Photocatalytic and Thermal Catalytic Reaction of Carbon Monoxide with Nitrous Oxide and Oxygen over Zinc Oxide

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Summary The photocatalytic and thermal catalytic oxidation of CO over ZnO is more complex than previously observed in that the illuminated and dark reactions obey different kinetics and that N_2O is also effective in oxidizing CO.

CATALYTIC activity on semiconductor surfaces has most often been studied using ZnO. The oxidation of CO over ZnO by O_2 has been stated[1] to be first order in CO under both dark and illuminated conditions at 400 °C with O_2 less effective in affecting the reaction. We report that N_2O also oxidizes CO on ZnO and that at 200 °C the reaction of CO with either N_2O or O_2 is more complex than observed previously because the light assisted and dark reactions obey different kinetics.

The apparatus and zinc oxide used here are the same as those used previously to study N_2O decomposition.[2,3] The reaction was followed by gas chromatographic analysis of N_2 in the reaction of N_2O with CO, and N_2 and O_2 in the case of the competitive reaction of CO with N_2O and O_2. Fresh ZnO which has been oxidized and evacuated at about 410 °C has a high catalytic activity for the reaction of N_2O with CO, but the activity decreases (rapidly at first) with each subsequent run, arriving at a stabilized activity after several runs. The stabilized catalyst gave a reproducible activity if the evacuation time between runs was kept constant. The catalyst used in the dark experiments was evacuated for 1 h at the reaction temperature and the catalyst used for the photocatalytic reaction was evacuated for 10 mins with illumination. In order to avoid complications due to retardation by product CO_2, the initial rates were determined and used to derive rate equations. It was determined that neither thermal nor photocatalytic decomposition of $\mathrm{N_2O}$ occur on zinc oxide with a detectable rate at 203 °C.

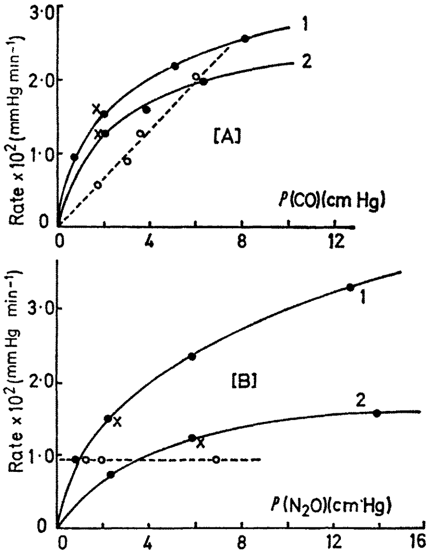

FIGURE 1. *Effect of* CO *pressure on the reaction rates* (A) *and the effect of* $\mathrm{N_2O}$ *pressure on the reaction rates* (B). (A): *Photocatalytic reaction. Initial pressures and reaction temperatures.* (1) $P(\mathrm{N_2O}) = 2{\cdot}42$—$2{\cdot}53$ cmHg; 202—204 °C. (2) $P(\mathrm{N_2O}) = 6{\cdot}05$—$6{\cdot}40$ cmHg; 192—193 °C. ○: *Dark reaction at* 203 ± 1 °C. +: *Estimated values from* (B). (B): *Photocatalytic reaction. Initial pressures and reaction temperatures.* (1) $P(\mathrm{CO}) = 1{\cdot}68$—$1{\cdot}75$ cmHg; 201—204 °C. (2) $P(\mathrm{CO}) = 1{\cdot}75$—$1{\cdot}85$ cmHg; 193 °C ○: *Dark reaction at* 201—202 °C. +: *Estimated values from* (A).

Figure 1 shows that the $\mathrm{N_2O}$ reaction with CO on ZnO in the dark may be expressed by the equation rate = $kP(\mathrm{CO})^{1\cdot0}P(\mathrm{N_2O})^{0}$, but under illumination the markedly different expression, rate = $kP(\mathrm{CO})^{0\cdot4}P(\mathrm{N_2O})^{0\cdot4}$ is obeyed. In the dark, the reaction of $\mathrm{N_2O}$ with CO is strongly retarded by oxygen (see Figure 2). The reaction is negligible if the oxygen pressure is higher than 1 mmHg but under illumination the reaction of $\mathrm{N_2O}$ with CO is not retarded by oxygen (Figure 3).

