Chapter 1

Introduction

1.1   Background and Motivation

This dissertation focuses on the widespread problem of removing low concentrations of volatile organic compounds from large volumes of air as in indoor ventilation systems. Volatile organic compounds (VOCs) represent a large class of substances that contribute to both indoor and outdoor air pollution. VOCs can be broadly defined as organic compounds that have a room temperature vapor pressure greater than 0.01 psia (0.0007 atm, 70 Pa). According to the U.S. EPA, VOCs are defined as compounds of carbon that have high photochemical activity but exclude elemental carbon, carbonate carbon, carbon monoxide, carbon dioxide, and compounds with metal-carbon bonds [1,2,3].

The damaging effects of VOCs are numerous, ranging from minor annoyances such as eyes, nose, and throat irritation, headaches, and nausea to serious dangers such as damage to the kidneys, liver, and central nervous system. Long-term exposure to some VOCs such as benzene is known to cause cancer [4]. Due to the possible dangers attributed to VOCs, tighter regulations have been enacted to control the emissions of these substances [5,6]. Many methods are currently used to control the release of VOCs. The ideal method is to reduce the amount of emissions leaving a point of origin, which

usually requires some type of improvement or redesign of the equipment or process. However, it is not always practical or even possible to eliminate all waste and pollution at the source. Therefore, other methods must be utilized to treat VOCs after they have been produced.

The various VOC control methods fall under three general categories. The first category involves the recovery of VOCs, and specific examples include condensation, adsorption, and absorption. The second category is made up of methods that utilize the conversion of wastes to less harmful products, and examples include biological and UV treatment. The third category involves combustion methods, and examples are thermal incineration, flaring, and catalytic incineration. Details of each of these methods can be found in several books that address the general subject of VOCs [1,2,7,8].

The applications of each of these methods depend on the nature of the VOC, concentration levels, and conditions (temperature, pressure, flow rate, etc.). For the problem addressed in this project involving large air streams contaminated with low concentrations of VOCs (< 500 ppm) such as found in indoor ventilation systems, there are specific problems with the general categories already discussed. Methods like condensation, adsorption, and absorption work best at high concentrations of VOCs and low flow rates. Methods such as biological and UV treatment are kinetically slow. Finally, the combustion methods like thermal incineration, flaring, and catalytic incineration are effective in removing high concentrations of VOCs from large volume gas emissions but are thermodynamically inefficient. They consume fuel and require large volumes of air to be heated in excess of 873 K and then cooled [9].

Therefore, this study focuses on an emerging technology that involves catalytic oxidation using ozone. Compared to the commonly used method of catalytic incineration to remove VOCs from waste gases [10], the use of ozone in the oxidation process allows for complete removal of VOCs at close to room temperature [11]. The lower reaction temperature results in considerable energy savings since the gas streams do not need to be significantly heated. One study even reported that the cost to catalytically oxidize VOCs using ozone was 1.5 times lower than the conventional catalytic incineration process [11].

1.2   Reacting System

Ozone (O_3) is an allotropic form of oxygen. It is a strong oxidizing agent with an oxidizing power that is exceeded only by fluorine, the perxenate ion, atomic oxygen, OH radicals, and a few other such species [12]. In the absence of ultraviolet radiation or catalyst, ozone decomposes very slowly up to 523 K ($250^{o}C$) [13]. Ozone is a very reactive species, which allows for catalytic oxidation reactions to be run at close to room temperature. Since VOCs are typically found at low concentrations (ten to hundred ppm levels) in large air streams, only a small amount of ozone is needed for their full conversion [2]. Considering that ozone can be produced at the low price of $ 1/lb [14,15], its use as the oxidizing agent in these reactions is cost effective.

The VOC used in this study was acetone. Acetone was chosen as the substrate because it is a common industrial solvent used, for example, to make paints, varnishes, resins, coatings, and polymers and because the health risks associated with acetone are similar to those of many other VOCs. Depending on the concentration levels of acetone,

the effects of breathing acetone range from minor irritation in the nose and throat to nausea and vomiting [16]. More importantly, however, acetone is interesting from a theoretical perspective due to its structural simplicity. The bonding of acetone with the metal sites located on catalyst surfaces is like that of compounds of similar molecular structure [17]. An understanding of the catalytic oxidation reaction of acetone with ozone can lead to valuable insight into the catalytic reactions of more complex compounds.

