# Ozone Decomposition over Manganese Oxide Supported on ZrO<sub>2</sub> and TiO<sub>2</sub>: A Kinetic Study Using *in Situ* Laser Raman Spectroscopy

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Ozone decomposition on ZrO<sub>2</sub>- and TiO<sub>2</sub>-supported manganese oxide was studied using in situ laser Raman spectroscopy along with simultaneous steady-state kinetic measurements. The Raman spectra showed the presence of an adsorbed peroxide species for both catalysts under reaction conditions. The experimental data were well represented by a nonuniform surface kinetic treatment that assumed that the activation energies of adsorption and desorption were linear functions of the surface coverage of the peroxide species. Steady-state reaction rates were monitored for varying ozone partial pressure (0.6-3 kPa) and temperature (293-343 K). The reaction order with respect to ozone partial pressure for the ZrO<sub>2</sub>-supported sample was 0.98 and that for the TiO<sub>2</sub>-supported sample was 0.85. At zero surface coverage of the peroxide species, the activation energy for adsorption was 6 and 7 kJ/mol for the ZrO<sub>2</sub>- and TiO<sub>2</sub>-supported catalysts, respectively. The activation energies for desorption at zero coverage were 62 and 44 kJ/mol, respectively, for the same catalysts. The difference in ozone decomposition activity for the catalysts was primarily due to the difference in desorption kinetic parameters. © 2001 Academic Press

*Key Words:* ozone; manganese oxide; kinetics; nonuniform surface; laser Raman.

# INTRODUCTION

Ozone is a toxic environmental pollutant and its abatement at ground level is important for protecting plant and animal life. Several academic studies and patents have reported on the development and testing of ozone decomposition catalysts (1-4) and many of these have identified manganese oxide as an excellent catalyst for ozone elimination. Manganese oxides have also found use in catalyzing a variety of oxidation (5-10) and reduction reactions (11-13). The chemical and catalytic properties of ozone are described in a recent book (14).

This paper presents a study of ozone decomposition on manganese oxide supported on  $TiO_2$  and  $ZrO_2$  using *in situ* laser Raman spectroscopy to quantify reaction intermedi-

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ates on the surface of the working catalysts. This follows recent work done in our laboratory (1, 2) on the mechanism and reaction kinetics for ozone decomposition on manganese oxide supported on  $Al_2O_3$ . The present study confirms the presence of an adsorbed peroxide species on the surface of the two new catalysts and the applicability of the earlier proposed kinetics. The result is a set of kinetic parameters that are compared to those obtained in the previous work and which help explain ozone decomposition activity differences for the various manganese oxide catalysts.

The detection of an adsorbed peroxide species on the catalyst surface by Raman spectroscopy was critical in obtaining coverage data which were used in the analysis. Raman spectroscopy is a powerful technique that has been widely used in heterogeneous catalysis (15). In situ Raman spectroscopy has emerged as a useful method for studying catalyst structure changes and adsorbed reaction intermediates (16-18). The information provided by these studies combined with kinetic measurements can be utilized to determine reaction mechanisms (19). Raman spectroscopy has been used to study several transition metal oxide systems. Among the materials that commonly appear in the literature are supported oxides of Mo (20, 21), V (15, 22), Cr (23), Nb (24), W (25), and Re (26). There have been very few Raman studies which present spectra for supported manganese oxide (1, 5, 27, 28). These studies have concentrated on manganese oxide supported on alumina (1, 5, 27, 28) or silica (28). Adsorption of ozone at low temperatures (77 K) has been studied earlier for ZrO<sub>2</sub> (29) and TiO<sub>2</sub> (30) substrates using infrared spectroscopy.

# EXPERIMENTAL

*Catalyst preparation and characterization.* Supported manganese oxide catalysts (3 wt%) were prepared by impregnating ZrO<sub>2</sub> (Degussa, VP ZrO<sub>2</sub>,  $S_g = 50 \text{ m}^2 \text{ g}^{-1}$ ) and TiO<sub>2</sub> (Degussa, Titanoxid P25,  $S_g = 50 \text{ m}^2 \text{ g}^{-1}$ ) with aqueous



solutions of manganese acetate  $(Mn(CH_3COO)_2 \cdot 4H_2O, Aldrich, >99.99\%)$  to the point of incipient wetness. For example, 1.69 g of manganese acetate was dissolved in 4 cm<sup>3</sup> of distilled water and this solution was added dropwise to 20 g of ZrO<sub>2</sub>. After impregnation, the sample was heated at 393 K for 6 h and calcined at 773 K for 6 h to produce 3 wt% MnO<sub>x</sub>/ZrO<sub>2</sub>. A similar method was used to prepare 3 wt% MnO<sub>x</sub>/TiO<sub>2</sub>.

