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REACTION RATE OSCILLATIONS DURING CATALYTIC CO OXIDATION– A BRIEF OVERVIEW.

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INTRODUCTION

It is not our intent here to present a comprehensive review of the dynamic behavior of the catalytic oxidation of CO. This reaction is one of the most widely studied in the field of catalysis. A review paper by Engel and Ertl [1] has examined the basic kinetic and mechanistic aspects, and a comprehensive paper by Razon and Schmitz [2] was recently devoted to its dynamic behavior. Those interested in further study of the subject should consult these reviews and a number of general review papers on catalytic reaction dynamics [3-12].

Our goal is to present here a brief overview of certain interesting aspects of the dynamic behavior of this reaction and to discuss a few questions and issues, which are still the subject of study and debate.

(I) THE DYNAMIC BEHAVIOR OF THE CO OXIDATION REACTION

Interest in the dynamic behavior of catalytic reactions started in 1968, when for the first time Hugo [13] observed reaction rate oscillations during decomposition of N_2O over a CuO catalyst. Since then, interest in such phenomena has grown and other reactions have been shown to exhibit interesting dynamic behavior, such as simple and complex types of hysteresis behavior, isolas, single-peak, multipeak and chaotic oscillations, propagating waves and spatial patterns.

Among the reactions exhibiting such behavior, one finds industrially important systems such as NH_3 [14] and hydrocarbon [15] oxidations and Fischer-Tropsch synthesis over zeolite-type and other catalysts [16]. The system that has received the greatest attention is CO oxidation over Pt-type catalysts. To date, over eighty experimental and/or review papers have appeared [2] which deal with some aspect of its steady-state and dynamic behavior.

The early studies were primarily of a qualitative character. Compared to more recent studies, relatively little attention was paid to issues such as catalyst cleanliness and preparation techniques, purification of reactants and reactor materials, or to control and monitoring of operating conditions.

The issue of impurities in the gas phase reactant streams became of particular concern to workers in the area for the first time in 1976 [17]. During the 4th ISCRE meeting in Heidelberg, Eigenberger attempted to explain the reaction rate oscillations observed, during CO oxidation, by Beusch et al. [18] by a four step kinetic scheme, which included CO and oxygen adsorption and desorption steps, a Langmuir-Hinshelwood surface reaction, and a slow buffer step involving an unidentified inhibitor. He pointed out that oscillations can result from the fact that the first three steps lead to multiple steady states for CO surface coverage at a fixed concentration of the unidentified inhibitor. The effect of the buffer step was to drive the value of CO surface concentration around a hysteresis loop. Eigenberger proposed gaseous oxygen as the so-called unidentified inhibitor, which reacts with the catalyst to create an inactive oxide species.

Experimental evidence of the role of gas phase impurities on the oscillatory behavior of this reaction appeared almost simultaneously. At the Sixth International Congress on Catalysis, in the discussion following the paper presented by Belyaev et al. [19], Jones reported that introduction of small amounts of TEP (triethylphosphate) triggered reproducible reaction rate oscillations during CO oxidation over a Pt wire. Similar observations were reported three years later by Gray and coworkers [20]. Jones et al. reported in 1977 [21] that oscillations were also triggered by the introduction of trace amounts of isopropyl methyl phosphofluoridate.

At about the same time additional experimental evidence was also presented by other groups apparently supporting the idea that trace amounts of impurities are primarily responsible for oscillations observed with CO oxidation. Cutlip, Kenney and coworkers [22,23] in their experiments over a 0.5% Pt/γ-Al_2O_3 catalyst for CO concentrations in the range of 0.5-3.0% and O_2 in the range 2-4% in Ar were unable to observe oscillations. They were, however, able to observe reproducible oscillations with a reaction mixture of 2% CO, and 3% O_2 and 1% Butene in Ar. Varghese et al. [24] reported a startling effect of hydrocarbon impurities on the oscillatory behavior in their system. Oscillations were observed, when an "impure" O_2 was used and disappeared when the "impure" O_2 was replaced by an "ultrapure" O_2. The only apparent difference between the "ultrapure" and "impure" O_2 was a 30 ppm impurity of hydrocarbons. Zhang [25] in 1980 reported that an aluminum coating on the inside reactor walls of the Illinois group [26,27] was the cause of the oscillations. The explanation advanced was that traces of a residual organic solvent entered the vapor phase.

