

# Exploring the influence of the support in vanadium oxide catalysts for partial oxidation of light alkanes

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## Introduction

Oxidative dehydrogenation (ODH) of light alkanes is an attractive process since the energy demand for this reaction is substantially lower than conventional cracking and dehydrogenation pathways currently applied in industry. Vanadium based catalysts have shown promise as effective catalysts in oxidative dehydrogenation reactions showing a comparatively high yield in, for example, oxidative dehydrogenation of propane [1,2]. 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). For methanol, ethanol, and propane ODH the activity of the catalyst increases in the order of  $\text{VO}_x/\text{SiO}_2 < \text{VO}_x/\text{Al}_2\text{O}_3 < \text{V}_2\text{O}_5 < \text{VO}_x/\text{ZrO}_2 < \text{VO}_x/\text{CeO}_2$ , with  $\text{VO}_x/\text{TiO}_2$  showing exceptionally high activity in ethanol and propane oxidation [3]. Though significant progress has been made in understanding the influence of the support effect on ODH reactivity, studies can be complicated by the fact that the supports of interest have widely different structural properties (e.g. surface area, pore size distribution), which can affect the dispersion of the vanadia phase. One way to deconvolute these factors is to employ bilayered inverted core-shell catalysts where a well-defined mesoporous support is used to stabilise a layer of metal oxide upon which vanadia may be deposited yielding a series of catalysts with different metal oxide guest phases that have a comparable surface area and pore size. In this manner, the surface vanadia density can be more readily controlled thereby assisting meaningful comparison between different catalysts. In addition, such layered materials mimic the planar model systems thus facilitating comparison with surface science measurements.

## Experimental

Catalyst series aiming to deposit a monolayer of each metal oxide within the pores of a well-defined high surface area mesoporous silica support (SBA-15) were synthesised by sequential grafting of metal alkoxides utilizing structural OH groups as defined anchoring points [4]. Sub-monolayer coverages of vanadia are then deposited upon the Ti oxide guest phase yielding a bi-layered inverted core-shell structure. An extensive matrix of catalysts has been synthesized including systematic combination of V and Ti loadings (Fig. 1).

## Results/Discussion

The anchorage of the metal oxide species in the hierarchical pore system of SBA-15 has been studied by nitrogen adsorption showing that vanadium oxide preferentially fills the micropores while titanium oxide is mainly located on the walls of the mesopores. Analysis of the pore volume upon increasing metal oxide coverage in the bi-layered materials suggests preferential grafting of vanadium on titanium oxide on sub-monolayer Ti/SBA-15 materials. This result is in agreement with FTIR spectroscopy of adsorbed CO that allows the detection of  $\text{TiO}_x$  species that are not covered by vanadia. However, total coverage of  $\text{TiO}_x$  has not been observed on sub-monolayer Ti/SBA-15, even in the presence of excess vanadia. Combined analysis by  $\text{N}_2$  adsorption and SAXRD revealed that the integrity of the mesopore system is maintained up to total metal loadings of greater than 25 wt.-% resulting in metal oxide films with a thickness of ca. 1-2 nm. Raman spectroscopy and diffuse reflectance UV-vis spectroscopy are used to detect the presence of 3D metal oxide structures, while infrared measurements reveal residual OH groups that can be used to anchor additional metal oxide species. The band maximum of the UV-vis spectra (200-300 nm) and the absorption edge energy values suggest progressive polymerization of  $\text{TiO}_x$  with increasing Ti-loading. Three dimensional polymeric titanium oxide domains start to form at loadings above 23 wt.-% Ti. UV-vis spectroscopy indicates that titania promotes de-polymerization of vanadia species in the bi-layered catalysts (Fig. 2). Accordingly, Raman spectroscopy suggests a different structure of supported vanadia species on Ti/SBA-15, which is indicated by a shift of the V=O stretching vibration from  $1033 \text{ cm}^{-1}$  in V/SBA-15 to  $1025 \text{ cm}^{-1}$  in V-Ti/SBA-15 and reflected in an enhancement in performance of vanadia deposited on amorphous sub-monolayer  $\text{TiO}_2/\text{SBA-15}$  supports relative to both  $\text{VO}_x/\text{SBA-15}$  and  $\text{VO}_x/\text{TiO}_2$  catalysts.

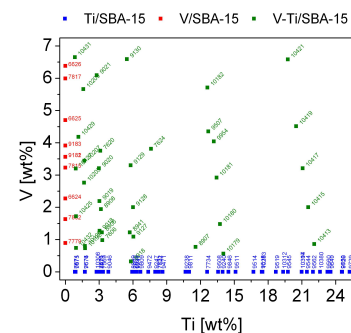


Fig. 1. Explored catalyst matrix.

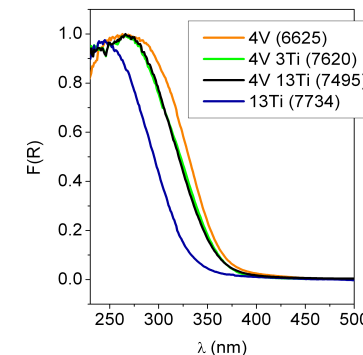


Fig. 2. UV-vis spectra of (V,Ti)/SBA-15.

## References

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