Oxygen Species Contributing to the Formation and the Decomposition of an Intermediate in the Complete Oxidation of Ethylene over a Silver Catalyst

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Summary The oxygen species formed on silver by the decomposition of N_2O contribute to the formation of an intermediate (In) in the complete oxidation of C_2H_4; the oxygen species from gaseous O_2 contribute to the decomposition of In.

Recently we demonstrated the existence of a stable intermediate (In) during the course of the complete oxidation of C_2H_4 on a silver surface.[1] We have now examined the form of the adsorbed oxygen species contributing to the formation and the decomposition of the intermediate In by applying a transient response method, using N_2O and O_2 gases which can produce, respectively, monoatomic and diatomic oxygen species on the surface in the initial stages of their adsorption. The catalyst and the transient response method used are as reported previously.[1] The total flow rate of the gases was maintained at 160 ml (N.T.P.) min^{-1}.

After the catalyst had been completely reduced by a pure H_2 stream at 91 °C for 24 h, the stream was changed to pure He (desorption of adsorbed H_2 and H_2O) and the catalyst was then exposed to a stream of C_2H_4–He (12·8 : 87·2). O_2 and N_2O gases were separately pulsed into the inlet stream of this mixture and the resulting amounts of CO_2 and C_2H_4O in the outlet stream in each case were measured (run 1). The same measurements were repeated ten times; typical results are in the Figure. Comparison between both pulses shows that, in the case of the O_2 pulse, the production of CO_2 and C_2H_4O was observed whereas, for N_2O, only N_2 was detected, which was formed in the initial stages of the measurements (not shown in the Figure). This difference may be reasonably attributed to the difference between the reactivity of the oxygen species adsorbed from O_2 and that from N_2O. The possibility of other factors contributing to the form of the response curve was eliminated by the following conclusions which had been drawn from the transient data; C_2H_4 and N_2O are not co-adsorbed on the reduced surface, gaseous C_2H_4 directly reacts with oxygen which had been irreversibly adsorbed, C_2H_4O and CO_2 produced are desorbed rapidly, and N_2O decomposes directly on the active sites which are free from adsorbed oxygen. Furthermore, O_2 or N_2O which had not been taken up by the surface could be detected for all pulses in the effluent gas. This indicates that the oxygen species adsorbed initially in each pulse are continuously distributed along the reactor length from the entrance to the exit of catalyst bed, with no significance differences between the O_2 and N_2O pulses.

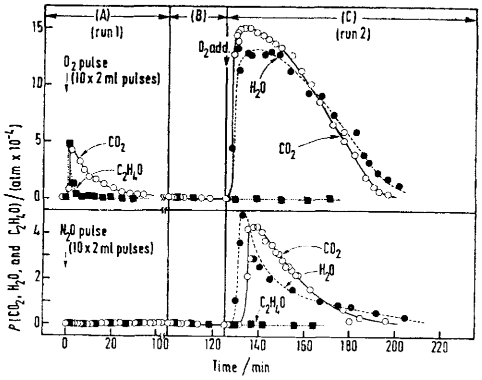

FIGURE. Formation of the intermediate In. (A), He–C_2H_4 stream: $P°(C_2H_4)$ 0·128, $P°(He)$ 0·872; (B), pure He stream; (C), O_2–He stream $P°(O_2)$ 0·10, $P°(He)$ 0·80. Temperature 91 °C.

The above consideration show that the response curves in run 1 can be explained by the supposition that monoatomic oxygen species produce only the intermediate In by reaction with C_2H_4 whereas diatomic oxygen species can produce C_2H_4O and decompose In to CO_2 and H_2O. In the case of the N_2O pulse, monoatomic oxygen species are formed initially which produce the intermediate In by reaction with gaseous C_2H_4 faster than their rate of recombination to diatomic oxygen. Conversely, with the O_2 pulse, the diatomic oxygen species adsorbed produce C_2H_4O and are also simultaneously dissociated into monoatomic species. These monoatomic species produce the intermediate In which is then decomposed to CO_2 and H_2O by reaction with the diatomic oxygen species. This explains why CO_2 and C_2H_4O were produced with the O_2 pulse but not the N_2O pulse. When the temperature was increased from 91 to 160 °C, small amounts of C_2H_4O and CO_2 were detected even with the N_2O pulse, indicating the production of diatomic oxygen species caused by the rapid recombination of monoatomic oxygen species at the higher temperature.

The formation of the intermediate In with both pulses was proved by the following subsequent experiments. The stream of C_2H_4–He which had been used in the foregoing experiments was changed to pure He and the catalyst was then exposed to a stream of O_2–He (20:80) (run 2). The amounts of CO_2 and H_2O produced were followed simultaneously. The results in the Figure show that the amount of CO_2 and H_2O produced in each pulse was similar; other products were not detected. This result indicates strongly that the intermediate In, which had already been formed during the pulse run, was easily decomposed to CO_2 and H_2O by the diatomic oxygen species in the O_2–He stream. In contrast, the N_2O–He stream did not cause decomposition of In.

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[1] M. Kobayashi, M. Yamamoto, and H. Kobayashi, 6th International Congress on Catalysis, London, A24, 1976; see also M. Kobayashi and H. Takegami, *J.C.S. Chem. Comm.*, 1976, 1033; 1977, 37.

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