Since then, and in contrast to the above, several published studies have reported oscillations for CO oxidation in the absence of gas phase impurities [28-30] several of them conducted under low-pressure or UHV conditions [31-37]. We have also considered the issue of gas phase impurities a few years ago [29] and attempted to duplicate Varghese's experiments. We found no effect of gas phase impurities in the O_2 stream, and oscillations were observed for both high and low purity O_2. Since then, experiments performed in our laboratories at intermediate and atmospheric pressure conditions (10^{-4} Torr - 1 atm) with elaborate purification techniques, in the absence of gas phase impurities (<1 ppm) and with spectroscopically clean catalyst surfaces have shown a variety of types of oscillatory behavior [28,37]. Based on our data and recent corroborating data of other groups we concluded in a 1985 paper [28] that "gas phase impurities are not the prime cause for the experimentally observed oscillatory behavior of this system." The issue of gas phase impurities is, of course, by no means closed, and it goes beyond the narrow confines of the field of catalytic reaction dynamics. To quote Razon and Schmitz [2], "It would be legitimate to ask what is the maximum amount of impurities tolerable in an experiment? Absolute purity is impossible. Indeed workers cannot even agree on how to approach the control of impurities as far as catalyst treatment steps are concerned. If ultrapurity levels are required in order to obtain reproducible results, then what resource must chemical engineers take in designing and controlling catalytic reactors for real conditions."

One of the primary reasons that CO oxidation has received attention in the field of catalytic reaction dynamics is its rich dynamic behavior. For a large range of experimental conditions, the reaction exhibits hysteresis behavior, i.e. regions where multiple steady states are observed. The typical steady state behavior reported, in a CSTR flow reactor, is shown in Figs. 1 and 2. Such figures are called bifurcation diagrams, and the independent experimental variable the bifurcation parameter (gas-phase, catalyst temperature in Figs. 1 and 2). The hysteresis behavior in Fig. 1a is of a counter-clockwise type (clockwise when the diagram is plotted in terms of CO surface-coverage, i.e., absorbance, Figs. 1b, 2a, 2b). Counter-clockwise hysteresis behavior, with temperature as the bifurcation parameter, is typical for CO oxidation and contrasts this reaction with other reactions such as H_2 oxidation. Note that multiple steady states (hysteresis behavior) have been observed even under isothermal, low-pressure conditions (Figs. 2a, 2b). This is important because even simple (first order) reactions can exhibit hysteresis behavior under non-isothermal conditions.

When inlet gas phase CO concentration is used as the bifurcation parameter, the behavior, in the presence of temperature gradients between the solid and gas phases, can be very complex, as shown both by our group [28,37] and Harold and Luss [38]. The observed behavior is best summarized in terms of the bifurcation set for this system (see Fig. 3), which is constructed by plotting the ignition and extinction points from the bifurcation diagrams (Figs. 1, 2) as a function of the inlet gas phase concentration.

Fig. 3 is for CO oxidation at atmospheric pressure conditions over a $Pt/\gamma\text{-}Al_2O_3$ catalyst. The upper line is, of course, the line of ignition points. Notice that the line of extinction points has a maximum value. The presence of such maximum implies interesting bifurcation behavior shown schematically in Fig. 4. Note in Fig. 4 steady states not directly connected to the main steady-state branch. The only way these states, commonly referred to as "isolas", can be accessed experimentally is by large perturbations in the operating variables. The behavior shown schematically in Fig. 4 was observed experimentally both by our group [37] and by Harold and Luss [38]. Under isothermal conditions, the maximum in the extinction line disappears and one is left with the clockwise hysteresis behavior [37].

In Figs. 1, 2, 4 there are at most two stable steady states.

This is the behavior reported by most studies of CO oxidation. There are, however, studies [25,38,39] reporting the existence of three stable steady states (five in total). Under non-isothermal conditions three stable states are, in principle, possible for this reaction [40]. In two of the above studies the authors have attributed the existence of three stable states to other causes. Hegedus et al. [39], who performed their experiments in an integral reactor, cite diffusional limitations. Zhang [25] implicates temperature non-uniformities along his Pt ribbon.