This study focuses on the reaction between acetone and ozone over a silica supported manganese oxide catalyst. Manganese oxide was the catalyst of choice for this study because it is a well-known complete oxidation catalyst [18] and is the most active transition metal oxide for VOC oxidation. In a study comparing the activity of Mn, Cu, Mo, Fe, V, Co, Ni, and Zn metals supported on γ-Al_2O_3, the Mn catalyst had the highest activity for temperatures below 533 K for the complete oxidation reaction of toluene (1000 ppm) with oxygen [5]. Previous work also showed manganese oxide to be an active catalyst for ozone decomposition [19], and this was confirmed by a study comparing different transition metal oxides, which showed that manganese oxide had a higher ozone decomposition rate than Co, Ni, Cr, Ag, Cu, Ce, Fe, V, and Mo oxides [20].

1.3 VOC Oxidation

There have been limited studies of acetone oxidation with molecular oxygen over manganese oxide catalysts, but the studies that have been made report high activity for manganese oxide in this reaction. One study used manganese nodules collected from the

Indian Ocean to test their activity in VOC oxidation reactions including acetone. These nodules were found to be very active catalysts, and complete oxidation was achieved for acetone at a temperature less than 573 K [21]. Another study on Mn_3O_4 showed that acetone conversion began as low as 473 K with selectivities to acetaldehyde and small amounts of acetic acid. However, in the temperature range of 510-563 K, higher acetone conversion values were achieved and only CO_2 was produced [22]. Catalytic acetone combustion studies were also performed over binary (α-Mn_2O_3) and ternary, perovskite-type ($SmMnO_3$) manganese oxides. In this study complete acetone conversion was achieved at 573 K for the single oxide compared to a lower temperature of 543 K for the perovskite-type oxide, with CO_2 and H_2O being the only reaction products formed. Activation energies were also reported for the complete oxidation of acetone over the single and perovskite-type manganese oxides with the values being 121 kJ/mol and 100 kJ/mol, respectively [23]. Enhanced activity for manganese oxide catalysts in acetone oxidation also have been reported when they were promoted with alkali metals [24] or when zirconia was used as a support [25]. Finally, a Fourier transform infrared spectroscopy (FTIR) study on Mn_3O_4 reported a molecularly adsorbed acetone species at 423 K [26].

There are also few studies that have looked at VOC catalytic oxidation using ozone, but these studies report enhanced oxidation in the presence of ozone. In two studies [27,28] that used bulk or supported manganese oxide as the catalyst, a dramatic decrease in activation energy was observed for the reaction using ozone compared to oxygen. In one study utilizing MnO_2 for the complete oxidation of benzene, the activation energy using ozone was reported to be 30 kJ/mol in the temperature range of

283 K to 353 K while the activation energy for the reaction using oxygen was 88 kJ/mol and required temperatures greater than 433 K [27]. Similarly, the activation energy for ethanol oxidation over MnO_2/Al_2O_3 using ozone was reported to be 3.7 kJ/mol for temperatures less than 400 K, while the activation energy for the reaction utilizing oxygen was 89 kJ/mol in the temperature range of 416 K to 526 K [28]. Silica-supported molybdenum oxide was also used to catalyze the ethanol oxidation reaction with ozone, and the same trends were observed. For temperatures less than 523 K, a low activation energy of 10 kJ/mol was observed when ozone was used as the oxidant while a high activation energy of 92 kJ/mol was observed for ethanol oxidation using oxygen alone over a temperature range of 475 K to 555 K [28]. An important finding in this study was that the main product from the ethanol oxidation reaction over molybdenum oxide was acetaldehyde with conversions ranging from 0 – 40 % while that for the reaction over manganese oxide was CO_2 with conversions ranging from 0 – 25 %. These results coincide with the known chemistry for both of these catalysts, as molybdenum oxide is known as a partial oxidation catalyst and manganese oxide as a complete oxidation catalyst [28]. Thus, the catalyst has an important role in controlling the reaction pathway.

