

## Kinetics and Mechanism of Ozone Decomposition on a Manganese Oxide Catalyst

Balamurugan Dhandapani and Shigeo Ted Oyama\*

Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0211, U.S.A.

(Received February 13, 1995)

The ozone decomposition reaction to molecular oxygen was studied in a flow reactor on a  $\text{MnO}_2 / \gamma\text{-Al}_2\text{O}_3 / \text{cordierite}$  catalyst. The rate expression is found to depend on ozone concentration,  $r_{\text{O}_3} = k(\text{O}_3)^{0.68}$ , but not on  $\text{O}_2$  or  $\text{H}_2\text{O}$  partial pressure. A reaction sequence based on an ionic type intermediate with superoxide ( $\text{O}_2^-$ ) or peroxide ( $\text{O}_2^{2-}$ ) character is proposed to explain the kinetics.

Ozone is a powerful oxidant, and in the range of 0.1 - 1 ppm causes headaches, throat dryness and damage to mucous membranes<sup>1</sup>, so must be removed from human environments. Major sources are photocopiers, laser printers, sterilizers, and aircraft air. Most of the work in the area of decomposition of ozone on heterogeneous catalysts is reported in patents, with very few fundamental studies published in the open literature<sup>2-4</sup>. In this paper the effect of  $\text{O}_3$ ,  $\text{O}_2$  and  $\text{H}_2\text{O}$  partial pressure on ozone decomposition was studied over a  $\text{MnO}_2 / \gamma\text{-Al}_2\text{O}_3 / \text{cordierite}$  substrate to obtain insight on the reaction mechanism.

Straight pore monoliths (5.1 cm x 5.1 cm x 1.3) made of cordierite ( $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ ) (Corning, part no. 9475) with a standard cell density of 400 cells per in<sup>2</sup> (cpsi) or 60 cells/cm<sup>2</sup>, (square pores of 0.12 cm size) were used. The monoliths were acid leached in 1.5 N  $\text{HNO}_3$  solution for 9 h at 368 K to open up clogged pores and to prepare the surface for wash coating<sup>5</sup>. Leaching the surface of the cordierite produces better bonding for the subsequent washcoat than the air-fired surface<sup>6</sup>. The surface area of the cordierite increased from 1.5 m<sup>2</sup>g<sup>-1</sup> to 6.5 m<sup>2</sup>g<sup>-1</sup> by this procedure. The leached cordierite was coated with a slurry of 20 %  $\gamma\text{-Al}_2\text{O}_3$  (Vista Chemical Co., 150 m<sup>2</sup>g<sup>-1</sup>, particle size 65  $\mu\text{m}$ ) in three stages with calcination at 773 K at each stage. A uniform coating of controllable thickness which typically was 5-6 wt % of the substrate was obtained. The  $\text{MnO}_2$  was deposited on the support by multiple impregnation of a  $\text{Mn}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$  (ultra pure, Johnson Matthey Company) solution. The sample was

dried at 423 K and calcined at 773 K for 3 h. The loading of  $\text{MnO}_2$  was 10 wt % of the  $\gamma\text{-Al}_2\text{O}_3$  support. Hall effect measurements indicated that  $\text{MnO}_2$  was a *p*-type conductor with  $5 \times 10^{14} \text{ cm}^{-3}$  carrier concentration and  $5 \times 10^2 \Omega \text{ cm}$  resistivity.

The effect of the partial pressures of  $\text{O}_3$ ,  $\text{O}_2$  and  $\text{H}_2\text{O}$  was determined in a flow reactor system (Figure 1) with an aluminum reactor constructed to accept a catalyst of square geometry. The system incorporated an ozone generator (Atlantic Ultraviolet Corporation, Model II-OZ), a two-stage water saturator with temperature control (PolyScience Model 900), an ozone monitor (OREC, Model O3DM-100), an anemometer (Velocicalc, Model 8350), a differential pressure gauge (Modus Instruments, Inc., Model T40), and a compressor (Spencer Turbines, Model VB002S), and operated at atmospheric pressure.

