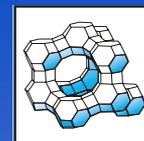




UV/Vis and solid-state NMR investigation of the effect of sequential reaction conditions on VPO catalysts during selective oxidation of *n*-butane

J. Frey and M. Hunger

Institute of Chemical Technology, University of Stuttgart, 70550 Stuttgart, Germany



INTRODUCTION

Recent papers [1-4] demonstrate the strong research activities in the field of selective oxidation of alkanes by VPO catalysts. These activities focus on the improvement of the catalyst materials, their better understanding, the development of new reactor types, such as fluidized catalyst-bed and membrane reactors, and sequential processing. In our present work, we utilized bulk VPO material (VPO/bulk) and VPO compounds supported on SBA-15 (VPO/SBA-15) in the selective oxidation of *n*-butane to maleic anhydride (MA) during sequential switching off and on of the oxygen in the feed. By *on-line* UV/Vis spectroscopy, the change of the oxidation state of the catalysts under reaction conditions in the fixed-bed reactor was observed. In this case, the ability of diffuse reflectance UV/Vis spectroscopy to distinguish V^{4+} and V^{5+} species in VPO catalysts by the d-d transition at ca. 900 nm and the charge-transfer at ca. 420 nm, respectively, was used [5]. Furthermore, quantitative ^{31}P MAS NMR measurements of VPO catalysts taken from the sequential-flow fixed-bed reactor without contact to air allowed the detailed investigation of the change of the active VOPO₄ phases upon the catalyst activation, reduction, and reoxidation under continuous *n*-butane flow. By $\{^1\text{H}\}^{31}\text{P}$ cross-polarization MAS NMR investigations of the *n*-butane-loaded VPO/SBA-15 catalyst, the preferential adsorption sites at the VOPO₄ surface compounds were identified. These investigations improve our knowledge on the catalytically active surface species of VPO catalysts.

EXPERIMENTAL SECTION

The VPO catalysts were prepared and activated as described in Ref. [6]. The selective oxidation of *n*-butane was studied using a fixed-bed reactor with an inner diameter of 10 mm, the reactant flow of 100 ml/min with a feed composition of 1.5 Vol.% *n*-butane in synthetic air or nitrogen under atmospheric pressure, and at 678 K. The reactor was equipped with a glass-fiber reflection probe FCR-7UV20-3-SR-S1 by Avantes (Fig. 1) connected with a HPSUV1000A fiber-optic UV/Vis spectrometer and an AvaLight-DH-S light source. The reaction products were analyzed after the activation time of 24 h in steps of 5 min by an *on-line* gas chromatograph HP 6890 equipped with a column HP-5 (30 m). ^{31}P MAS NMR studies were performed on a Bruker MSL-400 spectrometer at the resonance frequency of 161 MHz, with a 4 mm MAS NMR probe, the sample spinning rate of 10 kHz, the repetition time of 10 s, and ca. 4.000 scans per spectrum. Before the cross-polarization experiments, the sample obtained after treatment **C** was loaded with 200 mbar *n*-butane.

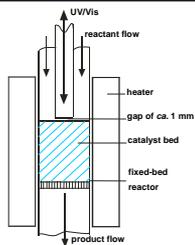


Figure 1: Setup for *on-line* UV/Vis observation of the oxidation state of vanadium in the VPO catalysts inside the fixed-bed reactor.

RESULTS AND DISCUSSION

Fig. 2 shows the *n*-butane conversion *X*, selectivity *S* to MA, and MA yield *Y* as a function of time-on-stream for periods of 40 min under a flow of 1.5 Vol.% *n*-butane in pure nitrogen (reduction period) and 15 min under a flow of 1.5 Vol.% *n*-butane in synthetic air (reoxidation period). For the solid-state NMR studies, catalyst samples were taken at the points **A** (end of the activation period of 24 h), **B** (end of the first reduction period of 40 min), as well as **C** and **D** (end of the first and fourth reoxidation period, respectively, of 15 min). *On-line* UV/Vis spectroscopy of the V^{5+} band at ca. 420 nm led to band intensities correlating with the reduction and reoxidation cycles of the selective oxidation reaction. The $\{^1\text{H}\}^{31}\text{P}$ CPMAS NMR spectra in Fig. 3 indicate an adsorption of *n*-butane at various VOPO₄ phases, but preferentially at δ -VOPO₄-like compounds (Tab. 1). The ^{31}P MAS NMR spectra of the VPO catalysts taken at points **A** to **D** were deconvoluted assuming signals of α_1 -, β -, δ -, and γ -VOPO₄ phases (Fig. 4). According to Tab. 2, only 0.5 % of all phosphorus atoms in the activated VPO/bulk sample **A** exist in the proximity of V^{5+} species (P/V^{5+}). After reduction of the VPO/bulk catalyst (sample **B**), there is a total decline of these species, while they appear again with contents of 0.3 to 0.4 % of all phosphorus atoms after the reoxidation procedures (samples **C** and **D**). For the VPO/SBA-15/A sample, the content of 2.6 % for the phosphorus atoms in P/V^{5+} and P/SiO_2 species was determined. In the reoxidized VPO/SBA-15 samples **C** and **D**, 0.9 to 1.3 % of the phosphorus atoms exist as P/V^{5+} and P/SiO_2 species. Considering the contents of phosphorus atoms in P/V^{5+} species of δ -VOPO₄-like compounds (Tab. 2, last column), ca. 0.2 % of all vanadium atoms contribute to the preferred *n*-butane adsorption sites of VPO/SBA-15. Based on the catalytic data (Fig. 1) and the number of P/V^{5+} species in δ -VOPO₄-like compounds, the turnover frequency of the surface sites on the VPO/SBA-15 material was estimated to be about 0.2 s⁻¹.

