Beamtime Report
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We have previously investigated the co-operative effect of introducing copper and vanadium in AlPO-5 by deposition (VCu:AlPO-5), a material active in the selective oxidation of propene. We previously proposed a synergistic redox effect when both copper and vanadium was promoting the activity of the reaction. The red-ox properties of these materials were previously established by cycling between propene and oxygen at 350°C and 450°C and for this experiment we carried out temperature programmed reduction in propene to establish the reduction characteristics of the metals. We performed a combined XAS and PXRD experiment whilst monitoring the outlet with a mass spectrometer. Secondly we monitored the stability of the metal species during reaction conditions for varying O_2:propene rations. Deactivation of these catalytic systems is believed to be due to sintering and formation of non-reversible oxide species. To achieve a complete assessment of the co-operative effect of copper and vanadium, the same procedures were performed on the monometallic analogues.

We carried out *in situ* XAS measurements done at the copper k-edge in transmission mode, and at the vanadium k-edge in fluorescence mode, to monitor the speciation of copper and vanadium during the reaction. Experimentally the reaction was studied by heating in propene (1.11 %) to 450°C with a ramp rate of 3°C/min, while collection XAS/PXRD. PXRD was collected by using the new 2D detector at SNBL. This was the first time we used the 2D detector and it worked very well, and made it possible to acquire PXRD data within seconds, a great addition to the SNBL B-station. Figure 1 show XANES at the copper K-edge for VCu:AlPO-5 (left) and copper deposited AlPO-5 (Cu:AlPO-5, right) during reduction. Interestingly VCu:AlPO-5 show a reduction to metallic copper at 450°C, while copper in Cu:AlPO-5 are only present as monovalent copper. Clearly our results show that the presence of vanadium promotes the reduction of copper in propene into metallic state, which has not previously been reported to our knowledge. Figure 2 shows the integrated PXRD diffractograms acquired from the 2D detector at room temperature and at 450°C. As seen in the figure metallic copper is detected at 450°C with PXRD.

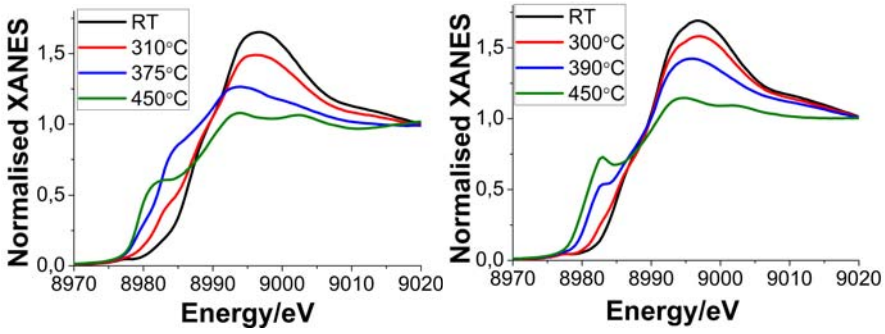

Figure 1: Left: Normalised XANES of VCu:AlPO-5; Right: Normalised XANES of Cu:AlPO-5

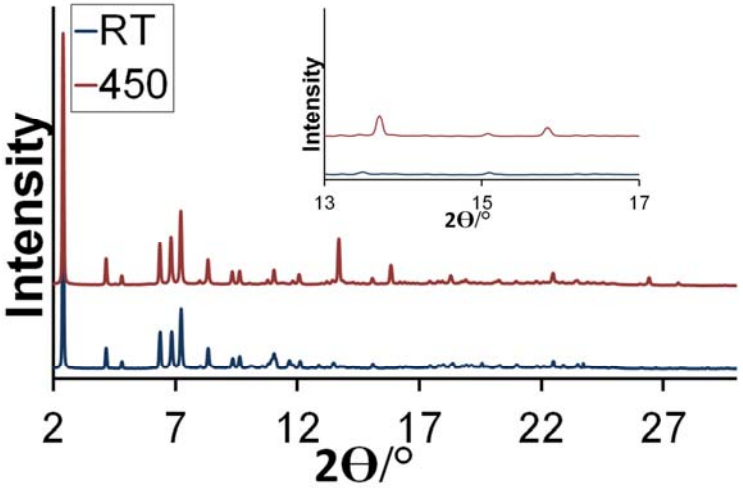

Figure 2: PXRD diffractograms of VCu:AlPO-5 at room temperature and at 450°C; inset: revealing peaks corresponding to metallic copper.