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ESR Evidence of CO Oxidation by More Than One Oxygen Species Sorbed on ZnO

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An approach is described for investigating the nature of sorbed oxygen species on a semiconductor catalyst surface and for determining their relative reactivities in a heterogeneous oxidation reaction. Experimental information as to the types of oxygen species on ZnO with presorbed oxygen, $ZnO \cdot O_2$, was obtained from measurements of ESR and sorption of carbon monoxide at 20°C. When CO is sorbed on $ZnO \cdot O_2$, the 1.96 line, associated with conduction electrons, rapidly increases and the 2.010 line, associated with a sorbed oxygen species, slowly decreases. These results indicate that CO reacts with two different sorbed oxygen species. The probable nature of these species is discussed.

INTRODUCTION

One goal of current research in heterogeneous oxidation catalysis is to develop experimental approaches suitable for the detection of reactive sorbed species and for the determination of their surface concentrations and reactivities. The present paper describes an ESR study of the CO oxidation reaction on ZnO, an approach which offers considerable potential for further extension. Emphasis is placed on the information that can be obtained by studying the electron transfer between the bulk and the surface of the semiconductor, ZnO, as surface reactions proceed. In this investigation, low oxygen surface coverages were used so that charged surface species would dominate over neutral species.

Earlier we reported that the ESR technique provided important information on heterogeneous reactions occurring on a semiconductor surface (*1*). In that study, when CO was sorbed on ZnO with presorbed oxygen, we observed that the ESR line at $g = 1.96$ increased, and a line in the vicinity of $g \sim 2.00$ increased in some experiments and decreased in others. The increase of the 1.96 line was attributed to a surface reaction between CO and a charged oxygen species which released electrons to the conduction band of the ZnO. The variable behavior of the 2.00 line suggested that better control of the ZnO pretreatment was required.

Some effects of ZnO pretreatment and of subsequent oxygen sorption have since been demonstrated in another ESR study (*2*). The results showed that for incompletely outgassed ZnO, oxygen sorption produces two new lines at g values of 2.004 and 2.010, both of which have some reversibility with oxygen pressure. However, after more outgassing, oxygen sorption shows no reversibility with oxygen pressure. The present study makes use of the latter surface treatment.

EXPERIMENTAL

The apparatus, techniques, and materials have been described (*1, 2*). All gas sorption and ESR measurements were made at about 20°C. Oxygen and CO were individually passed through traps at liquid nitrogen temperature before sorption on ZnO. The carbon dioxide (Matheson, C.P. grade) was distilled several times, and it was passed through a trap at dry ice temperature before sorption on ZnO. The ZnO was pretreated by heating at 500°C in vacuum for at least 30 min; hereafter it will be referred to as "pretreated ZnO." The pretreated ZnO with presorbed oxygen will be referred to as "$ZnO \cdot O_2$."

Results

Figure 1 shows the effect, on the pretreated ZnO, of oxygen sorption and subsequent carbon monoxide sorption on the first moments of the first derivative curves of the 2.010 and 1.96 lines, $M_{2.010}$ and $M_{1.96}$. The data were obtained with three separate 0.2-g samples of pretreated ZnO. When 0.2 torr-cc oxygen was admitted to the pretreated ZnO, the residual pressure rapidly decreased to less than 10^{-4} torr (30 cc volume). This sorption resulted in a surface coverage of 3×10^{16} O_2 molecules/g ZnO, and for these conditions it is estimated (*2*) that about ⅕ of the sorbed oxygen is present as charged species. No time scale is given in Fig. 1 for (1) the vacuum-heat pretreatment and (2) the oxygen sorption because the ESR lines remained stable for long periods of time after each of these treatments. The time scale applies only to the changes that occurred upon (3) CO sorption. Immediately after oxygen sorption, the $ZnO \cdot O_2$ samples were exposed to different amounts of CO, so that on the separate samples 0.3×10^{17}, 1×10^{17}, and 3×10^{17} CO molecules/g ZnO were sorbed with residual pressures after about 30 min of 2×10^{-3}, 30×10^{-3}, and 50×10^{-3} torr, respectively. The results in Fig. 1 show no significant effect due to different amounts of CO sorbed.

