Design of a VO$_x$-WO$_x$ Catalyst on Mesoporous Titania

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Introduction

Oxidative Dehydrogenation (ODH) possesses a great deal of beneficial characteristics and is a promising route toward selective olefin production (see Figure 1). ODH is more attractive than other processes such as steam cracking, FCC and catalytic dehydrogenation due to its exothermic characteristic and the lack of thermodynamic limitations.

The focus of this research lies on vanadium based catalysts. Vanadium containing catalysts are widely used for several oxidation reactions.

In this project VO$_x$ and WO$_x$ are deposited on commercially available mesoporous titania (Hombikat M311) via 2 different synthesis routes. For future work VO$_x$ and WO$_x$ will be deposited on in-house made mesoporous titania via the Evaporation Induced Self Assembly (EISA).

Synthesis Catalyst

Comparing the Raman spectra of the VO$_x$-WO$_x$ samples obtained via a dry impregnation and a wet impregnation route let us conclude the following:

1 – Considering Figure 2 there can be concluded that the mesoporous titania supporting material remains in the anatase phase and that no rutile is formed upon calcination after impregnation.

2 – The zoom of the Raman spectrum in Figure 2 shows a signal at ~1020 cm$^{-1}$ meaning that both samples contain VO$_x$ in the monovanadate phase. However for the sample generated by the MDD method there is no distinct signal, only a shoulder. H$_2$-TPR will give more information.

3 – In every sample there is a signal at 800 cm$^{-1}$ which is correlated with the presence of WO$_x$. The only sample which generates WO$_x$ signal at 975 cm$^{-1}$, is the MDD sample (see Figure 3). This would explain the plateau and the presence of a shoulder rather than a distinct peak.

H$_2$-TPR

Figure 4 gives additional information which confirms our interpretation of the Raman spectra. Due to the fact that both samples have a similar T$_{MAX}$ (~450°C), which correlates with the nature of the VO$_x$ species, there can be concluded that the VO$_x$ species is obtained in its isolated monovanadate formation which is independent of the synthesis route.

N$_2$ sorption

Figure 5 shows the N$_2$ isotherms of the VO$_x$-WO$_x$ samples. The surface area ($S_{BET}$) and pore volume ($V_p$) decreases due to the loading of the catalyst on the TiO$_2$. The pore diameter ($d_p$) on the other hand increases. This could be due to destruction of the porous structure during calcination.

<table>
<thead>
<tr>
<th>sample</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_p$ (cm$^3$/g)</th>
<th>$d_p$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>250</td>
<td>0.6</td>
<td>2</td>
</tr>
<tr>
<td>TiO$_2$ – VO$_x$WO$_x$ – DRY-1</td>
<td>70</td>
<td>0.5</td>
<td>9</td>
</tr>
<tr>
<td>TiO$_2$ – WO$_x$VO$_x$ – MDD-1</td>
<td>110</td>
<td>0.5</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Table 1: N$_2$ sorption results of the VO$_x$-WO$_x$ samples obtained via dry (TiO$_2$-VO$_x$WO$_x$-DRY-1) and wet impregnation (TiO$_2$-WO$_x$VO$_x$-MDD-1).

Acknowledgments

I.A. is grateful to the Long Term Structural Methusalem grant nr. 01M00409 Funding by the Flemish Government.