

Reaction Rate Oscillations during Propylene Oxidation on Platinum

INTRODUCTION

Sustained oscillations in reaction rate under isothermal conditions have been observed in several heterogeneous catalytic reactions including Pt catalyzed oxidation of hydrogen (1), carbon monoxide (2), ethylene (3), and a mixture of CO and 1-butene (4). Reviews of the theoretical and experimental studies were presented by Sheintuch and Schmitz (5) and Slin'ko and Slin'ko (6). It is of interest to determine whether oscillatory behavior is a peculiarity limited to small number of reactions or occurs in many reactions including hydrocarbon oxidation.

METHODS

We report here a study of oscillatory behavior during the isothermal oxidation of propylene on a platinum wire. The 5.2-cm-long and 0.005-cm-diameter high-purity platinum wire (United Mineral and Chemical Corp.) was placed in a flow reactor and maintained at a constant resistance, and hence temperature, by a constant temperature anemometer. Details of the experimental system and the instrumentation are described by Zuniga and Luss (1). The heat transmitted to the wire was calculated from the difference in the electric power required to maintain the wire at a preset resistance with and without reaction. The reaction rate was computed by assuming that all the heat generated by the reaction was transmitted to the wire and that the propylene was completely oxidized to CO_2 and H_2O (7). Extra-dry grade oxygen and nitrogen from gas cylinders (Lynde Inc.) were passed through activated charcoal beds and then mixed with CP-grade propylene by passing through a bed of Drierite pellets.

The platinum wire was activated by heating it in air to about 700°C for 1 hr before adding propylene (2% v) to the mixture.

The reaction sustained itself without electrical heating after about 1 hr, and the wire was kept at about 700°C for another 4 hr. Before each run the catalyst was reactivated by heating it in a 20% v O_2 in N_2 mixture for 5 min at 900°C followed by 30 min at 500°C . After the desired reaction temperature was set with a flow of the desired composition of N_2 and O_2 , propylene was introduced and the power input was recorded until either a time-invariant or a fully developed oscillatory state was achieved.

RESULTS

Sustained oscillatory states were observed for mixtures of less than 1% propylene in oxygen in the temperature range of 175 – 228°C . At 202°C oscillatory states appeared for propylene concentration between 0.2 to 1% v in oxygen (Fig. 1). The largest amplitude was observed for 0.38% v C_3H_6 and was about 0.3 of the average rate. For propylene concentrations higher than 1% v in oxygen, no oscillations were observed.

When the propylene concentration was increased from zero to 1.44% in a different run, another branch of the rate curve was found at the same temperature (202°C) and flow rate. The electrical power at this state was (within experimental error) the same as the power required without reaction. The nature and heat of the reaction taking place at this low activity branch are unknown. Thus, its reaction rate cannot be determined. We refer to it as the low activity state. A transition from the low to the high activity branch was observed as propylene concentration decreased to 0.2% v (Fig. 1). That branch was maintained upon subsequent increase in concentration. At 1.09% v the low activity state was established again following 1 min perturbation to room temperature.

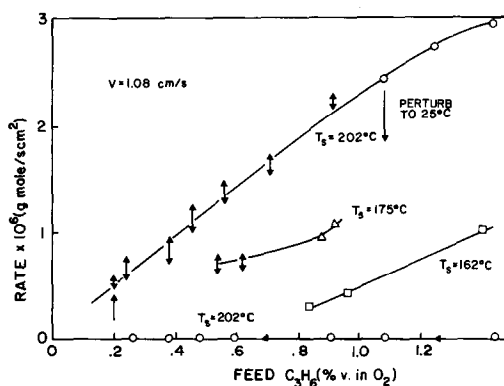


FIG. 1. High- and low-activity branches of the rate curve. Vertical arrows represent peak to peak amplitude of the oscillations.

The low-activity state was observed in a certain range of propylene concentration for temperatures below 207°C. Transitions between the two branches were established by temperature perturbations. At 175°C (Fig. 1) the high-activity branch was established by a temperature perturbation from the low-activity state at 0.91% *v* propylene. A small region of oscillatory behavior was observed when the concentration was decreased to 0.54% *v* (Fig. 1); transition to the low-activity branch occurred upon further decrease to 0.48% and this state was maintained for lower propylene concentrations. At very low propylene concentrations (<0.1% *v*) an appreciable increase in the rate was observed upon decreasing the reactant concentration before declining to zero for vanishing propylene concentration. Similar observations were made at 162°C (Fig. 1) where a stable high-activity branch existed for concentrations above 0.66%. An hysteresis loop was observed with 0.62% *v* propylene in oxygen as the temperature of the wire was varied; extinction and ignition occurred at 170 and 205°C, respectively.

The largest range of propylene concentration in oxygen for which oscillatory behavior existed was observed at 202°C. Upon diluting the reacting mixture with N₂ the region of oscillatory behavior dimin-

ished and the region of attraction of the low-activity state increased. Transitions from an oscillatory to a stable state and then to a low-activity state occurred upon replacing oxygen by nitrogen at a constant propylene concentration of 0.59% *v* (Fig. 2). After the low-activity state was established, the original state was not obtained after the nitrogen was eliminated. A temperature perturbation to 310°C was required to reestablish the oscillatory state.

