

Design and characterization of a small volume reactor for the high pressure invacuo study of catalytic surface reactions

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Abstract: A small volume reactor compatible with ultrahigh vacuum (UHV) surface-science instrumentation has been designed, modeled and tested for the study of the kinetics of surface chemical reactions on single crystals. The overall apparatus is composed of two chambers, one “main” UHV volume operating at a base pressure of 2×10^{-10} torr for crystal manipulation, Ar ion sputtering, low-energy electron diffraction (LEED) surface characterization, and gas-phase analysis using mass spectrometry (MS), and a second “probe” chamber operating at a base pressure of 2×10^{-9} torr and equipped with a second gas-phase MS and an ion gauge for the detection of products from the reactor. The small reactor consists of two concentric tubes, the inner inlet for the supply of the reactants and an outer cone to trap the gases within a nanoliter sized volume above the catalytic crystal surface, presumably feeding the gas mixture into the probe chamber. CO oxidation experiments have been carried out experimentally and found to approximately match two-dimensional multiphysics models carried out in COMSOL. However, the COMSOL model gives a flow profile that allows for doser design improvements that would optimize flow impingement onto the crystal surface, increasing reaction rate, and effectiveness of the doser on low probability reactions.

Keywords: carbon monoxide (CO) oxidation, surface catalysis, ultra-high-vacuum (UHV) system design, UHV system modeling

1. Introduction

The design and construction of ultra-high-vacuum (UHV) systems for the study of surface reactions has led to high impact innovation in a

myriad of industries, most notably in automobile catalysis and semiconductors. The impact of the study of reactive surfaces was recognized by the international community in 2007 through the award of the Noble Prize in chemistry to surface scientist Gerhard Ertl. This award was rendered in part for Ertl’s work in elucidating the mechanism of carbon monoxide oxidation on platinum surfaces¹.

Here carbon monoxide oxidation on Pt(111) is used as a well studied system to test and design a new UHV system. The system discussed here is designed to bridge the pressure gap in catalysis. Although groups have been successful in bridging the pressure gap between UHV (10^{-9} torr) and high pressure (<1 torr), these systems have been complex, expensive, and requiring operation as batch reactors^{2,3}.

In this work a simple invacuo test reactor has been tested using the carbon monoxide oxidation reaction as a benchmark reaction. Additionally, this reactor has been modeled using the computational multiphysics package COMSOL. This work has yielded agreement between model and experiment.

Through use of this experimentally verified model new invacuo reactor designs can be explored that without the cost of construction of a new apparatus. Ultimately it is hoped that this will lead to an optimized reactor design that will allow the study of low-probability catalytic reactions which will yield future surface science and catalysis breakthroughs.

2. Materials and Methods

2.1 UHV Apparatus

The UHV system used here is comprised of two differentially pumped chambers separated by an annular doser. Figure 1 gives a pictorial view

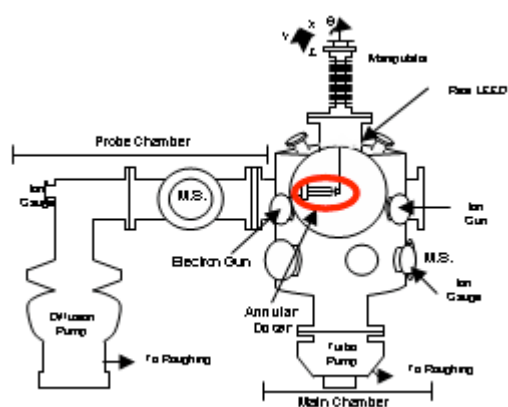


Figure 1: Pictorial diagram of UHV system.

of the UHV system. A detailed vacuum diagram of the system is provided in the appendix. The two chambers are labeled in Figure 1 as the main chamber and the probe chamber.

Contained in the main chamber is the Pt(111) crystal and all the surface preparation and analysis equipment. This surface analysis equipment includes: an Ar ion gun, a quadrupole mass spectrometer, a front view low-energy electron diffraction screen (LEED), and an electron gun for Auger Spectroscopy. The base pressure in the main chamber is 2×10^{-10} torr as measured by a nude UHV ion gauge. As stated before, the main chamber and the probe chamber are separated by the annular doser. This doser has been custom fabricated at the University of California, Riverside and is shown in detail in Figure 2. The crystal is brought to within 1mm of the doser nozzle. The reactant gas, in these experiments a carbon monoxide and oxygen mixture, is introduced through the center tube. The annulus of the doser nozzle is the only connection of the main chamber to the probe chamber.

