

## Evaluation and Structural Characterization of DuPont V-P-O/SiO<sub>2</sub> Catalysts

W. Weng\*, N.F. Dummer\*\*, C. Kiely\*, A.F. Carley\*\*, J.K. Bartley\*\*, G.J. Hutchings\*\* and C.J. Kiely\*

\* Department of Materials Science & Engineering, Lehigh University, Bethlehem, PA 18015, USA

\*\* Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, CF10 3AT, UK

For several decades vanadyl pyrophosphate, (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, has been used commercially as a catalyst for the partial oxidation of n-butane into maleic anhydride (MA) [1]. However due to the moderate specificity to MA production, many research groups still continue to investigate the V-P-O catalyst system with the aim of further improving its overall performance. Now a specialized form of V-P-O catalyst has been developed by DuPont for use in a fluidized bed reactor, which consists of a V-P-O core encased by a mechanically protective porous silica shell. Selected research centers worldwide have received samples of this material for analysis, aiming at combining the results generated, in an effort to further understand the functionality of the V-P-O catalyst.

In the current work a wide variety of standard microscopy (*e.g.* SEM and TEM) and spectroscopy (*e.g.* XPS) techniques have been used to understand the structural and chemical composition of this novel V-P-O/SiO<sub>2</sub> catalyst at various stages of its lifetime. In addition, a new SEM-based X-ray ultramicroscopy (XuM) method [2] has been applied for the first time to obtain transmission images and 3D-tomograms of unsectioned particulate catalysts that are in the 50-150 μm size scale. The microstructural and compositional changes occurring in this catalyst material over the course of its industrial lifespan in a fluidized-bed reactor will be described in detail.

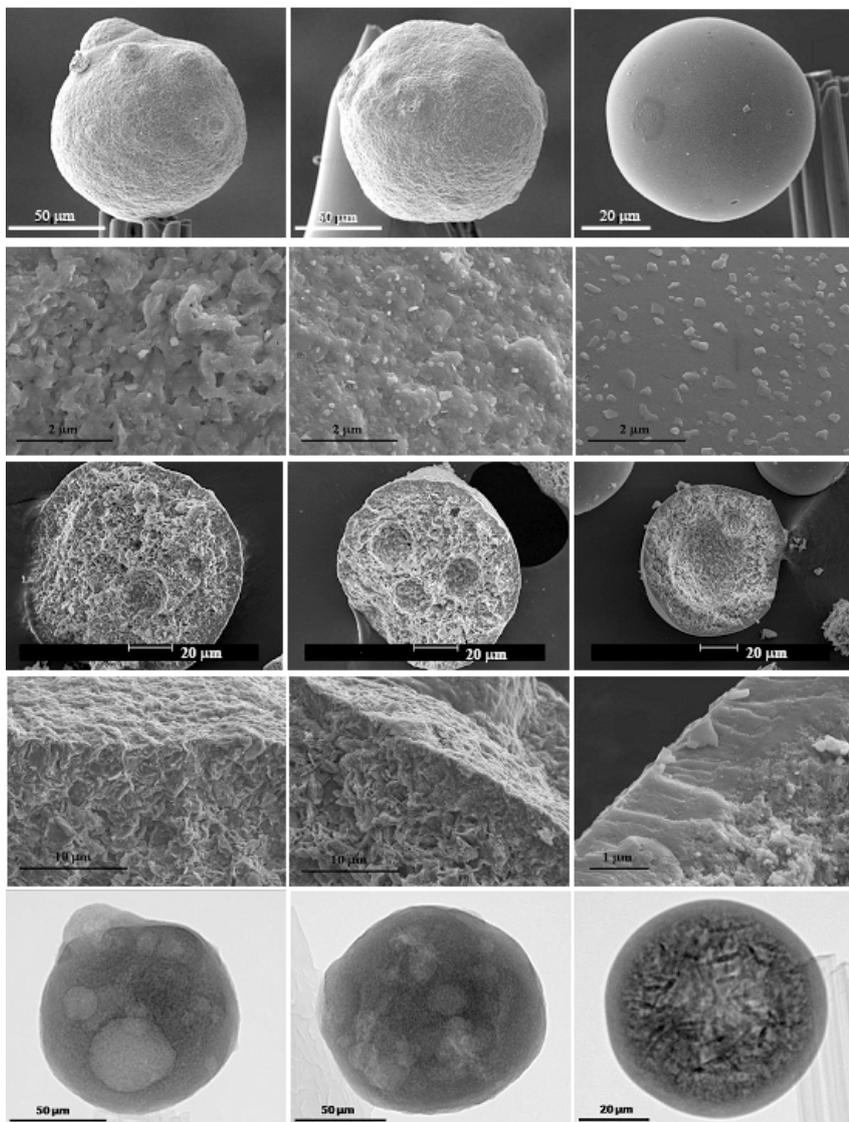
SEM shows that the protective SiO<sub>2</sub> shell surrounding the hemihydrate (VOHPO<sub>4</sub>·0.5H<sub>2</sub>O) precursor is highly microporous and contains multiple fissures (Fig. 1, column 1, row 2). The silica shell surrounding the freshly activated pyrophosphate ((VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>) catalyst still has a rough, porous texture but shows some evidence of additional surface debris (Fig. 1, column 2, row 2). After 100-days of exposure to mechanical agitation and abrasion in the reactor environment, the silica shell becomes markedly smoother, with numerous crystalline V-P-O fragments physically embedded in the surface (Fig. 1, column 3, row 2). When imaged by a combination of X-ray absorption and phase contrast in the XuM, the 2-5 μm thick SiO<sub>2</sub> shell is clearly visible as well as the interior V-P-O rosette material (Fig. 1, row 5). TEM imaging and electron diffraction studies (Fig. 2) indicate that the 100-day used catalyst contains significant amounts of β-VOPO<sub>4</sub> and δ-VOPO<sub>4</sub> phases, which are known to decrease the MA selectivity, in addition to (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> [3]. The appearance of V<sup>5+</sup> (*i.e.* VOPO<sub>4</sub>) species in the used catalyst is also confirmed by XPS analysis. In addition, our XuM studies (Fig. 3) show that a significant fraction of the 100-day used particles are hollow, having completely lost their internal V-P-O material, while still retaining an almost spherical morphology. Such drastically modified particles are also likely to be catalytically inactive. Our detailed microstructural observations will be correlated with catalytic performance measurements that have been performed on these V-P-O/SiO<sub>2</sub> materials.

