of this study.

Chapter 8 provides a summary of the work presented in Parts I and II. The results of Part I are summarized and followed by a discussion of the feasibility of using alkali—metal azide precursors for the synthesis of a zeolite supported super—basic catalyst. The reactivity data collected for the partial oxidation of ethane, ethylene, and ethanol in Part II are summarized. Conclusions and recommendations for the heteropolyanion systems are also discussed.