Chapter 1

Introduction

1.1　General properties of ozone

Ozone is a chemical compound that has gained considerable attention in the past few years. Ozone occurs naturally in the stratosphere 15 to 50 km above the surface of the earth in concentrations of 1-10 ppm [1]. Ozone in the upper atmosphere is beneficial because it can absorb harmful ultraviolet radiation; however, ground level ozone is harmful and is responsible for nausea, headaches, and other respiratory problems in human beings. Ozone is a powerful oxidant and according to OSHA (Occupational Safety and Health Administration), the threshold level for allowable exposure of a human being is 0.1 ppm in 8 h.

Ozone is an allotropic form of oxygen. It is a pale blue gas at ambient conditions, which condenses into an indigo blue liquid at 161 K, and freezes to a deep blue-violet solid at 80.5 K. The structure of ozone can be viewed as a hybrid of resonance structures (Figure 1-1).
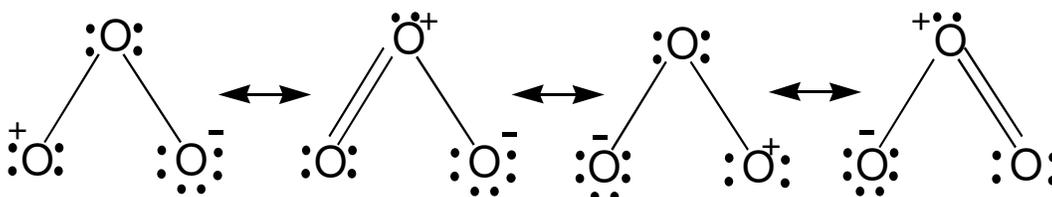

Figure 1-1. Resonance structure of ozone.

Ozone is thermodynamically unstable with a free energy of ΔG^0_{298} = -163 kJ mol^{-1}, and decomposes thermally to dioxygen with a heat of reaction of ΔH^0_{298} = -138 kJ mol^{-1} [2]. However, it is thermally stable up to 523 K so that catalysts are necessary to decompose it at lower temperatures [3].

1.2   Catalytic oxidation of VOCs using ozone

Catalytic oxidation is a promising method to control the emission of volatile organic compounds (VOCs), a class of airborne pollutants with harmful effects on human health and the environment. VOCs can be defined as organic compounds whose vapor pressures at room temperature are greater than 0.01 psia (0.0007 atm, 70 Pa). The U. S. Environmental Protection Agency defines VOCs as compounds of carbon that have high photochemical activity while excluding pure carbon, carbonate carbon, solid carbidic compounds in which the carbon is bonded to a metal, CO, and CO_2 [4]. The use of ozone as an alternative oxidant to perform complete oxidation in the catalytic oxidation of VOCs has been reported in the literature [5, 6, 7, 8]. Ozone has also been reported for the catalytic oxidation of gaseous reduced sulfur compounds [9]. Ozone is a strong oxidant with oxidizing power exceeded only by fluorine, the perxenate ion, atomic oxygen, OH radicals, and a few other such species [10].

Ozone has been found to be effective in reducing the conversion temperature for VOCs. This is important because for air pollution control it obviates the need for heating and then cooling large volumes of air. Naydenov et al. [11] studied the kinetics of complete oxidation of benzene over MnO_2 using ozone. They found that the decomposition of ozone and the oxidation of benzene occurred within the same temperature range (283-353 K) while the oxidation of benzene with oxygen took place at higher temperatures (> 433 K). They also found that the

apparent activation energy for ozone decomposition (32 kJ/mol) was similar to that of benzene oxidation using ozone (30 kJ/mol), and was lower than that of benzene oxidation using oxygen (88 kJ/mol). Oyama et al. [12] compared the catalytic oxidation of ethanol over supported molybdenum and manganese oxide catalysts and found a similar trend, with ethanol reacting with ozone at lower temperatures than with oxygen. For the case of a 10 wt % MnO_2/Al_2O_3 catalyst the activation energy for the reaction with ozone (3.7 kJ/mol) was lower than that with oxygen (89 kJ/mol) and occurred at low temperatures (< 400 K). For the case of a 9 wt % MoO_3/SiO_2 catalyst the activation energy for the reaction with ozone (10 kJ/mol) was similarly lower than that with oxygen (92 kJ/mol) and also occurred at low temperatures (< 523 K). A significant difference was found in the product distribution over the two catalysts, with carbon dioxide being the main product over the manganese oxide catalyst and acetaldehyde over the molybdenum oxide catalyst. Thus, the nature of the catalyst played a significant role in the reaction pathway. In another study Ragaini et al. [13] investigated the oxidation of VOCs with and without ozone over a barium promoted copper-chromite catalyst. They reported that styrene was more easily destroyed by the combined action of ozone and catalyst than without ozone. They also found that to convert styrene to a desired concentration (50 ppm) from the initial concentration (250 ppm), a lower temperature (< 388 K) was required in the presence of ozone than with oxygen (> 523 K).

