

CO Adsorption and Desorption in a Sample Cup Liner for Harrick HVC Reactors

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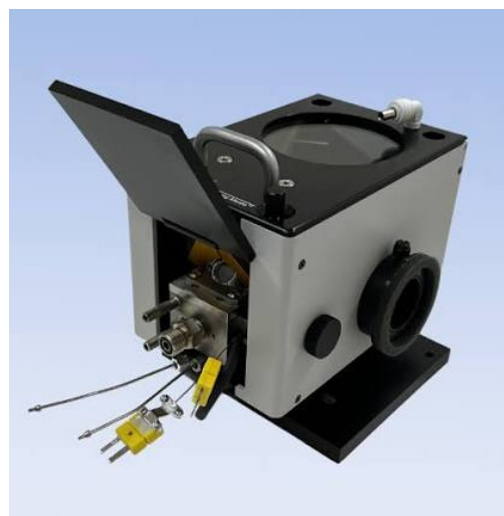
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Introduction

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is widely used to characterize heterogeneous catalysts under reaction conditions. In many catalytic studies, catalysts containing species known for contamination (e.g., Ni) may leave residual material in the sample cup, increasing the risk of cross-contamination between experiments.¹

A sample cup liner could address these practical challenges providing a barrier between the sample and permanent reactor hardware. Before adopting a liner for spectroscopic measurements, however, it is important to verify that the modified sample geometry does not alter catalyst heating or the resulting DRIFT spectra. Here, CO adsorption and desorption over a commercial Pd/Al₂O₃ catalyst are compared using the standard Harrick HVC cell with and without a sample cup liner installed. These measurements demonstrate that the sample cup liner produces equivalent CO-DRIFT spectra to those obtained using the permanent cup without measurably affecting catalyst heating.



Picture 1: Harrick Praying Mantis™ with its Low Volume High Temperature Reaction Chamber installed.

Methods

DRIFTS experiments were carried out in a Harrick Low Volume HVC reactor chamber equipped with ZnSe windows, which was installed in a Praying Mantis™ diffuse reflectance accessory mounted in the sample compartment of a Vertex 70 Fourier-Transform Infrared Spectrometer (FTIR) purged with dry N₂. The catalyst beds were prepared by first placing a 304 stainless steel disc (150 × 150 mesh) into the sample cup and then filling the sample cup to approximately 1mm from the rim with 46 grit SiC followed by a commercial 0.5 wt% Pd/Al₂O₃ catalyst (Sigma Aldrich, ESCAT 226) sieved to 212–300 µm particle size. Experiments in the standard Harrick HVC sample cup used 120 mg of SiC and 11.9 mg of Pd/Al₂O₃ catalyst, and the sample cup liner used 78.9 mg of SiC and 6.5 mg of Pd/Al₂O₃ ESCAT catalyst. The catalyst temperature was monitored using a thermocouple positioned external to the catalyst bed, and the thermal gradient between the thermocouple and the catalyst bed was calibrated with an optical pyrometer (emissivity = 0.95).

Reactant gases were supplied using a custom gas mixing system at a flow rate of 25 mL/min. Gas entered the reactor through the inlet located in the reactor dome and exited through the outlet at the bottom of the sample cup. The catalyst was first heated to 250 °C in 20% O₂/Ar at 30 °C/min, then held for 30 minutes, followed by a 1.2% H₂/Ar treatment

at 250 °C for 30 minutes, then the catalyst was cooled to 30 °C under flowing Ar. Background spectra were collected in Ar at 30 °C before introducing 0.4% CO/Ar, followed by a purge in Ar. DRIFT spectra were acquired using a liquid nitrogen-cooled HgCdTe (MCT) detector approximately 20 seconds apart. All spectral acquisition parameters were identical for both sample cup configurations.

Results and Discussion

Before comparing the CO-DRIFT spectra, sample bed temperatures were measured using an optical pyrometer to verify that the sample cup liner did not affect catalyst heating. During the pretreatments, average catalyst temperatures of 255 ± 4 and 257 ± 4 °C were measured for the standard Harrick HVC sample cup and sample cup liner, respectively. During the CO-DRIFTS measurements, average catalyst temperatures of 31 ± 1 °C were measured for both experiments. These results indicate that the sample cup liner does not measurably alter catalyst heating under the conditions investigated.