The total number of metal oxide sites on the surface of the catalysts was estimated through the temperatureprogrammed desorption (TPD) of oxygen. A detailed description of the experiment can be found elsewhere (31). Briefly, the procedure involved pretreatment of the catalyst at 773 K in oxygen flow followed by the introduction of a 2 mol% ozone/oxygen mixture at 233 K for 2 h. Subsequently, the catalyst was heated in helium flow at 0.17 K/s to 1173 K while monitoring the m/e signals at 16, 32, and 48 corresponding to the possibly desorbing molecular oxygen species. Desorption/decomposition peaks for molecular oxygen were detected and these were quantified through calibration pulses of to determine the amount of oxygen adsorbed per gram of catalyst. This value was used as the corresponding site density (sites per gram of catalyst) for turnover rate calculations. X-ray diffraction (XRD) patterns were acquired on a powder diffractometer (Scintag, Model ASC0007) with a Cu  $K_{\alpha}$  monochromatized radiation source (45 kV and 40 mA).

In situ Raman spectroscopy. Details about the experimental setup for the *in situ* Raman spectroscopy system can be found elsewhere (1). Briefly, the system used an argon ion laser (514.5 nm, Spex Lexel 95) as a light source, a holographic notch filter (Kaiser, Super Notch Plus) for removing Rayleigh scattering, a single-stage monochromator (Spex, 500 M) for light dispersion, and a CCD detector (Spex, Spectrum One) for spectral acquisition. The laser was operated at 200 mW and the detector slit width was set at 100  $\mu$ m. The resolution of the Raman spectrometer was 6 cm<sup>-1</sup>. The samples were in the form of thin wafers held at the end of a rotating cylinder (1500 rpm) in a Suprasil quartz *in situ* cell. Heating was carried out using heating tape around the samples. Cooling of the samples was achieved by passing chilled water through Teflon tubing wrapped around the cell.

Steady-state kinetic studies. A low volume sample cell (volume  $<25 \text{ cm}^3$ ) allowed effective investigation of surface reactions under varying pressure and temperature conditions. The temperature of the sample was monitored through a thermocouple placed 3 mm from the sample in a thermocouple well. The sample (0.3 g) was pressed into a thin cylindrical wafer with a diameter of about 15 mm and a thickness of 1 mm, which was rotated at approximately 1500 rpm to prevent local overheating due to the laser. The wafer was pretreated in flowing oxygen (Airco, >99.6%) at 773 K for 2 h. Ozone was generated

by passing filtered oxygen through a high-voltage silentdischarge ozone generator (OREC, V5–0). The total pressure in the system was maintained at 101 kPa and the generated ozone/oxygen mixture was introduced into the cell with ozone partial pressures varying from 0.4 to 3 kPa. The reaction temperature was varied from 293 to 340 K and the flow rate of the ozone/oxygen mixture was maintained at 744  $\mu$ mol s<sup>-1</sup> (1000 cm<sup>3</sup> min<sup>-1</sup>). The inlet and outlet ozone concentrations were monitored using a UV absorption-type ozone analyzer (IN-USA, AFX-H1). Steady-state turnover rates were based on ozone conversions and the number of Mn active sites calculated from the ozone desorption experiments, using the expression, rate = (conversion × flow rate) × (ozone concentration)/number of sites.

#### RESULTS

# **TPD** Traces

The TPD traces for molecular oxygen (m/e=32) from the ZrO<sub>2</sub>-supported manganese oxide are shown in Fig. 1. In no case was ozone (m/e=48) observed. The traces for the support ZrO<sub>2</sub> without ozone adsorption reveals no desorption/decomposition peak (Fig. 1a). However, when



FIG. 1. Oxygen (m/e=32) TPD trace for ZrO<sub>2</sub>-supported manganese oxide: (a) ZrO<sub>2</sub> without ozone adsorption; (b) ZrO<sub>2</sub> after ozone adsorption at 233 K; (c) Mn/ZrO<sub>2</sub> without ozone adsorption; (d) Mn/ZrO<sub>2</sub> with ozone adsorption at 233 K.



