Application Note

Materials Testing and Research

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# Measurement of Diffuse Reflection from Catalyst Powders

## Using the Praying Mantis accessory and Agilent Cary 5000 UV-Vis-NIR spectrophotometer


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## Introduction

Aluminum oxide ($Al_2O_3$), commonly known as alumina, is a widespread naturally occurring compound that has a broad range of industrial applications. Besides its use as a pigment or abrasive, alumina also plays a vital role as a catalyst support for desulfurization or hydrogenation reactions. In the latter case, the active phase on the catalyst often consists of nickel metal nanoparticles. The interactions initially established between nickel (II) salt and the alumina surface during the first steps of the $Ni/Al_2O_3$ catalyst preparation ultimately determine the active phase dispersion and the activity of the catalyst. It is thus of prime importance to follow the evolution of nickel speciation upon thermal treatments to improve the catalyst preparation.

The Agilent Cary 5000 UV-Vis-NIR spectrophotometer coupled with a Praying Mantis diffuse reflectance accessory is suited for gaining greater understanding of the chemical transformations taking place over wide temperature ranges. UV-Vis-NIR spectroscopy allows investigating electronic absorption spectra of transition metal ions. The spectra are interpreted by the number and position of absorption bands, which provides the electronic configuration of the element as well as the nature and symmetry of its chemical environment. Moreover, the near-infrared part of the spectrum provides information on the narrow IR overtone and combination bands originating from the metal ligands or from the support, which may effectively complement mid-range IR spectra.

The flexibility of the Praying Mantis sampling accessory allows reflection studies on solid samples within an environmental cell where temperature and gas atmosphere can be controlled. In this study, samples were measured using a small volume powder cup of the reaction chamber set inside the Praying Mantis. The Praying Mantis accessory gives results that are qualitatively very similar to an alternative diffuse reflectance accessory — an integrating sphere — but with the advantage of the measurement geometry being downward-looking, permitting the samples to be mounted horizontally, and with an ability to measure very small samples (approximately 0.1 $cm^3$) without loss of performance.

Further to its flexibility, the Cary UV-Vis-NIR system delivers a very high level of data for small power volumes. The Praying Mantis DRA uses mirrors rather than a sphere, which has a reflective coating. This gives better optical control over illumination and detection conditions, creating a highly efficient system over a defined range of reflection angles. This type of measurement is always made as a "percent of reference reflectance", making it qualitative in nature; the result is dependent on the reference material used. But, similar results can be obtained from the two approaches.

A primary advantage of Cary UV-Vis-NIR spectrophotometers is their ability to work with very small signals and very low light levels (very high absorbance or very low transmittance/reflectance). High-precision readings can be obtained even where the sample has low reflectance or when measurements are made under extreme sampling conditions, such as with the reaction chamber.

## Experimental

### Instrumentation

All readings were made using a standard Cary 5000 UV-Vis-NIR spectrophotometer (Figure 1) with a Praying Mantis accessory (Figure 2) fitted with a high-temperature reaction chamber, which had been mounted and aligned for use with the standard powder cell holders. The windows of the reaction chamber were $SiO_2$. The reference spectrum was collected on PTFE under ambient conditions (20 °C), and air flow was used for sample measurements.

**Figure 1.** Agilent Cary 5000 spectrophotometer.

**Figure 2.** Praying Mantis accessory with alignment tools and powder cell sample cups.

### Reaction chamber

The reaction chamber (Figure 3) enables a reaction gas to be introduced and reacted with the sample so that the reactions can be studied *in vivo*, reaction rates determined, and intermediate and reaction products identified. The reaction chamber is enclosed with a dome with three windows — two for the spectrometer radiation to enter and exit the chamber and the third for viewing, illuminating, or irradiating the sample. This enables the use of the reaction chambers for photochemical studies. The standard material provided with all three windows is UV quartz.

