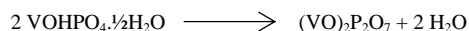


VPO calcination: What are the optimum conditions?

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Introduction

Maleic anhydride is commercially produced by partial oxidation of n-butane over vanadium phosphorous oxide (VPO) catalyst. Calcination of the VPO precursor is an important step in which the active phase of the catalyst, vanadium pyrophosphate, is developed. Development of the active phase takes place by elimination of structural water from hemihydrate precursor according to the following reaction:



Development of active phase during VPO calcination is accompanied by two major water removal periods [1-2]. In the first step, surface water is desorbed by evaporation and in the second step the active phase of the catalyst is formed by elimination of structural water at higher temperatures.

The development of the active phase during calcination is strongly dependent on the operating conditions. However, despite the large number of experimental studies, there is still no general consensus concerning the optimum calcination conditions. In this study, we examined over 60 articles and patents to identify the most common operating parameters as basis to begin to define the optimum conditions.

Materials and Methods

The precursor samples for calcination were provided by DuPont. A conventional thermogravimetric analysis (TGA) setup coupled with mass spectroscopic analysis was used for calcination of all precursor samples under a specified temperature ramp. A partial list of the experiments is presented in Table 1.

Table 1. Calcination experiments

Experiment	Ramp, °C/min	Atmosphere	Duration	Final temp., °C
TG-1	4	Argon/Oxygen	4 hr	260
TG-2	4	Argon/Oxygen	4 hr	390
TG-3	4	Argon/Oxygen	4 hr	480
CAT-1	20	Argon	40 min	500
CAT-2	20	Oxygen	30 min	500
CAT-3	20	Argon/Oxygen	70 min	450

The weight change of the catalyst samples during calcination was measured under oxygen and argon atmospheres at several temperatures and the evolution of gases during the transformation of the hemihydrate to pyrophosphate phase was measured by mass spectrometric analysis.

Results and Discussion

Figure 1 shows the mass loss of the precursor under argon during calcination at different temperatures. Two major water peaks are detectable. The second major water loss is detectable only when the temperature rises above 260°C. This shows that the development of catalyst structure and active phase occurs at temperatures between 260 to 390 °C.

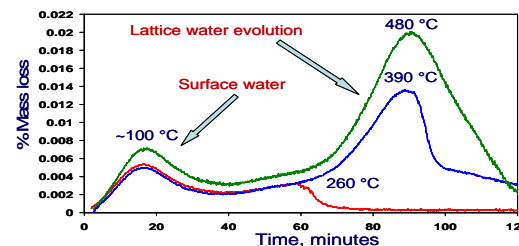


Figure 1. Lattice development during VPO calcination

The evolution of water during calcination was also confirmed by mass spectroscopic analysis. Figure 2, demonstrates the evolution of water and subsequent combustion of organics by switching argon to air. The total weight loss of water and organics was on the order of 12-16%. Regarding calcination in air a continuous uptake of oxygen (1-2% weight gain) was observed which might be due to transformation of V^{4+} to V^{5+} states.

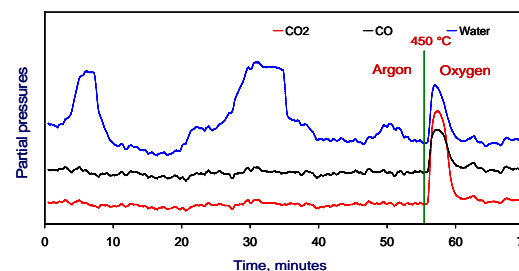


Figure 2. Evolution of water and combustion products during VPO calcination

Significance

n-Butane conversion to maleic anhydride over VPO catalyst is the only light alkane partial oxidation that has achieved commercial success. Identifying the underlying processes of the transformation of the precursor phase to the active phase may help identify more active catalyst as well as the development of new catalyst systems (propane to acrylic acid, for example).

References

- Wang, D., Kung, H.H. and Barteau, M.A. *Appl. Catal. A: General* 201, 203 (2000).
- O'Mahony, L., Curtin, T., Henry, J., Zemlyanov, D., Mihov, M. and Hodnett, B.K. *Appl. Catal. A: General* 285, 36 (2005).