

# Resolving Transient Responses of Catalyst Systems to Reactant Stream Modulation Using Low Volume HVC DRIFTS Reactor

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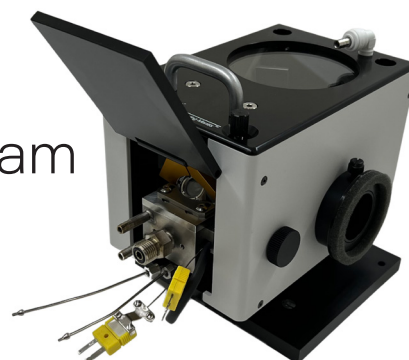


Figure 1. Praying Mantis™ with its [Low Volume High Temperature Reaction Chamber](#) installed.

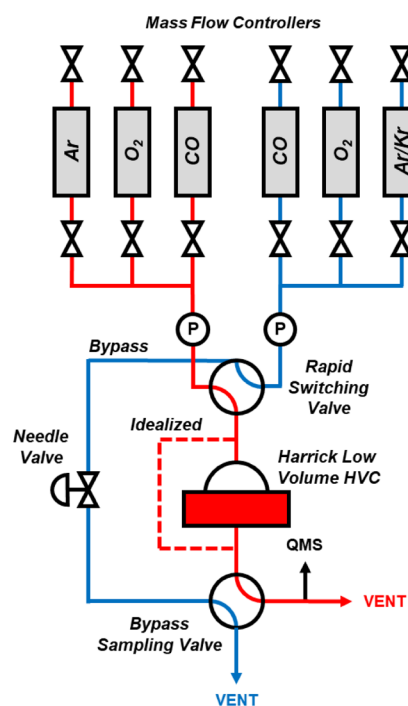


Figure 2. Schematic of idealized gas flow configuration and Low Volume HVC gas flow configuration.

## 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. There is a rapidly growing application of modulation excitation spectroscopy (MES), such as Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), to provide unprecedented insight into the mechanism and kinetics of heterogeneous catalyst systems (1). However, the application of MES DRIFTS is limited due to instrument design challenges, including the rapid switching of the reactor gas environment. Here, we investigate the feasibility of rapid reactor gas switching in the Harrick Low volume High Temperature Reaction Chamber for DRIFTS measurements. We demonstrate that it is possible to rapidly exchange gas phase species to a Harrick Low Volume Reaction Chamber and utilize DRIFTS measurements to observe the time evolution of reactant, surface-bound intermediates and products to provide mechanistic insight to a catalyst reaction system.

## EXPERIMENTAL

The experiments were performed using a Harrick Praying Mantis™ Low Volume High Temperature Reaction Chamber (**Figure 1**) with a rapid switching gas handling and quadrupole mass spectrometer (QMS) system attached to gas inlet and outlet. The rapid switching gas handling and QMS system has previously been described in detail (2). The reaction chamber was installed in a Praying Mantis™ diffuse reflectance accessory mounted in the sample compartment of a Bruker Invenio Fourier-Transform Infrared Spectrometer (FTIR) for detection of gas phase and catalyst surface-bound species. The idealized switching

gas environment tracers were performed with rapid switching gas handling directly bypassing the reaction chamber and connecting to the quadruple mass spectrometer characterization system. A schematic of the two experimental configurations is provided in **Figure 2**. A total flow rate of  $25 \text{ mL min}^{-1}$  was used unless otherwise stated.

The gas environment response sample was prepared in the sample cup by 1) inserting a 250-mesh stainless steel disc and 2) filling and packing 120-grit SiC to the top of the sample cup. The catalytic reaction testing 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) filling and packing a 50-70 mesh sieved Pt/SiO<sub>2</sub> catalyst up to the top of the sample cup. The Pt/SiO<sub>2</sub> catalyst was synthesized using a previously reported

method (3). The sample temperature was measured by a K-type thermocouple in the sample cup and the sample surface temperature was calibrated by an optical pyrometer due to a thermal gradient between the thermocouple contact and the exposed catalyst temperature (4). The sample temperature was maintained using a Harrick Temperature Controller (P/N: ATK-024-3). The catalyst was cleaned by an *in situ* O<sub>2</sub> treatment (5 % O<sub>2</sub> balanced in Ar) followed by H<sub>2</sub> treatment (5 % H<sub>2</sub> balanced in Ar) at 350 °C.

