

VOC Catalytic Oxidation on Manganese Oxide

Catalysts Using Ozone

Corey Reed

Dissertation submitted to the faculty of Virginia Polytechnic Institute and
State University in partial fulfillment of the requirement for the degree of

Doctor of Philosophy

in

Chemical Engineering

S. Ted Oyama, Chairman

David F. Cox

Rick M. Davis

Brian E. Hanson

Preston L. Durrill

May 27, 2005

Blacksburg, Virginia

Keywords: Manganese, VOC, Acetone, Ozone, Catalyst, Raman, EXAFS, XANES,

Kinetics, Mechanism

VOC Catalytic Oxidation on Manganese Oxide

Catalysts Using Ozone

by

Corey Reed

Chemical Engineering

Abstract

This dissertation describes the current and common problem of removing low concentrations of pollutants known as volatile organic compounds (VOCs) from large volume gas emissions. Silica-supported manganese oxide catalysts with loadings of 3, 10, 15, and 20 wt. % (as MnO_2) were characterized using x-ray absorption spectroscopy and x-ray diffraction (XRD). The edge positions in the x-ray absorption spectra indicated that the oxidation state for the manganese decreased with increasing metal oxide loading from a value close to that of Mn_2O_3 (+3) to a value approximating that of Mn_3O_4 (+ $2\frac{2}{3}$). The XRD was consistent with these results as the diffractograms for the supported catalysts of higher manganese oxide loading matched those of a Mn_3O_4 reference. The reactivity of the silica-supported manganese oxide catalysts in acetone oxidation using ozone as an oxidant was studied over the temperature range of 300 to 600 K. Both oxygen and ozone produced mainly CO_2 as the product of oxidation, but in the case of ozone the reaction temperature and activation energy were significantly reduced. The effect of metal oxide loading was investigated, and the activity for acetone oxidation was greater for a 10 wt. % $\text{MnO}_x/\text{SiO}_2$ catalyst sample compared to a 3 wt. % $\text{MnO}_x/\text{SiO}_2$ sample. A detailed

mechanistic study of acetone oxidation using ozone was performed on a 10 wt. % silica-supported manganese oxide catalyst utilizing Raman spectroscopy, temperature programmed desorption (TPD), and kinetic measurements. *In situ* Raman spectroscopy at reaction conditions identified a band at 2930 cm^{-1} due to an adsorbed acetone species on the silica support and a band at 890 cm^{-1} due to an adsorbed peroxide species on the manganese oxide. A steady-state kinetic analysis, which varied acetone partial pressure (101 – 405 Pa), ozone partial pressure (101 – 1013 Pa), and temperature (318, 333, 343, and 373 K), was used to determine reaction rate expressions, while a transient kinetic study (318 K) was used to determine the role of the adsorbed species in the reaction mechanism. It was found that the rates of the acetone and ozone reactions were equally well described by both a power rate law and a Langmuir-Hinshelwood expression. The transient experiments showed that the rates of formation and reaction of the observed peroxide surface species did not correspond to the overall reaction rate, and it was concluded that it was not directly involved in the rate determining step of the reaction. A mechanism is proposed involving the reaction of an adsorbed acetone intermediate with an atomically adsorbed oxygen species via a dual site surface reaction to form complete oxidation products.

*To my wonderful family
for the amazing support you have always provided*

Acknowledgements

I would first like to express my gratitude to my advisor, Dr. S. Ted Oyama, for his guidance and support throughout my tenure at Virginia Tech. Not only has his influence been critical to my development as a research scientist, but he has afforded me other wonderful opportunities to grow in the areas of communication, administration, and leadership. I feel well equipped for the world ahead, and I thank Dr. Oyama for challenging and pushing me to get to this point. I would also like to thank the other committee members, Dr. Cox, Dr. Davis, and Dr. Hanson, for their help throughout this project.

I would like to express additional thanks to my final committee member, Dr. Durrill, who I first met on my initial recruiting visit to Radford University. From that meeting on, he has been the most influential person in my professional development. I want to express my deepest gratitude for being a wonderful professor, mentor, role model, and friend.