The ESR changes produced by CO sorption were not due simply to CO or CO_2 sorption effects. This was demonstrated by sorbing CO and CO_2 separately on pretreated ZnO to a surface coverage far exceeding that in the above experiments. For example, sorption of either CO or CO_2 to a surface coverage of about 10^{18} molecules/g ZnO produced essentially no effect on the 1.96 line, and no new ESR line appeared.

The rapid change of the 1.96 line upon CO sorption, shown in Fig. 1, was studied by adjusting the magnetic field of the ESR spectrometer so as to record the peak intensity, $I_{1.96}$, with respect to time. Typical results are shown in Fig. 2, for which the $ZnO \cdot O_2$ was prepared by sorbing about 5×10^{15} O_2 molecules/g ZnO on pretreated ZnO. For this surface coverage, charged sorbed species are believed to predominate over neutral species. In Fig. 2, CO sorption was initiated at time 0 and steady state sorption after about 3 min was about 10×10^{15} CO molecules/g ZnO. The maximum of the curve is caused by line-broadening of the 1.96 line; however, $M_{1.96}$, if it were possible to measure its rapid changes, would presumably not pass through a maximum but just increase to a limiting value. The line-broadening is due to an increased concentration of conduction electrons in

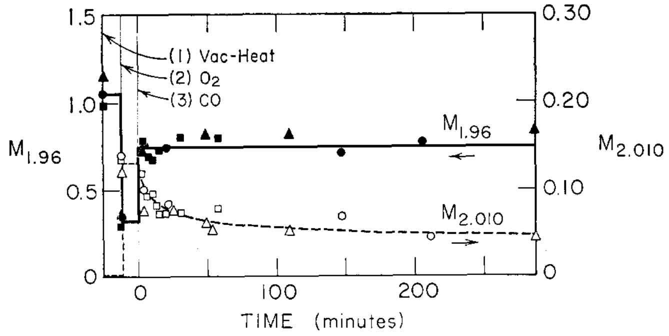

FIG. 1. Relative changes of the first moments, $M_{1.96}$ (solid symbols) and $M_{2.010}$ (open symbols), resulting from oxygen and carbon monoxide sorption on three samples of pretreated ZnO. (ESR and sorption carried out at 20°C.) (1) ZnO vacuum-heated at 500°C for 1 hr; (2) oxygen sorption of $0.3 \times 10^{17} O_2$ molecules/g ZnO; (3) carbon monoxide sorption of 0.3×10^{17} (○), 1.0×10^{17} (△), and 3×10^{17} (□) CO molecules/g ZnO.

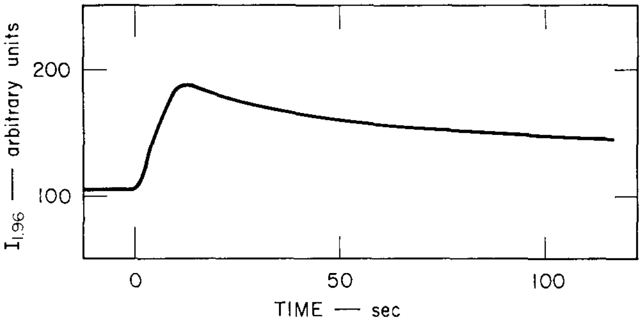

FIG. 2. Change of the peak intensity, $I_{1.96}$, upon sorbing CO on ZnO·O_2 at 20°C. CO introduced at time 0.

the bulk resulting from the reaction of CO with oxygen surface states.

The linewidth and spin density of the 1.96 line were found to be approximately proportional to one another for three separate ZnO samples and essentially independent of treatments such as vacuum heating, oxygen sorption, subsequent heating, and finally CO sorption. For example, for conditions that increased the spin densities in the range from 3×10^{15} to 15×10^{15} spins/g ZnO, the linewidths increased from 7 to 10.5 gauss, respectively.

DISCUSSION

The period of time for a one-half change of the ESR lines upon CO sorption is estimated from the data in Figs. 1 and 2 to be about 60 min for the 2.010 line and about 10 sec for the 1.96 line. The rates of change of these lines clearly differ by a factor of at least 10^2 despite the inherent difficulty in measuring the initial rapid change of the 1.96 line. The marked difference in rates of change of the two ESR lines upon CO sorption is taken as evidence of two different mechanisms by which CO reacts on the ZnO·O_2 surface. These mechanisms must involve reactions of CO with sorbed oxygen species, because CO, in the absence of presorbed oxygen, produced no change in the ESR spectrum of ZnO. It is further concluded that each of the two mechanisms involves a different oxygen species, since one oxygen species cannot account for two reactions of such different rates.