**FIG. 2.** Oxygen (m/e = 32) TPD trace for TiO<sub>2</sub>-supported manganese oxide: (a) TiO<sub>2</sub> without ozone adsorption; (b) TiO<sub>2</sub> after ozone adsorption at 233 K; (c) Mn/TiO<sub>2</sub> without ozone adsorption; (d) Mn/TiO<sub>2</sub> with ozone adsorption at 233 K.

ozone is adsorbed on the surface of  $ZrO_2$ , a desorption/decomposition peak at 532 K is observed (Fig. 1b). In the case of  $ZrO_2$ -supported manganese oxide, the trace without ozone adsorption (Fig. 1c) reveals a strong feature at 775 K and weaker features at 560, 790, and 1050 K. Adsorption of ozone on the catalyst surface at 233 K results in a TPD trace (Fig. 1d) which shows strong features at 370, 410, 549, and 780 K and weak features at 790 and 1060 K.

The corresponding oxygen (m/e=32) TPD traces for the TiO<sub>2</sub>-supported manganese oxide are shown in Fig. 2. The traces for the TiO<sub>2</sub> support (Figs. 2a, 2b) with and without ozone adsorption contain no desorption/decomposition peak. The TiO<sub>2</sub>-supported manganese oxide without any ozone adsorption (Fig. 2c) produces desorption/ decomposition peaks at 770, 836, and 1005 K. The catalyst with ozone adsorption at 233 K (Fig. 2d) shows desorption/ decomposition features at 378, 830, and 995 K.

# In Situ Laser Raman Spectra

Figure 3 shows the Raman spectra at room temperature (293 K) for manganese oxide on  $ZrO_2$ , under both oxygen flow and ozone/oxygen flow. Under oxygen flow (Fig. 3a), there were peaks at 336, 383, 470, 552, and 626 cm<sup>-1</sup>. The introduction of ozone (Fig. 3b) resulted in the appearance of a very intense peak at 880 cm<sup>-1</sup> along with a shoulder



**FIG. 3.** *In situ* Raman spectra of  $ZrO_2$ -supported manganese oxide: (a) in oxygen; (b) in 2 mol% ozone/oxygen mixture. Reactant flow = 1000 cm<sup>3</sup> min<sup>-1</sup> at room temperature. Spectrum acquisitions conditions (Figs. 1 and 2): laser power = 200 mW, resolution = 6 cm<sup>-1</sup>, exposure time = 60 s, n = 60 scans

feature at 852 cm<sup>-1</sup> and a broad band at 930 cm<sup>-1</sup>. This peak at 880 cm<sup>-1</sup> was accompanied by two overtone peaks at 1754 and 2615 cm<sup>-1</sup> (not shown). All the new peaks slowly disappeared once ozone flow was cut off. Similar measurements were carried out at different temperatures (273, 313, 328, and 343 K). It was found that the maximum peak intensity for the adsorbed species did not change for measurements at 273 and 293 K.

Figure 4 presents the Raman spectra for TiO<sub>2</sub>-supported manganese oxide under similar conditions, again at room



**FIG. 4.** *In situ* Raman spectra of  $TiO_2$ -supported manganese oxide: (a) in oxygen; (b) in 2 mol% ozone/oxygen mixture. Reactant flow = 1000 cm<sup>3</sup> min<sup>-1</sup> at room temperature.



FIG. 5. Effect of temperature and ozone partial pressure on ozone decomposition rates over  $ZrO_2$ -supported manganese oxide. Reactant flow = 1000 cm<sup>3</sup> min<sup>-1</sup>.

temperature (293 K). In oxygen flow (Fig. 4a), there were peaks at 390, 509, and 630 cm<sup>-1</sup>. Under continuous ozone flow (Fig. 4b), a peak at 878 cm<sup>-1</sup> appeared along with a very weak feature at 928 cm<sup>-1</sup>. The first and second overtone peaks in this case were at 1750 and 2614 cm<sup>-1</sup>, respectively. Again, similar measurements were made at different temperatures (273, 313, 328, and 343 K).

Blank experiments conducted with the supports indicated that the presence of ozone did not result in a decrease in the intensity of the support peaks. The intense support peaks for the  $ZrO_2$ - and  $TiO_2$ -supported manganese oxide prevented the observation of any manganese oxide peak or changes to it during the course of the reaction.



**FIG. 6.** Effect of temperature and ozone partial pressure on ozone decomposition rates over  $TiO_2$ -supported manganese oxide. Reactant flow = 1000 cm<sup>3</sup> min<sup>-1</sup>.



