



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

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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 oxidative dehydrogenation of propane [1,2]. The reactivity of supported vanadia catalysts has been shown to depend strongly on the support with reducible oxides (e.g. titania) exhibiting much higher turnover frequencies for ODH reactions compared to irreducible oxides (e.g. silica). VO_x/TiO_2 show significantly higher propane ODH activity than VO_x/SiO_2 analogues [3]. Understanding the influence of the support effect on ODH reactivity can be complicated by the fact that the supports have widely differing structural properties, 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 subsequently deposited. Such layered materials mimic the planar model systems thus facilitating comparison with surface science measurements.

Experimental

Catalyst supports aiming to deposit a monolayer of titanium oxide within the pores of a well-defined high surface area mesoporous silica support (SBA-15) were prepared by sequential grafting of titanium isopropoxide utilizing structural OH groups as defined anchoring points. The resulting materials were extensively characterized by complementary spectroscopic techniques (FTIR, Raman, UV-vis). Dispersed vanadium structures are subsequently deposited upon the Ti oxide guest phase with

the aim of producing 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

Infrared spectroscopy demonstrates the anchoring of titanium oxide structures via reaction with OH groups presented by the SBA-15 support. Combined analysis by N₂ adsorption and SAXRD revealed that the integrity of the mesopore system is maintained up to titanium loadings in excess of 25 wt.%. Raman spectroscopy shows the formation of nano-crystalline anatase domains at loadings in excess of a theoretical monolayer, i.e. where the number of deposited Ti atoms equals the number of native SBA-15 OH groups. Analysis of the line shape indicates these particles to be of exceptionally small dimension (2 nm), which therefore may be stabilised in the microporous corona of the SBA-15. Raman spectroscopy further indicates a different character of supported vanadia species on Ti/SBA-15 supports compared with pure SBA-15, which is demonstrated by a shift of the V=O stretching vibration from 1025 cm⁻¹ to 1033 cm⁻¹. This is further reflected by an enhancement in catalytic performance (Fig. 2), indicating a clear synergism between vanadia and titania deposits.

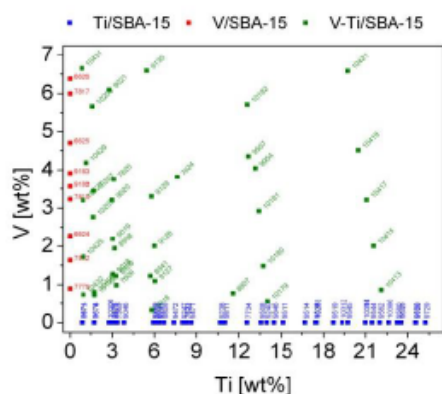


Figure 1: Extensive sample matrix.

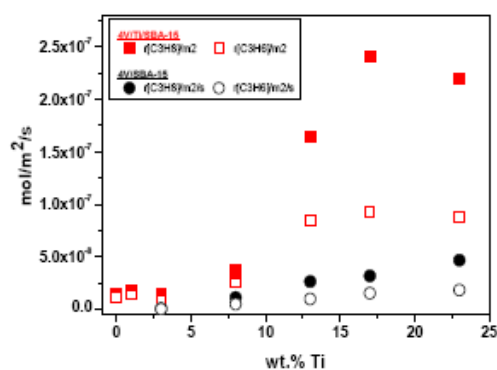


Figure 2: Catalytic activity comparisons

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2. M. Banares, *Catal. Today*, 51 (1999) 319.
3. A. Dinse, B. Frank, C. Hess, D. Habel, R. Schomacker, *J. Mol. Catal. A*, 289 (2008) 28.