CO oxidation has also been shown to exhibit various types of oscillatory behavior. Both single peak and multipeak regular (regular meaning oscillations having a periodic pattern) oscillations have been observed. Several studies report relaxation-type oscillations (Fig. 5) characterized by sudden sharp changes in reaction rate (bursts), followed by periods of relatively constant behavior.

Aperiodic or "chaotic" oscillations have also been reported. The term "chaotic" has been used rather loosely, as Razon and Schmitz have observed [12], to describe oscillations that appear not to have a repeat pattern. Until Razon et al. [41] recently calculated the fractal dimension of the chaotic (strange) attractor they observed for CO oxidation, no analysis had been done to show that the reported aperiodic behavior did indeed conform to the mathematical definition of chaos.

(II) THE MECHANISM RESPONSIBLE FOR OSCILLATIONS

Even amidst the early excitement of discovering new types of dynamic behavior, there were efforts to understand the mechanistic basis for oscillations. There were also hopes that the newly discovered dynamic phenomena would eventually enable one to discriminate amongst rival mechanisms for CO oxidation and other catalytic reactions, in situations where steady-state data cannot. The success of our efforts in this direction is still subject to debate.

As is often the case, most of the initial efforts to understand the causes of rate oscillations and hysteresis behavior for CO oxidation and other catalytic reactions were somewhat misguided. Little experimental data were available, most of it of questionable quality by today's standards. The first effort to bring a sense of order into the fairly confused state of affairs was made by Scheintuch and Schmitz [4]. They critically examined many of the proposed mechanisms for the oscillatory behavior of CO oxidation. Most of these failed the test because they were not able to predict oscillations for realistic values of experimental parameters and/or conditions. The serious reader should consult this work. Most of the mechanisms subsequently proposed to explain oscillations for CO oxidation and other catalytic reactions can either be found in this work or traced back to it.

By the late seventies, it became clear to most workers in the field that if a mechanism for oscillations was ever to be found, elaborate experiments would have to be performed, in which the catalyst surface state would be monitored in situ, during oscillations. Two research groups engaged in this approach and in 1982 almost simultaneously reported their findings on CO oxidation over supported Pt [29,42]. In these studies IR Transmission Spectroscopy was employed to monitor the catalyst surface during oscillations. A number of issues heretofore unsettled were clarified at this point, not the least of which was the question of whether surface processes were at all responsible for oscillations. Some of the previously suggested mechanisms were put to test and found to fail, for example, that an Eley-Rideal mechanism was responsible for the oscillations [4], that long period oscillations result from a slow interconversion process between bridge and linear adsorbed CO [43] etc. For further details, the reader should consult the original and follow-up publications by the above groups [28,30,37] and others [44] who have since used the same techniques to study the dynamic behavior of the CO oxidation.

The year 1982 also marked the appearance of the first paper [32] in a series [32-36] by Ertl and coworkers, on the dynamics of CO oxidation over Pt single crystals. In their kinetic studies of CO oxidation over Pt(100) using a scanning LEED technique and work function measurements, they observed rate oscillations for a wide range of experimental conditions. They attributed these to a reversible phase transition of the surface structure of Pt(100) between phases (i.e., hex ↔ 1×1), which both have distinctly different properties towards CO adsorption and oxidation. It was not clear in the beginning, whether this transition was the cause or the outcome of the observed rate oscillations. There were also a number of other questions. Ertl and coworkers have since then, however, refined their mechanistic ideas on low-pressure CO oxidation over Pt(100), culminating with an excellent recent publication [36]. Their proposed mechanism for low-pressure oscillations over Pt(100) single crystals is today well accepted. But what about the oscillations observed at high pressures, where such a phase transition does not occur, or with other crystal planes, which do not undergo such a phase transition? For example, Yeates et al. [45] have observed reaction rate oscillations during CO oxidation over Pt(100), Pt(111) and Pt(13,1,1) crystals at high pressures. What about reaction rate oscillations observed on supported Pt catalysts? The issues here are certainly not resolved.

