

Towards an understanding of the active site of VPO catalysts using nanostructured V_xO_y model catalysts

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Introduction

Despite extensive research and numerous contributions to the literature the understanding of the mode of functioning of vanadium-based partial oxidation catalysts such as vanadium-phosphorus-oxide (VPO) is still incomplete. It has been shown that the structure of the catalytically active species is only weakly related to the average bulk structure [1]. This suggests that the VPO catalyst acts as a support material and reservoir for the constituents of the active phase. Therefore, it seems necessary to investigate model systems with simplified structure but catalytically relevant properties. Previous results on binary vanadium oxide systems with long-range order such as thin V_2O_5 films of single crystal quality have shown only little reactivity. However, significant reactivity was observed after partial reduction by ion bombardment or hydrogen atoms [2]. Based on these results the hypothesis is put forward that catalytic activity depends on defects present in the V_xO_y phase. Proceeding in this direction we have studied nanostructured V_xO_y materials which should exhibit a lower kinetic barrier for restructuring into an active defective state from the long-range ordered matrix phase.

Materials and Methods

Calcined VPO was supplied by DuPont. V_xO_y nanocrystals were synthesised by an alkoxide/benzyl alcohol route in a steel autoclave at 200°C using vanadium (V) triisopropoxide as starting material [3]. For catalytic testing a micro-reactor was used, which was connected to a proton transfer reaction-mass spectrometer (PTR-MS). allows for sensitivity for oxygenated products down to the sub-ppb level. The catalytic characterization was carried out under industrially relevant conditions, i.e., oxygen-rich conditions, at atmospheric pressure. A mixture of *n*-butane (1 vol%), oxygen (16 vol%) and nitrogen (83 vol%) was fed into the reactor at a total flow rate of 22 sccm. The amount of sample introduced into the reactor was comparable to the amount typically deposited on a TEM grid. Changes in the electronic and geometric structure of the material before and after reaction were monitored by transmission electron microscopy (TEM) investigations including electron diffraction as well as electron energy-loss spectroscopy (EELS).

Results and Discussion

Figure 1 shows the catalytic activity of nanostructured V_xO_y at 300°C compared to that of calcined VPO. Interestingly, based on the PTR-MS data a comparable catalytic performance was observed for both materials strongly confirming the validity of the approach outlined in the introduction. Besides maleic anhydride, acetic acid, crotonaldehyde and furan were observed. Mass 71 is related to crotonaldehyde rather than dihydrofuran as the former has

been identified as a side product in selective C_4 olefin oxidation. Its presence indicates multiple redox sites, whereas the presence of acetic acid points to a C-C bond cracking function. Figure 2 shows TEM images of V_xO_y particles before and after butane partial oxidation reaction for 24h. Clearly, changes in the microstructure are observed after 24h reaction equilibration. This is supported by electron diffraction after reaction indicating a phase change from the initial V_2O_5 -like structure. The origin of the active, defective phase is currently under study.

Significance

V_xO_y materials are shown to be suitable model catalysts to obtain more insight into the mode of functioning of vanadium-based oxidation catalysts for *n*-butane oxidation to maleic anhydride.

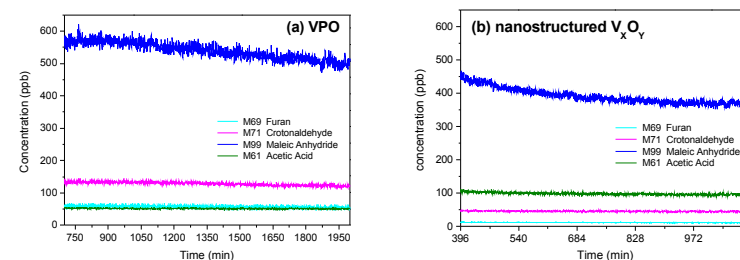


Figure 1. PTR-MS response during the selective oxidation of *n*-butane at 300°C using (a) commercial VPO (DuPont) and (b) V_xO_y nanoparticles.

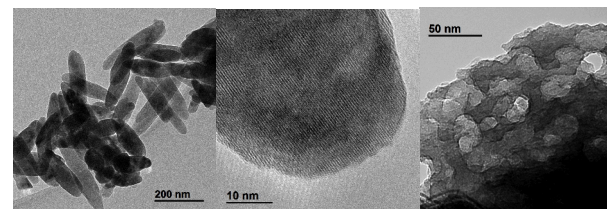


Figure 2. TEM images of V_xO_y particles before (left, center) and after reaction for 24h (right).

References

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