The reactor operated at differential conditions with a total flow rate of 800 cm<sup>3</sup> s<sup>-1</sup>. The effect of  $\text{O}_3$  partial pressure on the rate of ozone decomposition at 313 K and mole fraction of  $\text{H}_2\text{O}$  of 0.029 (relative humidity of 40%) is reported in figure 2. The inlet concentration of  $\text{O}_3$  in purified air was varied from 0.5 to 15 ppm (mole fraction =  $0.5 \times 10^{-6}$  to  $15 \times 10^{-6}$ ), with total air flow rate constant at 800 cm<sup>3</sup> s<sup>-1</sup> (contact time = 0.04 s). The order in  $\text{O}_3$  was determined to be 0.68 from the plot. At an ozone concentration of 8 ppm the rate was 1.24  $\mu\text{mol g}^{-1} \text{ s}^{-1}$  equivalent to a turnover rate of  $1.1 \times 10^{-4} \text{ s}^{-1}$ , assuming 100% dispersion of the supported  $\text{MnO}_2$ .

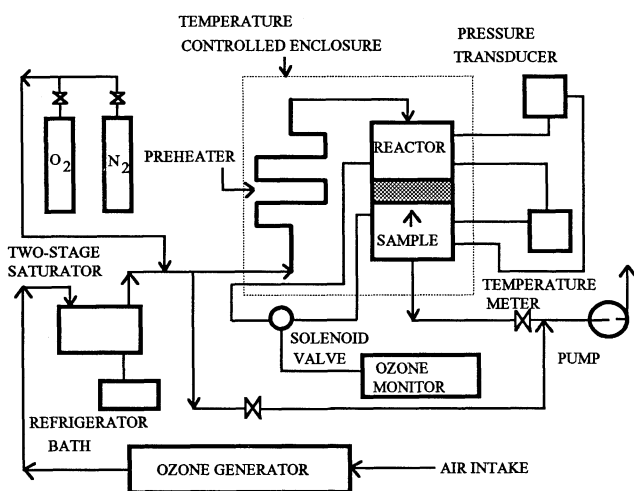


Figure 1. Schematic representation of the testing equipment.

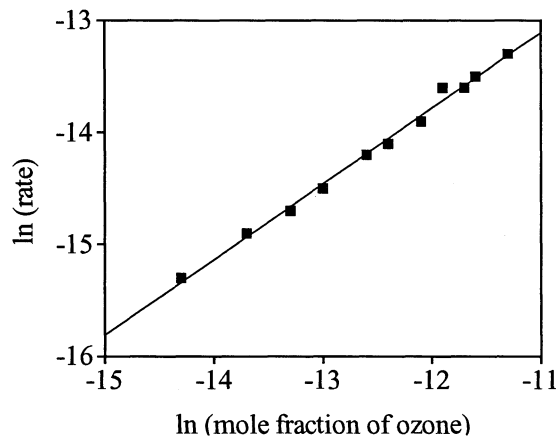


Figure 2. Plot of  $\ln(\text{rate})$  vs  $\ln(\text{mole fraction of O}_3)$ .

The effect of  $\text{O}_2$  partial pressure on the ozone conversion at 313 K and relative humidity 40% was obtained by varying the  $\text{O}_2$  mole fraction from 0.21 to 0.50 with diluent  $\text{N}_2$  in the inlet feed, while keeping the concentration of  $\text{O}_3$  and the total flow rate constant at 4 ppm and 1000 cm<sup>3</sup>/s, respectively. The  $\text{O}_2$  partial pressure did not change the conversion of  $\text{O}_3$  (Figure 3).

The effect of  $\text{H}_2\text{O}$  partial pressure on the ozone decomposition at 313 K was studied by varying the  $\text{H}_2\text{O}$  mole fraction from 0 to 0.04 in the inlet feed, while keeping the

concentration of  $O_2$  at 21%,  $O_3$  at 2 ppm, and total flow rate at  $800 \text{ cm}^3\text{s}^{-1}$ . Figure 3 shows that changing  $H_2O$  partial pressure had no effect on the conversion of  $O_3$ .