Our own group has been primarily involved with the study of the dynamics of CO oxidation over supported Pt catalysts. We have observed [27,28,37], both in the so-called "pressure-gap" region and under atmospheric conditions, that at least two types of adsorbed oxygen exist on supported Pt, with different physical and chemical characteristics. It appears that a species responsible for a CO adsorbance band around 2120 cm^{-1} (also observed by other investigators [46-48] and attributed to either CO adsorbed with oxygen atoms on Pt or CO adsorbed on oxidized Pt) is practically inert towards CO oxidation. As such, the formation and reduction of this species is a prime candidate for the slow mechanistic buffer step originally suggested by Eigenberger [17] and since then repeatedly mentioned in the literature as necessary for the generation of reaction rate oscillations. That this is the case is shown in Fig. 5. Note that the 2120 cm^{-1} band oscillates in phase with both the 2060 cm^{-1} (the band corresponding to linearly adsorbed CO) and the conversion. Note furthermore that both the conversion and the 2060 cm^{-1} band show multipeak oscillatory behavior, characterized by long period relaxation oscillations with superimposed oscillations of small period, the same order of magnitude as the reactor residence time. On the other hand, the 2120 cm^{-1} band shows only large period and apparently more regular oscillations. Such observations are direct evidence of multiple time scale phenomena and are in accord with the theoretical investigations, by Chang and Aluko [49].

There is additional experimental evidence [28,37] on the role of the 2120 cm^{-1} band in the generation of (large period) oscillations during CO oxidation over Pt/γ-Al$_2$O$_3$. We have observed, in agreement with Sarkany and Gonzalez [50] and Cant [51], that the 2120 cm^{-1} band forms to any appreciable extent only on catalysts with high metal dispersions and small Pt crystallites. In our experiments, we have been unable to observe long period oscillations during CO oxidation on any catalyst not forming a 2120 cm^{-1} band. On the other hand, catalysts that show oscillations, cease to exhibit any oscillations when they lose (by controlled sintering) the ability to form the 2120 cm^{-1} band. At the risk of sounding repetitious, it should be emphasized that the idea that formation and reduction of an "inactive" surface oxide is responsible for oscillations is neither original nor is specific to CO oxidation. Dating from Eigenberger's work, it has been the central theme of several theoretical investigations. Yeates et al. [45] proposed (but did not establish experimentally) the same mechanism for oscillations of CO oxidation at high pressures over single crystal and polycrystalline Pt catalysts. After all, the slow formation and reduction of an inactive surface oxide is probably the most plausible (the hex ↔ 1×1 transition for Pt(100) notwithstanding) mechanistic scheme to explain phenomena like the oscillations observed in CO oxidation, which are characterized by (long) periods orders of magnitude larger than the reactor residence time and the time constants typical of adsorption and reaction. It is well established [48] by now that noble supported catalysts do form inactive (at least towards CO oxidation) oxides both under intermediate and high (atmospheric) pressure conditions. The issues are, however, not very clear for single crystal and polycrystalline Pt catalysts, where the formation of similar oxide species has been attributed to bulk Si (and Al) impurities [2,28,37,45].

There is still much confusion surrounding the above issues. When it comes to explaining the oscillations, during CO oxidation, the need to postulate slow steps, such as a hex ↔ 1×1 transition or the slow formation and reduction of an oxide, arises from the clear difference between the time scales characterizing the oscillations (long periods) and the other plausible physico-chemical processes. If the oscillations observed with CO oxidation were of higher frequency, there would be no need to postulate slow mechanistic steps. There are many plausible causes ranging from the fluid mechanics of the process, the presence of diffusional limitations and nonisothermal phenomena to the existence of macroscopic roughness on the catalyst's surface (for polycrystalline catalysts) that could give rise to such oscillations [12]. The theoretical work of Chang and Aluko [49] should be very informative to anyone interested in further study on the subject.

When it comes to reaction rate oscillations observed for CO oxidation over supported catalysts, especially under isothermal and low-pressure conditions, there still remains a question for which there is no answer at present. For the catalyst to exhibit the observed type of behavior (oscillations, multiple steady states), there must be absolute synchronization in the behavior of all crystallites. The means of such perfect communication among the different crystallites still remains a mystery.