Steady-state CO-DRIFT spectra collected using the standard sample cup and sample cup liner are compared in Figure 1. The CO-DRIFT spectra taken after saturation with 0.4% CO exhibit the expected features associated with CO bound to metallic Pd and Al₂O₃ (Figure 1). Features 1–3 are associated with CO bound to metallic Pd, specifically linearly bound to

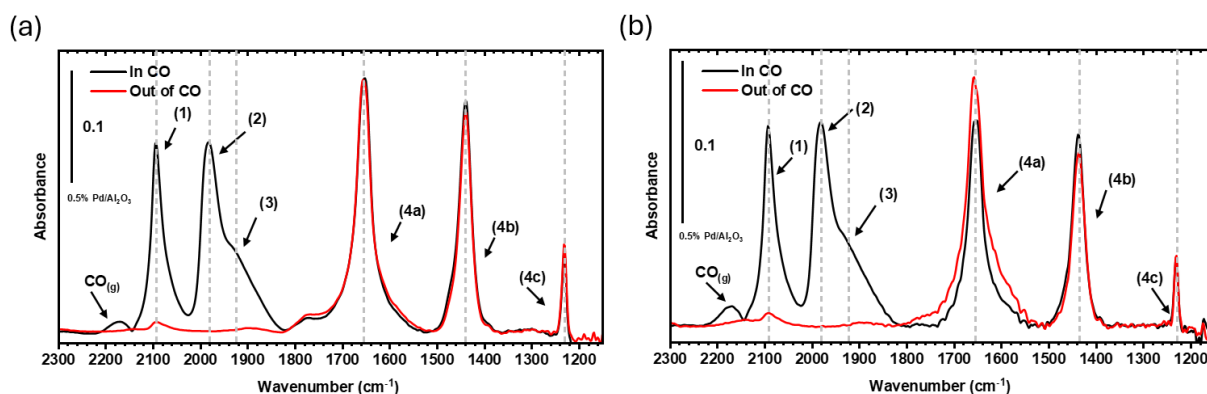


Figure 1. Baseline-corrected steady-state CO-DRIFT spectra of a 0.5% Pd/Al₂O₃ catalyst at 30°C under 0.4% CO/Ar (black) and 100% Ar (red) in (a) the permanent Harrick HVC reactor chamber cup and (b) the sample cup liner.

a single Pd atom (2092 cm⁻¹), bridge-bound to two Pd atoms (1980 cm⁻¹), and three-fold bound in a hollow site between three Pd atoms (1923 cm⁻¹).² Features 4a-c are associated with carbonate species on the alumina support.^{3,4} No additional absorption bands were observed when using the sample cup liner, and the positions of the observed Pd peaks agree within 1 cm⁻¹, which is below the spectral resolution of 4 cm⁻¹. Because the sample cup liner contains less total catalyst to maintain the same bed thickness, the overall absorbance intensity is reduced by a roughly proportional amount. Despite this, the spectral profile remains unchanged, indicating that the liner does not affect the interpretation of the CO adsorption spectra.

After CO saturation, the sample environment was switched to Ar and DRIFT spectra were collected every 20 seconds (Figure 2). During this time, some CO desorbed from Pd, which is observed in the decrease in intensity of features 1-3 over time in Ar. Importantly, the patterns of desorption remain

qualitatively similar from both the catalyst in the Harrick HVC sample cup and the catalyst in the sample cup liner. For both experiments, little change was observed in the carbonate peaks associated with the Al₂O₃ support, which indicates that these peaks are stable after being removed from the CO environment. Together, these spectra indicate that the sample cup liner does not measurably alter the observed CO adsorption or desorption behavior or affect qualitative interpretation of the spectra.

Overall, the results demonstrate that the Harrick sample cup liner does not measurably alter catalyst heating or CO adsorption and desorption behavior. It provides equivalent CO-DRIFT spectra and structural information while protecting the permanent sample cup from contamination, with the added benefit of reducing sample consumption.

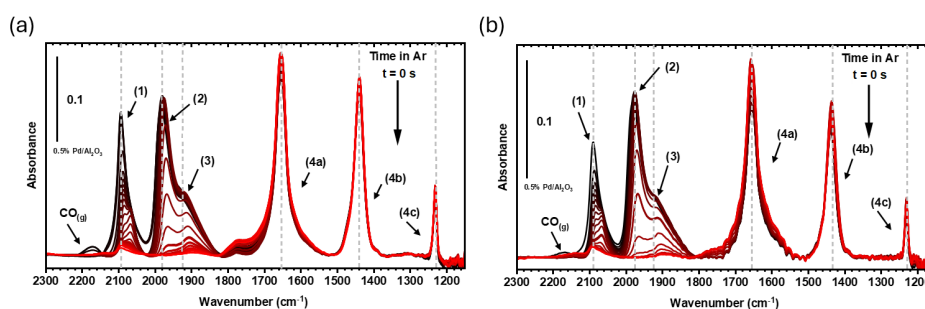


Figure 2. Time-resolved baseline-corrected DRIFT spectra of a 0.5 wt% Pd/Al₂O₃ catalyst at 30 °C under flowing Ar taken after saturation in 0.4% CO/Ar in (a) the permanent Harrick HVC reactor chamber cup and (b) the sample cup liner.

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