Adsorbed Species of Oxygen on Dark and on Illuminated Zinc Oxide

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Summary Oxygen adsorbed at room temperature on zinc oxide, which had been cooled in vacuum after activation, gave two oxygen desorption peaks with maxima at 180—190 and 280—290 °C, while oxygen adsorbed at 200 °C gave mainly the higher temperature peak; no desorption was observed from zinc oxide cooled under an oxygen atmosphere.

A TEMPERATURE programmed desorption technique has been applied to oxygen on dark and on illuminated zinc oxide Zinc oxide (Kadox-25) was mounted in a cell connected to a molecular sieve column of a gas chromatograph The cell, furnace, and illumination are as reported previously [1] Helium carrier gas was passed through the cell at various temperatures and desorbed oxygen was detected by a thermal conductivity cell

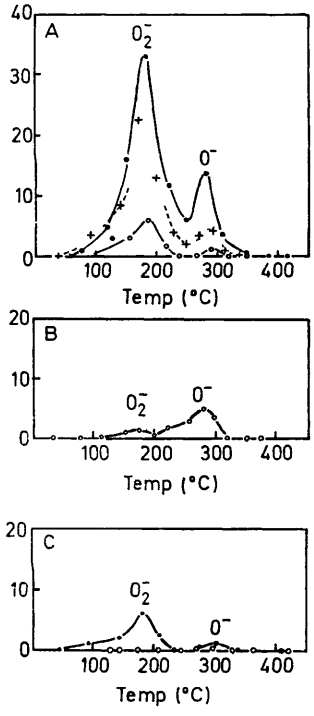

FIGURE A, *Desorption spectra (in arbitrary units of oxygen adsorbed) at room temperature* ●, *overnight exposure,* +, 6 h *exposure,* ○, 20 min *exposure* B, *Desorption spectrum of oxygen adsorbed at* 200° C *for* 1 h C, *Desorption spectra from inert surface* ○, *inert surface prepared by cooling under oxygen,* ●, *after* 30 min *illumination of inert surface*

Figure A shows typical desorption spectra of oxygen adsorbed at room temperature on zinc oxide which has been outgassed at 415—420 °C for 3–7 h and cooled *in vacuo* Before the desorption experiment the oxide was evacuated for 10 min at room temperature The heating rate was about 400 °C per hour The desorption spectra have two peaks, one at *ca* 180—190 and another at 280—290 °C On increasing the adsorption time from 20 min to overnight, the amount of desorbed oxygen increases proportionately in both peaks

When oxygen was adsorbed at about 200 °C for 1 h, instead of at room temperature, and then the surface cooled to room temperature under oxygen, the desorption spectrum is as shown in Figure B The lower temperature peak is greatly decreased

If zinc oxide evacuated at 415 °C for 2 h was cooled under oxygen from 415 °C to room temperature and kept overnight, no desorption peaks were observed (Figure C, open circles) Oxygen was admitted to this inert surface at room temperature and illumination carried out for 30 min after which a desorption spectrum (Figure C, solid circles) was observed

It has been established[2] that the main oxygen species adsorbed on zinc oxide at low temperature is O_2^- The O_2^- is estimated[3] to be stable up to *ca* 150 °C and changes to O^- on zinc oxide with some activation energy above 160 °C Accordingly, the two desorption peaks are proposed to correspond to O_2^- and O^- respectively The results suggest that both O_2^- and O^- may be formed on zinc oxide at room temperature, O_2^- being the predominant adsorbed species Figure B suggests that equilibration between O_2^- and O^- is not established as the temperature is lowered after oxygen has been adsorbed at 200 °C The fact that zinc oxide cooled under oxygen is relatively inert to oxygen adsorption as indicated by the amount of desorption (Figure C), reveals that the active sites for oxygen adsorption are destroyed by this treatment The recovery of adsorption ability by illumination indicates the reformation of active sites

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[1] K Tanaka and G Blyholder, *J Phys Chem*, 1971, **75**, 1037
[2] J H Lunsford and J P Jayne, *J Chem Phys*, 1966, **44**, 1487, M Codell, J Weisberg, H Gisser, and R D Iyengar, *J Amer Chem Soc*, 1969, **91**, 7763, A J Tench and T Lawson, *Chem Phys Letters*, 1971, **8**, 177
[3] H Horiguchi, M Setaka, K M Sancier, and T Kwan, 4th International Congress on Catalysis, Moscow, 1968