## RESULTS AND DISCUSSION

The gas switching response as a function of total gas flow rate was determined by switching the gas environment from pure Ar to 1 % Kr balanced in Ar (Kr/Ar) and using a QMS to track the time evolution of Kr ( $m/z = 84$ ) in the exit gas stream (**Figure 3**). The

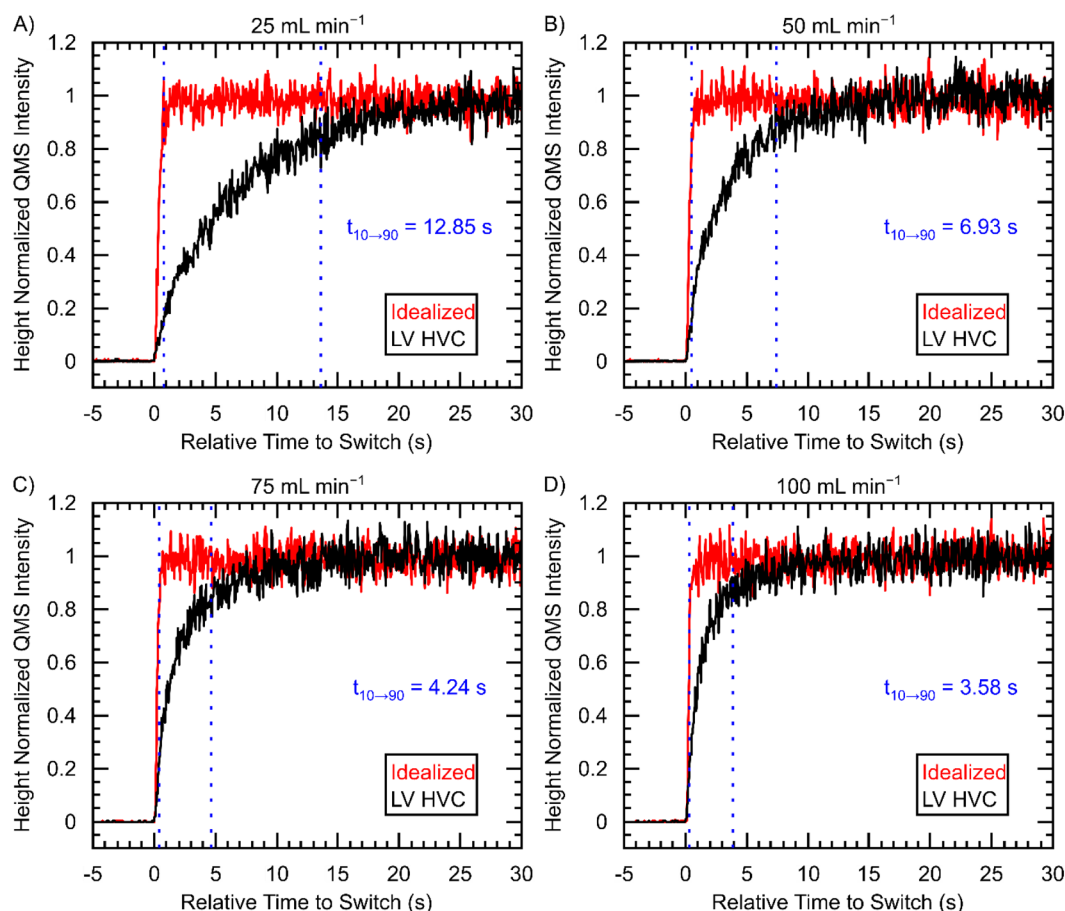


Figure 3. Gas environment exchange response of (black) Harrick Low Volume HVC cell and (red) idealized gas handling system response when switching from pure Ar to 1% Kr balanced in Ar with a flow rate of (A) 25, (B) 50, (C) 75 and (D) 100 mL min<sup>-1</sup>. Blue dashed lines denote the 10 % and 90 % signal rise times.

QMS Kr signal was normalized by dividing by the Kr signal intensity after equilibration in the Kr/Ar gas stream for 30 mins. The relative time to switch was determined by setting  $t = 0$  for the last data point with no Kr detection. The gas switching response for the idealized configuration of the gas handling and QMS system was rapid with complete gas environment exchanged in less than 1 s for total gas flow rates from 25 to 100 mL min<sup>-1</sup> (Figure 3, red traces). The gas switching response for the Low Volume HVC configuration of the gas handling and QMS system showed an initial rapid gas environment exchange that has a slower extended tail for total gas flow rates from 25 to 100 mL min<sup>-1</sup> (Figure 3, black traces). The rise time of the Kr signal from 10 % to 90 % of the equilibrated Kr signal ( $t_{10 \rightarrow 90}$ ) was measured to evaluate the relative rate of gas environment exchange as a function of total gas flow rate (Figure 3, vertical blue dashed lines). The gas environment exchange time ( $t_{10 \rightarrow 90}$ ) is strongly dependent on the total gas flow rate up to 50 mL min<sup>-1</sup>, after which increasing the total gas flow rate only slightly decreases the gas environment exchange time (Figure 4). The Low Volume HVC reactor cell facilitates rapid exchange of the reactor gas environment on the time scale of seconds which enables probing the transient response of gas phase and surface species interacting with catalyst surface to modulation of the reactant stream using DRIFTS.