FIG. 7. Reaction isotherms of ozone decomposition rates over  $ZrO_2$ -supported manganese oxide measured using *in situ* Raman spectroscopy. Reactant flow = 1000 cm<sup>3</sup> min<sup>-1</sup>. Spectrum acquisitions conditions (Figs. 5 and 6): laser power = 200 mW, resolution = 6 cm<sup>-1</sup>, exposure time = 60 s, n = 15 scans.

#### Steady-State Kinetics

Steady-state ozone decomposition rates were measured under varying temperature and ozone partial pressure conditions. For both catalysts, the decomposition rate increased with increasing ozone partial pressure and temperature (Figs. 5 and 6). The reaction order in ozone partial pressure was found to be 0.98 and 0.85 for the  $ZrO_2$ - and TiO<sub>2</sub>-supported catalysts, respectively. These reaction orders were found to be temperature independent.

The peak at 880 cm<sup>-1</sup> for the ZrO<sub>2</sub>-supported catalyst and the peak at 878 cm<sup>-1</sup> for the TiO<sub>2</sub>-supported catalyst were used to determine the surface coverage of the adsorbed species,  $\theta$ , under reaction conditions. This was done by integrating the peak intensities and normalizing the values to the peak area at saturation, at the highest ozone partial pressures and the lowest temperatures. Figures 7 and 8 present reaction isotherms of the surface coverage for ZrO<sub>2</sub>- and TiO<sub>2</sub>-supported manganese oxide catalysts. In both cases, the surface coverage increased with increasing ozone partial pressure, eventually reaching saturation. Surface coverage values decreased with increasing temperature as expected.

#### DISCUSSION

## TPD Spectra

The absence of desorption/decomposition peaks for the TPD trace of  $ZrO_2$  without ozone adsorption shows that no bulk reduction of the support occurred by heating to elevated temperatures. The TPD trace for the pure  $ZrO_2$  support after ozone adsorption showed a broad desorption/decomposition peak at 532 K (Fig. 1b). This



**FIG. 8.** Reaction isotherms of ozone decomposition rates over  $TiO_2$ -supported manganese oxide measured using *in situ* Raman spectroscopy. Reactant flow = 1000 cm<sup>3</sup> min<sup>-1</sup>.

peak is indicative of an adsorbed species on the surface of ZrO<sub>2</sub> upon exposure to ozone. Peaks at 775 and 1050 K (Fig. 1c) for zirconia-supported manganese oxide (without ozone adsorption) suggest reduction of manganese oxide at these high temperatures. These reduction peaks shifted slightly to 780 and 1060 K when ozone was adsorbed on the surface of the catalyst. The peaks at 370 and 410 K (Fig. 1d) can be attributed to the desorption/decomposition of adsorbed oxygen species. The oxygen species are identified as peroxide groups on the surface of the catalysts by their band positions as obtained from their Raman spectra. The range of vibrational frequencies expected for neutral  $O_2$  is 1460–1700 cm<sup>-1</sup>, that for  $O_2^-$  is 1015–1180 cm<sup>-1</sup>, and that for  $O_2^{2-}$  is 640–970 cm<sup>-1</sup> (32) and the observed bands clearly fall in the peroxide range. Also the bands are close to those of  $O_2^{2-}$  on MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> where isotopic substitution has unambiguously identified the peroxide intermediate (1). When the  $MnO_x/ZrO_2$  sample was heated to 500 K, the peroxide Raman signal disappeared. Thus, the desorption/decomposition peak observed at 549 K is likely a result of the recombination and desorption of atomic oxygen on the surface of the ZrO<sub>2</sub> support. This process, though, occurs at much higher temperatures than those at which reaction occurs (<350 K). Consequently, it probably does not contribute to the reaction in the lower range. Isotopic tracer studies had earlier indicated that atomic oxygen did not recombine at low temperatures on  $MnO_x/Al_2O_3$  (1, 2).

The desorption traces for the pure  $TiO_2$  support with and without ozone adsorption showed no signs of adsorbed species or bulk reduction (Figs. 2a, 2b). In the case of the Mn/TiO<sub>2</sub> catalyst with no adsorption, manganese oxide reduction features appeared at 770, 836, and 1005 K (Fig. 2c). When ozone was adsorbed on the surface of the catalyst, broad reduction peaks at 830 and 995 K appeared along with the adsorbed peroxide species peak at 378 K (Fig. 2d). An interesting observation here is the absence of a desortion peak from atomic oxygen. This suggests that the recombination reaction for adsorbed atomic oxygen species does not occur for the catalyst under the measurement conditions.