The probe chamber is presumably the analysis chamber for product gas, carbon dioxide, forming on the crystal surface. The base pressure of the probe chamber is 1×10^{-9} torr. The probe chamber has only an ion gauge and a quadrupole mass spectrometer.

During steady-state reaction on the crystal surface a high pressure large volume gas bulb is the source of the reactant mixture gas. The doser pressure prior to the introduction of the reactant gas to the crystal surface, as measured by a thermocouple gauge, is set to 1 torr. The cylindrical crystal, which is

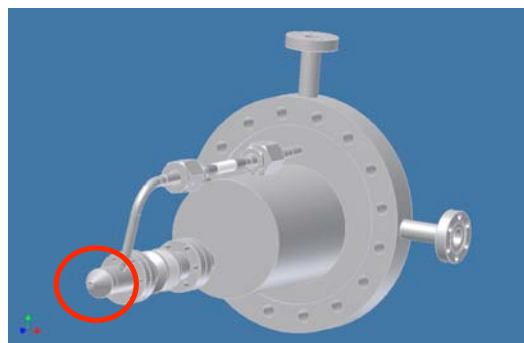


Figure 2: Design drawing of invacuo doser assembly with the annular doser nozzle is circled in red. This doser is mounted on a 6" CF flange to provide a barrier between the "main" and "probe" chambers.

resistively heated, is pressed within 1mm of the doser surface. The cylindrical Pt(111) crystal is 2 cm in diameter and 2 mm thick.

The oxygen is supplied by Matheson and is reported as 99.999% pure. The oxygen is mixed in the large volume high pressure bulb 2:1 with Matheson 99.5% pure carbon monoxide for all experiments reported here.

2.3 COMSOL Modeling

COMSOL Multiphysics was used to perform simulations on the reactive system. The system was modeled in two dimensions, as the system is symmetrical. Fluid dynamics, heat transfer, mass transfer and chemical reaction were taken into account using COMSOL. The system was assumed to be at steady state. Additionally the system was modeled as isothermal and weakly compressible.

3. Results and Discussions

Quadrupole mass spectrometer reaction data for CO oxidation are provided in Figure 3. In Figure 3 steady-state CO consumption is seen to increase with temperature as CO_2 production increases. While this is expected, data presented in Figure 3 verify that the reactor system is operating as anticipated. System properties can also be gleaned from the calibrated mass spectrometer trace in Figure 3. The mass spectrometer signal is labile and this noise is attributed to instrumentation artifacts. Mass spectrometer data for CO_2 and CO were taken in both the probe chamber and main chamber simultaneously and found to approximately match. However, the instrumentation artifacts

were different between the two mass spectrometers. The oscillations in the CO mass spectrometer trace are thought to be the oscillations seen by the CO oxidation mechanism proposed by Ertl et al¹. This oscillation is thought to involve surface atom reorganization.

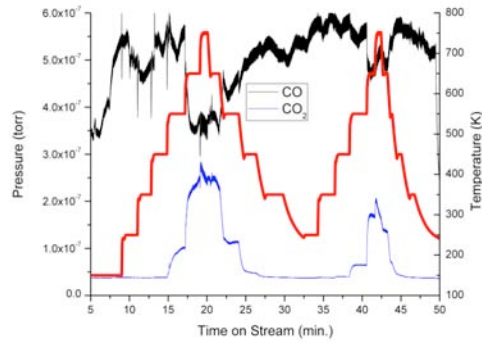


Figure 3: Calibrated Main Chamber Mass Spectrometer trace of a CO oxidation on Pt(111) using the annular reactor. Note: the red line is the temperature profile of the experiment.