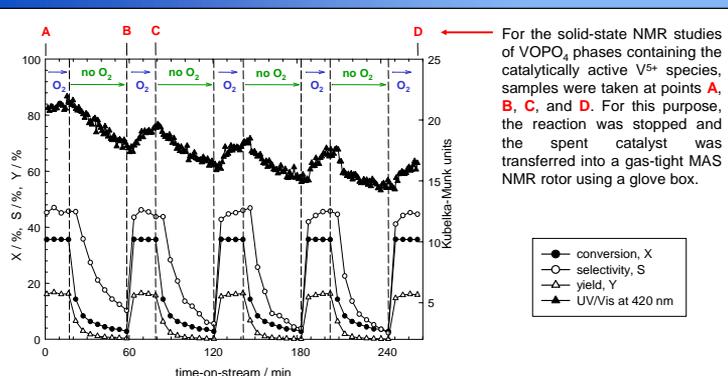


Figure 2: Selective oxidation of *n*-butane to maleic anhydride on the VPO/SBA-15 catalyst studied with sequential switching off (40 min) and on (15 min) of the oxygen in the reactant flow and *on-line* detection of V^{5+} species by evaluating (according to Kubelka-Munk) the UV/Vis band at ca. 420 nm.

SUMMARY

- Bulk VPO (VPO/bulk) and VPO compounds supported on SBA-15 (VPO/SBA-15) show similar catalytic activities in the selective oxidation of *n*-butane to maleic anhydride.
- Sequential switching off and on of the oxygen in the feed leads to a reversible change of the oxidation state of vanadium in the VPO catalysts from V^{5+} to V^{4+} and *vice versa*.
- The oxidation state of the vanadium in the VPO catalysts could be observed *on-line* by fiber-optic UV/Vis spectroscopy evaluating the charge-transfer band at ca. 420 nm.
- The slow decrease of the *n*-butane conversion and selectivity to maleic anhydride during the reduction period indicate the oxygen storage behavior of the VPO catalysts.

^{31}P CPMAS NMR experiments:

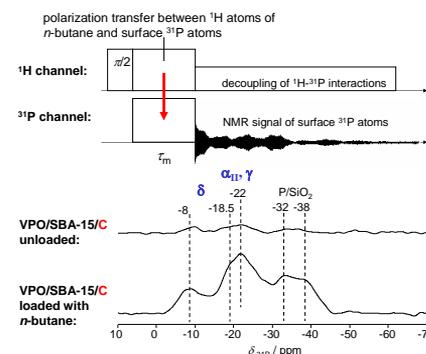


Figure 3: Scheme of the ^{31}P cross-polarization MAS NMR experiment (top) and spectra (bottom) of VPO/SBA-15/C recorded before and after loading of *n*-butane.

Tab. 1: ^{31}P MAS NMR signals of phosphorus atoms in VOPO₄ phases [7-9].

