Effects of Catalyst Particle Size on Multiple Steady States

S. H. Oh, K. Baron, E. M. Sloan, and L. L. Hegedus

General Motors Research Laboratories, Warren, Michigan 48090

Carbon monoxide oxidation experiments were carried out over Pt–alumina catalyst particles of various sizes. The width of the conversion–temperature hysteresis loop goes through a maximum as the degree of intrapellet diffusion resistances (i.e., catalyst particle size) is varied. No hysteresis was observed over finely powdered catalysts. The above observations are in agreement with the qualitative predictions of diffusion–reaction theory, and provide further evidence to suggest that the steady-state multiplicities observed here were caused by the interactions between reaction and intrapellet diffusion resistances. The hysteresis loop was found to shift along the temperature axis as the pellet size was varied. The hysteresis occurred at the lowest temperature when catalyst particles of an intermediate size were used. Both larger and smaller particles showed multiplicity at higher temperatures. This observation is also consistent with diffusion–reaction theory.

INTRODUCTION

Steady-state multiplicity during the oxidation of carbon monoxide over supported Pt catalysts has been the subject of numerous theoretical and experimental investigations. Much of the earlier experimental work in this area has been concerned with adiabatic, fixed-bed reactors, where thermal effects are significant (e.g., *1–3*). Due to its complex kinetics, however, this reaction system has also been shown to exhibit multiplicities under the condition of negligible thermal effects; such isothermal multiplicities were first observed by Wicke and collaborators (*4*) for CO oxidation in a single, porous, platinum-alumina catalyst pellet.

Experimental work on multiplicity in chemically reacting systems has been recently reviewed by Schmitz (*5*). It has been shown that negative-order reaction systems (such as CO oxidation over Pt), when coupled with transport resistances, can give rise to isothermal steady-state multiplicities. For example, Roberts and Satterfield (*6*), Schneider and Mitschka (*7*), Smith et al. (*8*), and Wei and Becker (*9*) have predicted isothermal multiplicities for negative-order reactions under the influence of *intrapellet diffusion* resistances. Recently Hegedus et al. (*10*) and Oh et al. (*11*) have shown that the steady-state multiplicities observed in an isothermal, integral reactor can indeed be well interpreted by diffusion-reaction interactions, and that more than two stable steady states can be generated by appropriate manipulations of the time history of the operating conditions.

Isothermal multiplicity can also be generated by the interaction between negative-order kinetics and *external mass transfer* resistances, as pointed out by Wei and Becker (*9*).

Steady-state multiplicities have been observed during isothermal CO oxidation

272

over Pt even in the absence of internal and external mass transfer resistances. In a well-mixed reactor (CSTR or recirculated reactor), for example, multiple steady states can be obtained under isothermal conditions when the reactor operating line intersects the rate versus concentration curve more than once (12-16). Such multiplicity is a direct consequence of the mass *feedback mechanism* inherent in a well-mixed reactor.

There also have been attempts to explain experimentally observed isothermal multiplicities by means of a *purely kinetic mechanism*. Beusch et al. (4) suggested that the multiplicities observed in their study of isothermal CO oxidation in a Pt/Al_2O_3 pellet were caused by the interactions between chemisorption rates and surface reaction rates. Eigenberger (17, 18) has shown theoretically that relatively simple Langmuir-type kinetic mechanisms can lead to isothermal multiplicities when more than one mechanistic step is allowed to be at nonequilibrium.

The purpose of this paper is to investigate the role of intrapellet diffusion resistances in the occurrence of isothermal steady-state multiplicities during CO oxidation. Of particular interest here is the magnitude of the hysteresis loop as a function of the degree of intrapellet diffusion resistances. Thus, only the upper and lower branches of the hysteresis loop were generated here, although more than two stable states have been observed under similar experimental conditions (10, 11). Since the degree of intrapellet diffusion resistances is a direct function of catalyst pellet size (19, 20), we carried out some experiments with catalyst particles of various sizes in order to cover a wide range of intrapellet diffusion resistances without changing the chemical properties of the system.

Although isothermal multiplicities can occur as a result of the various mechanisms mentioned above, a careful choice of experimental conditions allowed us to

TABLE 1

Catalyst Properties

Pt (wt%)	0.05
Pt dispersion (%)	80
a (cm^2 Pt/cm^3 pellet)	1196
V_{macro} (cm^3/g)	0.115
V_{micro} (cm^3/g)	0.48
$\bar{r}_{macro}$ (Å)	4327
$\bar{r}_{micro}$ (Å)	64.2
Surface area (BET, m^2/g)	96
Solid density (g/cm^3)	3.65
Pellet density (g/cm^3)	1.15
D (cm^2/s)^a	0.0311

^{a} Computed from the random pore model of Wakao and Smith [Smith (21)], and given here at 1 atm and 838 K. D increases with the 1.4th power of T.

isolate and study in detail the diffusion–reaction interactions without interference from the other mechanisms. For example, the inlet CO concentrations were kept low enough (about 0.3 vol. %) to ensure near-isothermal operation, and the flow rate was chosen to be high enough to operate the reactor under negligible external mass transfer resistances. Also, our reactor system was designed to provide a plug flow through the reactive section, thereby eliminating a feedback mechanism due to axial dispersion. Furthermore, the multiplicities reported here are not purely kinetic in nature, because multiplicities were found to disappear upon minimizing the transport resistances (i.e., over finely powdered catalysts, as we will see later).