The capability of the Low Volume HVC cell for using DRIFTS to observe the transient response of a catalytic system is demonstrated by modulation from a pure O<sub>2</sub> gas stream to a CO-rich reactant mixture for CO oxidation over Pt/SiO<sub>2</sub>. The Pt/SiO<sub>2</sub> catalyst was activated with an oxidation treatment by an O<sub>2</sub> treatment (5 % O<sub>2</sub>, 95 % Ar) for 30 mins followed by a reduction treatment using H<sub>2</sub> (5 % H<sub>2</sub>, 95 % Ar) at 350 °C for 30 minutes. The catalyst was then cooled to 160 °C in a pure Ar environment. The catalyst state was equilibrated in an O<sub>2</sub> environment (0.5 % O<sub>2</sub>, 99.5 % Ar) for 30 mins after which a background DRIFTS spectra was acquired. The O<sub>2</sub> stream was switched to a CO-rich reactant mixture for CO

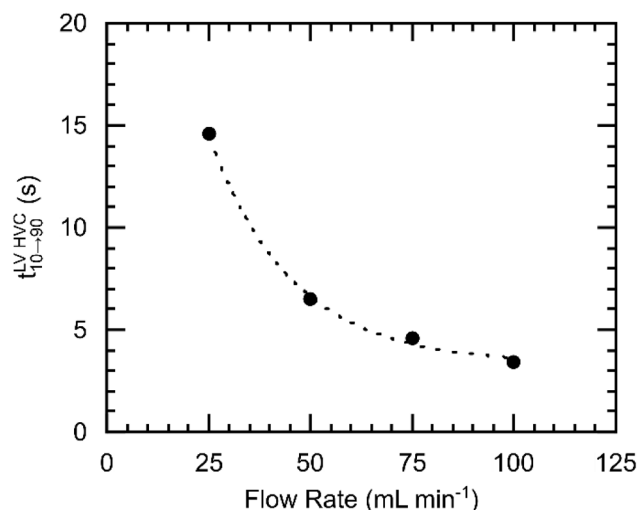


Figure 4. Comparison of 10 % to 90 % signal rise times ( $t_{10 \rightarrow 90}$ ) of the Harrick Low Volume HVC cell when switching from pure Ar to 1% Kr balanced in Ar with a total gas flow rate of (A) 25, (B) 50, (C) 75 and (D) 100 mL min<sup>-1</sup>. An exponential decay function is fit to illustrate the trend in the gas environment exchange response as a function of total gas flow rate.

oxidation (0.5 % O<sub>2</sub>, 1.5 % CO, 98 % Ar) and the time evolution of surface and gas phase species was monitored by acquiring rapid scan DRIFT spectra (Figure 5). The DRIFT spectra were characterized by 3 majority species: gas phase CO<sub>2</sub> (CO<sub>2</sub>(g), doublet maxima at 2362 cm<sup>-1</sup>), gas phase CO (CO(g), doublet maxima at 2176 cm<sup>-1</sup>) and linearly adsorbed CO on Pt (Pt-CO, maxima at 2070 cm<sup>-1</sup>) (3). The time evolution of the reactant CO(g), the surface-bound intermediate Pt-CO and the product CO<sub>2</sub>(g) was determined by the height normalized absorbance of the peak maxima denoted above. The rapid population of Pt-CO and production of CO<sub>2</sub>(g) is consistent with a high probability of CO adsorption and fast kinetics for CO oxidation for reaction of a CO-rich reaction mixture with an oxygen covered Pt-group surface (5). Similarly, the slow increase in CO(g) indicates the rapid uptake of CO by the Pt surface and consumption for CO<sub>2</sub>(g) production. The maximum CO<sub>2</sub>(g) production occurs as the Pt-CO population approaches saturation after which CO<sub>2</sub>(g) production decreases to a lower

