Bifurcation Behavior of a Catalytic Reaction Due to a Slowly Varying Parameter

Bifurcation problems with slowly varying control parameters are of interest in several research areas, including catalyst deactivation, combustion, and lasers and other nonlinear optical devices. Significant theoretical work has been devoted to the study of these dynamic phenomena, but very little directly relevant experimental information is currently available. Results are presented here from an experimental study of the dynamic behavior of a catalytic reaction system due to a deliberately slowly varied control parameter. Attention is focused on the dynamics due to slow passage through simple limit and Hopf points.

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Introduction

Bifurcation problems with slowly varying control parameters are of interest in several research areas. In many instances, the slow change of one or more system parameters occurs naturally. This is frequently the case with many catalytic reaction systems, for which the catalyst is undergoing slow deactivation due to the presence of poisons in the reactant or product streams, which adsorb on the catalyst surface or plug the catalyst's pore volume (Yortsos and Tsotsis, 1984; Tsakalis et al., 1984; Sahimi and Tsotsis, 1985). Since many catalytic reactions exhibit multiple steady states and hysteresis behavior (Sheintuch and Schmitz, 1977; Schmitz et al., 1984), slow deactivation of the catalyst, if left unattended, eventually leads to extinction of the catalyst bed. The bifurcation behavior of a bistable catalytic reaction system undergoing deactivation has been studied theoretically by Do and Weiland (1980) and Kapila (1983). Kapila, in particular, utilized a general asymptotic technique to study the jump phenomena associated with gradual catalyst deactivation and slow passage through an extinction point. This asymptotic analysis had been previously utilized by Kapila (1981) (see Haberman, 1979, for a detailed mathematical analysis) to study jump dynamics due to slow passage through a criticality in Arrhenius-type reaction systems.

In other cases, one might choose to deliberately vary one or more control parameters. This is typically the case with experiments in the area of lasers and other nonlinear optical devices (Erneux and Mandel, 1983, 1984; Arimondo et al., 1983; Scharpf et al., 1987). A growing number of experimental papers have also been devoted to the study of pulsed catalytic and electrochemical reactors and combustion chambers (Sheintuch and Schmitz, 1977; Schmitz et al., 1984). Recent theoretical and numerical studies of laser problems (Erneux and Mandel, 1984; Mandel and Erneux, 1984) have shown that the actual behavior due to the deliberate slow change of a control parameter is quite different from the static behavior. In a recent paper Erneux and Mandel (1986) have undertaken a systematic study of the bifurcation behavior due to a slowly varying bifurcation parameter. They consider a general class of imperfect bifurcation problems, relevant to the modeling of simple lasers and lasers with saturable absorbers, described by the following equation:

$$y_t = ky^p + \lambda(t)y + \delta \text{ with } k = +1 \text{ or } -1, p = 2, 3 \quad (1)$$

and the control parameter

$$\lambda(t) = \lambda_0 + \epsilon t; \lambda_0 < 0, 0 < \epsilon < 1. \quad (2)$$

When $\epsilon = \delta = 0$ the above equation exhibits at $\lambda = 0$ a simple bifurcation for the basic $y = 0$ solution to the nonzero steady states. When ($\epsilon \neq 0, \delta \neq 0$) Erneux and Mandel show that $\lambda = 0$ does not correspond to the transition between the two branches of slowly varying steady states. Instead this transition occurs at a larger value of $\lambda = \lambda_1$, which may depend on λ_0 (the starting value of the control parameter, from which the slow variation is initiated), that is, the system exhibits memory effects. These effects are particularly dramatic if δ is sufficiently small compared to ϵ. Erneux and Reiss (1986) and Baer et al. (1987) have also studied bifurcation phenomena due to slow passage through a Hopf bifurcation point. In particular, Erneux and Reiss investigated the behavior of the Brusselator problem described by

$$X_t = A + X^2Y - (B + 1)X \quad (3)$$

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$$Y_t = BX - X^2Y, \tag{4}$$

which shows a Hopf bifurcation at $B = B_0 = 1 + A^2$ when the control parameter B is varied as

$$B = B_i + \epsilon t, \quad B_i < B_0, \quad \epsilon \ll 1. \tag{5}$$

They again observe large delays in the dynamic response as well as memory effects.