In other reactions involving the catalytic oxidation of VOCs, ozone was found to increase oxidation at low temperatures but to have little effect at higher temperatures. A catalyst composed of a mixture of Co_3O_4 and MnO_2 was used in the complete oxidation of gas-phase n-heptane and n-octane [29]. Below 433 K, ozone enhanced the oxidation of the VOC, but above that temperature, its presence had no effect. In another study, the catalytic oxidation of methane with ozone was studied over Li/MgO, MgO, and γ-Al_2O_3 catalysts [30]. The same phenomenon was observed, where ozone was more effective

than oxygen at low temperatures (473-573 K) but had no effect at high temperatures (673 K). The one study that actually investigated the catalytic oxidation of acetone with ozone used a Ba-CuO-Cr$_2$O$_3$/Al$_2$O$_3$ catalyst and reported the same trends [31]. This study looked at the effect of temperature on the conversion of acetone (1,100 ppm) in the presence and absence of ozone at a space velocity of 20,000 h^{-1}. A dramatic increase in conversion was seen in reactions containing ozone compared to those without ozone for temperatures less than 373 K. However, ozone had no effect in the oxidation of acetone at temperatures greater than 473 K.

1.4 Role of Adsorbed Intermediates in Reaction Kinetics and Mechansim

Monitoring adsorbed intermediates on catalyst surfaces during reaction conditions is an effective means of elucidating mechanistic information for catalytic reactions [32]. However, proof that the observed surface species are true reaction intermediates is only infrequently provided. Such proof would include measurement of the rates of formation and consumption of the intermediates and confirmation that these rates were consistent with the overall reaction rate. This work carries out precisely such a quantitative comparison for the case of acetone oxidation with ozone on manganese oxide.

Many techniques have been employed to study surface intermediates. Notable among these are vibrational spectroscopies such as sum frequency generation (SFG), infrared spectroscopy (IR), and Raman spectroscopy, which provide direct molecular information. Sum frequency generation (SFG) was used to study the hydrogenation and dehydrogenation of cyclohexene on a Pt (111) surface [33]. A reaction mechanism was

proposed based on investigations of the nature of the adsorbed surface species and the reaction kinetics. Hydrogenation carried out for both 1,3- and 1,4- cyclohexadiene at 295 K showed that the 1,3-cyclohexadiene hydrogenated very fast with TOFs on the order of ~100 s^{-1} while 1,4-cyclohexadiene had a much lower rates of ~5 s^{-1}. Also, in the temperature range of 300 – 400 K, it was found that the surface concentration of the 1,4-cyclohexadiene was very low. This evidence suggested that in the temperature range of 300 – 400 K, the mechanism consisted of the hydrogenation of cyclohexene to cyclohexane through a 1,3-cyclohexadiene intermediate. At temperatures above 400 K, it was found that 1,3-cyclohexadiene was unstable on the Pt surface and either dehydrogenated to benzene or rearranged to 1,4-cyclohexadiene to continue the dehydrogenation path [33]. Another study [34] utilized reaction rate studies with SFG to determine molecular level information for the ethylene hydrogenation reaction on a Pt (111) surface. A TOF of ~5 s^{-1} was measured for the reaction of H$_2$ with C$_2$H$_4$ at 295 K, and three adsorbed species were identified to be ethylidyne, di-σ-bonded ethylene, and π-bonded ethylene. Previous work determined that the ethylidyne was not involved in the hydrogenation reaction and was a spectator species on the catalyst surface during reaction. When the reaction mixture was removed, the feature associated with the ethylidyne grew to saturation while the other two features disappeared. When the reaction mixture was turned back on, the ethylidye feature remained unchanged, the di-σ-bonded ethylene species did not appear, the π-bonded ethylene reappeared, and the TOF was consistent again at ~5 s^{-1}. Thus, it was concluded that the ethylidyne and the di-σ-bonded ethylene species competed for active sites, and hydrogenation occurred mainly through the π-bonded ethylene species [34].

