Desorption of an Intermediate in the Complete Oxidation of C_2H_4 over Silver Catalyst

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Summary It was found by applying the transient response method that a stable intermediate was formed during the complete oxidation of C_2H_4 over a silver catalyst which could be desorbed as acetic acid in a stream of pure H_2, whereas it was not desorbed in pure He and it was decomposed to CO_2 and H_2O in a mixture of O_2–He.

WE recently[1] demonstrated, by using the transient response method[2], the existence of a stable intermediate (In), of atomic composition $C:H:O = 1:2:(1\sim2)$, on the silver surface during the complete oxidation of C_2H_4 over silver· We have now attempted to desorb this intermediate without decomposition into CO_2 and H_2O.

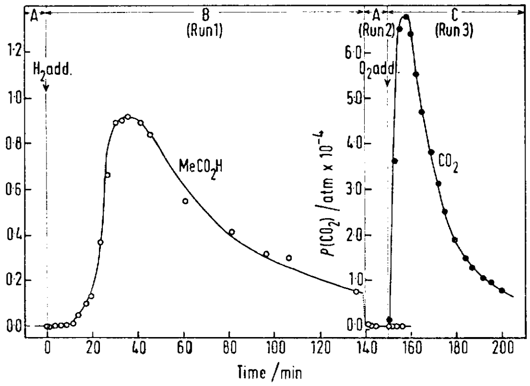

FIGURE. Desorption of (In) from the Ag surface under gaseous conditions. A: $P°$ (He) = 1·0; B: $P°$ (H_2) = 1·0; C: $P°$ (O_2) = 0·20, P° (He) = 0·80 atm. T = 91 °C.

The transient response method and the catalyst used in the study are as reported previously.[1]

After the reaction had attained steady-state conditions in a stream of mixed gases, $P°(C_2H_4) = 0{\cdot}021$, $P°(O_2) = 0{\cdot}20$, and $P°(He) = 0{\cdot}779$ atm at 91 °C, producing (In), the catalyst was reduced in a C_2H_4–He mixture, with $P°(C_2H_4) = 0{\cdot}021$ and $P°(He) = 0{\cdot}979$ atm, for 900 min until no CO_2 and C_2H_4O could be detected in the effluent gas stream, removing surface oxygen. The catalyst was then exposed to a pure He stream for 40 min until C_2H_4 was completely desorbed. He was then replaced by H_2, effectively removing any remaining surface oxygen and the effluent gas was continuously analysed by g.l.c. with a Porapak Q column. Acetic acid was detected by its smell, retention time, and the i.r. spectrum of a liquified sample as shown by Run 1 in the Figure. The desorption of acetic acid was instantaneously stopped by reverting to pure He (Run 2). When the catalyst was exposed to an O_2–He mixture, appreciable amounts of CO_2 and H_2O were observed but only the CO_2 desorption is shown (Run 3) in the Figure.

In the course of Run 1, the only component other than acetic acid detected was H_2O, produced by reduction of the surface with H_2. The amounts of acetic acid desorbed in Run 1 and CO_2 formed by the decomposition of (In) in Run 3 were estimated to be $1{\cdot}9 \times 10^{-7}$ and $5{\cdot}8 \times 10^{-7}$ mol per g of Ag, respectively. The total amount, estimated from stoicheiometry, $9{\cdot}6 \times 10^{-7}$ mol CO_2 per g of Ag, is close to the value, 11×10^{-7} mol CO_2 per g of Ag, obtained when (In) was decomposed under steady-state conditions, the catalyst being directly exposed to an O_2–He mixture. This, together with the experimental results obtained above indicate that (In) is an adsorbed species which can desorb as acetic acid in H_2 but not in He even when the catalyst is heated to 108 °C and it is decomposed to CO_2 and H_2O in O_2–He.

Although it is very difficult to determine the form of (In) on the surface, the fact that it desorbs as acetic acid enables us to consider a structure involving retention of the carbon–carbon bond and to exclude the formaldehyde form which has been generally assumed so far.[3]

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[2] M. Kobayashi and H. Kobayashi, *J. Catalysis*, 1976, **27**, 100; *Shokubai*, 1974, **16**, (2), 8; *Catalysis Rev.*, 1974, **10**, 139.

[3] L. Ya. Margolis, *Adv. Catalysis*, 1963, **14**, 429.