(III) FUTURE WORK

What the future should hold for further studies of the dynamics of CO oxidation and other catalytic reaction dynamics is probably a matter of personal predilection. There are, for example, those who find it difficult to accept that two or more mechanisms are needed to (or can possibly) explain the same type behavior (oscillations) for the same reaction (CO oxidation). For those, who have dealt with the complexities and peculiarities of non-linear systems, catalytic reactions being a prime example, this presents no conflict.

Resolving the issue of perfect communication among crystallites on a supported catalyst during oscillations will certainly occupy the thoughts and work of many. So also will efforts to understand and mathematically model new phenomena, such as propagating waves, chaos, and the phenomena resulting from external forcing of such reaction systems, which are, by themselves, intrinsically unstable.

The field is currently being shaped by two diametrically opposing forces. On one side, the newly observed phenomena are becoming more complex and the mathematical techniques and concepts required to model them are becoming progressively more difficult and esoteric. On the other hand, the experimental surface techniques needed to design and perform new and meaningful experiments are also rapidly becoming more complex, elaborate and expensive. In the face of current trends, the future probably holds little hope for the single investigator and further progress will require well-equipped and funded multidisciplinary efforts.

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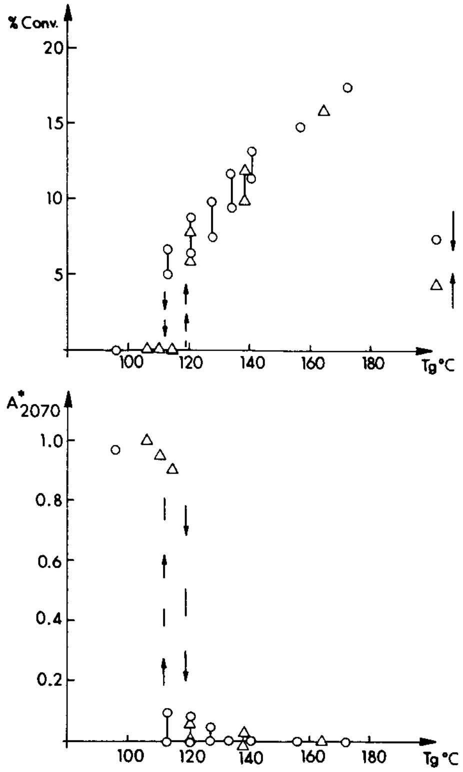
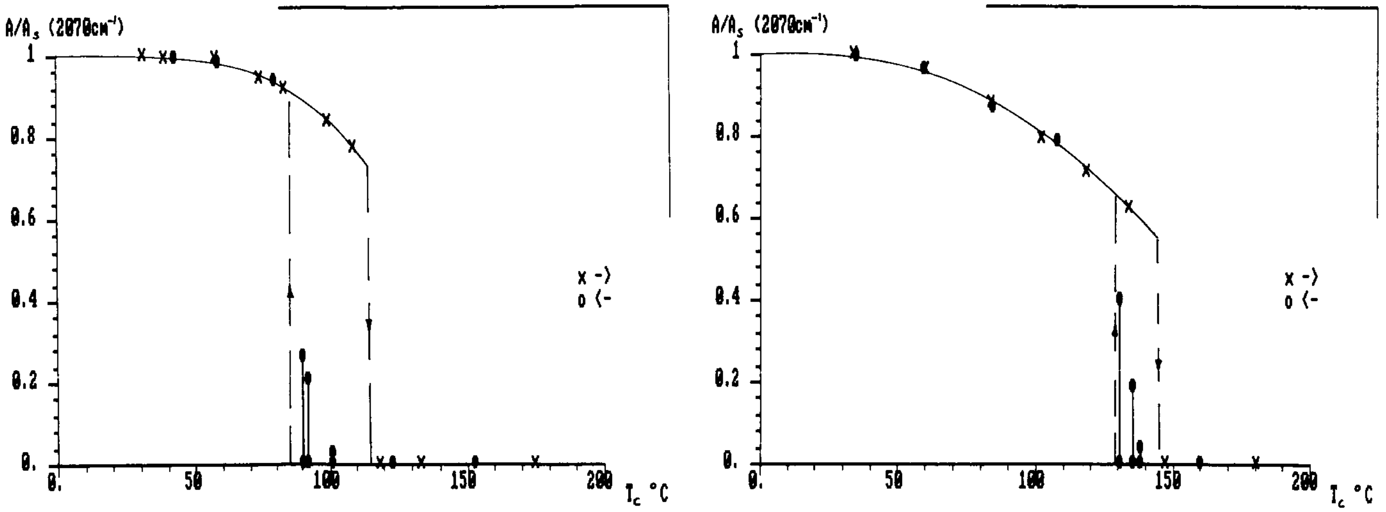


