Applied Catalysis A: General 391 (2011) 468–476

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Closing the operando gap: The application of high energy photons for studying catalytic solids at work

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ARTICLE INFO

Article history:
Received 13 March 2010
Received in revised form 13 May 2010
Accepted 15 June 2010
Available online 23 June 2010

Keywords:
In situ spectroscopy
X-rays
Multi-technique
Bulk oxide
Catalysis
MoO_3
Iron molybdate

ABSTRACT

Understanding the working principles of heterogeneous catalysts represents one of the great challenges in the field of materials science today. Ex situ bulk and surface science techniques provide information on such systems; however it is difficult to know whether any observed change in the physicochemical state of the catalyst would occur under the real working conditions. To counter this operando gap, the last decade has witnessed research efforts pushing towards more operando-like experimental setups to investigate 'catalysis in action'. The advances in this field have been considerable so that it is now feasible to observe catalytic materials using a variety of techniques (sometimes combined into a single experiment) under conditions approaching those used for commercial operation. There still remain, however, some key differences between the conditions under which the experiments and the measurements are performed and with those required to fully understand a catalyst material in an industrial setting. In this paper we aim to show how multiple high energy techniques can be employed to further close the operando gap and meet the relevant criteria of replicating industrially relevant conditions and gleaning useful high quality data, whilst minimizing sample effects. For this purpose, a new high energy source experimental setup is described. We present results from high energy X-ray experiments on a simple model parent oxide, molybdenum oxide (MoO_3) used for the selective oxidation of methanol as well as a new characterization study on the more complex iron molybdate ($Fe_2(MoO_4)_3$) catalyst. The advantages and limitations of high energy X-ray experiments will be discussed.

1. Introduction

To provide a comprehensive scientific understanding of an industrial-like catalyst material through laboratory/synchrotron-based measurements it is necessary to meet several criteria, the most important of which are:

1. *A realistic experimental setup that mimics the industrial process.* A realistic environment includes the ability to obtain and maintain the correct thermal and pressure conditions during the experiment (and ensure that the setup itself does not induce unexpected changes in these) and the use of a reactor sufficiently large in size to realistically replicate the industrial axial and radial distribution gradients across the catalyst bed for measurement in a spatiotemporal manner.
2. *The acquisition of useful data.* From our realistic experiment we must of course obtain useful experimental data, in terms of quality, time and spatial resolution. Quality is typically determined by both the source (e.g. high photon flux) and of the detector (e.g. resolution, sensitivity and low noise) and as data quality and rate of acquisition are in general inversely correlated, one must find a balance between the time frame and the quality of observations to suit a particular experiment (particularly at the limits of these two criteria). In addition, the need for spatial examination of the reactor must be considered as axial and radial phase variation may prove important with regard to understanding larger reactors. Again the ability to perform such measurements is determined by the quality and time resolution required.
3. *The acquisition of complementary information.* Where possible it is desirable to obtain information from a number of techniques in a single experiment, providing data over different length scales (local and long range order) and penetration depths (bulk vs. surface) that can be correlated to significantly enhance the understanding of changes within the sample. These can include X-ray Absorption Spectroscopy (XAS), Small Angle X-ray Scattering (SAXS) and Wide Angle X-ray Scattering (WAXS), providing

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doi:10.1016/j.apcata.2010.06.027

