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Structure and reaction dynamics of vanadium oxide surface species supported on Ti-SBA-15

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Introduction

V_2O_5 dispersed on high surface area metal oxides, such as SiO_2 , Al_2O_3 , TiO_2 , or ZrO_2 , has been the topic of many experimental and theoretical approaches targeted at a deeper understanding of heterogeneous oxidation catalysis on a molecular level.¹ Structure, reactivity and stability of the active, two-dimensional vanadium oxide surface species depend on catalyst synthesis, nature of the support and reaction conditions. In the present work, highly dispersed V_xO_y supported on mesoporous silica (SBA-15) modified with titania has been used as a model system to investigate the vanadia-support interaction and the effect of the degree of aggregation of vanadium oxo-species on the reactivity in oxidative dehydrogenation (ODH) of propane applying *in-situ* spectroscopic techniques.

2. Experimental

Two series of catalysts with either titania or vanadia supported on SBA-15 containing 1-20 wt.-% of the metal have been synthesized *via* wet impregnation with vanadium and titanium alkoxides. Moreover, the V content has been varied using Ti/SBA-15 with different Ti loadings as support. SBA-15 has been prepared in large scale in an automated laboratory reactor to minimize batch effects of the SBA-15 support.² The catalysts were characterized using a variety of techniques including XRD, TEM, NEXAFS, UV-vis, FTIR, and Raman spectroscopy.

3. Results and discussion

Highly ordered mesoporous supports with large surface area such as SBA-15 allow for the deposition of a high number of well-defined two-dimensional metal oxide species. The textural integrity of SBA-15 is maintained even at high titania, vanadia and V/Ti oxide loadings. The vanadium precursor reacts with all silanol groups available and preferentially fills the micropores of the support. Vanadia strongly increases the number of Brønsted acid sites on the catalyst surface. With increasing loading, vanadia oligomerizes to a mixture of species with different nuclearity. In contrast, titania forms distorted tetrahedral species at all loadings as shown by NEXAFS, FTIR, and UV-vis spectroscopy. In-situ UV-vis reveals similar electronic structure of the V species on SBA-15 and Ti-SBA-15 in the calcined catalysts. Under reaction conditions of propane ODH, differentiation occurs reflecting the presence of the Ti species. The catalyst becomes more selective when larger V-O-V oligomers characterized by a band at 390 nm disappear. This is in agreement with changes in the oxygen coordination observed by NEXAFS and interpreted in terms of spreading of vanadia on titania. Moreover, titania limits the reducibility of vanadium under reaction conditions.

4. Conclusions

Due to hydrolysis of V-O-Si bonds, silica supported vanadia species are structurally highly dynamic during thermal pretreatment of the catalyst and by varying the reaction conditions of ODH of propane. The combination of vanadia and titania suppresses the structural dynamics of vanadia surface species and prevents deep reduction of vanadium.

References

1. I. Muylaert, P. Van Der Voort, PCCP 11 (2009) 2826.
2. P. Gruene, T. Wolfram, K. Pelzer, R. Schlögl, A. Trunschke submitted to Catal. Today.