High Energy Diffraction and Open Cell Architectures for Studying Catalysts in Action

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Introduction

To fully understand the operation of a catalyst it is important to obtain as much high quality data over various parts of the reactor and in conditions as close to industrial as possible. Recent developments have demonstrated how congruent multiple technique measurements can provide additional insight compared to single or ex situ techniques [1]. However, these experiments are often performed on relatively low energy beamlines requiring capillary (or similar) setups with small restrictive sample environments. These do not mimic large volume industrial reactors, making the combination of techniques without significant loss of data quality difficult and thus severely limit the possibility of profiling different parts of the system. Many of these issues can be overcome by combining open cell architectures with high energy synchrotron radiation.

Here we detail such a setup, performing two 'test' experiments on the reduction of molybdenum oxide (MoO_3). MoO_3 is extensively studied as a 'parent' oxide of iron molybdate (FEMO) to reveal more detail about the more complex catalyst [2]. FEMO is used extensively in the production of formaldehyde from methanol and in this study we examined both the Mars-van Krevelen (MVK) oxygen extraction process believed to take place and the well known problem of FEMO deactivation due to molybdenum volatilization [3].

Materials and Methods

The sample cell consisted of a custom machined quartz tube orientated in an open cell environment that allowed all parts of the bed to be profiled. Heat was supplied from two air guns with specifically designed nozzles to reduce temperature gradients. When combined with programmable mass flow controllers, this setup can treat the samples under a range of environments in the temperature range 24 – 450 ºC. In this test the cell (∅ = 4 mm) provided a reactor considerably larger than a standard capillary setup, allowing a more realistic sample environment and a large number of techniques to be combined. To date diffraction, Raman, UV-Vis, Fluorescence/Compton scattering and online mass spectrometry (MS) have been successfully combined. To penetrate the sample and acquire X-ray data without a significant loss of quality and within a reasonable time frame, the very high energy (90 KeV) beam characteristic of station ID15B at the ESRF was used.

Results and Discussion

In the first example reduction was monitored at a single point in the reactor bed using high quality diffraction, Raman UV-Vis and MS. Rietveld parameters obtained from the diffraction revealed that of the 3 unique oxygen environments in the crystal structure (O1, O2 and O3 respectively), only the Mo-O1 bond length and thermal disorder increased significantly (figure 1a). This suggested the O1 atom is the most likely extracted during MVK transfer of bulk oxygen. This was supported by additional changes in the Raman intensities indicting the Mo-O1 bond is broken more rapidly than O2 or O3. In the second example the sample was profiled along the bed from the inlet (top) to outlet (bottom) during reduction. Here diffraction indicated the reappearance of MoO_3 after initial reduction at the bottom of the bed, whilst the concentration of forming MoO_2 after reduction also appeared to increase towards the bottom of the bed (figure 1b). Additionally combined Raman measurements indicate the reappearance of MoO_3 at the bottom of the bed. Interestingly, comparative experiments in a flow of water vapor did not present such changes; therefore it seems likely that the primary cause of volatilization (and therefore deactivation) within the FEMO system may be methanol and not water produced during formaldehyde production.

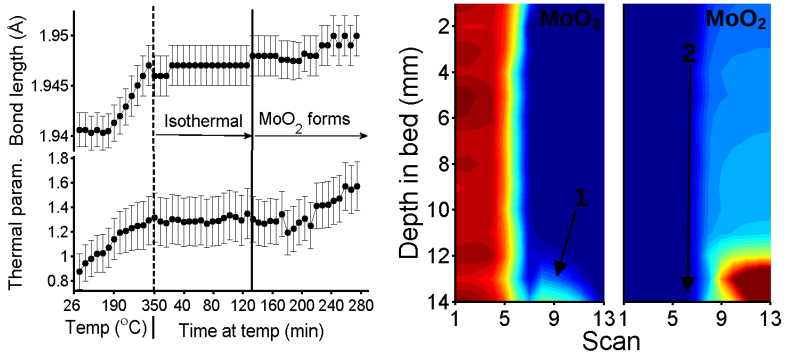

Figure 1. The bond length and thermal parameter of O1 both increase during the formation of MoO_2, indicating oxygen O1 is active within the bulk (a) and intensity plots of MoO_3 consumption and MoO_2 formation profiled along the bed indicating re-appearance (arrow 1) and increased concentration (arrow 2) towards the bottom of the bed (b).

Significance

This work has demonstrated the power of combining high energy diffraction and open cell architectures with multiple techniques to obtain high quality data on catalytic materials in more 'industrial like' environments. We have successfully identified the oxygen extracted from the bulk during MoO_3 reduction and identified that significant volatilization of Mo occurs in the presence of methanol. This knowledge is important in the understanding of the reactivity and deactivation of the industrial FEMO catalyst and demonstrates that the recording of such detailed information will be invaluable in understanding the processes in many catalytic systems, leading to improved performance and catalyst lifetimes.

References

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