

Unprecedented Molecular 'VPO' assembly with Catalytic Activity under Mild Conditions

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- The conversion of butane into maleic anhydride (MA) is one of the most complex catalytic processes utilized by the petrochemical industry. Industrial catalysts are based on vanadium-phosphorous-oxide (VPO) systems, which consist of a suitable *precursor* and a derived *active species* formed *in-situ* at high temperatures (~700 K).
- We have sought to prepare an active catalyst phase directly, at room temperature, as a discrete molecular assembly
- We have successfully built such a systems (see Figure 1) and studied it's crystalline phases (figure 1) and basic catalytic activity (see Figure 2 and table 1)

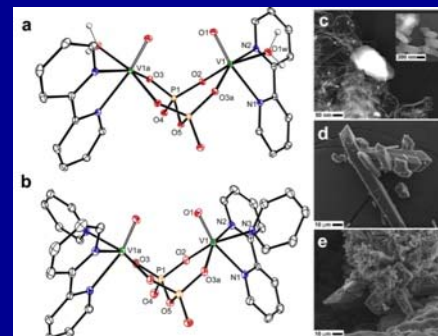


Figure 1. (a,b) ORTEP plots (20% probability level) of the vanadyl-pyrophosphate dimeric unit in **1** (a) and **1-pyr** (b) with the atom labeling scheme (bipy and pyridine-H atoms are omitted for clarity). Vanadyl (V=O) units are evidenced with the open-type bond. Selected bond lengths (Å) in **1**: V1-O1 = 1.611(3), V1-O2 = 1.979(3), V1-O3a = 1.960(3), V1-O1w = 2.038(3), V1-N1 = 2.294(4), V1-N2 = 2.143(3)

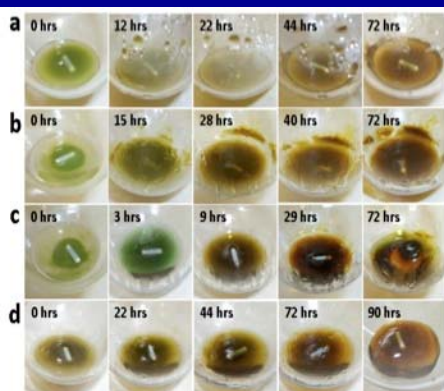


Figure 2. Snapshots of the reaction course at various time-points (only selected examples): (a) BA (1ml) + TEA (10mol%) + **1** (1mol%) under argon at 100°C; (b) BA (1ml) + pyridine (10mol%) + **1** (1mol%) under air at 100°C; (c) BA (1ml) + TEA (10mol%) + **1** (1mol%) under air at 100°C; (d) BA (1ml) + TEA (10mol%) + **1-anhyd** (1mol%) under air at RT.

Table 1. Aerobic oxidation of benzyl alcohol (route 1) or pinacol (route 2) catalyzed by complex **1**.^[a,b]

Entry	Substrate	mol% 1	atm	additive	% conversion
1	benzyl alcohol	none	argon	Et ₃ N	<1
2		none	air	Et ₃ N	<2
3		1	argon	pyr	<2
4		1	argon	Et ₃ N	<2
5		1	air	none	9
6		1	air	pyr	10
7 ^[d]		1	air	Et ₃ N	16
8 ^[c-d]		1	air	Et ₃ N	42
9		1	air	Et ₃ N	35 ± 4
10		0.5	air	Et ₃ N	33 ± 6
11		0.25	air	Et ₃ N	30 ± 4
12		0.1	air	Et ₃ N	10
13		2	air	Et ₃ N	50
14		5	air	Et ₃ N	46
13		pinacol	none	air	Et ₃ N
14	1		air	Et ₃ N	70
15	0.25		air	Et ₃ N	67

[a] Reaction conditions, unless otherwise stated: 1 ml substrate, no solvent (*neat*); [b] % conversion determined from ¹H NMR analysis (see the Experimental Section for further details); [c] Reaction conditions: 5 ml substrate, no solvent, 3 days at 100 °C under air; [d] % conversion after 11 days.