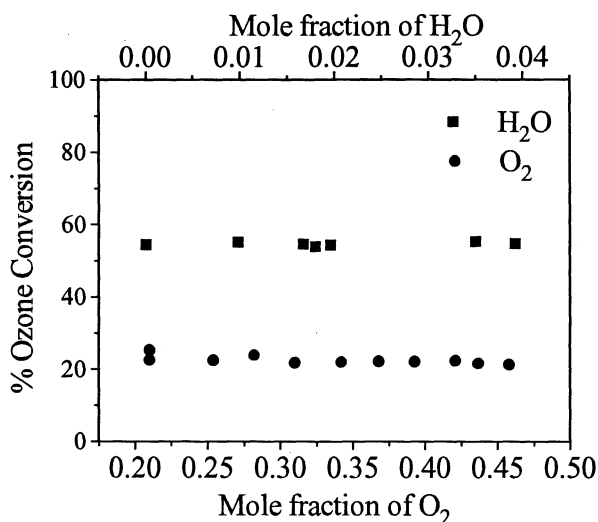
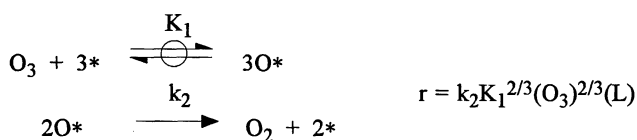


Figure 3. Effect of  $O_2$  and  $H_2O$  on conversion of ozone.

Over a limited range of mole fractions ( $y_{O_3} = 0.5 \times 10^{-6} - 15 \times 10^{-6}$ ,  $y_{O_2} = 0.21 - 0.5$ ,  $y_{H_2O} = 0 - 0.04$ ), the rate of decomposition obeys the following expression:

$$r_{O_3} = kP_{O_3}^{0.68} P_{O_2}^0 P_{H_2O}^0$$

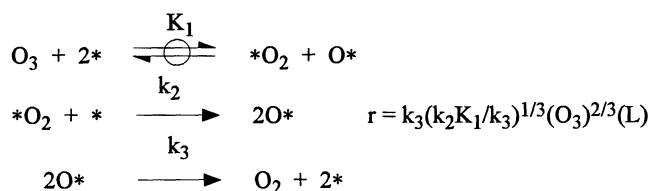
The dependence of the rate on oxygen partial pressure is zero, but the exponent on the ozone partial pressure is close to  $2/3$ , an unusual value. A simple rationalization is that the ozone is in equilibrium with three equivalent adsorbed oxygen atoms, and that these recombine in a rate-determining step to form  $O_2$ .



In the scheme above, \* represents catalytic sites and (L) the total concentration of sites. The derivation assumes the surface is almost bare,  $(L) \approx (*)$ . The mechanism is unlikely because the

first step requires three adjacent empty sites, and because the reverse reaction to produce ozone is improbable. Furthermore, the formation of three equivalent oxygen atoms from a nonsymmetrical reactant seems difficult.

The kinetic rate expression allows only a limited number of possible reaction schemes. An alternative is presented below:



The notable feature of this scheme is that the key intermediate  $*O_2$  does not immediately desorb. We propose that this is because it has partial ionic ( $O_2^-, O_2^{2-}$ ) character, and is stabilized by Coulombic interactions with the substrate. Such an intermediate was suggested earlier for ozone decomposition on silver<sup>2</sup>. The observation that  $MnO_2$  is a *p*-type oxide, which would tend to stabilize anionic species, gives support to this hypothesis.

In summary, for  $MnO_2/Al_2O_3$  the order of decomposition of ozone with respect to  $O_3$  partial pressure was close to  $2/3$ , while it was zero with respect to  $O_2$  and  $H_2O$ . A mechanism involving the formation of an ionic intermediate with partial superoxide or peroxide character was suggested to explain the kinetics.

This work was supported by the Director, Division for Chemical and Thermal Systems of the National Science Foundation under Grant CTS-9311876

#### References and Notes

- 1 R. E. Kirk and D. F. Othmer, *Encyclopedia of Chemical Technology*, vol 16, Wiley-Interscience Publication, 1981.
- 2 S. Imamura, M. Ikebata, T. Ito, and T. Ogita, *Ind. Eng. Chem. Res.*, **30**, 217 (1991).
- 3 P. H. Calderbank and J. M. O. Lewis, *Chem. Eng. Sci.*, **31**, 1216 (1976).
- 4 F. D. Toor, *Pakistan J. Sci. Ind. Res.*, **13**, 6 (1970).
- 5 T. H. Elmer, *Ceram. Eng. and Sci. Proc.*, **7**, 40 (1986).
- 6 M. D. Patil and I. M. Lachman, *Perspectives in Molecular Sieve Science*, ed by W. H. Flank and T.E. Whyte, Toronto, Canada, 1988.