1.3   Manganese oxide catalysts

Manganese oxide catalysts have been reported to be effective in catalytic combustion for the elimination of volatile organic compounds (VOCs) such as ethanol [7], benzene [11], acetone

3

[14, 15, 16, 17], methylethylketone [15] and C3 alcohols (1-propanol, 2-propanol, allyl alcohol) [18].

Manganese oxide was chosen as the catalyst in this study because it is a well-known complete oxidation catalyst for VOCs [19] and also an active catalyst for ozone decomposition [20]. Kim et al.[21] studied the complete oxidation reaction of toluene and found that Mn had the highest activity at lower temperatures (< 533 K) compared to Cu, Mo, Fe, V, Co, Ni, and Zn metals supported on γ-Al$_2$O$_3$. Mn oxide was reported to have a higher ozone decomposition rate than Co, Ni, Cr, Ag, Cu, Ce, Fe, V, and Mo oxides [20]. Previous work from our lab confirmed that manganese oxide was effective in the decomposition of ozone [7, 22, 23, 24].

Characterization and reactivity studies conducted on supported manganese catalysts have been reported in literature [25, 26, 27]. Buciuman et al. [25] studied γ-Al$_2$O$_3$ and SiO$_2$ supported manganese oxide catalysts using x-ray diffraction (XRD), Raman, and FTIR spectroscopies, and found that the predominant manganese oxide phases were β-MnO$_2$ and α-Mn$_2$O$_3$. Kepteijn et al [28, 29]. studied the precursor effect on the alumina-supported manganese oxide catalyst using XRD, temperature-programmed reduction (TPR), Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), and infrared (IR) spectroscopy. They found that to prepare manganese oxide catalyst from two different precursors resulted in significantly different supported manganese oxide phases, with Mn (III) and Mn (IV) oxides for the nitrate precursor and a highly dispersed Mn (III) oxide for the acetate precursor. The mechanism of ozone decomposition was also studied over alumina-supported manganese catalysts using *in situ* Raman spectroscopy [22, 24].

In this thesis the activity of the supported manganese oxide catalyst deposited on foam substrates during acetone oxidation reaction using ozone is studied. The investigation of the

4

structural properties of the manganese catalyst during ozone decomposition using an *in situ* x-ray adsorption spectroscopy is also described.

1.4   Objectives

The primary objectives of this thesis are to better understand the chemistry of ozone in the catalytic oxidation of acetone using manganese oxide catalysts, to characterize the catalysts, and to study the effect of the support on the catalyst during the ozone decomposition reaction. In order to achieve these objectives the following methodologies were used:

1. Synthesis of various manganese oxide catalysts with two different supports (Al_2O_3 and SiO_2) deposited on a reticulated foam substrates.

2. Application of XRD and EXAFS measurements to identify the structure of the foam supported catalysts.

3. Application of TPR (temperature-programmed reduction), oxygen chemisorption, and BET (Brunauer-Emmett-Teller) techniques to estimate the number of manganese active sites.

4. Testing of the activity of the foam supported manganese oxide catalysts in the acetone oxidation reaction using ozone.

5. Comparison of the effect of support on the ozone decomposition reaction using *in situ* XAS (x-ray absorption spectroscopy).

1.5   Organization

Chapter 1, "Introduction", describes the background, objectives, and organization of the thesis.

Chapter 2, "Acetone Oxidation Using Ozone on Manganese Oxide Catalysts", presents the preparation, characterization, and performance of the silica- and alumina-supported manganese oxide catalysts deposited on aluminum oxide foam substrates during the acetone oxidation reaction. A steady-state *in situ* Raman study on another powder manganese catalyst supported on higher surface area silica is also presented in this chapter.

Chapter 3, "*In Situ* X-ray Absorption Studies of Supported Manganese Oxide Catalyst During Ozone Decomposition", presents the study of the effect of the supports on the structure of the catalyst during the ozone decomposition reaction using *in situ* XAS measurements. The synthesis and characterization of the alumina- and silica-supported manganese catalysts with different loadings are also presented in this chapter.

Chapter 4, "Conclusions", presents the conclusions of this research.

