

Active Site Titration for CO Oxidation Catalyzed by Pt/SiO₂ using Pulse–Probe Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

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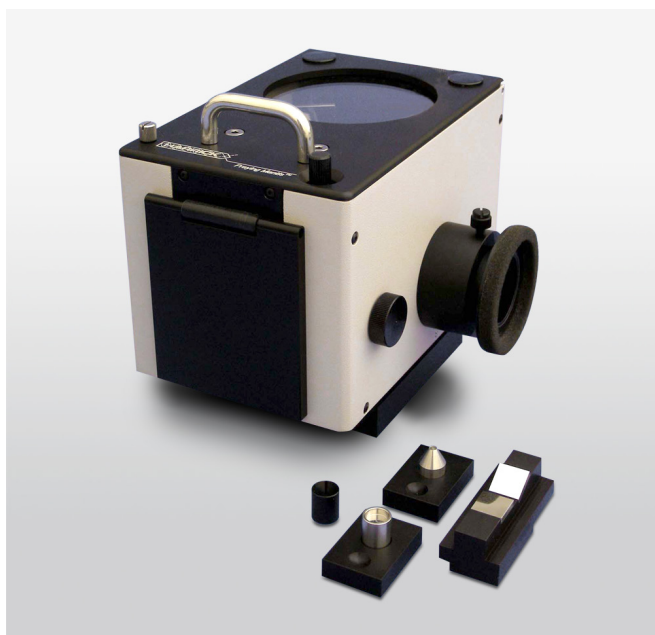


Figure 1. [The Harrick Praying Mantis™ Diffuse Reflectance Accessory.](#)

Figure 2. [The Praying Mantis™ Low Temperature Chamber.](#)

INTRODUCTION

A detailed understanding of the reaction kinetics for solid-gas heterogeneous catalysis can contribute to the design of novel catalyst materials for efficient chemical production processes. Model systems investigated using surface science tools can provide unprecedented insight into molecular-scale elementary steps for complex reactions. However, translating from ultra-high vacuum to ambient pressures ($\sim 10^{-10}$ to 760 Torr), cryogenic to reaction temperatures (often hundreds of degrees Celsius), and from planar single-crystals to complex supported catalysts can be challenging. Well controlled gas pulsing experiments at reaction temperatures under intermediate pressures on supported catalysts can provide an avenue for bridging the detailed understanding from surface science model systems to the design of real-world catalyst systems¹.



