Advanced X-ray absorption and emission spectroscopy: in situ catalytic studies

Advanced X-ray absorption and emission spectroscopy: *in situ* catalytic studies†

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Knowledge of the structure of catalysts is essential to understand their behavior, which further facilitates development of an active, selective, and stable catalyst. Determining the structure of a functioning catalyst is essential in this regard. The structure of a catalyst is prone to change during the catalytic process and needs to be determined in its working conditions. In this *tutorial review*, we have summarized studies done at synchrotron radiation facilities that illustrate the capability to determine catalyst structure using X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES). These studies aim at facilitating the determination of the dynamic structure-performance relationships during a catalytic process.

1. Introduction

It is essential to know the electronic and geometric structures of materials in order to understand their behavior. Nano-sized particles are of great interest, especially in catalysis where noble metal nanoparticles are often supported on various supports and are used in different reactions such as CO oxidation,[1] the water gas shift reaction,[2] hydrogenation[1d,3] methanation,[4] and hydrogenolysis.[5] The structure of nano-sized particles differs from that of bulk metals. Bulk metals lose their metallic character when the size reduces to less than a few nm.[6] There are many techniques to determine the structure of matter, all with pros and cons; their application depends on the required information and the conditions of measurement. Because of the large penetration depth of X-rays, the interaction of X-rays with matter has been applied extensively. X-ray absorption spectroscopy (XAS) is one of the most popular techniques for determining the structure of materials without long-range order.[7] An XAS spectrum can be divided into three regions, namely the pre-edge, the X-ray absorption near edge structure (XANES), and the extended X-ray absorption fine structure (EXAFS). The shape of XANES spectra gives the electronic structure and the local geometry around the atom that absorbs the X-ray radiation. It reflects the empty density of states (DOS) of the electronic transition. EXAFS spectroscopy provides the coordination geometry, such as bond length (with an accuracy of about 0.01 Å), the number of neighboring atoms, which indicates the size and shape of the nanoparticles, and the Debye–Waller factor.[8]

In an XAS experiment, an electron from a core level is excited through the absorption of a photon of the incoming X-rays. The excited electron is pushed above the Fermi level

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