

## The EPR Measurement of $O_2^-$ Species in Silver(II) Oxide (AgO) Related to the Catalysis

There has been considerable interest in the oxygen species of silver surface related to the catalytic oxidation of ethylene to ethylene oxide. Kilty *et al.* (1) suggested in their experimental work by using oxygen isotope and ir technique that the  $O_2^-$  species on the silver could be an important role of ethylene oxidation to form ethylene oxide. The work by Clarkson and Cirillo (2) reported the first spectroscopic identification of the adsorbed  $O_2^-$  species on the surface of silver metal supported on porous Vycor quartz glass, using an EPR technique.

In the present paper, we report the much clearer EPR spectra of  $O_2^-$  species in silver(II) oxide (AgO) and some observation of the chemical reactivity of  $O_2^-$  species with ethylene to form ethylene oxide.

Silver(II) oxide sample was prepared by the oxidation of silver nitrate by means of potassium peroxydisulfate in an alkaline medium following the method by Hammer and Kleinberg (3). The X-ray diffraction pattern of the sample used in this experiment is shown in Fig. 1, with the reference spectra of AgO and  $Ag_2O$ , where most of the observed reflections could be attributed to AgO and  $Ag_2O$ .

The EPR spectra were recorded on Varian spectrometer Model E-4, and the spectra were generally obtained at  $-196^\circ C$ , because of clearer resolution than at room temperature.

The variation of EPR spectra of  $O_2^-$  species with heating *in vacuo* are presented in Fig. 2, where very strong and clear spectra of  $O_2^-$  species with  $G_{xx} =$

1.9843,  $G_{yy} = 2.0026$  and  $G_{zz} = 2.0389$  could be observed. Also, other unexplainable signals were observed as the  $G$ -values, namely at  $G = 2.148$ , 2.124 and 1.940, respectively. As shown in Fig. 2, the intensity of EPR signal from  $O_2^-$  species was observed to decrease with heating at higher temperature *in vacuo*, and to disappear gradually at  $130^\circ C$  with the heating time. At the higher temperature, another signal at  $G = 1.940$  was increased slightly over  $200^\circ C$ . This signal might be due to the defect of lattice.

When the sample of AgO was contacted with ethylene gas, it was found that the superoxide ion  $O_2^-$  reacted with ethylene to reduce the signal intensity at  $100^\circ C$ , as shown Fig. 3.

To make clear the nature of  $O_2$  species, the stability of the radical to prolonged outgassing and thermal desorption of oxygen from the AgO sample, and also the reactivity with ethylene were examined. Figure 4 shows the thermal desorption curves of oxygen from AgO sample, where the raising rate of temperature was  $1^\circ C/6$  min and the desorbed gases (mainly  $O_2$  including small amount of  $CO_2$ ,  $H_2O$ , CO and HCHO) were analyzed simultaneously by a quadrupole mass spectrometer. It is to be noted in Fig. 4a that two kinds of oxygen were observed clearly in the temperatures of around 150 and  $400^\circ C$ , respectively. The former peak of oxygen might be due to  $O_2^-$  species and the latter  $O^{2-}$  species as  $Ag_2O$ . On the other hand, the thermal desorption curve of the AgO sample after contacting with ethylene of 40 Torr at  $100^\circ C$  for several

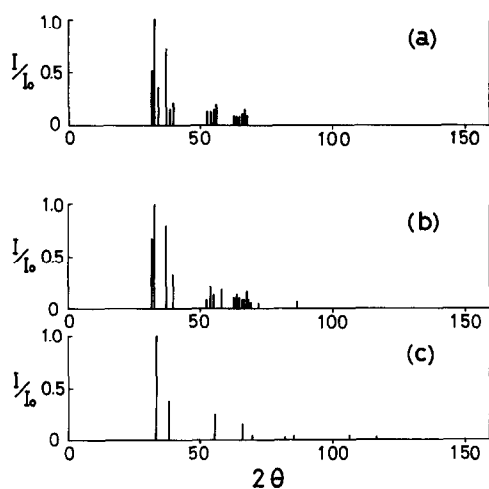


FIG. 1. X-Ray diffraction patterns of the AgO sample. (a) AgO sample prepared in the present study; (b) standard diffraction pattern of AgO from ASTM card; (c) standard diffraction pattern of  $\text{Ag}_2\text{O}$  from ASTM card.

