

## Smart Combinatorial *Operando* Spectroscopy Catalytic System

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### Introduction

With the recent introduction of the *operando* spectroscopic methodology that involves simultaneous spectroscopic characterization of catalysts and reaction product analysis to develop molecular structure-activity/selectivity relationships, there is currently a strong desire to obtain real-time catalyst spectroscopic and performance information *under relevant reaction conditions*. Only from such fundamental information will it be possible to establish molecular/electronic structure-activity/selectivity relationships for catalytic systems that will allow for the molecular engineering of advanced catalytic materials for specific targeted applications. The *operando* spectroscopic approach requires that the spectroscopic and catalytic information be able to provide the following:

- Real-time generation of spectroscopic and catalytic data
- Molecular structures of catalytic active sites
- Electronic structure of catalytic active sites
- Molecular structure of surface reaction intermediates
- Rate-determining-step
- Surface reaction mechanism
- Surface kinetics
- Overall reaction kinetics
- Spatial resolution
- Temporal resolution (on the order of second or less).

### Materials and Methods

The catalyst characterization methods based on electrons and ions will not be able to function under relevant reaction conditions since their operation requires vacuum conditions (XPS, AES, EELS, LEED, TEM, ISS and SIMS) and/or metallic single crystals or foils (STM). The criterion of spatial resolution can not be satisfied with the bulk characterization techniques of XRD, solid-state NMR, EXAFS/XANES and EPR. Optical characterization techniques (Raman, IR and UV-vis), however, can satisfy all of the *operando* spectroscopy and microscopy requirements. There are no temperature and pressure limitations on Raman spectroscopy and current technology allows for rapid data acquisition (as fast as 1 second) and spatial resolution better than a micron. Visible Raman spectroscopy is limited to  $\sim 800$  °C by black-body radiation, but this is circumvented by UV Raman spectroscopy since UV light is not absorbed by black bodies. Raman provides molecular structural information of the catalytic active sites, surface reaction intermediates, and their location on the catalyst surface. Complementary information is provided by IR, but thermal broadening limits the reaction temperature to less than  $\sim 500$  °C and the strong absorption of gas phase molecules needs to be spectroscopically subtracted to enhance the vibrations originating from the catalyst surface. The IR spectroscopy acquisition time is currently better than 1 second and spatial resolution of

$\sim 10$  microns can be achieved. In contrast to Raman and IR spectroscopy, UV-vis diffuse reflectance spectroscopy (DRS) provides electronic information (oxidation states and degree of aggregation of catalytic active sites). The current temperature limit on UV-vis DRS spectrometer systems is  $\sim 750$  °C with spectral acquisition time in milliseconds and spatial resolution of  $\sim 10$  microns. Whereas, Raman and UV-vis DRS can also function in aqueous environments, this is not the case for IR because of the strong absorption by H<sub>2</sub>O. Surface mapping capabilities can also be obtained with confocal microscopy, and temperature programmed surface reaction (TPSR) spectroscopy provides the surface mechanistic and kinetic details. Finally, real-time online product analysis with a mass spectrometer or a micro-GC can provide the desired overall catalytic activity, selectivity and kinetics.

### Results and Discussion

A smart combinatorial *operando* spectroscopy catalytic system has been designed (PCT International Patent Application #WO 2005/100993) that will allow achievement of all the criteria discussed above. The platform for this system is the Horiba-Jobin Yvon LabRaman-IR Spectrometer, which contains 6 spectroscopic techniques (Raman with 3 different excitations from UV to visible, IR, UV-vis, and TPSR) and confocal microscopy. The rapid data acquisition and spatial capabilities readily allows the system to be extended to a combinatorial mode with parallel micro-reactors so that more information can be generated in a given time period (7 characterization methods x 8 parallel reactors = 56 experiments in same time period). In addition, the channel micro-reactor can also be temperature programmed to provide more mechanistic and kinetic information, with an online mass spectrometer and a parallel micro-GC system for real-time and quantitative product analysis, respectively.

This presentation will discuss the design details and capabilities of this novel new *operando* spectroscopic system. Catalytic examples from CH<sub>3</sub>OH oxidation to H<sub>2</sub>CO over surface redox sites, CH<sub>3</sub>OH dehydration to CH<sub>3</sub>OCH<sub>3</sub> over surface acid sites, NO<sub>x</sub> storage on basic surface sites and several other applications will be discussed.

### Significance

Recent advances in optical spectroscopic instrumentation now allow for the collection of Raman, IR and UV-Vis spectra with temporal ( $\sim 1$  second) and spatial ( $\sim 1$  micron) resolution. Such a new *operando* spectroscopic system has been developed that can simultaneously provide multiple spectroscopic (IR, UV-Vis, Raman excitation from UV to visible and temperature programmed surface reaction) and confocal microscopic information for surface mapping. The reaction products from this *operando* spectroscopic catalytic system are monitored in real-time with an online mass spectrometer system. To further accelerate the amount of information being generated from such an *operando* spectroscopic catalytic system, eight multiple parallel fixed-bed reactors were installed to also allow for combinatorial studies. Thus, this smart combinatorial *operando* catalytic system can perform 6 spectroscopic and 1 microscopic experiments that allow for the rapid establishment of molecular/electronic structure-catalytic activity/selectivity relationships that will allow for the design of advanced catalytic materials for targeted catalytic reactions.