

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 7/3/01	3. REPORT TYPE AND DATES COVERED Final Technical: 6/1/97 - 5/31/01	
4. TITLE AND SUBTITLE Spatiotemporal Dynamics in Heterogeneous Catalysis			5. FUNDING NUMBERS N00014-97-1-0771	
6. AUTHOR(S) C. M. Surko				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Regents of the University of California University of California, San Diego			8. PERFORMING ORGANIZATION REPORT NUMBER Fin-1	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Program officer: Dr. M. F. Shlesinger, code 331 Ballston Centre Tower One, 800 North Quincy Street Arlington, VA 22217-5660			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE				
13. ABSTRACT (Maximum 200 words) This project studied the heterogeneous catalytic reaction of carbon monoxide and oxygen on the surface of thin platinum metal films to form carbon dioxide. Infrared imaging was used to study both the spatial and temporal behavior of the reaction. The mechanisms of spatial coupling in this system were studied as well as their effect on the resulting pattern formation. A complementary study was conducted to examine the effect of local perturbations in initiating catalytic behavior. An important conclusion of the work is that, while none of the currently proposed models completely describes the oscillatory catalytic behavior observed in this system, the oxidation-reduction model agrees best with the experimental results.				
14. SUBJECT TERMS			15. NUMBER OF PAGES 6	
			16. PRICE CODE N/A	
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT	

20010717 097

Final Technical Report
Spatiotemporal Dynamics in Heterogeneous Catalysis
ONR Grant #N00014-97-1-0771
6/1/97 - 5/31/01

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Summary

This is the final report for an AASERT training grant, associated with the project: "Study of Patterns and Dynamics in Heterogeneous Catalysis," Grant #N00014-95-0179, from 1/1/95 - 6/30/98. Progress made during parent grant from that Final Technical Report is restated, and the additional progress during the period 7/1/98 - 5/31/01 as a result of the AASERT grant is summarized. This project studied the heterogeneous catalytic reaction of carbon monoxide and oxygen on the surface of platinum metal to form carbon dioxide. While some aspects of oscillatory oxidation on platinum at atmospheric pressure are well studied, such as the time-series behavior of the surface temperature of the catalyst, many open questions remain. In this project, infrared imaging was used to study both the spatial and temporal behavior of the reaction. The catalytic reactor was designed to take advantage of a high-speed, high-resolution infrared imager. The mechanisms of spatial coupling in this system were studied as well as their effect on the resulting pattern formation. A complementary study was conducted to examine the effect of local perturbations in initiating catalytic behavior. An important conclusion of the recent work is that, while none of the currently proposed models completely describes the oscillatory catalytic behavior observed in this system, the oxidation-reduction model agrees best with the experimental results.

I. Introduction

Oscillations in the reaction-rate of CO oxidation on platinum surfaces are observed under two strikingly different pressure regimes: high vacuum and atmospheric pressure. Under UHV conditions, studies using *in situ* techniques such as photoemission electron microscopy have revealed a variety of spatial patterns such as target patterns and spiral waves. [1] These oscillations have been shown to be due to a reconstruction of the platinum surface. [2]

At atmospheric pressure, previous studies of oscillations in the temperature of a platinum catalyst during exothermic CO oxidation have used thermocouples to record time-series data. [3-5] In order to observe spatial pattern formation, a different technique is required. In other exothermic reactions, such as the oxidation of hydrogen over nickel catalysts, infrared imaging was found to be an effective method of observing spatiotemporal behavior. [6,7] In the hydrogen oxidation reaction, however, the amplitude of the oscillations was large and modeling proved to be difficult since the system cannot be considered isothermal. In CO oxidation over platinum, oscillations on pressed powder catalysts typically have similar fluctuation amplitudes. In order to study spatiotemporal dynamics in a catalytic system in more detail, a model system was required in which the temperature fluctuations were much smaller. After testing platinum wires and foils, we settled upon the use of vacuum-deposited platinum thin-films. The reasons for this decision are discussed in more detail in the next section.

This report provides an overview of the research accomplishments completed during both the parent and AASERT grants. We refer the reader to the published papers [8-13] which contain a more detailed description of the experiments, the analysis of the data and the results of this research.

II. Description of the Experiment

The experiment was conducted in a continuous-flow reactor which consists of a long quartz tube mounted in a furnace [9]. Before entering the reactor the reactant gases (carbon monoxide and oxygen), along with helium or argon buffer gases, are mixed and purified in a glass bead pack which is maintained at an elevated temperature. In the main reactor, the gas flow is laminar with a Reynolds number of ~ 10 . Thus the gas flow profile is parabolic, and cylindrical symmetry is maintained so that all parts of the catalyst experience identical reaction conditions. After flowing over the catalyst, the gases are vented downstream.

The catalysts used in the experiment are 1000 Å thick films evaporatively-deposited onto thin, ring-shaped quartz substrates. The use of thin films has several advantages over other types of catalysts. First, the purity and uniformity of films are much higher than other forms, resulting in higher repeatability. Second, by using masks during deposition, a variety of catalyst geometries can be made easily. Finally, the surface area of thin films is much smaller than pressed powder catalysts of equal dimensions, and this results in a lower total reaction rate and smaller temperature fluctuations. The catalyst is suspended perpendicular to the gas flow in the center of the reactor by three equally-spaced thermocouples.

