EUROPEAN SYNCHROTRON RADIATION FACILITY
INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

	Experiment title: Unveiling the Structure of Single-site Isolated Bimetallic V5+-Oxo Species by X-ray Absorption Spectroscopy	**Experiment number**: 30-02 1081
Beamline: 30B	**Date of experiment**: from: 23 Jul 2014 to: 30 Jul 2014	**Date of report**:
Shifts: 18	**Local contact(s)**: Isabelle Llorens	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Goh S.*, Hogerl M.*, Zhu, H.*, Ould-Chikh, S.*, D'Elia, V., Basset, J.-M., Barman, S., Maity, N

KAUST Catalysis Center (KCC), King Abdullah University of Science and Technology, Thuwal, Saudi Arabia

Report:

1) VO_x/SiO_2 Catalyst Prepared by Grafting $VOCl_3$ on Silica for Oxidative Dehydrogenation of Propane

Zhu, H., Ould-Chikh, S., Dong, H., Llorens, I., Saih, Y., Anjum, D.H., Hazemann, J.-L., Basset, J.-M *ChemCatChem* 2015, 7, 3332 –3339

Abstract

The VO_x/SiO_2 catalysts for oxidative dehydrogenation of propane were synthesized by a simple grafting method. The $VOCl_3$ was first grafted at the surface of SiO_2, which was dehydrated at different temperature (from 200 to 1000°C). The formed grafted complexes were then calcined in air, leading to the formation of VO_x/SiO_2 catalysts. The synthesized catalysts were characterized by nitrogen adsorption, SEM, Raman spectroscopy, temperature-programmed reduction, and extended X-ray absorption fine structure analysis. The SiO_2 pretreatment temperature has an

evident effect on the loading and dispersion of VO_x on SiO_2, which finally affects their catalytic performance. High SiO_2treatment temperature is beneficial to dispersing the vanadium oxide species at the SiO_2 surface. These materials are efficient catalysts for the catalytic oxidative dehydrogenation of propane to propylene. The best selectivity to propylene is achieved on the $VO_x/SiO_{2\text{-}(1000)}$ catalyst. The high selectivity and activity are well maintained for three days catalytic reaction. Silica likes it hot: The SiO_2 pretreatment temperature of grafted VO_x/SiO_2 catalysts has an evident effect on the loading and dispersion of VO_x on SiO_2, which finally affects the catalytic performance. The high selectivity and activity in propane oxidative dehydrogenation obtained on the VOx/SiO2-(1000) catalyst persists over three days reaction time.

2) Single-Site VOx Moieties Generated on Silica by Surface Organometallic Chemistry: A Way To Enhance the Catalytic Activity in the Oxidative Dehydrogenation of Propane

Barman, S., Maity, N., Bhatte, K., Ould-Chikh, S., Dachwald, O., Haeßner, C., Saih, Y., Abou-Hamad, E., Llorens, I, Hazemann, J.-L, Köhler, K., D'Elia, V., Basset, J.-M., *ACS Catalysis.*, 2016, 6 (9), pp 5908–5921

Abstract

We report here an accurate surface organometallic chemistry (SOMC) approach to propane oxidative dehydrogenation (ODH) using a μ^2-oxo-bridged, bimetallic $[V_2O_4(acac)_2]$ (1) (acac = acetylacetonate anion) complex as a precursor. The identity and the nuclearity of the product of grafting and of the subsequent oxidative treatment have been systematically studied by means of FT-IR, Raman, solid-state (SS) NMR, UV-vis DRS, EPR and EXAFS spectroscopies. We show that the grafting of 1 on the silica surface under a rigorous SOMC protocol and the subsequent oxidative thermal treatment lead exclusively to well-defined and isolated monovanadate species. The resulting material has been tested for the oxidative dehydrogenation of propane in a moderate temperature range (400-525 °C) and compared with that of silica-supported vanadium catalysts prepared by the standard impregnation technique. The experimental results show that the catalytic activity in propane ODH is strongly upgraded by the degree of isolation of the VO_x species that can be achieved by employing the SOMC protocol.