It is clear from the above discussion that a significant amount of theoretical work has been devoted to the study of bifurcation phenomena due to slowly varying control parameters near both limit and bifurcation points. On the other hand, very little, if any, directly relevant experimental work exists on the bifurcation behavior of a catalytic reaction system due to a deliberately slowly varied control parameter. Our attention is primarily focused here on the dynamics due to slow passage through simple limit and Hopf points.

Reaction System

The catalytic reaction system we have studied is the CO oxidation over $Pt/\gamma\text{-}Al_2O_3$ at low total pressure conditions ($P_t < 10$ torr [1.33kPa]). The reaction is carried out in a single-pellet continuous stirred-tank reactor (CSTR). Under the conditions employed, the reactor operates isothermally and without external/internal heat and mass transport limitations. The reactor system utilized has been described in detail elsewhere (Lindstrom, 1985). With this apparatus, the reactor total pressure, the inlet gas phase composition, the catalyst temperature as well as the reactant flow rates can all be independently set and adjusted.

The reactor cell body is made out of quartz glass and Teflon. CaF_2 windows are sealed to this body with Viton O-rings. The catalyst holder is made of Pyrex glass and one arm of this holder provides access for a thermocouple into the reactor through a capillary channel. With the exception of this thermocouple tip, the reactant gases do not come in contact with any other material but the quartz and Teflon walls, the Pyrex holder, and the CaF_2 windows. Reaction rates are continuously monitored by a UTI 100c mass analyzer. The catalyst surface is monitored using a Perkin-Elmer model 681 IR spectrophotometer. The catalyst temperature is continuously monitored and controlled by an Omega CN-2012 temperature controller.

Sonic orifice meters are used to provide constant gas phase compositions, free from downstream pressure perturbations. The reactant gases are purified by a series of purification steps in order to remove undesirable gaseous impurities.

The catalyst wafer (1 in. [25.4 mm] dia.) was prepared by impregnation of $\gamma\text{-}Al_2O_3$, Degussa type C, with a $H_2PtCl_6 \cdot 6H_2O$ solution up to a total Pt content of 3.2%. Further details of the catalyst properties and preparation techniques can be found elsewhere (Lindstrom, 1986).

There have been numerous papers devoted to the study of both the steady-state and the dynamic behavior of the CO oxidation reaction over supported and unsupported Pt group metal catalysts (Sheintuch and Schmitz, 1977; Schmitz et al., 1984; Razon and Schmitz, 1986). Thorough review papers by Engel and Ertl (1979) and by Razon and Schmitz (1986) have addressed different experimental and theoretical aspects pertaining to this reaction system. The CO oxidation reaction has exhibited a variety of interesting dynamic phenomena. Ignition and extinction phenomena and reaction rate oscillations (single peak, multipeak, and chaotic type) have been observed and reported (Razon and Schmitz). Most of these oscillations have been shown to be of spatio-temporal type, that is, in the form of temperature and/or surface concentration waves propagating along the catalyst surface (Cox et al., 1985), although under well-controlled experimental conditions uniform temporal oscillations have also been observed (Lindstrom and Tsotsis, 1986a,b).

For atmospheric pressure experiments (Lindstrom and Tsotsis, 1984; Harold and Luss, 1985), isolas have been observed and reported with this reaction system. The overall steady state bifurcation behavior at atmospheric pressure conditions is indicative of pitchfork-type bifurcation. At lower pressures, however, isolas have yet to be observed but the reaction system still exhibits bistable behavior (multiple steady states, ignition and extinction phenomena).

Although several mechanistic aspects of this reaction system have been studied and are presently well understood, a number of issues and questions concerning its mechanism still remain to be resolved. It is now believed that the surface reaction is of the Langmuir-Hinshelwood type and involves adsorbed CO and oxygen atoms (resulting from the dissociative adsorption of O_2). The adsorption and reaction constants, however, have been shown to be surface-coverage (concentration-) dependent. Furthermore, CO adsorbs in (at least) two forms on reduced metal surfaces, linear and bridge CO, and it is unclear at this point to which degree these two forms participate in the surface reaction. The effects of metal-support interaction (for supported catalysts) and Al and Si impurities present in the unsupported catalyst are also not well understood. On supported catalysts, several studies have reported CO island formation, that is, regions of the surface predominantly occupied by CO molecules. Under such conditions the surface reaction occurs primarily at the periphery of these islands (contradictory evidence also exists). Models utilizing ordinary differential equations are not applicable to this situation (Razon and Schmitz, 1986).