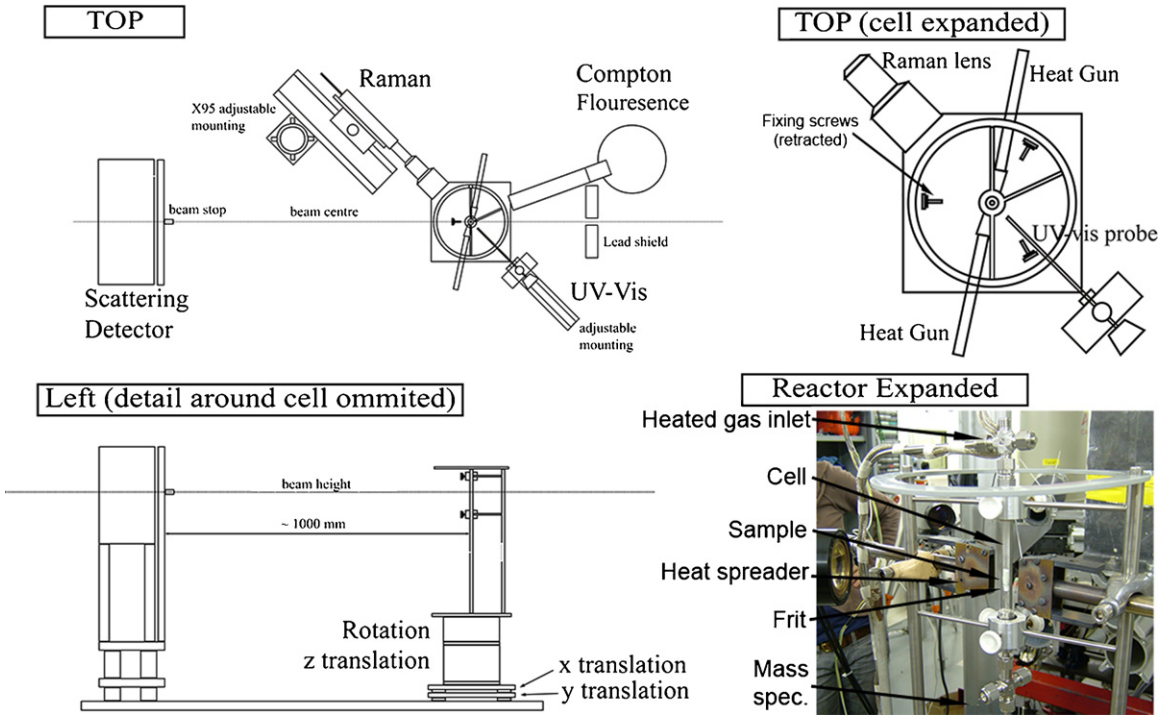

Fig. 1. A detailed schematic view of the experimental set-up for measuring catalytic solids at work with high energy photons. The top view demonstrates the angle at which each of the techniques was located; the left view demonstrates the available reactor translation, the expanded view details the area around the reactor and the photograph of the reactor demonstrates more detail of this area.

local, short and long range order information respectively and in the case of high energy setups, 'secondary' information, such as Compton and fluorescence, can provide additional elemental and density analysis. Data on the state of the catalyst may also be obtained from numerous non-synchrotron-based techniques, such as Raman, UV–vis and IR spectroscopy.

4. *Maintenance of sample stability*. Although any measurement will always result in a perturbation of the sample, it is desirable to minimize the 'side effects' of this. In extreme cases this can result in induced sample damage caused by a number of mechanisms, including photo-excitation, localized heating, photoelectric and Compton effects.

By improving on each of these criteria we can obtain experimental physicochemical information that is of greater use for the analysis of large scale industrial processes. Of course it is not always possible to implement each of these, however this does not preclude obtaining useful information—for example many high quality ex situ studies have provided vital insight into the behavior of catalytic materials. Such measurements cannot always provide information on the dynamic/kinetic aspects of the system, however with the continued development of high-brilliance synchrotron sources and high quality detectors, in situ studies with increasing signal quality and time resolution can now provide such detailed kinetic information [1–8]. Recent examples include the combination of synchrotron radiation (SR) and non-SR techniques in a multi-technique experiment that can provide additional insight over that provided by single in situ techniques [1,9,10] and in situ [11,12] or pseudo-in situ [13] spatiotemporal mapping of axial and radial variations in catalytic materials. Whilst these multi-technique in situ setups are then close to closing the operando gap they do suffer from a considerable disadvantage in that they generally utilize SR-radiation from bending magnet beamlines working within a relatively low energy range of 5–30 keV. These photons then do not have a high penetration depth, restricting the maximum diameter of the experimental reactor to at most a couple of millimeters (to allow transmission). These conditions are then far removed from those encountered in industrial reactors, result in increased interference (parasitic radiation) between complementary spectroscopic techniques and make bulk measurements more difficult (increase ratio of surface to bulk). The reduced photon transmission also decreases the data quality per unit time (for a fixed sample diameter) and therefore reduces the opportunity for useful spatiotemporal mapping. In addition low energy photons may increase the risk of induced change within the sample *via* for example the photoelectric effect.

The solution for many of these problems is then a move towards higher X-ray energy experimental setups such as the one described in detail in this paper. Constructed on the ID15b beamline at the ESRF (Grenoble, France), this powerful setup has been previously used to collect very high quality information on the bulk nature of simple oxides [14] and examine spatiotemporal changes of these systems in situ [15]. Here we provide further details on this experimental approach and discuss its advantages with reference to the criteria above and with examples from previous work and novel measurements on an industrial-like $Fe_2(MoO_4)_3$ catalyst for formaldehyde production. In this manner, we will demonstrate how the use of high energy X-ray photon setups allows to further push towards closing the operando gap in heterogeneous catalysis research.

2. The experimental setup and reaction conditions

A detailed schematic of the novel experimental setup is given in Fig. 1, whilst detailed descriptions of the experimental equipment and data analysis procedures are given in Supplementary information S1. The top elevation details the position of the techniques which can be applied in a single experiment, with scattering being obtained in transmission geometry and Compton/fluorescence in a back-scattered orientation. The advantage of