Utilizing Raman spectroscopy to monitor catalysts in action
10 December 2010, by Chris Keturakis

Israel E. Wachs, G. Whitney Snyder Professor of Chemical Engineering at Lehigh University, and Charles A. Roberts, a graduate student at Lehigh, have published a critical review on Raman spectroscopy entitled "Monitoring surface metal oxide catalytic active sites with Raman spectroscopy." The review focuses on the ability of Raman spectroscopy to determine the molecular structures of catalytic active sites, the location in a catalyst responsible for chemical transformations, under all environmental conditions (gaseous and aqueous environments under a broad range of temperatures and pressures).

In the early period of Raman spectroscopy studies (1970-1980), researchers simply explored the kind of molecular structural information that can be obtained from a Raman spectrum. From 1980-2000, Raman studies began to employ controlled atmosphere, or in situ, conditions to determine the molecular structure of catalytic active sites under different environmental conditions. The in situ Raman spectroscopy studies now account for ~25% of all reported Raman publications, reflecting the realization that the molecular structures of catalytic active sites are dynamic and depend on the specific environmental conditions.

Most recently, researchers have been employing real time monitoring of the catalytic active site with in situ Raman spectroscopy and the simultaneous analysis of product formation with techniques such as mass spectrometry and gas chromatography. This approach has been termed operando spectroscopy in the catalysis literature and has proven to be extremely beneficial in the elucidation of the dynamic evolution of the catalytic active sites under reaction conditions and its relationship to the catalyst performance. Only such cutting edge operando Raman spectroscopy investigations will allow for the establishment of definitive catalytic active site structure-performance relationships on a molecular level.

When asked about the versatility of Raman spectroscopy, Charles Roberts stated "Raman spectroscopy has come a long way with regards to its ability to efficiently collect meaningful, quality spectroscopic data. The state-of-the-art commercially available systems have greatly improved collection time and increased signal intensity, while decreasing the necessary laser power, which is critical to avoid detrimental effects like sample damage and fluorescence. Given the current state of technology, Raman spectroscopy is the perfect technique to be employed during operando spectroscopy studies of catalysts and their active sites. No other technique is so easily employed under so many reaction conditions.

Raman spectroscopy can be used at temperatures ranging from sub-ambient to greater than 1000 °C and pressures as high as those found in Earth's crust by using diamond-anvil cells to achieve pressures of excess of 50,000 atmospheres! A researcher is only limited by the capabilities of the reaction cell being employed. As for the materials that can be studied, the molecular nature of Raman spectroscopy is well suited to probe the nature of catalytic active sites that are responsible for the overall catalytic performance, as one can see from the multitude of examples in our review."

The review is broken down into several sections including the use of Raman spectroscopy with aqueous solutions, bulk metal oxides (pure oxides, mixed oxides, polyoxo metallates (POMs), layered metal hydroxides, zeolites, etc.), supported metal oxides, and catalyst synthesis.

Two special sections are dedicated to cutting edge operando Raman spectroscopy and Raman spectroscopy combined with other techniques (e.g. Raman-UV-vis, Raman-IR, Raman-EPR) that significantly advance the field of catalysis science. Some unique examples of the capability of Raman spectroscopy discussed include tracking the structure of aqueous ammonium heptamolybdate,
(NH₄)₆Mo₇O₂₄·4H₂O, as a function of solution pH, examining the hydrated and dehydrated structures of supported metal oxides using the isotopic exchange of oxygen to probe local molecular structures (terminal oxo (metal=O) bonds, terminal hydroxyl (metal-OH) bonds, bridging metal-O-metal bonds, peroxy (\(-O-O\))² species, superoxo (\(-O-O\))⁻¹ species and physically adsorbed molecular O₂), and monitoring the dynamic changes of catalytic active sites.

For example, the catalytic active surface MoOₓ sites on SiO₂ are present as surface (O=)₂MoO₂ species during methane oxidation reaction conditions and transform to beta-MoO₃ nanoparticles during methanol oxidation reaction conditions.

Professor Wachs stated that "Raman spectroscopy is turning out to be one of the most informative catalyst characterization techniques, as well as many non-catalytic materials, because of its ability to provide time-resolved molecular structural information about catalytic active sites under all reaction conditions."

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