

Pulse Chemisorption in a Low Volume HVC DRIFTS Reactor

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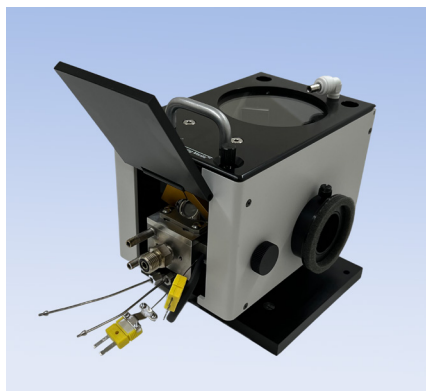


Figure 1. [Praying Mantis™](#) with its [Low Volume High Temperature Reaction Chamber](#) installed.

The ability to rapidly alter the environment inside of spectroscopic cells is of vital importance for the growing application of transient experiments (e.g., modulation excitation spectroscopy, chemical transient kinetics) to characterize catalytic materials and determine the kinetics and mechanisms for heterogeneous catalytic processes. Key to this is the need for cells that have a low dead-volume to allow for the efficient introduction and removal of gases. It has been demonstrated that for step transient experiments it is possible to exchange the gas environment in a reaction chamber in < 4 s at high flow rates (1), but its applicability to more complex experiments have not yet been tested. Herein, we demonstrate that the Harrick Low Volume HVC reactor chamber can be utilized for pulse chemisorption experiments. Using the test case of CO pulsed chemisorption over a Pt/SiO₂ catalyst we demonstrate that the reactor cell allows precisely controlled pulses of CO to be introduced sequentially over the catalyst surface, affording calculation of the surface site density and to visualize the saturation of different sites.

The Harrick Low Volume HVC 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) that was purged with dry N₂, with the inlet and outlet of the reaction chamber attached to a rapid switching gas handling system (2). The Pt/SiO₂ catalyst was synthesized and packed into the reactor using the previously reported method (3). The sample temperature was measured by a K-type thermocouple in the sample cup and was maintained using a Harrick ATK Temperature Controller. 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 catalyst was cleaned by an in situ O₂ treatment (5 % O₂ balanced in Ar) followed by H₂ treatment (5 % H₂ balanced in Ar) at 350 °C. The FTIR spectra were acquired with

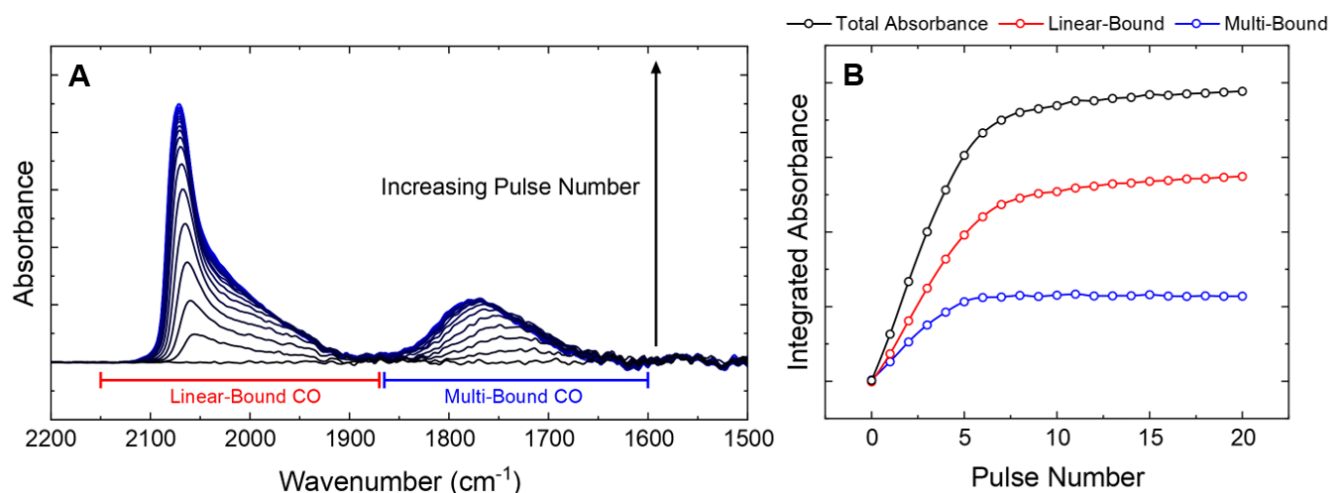


Figure 1. A) DRIFT spectra of a Pt/SiO₂ catalyst at 15°C during 20 sequential pulses of a 0.2% CO 1% Kr stream balanced in Ar. B) Integrated absorbance of the multi-bound CO region, linear-bound CO region, and the total spectra. The number of multi-bound CO sites saturates rapidly within 5 pulses, whereas the number of linear bound CO molecules is still slowly increasing after 20 pulses.

200 scans with a resolution of 4 cm⁻¹ using a liquid-nitrogen-cooled MCT detector. The background measurement was acquired in Ar at 15°C following the H₂ treatment. Using the rapid gas switching system a series of 20 pulses were generated by rapidly switching between a stream of Ar and a stream of 0.2% CO and 1% Kr balanced in Ar for 500 ms with a 60 s pulse spacing at a total flow rate of 25 SCCM (Figure 1). Using this method, sub-monolayer amounts of CO could be adsorbed onto the surface of the catalyst per pulse, allowing efficient titration of empty sites on the catalyst. We find that during saturation, the multi-bound CO sites saturate within 5 pulses, but the linear-bound CO had still not saturated after 20 pulses of CO. This work demonstrates that precisely controlled pulse experiments are possible in a Harrick Low Volume HVC Reaction chamber.

REFERENCES

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