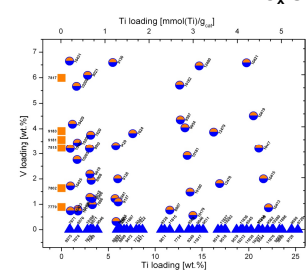
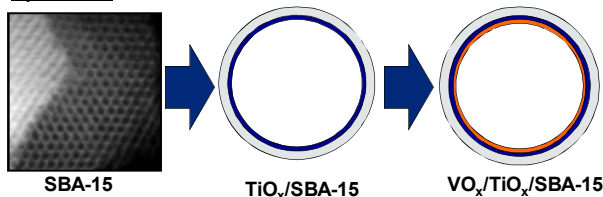


Introduction:

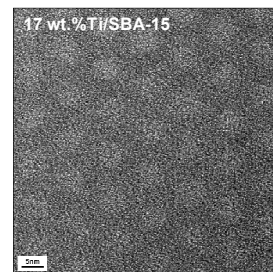
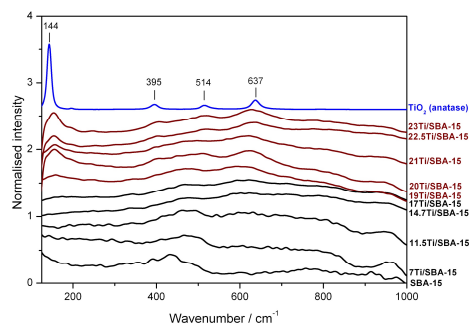
Vanadium based catalysts have shown promise as catalysts in ODH reactions exhibiting a comparatively high yield in oxidative dehydrogenation of propane. The reactivity of supported vanadia catalysts has been shown to depend strongly on the oxide support with reducible oxides (e.g. titania) exhibiting much higher turnover frequencies for ODH reactions compared to irreducible oxides (e.g. silica). Studies addressing the influence of the support on ODH reactivity are complicated by the different structural properties of the supports of interest, which can affect the dispersion of the vanadia phase. Here, we report the synthesis and characterisation of bilayered, inverted core-shell catalysts where a well-defined, mesoporous SBA-15 support is used to stabilise a layer of titania upon which vanadia is deposited.

Synthesis:



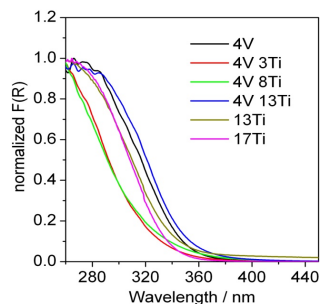
- Catalyst samples prepared by sequential grafting of titania and vanadia on mesoporous SBA-15.
- Variation of the Ti and V content lead to the development of a **comprehensive sample matrix**.

TiOx/SBA-15 supports:

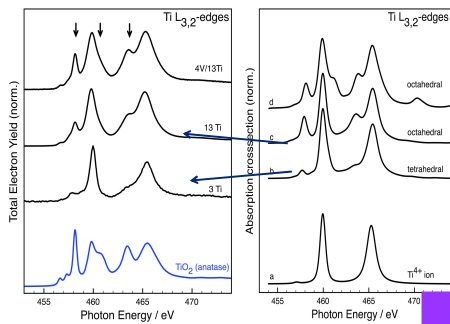


- Sequential deposition of titania on SBA-15 lead to unsurpassed loading of dispersed titania species.
- 3D titania species observed only when the Ti concentration exceeds OH concentration of the SBA-15 support.

Electronic structure:

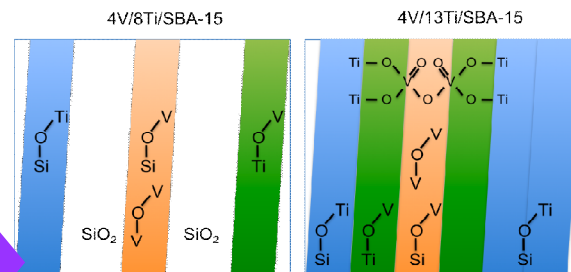


- Sub-monolayer titania stabilises Td vanadia clusters.
- Higher titania coverage favours the situation observed for 4V/SBA-15.
- 4V/13Ti/SBA-15 approximate 'monolayer' concentration of V & Ti components.



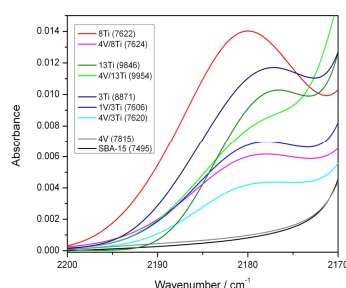
- Pre-peak at 458.1 eV and shoulder at 460.7 eV indicates Ti-O-Ti linkages.
- CTM calculations – show sensitivity of Ti-NEXAFS to local bonding.
- NEXAFS is in agreement with UV-vis: 3Ti has mainly Td, 13Ti more Od.

Enhancement of catalytic activity via self-organization of the active phase

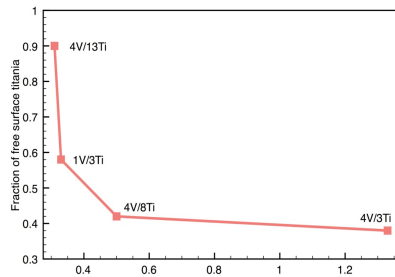


- Mixed V-Ti 'monolayer' catalysts exhibit maximum productivity in propylene formation. We attribute this to the high abundance of V-O-Ti bonds.
- That these catalysts exhibit higher selectivity compared to V/TiO2 catalysts is attributed to the unique 2D surface condition created by the interaction between dispersed vanadia species with polymeric titania domains.

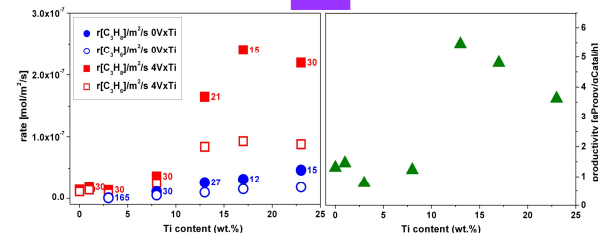
FTIR spectra of adsorbed CO:



- 2180 cm⁻¹ band reveals accessible Ti⁴⁺ sites and generally increases with Ti loading.
- Attenuation of this feature with addition of V indicates formation of Ti-O-V bond(s). The level of attenuation is greatest for low Ti loaded samples.
- When V is present in excess some Ti⁴⁺ sites persist.



Catalytic testing:



- Promotional effect of Ti observed by comparing V/Ti/SBA-15 with V/SBA-15.
- 4V/13Ti/SBA-15 sample shows unprecedented high propylene productivity.