1. Bifurcation diagrams for the CO oxidation over Pt/γ-Al$_2$O$_3$ in a CSTR, at atmospheric pressures: (a) % conversion versus T_g (gas phase temperature); (b) normalized absorbance (2070 cm^{-1}) versus T_g. From [28].*



2. Bifurcation diagrams for the CO oxidation in the "pressure-gap" region. Normalized absorbance versus T_c (catalyst temperature): (a) P_t (total pressure) = 2.1 Torr; (b) P_t = 10 Torr. From [37].*

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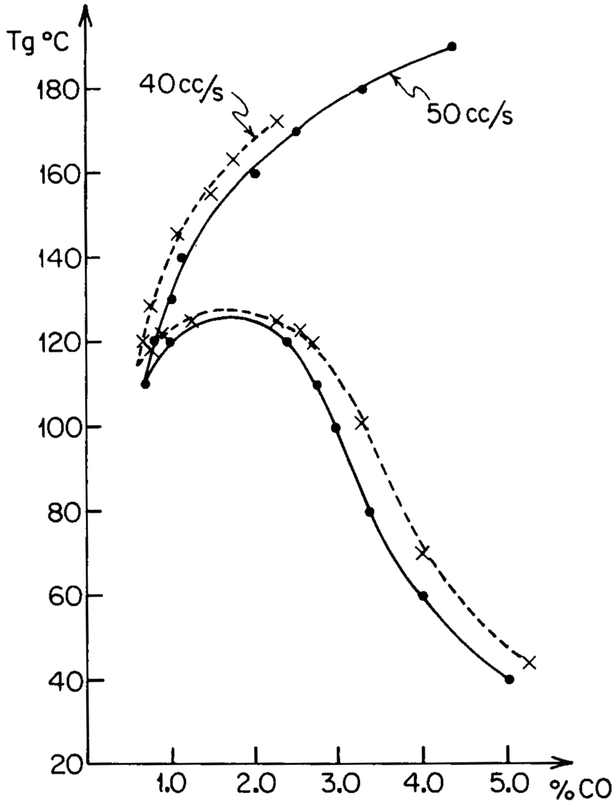
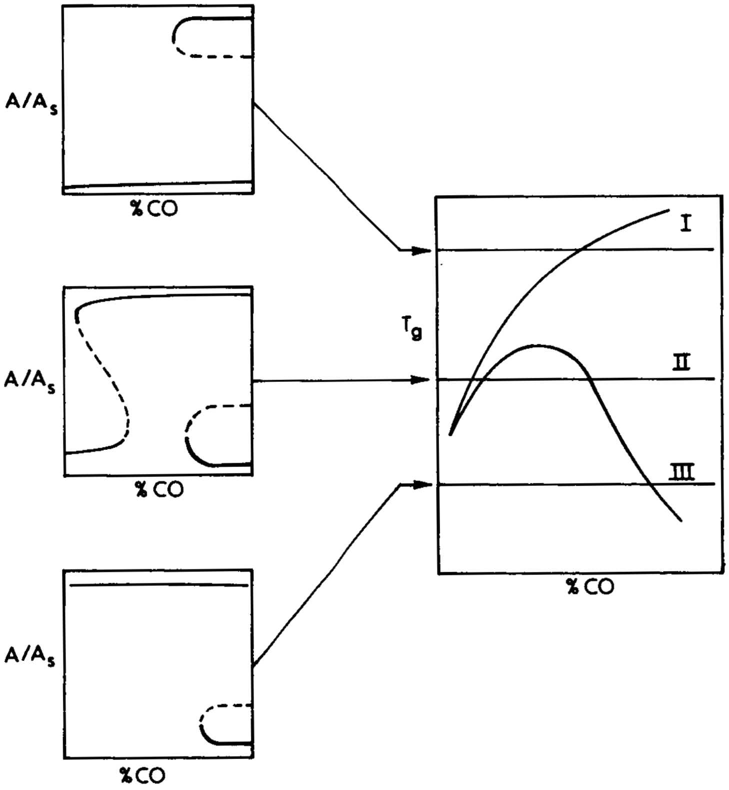