I would also like to thank each group member, past and present, that I have worked with during my time in the Environmental Catalysis and Nanomaterials Laboratory. I have learned something from every one of you, from science to culture, but most importantly, I have appreciated your friendship. Current group members include Yong-Kul Lee, Yan Xi, Pelin Hacarlioglu, Travis Gott, Hankwon Lim, Jason Gaudet, Haiyan Zhao, and Yunfeng Gu. Former group members include Viviane Schwartz, Lixiong Zhang, Wang-Jae Chun, Paige Hunter, Paul Clark, Rakesh Radhakrishnan, Xianqin Wang, Doo-Hwan Lee, Juan Bravo, Ben Cormier, Hiroyuki Imai, and Yuying Shu. I would like to give a special thanks to Yong-Kul Lee for his help in the x-ray

absorption fine structure experiments and analysis, Yan Xi for her contribution to the x-ray absorption fine structure and kinetics experiments, and Jason Gaudet for his aid in the oxygen chemisorption experiments. I would also like to thank Dr. Gibbs for his continuous aid and advice with various projects involving Gaussian calculations.

A big thank you goes to all the members of the Chemical Engineering Department Staff who make our lives easier on a daily basis. Specifically, I would like to thank Chris Moore, Diane Cannaday, Riley Chan, Michael Vaught, and Wendel Brown.

Finally, I would like thank my family for their support throughout this process and in every other endeavor for which I have partaken. I would like to show my sincerest gratitude to my parents, Jan and Kent Reed, my sister, Jenny Reed, and my grandmother, Doris Snider. My sister and I have been very fortunate to grow up in a family like the one we have, and I only hope that I can someday provide similarly for my children.

Table of Contents

Chapter 1

Introduction

| | | |
|-----|---|----|
| 1.1 | Background and Motivation | 1 |
| 1.2 | Reacting System | 3 |
| 1.3 | VOC Oxidation | 4 |
| 1.4 | Role of Adsorbed Intermediates in Reaction Kinetics and Mechanism | 7 |
| 1.5 | Objectives | 12 |

Chapter 2

Structure and Oxidation State of Silica-Supported Manganese Oxide Catalysts and Reactivity for Acetone Oxidation Using Ozone

| | | |
|-----|---|----|
| 2.1 | Introduction | 20 |
| 2.2 | Experimental Section | 21 |
| | 2.2.1 Materials | 21 |
| | 2.2.2 Characterization | 22 |
| | 2.2.3 Spectroscopic and Reactivity Measurements | 24 |
| 2.3 | Results and Discussion | 27 |
| | 2.3.1 TPR, Oxygen Chemisorption, Surface Area, and XRD Measurements | 27 |
| | 2.3.2 X-ray Absorption Fine Structure (XAFS) | 34 |
| | 2.3.3 Reactivity Studies | 46 |

| | | |
|-------|---|----|
| 2.3.4 | Laser Raman Spectroscopy | 56 |
| 2.4 | Relationship Between Structure and Reactivity | 61 |
| 2.5 | Conclusions | 63 |

Chapter 3

Distinguishing between Reaction Intermediates and Spectators: A Kinetic Study of Acetone Oxidation Using Ozone on a Silica-Supported Manganese Oxide Catalyst

| | | |
|-------|--|----|
| 3.1 | Introduction | 68 |
| 3.2 | Experimental Section | 69 |
| 3.2.1 | Materials | 69 |
| 3.2.2 | Spectroscopic and Kinetic Measurements | 69 |
| 3.2.3 | Temperature Programmed Desorption (TPD) Measurements | 72 |
| 3.3 | Results | 73 |
| 3.3.1 | Temperature Programmed Desorption (TPD) Measurements | 73 |
| 3.3.2 | Steady-State Raman Spectroscopy Measurements | 75 |
| 3.3.3 | Steady-State Kinetic Measurements | 81 |
| 3.3.4 | Transient Kinetic Measurements | 87 |
| 3.4 | Discussion | 93 |
| 3.4.1 | Acetone Oxidation With Ozone | 93 |
| 3.4.2 | Temperature Programmed Desorption (TPD) Measurements | 94 |
| 3.4.3 | Steady-State Raman Spectroscopy Measurements | 95 |
| 3.4.4 | Steady-State Kinetic Analysis | 99 |

| | | |
|-------|----------------------------|-----|
| 3.4.5 | Transient Kinetic Analysis | 112 |
| 3.5 | Conclusions | 118 |

Chapter 4

Conclusions and Recommendations for Future Work

| | | |
|-------|--------------------------------------|-----|
| 4.1 | Conclusions | 121 |
| 4.2 | Recommendations for Future Work | 124 |
| 4.2.1 | <i>Ab Initio</i> Calculations | 124 |
| 4.2.2 | Non-Uniform Surface Kinetic Analysis | 124 |
| 4.2.3 | Loading and Support Effects | 126 |

