

## VII Historical Perspective of Raman Spectroscopy in Catalysis

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Raman spectroscopy is a very powerful catalyst characterization technique because it can provide fundamental and molecular-level information about catalyst structures, bulk as well as surface, and surface reaction intermediates. Furthermore, Raman spectroscopy is among a handful of characterization techniques that can provide such fundamental information about heterogeneous catalysis under in situ reaction conditions. Consequently Raman spectroscopy has been used to examine essentially every type of catalytic material: bulk metals, supported metals, bulk mixed metal oxides, supported metal oxides, bulk and supported metal sulfides, zeolites and molecular sieves, heteropoly anions and clays.

The combination of fundamental molecular structural information and in situ capabilities has resulted in an explosion of Raman spectroscopy characterization studies in the catalysis literature (see Fig. VII.1). The Raman instrumentation that was available in the 1970's, double monochromators with single-channel photo-multiplier detectors, primarily allowed only strong Raman signals to be detected. Thus, much of the early catalyst characterization studies focused on materials that gave strong Raman signals (e.g.,

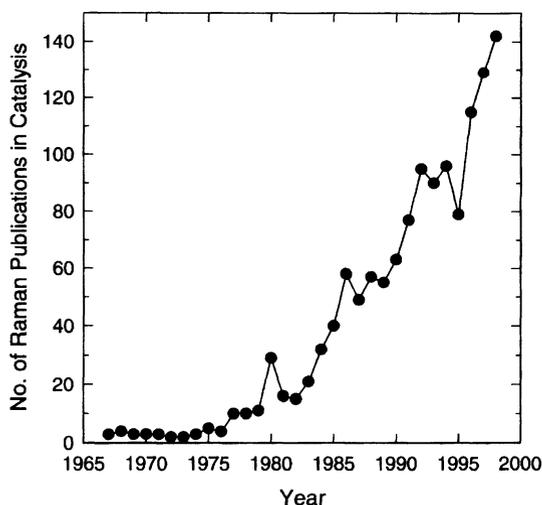


Fig. VII.1. Raman papers on catalysis versus publication year

crystalline mixed metal oxides). However, the Raman structural information was not unique, since the bulk structures of these materials could also be obtained with X-ray diffraction techniques. The first major growth in Raman characterization in catalysis occurred in 1977, when it was found that Raman spectroscopy can detect the very weak signals of materials that were X-ray amorphous (e.g., metal oxide crystallites smaller than  $\approx 40 \text{ \AA}$  and 2D metal oxide overlayers) [1–3]. The weak Raman signals and fluorescence problems, however, dampened much of the initial enthusiasm. The development of optical multi-channel analyzers (OMA's) and triple monochromators in the early 1980's resulted in significantly stronger Raman signals and renewed interest in Raman spectroscopy. This renewed interest was also fueled by the appearance of several in situ Raman studies that demonstrated the dynamic nature of heterogeneous catalysis surfaces [4–8]. The introduction of commercial Raman systems with CCD detectors, notch filters, and single monochromators in the 1990's resulted in even stronger signals and the ability to perform real-time Raman analyses of heterogeneous catalysts under reaction conditions [9].

As catalysis science turns to a molecular-level understanding of the molecular structure – reactivity/selectivity relationships of heterogeneous catalysis, the unique information that can be provided by Raman spectroscopy becomes even more critical (especially with real-time analysis under in situ reaction conditions). Thus, the exponential growth of Raman spectroscopy in catalysis should continue for many more years. Eventually it may result in the molecular design and engineering of heterogeneous catalytic materials and their surfaces from fundamental principles.

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