Reaction rate oscillations observed with this reaction have periods often orders of magnitude larger than the time scales associated with the adsorption, desorption, and surface reaction processes (Razon and Schmitz, 1986; Cox et al., 1985; Lindstrom and Tsotsis, 1985). This has prompted a number of investigators (Cox et al., 1985; Lindstrom and Tsotsis, 1985, 1986; Ertl, 1985; Yeates et al., 1985) to postulate an additional slow mechanistic step, which presumably drives the catalyst surface between two states of distinctly different catalytic activity. Two such slow mechanistic steps have so far been postulated. For Pt(100) single-crystal catalysts and low pressures ($\sim 10^{-4}$ torr [1.33_{10}^{-4}kPa]) Ertl and coworkers (Cox et al., 1985; Ertl, 1985) have proposed the slow step to be a reversible (hex $\leftrightarrow$ 1 $\times$ 1) phase transition. For polycrystalline and supported catalysts and at higher pressures Lindstrom and Tsotsis (1985, 1986) and Yeates et al. (1985) have proposed a step that involves the slow oxidation and reduction of the active metal.

Many theoretical models have been proposed to describe the steady state and dynamic behavior of the CO oxidation reaction system. Although a number of these models have been successful in qualitatively describing at least some of the features of its dynamic behavior, a generally accepted and applicable model has yet to emerge (Razon and Schmitz, 1986). The development

of such a model goes beyond the scope of this publication. We believe that some of the basic features of the work of Kapila (1981, 1983) are also of direct relevance to this problem.

Experimental Results

Limit point

As mentioned above, the CO oxidation reaction system exhibits its bistable behavior (Razon and Schmitz, 1986; Lindstrom and Tsotsis, 1985, 1986). Figure 1 shows a typical bifurcation diagram for this reaction system. This diagram was constructed by keeping all other system control parameters constant (gas phase concentration, flow rate, and total pressure) and varying the catalyst surface temperature (due to the isothermal low pressure conditions, the catalyst temperature is an independent control parameter). By varying the catalyst surface temperature, one in effect varies the reaction rate constants, due to their Arrhenius dependence on temperature. The situation is not as simple as with the model studied by Kapila (1981), since changes in the catalyst temperature not only affect the Damkohler number but simultaneously various other rate and thermodynamic equilibrium constants, which are part of the overall rate expression.

In view of what follows, a discussion is in order on how one accurately generates a bifurcation diagram such as the one shown in Figure 1. This diagram was generated by raising the catalyst temperature in a stepwise fashion and allowing the catalyst sufficient time to equilibrate after each step. As one approaches the limit point the process becomes tedious, since critical slowdown and jump phenomena come into play. We have deliberately exercised great care in identifying the ignition point (Figures 1 and 2) so that the last steady state point shown on line *S*, Figure 2, is within 0.5°C of the true ignition point. We were aided in our effort by two fortuitous events. First, the catalyst does not deactivate (care is exercised in exhaustively purifying the gases), and second, the CO oxidation reaction system has fast inherent dynamics. We have not been so fortunate with

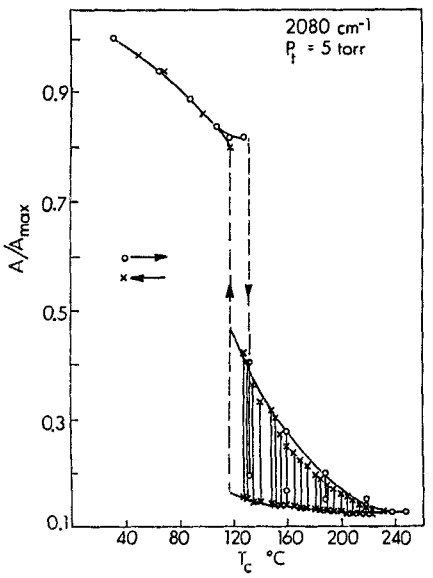

Figure 1. Bifurcation diagram for CO oxidation reaction system for catalyst 1.
(A/A_{max}) for 2,080 cm^{-1} band vs. T_c
P_t = 5 torr; feed composition: 5% CO, 20% O_2, 75% Ar

