

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

Probing the surfaces of heterogeneous catalysts by in situ IR spectroscopy

This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/82881> since

Published version:

DOI:10.1039/c0cs00117a

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

Probing the surfaces of heterogeneous catalysts by *in situ* IR spectroscopy†

Carlo Lamberti,^a Adriano Zecchina,^a Elena Groppo^b and Silvia Bordiga^{*b}

Received 21st September 2010

DOI: 10.1039/c0cs00117a

This *critical review* describes the reactivity of heterogeneous catalysts from the point of view of four simple, but essential for Chemistry, molecules (namely dihydrogen, carbon monoxide, nitrogen monoxide and ethylene) that are considered as probes or as reactants in combination with “*in situ*” controlled temperature and pressure Infrared spectroscopy. The fundamental properties of H₂, CO, NO and C₂H₄ are shortly described in order to justify their different behaviour in respect of isolated sites in different environments, extended surfaces, clusters, crystalline or amorphous materials. The description is given by considering some “key studies” and trying to evidence similarities and differences among surfaces and probes (572 references).

1. Introduction: Probing a surface

Heterogeneous catalysts are complex systems whose properties are given by a combination of multiple factors. Activity, selectivity and life-time of the catalyst are determined by the optimum combination of specific features that range from nano to micro and macro properties of the surface properties of the catalyst.¹ A powerful tool to obtain a detailed description of the catalyst surface properties is the use of probe

molecules in combination with an investigative technique able to monitor with the sufficient sensitivity the probe–surface interaction.^{2–22} One of the most widely used techniques that follows this approach, is Mid-infrared spectroscopy (4200–400 cm^{−1}) using appropriate probe molecules. The method is indirect, in the sense that it monitors the surface through the perturbation inferred to the probe. The observables are the changes in vibrational frequency and intensity of the probe modes. IR-inactive modes can also be observed as a result of the interaction with the surface. In some cases it is also possible to follow induced changes of skeletal and surfaces modes of the catalysts^{23–25} and or to follow a reaction-dynamic on the surface.^{16,20,26,27} In this respect, time- and temperature-resolved FTIR spectroscopy has the potential to detect intermediate species in a reaction chain.²⁰ In this contribution we have chosen four probe molecules (H₂, CO, NO and C₂H₄) and for each of them we will report some “case studies” in which they behave as probe molecules and or as reagent.

^a Department of Inorganic, Physical and Materials Chemistry, NIS Centre of Excellence, and INSTM reference center, University of Turin. Via P. Giuria 7, 10125 Torino, Italy

^b Department of Inorganic, Physical and Materials Chemistry, NIS Centre of Excellence, and INSTM reference center, University of Turin, Via Quarellio 11, 10135 Torino, Italy. E-mail: silvia.bordiga@unito.it; Fax: +39011-6707855; Tel: 39011-6708373

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



Carlo Lamberti

Carlo Lamberti: born in 1964; degree in Physics in 1988; PhD in solid state physics in 1993. He has been a professor in Physical Chemistry at Torino University since 2006. His research activities are focused on the multitechnical characterization of nanostructured materials, combining (in collaboration with expert colleagues) laboratory techniques (IR, UV-Vis, photoluminescence, EPR, XRD, TEM) with synchrotron (XAFS, XES, XRD, XRF)

and neutron (diffraction and INS) based techniques. He edited the book *Characterization of Semiconductor Heterostructures and Nanostructures*, Elsevier, 2008. He has authored and coauthored more than 200 research papers, 8 review articles and 6 book chapters, that have received more than 7000 citations (*h-index* 48).



Adriano Zecchina

Adriano Zecchina is Emeritus Professor at University of Turin. He is Director of the Inter-departmental Centre of Excellence “Surfaces and nano-structured interfaces (NIS)” as well as being a member of the Accademia delle Scienze di Torino and of the Accademia dei Lincei. He is coauthor of about 430 papers and 5 reviews published in the main journals of Chemistry, Physical Chemistry, Surface Science and Catalysis (number of citations: 12000; *h-index* 59). His research activities are mainly focused on high surface area systems and catalysts studied by IR, Raman, UV-Vis, XANES and EXAFS techniques. Recent attention is on the structure characterization of catalytic sites under reaction conditions.