The identities of the reactive oxygen species and the CO oxidation mechanisms cannot be unequivocally deduced from the above largely qualitative information. The results of various investigators (*2, 3–13*) on the probable identity of sorbed oxygen species on ZnO lead to the consensus that oxygen sorption at low temperatures leads primarily to O_2, O_2^-, and O^-, and at higher temperature primarily to O^- and O^{2-}. We therefore assume that in the present study the oxygen species reactive with CO are among O_2, O_2^-, and O^-.

The rapidly reacting species must be negatively charged to account for the observed electron transfer to the bulk upon CO sorption, i.e., the increase of $M_{1.96}$. It is difficult to decide whether the slowly reacting species reacts with or without electron transfer to the ZnO bulk, because the experimental variation in the measurement of $M_{1.96}$ is of the same order of magnitude as the change in $M_{2.010}$. Therefore at present it is not possible to recognize a slow change of $M_{1.96}$ which corresponds to the slow change of $M_{2.010}$. If the slow reaction proceeds with electron transfer, the oxygen species is charged; if no electron transfer occurs, the species is either neutral or it is charged and reacts to form a sorbed product that retains the electron.

We tentatively propose that the reactive oxygen species at room temperature are O_2^- and O^-. The O_2^- species is assumed to be the slowly reactive species associated with the 2.010 line; actually the 2.010 line is one of three lines (2.003, 2.008, and 2.05) attributed to anisotropic g values of this species (*14*). This species may react with or without electron transfer to the ZnO bulk. The O^- species is then assumed to be the rapidly reactive species which has no observable resonance and which reacts with electron transfer to the bulk, probably by $CO + O^- \rightarrow CO_2 + e$. Expectations that the principal product of the fast reaction is CO_2 are supported by the fact that this molecule is neither an electron acceptor nor donor, as shown in this study and in others (*3–5*). Thus, if an intermediate complex such as CO_2^- were to be formed, it would rapidly release its electron to the solid. Finally, we must postulate formation of a sorbed product, such as CO_3^- which traps electrons at the surface. Such a species is required because sorption of CO on $ZnO \cdot O_2$ does not entirely restore $M_{1.96}$ to the original value before oxygen sorption.

Because of the importance of the electron transfer process with respect to bulk ZnO in the interpretation of our CO oxidation results, it is valuable to assess the findings of other investigators in this connection. Several such studies have been made in which an electron transfer process has been observed (*3, 12, 13*); however, the results of these studies are not entirely comparable with the present study, nor in some cases in agreement among themselves. The principal reason for the discrepancies appears to be due to differences in the ZnO pretreatment and in experimental conditions such as residual oxygen pressure.

Chon and Prater used the Hall effect to study the CO oxidation and concluded that O^- is the dominant, but probably not the only, reactive species in a reaction with electron transfer to the ZnO in the temperature range of 200° to 350°C (*3*). Their values for the half-time τ of the electron transfer reaction were larger by a factor of about 10^2 than that observed in the present study. Amigues and Teichner (*5*) also observed that the reaction between CO and O_2 at 261°C produced in ZnO a slow increase of the electrical conductivity ($\tau \sim$ 10 to 70 min), and they concluded that a nonionic sorbed oxygen species reacts with CO. These large values of τ are probably due to the large residual oxygen pressures that these investigators used. That is, until the partial pressure of oxygen is reduced by the CO reaction, the electrons of the bulk will tend to be localized on sorbed oxygen species. A comparable effect of oxygen on sorbed species was noted by Kwan and Setaka, who showed by means of ESR that in the presence of CO the rate of disappearance of a sorbed oxygen species, identified with a line at $g = 2.008$, depended in some reciprocal way on the oxygen pressure (*6*); however, they did not examine the 1.96 line. In the present study the residual oxygen pressure was very low, so that only the presorbed oxygen was available for CO oxidation.

Amberg and Seanor, by means of infrared, observed a slow transfer of electrons from the surface to the bulk when CO was sorbed on ZnO at 30°C, but only for oxidized ZnO (*12*). However, for a similar system Doeffler and Hauffe report from electrical conductivity studies that electron transfer occurs in the opposite direction, from the bulk to the surface, when CO is sorbed on oxidized ZnO at 150°C (*13*).

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