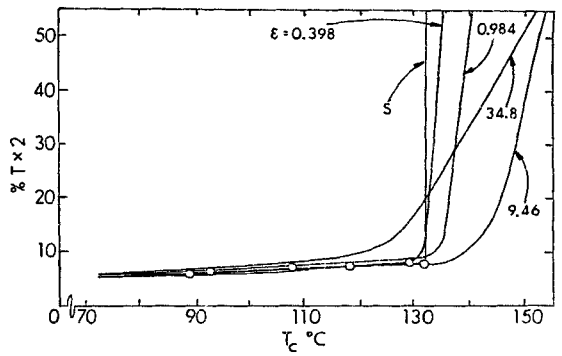

Figure 2. Dynamic response of catalyst 1 to a slowly varying bifurcation parameter (catalyst temperature T_c) for various values of ϵ.
P_t = 5 torr; feed composition: 5% CO, 20% O_2, 75% Ar

other reaction systems. For example, for the CO/NO reaction, even under the best of circumstances we have been unable to locate the ignition point with an accuracy better than 3°C (Lindstrom et al., 1985).

After the completion of the bifurcation diagram, we performed a series of experiments in which all other control parameters were kept constant and the catalyst temperature was raised in a linear fashion, that is:

$$T_c = T_{c0} + \epsilon t, \epsilon \quad \text{C/min} \tag{6}$$

The catalyst's behavior was monitored by measuring the IR transmission of the 2,080 cm^{-1} band, which corresponds to the linearly adsorbed CO. Five curves are shown in Figure 2 (for all curves, T_{c0} is the same, 74°C). In this figure, we plot percent transmission of the 2,080 cm^{-1} band as a function of catalyst temperature T_c. Note that high IR transmission values correspond to low absorbances—compare Figures 1 and 2—and surface concentrations of CO, and vice versa. In terms of the IR transmission of the 2,080 cm^{-1} band, the CO oxidation reaction system exhibits a counterclockwise hysteresis behavior. Since CO not only acts as a reactant but also as an inhibitor for this reaction, high surface concentrations of CO correspond to low reaction rates.

As can be seen from these curves, the dynamic behavior strongly depends on ϵ, the rate of change of the bifurcation parameter T_c. What is apparent, furthermore, from Figures 2 and 3 is that for $\epsilon \neq 0$ one can no longer uniquely identify a true ignition point. We have chosen here as ignition temperature, T^{ϵ}_{cI}, the temperature at which the catalyst transmission is 5%. The transmission at the true ignition point T^{0}_{cI} is 3% (curve *S*). Note that the different curves in Figures 2 and 3 cross each other. If one plots, Figure 4, $(T^{\epsilon}_{cI} - T^{0}_{cI})$ as a function of ϵ, as expected in view of the crossover points of Figures 2 and 3, a maximum appears. This maximum is not predicted by the asymptotic theoretical studies of Kapila and Erneux et al., which are formally valid for $\epsilon \ll 1$ $(\epsilon \to 0)$. However, its presence is not totally unexpected. A similar behavior has been found *numerically for* a Hopf bifurcation problem (Baer et al., 1987). For small values of ϵ, $(T^{\epsilon}_{cI} - T^{0}_{cI})$ has an ϵ^{p} $(p < 1)$ dependence, as expected from the asymptotic theory (Kapila, 1981).

One of the many issues of significance that was raised by the work of Erneux and Mandel (1986) is the possible memory

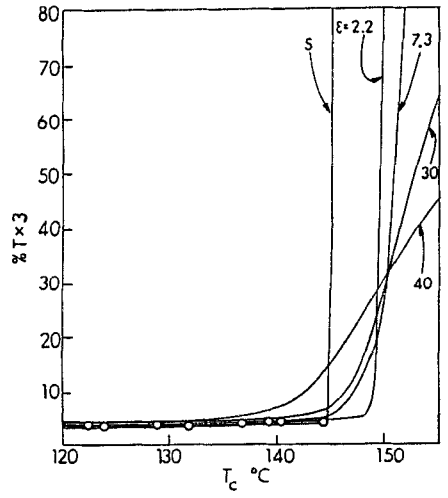

Figure 3. Dynamic response of catalyst 2 to slowly varying catalyst temperature T_c for various values of ϵ.