Infrared spectroscopy is a common technique used to monitor adsorbed intermediates during catalytic reactions and gives direct molecular structure information. *In situ* Fourier transform infrared spectroscopy (FTIR) was used to study the oxidation of methanol over a MoO_3/SiO_2 catalyst [35,36]. The studies showed that the methanol formed mobile methoxide species on the silica support which migrated and reacted to form formaldehyde on the Mo centers. The silica support displayed non-innocent behavior [36], actively participating in the reaction by holding reactive intermediates. *In situ* FTIR was also used to study the reaction between CO and H_2 to form CH_4 on a Rh/Al_2O_3 catalyst at 220 K to investigate the evolution of adsorbed intermediates during reaction conditions [37]. The study, which focused on the quantity of adsorbed species and their reactivity towards hydrogenation, found that there were small concentrations of surface carbon species, CH_x, but large amounts of adsorbed CO species, which formed CH_4 during reaction. Also present on the Rh surface during reaction conditions were spectator C_xH_y species that increased with time but did not participate in the mechanism of methane formation. Other spectator species (formate and ionic carbonate) were found to adsorb on the alumina support. The rate of methane formation at 220 K was found to be primarily controlled by the dissociation of CO over the catalyst surface [37]. Another IR study [38] examined the decomposition of methanol over Cu/SiO_2, ZrO_2/SiO_2, and $Cu/ZrO_2/SiO_2$ catalysts to determine the mechanism of reaction. When the Cu/SiO_2 catalyst was exposed to methanol in the gas-phase, an adsorbed methoxide species was observed on both Cu and SiO_2 at 323 K. Further exposure to gas-phase methanol resulted in the formation of methyl formate, CO_2, and H_2. When methanol was removed from the reaction mixture, the adsorbed methoxide species on Cu dehydrogenated to form

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formaldehyde at 340 K, which was oxidized to a formate species at 373 K and was then decomposed to CO_2 and H_2 at 390 K. For the ZrO_2/SiO_2 catalyst, exposure to gas-phase methanol resulted in an adsorbed methoxide species formed on the zirconia and silica at 323 K. At 523 K, the methoxide species on the zirconia slowly decomposed. When Cu was added to the ZrO_2/SiO_2 catalyst, however, the adsorbed methoxide dehydrogenated to formaldehyde at 325 K, which was then oxidized at 373 K to form an adsorbed formate species on the zirconia. The formate then decomposed to CO, CO_2, and H_2 at 400 K. Thus, the decomposition of methanol over $Cu/ZrO_2/SiO_2$ took place mainly over the zirconia with the Cu being used solely to remove hydrogen.   In comparing the effectiveness of Cu/SiO_2 and $Cu/ZrO_2/SiO_2$ for methanol decomposition, methanol temperature program desorption (TPD) measurements were used. It was found that almost 6 times as much CH_2O and about 2 times as much CO_2 was formed using the $Cu/ZrO_2/SiO_2$ catalyst indicating it to be the most active for the decomposition reaction [38]. Finally, an *in situ* IR study [39] was combined with kinetic experiments to determine a mechanism and rate expression for the formation of propionaldehyde from the reaction of CO, H_2, and C_2H_4 over a 4 wt. % $Mn-Rh/SiO_2$ catalyst at 513 K. It was found that adding a Mn-O promoter to the Rh/SiO_2 catalyst resulted in drastic changes in reaction rate, transient response, and adsorbed C_2H_5CO coverages with the partial pressures of the reactants. A Langmuir-Hinshelwood-Hougen-Watson (LHHW) analysis, which included the assumption of a single rate-determining step, was used to determine a rate expression that fit the data well, but did not fit the coverage expression for the adsorbed acyl intermediates. It was found that the hydrogenation of adsorbed acyl intermediates and CO insertion were significant kinetic steps and was thus determined

that the changes in reaction rate and adsorbed C_2H_5CO coverage with the reactant partial pressure brought on by the Mn-O promoter were due to its effect on the rate-determining step [39].

Raman spectroscopy is also a useful technique in identifying surface intermediates during catalytic reactions. One study [40] used *in situ* Raman spectroscopy along with conventional kinetic experiments to determine mechanistic information about the decomposition of nitrous oxide over a 14 mol % BaO on MgO (Ba/MgO) catalyst. Specifically, Raman spectroscopy was used to investigate the role of adsorbed peroxide ions that have been identified as known intermediates for the reaction. According to the general mechanism for alkaline earth oxides, the first step involves the decomposition of N_2O on oxide ions to form gaseous nitrogen and a peroxide intermediate. Two peroxide species then react in the second step of the mechanism to yield molecular oxygen and regenerate the surface oxide ions. However, when barium oxide supported on magnesium was used as the catalyst, the second step can occur in reverse with molecular oxygen reacting with BaO to form peroxide ions. Thus, peroxide ions were formed from both the decomposition of N_2O and from the reverse reaction of the second step. From this, it can be inferred that peroxide ions serve as both an intermediate and a poison when the BaO/MgO catalyst is used [40].

