The Effect of Traces of Sulphide on the Catalytic and Magnetic Properties of Indium Oxide

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THE catalytic properties of SnO_2, for oxidative dehydrogenation of butenes have been described.[1] Since Ag^+, In^{3+}, and Sn^{4+} ions have all the $4d^{10}$ electronic configuration and a small amount of sulphide is known to improve silver oxide catalysts for oxidising ethylene to ethylene oxide,[2] we have investigated the effect of traces of sulphide on the oxidative dehydrogenation of butenes on In_2O_3 and SnO_2.

In_2O_3 (A) containing 0·4 wt. % sulphur was prepared by heating In_2S_3 in air at 600° for 7 hr. *X*-Ray powder photographs of A were identical to those of a very pure sample of In_2O_3 (B). While samples of A were initially more active than those of B for converting but-1-ene into buta-1,3-diene at 340°, or above, using a 1 : 1 mixture of olefin and oxygen, the effect was very short-lived as the residual sulphide was rapidly eliminated as SO_2, in contrast to its stability during prior heating in oxygen alone at much higher temperatures. However, the most striking difference was that but-1-ene isomerised very rapidly to an equilibrium mixture of n-butenes, whereas, isomerisation on B was slow compared to oxidative dehydrogenation. The catalytic properties of used samples of A were then identical to those of B.

Because of the high initial activity of A, we examined isomerisation reactions in the absence of oxygen at 20°. A static reaction vessel containing 0·2 g. of A or B was heated in oxygen at 400°, evacuated, cooled, and charged with but-1-ene (8×10^{19} molecules). Small portions of the reaction mixture were periodically expanded into a sampling valve and analysed by g.l.c. There was rapid initial conversion of but-1-ene to but-2-enes (*cis*/*trans* = 1·2), but the activity quickly declined. When the vessel was evacuated and a second dose of but-1-ene admitted, isomerisation was very slow (*cis*/*trans* = 2·7). The results are plotted in Figure 1. Cyclopropane and methylcyclopropane also isomerised readily to propene and only n-butenes respectively, but again the activity of fresh samples of A at 20° fell off quickly and conversion of second doses on the used samples were negligible. On the other hand, slow isomerisation of but-1-ene and the cyclopropanes on samples of B required temperatures of 200 and 400°, respectively.

Samples of A and B which had been evacuated at 400° were subjected to e.s.r. analysis.† The e.s.r. spectrum of A contained a single broad line (6×10^{15} spins g.$^{-1}$, $g = 1{\cdot}875$) which was absent in the spectrum of B. When but-1-ene or cyclopropane was added at 20° the intensity of this e.s.r. signal quickly diminished and a much smaller signal ($g = 1{\cdot}997 \pm 0{\cdot}005$) appeared, but eventually both vanished. The effect of but-1-ene is shown in Figure 2. The second signal is just apparent on the low-field side in the spectra of Figure 2 but was much more pronounced using the less reactive cyclopropane. The initial signal and catalytic activity were largely restored by evacuation, followed by heating in oxygen to 400°, evacuating, and cooling to 20°. Ethylene had no effect on the initial e.s.r. spectrum of A even after 12 hr.

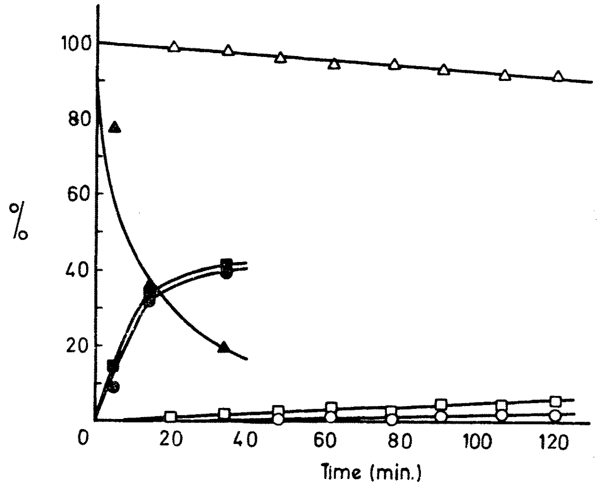

FIGURE 1. *Isomerisation of but-1-ene at 20° on* In_2O_3 *containing 0·4 wt. % sulphur. Filled symbols, first run; open symbols, second run.* △, *but-1-ene;* □, cis-*but-2-ene;* ○, trans-*but-2-ene.*

The g-value of the e.s.r. signal in A indicates strong spin–orbit coupling, so the paramagnetic centres are probably In^{2+} ions ($4d^{10}\ 5s^1 \rightarrow 4d^9\ 5s^2$) due to electron transfer to In^{3+} ions from the sulphide ions in the oxide lattice. Since ethylene had no effect on the initial signal, but-1-ene seems to isomerise initially *via* formation of 1-methylallyl radicals at the paramagnetic centres. Such intermediates should give almost equal amounts of but-2-enes.[3] This is a fast reversible process as $\sim 10^5$ molecules per centre are converted. Simultaneously a slower irreversible process occurs during which unpaired electrons eventually become spin-paired in surface–organic complexes, and the catalytic activity disappears. This interpretation is supported by the intermediate appearance of the second e.s.r. signal whose g-value is close to that of the spin-free value.

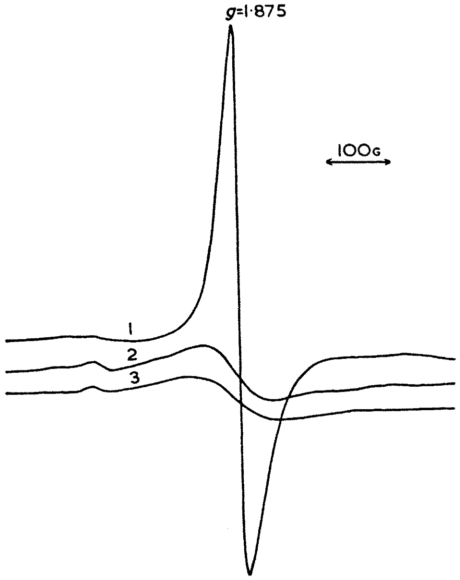

FIGURE 2. *Effect of but-1-ene on e.s.r. spectrum of* In_2O_3 *containing 0·4 wt. % sulphur. 1, initial spectrum; 2 and 3, spectra at 9 and 12 min., respectively, after addition of olefin.*

SnO_2 containing 0·3 wt. % sulphur, which was also prepared from the sulphide, had very similar catalytic and magnetic properties.

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† E.s.r. spectra were obtained using a Decca X-1 spectrometer operating at 9270 MHz with a magnetic field modulation of 100 kHz.

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