Integration of the desorption/decomposition peaks for oxygen from the catalysts can be used to calculate the amount of adsorbed oxygen on the surface. Taking values at the lowest temperatures (233 K) and highest pressures (3 kPa) gives coverages at saturation, and allows deduction of the active center site density on the surface of the catalyst (moles per gram of catalyst). Measurements at slightly higher temperatures showed insignificant changes, confirming that saturation had been reached. The corresponding values were 163 and 31  $\mu$ mol g<sup>-1</sup> for the Mn/ZrO<sub>2</sub> and Mn/TiO<sub>2</sub> catalysts, respectively.

## Laser Raman Spectra

The Raman spectrum obtained for each of the supported samples is indicative of dispersed species at the surface. In the absence of ozone for both the ZrO<sub>2</sub>- and TiO<sub>2</sub>supported samples, the only peaks visible are those of the support. For the ZrO<sub>2</sub> supported sample, the peaks at 336, 383, 470, 552, and 626 cm<sup>-1</sup> belong to ZrO<sub>2</sub>. Similarly, for the  $TiO_2$ -supported sample, the peaks at 390, 509, and 630 cm<sup>-1</sup> can be assigned to  $TiO_2$ . In addition, no XRD peaks besides those of the support are observed in these samples. Nevertheless, the supported samples do undergo reduction, and chemisorb oxygen. This evidence suggests that the manganese oxide is in a dispersed state in the near surface of the support. The degree of dispersion calculated from the active site density assuming one oxygen molecule per site was 47% for the Mn/ZrO<sub>2</sub> catalyst and 9% for the Mn/TiO<sub>2</sub> catalyst.

These conclusions are confirmed by studies conducted by Ma *et al.* (7, 8) for ZrO<sub>2</sub>- and Al<sub>2</sub>O<sub>3</sub>-supported manganese oxide samples also using manganese acetate as a precursor. The catalysts were characterized using XPS, TPR, and XRD, and it was deduced that the low loading catalysts prepared through incipient wetness resulted in well-dispersed manganese oxide systems with oxidation states between +2and +3. Kapteijn *et al.* have also studied the effect of precursor and metal loading on Al<sub>2</sub>O<sub>3</sub>-supported manganese oxide (5) using XPS, TPR, Raman, and IR spectroscopy. They observed that at low loadings (<10%), manganese oxide prepared from manganese acetate was a mixture of well-dispersed manganese oxide phases, MnO and Mn<sub>2</sub>O<sub>3</sub>. Earlier work done in our laboratory has identified a peak at 654 cm<sup>-1</sup> which was assigned to the mixed-valency species Mn<sub>3</sub>O<sub>4</sub> species (1). The presence of very intense support peaks in this region for  $ZrO_2$  and  $TiO_2$  precludes the

$$O_3 + {}^* \rightarrow O_2 + O^* \tag{i}$$

$$\mathrm{O}_3 + \mathrm{O}^* \to \mathrm{O}_2^* + \mathrm{O}_2 \tag{ii}$$

$$O_2^* \rightarrow O_2 + ^*$$
 (iii)

SCHEME 1. Proposed Ozone Decomposition Mechanism.

observation of this feature in the present studies. Additionally, the presence of MnO,  $Mn_2O_3$ , and  $MnO_2$  phases, which are weakly Raman active, cannot be ruled out. These phases are usually identified through XRD, but only for catalysts with high metal loading (>10%). Recently, Buciuman et al. (28) have also studied manganese oxide supported on  $Al_2O_3$  and  $SiO_2$  (0.05–18 mol%) using XRD, FTIR, and Raman spectroscopy. These studies have confirmed the presence of bulk phases at high loading (>6 wt%) by the observation of Raman features corresponding to  $\gamma$ -Mn<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>, MnO, and Mn<sub>3</sub>O<sub>4</sub> and XRD features for  $\beta$ -MnO<sub>2</sub>. In conclusion, based on comparisons to the literature, our results indicate that the supported manganese species are in a dispersed state with likely varied structures and oxidation states. Crystallites of some bulk oxide species are possible, but if present these would be smaller than 4 nm.