P_t = 10 torr; feed composition: 7% CO, 19.4% O_2, 73.6% Ar

effect, namely the fact that the system dynamics seemed to be dependent (for the same ϵ value) on the starting point from which the change in the control parameter was initiated. To test the existence of memory effects with the CO oxidation reaction system, a series of experiments were run in which ϵ was kept constant and the initial starting temperature T_{c0} was varied. In Figure 5 we plot T'_{cl} as a function of T_{c0}. Note that there is no apparent effect of T_{c0}; that is, there are no memory effects for this reaction system. To emphasize this point further, in Figure 6 we plot percent transmission (2,080 cm^{-1} band) vs. T_c for this catalyst for the same value of ϵ and four different T_{c0} values. The dynamics for all four cases are very similar. The lack of memory effects is in agreement with Kapila's study devoted to a simple limit point instability.

Hopf point

Our attention in this investigation was subsequently focused on the dynamics due to slowly varying control parameters on the ignited upper steady state branch. As has already been reported in numerous publications (Razon and Schmitz, 1986), in this region the CO oxidation reaction exhibits autonomous reaction

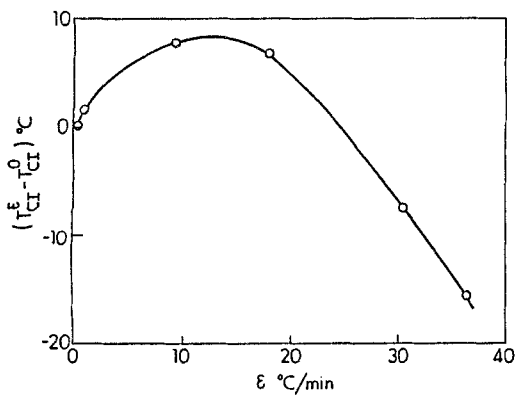

Figure 4. $(T'_{cl} - T^0_{cl})$ vs. ϵ.

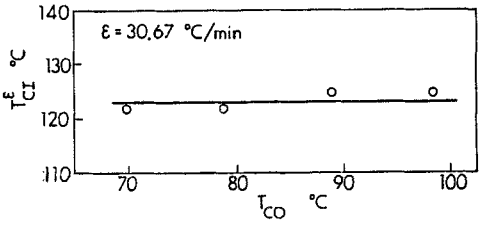

Figure 5. T'_{cl} vs. T_{c0}.

rate oscillations. Under isothermal low-pressure conditions with the catalyst surface temperature being used as the independent control parameter, these oscillations appear first at higher temperatures as small-amplitude, period oscillations (Hopf-type bifurcation), grow in amplitude and period and complexity as the temperature decreases, and finally disappear through what appears to be a saddle-node type bifurcation. The dynamic response in this region due to a slowly varying parameter has yet to be studied in any systematic fashion. The dynamics in this region are expected to be very complex because they involve both a Hopf bifurcation and a limit point. This problem is mathematically difficult and has not yet been analyzed. We will report here only on two aspects of this behavior, the rest to be reported in a future publication when our investigation is completed.

As the catalyst temperature is lowered in a linear fashion, that is,

$$T_c = T_{c0} - \epsilon t, \epsilon \text{ °C/min} \tag{7}$$

the IR transmission of the 2,080 cm^{-1} band (and the corresponding CO surface concentration) oscillates with increasing amplitude—Figures 7 and 8; the straight lines in these figures represent the catalyst temperature. This is to be expected, as also is the fact that the width and amplitude of the oscillatory envelope is a strong function of ϵ. The oscillations, however, bear no direct relationship with the oscillations observed under steady state conditions. Their amplitude and type is quite different from the oscillations observed with this reaction under steady state conditions. One observes a variety of interesting phenomena. For example, note that in Figures 7c and 8 the catalyst surface concentration reaches a temporary plateau, stays

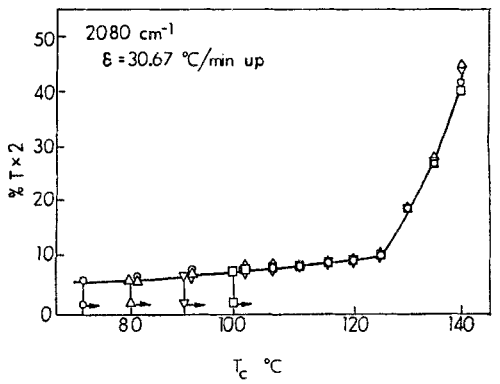

Figure 6. Dynamic response of catalyst 1 to slowly varying catalyst temperature T_c for ϵ = 30.67°C/min and different values of T_{c0}.