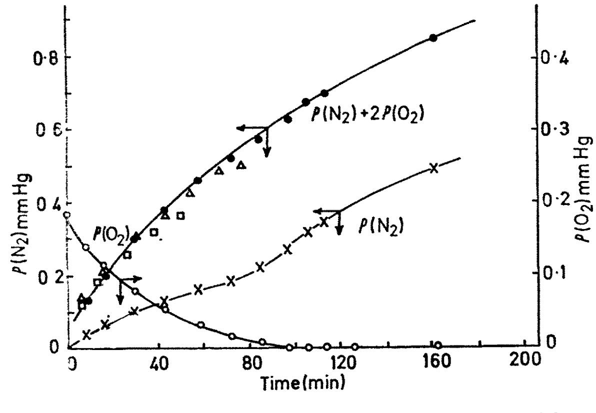

FIGURE 2. *Competitive thermal catalytic reaction of* CO *with* $\mathrm{N_2O}$ *and* $\mathrm{O_2}$ *at* 204 °C. *Initial pressures:* $P(\mathrm{N_2O}) = 2{\cdot}77$ cmHg; $P(\mathrm{CO}) = 1{\cdot}92$ cmHg; $P(\mathrm{O_2}) = 0{\cdot}19$ mmHg. ●: *Total reaction*; $P(\mathrm{N_2}) + 2P(\mathrm{O_2})$ (*reacted*). △: $P(\mathrm{CO}) = 1{\cdot}78$ cmHg, $P(\mathrm{N_2O}) = 2{\cdot}31$ cmHg, $P(\mathrm{O_2}) = 0$. □: $P(\mathrm{CO}) = 1{\cdot}69$ cmHg, $P(\mathrm{N_2O}) = 2{\cdot}91$ cmHg, $P(\mathrm{O_2}) = 0$.

In the dark the reaction of $\mathrm{N_2O}$ with CO accelerates when oxygen is completely removed from the gas phase, but the total reaction (Figure 2) gives a smooth curve. From the stoicheiometry of the reactions the rate of CO reaction is equal to the rate of increase of $P(\mathrm{N_2})$ for the reaction with $\mathrm{N_2O}$ and equal to twice the rate of decrease in $P(\mathrm{O_2})$ for the reaction with $\mathrm{O_2}$. Thus the total reaction of CO is proportional to $P(\mathrm{N_2}) + 2P(\mathrm{O_2})$ (reacted). This total reaction curve is identical with the reaction curves obtained in the absence of oxygen as plotted (squares and triangles in Figure 2). This indicates that the surface oxide which reacts with CO is the same whether produced from $\mathrm{O_2}$ or $\mathrm{N_2O}$. The fact that the initial reaction rates are first order in CO pressure and zero order in $\mathrm{N_2O}$ or $\mathrm{O_2}$ pressure suggests that the active sites on the surface are covered with oxide which reacts in the rate determining step with either gas phase CO or weakly adsorbed CO which is in equilibrium with the gas phase. Equations (1) and (2) show a possible reaction scheme where [ ] indicates the

$$\mathrm{N_2O}\ (g)\ \text{or}\ \mathrm{O_2}\ (g) + [\ \ ] \rightarrow [\mathrm{O}^*] \qquad (1)$$