An increase in temperature or oxygen concentration decreased the range of propylene concentration for which a low-activity state existed. For sufficiently high temperatures, the low-activity state disappeared.

Most oscillatory states were aperiodic (also termed chaotic) in nature, showing a sharp increase in reaction rate followed by a slow relaxation (Fig. 3). At large oxygen concentration, low propylene concentrations and at high temperatures, the oscillation exhibit several components of frequency ranging from several seconds to several minutes (Fig. 3b). Only the low-frequency components are maintained at higher propylene concentrations (Fig. 3c) and lower temperatures (Fig. 3a) or lower oxygen concentrations. These features were maintained for a long period of time;

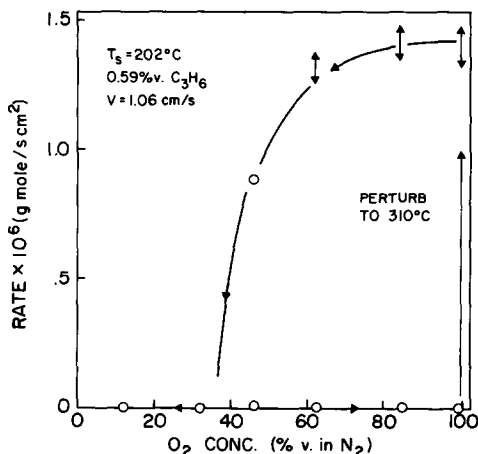


FIG. 2. Hysteresis observed upon variation in oxygen concentration.

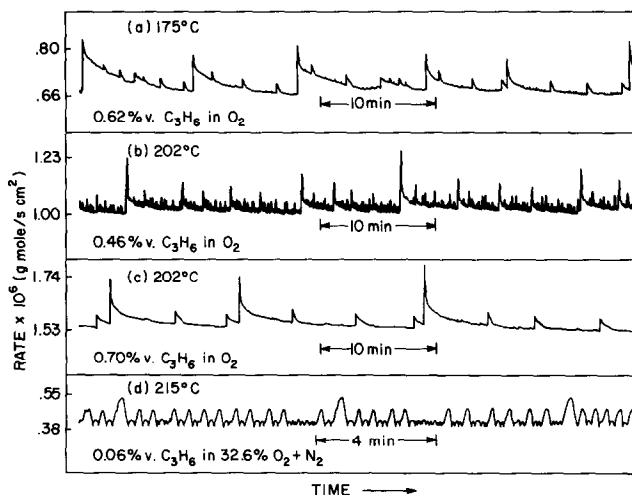


FIG. 3. Characteristic aperiodic states [time trace of the anemometer voltage, proportional to $(\text{rate})^{1/2}$.]

some of the states were recorded for 12 hr. In one state (Fig. 3d) the oscillations seem to be periodic over a short time span, but the features varied with time.

DISCUSSION

Oscillations in reaction rate and in surface oxygen activity were recently reported for Pt catalyzed oxidation of ethylene in a stirred reactor (3). These oscillations were observed at temperatures between 220 and 360°C and with hydrocarbon concentrations similar to those employed in this study, yet at low oxygen concentrations. They were attributed to cyclic oxidation and reduction of the surface. Studies of the oscillatory behavior during the oxidation of CO on Pt at 100–400°C, with reactant concentrations similar to those employed in this study, indicate that the instability is induced by the existence of minute concentrations of some poisonous component (2).

Recent theoretical studies (8) have shown that if the main reaction exhibits strong inhibition effects an oscillatory behavior may be induced either by surface oxidation and reduction or by reversible poison chemisorption. Such auto inhibition effects, indicated by negative order kinetics with respect to propylene, were observed

in propylene oxidation on supported Pt at the temperature range of 100–147°C (7, 9). Hydrocarbons are characterized by strong adsorption on Pt at relatively low temperatures (50–200°C), resulting in reaction rate inhibition of mixtures with excess oxygen (10). Thus, oscillatory behavior is expected to exist for a large class of hydrocarbon oxidation reactions on Pt.

The multiplicity pattern observed in Fig. 1 is quite surprising; at low temperatures (e.g., at 175 and 162°C) the high-activity branch extinguished upon a decrease in the propylene concentration, while at higher temperatures (202°C) ignition occurred upon a similar variation in concentrations. This behavior may be explained by the occurrence of a heterogeneous–homogeneous reaction, i.e., one which is initiated on the catalytic surface and continues in the gas phase. In such cases, part of the heat generated by the gas phase reaction may not be transmitted to the surface, so that the actual reaction rate exceeds that computed from an energy balance on the wire. Bakaev *et al.* (11) observed such a behavior during the oxidation of propylene in air at temperatures above 215°C. We suggest that the low-activity state may be attributed to a slow auto-inhibitory surface reaction and

the high-activity branch to a heterogeneous-homogeneous reaction. At low temperatures the usual extinction of high-activity branch upon a decrease in the reactant concentration occurred. At the higher temperature of 202°C the increased surface reaction rate caused by the decreased propylene concentration was apparently sufficient to initiate the homogeneous reaction and led to ignition. A more detailed investigation of the multiplicity features of this system will be reported elsewhere.

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