Materials	Signals
γ -VOPO ₄	-21.2 ppm, -17.3 ppm (ca. 1:1)
	-14.9 ppm (very weak shoulder)
α_1 -VOPO ₄	-20.5 ppm
δ -VOPO ₄	-17.6 ppm, -8.4 ppm (ca. 1:1)
	-6.5 ppm (very weak shoulder)
β -VOPO ₄	-11.5 ppm
α_2 -VOPO ₄	2.7 to 3.6 ppm
P species on SiO ₂	ca. -25 to -37 ppm

^{31}P MAS NMR spectra of VPO/SBA-15/A to VPO/SBA-15/D:

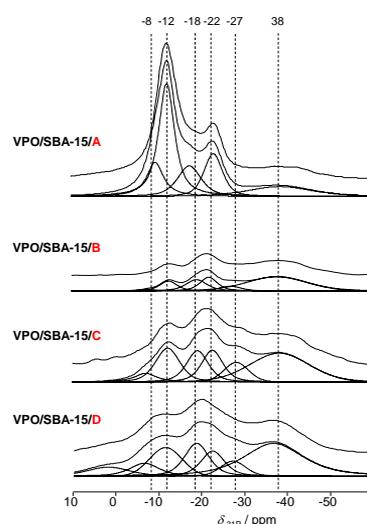


Figure 4: ^{31}P MAS NMR spectra of the VPO/SBA-15 in different activation states recorded at a resonance frequency of 161.9 MHz and the sample spinning rate of 8.0 kHz.

Tab. 2: Contents of phosphorus atoms in P/V^{5+} and P/SiO_2 species of the VPO/bulk and VPO/SBA-15 samples **A** to **D** as determined by quantitative evaluation of the ^{31}P MAS NMR spectra (e.g. of Fig. 4).

Materials	Type	Contents of P/V^{5+} and P/SiO_2 ¹⁾	Contents of P/V^{5+} in δ -VOPO ₄ phases ²⁾
VPO/bulk	A	0.5 %	
	B	0 %	
	C	0.35 %	
	D	0.4 %	
VPO/SBA-15	A	2.6 %	0.80 %
	B	0.3 %	0.05 %
	C	0.9 %	0.20 %
	D	1.3 %	0.30 %

1) Contents of phosphorus atoms causing signals at chemical shifts of -40 to 10 ppm, i.e., in the vicinity of V^{5+} compounds (P/V^{5+}) and on the SBA-15 support (P/SiO_2), accuracy $\pm 10\%$.

2) Contents of phosphorus atoms causing signals at chemical shifts of -8 to -18 ppm, i.e., exclusively in the vicinity of V^{5+} species contributing to δ -VOPO₄-like phases, accuracy $\pm 10\%$.

REFERENCES

- [1] G.J. Hutchings, J. Mater. **14** (2004) 3385-3395.
- [2] N. Ballarini, F. Cavani, C. Cortelli, S. Ligi, F. Pierelli, F. Trifiro, C. Fumagalli, G. Mazzoni, T. Monti, Top. Catal. **38** (2006) 147-156.
- [3] C.J. Kiely, G.J. Hutchings, Appl. Catal. A: General **325** (2007) 194-197.
- [4] J. Frey, Y.S. Ooi, B. Thomas, V.R. Reddy Marthala, A. Bressel, T. Schoelkopf, T. Schleid, M. Hunger, Solid State Nucl. Magn. Reson. **35** (2009) 130-137.
- [5] G. Bignardi, F. Cavani, C. Cortelli, T. De Lucia, F. Pierelli, F. Trifiro, G. Mazzoni, C. Fumagalli, T. Monti, J. Mol. Catal. A: Chemical **244** (2006) 244-251.
- [6] H.S. Horowitz, C.M. Blackstone, A.W. Sleight, G. Teufer, Appl. Catal. **38** (1988) 193-210.
- [7] F.B. Abdelouhab, R. Olier, N. Guilhaume, F. Lefebvre, J.C. Volta, J. Catal. **134** (1992) 151-167.
- [8] K.E. Birkeland, S.M. Babitz, G.K. Bethke, H.H. Kung, G.W. Coulston, S.R. Bare, J. Phys. Chem. B **101** (1997) 6895-6902.
- [9] S.A. Ennaciri, C. Rkha, P. Bardoux, J. Livage, Eur. J. Solid State Inorg. Chem. **30** (1993) 227-236.

ACKNOWLEDGEMENTS

Financial support by Deutsche Forschungsgemeinschaft, Volkswagenstiftung Hannover, and Fonds der Chemischen Industrie is gratefully acknowledged.

- $\{^1\text{H}\}^{31}\text{P}$ cross-polarization MAS NMR investigations of reoxidized VPO/SBA-15 loaded with *n*-butane hint to a preferred adsorption of the reactants at δ -VOPO₄-like phases.
- Catalyst samples taken from the fixed-bed reactor after the activation, reduction, and reoxidation periods show significant differences in the ^{31}P MAS NMR signals of VOPO₄ phases and their intensities.
- Quantitative evaluation of the ^{31}P MAS NMR spectra gives contents of 0.3 to 0.4 % and 0.9 to 1.3 % of phosphorus atoms in the vicinity of V^{5+} species (P/V^{5+}) in catalytically active VPO/bulk and VPO/SBA-15 materials, respectively.