Reactivity of O_2^- on ZnO

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Summary O_2^- adsorbed on ZnO is inactive for oxygen exchange reactions as well as for the oxidation of CO on ZnO; O_2^- is heterogeneous in its adsorption strength.

We have reported that the active component in the catalytic oxidation of CO on ZnO is O^- and not O_2^-;[1-3] however, Morrison *et al.*[4] suggested recently that O_2^- is the active form. In the present study, a temperature programmed desorption and isotopic analysis of the desorbed gases were carried out simultaneously by mass spectrometry providing information on the reactivity of O_2^- on ZnO (Kadox-25). ZnO, evacuated at *ca.* 410 °C for > 12 h and cooled *in vacuo*, was exposed to *ca.* 7—10 mmHg of $^{18}O_2$ (93 atom%) at room temperature, and, after evacuation, was recontacted with 6—7 mmHg of $^{16}O_2$ at room temperature and then evacuated. The adsorption cell was connected directly to the mass spectrometer.

Exchange reactions between O_2^- and adsorbed CO or CO_2 were studied by adding CO or CO_2 to ZnO treated as above with $^{18}O_2$. E.s.r. spectroscopy has shown that oxygen is desorbed as O_2^- from ZnO at *ca.* 185 °C and also from hydrogen-treated ZnO at lower temperatures.[2,3,5]

Figure 1 shows the typical isotopic composition of oxygen desorbed from ZnO on which $^{18}O_2$ had been adsorbed for 2 h followed by evacuation for 1 h and adsorption of $^{16}O_2$ for 2 h at room temperature. Before the temperature was raised, the sample was evacuated for 2 h at room temperature.

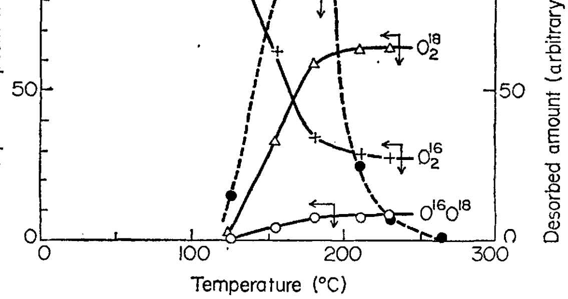

Figure 1. Isotopic composition of oxygen desorbed from ZnO. Dotted line indicates approximate desorption.

The isotopic composition of the desorbed oxygen changes with increasing temperature, approaching a uniform comcomposition without isotopic mixing, indicating that O_2^- is heterogeneous in its adsorption strength.

$^{16}O_2$ and $^{18}O_2$ were co-adsorbed on hydrogen-preadsorbed ZnO. In contrast to evacuated ZnO, the isotopic composition of the oxygen from hydrogen-preadsorbed ZnO does not approach a uniform value even at high temperatures, showing an enhancement of heterogeneity for the adsorption of O_2^-, as suggested by desorption experiments.[3]

The conservation of the molecular identity of the desorbed oxygen observed on both evacuated ZnO and hydrogen-adsorbed ZnO rules out the equilibrium $O_2^- \leftrightharpoons 2O^-$ on the surfaces below 200 °C.

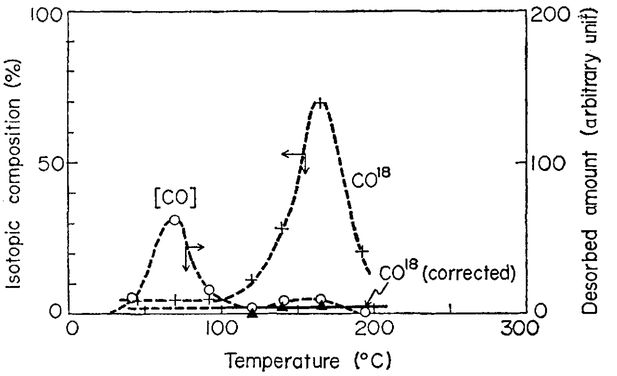

FIGURE 2. Isotopic composition of desorbed CO when CO was admitted on $^{16}O_2$ and $^{18}O_2$ coadsorbed ZnO. --+-- $C^{18}O$: apparent $C^{18}O$ in desorbed CO. --▲-- $C^{18}O$: corrected for exchange in the mass spectrometer.

Figure 2 shows the results when CO was added to ZnO preadsorbed with $^{18}O_2$ and $^{16}O_2$ at room temperature. One oxygen desorption peak and two CO desorption peaks were observed below 200 °C, indicating that O_2^- is less reactive for CO oxidation.[1,3] The isotopic composition of the desorbed oxygen is similar to that in Figure 1. The apparent amount of $C^{18}O$ in the desorption of CO is a maximum at the temperature of the oxygen desorption maximum. However, CO and $^{18}O_2$ were found to exchange in the mass spectrometer, and, if this exchange is allowed for, the amount of $C^{18}O$ in the desorption peaks of CO is negligible.

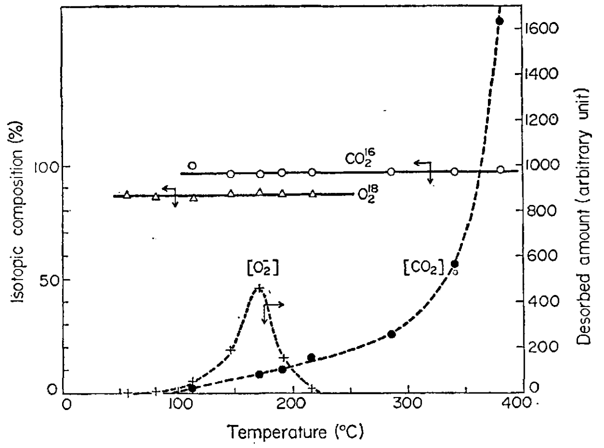

FIGURE 3. Isotopic composition of desorbed oxygen and desorbed CO_2 when CO_2 was admitted on $^{18}O_2$ adsorbed ZnO.

Figure 3 shows the results when CO_2 was adsorbed on ZnO preadsorbed with $^{18}O_2$ at room temperature. No isotopic mixing was observed for the desorptions of either O_2 or CO_2.

These results show that O_2^- on ZnO is inactive for exchange reactions with CO and CO_2 as well as for the catalytic oxidation of CO.[1]

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