Operando X-ray Diffraction Tomography for Revealing Insight into Active Phase Evolution in Catalyst Bodies

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Introduction and Objectives

Industrial catalysis utilizes mm-sized catalyst bodies in fixed bed reactors so as to minimize pressure drops across the reactor vessel. The efficiency of the final catalytic system depends on the nature and distribution of metal/metal oxide 'active species' across the catalyst body although this can normally be affected during the multi-step preparation process. The evolution of the active species from an initial precursor complex delivered via liquid phase impregnation is often a highly convoluted process. In recent times several analytical techniques have been utilized in order to obtain real time 2D and 3D spatial information on the nature of chemical species present on the catalyst during preparation, in order to identify the key physicochemical processes occurring that govern both their spatial distribution and final properties. It is envisaged that, armed with such information better control over these properties could be realized leading to improvements in catalyst performance [1]. Recently we employed the novel technique of synchrotron X-ray Diffraction Computed Tomography (XRD-CT) [2] and demonstrated its capability to image a catalyst body as a function of time to follow the preparation process and to study the catalyst as a reaction (CO methanation) takes place.

Results and Discussion

The experiments were performed at stations ID15A and ID15B of the ESRF (Grenoble, France) using a monochromatic (E = 86.88 (ID15B) or 69.95 keV (ID15A)), 100 μm square section pencil beam with diffracted X-rays recorded on a Pixium 4700 flat panel detector. Dynamic diffraction imaging was employed to follow the in situ calcination (ambient to 500 °C at 2.5 °C/min with dwell of 2 h) and catalytic reaction of a cylindrical catalyst body (diameter = 3 mm; length = 3 mm) impregnated with Ni catalyst precursor materials ($[NiCl_2(en)(H_2O)_4]$ or $[Ni(NO_3)_2(en)(H_2O)_4]$ where en = ethylenediamine). Calcination was performed under an inert gas atmosphere whereas catalytic methanation was performed in a mixture of CO/H_2 in N_2.

Catalyst preparation normally involves two or three steps; impregnation of the catalyst body with the active metal in the form of a metal complex, calcination at high temperatures and in some cases 'activation' in a pre-conditioning gas. XRD-CT was employed to examine this second step (calcination in N_2) of a Ni supported γ-Al_2O_3 catalyst body starting from a $NiCl_2$ source. Crucially we observed the formation of the cubic (fcc) metallic Ni phases via a number of complex intermediate phases. Importantly 2D XRD-CT scans revealed two different crystalline phases forming located at the periphery and in the centre of the body accordingly. Although both phases yielded fcc Ni, the precursor at the periphery did so in one step, while the phase in the centre did so via a 3-4 step process (Fig. 1). This appeared to affect the particle size of the fcc Ni phase with

the fcc Ni particles in the centre of the pellet larger than those seen at the periphery [3]. This will have important implications for the activity/selectivity of these bodies in a catalytic reaction.

In a second recent study, XRD-CT was also combined with absorption-CT to study the phase evolution process in $NiNO_3$ impregnated Ni/γ-Al_2O_3 catalyst bodies during calcination and activation, but more importantly, under true catalytic conditions. As with $NiCl_2$ impregnated catalyst bodies two different, inhomogenously distributed precursors result after the impregnation process although the breakdown of these precursors resulted in the formation of more uniformly-sized fcc Ni nanoparticles. Particles located towards the periphery undergo uncontrolled sintering on exposure to O_2 although this appears to be dependent on both the concentration/ distribution of the Ni and its form (where it is expected that Ni is present in the sample in both crystalline and diffraction silent forms). Reduction in H_2 did not induce further sintering but results in an active fcc Ni containing catalyst for CO methanation. Operando catalytic measurements performed during CO methanation, demonstrated the crystalline metallic fcc Ni component to be remarkably stable over the duration of reaction (~ 3 h @ 450 °C), undergoing no change in phase constitution, spatial distribution or average particle size, leading us to conclude that metallic fcc Ni is the active component of the catalyst for CO methanation [4].

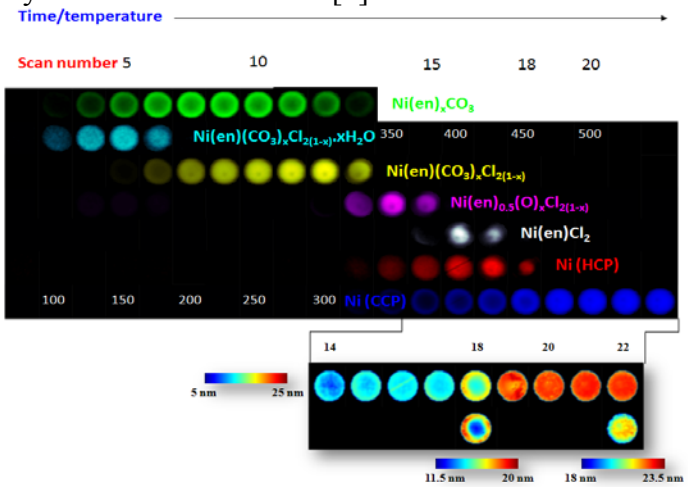

Fig. 1 Reconstructed 2D images of crystalline components features observed in the diffraction patterns as a function of time/temperature during thermal activation of a γ-Al_2O_3-supported $NiCl_2$ catalyst precursor. The color maps indicate the distribution of various solid-state phases. Below, thermal color maps showing the variation in crystallite size (nm). When plotted with a common color axis (top) these indicate the growth of fcc Ni crystallite size as the growth of the phase proceeds. For slices, 18 and 22, the data have been re-plotted with bespoke color axes (shown beneath).

Conclusions

By exploiting rapid, time resolved XRD-CT imaging it has been possible to obtain detailed insight into the complex chemistry occurring within catalyst bodies during catalyst preparation and under reaction conditions and how this influences the distribution of these phases and their final properties.

References

[1] L. Espinosa-Alonso, A. M. Beale and B. M. Weckhuysen, *Acc. Chem. Res. 43*, 1279 (2010).
[2] P. Bleuet, E. Welcomme, E. Dooryhee, J. Susini, J. L. Hodeau, P. Walter, *Nat. Mater. 7*, 468 (2008).
[3] S. D. M. Jacques, M. Di Michiel, A. M. Beale, T. Sochi, M. G. O'Brien, L. Espinosa-Alonso, B. M. Weckhuysen, Paul Barnes *Angew. Chem. Int. Ed. 50*, 10148, (2011).
[4] M. G. O'Brien, S. D. M. Jacques, M. Di Michiel, Paul Barnes, B. M. Weckhuysen, A. M. Beale *Chem. Sci.* (DOI: 10.1039/C1SC00637A).