List of Tables

| | | |
|-------------------|--|----|
| Table 2.1 | Surface area, molecular oxygen chemisorption, and dispersion values for the catalyst series and pure silica. | 30 |
| Table 2.2. | X-ray diffraction data, particle size, and dispersion values for the 10 and 15 wt. % MnO _x /SiO ₂ catalysts. | 33 |
| Table 2.3. | Coordination numbers and bond lengths for the crystal structures of β-MnO ₂ , β-Mn ₂ O ₃ , and Mn ₃ O ₄ . | 37 |
| Table 2.4. | EXAFS curve-fitting results for MnO _x /SiO ₂ catalyst series. | 42 |
| Table 3.1. | Acetone and ozone surface area, molecular oxygen uptake, and TPD values for 10 wt. % MnO _x /SiO ₂ and pure SiO ₂ . | 74 |

| | | |
|-------------------|--|-----|
| Table 3.2. | Non-linear least squared regression results for the kinetic data utilizing the power rate law expressions. | 102 |
| Table 3.3. | Non-linear least squared regression results for the kinetic data utilizing the Langmuir-Hinshelwood expressions. | 111 |
| Table 3.4. | Steady-state and transient coverage comparison. | 118 |

List of Figures

| | | |
|--------------------|---|----|
| Figure 2.1. | <i>In situ</i> Laser Raman spectroscopy system. | 25 |
| Figure 2.2. | TPR traces for the MnO _x /SiO ₂ catalytic series. | 29 |
| Figure 2.3. | XRD results for the MnO _x /SiO ₂ catalytic series along with reference lines for Mn ₃ O ₄ . | 32 |
| Figure 2.4. | Crystal structure and unit cell for Mn ₃ O ₄ . | 35 |
| Figure 2.5. | Crystal structure and unit cell for β-Mn ₂ O ₃ . | 36 |
| Figure 2.6. | Crystal structure and unit cell for β-MnO ₂ . | 36 |
| Figure 2.7. | Simulated EXAFS spectra for β-MnO ₂ , β-Mn ₂ O ₃ , and Mn ₃ O ₄ using FEFF 8.2. | 38 |
| Figure 2.8. | Mn K-edge EXAFS spectra for the MnO _x /SiO ₂ catalytic series and the reference compounds MnO, Mn ₃ O ₄ , Mn ₂ O ₃ , and MnO ₂ a) in k ³ -weighted space and b) the corresponding Fourier transforms. | 40 |
| Figure 2.9. | Manganese oxide clusters formed with increased loading from a) 3 wt. % MnO _x /SiO ₂ to b) 10 wt. % MnO _x /SiO ₂ , and c) 15 and 20 wt. % MnO _x /SiO ₂ . | 43 |

- Figure 2.10.** a) Mn K-edge XANES spectra and E_0 values for the $\text{MnO}_x/\text{SiO}_2$ catalytic series and the reference compounds MnO , Mn_3O_4 , Mn_2O_3 , and MnO_2 and b) white line area analysis on the Mn K-edge XANES spectra for the $\text{MnO}_x/\text{SiO}_2$ catalytic series. 46
- Figure 2.11.** Acetone a) conversion and b) TOF versus temperature for 3 and 10 wt. % $\text{MnO}_x/\text{SiO}_2$ in the presence and absence of ozone (0.2 mol % acetone, 1 mol % O_3 , 34 mol % O_2 , 64.8 mol % He). 48
- Figure 2.12.** Ozone a) conversion and b) TOF versus temperature for 3 and 10 wt. % $\text{MnO}_x/\text{SiO}_2$ in the presence and absence of acetone (0.2 mol % acetone, 1 mol % O_3 , 34 mol % O_2 , 64.8 mol % He). 50
- Figure 2.13.** Arrhenius plots for acetone conversion over the a) 3 wt. % $\text{MnO}_x/\text{SiO}_2$ catalyst and b) the 10 wt. % $\text{MnO}_x/\text{SiO}_2$ catalyst for reactions with and without ozone (0.2 mol % acetone, 1 mol % O_3 , 34 mol % O_2 , 64.8 mol % He). 53
- Figure 2.14.** Arrhenius plots for ozone conversion over the a) 3 wt. % $\text{MnO}_x/\text{SiO}_2$ catalyst and b) the 10 wt. % $\text{MnO}_x/\text{SiO}_2$ catalyst for reactions with and without acetone (0.2 mol % acetone, 1 mol % O_3 , 34 mol % O_2 , 64.8 mol % He). 54
- Figure 2.15.** Raman spectra of the 10 wt. % $\text{MnO}_x/\text{SiO}_2$ exposed to different gas mixtures: a) O_2/He (35 mol % / 65 mol %), b) acetone/ O_2/He (0.2 mol % / 35 mol % / 64.8 mol %), c) $\text{O}_3/\text{O}_2/\text{He}$ (1 mol % / 34 mol % / 65 mol %), d) acetone/ $\text{O}_3/\text{O}_2/\text{He}$ (0.2 mol %, 1 mol %, 34 mol %, 64.8 mol %). 57

