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Surface Propagation Speed of Kinetic Phase Transition in the Catalytic Oxidation of Carbon Monoxide over Platinum Thin Films

Recently, Ertl and co-workers have proved that the kinetic oscillations of carbon monoxide oxidation propagate along the platinum (100) surface at low pressure (*1–3*). Using selected area Fourier transform infrared spectroscopy, Kaul and Wolf have shown that oscillations tend to have the same behavior at atmospheric pressure on supported platinum and palladium catalysts (*4–6*). In a previous paper, we have studied the transition between the two CO oxidation stationary states (corresponding respectively to a low and a high reaction rate) at atmospheric pressure over polycrystalline platinum thin films (*7*). The work mentioned above and that of Dauchot and Bertouil (*8*) strongly suggest that this transition can also propagate.

In the present work, the transition from the low to the high reaction regime has been initiated by using a laser beam and its propagation has been detected by measuring the electrical resistance locally along the catalytic strip (the resistivity of polycrystalline films varies about 10% when the transition occurs (*7*).

The samples are prepared as PtO_2 deposited on oxidized silicon wafers as substrates (500 nm of SiO_2) by dc reactive sputtering in an argon–oxygen mixture. They are stored in this form and decomposed into platinum just before the experiment. The platinum film is about 20 nm thick. The electrical resistance is measured by means of small gold contacts every 2.5 mm along the catalytic strip (length, 12.5 mm; width, 0.1 mm) (Fig. 1). At one end of the strip a larger area has been added, from which the transition can be initiated by laser irradiation (Chromatix CMX-4 with Rhodamine 6G, 1 J/ms, 600 nm).

The experimental setup is pictured in Fig. 2. Two Brooks thermal flow meters control the $(CO)/(O_2)$ ratio. The gas mixture inlet (flow, 2 cm^3/s) is made of small holes (diameter, 0.3 mm) placed along the catalytic strip so that the reactant concentration can be assumed to be homogeneous. All the measurements are made under dynamical conditions. The sample is put on a heated gold-plated copper block placed in a small Dewar vessel. A thermocouple is pasted with silverdag on an oxidized silicon chip identical to the sample substrate.

The $(CO)/(O_2)$ ratio is fixed at a value where the reaction is inhibited. The catalyst temperature is increased slowly (2°C/min) while the extremity of the catalytic strip is irradiated. When the transition reaches the first electrical contacts, the corresponding resistance jump triggers a digital voltmeter which measures the voltage of the thermocouple. At the same time, chronometers attached to each following pair of contacts engage. The chronometers stop when the transition occurs at their position. In such a way, the time taken by the transition to travel over the distance between each pair of contact of the catalytic strip can be measured. The circuit is made by photolithography: the distance between all contacts (2.5 mm) is then known with good accuracy. The temperature increase between the transition at the first contacts and the transition at the last ones does not exceed 0.1°C.

It appears that the transition propagation rate is very sensitive to the state of the catalyst, e.g., thickness, defects, crystallite size. It was not always possible to avoid spontaneous ignition, i.e., not induced by the laser beam irradiation. At first, it was thought that the main cause of such a phe-

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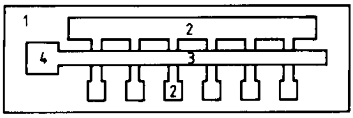

FIG. 1. Catalyst sample for propagation speed measurement. 1, Oxidized silicon substrate; 2, gold contacts; 3, platinum strip; 4, ignition area.

nomenon was the nonuniform thickness of the samples: special care has been taken to synthesize catalyst deposits with as regular a thickness as possible. Despite this, erratic transitions can always occur and propagate concurrently along the surface. Figure 3A gives an example of such behavior: the propagation time has been plotted versus the strip length and it appears that the transition has occurred at two different places.

By adjusting the (CO)/(O_2) ratio, the propagation speed has been measured versus temperature. The transition propagation is thermally activated: the higher the temperature, the faster the propagation (Fig. 3B). Unfortunately, due to the great number of uncontrolled transitions, no further systematic measurements were carried out.

Another point to emphasize is the increase in the propagation time (or the decrease in the propagation speed) versus the number of measurements at the same temperature (Fig. 3C). In our previous work (*7*), a rise in critical temperature (i.e., transition temperature) was observed after each measurement and a treatment under pure CO was found to restore the initial value. This fact was attributed to a "suboxide" which is formed during the transition from CO to oxygen coverage and reduced by carbon monoxide. The latter again returns small crystallites, whose critical temperature is lower (locally) from where the transition is initiated. In the framework of this interpretation, the formation of oxide patches on the surface of the catalyst increases the "transition path" and in turn the propagation time. Thus the same CO treatment has been considered in order to restore the initial speed but, as can be expected from the interpretation above, it raises the frequency of spontaneous ignition and makes the speed measurement more hazardous.

Finally, in the temperature range between 100 and 135°C, a speed of about 0.1 cm/s can be estimated from our measurements (see Figs. 3A–3C).