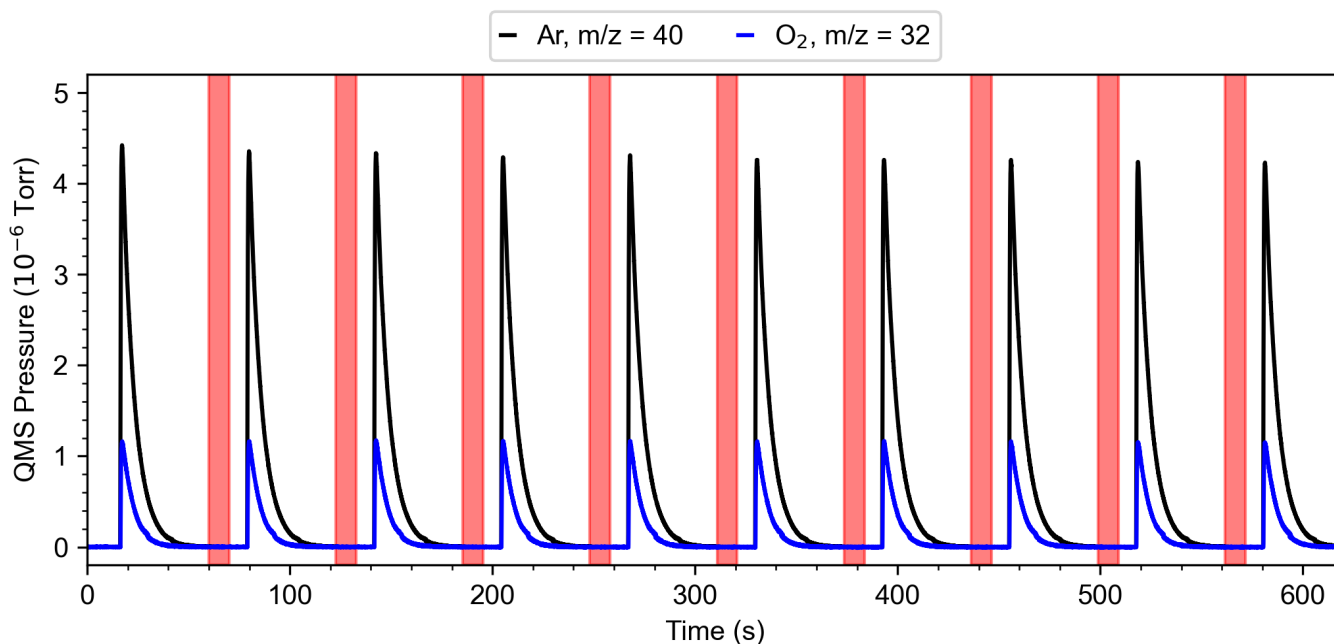


Figure 3. Transient response of (black) Ar and (blue) O₂ from a pulse probe experiment consisting of multiple gas pulses (20 % O₂ balanced in Ar, 170 μ s) over a surface site saturated Pt/SiO₂ at 25 °C. The red highlighted regions denote FTIR probe measurements.

Here we employ pulse-probe Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) on a supported catalyst to investigate the evolution of surface-bound intermediates using CO oxidation as a probe reaction. We demonstrate that it is possible to rapidly introduce gas phase species to an evacuated Harrick Praying Mantis™ Low Temperature Reaction Chamber and perform pulse-probe DRIFTS measurements by placing it between a pulsing valve and an ultra-high vacuum (UHV) chamber.

EXPERIMENTAL

The experiments were performed using a Harrick Praying Mantis™ Low Temperature Reaction Chamber (CHC-CHA-4) with a pulse valve (Parker Miniature High Speed High Vacuum Dispense Valve) attached to one of the 1/4" VCO inlet ports on the side of the chamber and a UHV chamber attached to the 1/4" VCO port leading from directly from below

the sample cup. A typical base pressure for the vacuum chamber was $< 2 \times 10^{-8}$ Torr and the pressure at the pulse valve was measured to be $< 1 \times 10^{-5}$ Torr. The vacuum chamber was equipped with a quadrupole mass spectrometer (SRS RGA 200) for detection of gas phase species. The reaction chamber was installed in a Praying Mantis™ diffuse reflectance accessory (DRP-BR4) mounted in the sample compartment of a Bruker Invenio Fourier-Transform Infrared Spectrometer (FTIR) for detection of catalyst surface-bound species. We found that the pulses were highly reproducible with little pulse-to-pulse deviation (**Figure 3**).

The sample was prepared in the sample cup by 1) inserting a 250-mesh stainless steel disc, 2) filling and packing 120-grit SiC up to 1 mm from the top of the sample cup, 3) inserting a 250-mesh stainless steel disc with a catalyst pressed onto it composed of 2 nm Pt nanoparticles supported on SiO₂ (Pt/SiO₂).

