

Synthesis and Characterization of Supported Vanadium Oxides for the Oxidative Dehydrogenation of Cyclohexane

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Introduction

In recent years, oxidative dehydrogenation (ODH) has been proposed as a promising alternative to traditional dehydrogenation processes for the production of light olefins [1,2]. Among ODH catalysts, supported vanadium oxides (VOx) have high activity and are well studied in the literature [3]. The active and selective sites of these catalysts, however, remain ill-defined and are not well known. Furthermore, the ODH reaction is limited by overoxidation to CO_x products. Since both the partial and total oxidation reactions share common mechanistic features, a major challenge lies in the design of a selective catalytic system that favors partial oxidation. A better understanding of the catalytic properties of supported vanadium oxides requires a well defined catalyst system. In the presented work, a series of supported VO_x catalysts with varying nuclearity were prepared using organometallic grafting and studied in the ODH reaction of cyclohexane.

Materials and Methods

All syntheses were carried out with rigorous exclusion of oxygen and moisture in flame- or oven-dried Schlenk-type glassware on a dual-manifold Schlenk line, interfaced to a high-vacuum manifold (10⁻⁶ Torr). All hydrocarbon solvents were dried and degassed over Na/K alloy and transferred in vacuo immediately prior to use. Ziegler θ-Al₂O₃ (S_{BET} = 137 m²/g), precipitated θ-Al₂O₃ (S_{BET} = 121 m²/g), and γ-Al₂O₃ (S_{BET} = 127 m²/g) supplied by Johnson Matthey were crushed and sieved to 80-120 μm, dried at 120°C overnight, calcined in O₂ at 550°C for 8hrs, then evacuated under 10⁻⁶ Torr at 400°C. A series of organometallic vanadium cluster compounds: VO(Mes)₃, [(Mes)₃V]₂(μ-O)₂ and [(η-C₅Me₅)V]₄(μ-O)₆ were synthesized according to literature procedures [4-7]. Supported catalysts were prepared using the organometallic grafting technique. Following grafting, the supported catalysts were calcined at 550°C in O₂ for 2hrs, then heated at 400°C at 10⁻⁶ Torr. Catalyst loadings ranged from 0.05 to 0.75 atoms V/nm² as determined by ICP-AES with a Varian Vista-MPX instrument. Diffuse reflectance UV-Vis spectra were measured in the range of 200-800 nm on a Varian Cary 500 UV-Vis-NIR spectrophotometer equipped with a diffuse-reflectance attachment, with MgO as a reference. UV-Raman spectra were excited at 244nm generated by an argon ion laser (Lexel 95 SHG). Catalysis experiments were carried out in a quartz flow reactor.

Results and Discussion

Through controlled surface reactions with the highly reactive organometallic precursors, a series of supported VOx catalysts were prepared. The predicted reactions are shown in Figure 1 below. The grafting reactions were monitored by ¹H NMR and stoichiometric ligand removal was observed.

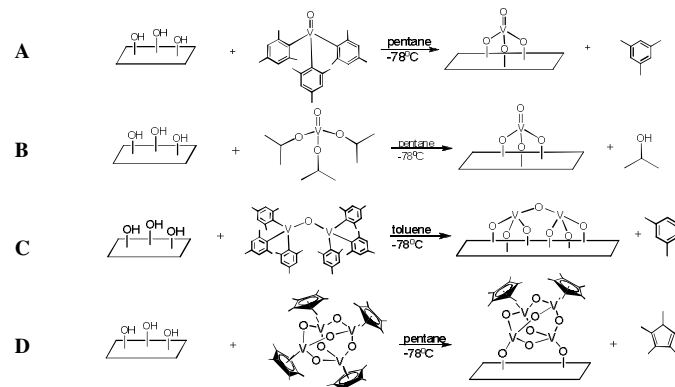


Figure 1. Grafting reactions for A) VO(Mes)₃, B) VO(OⁱPr)₃, C) [(Mes)₃V]₂(μ-O)₂, and D) [(η-C₅Me₅)V]₄(μ-O)₆ alumina supports

Edge energies of the supported catalysts, determined by DRS UV-Vis, decrease as the vanadium cluster size of the organometallic precursor increases. This signifies an increase in the number of V-O-V type bonds present in the samples prepared with the [(η-C₅Me₅)V]₄(μ-O)₆ precursor compared with samples prepared using the monomeric VO(Mes)₃ precursor. Further evidence of cluster size dependence on catalyst precursor was observed with a shift in the V=O band frequency in the UV-Raman spectra. The V=O band was shifted to higher frequency than that of the monomer when the catalysts were loaded with [(Mes)₃V]₂(μ-O)₂. Similar shifts have previously been observed with increasing vanadium loading [8]. EXAFS, solid state ⁵¹V NMR, and ODH catalytic experiments are currently underway.

Significance

Through controlled catalyst synthesis, we hope to design catalyst surface species for further understanding of catalytic mechanisms. In particular, we are working toward the development of a structure-function relationship for the ODH reaction mechanism.

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