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Synthesis of vanadium and titanium oxides on SBA-15 as catalysts for the oxidative dehydrogenation of propane

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V₂O₅ dispersed on high surface area metal oxides, such as SiO₂, Al₂O₃, TiO₂, CeO₂ or ZrO₂, has been the subject of many experimental and theoretical approaches targeted at a deeper understanding of heterogeneous oxidation catalysis on a molecular level. 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, structure and reactivity of vanadia supported on titania-modified mesoporous silica (SBA-15) was studied. Large batches of SBA-15 have been synthesized in an automated laboratory reactor applying a procedure that has been adopted and up-scaled from literature recipes. Reduced temperature gradients within the reaction vessel allow the synthesis of homogeneous, well-defined SBA-15 in large batch sizes.^[1] Two-dimensional titania species have been grafted

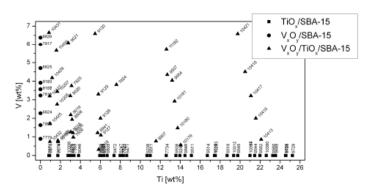


Fig. 1. Matrix of synthesized V/Ti-SBA-15 catalysts

onto silica approaching stepwise a monolayer coverage. The complex interaction between vanadium oxide and silica or molecular titanium oxide species has been studied by preparing a whole matrix of mono- and bilayered model catalysts (Fig. 1). In-situ spectroscopic techniques, such as Raman, UV-vis, FTIR, and photoelectron spectroscopy have been ap-

plied to investigate molecular structure and distribution of the surface vanadium oxide species. By anchoring the metal oxides using a multiple sequential procedure, the integrity of the mesopore system of the SBA-15 was maintained within the whole matrix. The maximum metal loading corresponds to 2.7 mmol V/g_{SBA-15} and 5.8 mmol Ti/g_{SBA-15}, respectively. Titania forms distorted tetrahedral species with different degree of oligomerization. A mixture of 1 D and 2 D tetrahedral vanadia species are present at all loadings, whereas 5-fold coordinated vanadium is found in the catalysts containing V loadings close to the monolayer. The application of in-situ methods with verified catalytic performance and contact times revealed that vanadia species are subjected to structural changes under reaction conditions of oxidative dehydrogenation of propane. At steady state, the molecular structure of vanadia species is similar for catalysts with different V loadings. Titania and steam favour re-structuring by stabilization of selective oligomeric vanadia species in tetrahedral coordination.

[1] P. Gruene, T. Wolfram, K. Pelzer, R. Schlögl, A. Trunschke, Catalysis Today 157 (2010) 137.