JOURNAL OF CATALYSIS **100**, 552–554 (1986)

Multiplicity Patterns of Hydrogen Oxidation on Several Platinum Wires

Many investigators have studied experimentally the multiplicity features of reactions catalyzed by a single pellet or wire (*1–4*) since the pioneering study of Davies in 1934 (*5*). The multiplicity was usually found by constructing bifurcation diagrams which show the dependence of a state variable of the system, such as reaction rate or surface temperature, on an operating condition such as feed concentration or temperature. The features of the multiplicity patterns may be used to predict the qualitative features of the rate expression (*3, 6*).

It is well known that small variations in the method of preparation or activation of catalysts lead to large differences in the activity of catalysts. In the case of a single reaction these differences are usually manifested by differences in the preexponential factor with only small changes in the activation energies. An interesting question, which has not yet been addressed in literature, is whether it is possible to get qualitatively different multiplicity features by the same reaction when using (supposedly) identical catalytic wires or pellets. The purpose of this letter is to describe a case in which such differences were observed and to analyze these data.

Three effects may lead to differences in the multiplicity features. First, changes in the activity may eliminate or create a new steady-state branch. For example, Harold and Luss (*4*) found in the oxidation of CO on a Pt-on-alumina pellet that only one of two "equal" pellets admitted three stable steady states. The second cause for different multiplicity features on similar catalytic wires is that different temperature distributions may exist at the same average temperature, leading to different observed reaction rates. For example, a reduced local heat conduction at a "neck" on a wire, may create a situation in which two different stable states exist on both sides of the neck. The observed rate of these nonuniform states is determined by the inhomogeneity of the wire. These nonuniform states may not be detected as such in the usual mode of experimentation and lead to several different multiplicity patterns as noted by Sheintuch and Schmidt (*7*) during the oxidation of ammonia on Pt wires.

The third effect is the existence of an inhomogeneous state on a *homogeneous* surface. Clearly, under the conditions that two or more stable states exist, each point on the surface may be at a different state unless some form of communication among the various points brings them to the same state. In the case of nonisothermal reactions the communication is usually caused by thermal conduction. In isothermal systems the synchronization is caused by a chemical mechanism. In certain cases the wire will attain an inhomogeneous state in which a stable narrow stationary front separates two regions occupied by two different stable homogeneous solutions. This front may be positioned at any point along the wire, as was shown by Barelko *et al.* (*8*). Thus, it is possible to obtain a large number of states having a different average rate or temperature under the same operating conditions. Pismen (*9*) suggested several mechanisms which can lead to stable inhomogeneous states.

We have recently conducted an experi-

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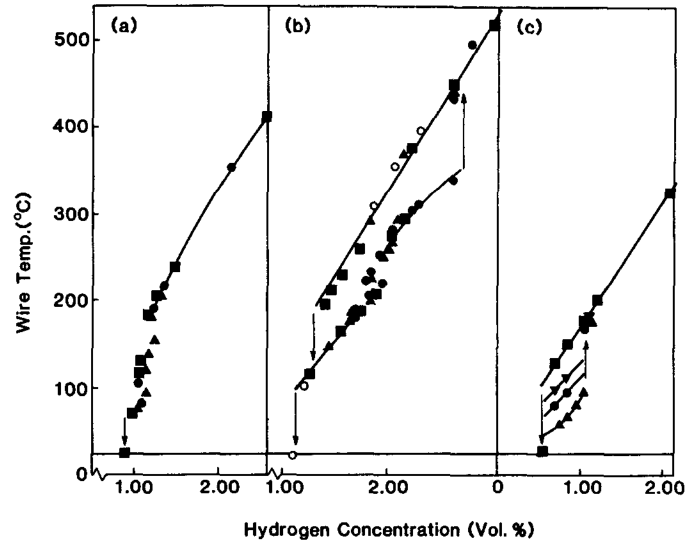

FIG. 1. Three different multiplicity patterns observed during H_2 oxidation in oxygen at ambient room temperature. Different symbols denote different scanning cycles.

mental study in order to test the reproducibility of the multiplicity patterns found on catalytic wires using 10 different sections of a 0.05-mm-diameter Pt wire, each about 50 mm long. The wire (average) temperature was determined from measurements of its resistance by a hot-wire anemometer (Thermo Systems Model 1054). Details of the experimental system and procedure are reported by Xiau *et al.* (*10*).

We selected the oxidation of hydrogen (0–3 vol%) in oxygen to be the test reaction. Reproducible results were always obtained with the same wire. However, three different types of multiplicity patterns were observed (Fig. 1). An extinguished state existed over the whole range of hydrogen concentrations for every wire. The ignited branch(es) were reached following a transient electrical heating of the wire. Very slow transients were observed at low surface temperatures (close to the extinction point). That was especially noticeable in the wire shown in case c for which the temperature declined at the very slow rate of 3°C/hr next to the extinction point.

There exist major qualitative differences between the three observed patterns. Patterns a and b differ in the number of steady states as well as in their inverse multiplicity: the ability to sustain the same wire temperature at different reactant concentrations. At most one ignited steady state exists for any wire temperature in case a. However, in case b more than one ignited state is found for a range of wire temperatures.

Four ignited branches were observed in case c. The three lower ones were obtained by interrupting the slow extinction process by a sudden small increase in the H_2 concentration. The ignition temperatures of these three branches were identical, and the ignition was relatively fast. The procedure used to get these ignited branches suggests that it is possible to attain a very large number of different states in this case.

The observation shown in cases a and b suggest that H_2 oxidation may admit up to three uniform stable states under nonisothermal conditions (Fig. 1). The connecting lines in sections of the ignited branches in cases a and b are not marked, since they may be interpreted as a very narrow hysteresis loop. The upper branch in case c is probably of a uniform state and corresponds to the ignited branch in cases a and b. There may be in case c another branch of uniform states similar to the intermediate branch in case b. The other branches found in case c are asymmetric and are bounded within the ignition and extinction of the uniform ignited states. The apparent absence of asymmetric states in case b is surprising and may be explained by their instability at high temperatures.

The inverse multiplicity noted in case b implies that the isothermal rate expression is not a single valued function of hydrogen concentration. Isothermal multiplicity was reported by Volodin *et al.* (*2*) for hydrogen oxidation in oxygen at temperatures below 85°C and concentrations exceeding 1 vol% H_2.

The case presented here is an extreme example of qualitative differences in the multiplicity patterns on different wires. It emphasizes the need to conduct such a comparison in order to obtain meaningful results. The relation between catalytic activity and surface morphology or composition is not well defined to provide an analytical tool for comparing different catalysts. Marked inhomogeneity in the catalytic activity of commercial catalytic pellets was shown recently by Brown *et al.* (*11*). These considerations underscore the uncertainty involved in deriving the kinetics from studies with one wire or pellet.

ACKNOWLEDGMENT

Financial support of this research by the Welch Foundation is gratefully acknowledged.

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Received August 27, 1985

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