Furthermore the raw data presented in Figure 3 was analyzed using the Arrhenius method and found to approximately match (within 20%) the literature values for CO₂ production on Pt in a well-studied high pressure surface science reactor system². The mechanism found by Goodman et al. for the production rate of CO₂ on Pt(111) is provided in Equation 1.

$$\frac{dC_{CO_2}}{dt} = ke \frac{-E_{des,CO}}{RT} \left(\frac{P_{O_2}}{P_{CO}} \right) \quad (1)$$

In Equation 1: C_{CO_2} is the concentration of CO₂, k is the rate constant, E_{des} is the desorption activation energy of CO desorption, R is the gas constant, T the reaction temperature, P_{O_2} the partial pressure of oxygen, and P_{CO} the partial pressure of carbon monoxide. Figure 4 gives an Arrhenius plot for CO oxidation performed on Pt(111) in the invacuo reactor system reported here. The data in Figure 4 shows two kinetic regimes. This is attributed by Goodman et al. to the desorption energy of CO on Pt. As the system reaction temperature reaches the desorption temperature of CO the activation energy for desorption decreases.

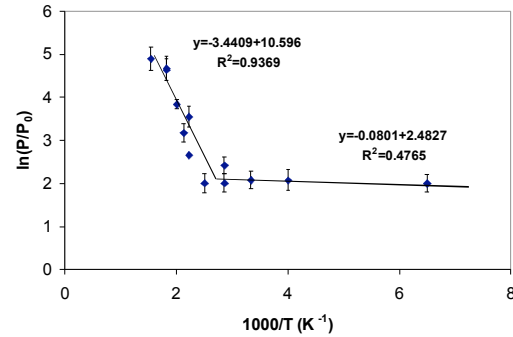


Figure 4: Arrhenius Plot of CO oxidation data, where P is the partial pressure of CO₂ produced at a given temperature and P_0 is the background pressure of CO₂ in the vacuum chamber.

Equation 1 was used in the two dimensional COMSOL model as the chemical reaction rate on the Pt(111) surface with a literature activation energy of 33 kcal/mol and a system temperature of 500K. Figure 5 gives the COMSOL output of the partial pressure of CO₂ in torr as a function of x and y position along the doser axis. Within an order of magnitude, which is often the error attributed to the measurement of vacuum pressure with an ion gauge, the COMSOL model matches the experimental data presented here. However, the model provides a visual representation of the physics going on in the surface science reaction system. Figure 5 shows that there are “hot spots”, shown in red where increased rates of CO₂ production are seen. It is desirable to eliminate these “hot spots” in future designs; an increased uniform reaction rate across the crystal surface is preferred.

These reaction rate “hot spots” are artifacts of the doser design; the system total pressure has hot spots at the same location. Instead of a pressure of 1 torr across the maximum area of crystal surface which was the desired design consequence of this reactor system the total pressure was modeled as being 1 torr only at the exit of the doser to the probe chamber. This indicates that the current reactor design does not use the entire reactive surface and is therefore not optimized for use in low probability catalytic reactions.

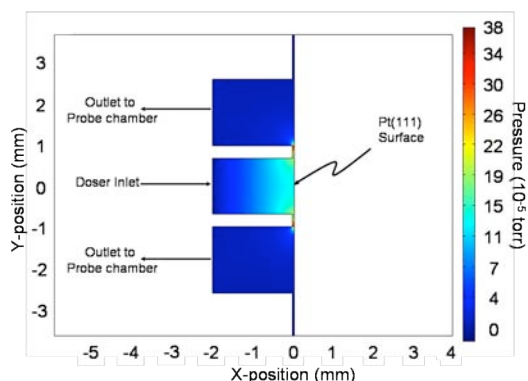


Figure 5: CO₂ production results of the 2-D COMSOL reactor model.

4. Conclusions

It has been shown here that the current high local pressure surface science reactor design is functional and can mimic more complex systems found in the literature. Furthermore the system can be modeled using COMSOL Multiphysics software. This model is found to approximately match the experimental data presented here, but allows a better understanding of the underlying flowing system. The conclusion of the model is that the current reactor system is not optimized for study of low probability catalytic surface reactions.

5. References

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9. Acknowledgements

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10. Appendix

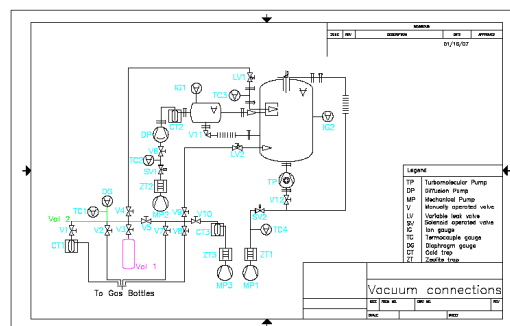


Figure 6: Detailed vacuum diagram of UHV apparatus.