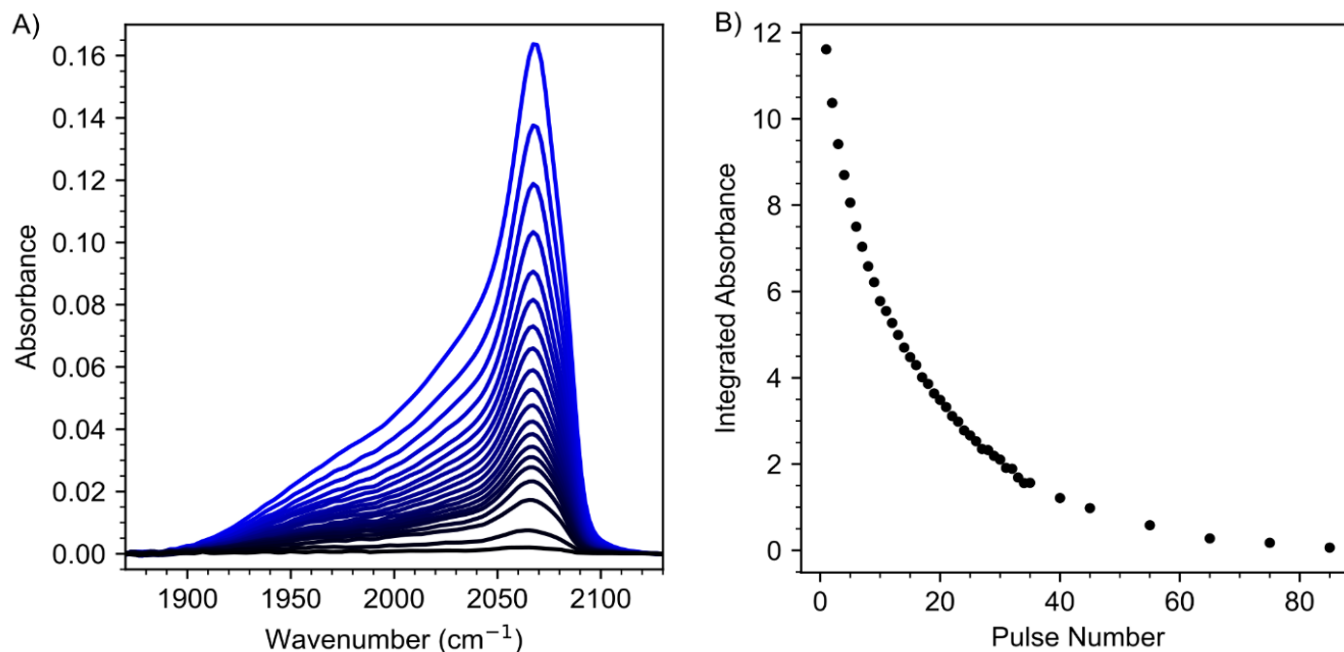


Figure 4. (A) FTIR spectra of CO adsorption on Pt/SiO₂ acquired in between consecutive O₂ gas pulses at 150 °C. (B) Change in the integrated absorbance of the CO band (1870 – 2130 cm⁻¹) in A) with O₂ pulsing. All oxygen pulses used a 20 % O₂ balanced in Ar mixture with a pulse length of 170 μs.

The 5 weight %, Pt/SiO₂ catalyst was synthesized using a previously reported method². The sample temperature was measured by a K-type thermocouple inserted into the SiC zone and the sample temperature was maintained at 150 °C using a Harrick ATK Temperature Controller (ATK-024-3). The catalyst was cleaned by an *in situ* O₂ pulsing followed by H₂ pulsing at 350 °C. The gas mixtures used were 20% O₂ balanced in Ar for O₂ pulsing, 10% H₂ balanced in Ar for H₂ pulsing and 20% CO balanced in Ar for CO pulsing.

RESULTS AND DISCUSSION

The Pt/SiO₂ catalyst was activated with an oxidation treatment by pulsing O₂ at 350 °C for 1 hour followed by a reduction treatment by pulsing H₂ at 350 °C for 30 minutes. The catalyst was determined to be clean once no CO₂ production was detected during the O₂ pulsing. The catalyst was then cooled to 150 °C and CO was pulsed until the saturation of active

sites as determined by DRIFT spectra. The adsorption of CO was associated with the appearance of a vibrational stretch between 2060–2075 cm⁻¹ (**Figure 4A**, highest absorbance blue trace). The vibrational stretch (2060–2075 cm⁻¹) was assigned to the collective oscillation of linearly adsorbed CO molecules on undercoordinated Pt sites in agreement with previous work on 1.4 nm Pt supported on Al₂O₃³.

Pulse-probe DRIFTS measurements were performed to provide spectroscopic “snapshots” during an experiment where the CO adsorbed at active sites was titrated by reaction with O₂ pulses (similar experimental sequence as **Figure 3**). The FTIR spectra demonstrates the titration of adsorbed CO by the decrease in absorbance of the CO band observed during the O₂ pulsing (**Figure 4A**, blue to black trace). The O₂ pulsing was performed until there was no evidence of adsorbed CO in the FTIR spectra. The integrated absorbance of the CO band shows an exponential decay in absorbance with O₂

pulse number, which is associated with first-order reaction kinetics (**Figure 4B**). This result suggests that a detailed investigation to quantify the initial concentration of adsorbed CO and modelling of the gas pulses may enable an accurate measurement of reaction kinetic parameters, similar to mass spectrometry methods that are currently utilized¹.

CONCLUSIONS

The Harrick Praying Mantis™ Low Temperature Reaction Chamber enables characterization of catalytic materials under reaction temperature using pulse-probe DRIFTS. The reaction chamber can be evacuated by connection to a vacuum chamber and rapid introduction of gas phase species to the catalyst surface can be performed using a pulse valve. When combined, this allows for the controlled titration of reactive intermediates by sequential pulsing. The Harrick accessory provides a new platform for determining reaction kinetics promoted by catalyst materials for solid-gas heterogeneous catalysis.

ACKNOWLEDGEMENTS

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