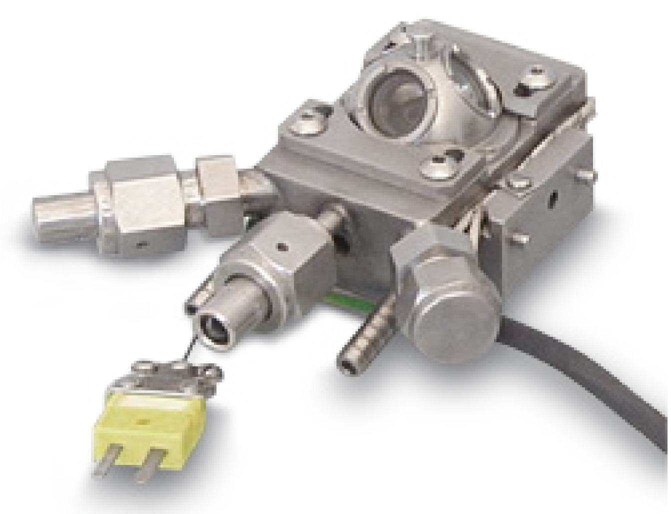

**Figure 3.** Reaction chamber.

## Results and discussion

Spectral results are presented in Kubelka-Munk (F(R)) units versus wavelength in nanometers. F(R) are a mathematical transformation of the %R to aid in the correlation between reflectance and concentration.

$Ni^{2+}$ ions in an octahedral geometry exhibit three absorption bands, two in the visible region (around 400 and 600 nm) and a broader one in the NIR region (around 1,200 nm). Shifts of the 390 nm band with temperature up to 110 °C evidence the changes around nickel ions upon transformation of hydrated nickel nitrate to nickel hydroxynitrate, while NiO forms above 230 °C.

Spectra in the NIR range both highlight development of hydroxynitrates between room temperature and 110 °C, (shift of the 1,153 nm band to 1,240 nm), but also dehydration of the nickel salt and support (loss of the -OH overtone band at 1,450 nm). Two more bands by adsorbed water and alumina hydroxyl groups are found at 1,950 and 2,300 nm.

The dehydration process is clearly seen through the decrease of the initially intense band at 1,950 nm, with some hydroxyl groups remaining on the alumina surface after thermal treatment at 250 °C.

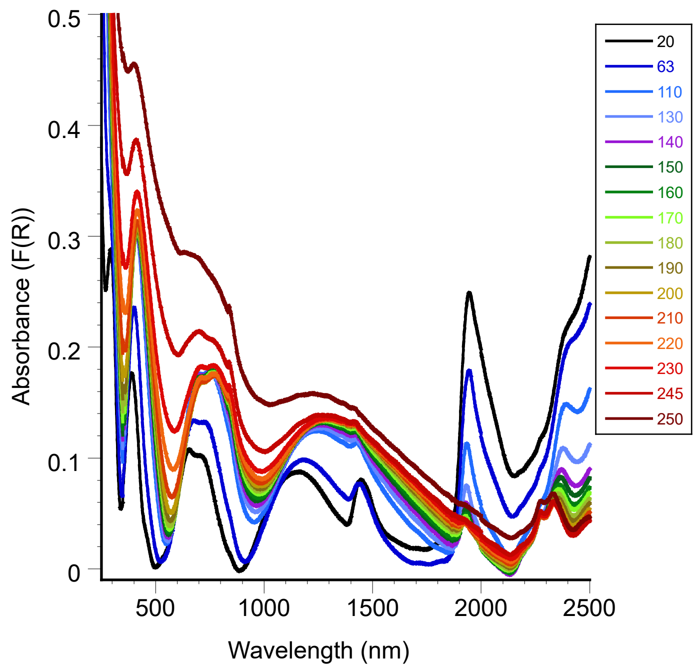


**Figure 4.** Praying Mantis in an Agilent Cary 5000 UV-Vis-NIR (overlaid scans). Thermal transformations of $Ni[H_2O]_6(NO_3)_2/Al_2O_3$ from 20 °C up to 250 °C.