Considering the work of Ertl *et al.*, a propagation speed can be deduced from Ref. (*22*, Fig. 22). In the latter the delay between two inflection points on the curve

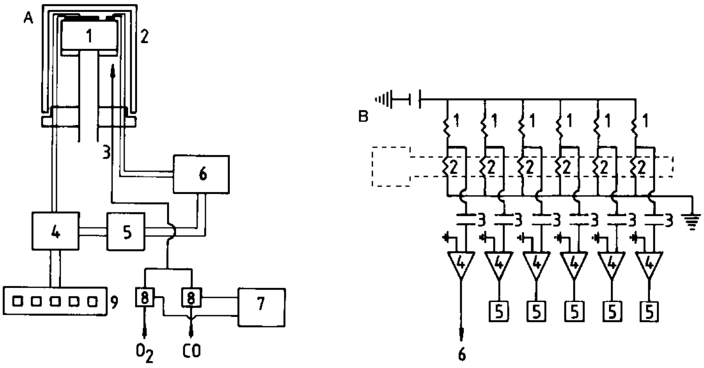

FIG. 2. Experimental setup. (A) 1, Gold-plated copper block; 2, Dewar vessel; 3, gas mixture inlet; 4, resistance measurement circuit; 5, amplifier; 6, digital voltmeter; 7, thermal flow meters; 8, electromagnetic valves; 9, chronometers. (B) 1, Loading resistances; 2, equivalent platinum thin-film resistances; 3, capacitors; 4, amplifiers; 5, chronometers; 6, chronometer starter.

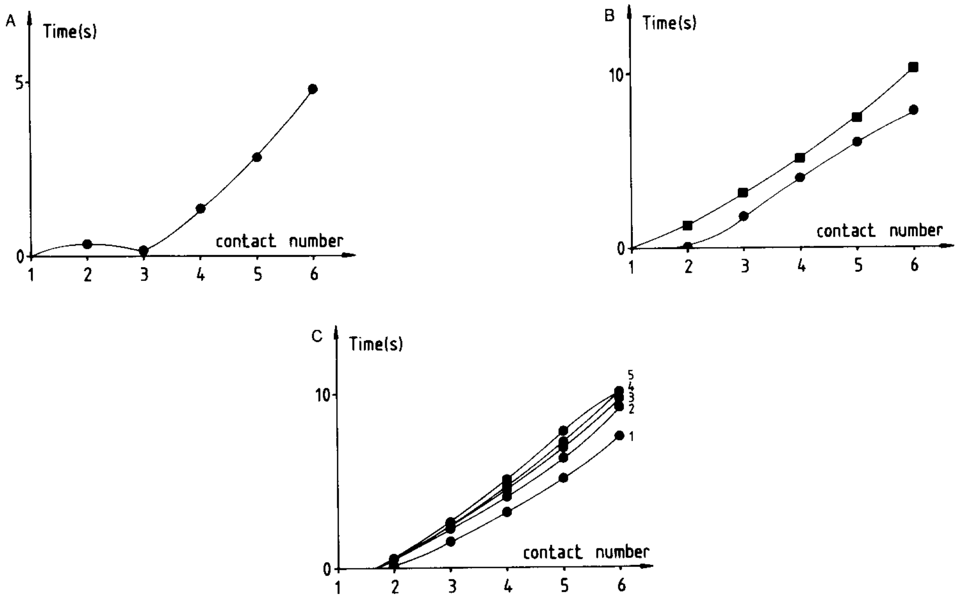

FIG. 3. Propagation time as a function of strip length. (A) Two ignitions have occurred at two different places (temperature, 107°C). (B) Temperature dependence of the propagation speed (■, 116.25°C; ●, 134.5°C). (C) Increase in the propagation time with the number of measurements at the same temperature (114°C). The numbers give the measurement sequence.

of the $c(2 \times 2)$ pattern intensity is 50 s for two points 2 mm apart (see for instance the points (4 mm, 50 s) and (2 mm, 100 s)), which corresponds to a speed of 0.004 cm/s for the CO coverage lowering front.

The values obtained previously by Dauchot and Bertouil (*8*) are spread out between 0.5 and 5 cm/s. They seem to depend on the sample history (preparation, treatment, and aging) and its thickness (which is not determined accurately). Thus they do not differ significantly from those of the present work.

In the interpretation of Ertl and co-workers (Ref. (*2*, Fig. 24) the propagation of the coverage transition is initiated where "defect sites are not so effectively blocked by adsorbed CO and allow oxygen adsorption." The situation in our experiments is very similar since a hole in the CO layer is created by laser impact where oxygen is preferentially adsorbed.

Following this interpretation three processes may be regarded as driving the transition propagation: surface reaction, oxygen adsorption, and CO diffusion on the surface. From the values of the corresponding parameters and of the surface diffusion constant (see, for instance, Ref. (*1*, Table 1)), it may be expected that at least two of these processes are coupled. At atmospheric pressure, the oxygen adsorption rate is greater than that of the surface reaction: the propagation speed is then determined by coupling the surface reaction and the CO surface diffusion. On the other hand, at low pressure (5.10^{-4} Torr), the oxygen adsorption rate becomes lower than the surface reaction rate: CO surface diffusion and oxygen adsorption are coupled to control the propagation speed. According to numerous studies dealing with reacting and diffusing systems (*9*, *10*), "the front propagation velocity" is of the order of $V_p = (D \cdot k)^{1/2}$ whre D and k are respectively the CO surface diffusion coefficient and the rate constant (i.e., the frequency factor) of the coupled process (surface reaction or oxygen adsorption). On the basis of this relationship in the two situations, we have

at atmospheric pressure:

$$V_p = (D \cdot k)^{1/2} = (10^{-7} \cdot 10^5)^{1/2} = 0.1 \text{ cm/s}$$

at 5.10^{-4} Torr:

$$V_p = (D \cdot k)^{1/2} = (10^{-7} \cdot 280)^{1/2} = 0.005 \text{ cm/s}.$$

These values (calculated from the data given in Ref. (*1*)) are strikingly near the experimental ones but only the orders of magnitude may be considered. However, this similarity tends to confirm the phenomenological mechanism described above for the propagation of the transition (*2*).

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