HARRICK

Application Note

HIGH TEMPERATURE TRANSMISSION CELL

NO. 21179

Characterization of Surface Hydroxyls on Metal-Oxide Catalysts Using High Temperature Transmission FTIR Coupled with Thermogravimetric Analysis

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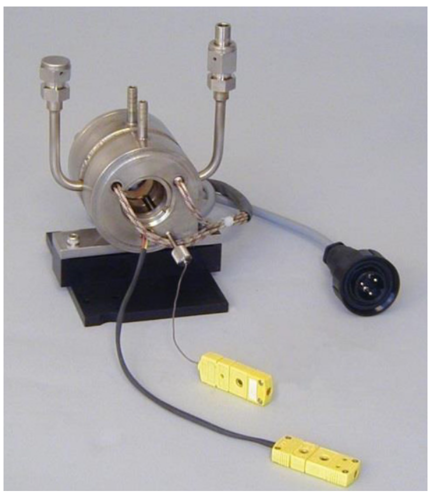

Figure 1. High Temperature Transmisson Cell.

INTRODUCTION

Transmission FTIR is commonly used to determine and quantify functional groups on solid samples, particularly metal oxide and oxide supported heterogeneous catalysts. The diverse surface features on an individual catalyst material give rise to multiple types of surface hydroxyls, which can vary in coordination environment, may or may not participate in hydrogen bonding, and may manifest as both acidic and basic hydroxyls simultaneously present on the same surface. Direct quantification of surface hydroxyl density can therefore be challenging. This application note shows how the Harrick High Temperature Transmission Cell (HTC) can be coupled with thermogravimetric analysis (TGA) to quantify hydroxyl groups on metal-oxide surfaces.

RESULTS AND DISCUSSION

Infrared spectra were collected on a Bruker Invenio-R FTIR spectrometer equipped with the Harrick High Temperature Transmission

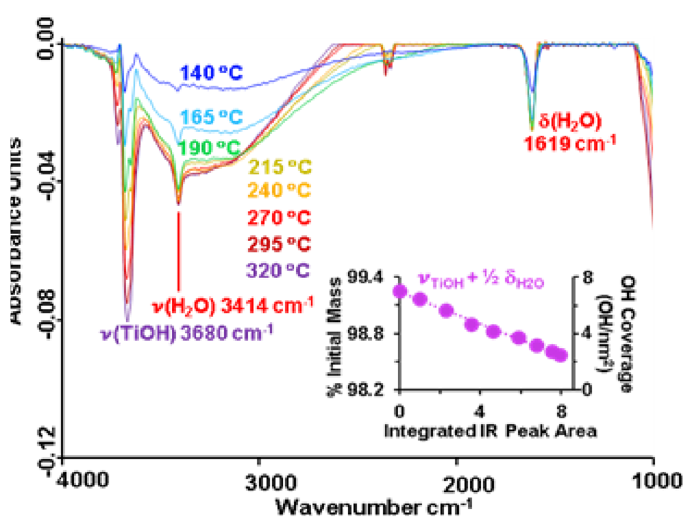

Figure 2. (A) Representative FTIR spectra collected during catalyst heating; the catalyst temperature was maintained at each temperature for 10 minutes prior to collecting each spectrum. Spectra were referenced to a pellet background collected at 120 °C under argon, so negative peaks show losses of surface species. Inset: Calibration curve correlating the FTIR and TGA data. The isolated OH stretching (ν_{OH} 3680 cm^{-1}) and molecularly adsorbed water bending (δ_{HOH} 1700 – 1550 cm^{-1}) regions were integrated and combined to generate the calibration plot.

Cell. Catalyst sample (17.4 mg) was pressed into a 13mm pellet with a hydraulic press and mounted in the High Temperature Transmission Cell. The sample pellet was heated to 120 °C, under Ar to remove physisorbed water. A pellet background was collected at 120 °C and spectra were recorded during stepwise heating to 320 °C, holding the temperature at each step for 10 minutes.[1, 2] These spectra are shown in Figure 2. TGA mass loss measurements were collected on a Discovery TGA 550—Water™ analyzer following the same protocol as the FTIR experiments.

The spectra in Figure 2 were referenced to a sample background collected at 120 °C, so peaks with negative absorbance values correspond to the loss of surface vibrations. Three primary regions of change are apparent: (1) narrow ν_{OH} band centered near 3680 cm^{-1} attributable to the loss of isolated surface hydroxyls; (2) a wide band spanning 3600-2500 cm^{-1} attributable to the loss of surface hydroxyls participating in hydrogen bonding; and (3) a narrow band at 1619 cm^{-1} is associated with the loss of the dHOH bending vibration of molecularly adsorbed water on the surface.3-6

Figure 2 inset shows the correlation the IR peak areas (isolated hydroxyl integrated area added to the molecularly adsorbed water integrated area) and TGA mass loss data collected using an identical heating protocol. This calibration allows us to determine the surface hydroxyl / water surface density at any time during subsequent experiments on the sample using only FTIR data.

CONCLUSION

When coupled with the right techniques, the Harrick High Temperature Transmission cell can be used to provide quantitative surface data. Coupling transmission FTIR with TGA provides a method of determining *in-situ* water and surface hydroxyl coverage within a 5% uncertainty at various temperatures and under a variety of gas atmospheres using only the FTIR data.

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