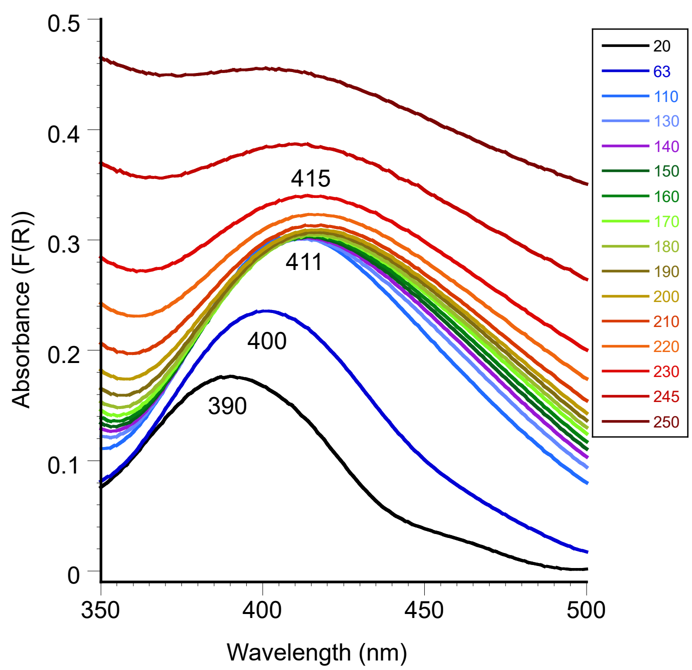


**Figure 5.** UV-Vis range.

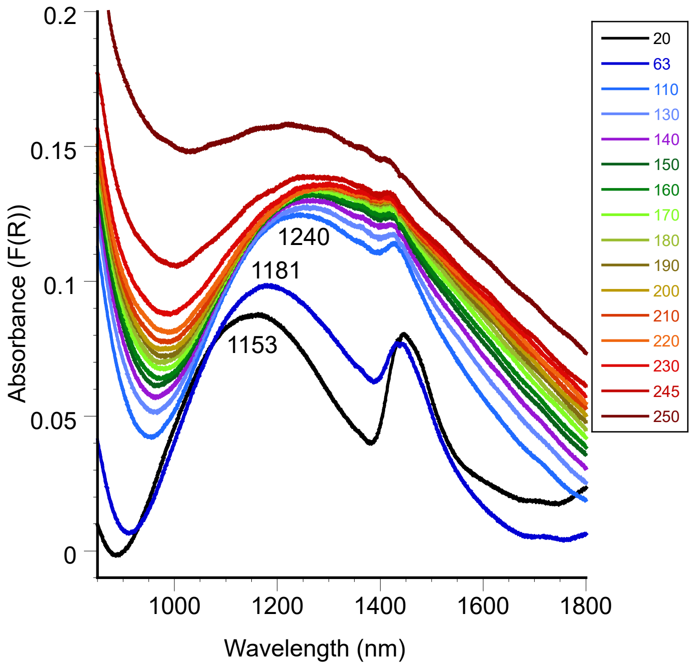


**Figure 6.** NIR range.

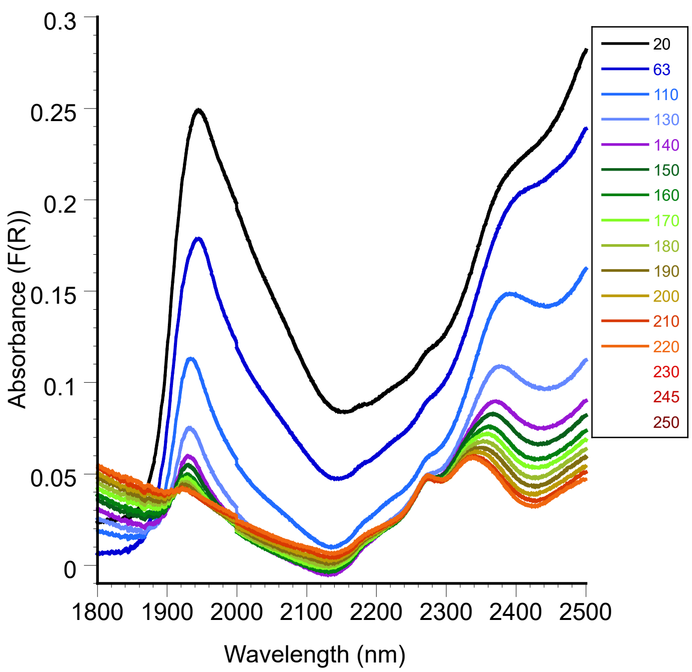


**Figure 7.** NIR range up to 1,800 nm.

## Conclusion

The results demonstrate the use of the Agilent Cary 5000 UV-Vis-NIR system in the analysis of a small volume of catalyst powder samples over temperatures from 20 to 250 °C. The combination of the wide dynamic range of the Cary 5000 and excellent signal-to-noise ratio evidenced the transformation of nickel salt and dehydration of the supported system using a high-temperature reaction chamber in combination with the Praying Mantis accessory. This makes diffuse reflectance a valuable tool for studying powders involved in heterogeneous catalysis or reactions at the gas-solid interface.

**www.agilent.com/chem/cary5000**

DE28029956


Printed in the USA, January 3, 2023
5990-9787EN

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