As discussed in the previous section, the new signals that appear upon ozone exposure at 880 and 878  $\text{cm}^{-1}$  for the ZrO<sub>2</sub>- and TiO<sub>2</sub>-supported manganese catalysts can be attributed to an adsorbed peroxide species derived from ozone. There are also smaller features at 930 and 928  $\rm cm^{-1}$ , respectively, that accompany the main peaks. These are likely due to Mn=O vibrations formed from atomically adsorbed oxygen (Scheme 1, vide infra). These are consistent with the expected vibrational frequencies for such M=O as summarized by Che *et al.* (32) (900–1100 cm<sup>-1</sup>). Atomically adsorbed oxygen species are known to be more thermally stable than adsorbed peroxide species (33). Table 1 presents the coverage of the two species as a function of increasing temperature at 3000 Pa and supports our assignment for the vibrations. The ratio of the two coverages clearly indicate the thermal stability of the atomic oxygen species compared to the peroxide species. These signals were not observed during blank experiments when the supports alone were used. Ozone decomposition work done on Al<sub>2</sub>O<sub>3</sub> supported manganese oxide using Raman spectroscopy (1) has identi-

#### TABLE 1

Effect of Temperature on Adsorbed Species Coverages

Temperature/K	$\theta_{\mathrm{O}_{2^*}}$	$\theta_{O^*}{}^a$	Ratio $(\theta_{O^*}/\theta_{O_2^*})$
293	0.80	0.05	0.06
313	0.69	0.06	0.09
328	0.58	0.12	0.21

<sup>*a*</sup>These coverages are qualitative. They were calculated from peak areas assuming the same calibration factor as for the  $O_2^*$  species.

fied an adsorbed peroxide species at  $884 \text{ cm}^{-1}$  on the catalyst surface through isotopic work and *ab initio* calculations. According to these studies, the vibrational mode for the adsorbed species is highly localized. This could be the reason for the very small change in the vibrational frequency for the peroxide species on  $ZrO_2$ - and  $TiO_2$ -supported catalysts as compared to that for the  $Al_2O_3$ -supported catalyst.

For the Mn/ZrO<sub>2</sub> catalyst, the peak at 880 cm<sup>-1</sup> had a shoulder on the low wavenumber side at 852 cm<sup>-1</sup> indicative of two different adsorbed peroxide species on the catalyst surface. The presence of these species was also indicated in the oxygen TPD results (Fig. 1). It is likely that in the case of the Mn/ZrO<sub>2</sub> catalyst, there are two peroxide species. The structure of these peroxide species is uncertain. They could be bidentate  $\eta^2$ -O<sub>2</sub> complexes as likely on the monoatomic Mn center on Mn/Al<sub>2</sub>O<sub>3</sub> (31), or they could be bridging dioxygen species as possible on the multinuclear Mn center on the Mn/TiO<sub>2</sub> and Mn/SiO<sub>2</sub> catalysts (31). The bands on the Mn/ZrO<sub>2</sub> samples could also arise from different interactions of the peroxide species with the ZrO<sub>2</sub> support.

Adsorbed ozone on  $\text{ZrO}_2$  and  $\text{TiO}_2$  at low temperatures (77 K) has been observed earlier (29, 30) using infrared spectroscopy. On  $\text{ZrO}_2$  bands were observed at 2122 cm<sup>-1</sup>  $(\nu_1 + \nu_3)$ , 1138 cm<sup>-1</sup>  $(\nu_1)$ , and 1001 cm<sup>-1</sup>  $(\nu_3)$  while on TiO<sub>2</sub> (anatase) bands were seen at 2137 cm<sup>-1</sup>  $(\nu_1 + \nu_3)$ , 1147 cm<sup>-1</sup>  $(\nu_1)$ , and 989 cm<sup>-1</sup>  $(\nu_3)$ . These correspond to distorted molecular ozone vibrations with interaction of O<sub>3</sub> with Lewis sites on the oxides. No adsorbed peroxide species were observed at these low temperatures.

#### Steady-State Kinetics

The proposed ozone decomposition mechanism from the studies done on an  $Al_2O_3$ -supported manganese oxide catalyst (1) is presented in Scheme 1. The symbol \* is used to denote surface sites. Briefly, experiments involving isotope ( $^{18}O_3$ ) (1, 2) substitution ruled out the possibility of oxygen atom recombination and the finding that the adsorbed ozone never desorbed established the irreversibility of steps (i) and (ii). Furthermore, the finding that the peroxide species could not be formed from molecular oxygen at any conditions showed the irreversibility of step (iii).

