## Beamtime SNBL April 2011 SNBL BM01B

Vanadium supported on micro and mesoporsous materials were studied during propene oxidation The selectove oxidation of propene is of interest as it yields oxygenates which are used industrially.<sup>1-4</sup> Prior to the beamtime, catalytic measurements were done in an in situ cell coupled to a GC-MS. The *in situ* XANES experiments were performed at the vanadium k-edge combined with online mass spectrometer and Raman. We wished to establish the reaction mechanism during the propene oxidation for the vanadium supported materials. The reaction gas consists of propene and oxygen, and as the oxidation of propene is rapid, we needed to cycle the reaction. Meaning first oxygen was sent over the sample, and then oxygen was switched off and propene was introduced to the vanadium systems. By doing this it became possible to see the changes in the pre-edge and absorption edge for vanadium. The XANES datacollection was done in fluorescence mode due to the vanadium k-edge (5465 eV).

Figure 1 a) show the variation in the threshold energy during the reaction and figure 1 b) show the variation in the pre-edge energy during the reaction. It is known from our reference compounds that tetravalent vanadium have a pre-edge energy at 5469.97 eV and a corresponding threshold energy at 5479.88 eV, and pentavalent vanadium have a pre-edge energy at 5470.57 eV and a corresponding threshold energy at 5481.12 eV. From Figure 1 it is clear that vanadium is pentavalent when treated in oxygen, and is reduced in propene to tetravalent vanadium. Upon treatment in oxygen after reduction, vanadium is involved during oxidation of propene, which is rapid, and can therefore not be observed when oxygen and propene is both present in the reaction gas.

Raman scattering provides useful information about the vanadium species present in the sample. Figure 2 show the Raman spectra of the vanadium sample in room temperature and bulk vanadium pentoxide ( $V_2O_5$ ). As seen in the figure, many of the same characteristic peaks for  $V_2O_5$  is present in our sample. This is and indication of  $V_2O_5$  nanoparticles (NP) on the support. Although some of the peaks are shifted to lower wavenumbers, this can be due to different bond distances between the bulk  $V_2O_5$  and the  $V_2O_5$  NPs.<sup>5</sup>

These studies reveal the interaction with  $V_2O_5$  nanoparticles on microporous supports and propene, in which vanadium is reduced by propene, and reoxidised in oxygen.



Figure 1 a) show the variation in the threshold energy during the reaction, b) shows the variation in the pre-edge energy during the reaction



Figure 2 Raman scattering spectra of a) the vanadium sample and b) of bulk V<sub>2</sub>O<sub>5</sub>

## References

- (1) Bettahar, M. M.; Costentin, G.; Savary, L.; Lavalley, J. C. Appl. Catal. A-Gen. 1996, 145,
- (2) Dadyburjor, D. B.; Jewur, S. S.; Ruckenstein, E. Catalysis Reviews: Science and Engineering 1979, 19, 293
- (3) Zhao, C. L.; Wachs, I. E. *Journal of Catalysis* 2008, 257, 181.
- (4) Zhao, C. L.; Wachs, I. E. J. Phys. Chem. C 2008, 112, 11363.
- (5) Hardcastle, F. D.; Wachs, I. E. *The Journal of Physical Chemistry* 1991, 95, 5031.