- Figure 2.16.** Effect of temperature on the Raman spectra for the 10 wt. % MnO_x/SiO₂ catalyst in acetone/O₂/He (0.2 mol % / 35 mol % / 64.8 mol %) flow. 60
- Figure 2.17.** Effect of temperature on the Raman spectra for the 10 wt. % MnO_x/SiO₂ catalyst in acetone/O₃/O₂/He (0.2 mol % / 1 mol % / 34 mol % / 64.8 mol %) flow. 61
- Figure 3.1.** Steady-state, *in situ* Raman spectroscopy results (298 K) for the a) 10 wt. % MnO_x/SiO₂ sample in acetone flow (0.2 mol %), b) 10 wt. % MnO_x/SiO₂ sample in acetone flow (0.4 mol %), c) pure SiO₂ in acetone flow (0.2 mol %), and d) pure SiO₂ in acetone flow (0.4 mol %). 76
- Figure 3.2.** Steady-state Raman spectra taken at 318 K when acetone partial pressure is varied and ozone partial pressure is constant at ~790 Pa. 78
- Figure 3.3.** Steady-state Raman spectra taken at 318 K when ozone partial pressure is varied and acetone partial pressure is constant at ~193 Pa. 79
- Figure 3.4.** Steady-state surface coverage values at 318 K for adsorbed acetone and ozone intermediates when acetone partial pressure is varied and ozone partial pressure is constant at ~790 Pa. 80
- Figure 3.5.** Steady-state surface coverage values at 318 K for adsorbed acetone and ozone intermediates when ozone partial pressure is varied and acetone partial pressure is constant at ~193 Pa. 81
- Figure 3.6.** Steady-state kinetic data for acetone TOF as a function of acetone partial pressure when the partial pressure of ozone is constant at ~790 Pa for the a) power rate law expression and b) Langmuir-Hinshelwood expression. 83

- Figure 3.7.** Steady-state kinetic data for acetone TOF as a function of ozone partial pressure when the partial pressure of acetone is constant at ~ 193 Pa for the a) power rate law expression and b) Langmuir-Hinshelwood expression. 84
- Figure 3.8.** Steady-state kinetic data for ozone TOF as a function of acetone partial pressure when the partial pressure of ozone is constant at ~ 790 Pa for the a) power rate law expression and b) Langmuir-Hinshelwood expression. 85
- Figure 3.9.** Steady-state kinetic data for ozone TOF as a function of ozone partial pressure when the partial pressure of acetone is constant at ~ 193 Pa for the a) power rate law expression and b) Langmuir-Hinshelwood expression. 86
- Figure 3.10.** Schematic depictions of transient experiments, which include a) acetone addition, b) acetone removal, c) ozone addition, and d) ozone removal. 87
- Figure 3.11.** Transient acetone addition results at 318 K showing coverage values for adsorbed acetone and ozone intermediates as a function of time; Inset shows the inlet partial pressure profiles used for the experiment. 89
- Figure 3.12.** Transient acetone removal results at 318 K showing coverage values for adsorbed acetone and ozone intermediates as a function of time; Inset shows the inlet partial pressure profiles used for the experiment 90
- Figure 3.13.** Transient ozone addition results at 318 K showing coverage values for adsorbed acetone and ozone intermediates as a function of time; Inset shows the inlet partial pressure profiles used for the experiment 91

- Figure 3.14.** Transient ozone removal results at 318 K showing coverage values for adsorbed acetone and ozone intermediates as a function of time; Inset shows the inlet partial pressure profiles used for the experiment 92
- Figure 3.15.** Transient kinetic analysis example for a) acetone addition and b) acetone removal. 114
- Figure 3.16.** Transient kinetic analysis results to determine steady-state coverages and rates for a) acetone and b) ozone. 116