The previous studies show examples where adsorbed intermediates were identified during reaction conditions to help provide mechanistic information for catalytic reactions. The present work will focus on the oxidation of acetone using ozone. As will be seen, adsorbed surface species observed by Raman spectroscopy respond to reaction conditions in a manner resembling the reaction intermediates. However, transient

experiments show that these species do not respond at rates consistent with the overall reaction rate and therefore, are not the principal reactive intermediates. This work is important because it highlights the need to carry out dynamic experiments to prove that spectroscopically observed species are involved in a mechanism.

To the knowledge of the authors, there has not been a study of the mechanism and kinetics of the oxidation of acetone by ozone over a manganese oxide catalyst. Previous work [41,42] looked at the kinetics and mechanism for ozone decomposition over manganese oxide and will be discussed later. An understanding of this mechanism is important for the present study because ozone decomposition proceeds simultaneously with acetone oxidation. The kinetics for the ozone decomposition reaction used steady-state measurements that were confirmed by transient measurements [42]. This technique was first used to derive kinetic information for the ammonia decomposition reaction on tungsten [43], and the technique can be called the Tamaru Method, after its originator.

1.5   Objectives

This study concentrates on the oxidation reaction between acetone and ozone over a silica-supported manganese oxide catalyst. The primary objectives of this work are listed below.

- Synthesize a series of silica-supported manganese oxide catalysts of different loading

- Characterize the catalyst series using Brunauer-Emmett-Teller (BET), temperature programmed reduction (TPR), and atomic oxygen chemisorption to

determine the surface areas, active site densities, and dispersions for the catalysts of different metal oxide loading.

- Characterize the catalyst series using x-ray diffraction (XRD) to determine information on the crystallinity and particle size of the catalyst materials.

- Characterize the catalyst series using x-ray absorption fine structure (XAFS) to investigate the catalysts' oxidation state and provide structural information such as bond distances and coordination numbers.

- Utilize Raman spectroscopy measurements to identify adsorbed interemediates on the catalyst surface during the course of the reaction.

- Measure the reactivity of the catalyst for the reaction of acetone with both ozone and oxygen. Relate the structure of the catalyst to its reactivity for the reaction.

- Perform a detailed steady-state kinetic experiment to determine rates of reaction for both acetone and ozone conversion on the catalyst surface. Use both a power rate law and Langmuir-Hinshelwood model to fit the data and determined kinetic parameters.

- Propose a verifiable reaction mechanism for the catalytic reaction between acetone and ozone. The Langmuire-Hinshelwood rate expressions are derived from this mechanism.

- Perform Raman spectroscopy experiments using the same conditions as the kinetic study to determine adsorbate coverages. The signal intensity will be calibrated by measuring the desorption amounts in temperature programmed desorption (TPD) experiments. Determinations at both steady-state and transient conditions will be made.

- Compare steady-state coverages determined by both transient and steady-state experiments to validate the role of adsorbed intermediates in the reaction mechanism.

References

1   N. de Nevers, "Air Pollution Control Engineering," McGraw-Hill: New York, 1995.

2   P. Hunter, S. T. Oyama, "Control of Volatile Organic Compound Emissions, Conventional and Emerging Technologies," John Wiley & Sons: New York, 2000.

3   R. G. Derwent, in: R. E. Hester, R. M. Harrison (Eds.), "Volatile Organic Compounds in the Atmosphere," The Royal Society of Chemistry, 1995.

4   http://www.epa.gov/iaq/voc.html

5   S. C. Kim, The catalytic oxidation of aromatic hydrocarbons over supported metal oxide, *J. Haz. Mater. B*, **2002**, 91, 285

6   J. J. Santoleri, D. L. Corwin, J. J. Sudnick, Air toxics emissions control: application and design, Air & Waste Mangement Assocation, 87th Annual Meeting & Exhibition, Cincinnati, OH, 1994, 1.

