Structure Sensitivity of Oscillation in the Partial Oxidation of Propene over Pt–SiO_2

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Oscillatory behaviour has been observed in the partial oxidation of propene to propanal by nitrous oxide on silica-supported platinum catalysts, whereas no oscillation appeared in the complete oxidation occurring in parallel; the extent of oscillation increased with increasing percentage exposed, indicating that the reaction is structure sensitive.

Many investigators have studied oscillatory phenomena in heterogenously catalysed complete oxidations of *e.g.* CO and H_2 on supported metal catalysts.[1] In the present study, the partial oxidation of propene to propanal on Pt–SiO_2, with various percentages exposed, has been studied using nitrous oxide as the oxidant.

Four catalysts were used with 7, 16, 40, and 81 percent of the surface platinum atoms exposed (D_h, measured by H_2 adsorption).[2] The catalysts (0.825—1.91 wt% Pt, 1.0—2.4 g, 60—80 mesh) were packed into a Pyrex tube which was immersed in a fluidized sand bath, the temperature of which was controlled to within ±0.5 °C. The reaction conditions were chosen to satisfy the conditions for a differential flow reactor with conversions of a few percent, using temperatures in the range 160 to 370 °C and a total gas flow rate of 80—320 (±2) ml min^{-1}. The oscillatory behaviour was followed manually using gas chromatography. The transient response method[3,4] was used to observe changes in the oscillation behaviour due to stepwise changes in the gas composition. Figure 1 illustrates the gas chromatographic response for the products propanal and carbon dioxide caused by the stepwise change in gas composition. Propanal formation clearly exhibited a regular oscillation, whereas no oscillation was observed for the response of carbon dioxide which showed instead a typical overshoot mode. The amplitude of the oscillation was increased immediately by a stepwise increase of the concentration of propene (conditions B). When the reactant gas stream reverted to pure helium (conditions A′), the amplitude of oscillation gradually decreased to zero over 30 min. However, the concentration of CO_2 quickly decreased to zero. From these results, one may conclude that CO_2 is not formed by further oxidation of propanal, since, were this so, the concentrations of both products would oscillate in parallel.

Figure 2 shows the turnover frequency (N_t, molecules site^{-1} s^{-1}) for propanal formation as a function of D_h and the ratio R of propene and nitrous oxide pressures. Since N_t increases with increasing D_h, the reaction is structure sensitive. Interestingly, the amplitude of the propanal oscillation increases markedly with increasing D_h and R. For the catalysts with D_h < 16, N_t becomes very small, although the oscillation still occurs. The selectivity for propanal, on the other hand, increases with increasing D_h and R.

The activation energies were calculated separately at the maximum and minimum of the oscillation to be 166 (±2) and 32 (±12) kJ mol^{-1}, respectively. This difference indicates that a transition occurs between two different surface structures as demonstrated in CO oxidation by Ertl *et al.*[5] The amount of

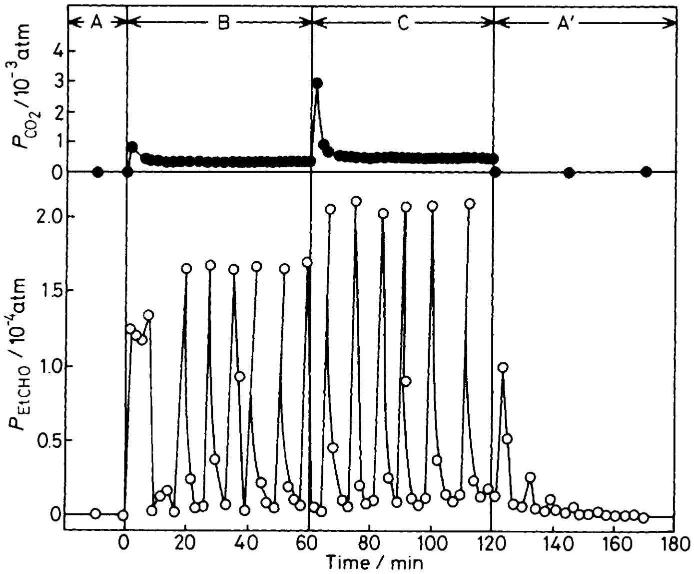

Figure 1. Transient oscillation of carbon dioxide (●) and propanal (○) partial pressures during the oxidation of propene over Pt–SiO_2; T = 310 °C, D_h = 16, F = 80 ml min^{-1}. Conditions: A,A′, $P^0(C_3H_6)$ = $P^0(N_2O)$ = 0, $P^0(He)$ = 1.000 atm; B, $P^0(C_3H_6)$ = $P^0(N_2O)$ = 0.050, $P^0(He)$ = 0.900 atm.; C, $P^0(C_3H_6)$ 0.100, $P^0(N_2O)$ = 0.050, $P^0(He)$ = 0.850 atm.

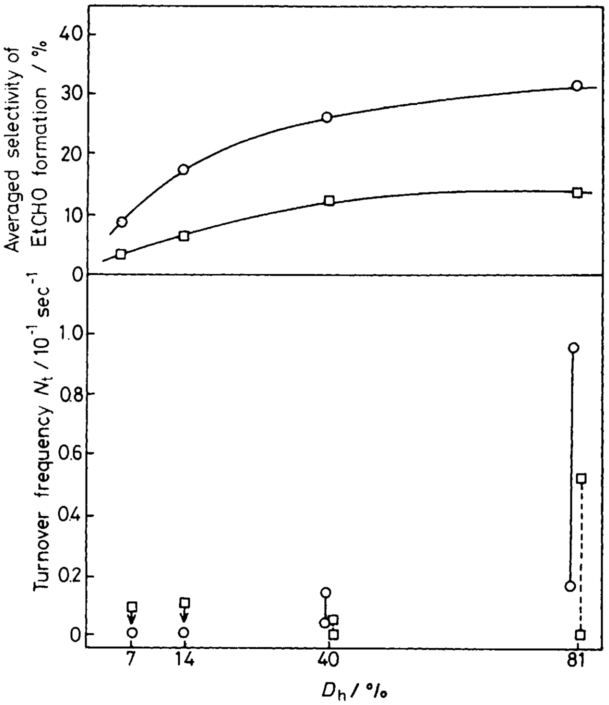

Figure 2. Effect of percentage of surface exposed (D_h) on (a) selectivity of formation of EtCHO with R = 10 (○) or R = 1 (□); and (b) amplitude of EtCHO oscillation in terms of turnover frequency N_t. T = 310 °C, F = 80 ml min^{-1}. R = $P^0(C_3H_6)/P^0(N_2O)$.

propene adsorbed was found to oscillate with the oscillation of propanal, suggesting that the adsorption of propene in some way triggers the switch between two different catalytic surface structures.

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