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Characterization of VPO catalysts for n-butane oxidation using in- situ XPS

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Introduction

Vanadium phosphorous oxides (VPO) are well-known as industrial catalysts for the selective oxidation of n-butane to maleic anhydride in the reaction

$$C_4H_{10} + 7/2\ O_2 \rightarrow C_4H_2O_3 + 4H_2O.$$

Usual industrial conditions for this reaction are p=1 atm. and T=375-480°C. It is known from measurements using a variety of different methods that VPO catalysts undergo significant structural changes during the activation process [1].

X-ray photoelectron spectroscopy (XPS) has been a powerful tool in catalytic research for decades. [2] This technique was used by numerous authors to investigate the properties of the VPO surface, in particular the P/V ratio and the vanadium oxidation state at the surface. [3-6]

Due to the short mean free path of electrons in a gas electron spectroscopies generally must operate in high vacuum conditions. Traditional XPS is therefore not suited for the characterization of catalytic surfaces under reaction conditions. To overcome this limitation, we have developed a new high-pressure electron spectrometer.

Experiment

The in-situ XPS spectrometer is a modified standard XPS spectrometer. The electrostatic lenes of the spectrometer were combined with a 3-stage differential pumping system. The pressure in the analyzer was in the 10^{-8} mbar range when the reaction cell pressure was several mbar. The reaction cell was separated from the synchrotron beamline by a 100 nm thick SiN_x window.

The VPO catalyst was activated ex- situ by heating vanadyl hydrogen phosphate hemihydrate $VOHPO_4 \cdot 0.5\ H_2O$ precursors at 400°C in vacuum. The conversion and the selectivity of the material were measured at standard conditions (1 bar, 400°C) prior to the spectroscopic investigations.

The samples were investigated in a constant reactant flow of 0.4 mbar of O_2 + 1.6 mbar of a He+butane (1.5%) gas mixture (total pressure 2 mbar). The sample temperature was cycled several times from 250°C (far below the reaction temperature) to 400°C (the reaction temperature). The goal of the experiment was to detect changes in the surface stoichiometry between the working and non-working catalyst. Two sets of incident photon energies were used in the in situ XPS experiments to provide different information depths (about 3 and 7 monolayers).

Results and discussion

XPS spectra of the catalyst showed changes of shape both with temperature and information depth (Fig. 1). The V oxidation state was estimated by fitting the O1s and V2p3/2 peaks using Gaussian profiles after Shirley background subtraction. Because of the inhomogenity of the VPO catalyst's surface numerous types of phosphor, vanadium and carbon oxides can occur. The O1s peak was fitted by four peaks (O_I, O_{II}, O_{III}, O_{IV}). The O_I peak was assigned to oxygen bound to vanadium. Thus, only the O_I peak area was used in O/V ratio calculations. The O_{II} O_{III} and O_{IV} peaks nature was not clearly identified. The phosphorous/vanadium and oxygen/vanadium atomic ratios were calculated using photoionisation cross-sections from [7]. The oxygen/vanadium ratio increased at the surface under reaction conditions. The phosphorous/vanadium ratio decreased with increasing information depth. This indicates an enrichment of phosphorous at the surface. Additionally, the P/V ratio decreased with time on stream. This effect is in agreement with the observation of phosphor depletion in industrial catalysts [1]. The atomic ratios of V, P and O for the different measurement conditions are summarized in table 1.

Table 1

	O/V		P/V	
T, °C	1 nm depth	3 nm depth	1 nm depth	3 nm depth
250	5.7	5.5	3.2	2.4
400	7.8	6.2	3.1	2.7
250	6.1	5.7	3.1	2.5
400	8.5	6.2	2.8	2.6

The difference in BE between the O1s peak and the $V2p_{3/2}$ peak for different V oxidation states was used to deconvolute the $V2p_{3/2}$ peak into its V^{5+},V^{4+} and V^{3+} contributions. The BE values for the different V oxidation states are known from XPS investigations of single-crystal vanadium oxides ([8], [9]). The fitting parameters that were used can be found in table 2. After peak fitting the BE scale was calibrated to 530 eV for the O_I peak position ([9]).

Table 2

	O_I	O_{II}	O_{III}	O_{IV}	V^{5+}	V^{4+}	V^{3+}
BE relative O_I, eV	0	2.1	1.1	-1.3	-12.9	-14.0	-15.1
FWHM, eV	1.5	1.8	2.2	1.5	1.8	1.8	1.8

It was found that the oxidation state of the catalyst surface was V^{4+} under reaction conditions and a mixture of V^{4+} and V^{3+} for the non-active material at 250°C. The oxidation state of deeper layers did not show significant changes and remained V^{4+} at both temperatures.

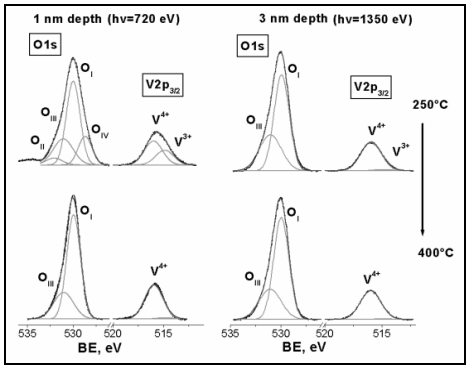

Fig. 1 Changes in O1s and $V2p_{3/2}$ XPS peaks with temperature and depth (Shirley background subtracted, the BE scale calibrated to $BE(O_I)$=530eV)

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