7   H.J. Rafson (Ed.), "Odor and VOC Control Handbook," McGraw-Hill: New York, 1998.

8   R. M. Heck, R. J. Farrauto, "Catalytic Air Pollution Control," Van Nostrand Reinhold: New York, 1995.

9   A. Gervasini, G. C. Vezzoli, V. Ragaini, VOC removal by synergic effect of combustion catalyst and ozone, *Catal. Today*, **1996**, 29, 449.

10 C. A. Clausen, C. D. Cooper, M. Hewett, A. Martinez, Enhancement of organic vapor incineration by using ozone, *J. Haz. Mater.*, **1992**, 31, 75.

11 D. V. Maksudov, F. R. Ismagilov, I. Kh. Khairulin, S. R. Khairulin, Z. R. Ismagilov, Study of ozone generation in the bed of heterogeneous catalysis of various geometry, *Eurasian Chem.-Technol. J.*, **2002**, 4, 271.

12 J. A. Wojtowicz, "Ozone," in *Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Ed.*, John Wiley & Sons: New York, 1996, pp. 953.

13 F. A. Cotton, G. Wilkinson, "Advanced Inorganic Chemistry, Fifth Ed.," John Wiley & Sons: New York, 1988, pp. 452.

14 E. Merz, F. Gaia, Comparison of economics of various ozone generation systems, *Ozone Sci. Eng.*, **1990**, 12, 401.

15 A. Shadiakhy, D. Blankenfeld, Potable water treatment with ozone of high concentration, *Water Supply*, **1995**, 13, 231.

16 http://www.ccohs.ca/oshanswers/chemicals/chem_profiles/acetone/basic_ace.html

17 W. S. Sim, D. A. King, Mechanism of Acetone Oxidation on Ag{111}-p(4 × 4)-O, *J. Phys. Chem.*, **1996**, 100, 14794.

18 G. K. Boreskov, in: J. R. Anderson, M. B. Boudart (Eds.), "Catalysis Science and Technology, Vol. 3," Springer: Berlin, 1982, p 39.

19 B. Dhandapani, S. T. Oyama, Kinetics and mechanism of ozone decomposition on a manganese oxide catalyst, *Chem. Lett.*, **1995**, 6, 413.

20 B. Dhandapani, S. T. Oyama, Gas phase ozone decomposition catalaysts, *Appl. Catal.B: Env.*, **1997**, 11, 129.

21 K. M. Parida, A. Samal, Catalytic combustion of volatile organic compounds on Indian Ocean manganese nodules, *Appl. Catal. A: Gen.*, **1999**, 182, 249.

22 M. Baldi, E. Finocchio, F. Milella, G. Busca, Catalytic combustion of C3 hydrocarbons and oxygenates over Mn_3O_4, *Appl. Catal. B: Env*., **1998**, 16, 43.

23 A. Gil, N. Burgos, M. Paulis, M. Montes, L. M. Gandia, Activity and stability of single and perovskite-type manganese and cobalt oxides in the catalytic combustion of acetone, *Stud. Surf. Sci. Catal.*, **2000**, 130, 2153.

24 L. M. Gandia, A. Gil, S. A. Korili, Effects of various alkali-acid additives on the activity of a manganese oxide in the catalytic combustion of ketones, *Appl. Catal. B. Env*., **2001**, 33, 1.

25 L. M. Gandia, M. A. Vicente, A. Gil, Complete oxidation of acetone over manganese oxide catalysts supported on alumina- and zirconia-pillared clays, *Appl. Catal. B. Env*., **2002**, 38, 295.

26 M. Baldi, F. Milella, G. Ramis, V. Sanshez Escribano, G. Busca, An FT-IR and flow reactor study of the selective catalytic oxy-dehydrogenation of C3 alcohols on Mn_3O_4, *Appl. Catal. A: Gen*., **1998**, 166, 75.

27 A. Naydenov, D. Mehandjiev, Complete oxidation of benzene on manganese dioxide by ozone, *Appl. Catal. A: Gen*., **1993**, 97, 17.