EXPERIMENTAL PART

Alumina-supported Pt catalyst particles of various sizes were used in the experiments. The original catalyst was in the form of uniformly impregnated, spherical pellets 3360–4000 μm in diameter. Catalyst particles of smaller sizes were prepared by cleaving or pulverizing the pellets. The characteristics of the catalyst employed are given in Table 1.

The integral reactor used in the experiments has been described previously (10).

OH ET AL.

The reactor essentially consists of a catalytically active section sandwiched between two SiC layers. The reactor was placed vertically and the gases were allowed to flow downward to minimize the possibility of flow channeling.

In an attempt to keep the Pt content constant, the reactive section was packed with the same weight of catalyst (approximately 8.3 g) in all the experiments. In the experiments with powdered catalysts, a plug of quartz wool was placed above and below the reactive section to prevent movement of the catalyst.

All the experiments were run at a feed flow rate of 81 cm³/s (STP). The feedstream composition was 0.3 vol% CO and 2 vol% O_2 (balance N_2). At the beginning of each

series of experiments, the catalytic reactor was heated in the aforementioned feedstream to 500°C and maintained at this temperature for 30 min. The reactor temperature was then decreased step by step, and the conversion of CO was determined after the reactor was stabilized at each selected temperature. After reaching a temperature low enough to give a negligible conversion ($<5\%$), the direction of temperature change was reversed and the reactor temperature was increased step by step in the same manner. The measured temperature difference between the inlet and outlet of the reactive section was less than 5°C even at high CO conversions.

The conversion versus temperature curves were found to be reasonably well reproducible when the catalyst was pretreated according to the aforementioned procedure at the beginning of each experiment. Minor irreproducibility in the pretreatment from run to run tended to cause a small shift of the hysteresis loop (usually less than 5°C on the T_{in} axis) without significantly changing its shape.

RESULTS AND DISCUSSION

Figure 1 shows the observed conversion of CO as a function of reactor inlet temperature for various sizes of catalyst particles. The conversion data for the full pellets (case a) exhibit relatively gradual changes with temperature, combined with some degree of steady state multiplicity. The hysteresis loop was found to become more pronounced as the pellet size was reduced to the half pellets (case b), and the largest hysteresis loop was observed with the quarter pellets (case c). However, further reduction of the pellet size diminished the width of the hysteresis loop (case d), and eventually the very fine powder (case e) showed virtually no multiplicity.

It is interesting to note that besides its size variation, the hysteresis loop also
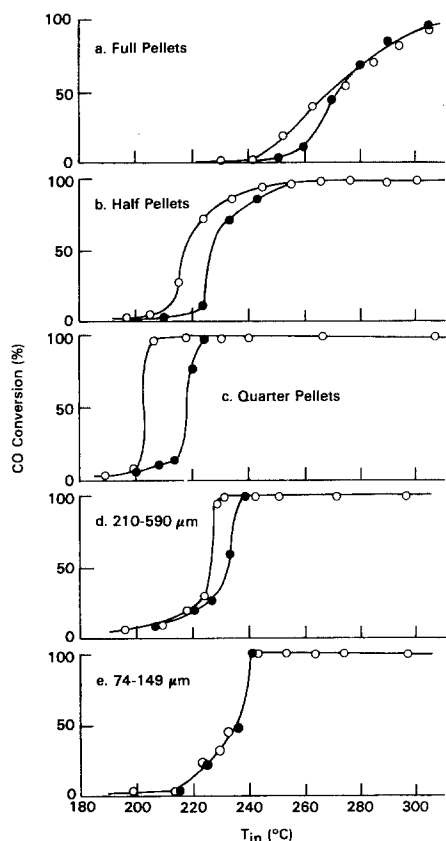

FIG. 1. Observed conversion–temperature behavior for various catalyst particle sizes. ● = increasing T, ○ = decreasing T.
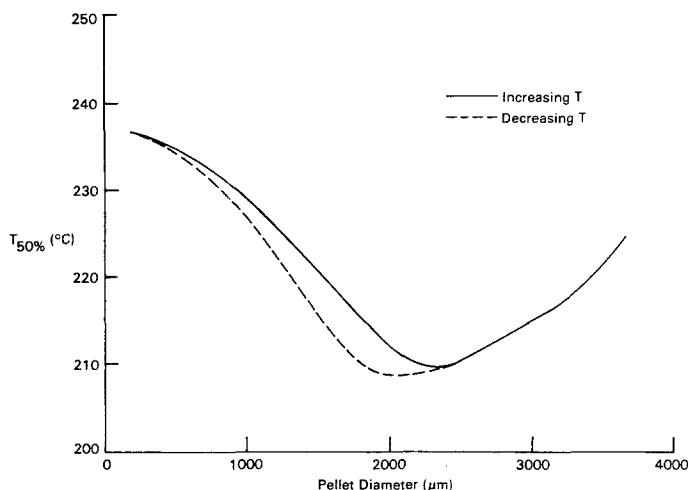
FIG. 2. Computed reactor temperature for 50% CO conversion as a function of catalyst pellet diameter.