The acquired steady-state data were analyzed with a uniform surface kinetic analysis using a Langmuirian expression for the coverage  $\theta$  with an equilibrium constant *K* and a reaction rate constant *k*:

$$\theta_{\rm ss} = \frac{K(\rm O_3)}{1 + K(\rm O_3)} \tag{1}$$

$$r_{\rm ss} = k\theta_{\rm ss}.$$
 [2]

The results of the analysis for the  $MnO_x/ZrO_2$  and  $MnO_x/TiO_2$  coverage fits are presented in Figs. 9 and 10. It is clear that the quality of the fit is not good and the

3000

FIG. 9. Surface coverage vs ozone partial pressure:  $MnO_x/ZrO_2$ . Fits based on the Langmuir coverage expression.

1500 2000 2500

O Partial Pressures / Pa

1000

average  $\chi^2$  value for these fits was found to be  $10^{-2}$ . Figures 11 and 12 present the rate versus coverage plots for the two catalysts. From Eq. [2], a linear dependency of steady-state rates on coverage is expected. The plots clearly show a nonlinear dependency of rates on coverage. It can be ascertained from these results that the experimental data are inadequately predicted by a uniform surface kinetic analysis.

As a result, a nonuniform surface kinetic treatment (2) was used to fit the acquired steady-state experimental data. The interaction of the dispersed Mn oxide species with different sites on the support surface probably gives rise to a heterogeneous surface. This is compounded by the



FIG. 11. Rate vs coverage: MnO<sub>x</sub>/ZrO<sub>2</sub>. A linear relationship is expected for a uniform surface.

likely presence of multiple manganese oxidation states on the surface of the catalyst which give rise to manganese oxide species with slightly different activities for ozone decomposition. The nonuniform analysis uses an adsorption activation energy which increases linearly with coverage ( $E_a = E_a^0 + gRT\theta$ ) and a desorption/decomposition activation energy that decreases linearly with coverage ( $E_d = E_d^0 - hRT\theta$ ). Equations [3] and [4] are the resulting rate expressions obtained for adsorption and desorption/decomposition, respectively.

$$r_{\mathbf{a}} = k_{\mathbf{a}}^{\mathbf{0}}(\mathbf{O}_3)e^{-g\theta}$$
[3]

$$r_{\rm d} = k_{\rm d}^0 e^{-h\theta}.$$
 [4]

In these expressions  $k_a^0$  and  $k_a^0$  are the adsorption and desorption/decomposition rate constants at zero coverage.

293 K

– 313 K – 328 K

0.05

0.25

0.20

0.15

0.10

0.05

0.00

0.00



0.15

Coverage / θ

0.20

0.25

0.30

0.10





Coverage / 0

1.0

0.8

0.6

0.4

0.2

0.0

0

293 K

313 K

328 K

500

Setting the adsorption and desorption rate expressions equal provides equations for both the steady-state rate and the steady-state coverage, Eqs. [5] and [6].

$$r_{\rm ss} = k_{\rm d}^0 \left[ \frac{k_{\rm a}^0}{k_{\rm d}^0} (\mathbf{O}_3) \right]^{h/g+h}$$
[5]

$$\theta_{\rm ss} = \frac{1}{g+h} \ln \left[ \frac{k_{\rm a}^0}{k_{\rm d}^0} (\mathcal{O}_3) \right].$$
 [6]

The steady-state coverage and rates were monitored as a function of ozone partial pressure and temperature. The values for the various kinetic parameters in Eqs. [5] and [6] were obtained through a least-squares fitting of the experimental data. The linear fits of the steady-state rate versus the ozone partial pressure (Figs. 5 and 6) and those of the steady-state coverage of the peroxide species against the logarithm of the ozone partial pressure (Figs. 13 and 14) were used to simultaneously solve for the parameters in Eqs. [5] and [6]. Clearly, the data fit the equations very well throughout the entire range of variation of experimental conditions. The average  $\chi^2$  value for the coverage fits was found to be  $10^{-4}$  while the rate fits produced an average  $\chi^2$ value of  $10^{-5}$ . The pre-exponential and activation energy values calculated for adsorption and desorption from the analysis are presented in Table 1 and are compared with the corresponding values obtained in the previous study for the Al<sub>2</sub>O<sub>3</sub>-supported catalyst.

The steady-state rates for both catalysts were found to have a fractional order dependency on ozone partial pressure which was independent of temperature. This is consistent with the fractional order h/(g+h) predicted by Eq. [3] with a value <1. The kinetic parameters for ozone decom-



FIG. 13. Plots for the surface coverage vs logarithm of ozone partial pressure:  $ZrO_2$ -supported manganese oxide. A linear relationship is expected for a nonuniform surface.