28 S. T. Oyama, W. Li, W. Zhang, in: H. Hattori, K. Otsuka (Eds.), A comparative study of ethanol oxidation with ozone on supported molybdenum and manganese oxide catalysts, "Science and Technology in Catalysis 1998," (Studies in Surface Science and Catalysis, Vol. 121), Elsevier: Tokyo, 1999, 105.

29 K. Hauffe, Y. Ishikawa, Catalytic oxidation of hydrocarbons in the presence of ozone, *Chem. Ing. Techn*., **1974**, 46, 1053.

30 G. J. Hutchings, M. S. Scurrell, J. R. Woodhouse, in: D. M. Bibby, C. D. Chang, R. F. Howe, S. Yurchak (Eds.), Effect of O_3 versus O_2 as oxidants for methane, "Methane Conversion," (Studies in Surface Science and Catalysis, Vol. 36), Elsevier Science Publishers B. V.: Amsterdam, 1988, 415.

31 A. Gervasini, C. L. Bianchi, V. Ragaini, in: J. N. Armor (Ed.), Low-temperature catalytic combustion of volatile organic compounds using ozone, "Environmental Catalysis," ACS Symposium Series No. 552, American Chemical Society: Washington, D. C., 1994, 353-369.

32 S. T. Oyama, W. Li, Absolute determination of reaction mechanisms by in situ measurements of reaction intermediates, *Top. Catal*., **1999**, 8, 75.

33 X. Su, K. Y. Kung, J. Lahtinen, Y. R. Shen, G. A. Somorjai, 1,3- and 1,4-cyclohexadiene reaction intermediates in cyclohexene hydrogentation and dehyrogentation on Pt(111) crystal surface: a combined reaction kinetics and surface vibrational spectroscopy study using sum frequency generation, *J. Mol. Catal. A: Chem*., **1999**, 141, 9.

34 P. S. Cremer, G. A. Somorjai, Surface science and catalysis of ethylene hydrogenation, *J. Chem. Soc. Faraday Trans*., **1995**, 91, 3671.

35 M. Seman, J. N. Kondo, K. Domen, C. Reed, S. T. Oyama, Direct observation of surface intermediates formed by selective oxidation of alcohols on silica-supported molybdenum oxide, *J. Phys. Chem. B*, **2004**, 108, 3231.

36   S. T. Oyama, R. Radhakrishnan, M. Seman, J. N. Kondo, K. Domen, K. Asakura, Control of reactivity in C-H bond breaking reactions on oxide catalysts: methanol oxidation on supported molybdenum oxide, *J. Phys. Chem. B*, **2003**, 107, 1845.

37   A. M. Efstathiou, T. Chafik, D. Bianchi, C. O Bennett, A transient kinetic study of the CO/H$_2$ reaction on Rh/Al$_2$O$_3$ using FTIR and mass spectroscopy, *J. Catal*., **1994**, 148, 224.

38   I. A. Fisher, A. T. Bell, A mechanistic study of methanol decomposition over Cu/SiO$_2$, ZrO$_2$/SiO$_2$, and Cu/ZrO$_2$/SiO$_2$, *J. Catal*., **1999**, 184, 357.

39   M. A. Brundage, M. W. Balakos, S. S. C. Chuang, LHHW and PSSA kinetic analysis of rates and adsorbate coverages in CO/H$_2$/C$_2$H$_4$ reactions on Mn-Rh/SiO$_2$, *J. Catal*., **1998**, 173, 122.

40   S. Xie, J. H. Lunsford, A catalytic and in situ Raman spectroscopy study of nitrous oxide decomposition over barium oxide supported on manganese oxide, *Appl. Catal. A.*, **1999**, 188, 137.

41   W. Li, S. T. Oyama, Mechanism of ozone decomposition on a manganese oxide catalyst. 1. In situ Raman spectroscopy and ab initio molecular orbital calculations, *J. Am. Chem. Soc*., **1998**, 120, 9041.

42   W. Li, S. T. Oyama, Mechanism of ozone decomposition on a mangense oxide catalyst. 2. Steady-state and transient kinetic studies, *J. Am. Chem. Soc.*, **1998**, 120, 9047.

43   H. Shindo, C. Egawa, T. Onishi, K. Tamaru, Reaction mechanism of ammonia decomposition on tungsten, *J. C. S. Faraday I*, **1980**, 76, 280.