The catalysts and substrates were made in the form of annular rings, with the radial extent of the rings small in comparison to the characteristic scale length of the patterns. This resulted in patterns that were "one-dimensional" (1D) in the direction around the annulus. Such patterns are much easier to compare with the predictions of theoretical models than less restrictive geometries that admit to 2D or 3D variations.

Spatiotemporal data was taken using a high-speed, high-resolution infrared imager located outside the reactor. Data from the imager was calibrated using temperature information from *in situ* thermocouples mounted near the catalyst. The emissivity of the quartz substrate (0.93) is much higher than that of platinum (0.03) in the wavelengths of interest. Consequently, the catalyst was imaged through the back surface of the quartz substrate in order to increase the sensitivity of the imaging process. Since the thickness of the substrate is small compared to the characteristic dimensions of the pattern, and the thermal conductivity of the substrate is large compared to that of the gas in the reactor, this procedure did not result in a significant degradation in spatial resolution.

III. Research Results

Spatial coupling in this system can come about through either surface- or gas-phase diffusion of either reactant concentration or temperature. By systematically blocking the possible mechanisms using physical barriers, we found that the dominant coupling mechanism is gas-phase diffusion of the reactants. [10] In order to reduce the amplitude of the temperature fluctuations in the system, helium and argon buffer gases are used to dilute the gas stream. Since these gases do not adsorb on the platinum surfaces, they do not play a role in the kinetics of the reaction. Because the spatial coupling occurs through the gas stream, however, these non-participant gases do affect the spatiotemporal dynamics.

A series of tests was conducted to determine how varying the buffer gas affects the synchronization of the oscillations. [12] Under typical operating conditions, the buffer gas stream is 90% helium and 10% argon. Since diffusion through the buffer

depends on the mass density of the gas, two sets of data were taken using a pure helium buffer in one case and a pure argon buffer in the other. The correlation between different parts of the catalyst was used to measure changes in spatial synchronization. When the helium is replaced with argon, the mass density is a factor of 10 higher, which decreases the diffusion coefficient of the composite gas stream by a factor of about 4. Remarkably, however, very little change was observed in the synchronization due to this change.

Since the reactions are studied in a continuous-flow reactor, fluctuations in the local concentration of the reactants are swept away from the catalyst after a short time. Thus, the degree of spatial coupling would be expected to decrease as the flow rate of the gas stream increases. To test this hypothesis, another data set was taken using a faster-flowing, pure argon buffer gas in which the total gas flow rate was four times the normal value. Comparison of spatiotemporal correlations using the fast and slow buffers showed a marked drop in the synchronization in the case of the faster flow rate. Thus, by changing the flow rate of the gas stream, spatial pattern formation can be affected without disrupting the cylindrical symmetry of the system. This is potentially an important tool for studying patterns and dynamics in this system.

In a related experiment, a small tube was mounted upstream from the catalyst with the mouth of the tube pointing at the platinum surface. [11] Using a gas-tight syringe located outside the reactor, a perturbation in the form of a small puff of pure reactant could be applied directly to the catalyst surface through this tube. The perturbation will react and then be advected away from the platinum, thereby limiting both the spatial and temporal duration of the perturbation. Since the high reaction-rate branch is characterized by low CO concentration and the low reaction-rate branch is characterized by high CO concentration, a CO perturbation applied to the surface during the high branch in the oscillatory cycle is expected to induce a transition to the lower branch.

When a small puff of CO was applied to an oscillating catalyst, the entire catalyst made a transition to the lower reaction-rate branch. Thus the *local* perturbation induced a *global* reaction in the catalyst. This transition persisted for a duration comparable to the natural oscillation of the catalyst, suggesting that the induced oscillation was identical to a natural one. However, the total time delay between the naturally-occurring oscillation previous to the triggered oscillation and the naturally occurring oscillation following the triggered oscillation was the same as the period of the natural oscillatory cycle. Thus, the induced transition did not affect the phase of the oscillatory cycle. This behavior is unexpected and remarkable, since numerical models for this system all predict that the phase of the oscillations should shift to that of the perturbation. To date, we have not been able to explain this behavior, but attempts to understand it continue.

Studies involving CO perturbations showed that they irreversibly altered the surface of a catalyst in an unknown way which "quenched" the oscillatory behavior of part of the surface. This region still converted CO to CO₂, but without oscillations. After this change, oscillations observed on the rest of the catalyst were in the form of low-amplitude, rapid pulses which began on one side of the quenched region and propagated to the other. These pulses were found to be repeatable and robust, persisting under changes in system temperature. In an earlier experiment, a similar low-amplitude, rapid pulse was observed in the system. [8] This pulse, unlike the more recent one, was a transient state which, after rotating for an hour, spontaneously made a transition to global oscillations and could not be repeated. While these pulses differ in robustness, they are similar in amplitude, velocity, and were found under similar reactor conditions. Studies of this behavior continue, comparing the propagation of the observed pulses with models of the reaction dynamics on a non-uniform ring.