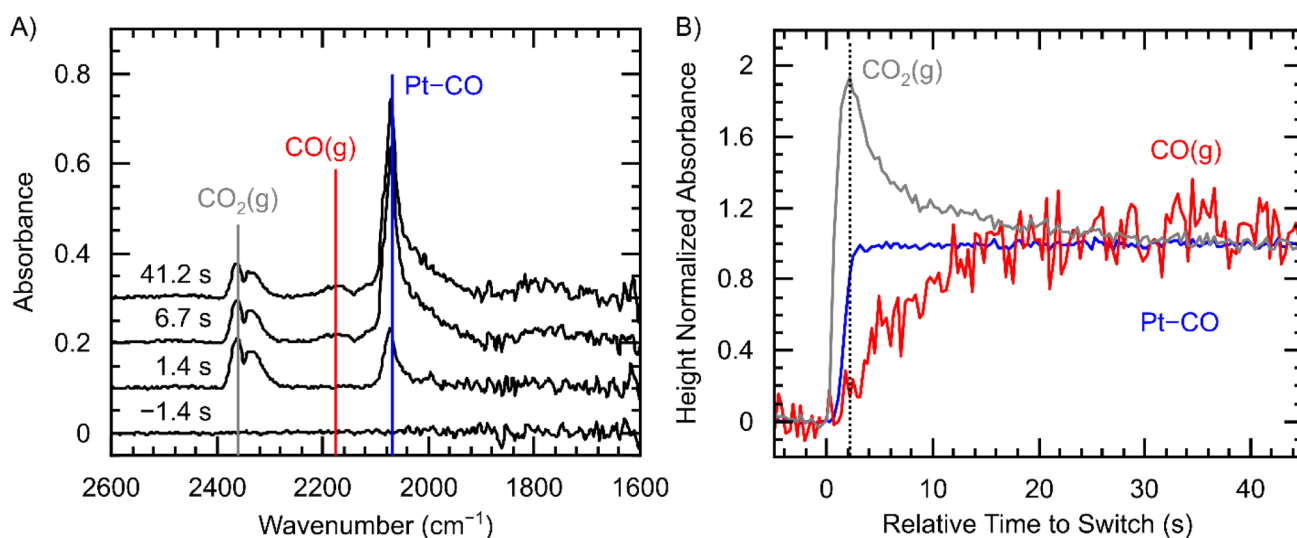


Figure 5. (A) DRIFTS spectra of 2 nm Pt/SiO<sub>2</sub> catalyst at 160 °C for gas environment switching from an O<sub>2</sub> environment (0.5 % O<sub>2</sub>, 99.5 % Ar) to an O<sub>2</sub>/CO mixture (0.5 % O<sub>2</sub>, 1.5 % CO, 98 % Ar) using a total flow rate of 25 mL min<sup>-1</sup>. (B) Time evolution of the height normalized absorbance of observed species relative to the gas environment switch. The absorbance is normalized with respect to the height under steady-state conditions in the O<sub>2</sub>/CO mixture. DRIFTS species assignments: CO<sub>2</sub>(g): 2362 cm<sup>-1</sup>; CO(g): 2176 cm<sup>-1</sup>; Pt-CO: 2070 cm<sup>-1</sup>.

steady-state activity. This is consistent a transition in activity as a CO-poisoned surface is formed where the slowing of CO<sub>2</sub>(g) production can be attributed to the high CO population blocking sites for O<sub>2</sub> adsorption and subsequent reaction. This results clearly demonstrates that the rapid exchange of the gas environment in the Low Volume HVC cell enables the observation of transient responses of catalytic systems to the modulation of the gas environment.

## CONCLUSIONS

The Harrick Praying Mantis™ Low Volume HVC Reaction Chamber enables probing the transient responses from the modulation of the gas environment in the reactants, surface-species and products using DRIFTS. The Harrick accessory provides a new platform for examining transient responses of catalytic activity promoted by catalyst materials for solid-gas heterogeneous catalysis.

## ACKNOWLEDGEMENTS

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## REFERENCES

1. P. Müller, I. Hermans, Applications of Modulation Excitation Spectroscopy in Heterogeneous Catalysis. *Ind. Eng. Chem. Res.* **56**, 1123–1136 (2017).
2. E. A. High, E. Lee, C. Reece, A transient flow reactor for rapid gas switching at atmospheric pressure. *Review of Scientific Instruments* **94**, 054101 (2023).
3. T.-S. Kim, C. O'Connor, C. Reece, Interrogating site dependent kinetics over SiO<sub>2</sub>-supported Pt nanoparticles (2023) <https://doi.org/10.21203/rs.3.rs-3235489/v1>.
4. H. Li, M. Rivallan, F. Thibault-Starzyk, A. Travert, F. C. Meunier, Effective bulk and surface temperatures of the catalyst bed of FT-IR cells used for in situ and operando studies. *Phys. Chem. Chem. Phys.* **15**, 7321 (2013).
5. J. Libuda, *et al.*, The CO oxidation kinetics on supported Pd model catalysts: A molecular beam/in situ time-resolved infrared reflection absorption spectroscopy study. *The Journal of Chemical Physics* **114**, 4669 (2001).