**FIG. 14.** Plots for the surface coverage vs logarithm of ozone partial pressure: TiO<sub>2</sub>-supported manganese oxide.

position on the  $Mn/ZrO_2$  and  $Mn/TiO_2$  catalyst are compared to those obtained for  $Mn/Al_2O_3$  in the earlier work (2) in Table 2.

The values for the pre-exponential for adsorption on each of the catalysts is in the range of  $10^{-18}$  cm<sup>-3</sup> s<sup>-1</sup> and the activation energy for ozone adsorption on each of the catalysts is low (<10 kJ/mol). The activation energy for desorption/decomposition is significantly larger than the activation energy of adsorption for each catalyst. This could be the reason why a stable reaction intermediate was observed for the catalytic process. The activation energies and pre-exponentials for the desorption/decomposition process follow the trend  $Al_2O_3 > ZrO_2 > TiO_2$ . This suggests that for the ozone decomposition process on supported manganese oxide catalysts, the desorption/decomposition step is rate determining.

There has been considerable work done in examining the effect of support on the reactivity of transition metal oxides. Work done in our laboratory with ethanol oxidation over  $MoO_3$  catalysts has shown that metal oxide-support

## TABLE 2

## Kinetic Parameters for Ozone Decomposition on Supported Manganese Oxide Catalysts

Parameter	Al <sub>2</sub> O <sub>3</sub> support	ZrO <sub>2</sub> support	TiO₂ support
h	11.8	11.1	23.8
g	0.75	0.2	4.2
$E_{ m a}^0$	6 kJ/mol	6 kJ/mol	7 kJ/mol
$E_{ m d}^0$	69 kJ/mol	62 kJ/mol	44 kJ/mol
$A^0_{ m a}$	$3.1\times 10^{-18}\ cm^3\ s^{-1}$	$1.1\times 10^{-18}\ cm^3s^{-1}$	$1.2\times 10^{-18}\ cm^3\ s^{-1}$
$A_{ m d}^0$	$1.6\times 10^7~s^{-1}$	$8\times 10^5 \ s^{-1}$	$1.9\times10^3s^{-1}$

interactions are responsible for changing activities and selectivities (18). The difference in the activities of the various support MoO<sub>3</sub> catalysts for ethanol oxidation studies is reported to have resulted from a difference in the pre-exponential term in the reaction rate constant (because there was little activation energy variation among all the catalysts). The reactivity trend in this case followed the order TiO<sub>2</sub> > Al<sub>2</sub>O<sub>3</sub> > SiO<sub>2</sub>. Similar trends in activity were observed for methanol oxidation on supported MoO<sub>3</sub> (34) and V<sub>2</sub>O<sub>5</sub> (35) catalysts. The greater lability of the metal–oxygen–support bridging bond for ZrO<sub>2</sub>- and TiO<sub>2</sub>supported catalysts was given as a reason for their higher activities.

The desorption/decomposition step in the ozone decomposition process can be viewed as a reductive elimination involving the transfer of electrons from the peroxide species to the manganese active center to form molecular oxygen. NEXAFS (near-edge X-ray absorption fine structure) measurements on the catalysts (31) revealed that there was a chemical shift to lower energies in the Mn L-edge features which followed the trend  $Al_2O_3 > ZrO_2 > TiO_2$ . The shift toward lower energy with respect to bulk MnO<sub>2</sub> indicates more reduced species and larger number of unoccupied *d* levels. Since it is the unoccupied *d* levels which accept electrons, the NEXAFS results support the likely importance of electron transfer in the reduction of the active center during ozone decomposition.

#### CONCLUSIONS

The presence of an adsorbed peroxide species on the surface of ZrO<sub>2</sub> and TiO<sub>2</sub> during ozone decomposition was confirmed using in situ laser Raman spectroscopy. Simultaneous steady-state kinetic measurements revealed a fractional order dependency of the turnover rates with respect to ozone partial pressure of 0.98 and 0.85 for the ZrO<sub>2</sub>- and TiO<sub>2</sub>-supported catalysts. The nonuniform surface kinetics analysis used in an earlier study on Al<sub>2</sub>O<sub>3</sub>-supported manganese oxide was found to work very well for the catalysts in this study. There was substantial variation in the activation energy and pre-exponential values for the desorption/decomposition step among the catalysts. Differences in the structure of the manganese active center seems to be the origin of the support effect on the desorption/decomposition kinetic parameters. The trend in these parameters,  $Al_2O_3 > ZrO_2 > TiO_2$ , seems to follow the reducibility of the manganese active center.

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