Fingering instabilities in propagating fronts of the CO oxidation reaction on Pt(100)

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Introduction

Interfacial patterning is a common feature of many non-linear systems ranging from isothermal chemical reactions [1] to viscous flow systems [2]. Underlying this behavior is the spatial decoupling of chemical species due to differences in convective or diffusive transport. The oxidation of CO on Pt(100) represents a non-linear system where adsorbed CO and O are significantly decoupled due to differences in binding energy on the Pt surface. However, patterns on reaction-diffusion fronts are not typically observed in this system as diffusive transport naturally adds curvature and therefore stability to propagating fronts. We have offset this natural tendency towards curvature by locally forcing the surface reaction to generate planar reaction fronts on an otherwise stable surface. Under these unique reaction conditions, reaction fronts were observed to undergo fingering bifurcations and subsequent finger tip-splitting [3].

Materials and Methods

Experiments were carried out on a Pt(100) single crystal mounted in a stainless steel ultra-high vacuum (UHV) chamber containing reactants at constant pressure. The Pt surface was cleaned by repeated cycles of annealing to 1200 K, Ar ion sputtering under $1x10^{-4}$ Torr Ar, and oxidation at 950 K and $1x10^{-6}$ Torr O_2. The catalyst surface was continuously analyzed using ellispomicroscopy for surface imaging (EMSI), which detects different adsorbates based on local changes in the optical properties of the surface [4].

External forcing was used to locally perturb the surface and create reaction fronts under global reaction conditions which do typically support the formation of spontaneous chemical fronts. This was done by locally dosing gas onto the surface via a capillary tube positioned 500 µm from the surface. A glass capillary with a square shaped internal channel with a cross-sectional area of 2500 μm^2 was used to promote the development of a square shaped perturbation on the surface, thereby creating the necessary planar wave fronts which preceded the fingering instability. The local gas doser was mounted on an x-y-z manipulator for precision movement and was supplied with reactant maintained at a desired pressure to control the intensity of the surface perturbation.

Results and Discussion

Planar CO fronts were initiated on the surface by locally dosing CO onto an O-covered surface maintained at 403 K and $4x10^{-4}$ Torr O_2 using a capillary tube. At these conditions, oxygen, acting as the activating species, was essentially immobile on the surface and could not diffuse to the reaction front and provide stability to the planar geometry. In contrast, the inhibiting species CO diffused with relative ease towards the reaction zone destabilizing the planar front. The instability took the form of narrow fingers of adsorbed CO extending into the O adlayer ahead of the reaction front as shown in figure 1. As the reaction front advanced on the surface, the continuously growing length of the front pulled the fingers apart increasing the wavelength between adjacent fingers. Once the critical wavelength (λ_c) of approximately 40 µm was surpassed, additional fingers were created in a tip-splitting bifurcation as the fingers attempted to restore the critical separation distance.

The initial conditions from which the system evolved towards λ_c were found to be crucial to the growth behavior of the fingered fronts. On bifurcated fronts where adjacent fingers were separated by distances greater than λ_c, new fingers formed not in tip-splitting bifurcations, but grew in at the trough between two existing fingers. A decrease in shielding, which is expected to be more significant for λ less than λ_c due to competition between growing fingers, may have facilitated finger growth from the trough position. This behavior suggests that the drive towards the apparent characteristic wavelength is a somewhat ordered and efficient process, with tip-splitting and finger growth at trough positions occurring selectively to create the critical separation distance.

Significance

This work demonstrates the effectiveness of local forcing in generating and exploring novel behavior on heterogeneous catalysts. The ability to perturb the system, while simultaneously monitoring the response of the system, provides for a better understanding of the reaction-diffusion properties of surface reactive systems.

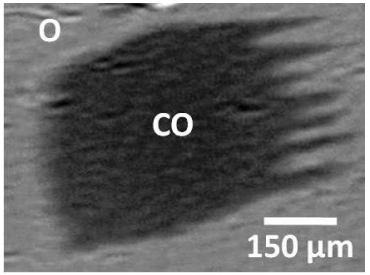

Figure 1. EMSI image showing the formation of CO fingers at the reaction interface between CO (black) and O (grey). (T=403 K, $p_{O2}=4x10^{-4}$ Torr)

References

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