3. Bifurcation set for CO oxidation at atmospheric pressures. T_g versus %CO in inlet stream. From [28].*



4. Schematic of the bifurcation set and the bifurcation diagrams for CO oxidation. From [28].*

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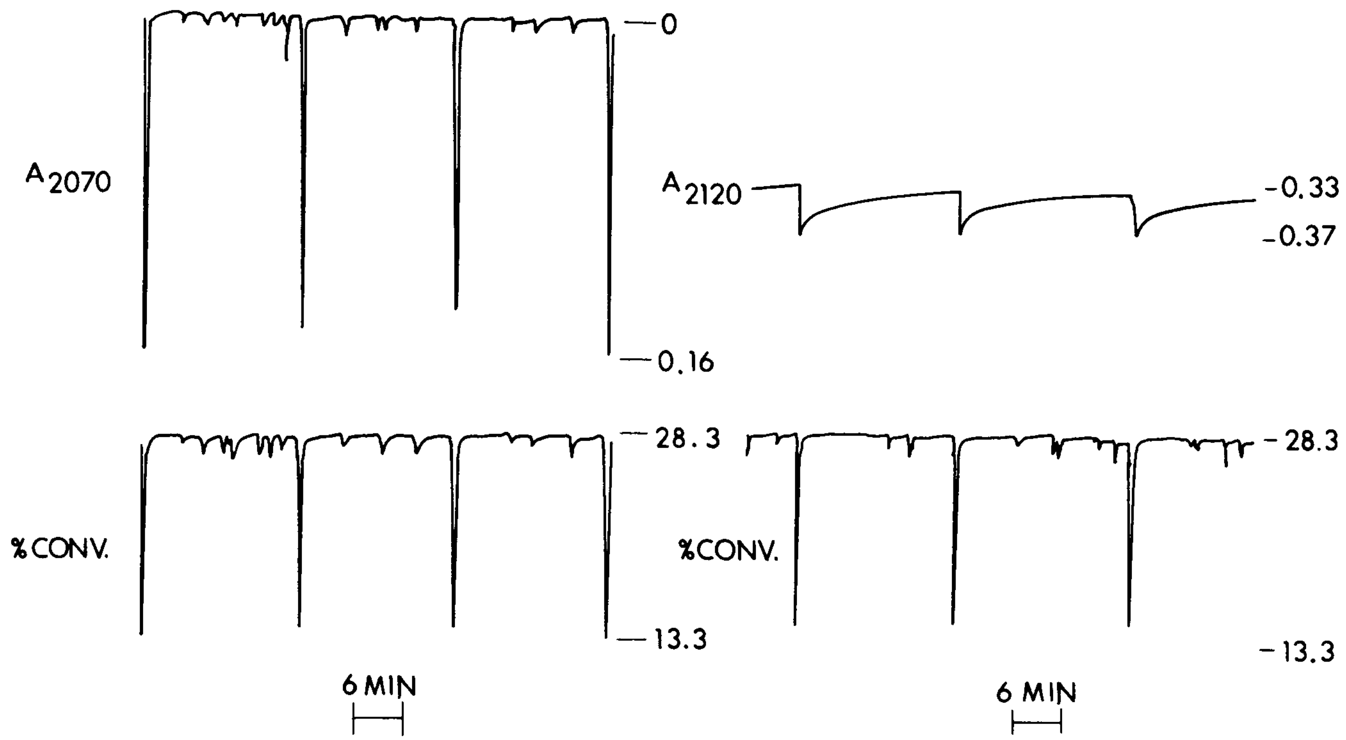

5. Conversion and surface concentration oscillations during CO CO oxidation over Pt/γ-Al_2O_3 in a CSTR at atmospheric pressures. From [28].*

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