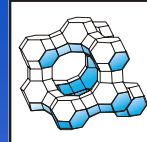


Vanadium phosphates on mesoporous supports: Model catalysts for solid-state NMR studies of the selective oxidation of alkanes

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INTRODUCTION

Selective oxidation of *n*-butane to maleic anhydride (MA) is the only commercially utilized chemical process for light alkanes. Bulk vanadium phosphorous oxide (VPO) is the catalyst commonly used for this reaction.¹ VPO catalysts are composed of a large number of phases, such as α -, α_1 -, β -, γ -, and δ -VOPO₄ (vanadyl orthophosphate, V⁵⁺), vanadyl pyrophosphate (VPP, V⁴⁺), VPO₄ (V³⁺) etc. For a long time, it was accepted that (VO)₂P₂O₇ is the main component of the active catalyst. Till date, however, little is known about the exact nature of the active sites.¹⁻⁵

Supported catalysts offer several advantages, such as (1) higher surface area to volume ratio of the active phase, (2) high mechanical strength, (3) improved heat transfer characteristics, and (4) controllable catalyst texture.^{2,3,5} In the case of VPO catalysts, strong support-oxide interactions can hinder the formation of the pyrophosphate phase or cause changes in the phase composition affecting the *n*-butane conversion and/or MA selectivity. The resulting material generally consists of phases that resemble, e.g. α -VOPO₄ or γ -VOPO₄.^{2,4}

In the present study, siliceous SBA-15 was used as support for VPO compounds to take advantage of the efficient dispersion of catalytically active components.

RESULTS AND DISCUSSION

The ²⁹Si MAS NMR spectra (Fig. 1) reveal characteristic signals of Q², Q³, and Q⁴ silicon species. A clear dependence of the number of SiOH groups on the VPO loading as determined by the quantitative ¹H MAS NMR studies further confirms the above-mentioned observation.

Decrease in surface area upon VPO loading on SBA-15. The small angle XRD patterns show characteristic (100), (110) and (200) reflections, but with an attenuation in intensity with increasing VPO loading. The wide-angle patterns exhibit lines due to VPO phases.

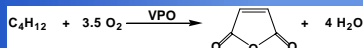
Table 1. Physicochemical characterization of the SBA-15 and VPO loaded catalysts.

Catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)	P/V
SBA-15	1164	1.25	-
20%VPO/SBA-15	662	0.80	1.09
60%VPO/SBA-15	456	0.54	1.04

³¹P MAS NMR spectrum (Fig. 2) of non-activated VPO/SBA-15 exhibits a broad peak at ca. 1650 ppm typical of the hemihydrate (VOHPO₄ · 0.5 H₂O) VPO precursor.

The activated catalysts show peaks characteristic of phosphorus in the vicinity of V⁵⁺ (orthophosphate phases) centers. The absence of broad signals at ca. 2600 ppm indicates that no vanadyl pyrophosphate phases were formed. It is well-known that VPO compounds dispersed on silica supports are composed of various VOPO₄ phases.²

Maleic anhydride (2,5-furandione) is produced from *n*-butane in a 14-electron oxidation involving the abstraction of 8 hydrogen atoms and insertion of 3 oxygen atoms. It is the most complex selective oxidation reaction industrially practiced. Generally, pure VPO material is the catalyst used for this reaction.¹



³¹P MAS NMR signals (Fig. 3) characteristic of phosphorus atoms in the neighbourhood of V⁵⁺ species were observed before and after catalytic oxidation of *n*-butane at 573 K.

Changes in the signal intensities occurred upon performing the oxidation reaction at 523 K.

Isovalent phase transformation from one orthophosphate phase to another one is the reason for the change in the intensity distribution of the ³¹P MAS NMR signals.⁵

During the oxidation reaction, a phase transformation from δ -VOPO₄ to α_1 -VOPO₄ is observed.

Acknowledgements

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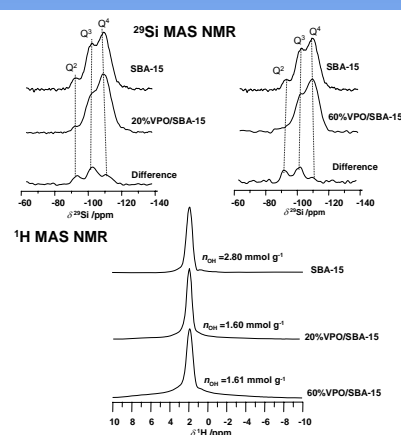


Figure 1. ²⁹Si and ¹H MAS NMR spectra of SBA-15, 20%, 60%VPO/SBA-15 catalysts recorded at room temperature. The spectra were recorded at 79.49 and 400.13 MHz using excitation pulses of 5.0 and 4.0 μ s, respectively. 180 and 64 free induction decays were collected for each spectrum with repetition times of 30 and 10 s, respectively.

