MECHANICAL ACTIVATION OF VPO

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Introduction

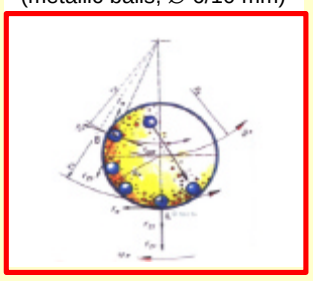
Mechanical treatment of VPO catalyst causes a substantial increase of both catalytic activity in *n*-butane oxidation and the selectivity to maleic anhydride (MA). Changes in specific surface area and anisotropic deformation take place. Mechanochemical treatment of the initial reagent impairs such properties that they remarkably influence the catalytic properties of the final catalyst.

Approach

$VOHPO_4 \cdot 0.5H_2O$ (VHP) was mechanotreated in ethanol and air for a duration of time and the morphologies studied by scanning and transmission electron microscopy (SEM, TEM) and by x-ray powder diffraction (XRD). This was compared to the morphologies of the initial material and to a sample thermally treated in vacuum. Also the equilibrated product $(VO)_2P_2O_7$ (VPP), which was obtained from $VOHPO_4 \cdot 0.5H_2O$ heated in a reactor under butane/air gas mixture, was compared. Bismuth was added to the precursor as a promoter.

Catalyst preparation and tribomechanical activation

Planetary ball mill
(metallic balls, ∅ 6/10 mm)



Precursor (VPO1)

$V_2O_5 + H_3PO_4$

↓

VHP

High-speed planetary ball-mill with metallic drums and balls. The balls were of two diameters: d=10mm and d=6 mm. About 65-75 percent of the total drum volume was loaded by them. The quantity of milled powder was varied, but did not exceed 4 percent (mass) of balls. Milling duration was varied from 2 to 60 min. The milling process was performed in ethanol, water and without any dispergant: "dry milling".

Sample preparation

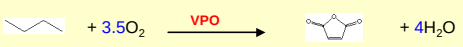
VPO-1 – Precursor [$VOHPO_4 \cdot 0.5H_2O$]
VPO-2 – VPO-1 mechanically activated during 5 min. in ethanol
VPO-3 – VPO-1 mechanically activated during 28 min. in air
VPO-4 – VPO-1 mechanically activated during 30 min. in air
VPO-5 – VPO-1 thermally activated in vacuum at 400 °C
VPO-6 – VPO-1 thermally activated in *n*-butane/air at 440°C

Effects of VHP treatment on VPO activity and MA selectivity and yield

Sample	$SA_{initial}$	X = conversion	S = selectivity	Y = yield	X´ = conversion	Y´ = yield
					Per m^2g^{-1}	
	m^2g^{-1}	%	%	%	%	%
VPO-1	6.0	62	61	38	10.3	6.3
VPO-2	7.8	66	64	42	8.5	5.4
VPO-3	20.1	75	68	51	3.7	2.5
VPO-4	19.2	78	69	54	4.1	2.8
VPO-5	7.6	50	46.5	24	6.6	3.2
VPO-6*	4.6	68	60	41	14.8	8.9

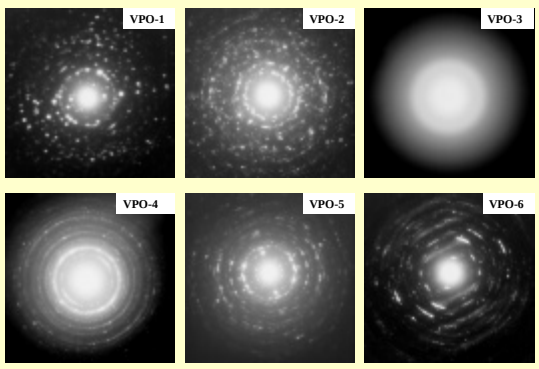
n-butane oxidation (T = 440°C, GHSV = 3200h[1]); * *n*-butane oxidation (T = 440°C, GHSV = 1500h[1])

Mechanotreatment increases the surface area and hence increases the butane conversion and maleic anhydride selectivity and yield, which does not require an extensive pre-treatment or activation period to establish full catalytic activity. In contrast comparing the conversion and selectivity per unit surface area we observe a decrease with milling, this may be due to the loss of active site.



