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Preface

A marked increase in the number of papers dealing with spectroscopic investigations of catalytic reactions has been observed in recent years. This fact reflects the desire of scientists to monitor at the molecular level the details of chemical reactions. Traditional microkinetic studies can offer reasonable models of the processes taking place, using calculations partly based on thermodynamics and other theoretical considerations. However, such analyses are in some instances merely a curve-fitting exercise, based on the measure of the concentrations of reactants and products under varying experimental conditions, without any actual direct observation inside the reactor. The use of spectroscopy can be very beneficial in supporting microkinetic analysis by literally turning on the light inside the reactor, which is no longer a ''black box'' to the scientist.

Spectroscopic techniques had been mostly used in the past to characterise fresh or used catalysts, in order to obtain structural information relating to the bulk and surface of the solids. In the second half of the last century, and in particular at the end of the 1970s, a few scientists realised that such characterisation would be so much more useful when used in the conditions of temperature and pressure relevant to the catalytic tests. This was the dawn of in situ analyses, which went on spreading to most fields of the chemical sciences, supported by the increased availability of commercial in situ cells. One of the great achievements of in situ techniques was the realisation that the behaviour of a catalytic surface in the presence of reagents under relevant pressures and temperatures was often significantly different from that observed ex situ, for example, under vacuum or room temperature conditions.

A molecular approach to the study of chemical reactions requires the determination of active sites, reaction elementary steps and, when possible, intermediate species. Such investigations are relevant only when the catalyst is studied in situ and heterogeneous catalytic systems are now routinely investigated under continuous flow conditions at concentrations, pressures, temperatures and contact times typical of use, i.e. *modus operandi*. Therefore, in order to identify these more focussed analytical techniques a new expression, i.e. ''*operando*'', was put forward. We should recall that the term *operando* spectroscopy refers to spectroscopic measurements of catalysts under working conditions (appropriate temperature, pressure and reactant composition—gas as well as liquid) with simultaneous on-line product analysis. This term was used in the literature starting from 2002 [see, for example: B.M. Weckhuysen, Chem. Commun. (2002) 97; M.A. Bañares, et al., Chem. Commun. (2002) 1292] with the aim to distinguish work in which on-line activity measurement was performed alongside spectroscopic measurements (i.e. *operando*) from those in which only spectroscopic data were recorded (i.e. in situ). [*Operando*, a gerund verbal form, is the Latin word for working or operating.] The on-line analysis of the reaction effluents is needed to ensure that the activity data obtained in the *operando* reactor are consistent with those observed in a conventional reactor. These conditions required the (often challenging) development of reaction cells operating in a kinetically relevant mode, able to withstand extreme conditions, while still allowing the electromagnetic radiation to escape from the reactor. In spite of the technical difficulties, the success of *operando* techniques is such that the number of teams switching their studies towards this methodology is increasing and the simultaneous utilisation or coupling of different spectroscopies is also receiving much attention, pushing further the boundaries and thresholds for investigation.

In 2003 the first conference on *operando* spectroscopy took place in Lunteren (The Netherlands). One year later, at the occasion of the 13th ICC Conference, the ISOSCAT symposium held in Caen (France) was devoted to the recent progress in ''In Situ and Operando Spectroscopy for Catalysis''. This Special Issue reports a combination of reviews and original results in this fast-moving field of in situ and *operando* spectroscopy by some scientists who attended the meeting or who are known in the literature for their outstanding contributions in these domains. Among others, Weckhuysen et al., Brückner, Anderson et al. and Payen et al. report on the recent developments of combined *operando* techniques. Stair et al. and Bañares et al. detail the possibilities and limitations of quantitative Raman spectroscopy. FT-IR spectroscopy is among the most used *operando* techniques, and this special issue of *Catalysis Today* reports contributions by Topsøe, Lamberti et al., Mondelli et al., Romero-Sarria et al. and Meunier et al. Finally, Gedeon et al. report on in situ NMR studies while

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Hunger and Ivanova et al. discuss the application of *operando* NMR spectroscopy.

Frederic Meunier*
Queen's University,
School of Chemistry and Chemical Engineering,
David Keir Building,
Stranmillis Road, Belfast BT9 5AG,
United Kingdom

Marco Daturi*
Laboratoire Catalyse et Spectrochimie,
UMR 6506,
CNRS, ENSICAEN and University of Caen, 6,
boulevard Maréchal Juin,
14050 Caen Cedex,
France

*Corresponding authors. Tel.: +44 28 90974420;
fax: +44 28 909 74890 (F. Meunier);
Tel.: +33 2 31 45 27 30;
fax: +33 2 31 45 28 22 (M. Daturi)
E-mail addresess: F.Meunier@qub.ac.uk (F. Meunier),
Marco.Daturi@ensicaen.fr (M. Daturi)