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This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/79193> since

Published version:

DOI:10.1039/c0cs00054j

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

Jagdeep Singh,^a Carlo Lamberti^b and Jeroen A. van Bokhoven^{*ac}

Received 26th July 2010

DOI: 10.1039/c0cs00054j

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

^a Institute for Chemical and Bioengineering, HCI E 127, Wolfgang Paulistrasse 10, 8093, Zurich, Switzerland.
Fax: +41446321162; Tel: +41446325542

^b Department of Inorganic, Physical and Materials Chemistry, NIS Centre of Excellence, and INSTM Reference Center, University of Turin, Torino, Italy

^c Paul Scherrer Institute, Villigen, Switzerland

† Part of the themed issue covering recent advances in the *in-situ* characterization of heterogeneous catalysts.



Jagdeep Singh

Jagdeep Singh, born and raised in Patiala, India, earned a BE in Chemical Engineering from Thapar University, Patiala in 2004 and a MTech degree in Chemical Engineering from Indian Institute of Technology, Roorkee, India in 2006. He completed his PhD under the guidance of Prof. Dr Jeroen A. van Bokhoven in October 2010 at ETH Zurich. His PhD research focused on the exploration of new tools of X-ray absorption and emission spectroscopy for *in situ* catalytic research.



Carlo Lamberti

Carlo Lamberti: born in 1964; degree in Physics in 1988; PhD in solid state physics in 1993. He is professor in Physical Chemistry at the Torino University since 2006. He has performed more than 100 experiments with synchrotron and neutron sources at ADONE, LURE, ESRF, Elettra, Daresbury, SLS, APS, ISIS, FRM-II, ILL. He has been member of the review committees of ESRF and SLS. His research activities are focused in the multitechnical

characterization of nanostructured materials. He edited the book *Characterization of Semiconductor Heterostructures and Nanostructures*, Elsevier, 2008.