P_t = 5 torr; feed composition: 5% CO, 20% O_2, 75% Ar

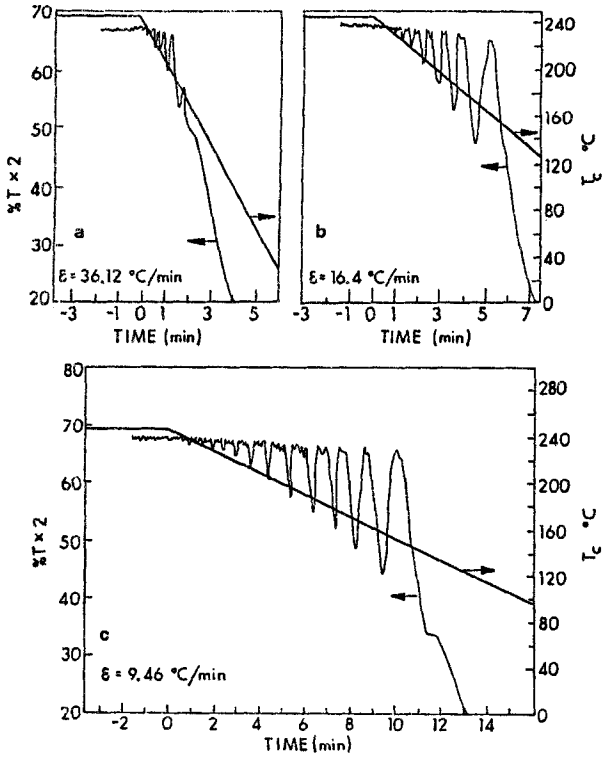

Figure 7. Dynamic response of catalyst 1 to slowly varying catalyst temperature T_c for various values of ϵ.

Upper ignited branch; P_t = 5 torr; feed composition: 5% CO, 20% O_2, 75% Ar

there for a few minutes, and then evenutally drops to the low extinguished state.

One aspect of the dynamic behavior that was surprising to us is shown in Figure 9. Here at the start of the experiment, the initial catalyst temperature was 74°C. The catalyst temperature was raised in a linear fashion with ϵ = 9.46°C/min. until the temperature reached 248°C (note the transition from the lower to the upper branch). After that point, the catalyst temperature

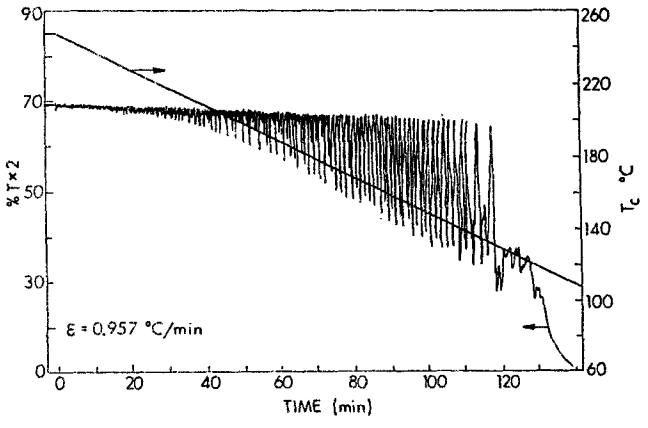

Figure 8. Dynamic response of catalyst 1 to slowly varying catalyst temperature T_c for ϵ = 0.957°C/min.

Upper ignited branch; P_t = 5 torr; feed composition: 5% CO, 20% O_2, 75% Ar

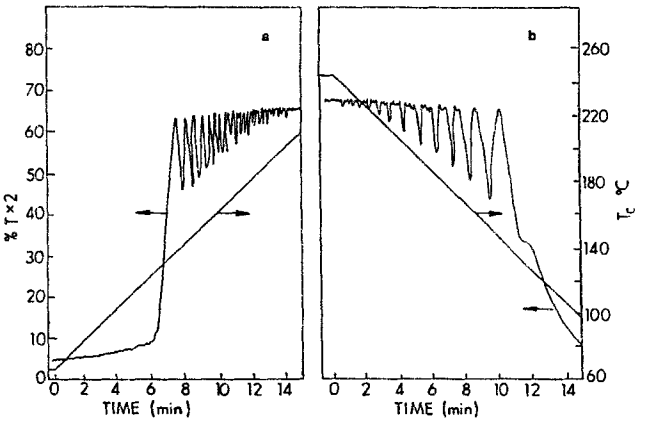

Figure 9. Dynamic response of catalyst 1 to slowly varying catalyst temperature T_c.

