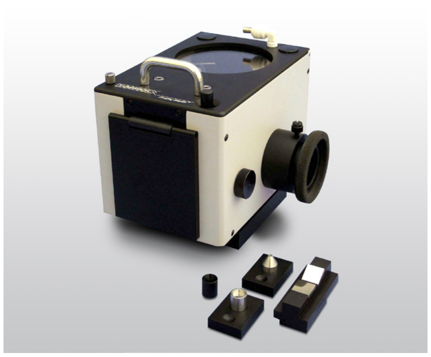

Figure 1. The Praying Mantis™ Diffuse Reflectance Accessory.

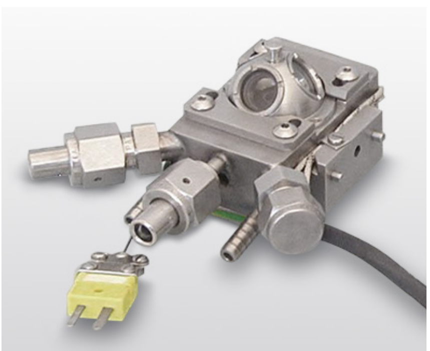

Figure 2. The Praying Mantis™ High Temperature Reaction Chamber.

Exploring the Ag-Pd Local Structure by DRIFTS

INTRODUCTION

Fourier Transform Infrared Spectroscopy is a very powerful technique used to analyze the chemical composition of a sample, specifically identifying organic, polymeric and the resulting spectrum provides information about the molecular vibrations and chemical functional groups present in the sample, allowing for the identification of the sample's chemical composition. In addition to that, Diffuse Reflection FTIR spectroscopy is also a very powerful tool for the surface characterization of nanoparticles to study the active sites and reaction mechanisms of various catalytic processes. Carbon monoxide chemisorption followed by Diffuse Reflection FTIR spectroscopy has been well-established and used to characterize supported or unsupported transition metals.[1] The adsorption of CO on the catalyst surface leads to characteristic infrared vibrations that can be collected by FTIR. This valuable information can be further used to study the local environment of the metal atoms.

Here, we present an example of the utilization of CO adsorption study by DRIFTS to gain insights into the local structure of Ag-Pd alloy nanoparticles (AgPd NPs) supported on CeO_2 nanofiber.

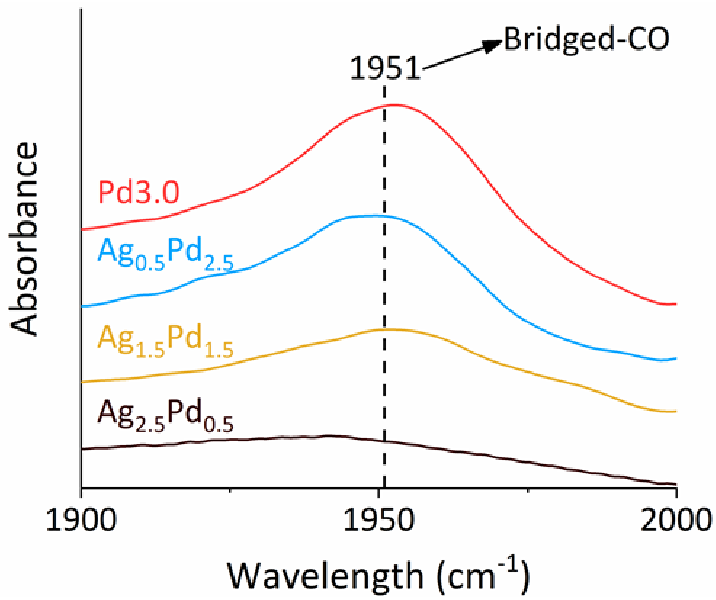

Figure 3. DRIFTS spectra of CO adsorption on Pd3.0 catalyst and AgPd alloy catalysts.

EXPERIMENTAL

A Nicolet iS50 spectrometer, fitted with a KBr beamsplitter, and a dedicated MCT detector (Thermo Fisher Scientific Inc., Madison, WI, USA) cooled by liquid nitrogen, was employed to conduct in-situ DRIFTS analysis. For each measurement, around 60 mg of catalyst was loaded into the High Temperature Reaction Chamber (HVC-DRM-5), and equipped with a Temperature Controller (ATK-024-04). Before the test, the sample was heated to 250 °C under He flow at 60 sccm to clean the surface and a chiller was used to circulate coolant through the reaction chamber. Then the temperature was reduced to 50 °C and the background was recorded. Finally, CO was induced to the reactor at 10 sccm. For each analysis, 64 scans were collected over the spectral range of 4000–800 cm^{-1} with a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

The FTIR spectra in Figure 1 displays a comparison of bridge-bonded CO (~1951 cm^{-1}) among Pd or Pd alloyed NPs surface. The peak intensity increases when the Ag/Pd ratio decreases, indicating inducing Ag atoms into Pd (forming AgPd alloy NPs) results in a decrease in Pd-Pd surface sites. The figure also highlights that in the case of $Ag_{2.5}Pd_{0.5}$, the contribution of bridging stretching vibration of CO on Pd significantly decreased (almost absent), which can be attributed to the presence of atomically dispersed Pd atoms and the decrease in Pd content. Thus, $Ag_{2.5}Pd_{0.5}$ NPs comprise fewer bridged Pd sites than $Pd_{3.0}$ NPs. It is also noteworthy that Pd clusters are present on the Ag-rich surface ($Ag_{1.5}Pd_{1.5}$ NPs).[2]

CONCLUSION

The DRIFTS technique provides an easy way to understand the local environment of nanomaterials and how the CO molecule can be used as a probe molecule. Overall, in-situ FTIR spectroscopy proves to be a valuable tool that enables researchers to deeply understand the surface interactions, such as solid-gas and solid-liquid interactions.

REFERENCES

1. Little, L. H. (1966). Infrared spectra of adsorbed species.

2. Jin, Y., Sarina, S., Liu, H., Martens, W., Waclawik, E. R., Peiris, E., ... & Zhu, H. Y. (2022). Aerobic oxidation of 5-hydroxymethyl-furfural to 2,5-Furandicarboxylic acid at 20 °C by optimizing adsorption on AgPd alloy nanoparticle catalysts. *ACS Catalysis*, **12**, 11226-11238.