shifted along the temperature axis as the pellet size was varied. The hysteresis occurred at the lowest temperature when catalyst particles of an intermediate size (case c) were used. Both larger (case a) and smaller (case d) particles showed multiplicity at higher temperatures.

Recent studies in our laboratories (10, 11) have shown that the steady-state multiplicities observed under similar operating conditions can be well interpreted by the interaction between intrapellet diffusion resistances and the complex kinetics of CO oxidation. In an attempt to examine in more detail the validity of the diffusion–reaction theory for this problem, calculations were carried out using a mathematical model which accounts for diffusion–reaction interactions within the catalyst pellets. Although the catalyst particles used in our experiments were not spherical (except the full pellets), a spherical-equivalent pellet geometry was conveniently assumed for the calculations because it was expected that this assumption would not interfere with the essential features of the system.

The bimolecular Langmuir–Hinshelwood type of rate expression given by Hegedus et al. (10) was employed in our computa-

tions. In view of various idealizations invoked in our model (such as the assumption of spherical pellet geometry, uniform noble metal concentration throughout the pellet, strict isothermicity, and an explicit reaction rate expression), no attempts are made here to match the experimental data. However, as will be seen later, the computational results are useful in elucidating some interesting aspects of the system's behavior.

Figure 2 shows the computed reactor temperature required to achieve 50% CO conversion, as a function of pellet diameter. The vertical distance between the solid (obtained with increasing T) and the dotted (obtained with decreasing T) curves represents the width of the hysteresis loop at 50% CO conversion. While the calculations did not exactly reproduce the experimental observations, the computational results were instructive because they correctly described the trend of the variation of both the hysteresis loop's magnitude and its location on the temperature axis with particle size. (That is, as observed in our experiments, the width of the hysteresis loop goes through a maximum as the pellet size is varied, and the hysteresis occurs at

the lowest temperature over catalyst particles of an intermediate size.)

The occurrence of the largest hysteresis loop at an intermediate catalyst particle size may not be surprising in view of the fact that the isothermal effectiveness factor for negative-order kinetics exhibits multiple solutions at intermediate values of the Thiele modulus (6, 7, 9). The qualitative agreement provided by the diffusion-reaction model, as well as the observation of complete disappearance of the hysteresis loop over the fine powder (case e, Fig. 1), indicates that the multiplicites observed here were caused by the interactions between reaction and intrapellet diffusion resistances, and not by the chemical properties of the system alone.

The fact that the hysteresis loop shifts along the temperature axis as the pellet size is varied (see Figs. 1 and 2) indicates that the catalyst's activity changes with particle size. The observation of the highest activity (i.e., the lowest $T_{50\%}$) at the intermediate particle size is a direct consequence of the fact that the isothermal effectiveness factor for negative-order kinetics exceeds unity in the range of an intermediate Thiele modulus. When the Thiele modulus is smaller or larger than these intermediate values, the effectiveness factor becomes smaller, resulting in a decrease in the catalyst's activity. For this reason, the temperature required for 50% conversion goes through a minimum at an intermediate particle size, as illustrated in Figs. 1 and 2.

The possibility of generating isothermal steady state multiplicities by the interaction between negative-order reactions and *external* mass transfer resistances has been pointed out by Wei and Becker (9). However, this is not the cause for the multiplicities reported here because our reactor system was operated under negligible external mass transfer resistances; that is, even a twofold increase of the external mass transfer coefficient in the

model [estimated from the correlation of Petrovic and Thodos (22)] did not significantly change the computed conversion-temperature curves.

The possibility of thermally generated multiplicity can also be ruled out, because the temperature difference between the inlet and outlet of the reactor was kept minimal, as pointed out in the experimental part. The interphase and intrapellet temperature gradients were also found to be negligible, according to calculations using a recently developed estimation technique (23).

It may be worth mentioning that no oscillations were observed in the experiments reported here.

NOMENCLATURE

a (cm² Pt/cm³ pellet)	Local Pt surface area
D (cm²/s)	Effective diffusivity of CO
$\bar{r}_{\text{macro or micro}}$ (Å)	Integral averaged pore radii
T_{in} (°C)	Reactor inlet temperature
$T_{50\%}$ (°C)	Temperature for 50% conversion
$V_{\text{macro or micro}}$ (cm³/g)	Pore volumes

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