(a) T_{c0} = 74°C, ϵ = +9.46°C/min; (b) T_{c0} = 248°C, ϵ = −9.46°C/min

P_t = 5 torr; feed composition: 5% CO, 20% O_2, 75% Ar

was subsequently lowered again in a linear fashion with the same ϵ, 9.46°C/min. Note the obvious differences in the catalytic dynamic response. The amplitude, periods, and waveforms seen in Figure 9b are different from those observed in Figure 9a where the temperature is increasing. The differences are not due to catalyst deactivation or other changes in catalytic activity since the same experimental behavior can be reproduced time and time again.

The dynamic behavior shown in Figure 9 contradicts another series of experiments we performed, which are shown schematically in Figure 10. In these experiments the catalyst temperature was lowered in a linear fashion, while ϵ was kept constant but T_{c0} was varied. Note that the dynamic response is similar in

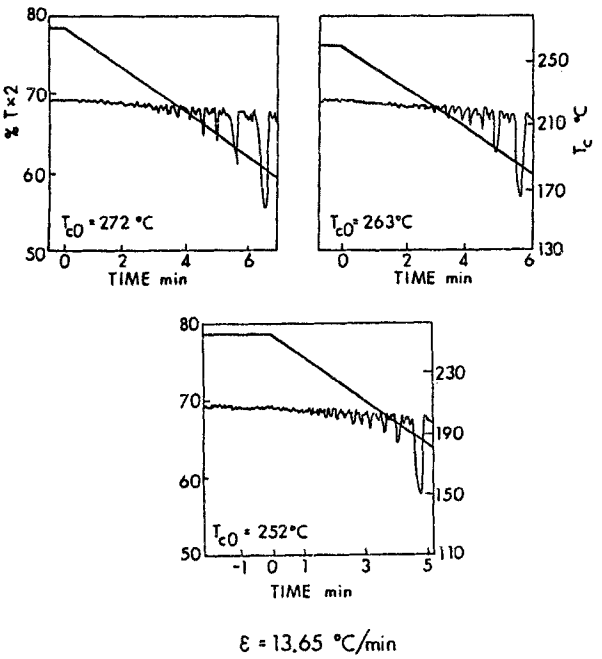

Figure 10. Dynamic response of catalyst 1 to slowly varying catalyst temperature T_c with ϵ = 13.65°C/min for different values of T_{c0}.

P_t = 5 torr; feed composition: 5% CO, 20% O_2, 75% Ar

all three cases, indicating absence of memory effects, as was also the case on the lower branch.

These are just a few examples of the intricate dynamic behavior one observes by slowly varying a bifurcation parameter in the oscillatory region. It goes without saying that our understanding of such phenomena is at this point at best very incomplete. Our experimental and theoretical studies of such phenomena are continuing.

Conclusions

We have presented here the results of our study of the dynamic behavior of a catalytic reaction system due to a deliberately slowly varied control parameter. We have, in particular, followed the jump phenomena due to slow passage through simple ignition and extinction type limit and Hopf bifurcation points.

For the particular experimental system under study the dynamic response due to a slowly varying parameter is quite different form the static behavior. Whether this is generally true for other catalytic reaction systems is the subject of our ongoing investigations. For the CO oxidation over $Pt/\gamma\text{-}Al_2O_3$ system, in our studies of jump phenomena due to slow passage through a limit point we have not observed memory effects similar to those suggested by the theoretical analysis of Erneux and Mandel (1986). The behavior becomes quite complex when one studies the dynamics due to a slow passage through a Hopf point and saddle-node type bifurcations. This is particularly true for systems with nested multiple steady state loops such as the $CO/NO/O_2$ or $CH_4/CO/O_2$ over $Pt/\gamma\text{-}Al_2O_3$ reaction systems (Lindstrom et al., 1985). These and other types of dynamic behavior will be the subject of future publications.

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