An Oxidative Dehydrogenation catalyst: a VO_x/WO_x catalyst on mesoporous silica

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Introduction

Olefins, more specific in this case propylene, are used for a great vary of chemical processes such as e.g. production of plastics (polypropylene). Due to an increase in propylene consumption for these processes there is a necessity to replace existing endothermic processes such as e.g. steam cracking to answer to this high propylene demand.
Oxidative Dehydrogenation (ODH) is in comparison to these processes energetically more favorable due to its exothermic characteristic (Figure 1). Only the availability of an appropiate catalyst with a high yield (=combined high conversion and selectivity) is lacking at this point.

We are investigating a VO_x/WO_x catalyst supported on silica for the ODH of propane. In this part of the research program the activity of pure VO_x systems are studied and compared to VO_x/WO_x systems.

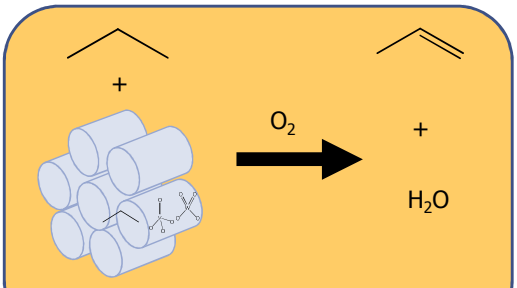

Figure 1: ODH of propane to propylene over a VO_x/WO_x supported catalyst.

Synthesis

Mesoporous silica was impregnated with a NH_4VO_3 solution via a dry impregnation method, Incipient Wetness Impregnation. This impregnation method only requires a NH_4VO_3 solution with a volume equal to the pore volume of the mesoporous material, in this case 0.75 mL/g (see Figure 2). The concentration of the NH_4VO_3 solution varies between 0.1 – 2.0 mmol V/g silica.

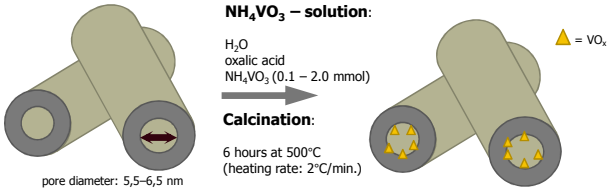

Figure 2: Graphical presentation of the impregnation of silicagel with NH_4VO_3

VO_x/WO_x samples were synthesized by applying the same method with the only difference that a mixed NH_4VO_3 – $(NH_4)_{10}H_2(W_2O_7)_6$ solution was impregnated.

X-Ray Diffraction - XRD

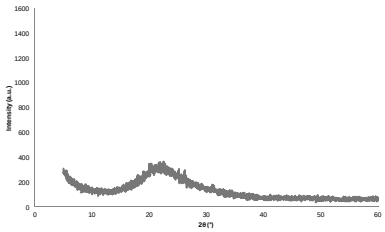

Figure 3: XRD diffractogram of sample 2.0 mmol V/g silica.

XRD diffractograms of all the VO_x samples do not show any reflections originating from V_2O_5 crystals indicating that there are no detectable clusters formed even at high loadings (see Figure 3). The crystallites found in Raman are therefore very small and thus below the detection limit of the XRD (< 3 nm).

Temperature Programmed Reduction - TPR

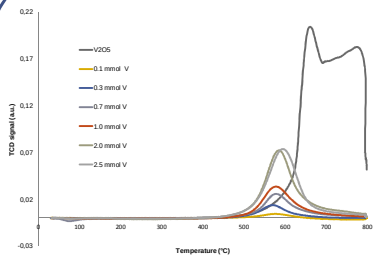

Figure 3: H_2-TPR of VO_x impregnated samples.

H_2-TPR (Figure 3) shows that the bulk V_2O_5 exhibits a different activity in comparison with supported VO_x sites. There is no remarkable difference in reactivity with increasing loading, T_{max} (~580°C) remains more or less the same. Surprisingly the 2.0 mmol VO_x sample, showing crystalline peaks in Raman, does not perform differently in TPR.

The doping with WO_x does not reduce the T_{max} and the presence of WO_x has no effect on the reactivity of the VO_x sites during H_2-TPR (Figure 4). It is supposed that the WO_x reduces the coalescence but shows no catalytic synergy.

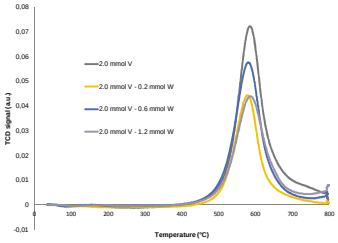

Figure 4: H_2-TPR of VO_x/WO_x impregnated samples.

Raman Spectroscopy

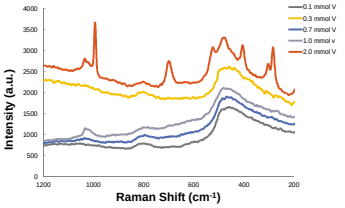

Figure 5: Raman spectra of VO_x impregnated samples.

Figure 5 shows the typical bands of crystalline V_2O_5 at a loading of 2.0 mmol V/g silica. The other samples contain isolated as well as oligomeric vanadium species.

Adding WO_x to the mixture reduces the coalescence of the samples. Figure 6 clearly shows that the crystalline V_2O_5 vibrations disappear.

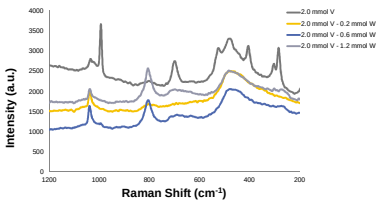

Figure 6: Raman spectra of VO_x/WO_x impregnated samples .

Acknowledgments

I. Ascoop is grateful to the Long Term Structural Methusalem grant nr. 01M00409 Funding by the Flemish Government and Ghent University.

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