References:

(1)   *Ulmann's Encyclopedia of Industrial Chemistry*, vol A 18, **1991,** 349.

(2)   R. H. Perry, D. Green, *Perry's Chemical Engineering's Handbook*, McGraw-Hill, New York, **1989**, 3.

(3)   F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, **1988**.

(4)   P. Hunter, S. T. Oyama, *Control of Volatile Organic Compound Emissions, Conventional and Emerging Technologies*, **2001**, John Wiley & Sons, New York.

(5)   A. Gervasini, G. C. Vezzoli, V. Ragaini, *Catal. Today*, **1996**, 29, 449.

(6)   A. Gervasini, C. L. Binachi, V. Ragaini, In *Environmental Catalysis*; J. N. Armor, Ed., ACS Symp. Ser. 552; ACS: Washington, DC, **1994**, 352.

(7)   W. Li, S. T. Oyama, In *Heterogeneous Hydrocarbon Oxidation*; B. K. Warren, S. T. Oyama, Eds., ACS Symp. Ser. 638; ACS: Washington, DC, **1996**, 364.

(8)   V. Ragaini, C. L. Bianchi, G. Forcella, A. Gervasini, In *Trends in Ecological Physical Chemistry*; Bonati, L., Ed., Elsevier: Amsterdam, **1993**, 275.

(9)   J. R. Kastrer, Q. Buqusi, R. Ganagavaram, K. C. Das, *Environ. Sci. Technol.*, **2005**, 39, 1835.

(10)   J. A. Wojtowicz, *"Ozone", In Kirk-Othmer Encyclopedia of Chemical Technology*, Fourth Ed., John Wiley & Sons: New York, **1996**, 953.

(11)   A. Naydenov, D. Mehandjiev, *Appl. Catal. A*, **1993**, 97, 17.

(12)   S. T. Oyama, W. Li, W. Zhang, *Stud. Surf. Sci. Catal.*, **1999**, 121, 105.

(13)   V. Ragaini, C. L. Bianchi, G. Forcella, A. Gervasini, *Trends in Ecological Physical Chemistry*, Milan, Italy, **1992**, 275.

(14) M. Paulis, L. M. Gandía, A. Gil, J. Sambeth, J. A. Odriozola, M. Montes, *Appl. Catal. B*, **2000**, 26, 37.

(15) L. M. Gandía, A. Gil, S. A. Korili, *Appl. Catal. B*, **2001**, 33, 1.

(16) M. Baldi, E. Finocchio, F. Milella, G. Busca, *Appl. Catal. B*, **1998**, 16, 43.

(17) A. Gil, N. Burgos, M. Paulis, M. Montes, L. M. Gandía, *Stud. in Surf. Sci. and Catal.*, **2000**, 130, 2153.

(18) M. Baldi, F. Milella, G. Ramis, V. S. Escribano, G. Busca, *Appl. Catal.*, **1998**, 166, 75.

(19) G. K. Borekov, In *J. R. Anderson*; M. B. Boudart, Ed., Catalysis Science and Technoloy, vol. 3, Springer: Berlin, **1982**, 39.

(20) B. Dhandapani, S. T. Oyama, *J. Appl. Catal. B*, **1997**, 11, 129.

(21) S. C. Kim, *J. Haz. Mater. B*., **2002**, 91, 285.

(22) R. Radhakrishnan, S. T. Oyama, J. G. Chen, K. Asakura, *J. Phys. Chem. B*, **200**1, 105, 4245.

(23) W. Li, G. V. Gibbs, S. T. Oyama, *J. Am. Chem. Soc.*, **1998**, 120, 9041.

(24) W. Li, S. T. Oyama, *J. Am. Chem. Soc.*, **1998**, 120, 9047.

(25) F. Buciuman, F. Patcas, R. Craciun, D. R. T. Zhan, *Phys Chem. Chem. Phys.*, **1999**, 1, 185.

(26) A. K. H. Nohman, *Monatshefte für Chemie*, **2004**, 135, 269.

(27) R. N. Nickolov, D. G. Stolova, K. T. Cheshkova, *J. Colloid and Interface Sci.*, **1999**, 212, 324.

(28) F. Kapteijn, A. D. Vanlangeveld, J. A. Moulijn, A. Andreini, M. A. Vuurman, A. M. Turek, J. M. Jehng, I. E. Wachs, *J. Catal.*, **1994**, 150, 94

(29) F. Kapteijn, L. Singoredjo, M. Vandriel, A. Andreini, J. A. Moulijn, G. Ramis, G. Busca, *J. Catal.*, **1994**, 150, 105.