

Investigation of gas-phase coupling in the CO oxidation reaction on polycrystalline Pt

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Introduction

The oxidation of CO on Pt catalysts has been shown to exhibit complex, non-linear behavior, such as reaction rate oscillations and spatio-temporal pattern formation over a wide range of reaction conditions [1]. At pressures above 1×10^{-3} Torr, individual regions of the catalyst surface are primarily coupled through thermal fluctuations within the catalyst itself or by variations in reactant pressure in the gas phase above the surface. At lower pressures, where the system is isothermal, coupling through the gas-phase [2] and by surface diffusion of adsorbates results in spatial synchronization. For the gas-phase coupling mode in particular, little is known about the spatial limits in which different surface regions may communicate through the gas phase. This is primarily due to experimental difficulties associated with locating and imaging dynamic behavior on the surface while simultaneously detecting local changes in the gas phase above the surface. In this study, we employ real time surface imaging combined with scanning mass spectrometry to analyze the gas phase above a polycrystalline Pt foil during CO oxidation to investigate gas-phase coupling behavior.

Materials and Methods

Experiments were carried out on a recrystallized polycrystalline Pt foil 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 1×10^{-4} Torr Ar, and oxidation at 950 K and 1×10^{-6} Torr O_2 . The catalyst surface was monitored using ellipsomicroscopy for surface imaging (EMSI) [3], which detects different adsorbates based on local changes in the optical properties of the surface. A second UHV chamber, connected to the main reaction chamber by way of a micro-orifice at the end of a glass capillary, contained a mass spectrometer used for the analysis of gas-phase species. By positioning the orifice at various locations above the surface, the gas-phase signal due to individual catalyst grains, identified using EMSI, could be resolved.

Results and Discussion

A necessary step in the investigation of gas-phase coupling is the creation of a distinct, spatially localized signal originating from the surface. This localized signal was generated by adjusting the reaction conditions to $P_{O_2} = 1.82 \times 10^{-3}$ Torr, $P_{CO} = 1.4 \times 10^{-4}$ Torr, and $T = 533$ K. At these conditions, a limited number of catalyst grains began to oscillate between a CO and O-covered state, thereby inducing an oscillating CO_2 signal in the gas phase which could be analyzed with the mass spectrometer. As shown in figure 1, the oscillatory CO_2 signal varied as the orifice was moved away from the surface, as the effects of individual grains became less significant and the oscillations reflected global system behavior. The distinct

features observed in the oscillations (e.g., at 330 s on the 2000 μm scan) are correlated with the kinetic behavior of individual grains on the surface using the EMSI data, allowing for estimation of the length scales associated with gas phase coupling in this pressure regime.

Significance

The impact of this work lies in the ability to simultaneously image dynamic behavior on the surface while locally monitoring variations in the gas-phase directly above the surface. Such experiments provide a quantitative estimate of the length scales associated with the gas-phase coupling mode which plays an important role in the dynamics of surface reactions.

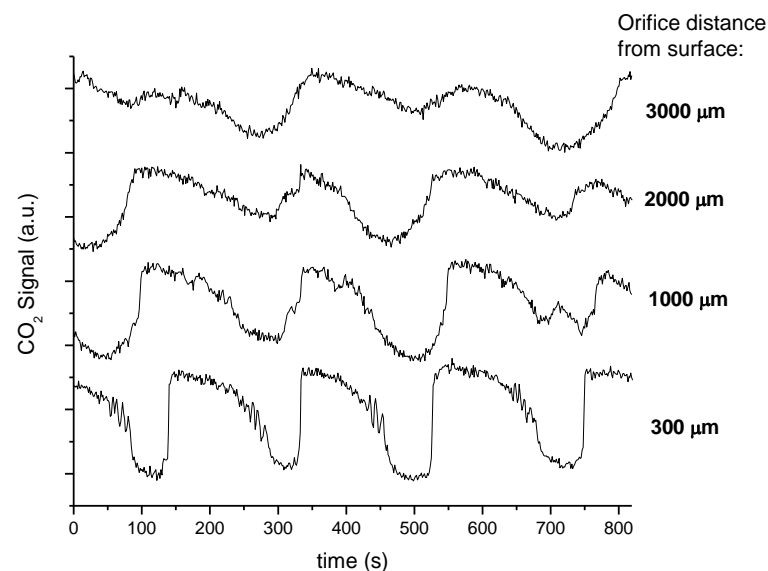


Figure 1. Mass spectrometer spectra (44 amu) taken at increasing distances from the reactive surface.

References

1. Imbihl, R., and Ertl, G. *Chem.Rev.* 95, 697 (1995).
2. Lauterbach, J., and Rotermund H.H. *Cat. Lett.* 27, 27 (1994).
3. Rotermund, H.H., Haas, G., Franz, R.U., Tromp, R.M., and Ertl, G. *Science* 270, 608 (1995).