Most studies of spatiotemporal behavior have examined oscillations at times well after the system has begun oscillations and all of the initial transients have died away. Under these conditions, different models for the oscillations predict relatively similar behavior. Thus, the easily measurable oscillations in the catalyst's temperature do not

provide a good discriminate between the models. However, if one starts from an initial condition not on the oscillatory cycle, the models predict different paths to oscillation. We devised a test to use these differences in transient response to try to distinguish between two models which appeared to best describe the oscillations which we observe.

In the "oxidation-reduction" model, [14] the change in the rate of reaction is controlled by a subsurface oxide which slowly forms from oxygen adsorbed on the surface. This oxide state blocks CO adsorption, thereby limiting the rate of reaction. Since adsorbed CO slowly reacts with the oxide, it is removed from the surface until there is a sufficiently small amount of oxide for the reaction to switch to the upper branch. In the carbon model, [15] on the other hand, the species responsible for the blocking of adsorption sites is adsorbed carbon atoms. The carbon impurities are removed by a slow reaction with adsorbed oxygen, which leads to the characteristic oscillations that are observed.

A test involving a series of reactant-gas pretreatments was developed to take advantage of the different site blocking mechanisms in order to determine which model describes the observed oscillations most accurately. The catalyst was first exposed to a gas stream consisting purely of one of the reactants. The second reactant was then added to the gas stream and the resulting transient behavior was recorded. For example, in the case of a CO pretreatment, CO was flowed over the catalyst for about 20 minutes. After this, oxygen was added to the CO stream. If the oxidation-reduction model is correct, the CO pretreatment will reduce the platinum surface thereby covering it with CO. Added oxygen will then react with the adsorbed CO at a high rate. In the carbon model, on the other hand, a CO pretreatment will allow carbon impurities to build up on the surface. Added oxygen will then react at a low rate as the carbon is slowly removed from the surface. In the oxygen pretreatment, the opposite behavior is expected.

The results of the pretreatment tests were inconclusive. After both the CO *and* oxygen pretreatments, the catalyst responded to the application of the full gas stream by reacting at a high rate. In the case of the CO pretreatment, this behavior matched the expected results of the oxidation-reduction model; while in the case of the oxygen pretreatment, the results matched the predictions of the carbon model. In retrospect, this result can be understood by realizing that both models were developed to describe the behavior under stable oscillatory conditions. Thus, the differences in the models in accurately describing the reaction is not optimally highlighted in steady-state conditions.

To proceed further, following oxygen and carbon monoxide pre treatments, we studied the transient response of the catalyst to reacting gas injected through a hypodermic needle directly above the catalyst (i.e., to achieve a faster change than can be achieved changing gas flow through the reactor) [13]. This proved to be a more discriminating test of the models. A novel scheme was used to analyze the data, which involved plotting the temperature responses to the two pre treatments against each other, at each time delay in the transient response and for various values of time delay. In this way, the separate, intrinsic time scales of the models drops out of the comparison, and each model could be compared with the observations. The key conclusion [13] is that while neither model provided an absolutely faithful description of the dynamics, the oxidation-reduction model was much better and appears to have essentially the correct features.

IV. Publications

1. S. Y. Yamamoto, C. M. Surko, M. B. Maple, and R. K. Pina, Phys. Rev. Lett. 74, 4071 (1995).
2. S. Y. Yamamoto, C. M. Surko, M. B. Maple, and R. K. Pina, J. Chem. Phys. 102, 8614 (1995).

3. S. Y. Yamamoto, C. M. Surko, and M. B. Maple, *J. Chem. Phys.* 103, 8209 (1995).
4. C. D. Lund, C. M. Surko, M. B. Maple, and S. Y. Yamamoto, *Applied Nonlinear Dynamics Near the Millennium* edited by James B. Kadtko and Adi Bulsara, AIP Conf. Proc. No. 411 (AIP, New York, 1997), p. 18.
5. C. D. Lund, C. M. Surko, M. B. Maple, and S. Y. Yamamoto, *J. Chem. Phys.* 108, 5565 (1998).
6. C. D. Lund, C. M. Surko, M. B. Maple, and S. Y. Yamamoto, *Surface Science*, 459, 413 (2000).

V. Summary and Concluding Remarks

We have extended the understanding of oscillatory CO oxidation at atmospheric pressure in several ways. One of the greatest challenges in studying this system is to fabricate catalysts with uniform, repeatable behavior. We found that, by using evaporatively-deposited films instead of prefabricated bulk platinum (e.g. wires and foils) catalysts, there is more control over the quality of the catalyst. This resulted in increased uniformity of a given catalyst and increased repeatability of behavior between different catalysts. We advanced the understanding of the mechanisms underlying spatial coupling in this system and how this degree of coupling can be controlled by changing the parameters of the buffer gas. Finally, transient perturbations applied to pretreated catalysts provided a key test to discriminate between models, indicating that the oxidation-reduction model best describes the reaction.

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