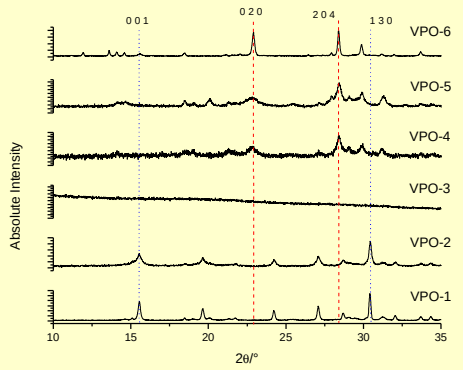
Microstructural analysis

Electron diffraction



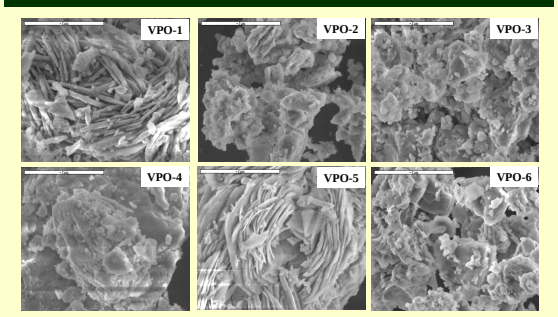
VPO-1	VPO-2	$VOHPO_4 \cdot 0.5H_2O$	VPO-4	VPO-5	VPO-6	$(VO)_2P_2O_7$
	5.92	5.901		6.22	6.27	6.280
5.63		5.719	3.07	3.17	3.14	3.137
3.66	3.69	3.684		3.01		2.982
	3.29	3.300	2.32	2.44	2.45	2.435
3.15	3.15	3.116	2.09	2.09	2.09	2.083
2.91	2.94	2.943		1.58	1.57	1.567

X-ray diffraction



The ED and XRD patterns for VPO-1 and VPO-2 show $VOHPO_4 \cdot 0.5H_2O$ phase, VPO-4, VPO-5 and VPO-6 show $(VO)_2P_2O_7$ phase.
The ED and XRD pattern from VPO-3 showed an amorphous phase after milling for 28 minutes in air. Milling the sample for 30 minutes (VPO-4) transforms $VOHPO_4 \cdot 0.5H_2O$ to $(VO)_2P_2O_7$. The catalysts are generally produced by activating VHP in a reaction feed of *n*-butane/air mixture at about 400°C for an extended time period.

SEM



The particle size becomes smaller (VPO-2 and VPO-3) and agglomeration occurs as milling time increases (VPO-4). Mechanotreated samples showed more rounded particles compared with VPO-1, which showed needle like particles. VPO-5 after heating in vacuum revealed a similar morphology as VPO-1.

Conclusions

- Mechanochemical treatment of VPO catalysts increases their activity in *n*-butane oxidation and the selectivity and yield to maleic anhydride. In contrast comparing catalytic activity on a surface area basis, a decrease with milling is observed
- $VOHPO_4 \cdot 0.5H_2O$ milled in air for 28 minutes gives an amorphous phase, milling for a longer time gives $(VO)_2P_2O_7$
- Samples mechanotreated showed more rounded particles compared with VPO-1, exhibiting needle like particles, but VPO-5 heated in vacuum revealed similar morphology to VPO-1

Acknowledgements

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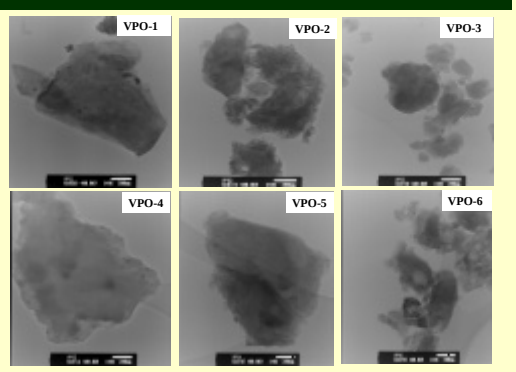
TEM



Mechanotreatment breaks down the particles (VPO-2), continuous milling in air courses amorphorisation (VPO-3). Milling for longer duration in air induces agglomeration of particles increasing the size and transformation from VHP to VPP (VPO-4).