### References

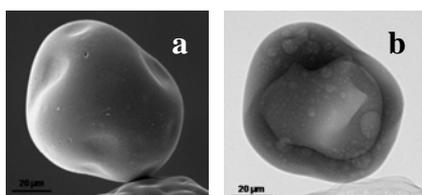
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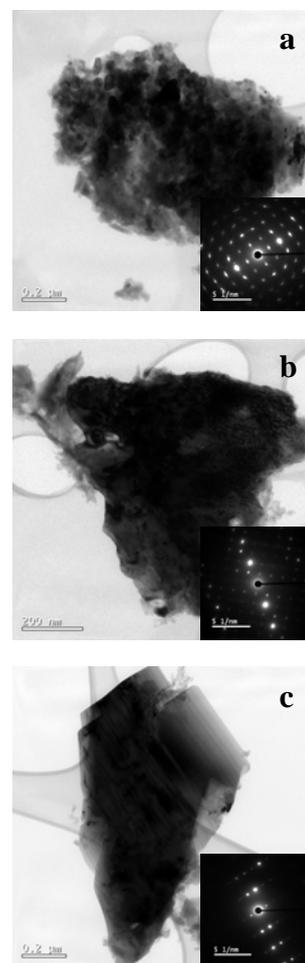
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**Fig. 1** SEM (rows 1-4) and XuM (row 5) micrographs of the precursor material (column 1), freshly activated catalyst (column 2) and 100-day used catalysts (column 3).



**Fig. 3** (a) SEM and (b) XuM micrographs of a 100-day used particle showing the presence of internal porosity.



**Fig. 2** TEM micrographs and diffraction patterns (inset) of 100-day used particles showing the presence of (a)  $(VO)_2P_2O_7$ , (b)  $\beta$ - $VOPO_4$  and (c)  $\delta$ - $VOPO_4$  phases.