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 appropriate 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.

Synthesis

Mesoporous silica was impregnated with a NH$_4$VO$_3$ solution via a dry impregnation method, Incipient Wetness Impregnation. This impregnation method only requires a NH$_4$VO$_3$ 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$_4$VO$_3$ solution varies between 0.1 – 2.0 mmol V/g silica.

**Figure 2:** Graphical presentation of the impregnation of silicagel with NH$_4$VO$_3$.

VO$_x$/WO$_x$ samples were synthesized by applying the same method with the only difference that a mixed NH$_4$VO$_3$ – (NH$_4$)$_2$H$_2$(W$_2$O$_7$)$_3$ solution was impregnated.

Raman Spectroscopy

Figure 5 shows the typical bands of crystalline V$_2$O$_5$ at a loading of 2.0 mmol V/g silica. The other samples contain isolated as well as oligomeric vanadium species.

**Figure 5:** Raman spectra of VO$_x$ impregnated samples.

**Figure 6:** Raman spectra of VO$_x$/WO$_x$ impregnated samples.

Raman spectroscopy of VO$_x$/WO$_x$ samples. Adding WO$_x$ to the mixture reduces the coalescence of the samples. Figure 6 clearly shows that the crystalline V$_2$O$_5$ vibrations disappear.

X-Ray Diffraction - XRD

XRD diffractograms of all the VO$_x$ samples do not show any reflections originating from V$_2$O$_5$ 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).

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

**Figure 4:** H$_2$-TPR of VO$_x$/WO$_x$ impregnated samples.

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.

Temperature Programmed Reduction - TPR

H$_2$-TPR (Figure 3) shows that the bulk V$_2$O$_5$ 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.

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