$$[\mathrm{O}^*] + \mathrm{CO} \rightarrow \mathrm{CO_2} + [\ \ ] \qquad (2)$$

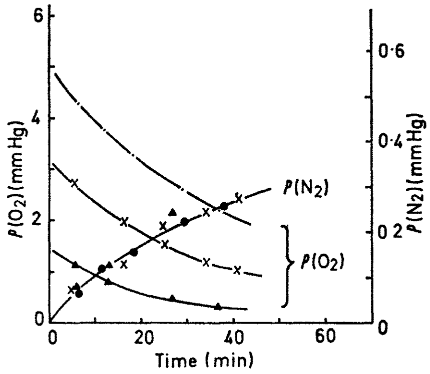

FIGURE 3. *Competitive photocatalytic reaction of* CO *with* $\mathrm{N_2O}$ *and* $\mathrm{O_2}$. ●: $P(\mathrm{N_2O}) = 1{\cdot}53$ cmHg, $P(\mathrm{CO}) = 2{\cdot}04$ cmHg, $P(\mathrm{O_2}) = 0{\cdot}49$ cmHg; 190 °C. +: $P(\mathrm{N_2O}) = 1{\cdot}63$ cmHg, $P(\mathrm{CO}) = 1{\cdot}99$ cmHg, $P(\mathrm{O_2}) = 0{\cdot}32$ cmHg; 190 °C. ▲: $P(\mathrm{N_2O}) = 1{\cdot}58$ cmHg, $P(\mathrm{CO}) = 2{\cdot}05$ cmHg, $P(\mathrm{O_2}) = 0{\cdot}15$ cmHg; 189 °C.

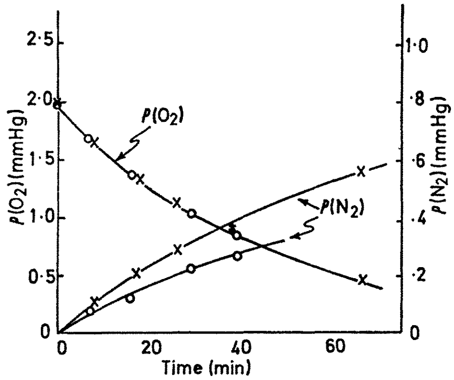

FIGURE 4. *Effect of* CO *pressure on the competitive photoreaction of* $\mathrm{N_2O}$ + CO *and* $\mathrm{O_2}$ + CO. ○: $P(\mathrm{O_2}) = 0{\cdot}19$ cmHg, $P(\mathrm{N_2O}) = 3{\cdot}39$ cmHg, $P(\mathrm{CO}) = 1{\cdot}35$ cmHg, 195 °C. +: $P(\mathrm{O_2}) = 0{\cdot}19$ cmHg, $P(\mathrm{N_2O}) = 3{\cdot}33$ cmHg, $P(\mathrm{CO}) = 5{\cdot}04$ cmHg, 195 °C.

active surface sites and O* the active oxygen species on the surface may be either neutral or charged. If N_2O is used in reaction (1), gas phase N_2 is also produced. This corresponds to the decomposition of N_2O on highly evacuated ZnO[4] which produces over 95% N_2 as the gaseous product. The retardation of oxygen in the competitive reaction indicates that the sites are occupied preferentially by the oxygen from gas phase O_2 rather than from the decomposition of N_2O.

The reaction of CO with O_2 under illumination is obviously much faster than that with N_2O (Figure 3) and the reaction rate is proportional to $P(O_2)^{0 \cdot 5}$ while being zero order in CO pressure (Figure 4). The fact that the orders, with respect to CO, for the competitive photo-oxidation with N_2O and O_2 are different (see Figure 4), indicates that the CO surface intermediate for the reaction with N_2O is not involved in the slow step of the reaction with O_2. Assuming rapid photoreaction of CO with adsorbed oxygen,[5] a possible reaction scheme in agreement with the observed results is as shown in equation (3), (4), and (5).

$$O_2\ (g) \rightleftharpoons 2\ O\ (a) \qquad (3$$

$$O\ (a) + [e^-] \rightarrow O^-\ (a) \qquad (4)$$

$$O^-\ (a) + CO \rightarrow CO_2 + [e^-] \qquad (5)$$

where O (a) is adsorbed oxygen, (4) is the rate determining step and (5) is fast.

Thus the thermal oxidation of CO over ZnO with O_2 and N_2O are similar while the photo-oxidations with O_2 and N_2O are dissimilar to each other.

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