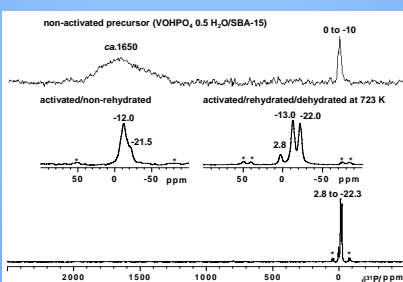


Figure 2. ³¹P MAS NMR spectra of the non-activated precursor, activated/non-rehydrated, and activated/rehydrated/dehydrated 60%VPO/SBA-15 catalyst. The spectra were recorded at 161.98 MHz using an excitation pulse of 0.61 μ s with 30 s repetition time. Approximately 320 free induction decays were collected at the sample spinning rate of 10.0 kHz. Asterisks indicate spinning side bands.

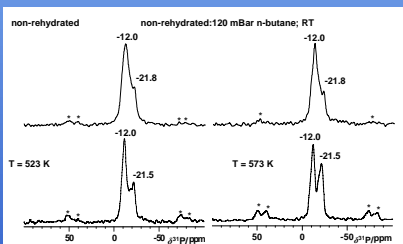


Figure 3. ³¹P MAS NMR spectra of calcined 60%VPO/SBA-15 catalyst recorded upon loading with 120 mbar *n*-butane and heating at 523 and 573 K. The spectra were recorded at 161.98 MHz using an excitation pulse of 0.61 μ s with 30 s repetition time. Approximately 320 free induction decays were collected at a spinning rate of 10.0 kHz.

EXPERIMENTAL PART

Siliceous SBA-15 was synthesized via liquid crystal template (LCT) method. Mixed (iso-butyl/benzyl) alcohol route was adopted as the preparation media for the effective dispersion of VPO on to SBA-15.

The hemihydrate VPO precursor (VOHPO₄ · 0.5 H₂O) was activated in air/butane/nitrogen mixture at 673 K for 16 h. Activated catalysts were characterized by chemical analysis (ICP-OES), X-ray diffraction (D8 Advance), nitrogen adsorption (ASAP2000), and solid-state NMR.

All NMR studies were performed on a Bruker MSL-400 spectrometer using 7 mm (²⁹Si) and 4 mm MAS probes (¹H, ³¹P, ⁵¹V) at room temperature.

Analysis of the side band intensities of ⁵¹V MAS NMR spectra (Fig. 4) gives chemical shift anisotropies corresponding to vanadium in distorted octahedral environments.⁶⁻⁷ Large values of CSA indicates a very short V=O bond.⁶

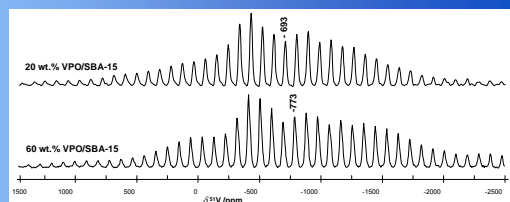


Figure 4. ⁵¹V MAS NMR spectra of the 20% and 60%VPO/SBA-15 catalysts. The spectra were recorded at 105.25 MHz using an excitation pulse of 0.61 μ s with 500 ms repetition time. Approximately 20,000 free induction decays were collected with the sample spinning rate of 10.0 kHz.

Table 2. Parameters obtained by simulation of the ⁵¹V MAS NMR spectra.

Catalyst	δ_{iso} (ppm)	δ_{cs} (ppm)	η_{cs}	C_{QCC} (MHz)	η_{Q}
20%VPO/SBA-15	-693	-830	0.07	1.99	0.71
60%VPO/SBA-15	-773	-900	0.10	1.99	0.59

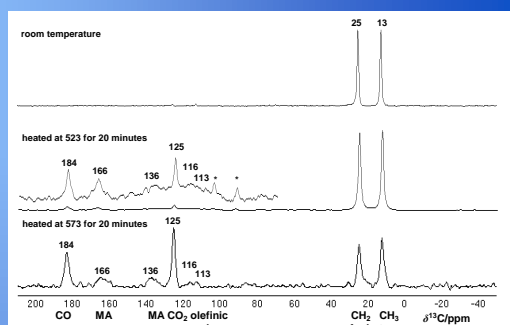


Figure 5. ¹³C MAS NMR spectra of calcined 60%VPO/SBA-15 catalyst loaded with ca. 120 mbar *n*-butane-¹³C at room temperature and heated at 523 K and 573 K for 20 minutes. The spectra were recorded at 100.61 MHz using an excitation pulse of 4.5 μ s with 10 s repetition time. Approximately 8,000 free induction decays were collected at a spinning rate of 8.0 kHz.

SUMMARY

In this study, VPO catalysts supported on siliceous SBA-15 were prepared and *ex situ* MAS NMR studies of *n*-butane oxidation to maleic anhydride performed. The 20%VPO/SBA-15 and 60%VPO/SBA-15 catalysts were composed mainly of various orthophosphate phases. Initial catalytic studies of *n*-butane-loaded samples at 523 and 573 K by ¹³C MAS NMR spectroscopy confirmed the formation of MA. ³¹P MAS NMR studies of the spent catalysts show changes in the phase composition upon the catalytic oxidation.

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