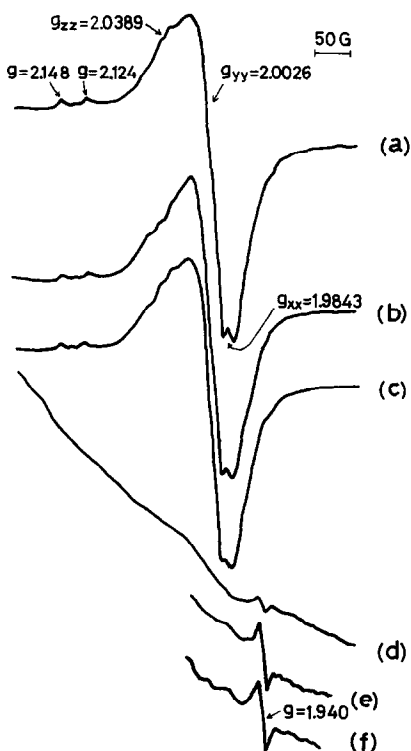


FIG. 2. Changes of EPR spectra of the AgO sample by heating *in vacuo*. (a) 20°C for 20 hr; (b) 100°C for 12 hr; (c) 130°C for 2.5 hr; (d) 130°C for 30 hr; (e) 260°C for 10 hr; (f) 325°C for 10 hr. All the spectra were recorded at  $-196^\circ\text{C}$ .

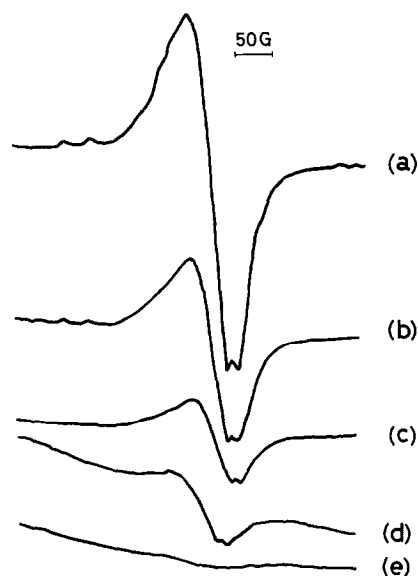


FIG. 3. Changes of EPR spectra of AgO sample by contact with ethylene (40 Torr) at  $100^\circ\text{C}$ . (a) AgO sample before contact; (b) AgO sample after contact with ethylene for 18 hr; (c) for 36 hr; (d) 56 hr; (e) 74 hr. All the spectra were recorded at  $-196^\circ\text{C}$ .

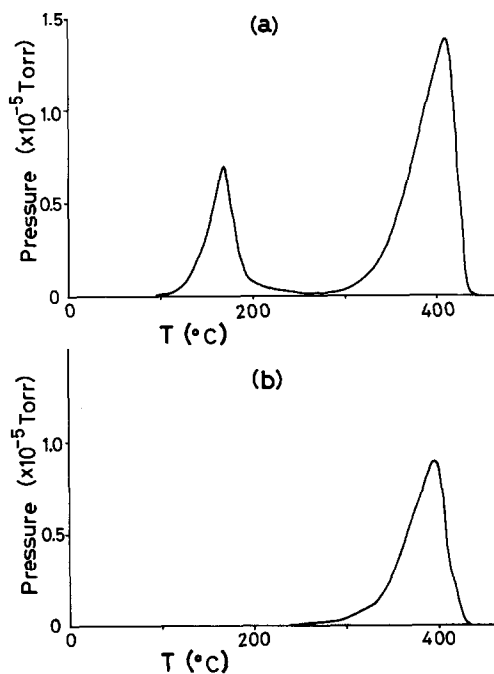


FIG. 4. Thermal desorption curves of oxygen. (a) AgO sample; (b) AgO sample after reacted with ethylene (40 Torr) at  $100^\circ\text{C}$  for 4 days.

days is presented in Fig. 4b, in which obviously only one peak from oxygen was observed at around 400°C, and most of oxygen desorbed at around 150°C in Fig. 4a may be reacted with ethylene very easily (1 Torr = 133.3 N m<sup>-2</sup>). Results of mass spectroscopic observation on the product gases showed that the selectivity of C<sub>2</sub>H<sub>4</sub>O formation at 100°C as the reaction temperature was approximately 60% for the first peak at 150°C and 40% for the second peak at 400°C.

Comparing the data of thermal desorption study with those of EPR study, it may be concluded that the O<sub>2</sub><sup>-</sup> species which could be contained mostly in the first desorption peak at the lower temperature could react with ethylene easier than the oxygen in the second desorption peak in

which large amount O<sub>2</sub><sup>-</sup> species could be contained.

## REFERENCES

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