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A New Catalyst for the Selective Oxidation of Butane and Propane**

Mark E. Davis,* Christopher J. Dillon,
Joseph H. Holles, and Jay Labinger

The abundance and low cost of light alkanes has motivated the search for new catalytic materials that can accomplish selective oxidation processes. The conversion of *n*-butane to maleic anhydride over V-P-O catalysts with molecular oxygen is commercially well established.[1] Other reactions of current interest are the production of acetic acid from ethane and acrylic acid from propane. Polyoxometalates are among the numerous catalytic materials that have been extensively investigated for each of the aforementioned reactions. Typically different polyoxometalate compositions have been used for each alkane. These compounds (and other mixed-metal oxides) have not been found to perform as well as V-P-O catalysts for the conversion of *n*-butane to maleic anhydride,[2] or as well as mixed-metal oxides containing Mo-V-Nb-Te[3a,b] or Mo-V-Nb-Sb[4] for conversion of propane to acrylic acid.

We have discovered a new catalyst system that achieves selective oxidation of both *n*-butane and propane. Li et al. reported that a solid obtained by treating molybdophosphoric acid, $H_3PMo_{12}O_{40}$ (henceforth denoted as PMo_{12}) with pyridine followed by activation in nitrogen at 420 °C exhibits catalytic activity for oxidation of propane to acrylic acid.[5] Ueda and Suzuki also showed that molybdovanadophosphoric acid (denoted as $PMo_{11}V$) similarly treated gives a less active and selective catalyst.[6] Our catalysts are obtained from PMo_{12} and $PMo_{11}V$ (prepared by known methods[7]), exchanged sequentially with niobium oxalate (giving $NbPMo_{12}$ and $NbPMo_{11}V$) and pyridine (giving $NbPMo_{12}$pyr and $NbPMo_{11}V$pyr) in aqueous media, followed by heating to 420 °C in flowing helium. The elemental compositions of the solids thus obtained are typically $Nb_{0.1-0.25}PMo_{12}(pyr)_{3-4}$ or $Nb_{0.1-0.25}PMo_{11}V(pyr)_{3-4}$ within experimental error.

Table 1 reports the catalytic performance of various materials for *n*-butane oxidation under hydrocarbon-rich conditions ($C_4/O_2 = 2/1$). All the solids prepared from precursors containing *both* pyridine and niobium are very active and selective. Note particularly the high space time yield (STY) for $NbPMo_{12}$pyr and $NbPMo_{11}V$pyr achieved by increasing the total flow rate by a factor of eight (15 mL min^{-1} to 120 mL min^{-1}; see entries 6 and 7, and 13 and 14, respectively, in Table 1). In contrast, the polyoxometalates that have not been exposed to pyridine do not exhibit significant activity (entries 1, 2, 8, and 9, Table 1), while samples treated with pyridine but without niobium do not give the highest activities

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[*] Prof. M. E. Davis, C. J. Dillon, J. H. Holles
Chemical Engineering
California Institute of Technology
Pasadena, CA 91125 (USA)
Fax: (+1) 626-568-8743
E-mail: mdavis@cheme.caltech.edu

Dr. J. Labinger
Beckman Institute
California Institute of Technology
Pasadena, CA 91125 (USA)

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Tabelle 1. Reactivity of *n*-butane.

Entry	Catalyst	T [°C]	Flow rate [mL min^{-1}][a]	Conversion [%]		Selectivity [%][c]				
				C_4	O_2	CO_x	Ac	AA	MA	STY[d]
1	PMo_{12}	380	4:2:4:5	0.2	7	64	34	2	–	–
2	$NbPMo_{12}$	380	4:2:4:5	3	32	13	7	2	70	0.017
3	PMo_{12}pyr	380	4:2:4:5	13.5	89	14	3	1	82	0.097
4	PMo_{12}pyr	340	4:2:4:5	7	55	10	4	1	83	0.050
5	$NbPMo_{12}$pyr	380	4:2:4:5	15[b]	100	25	3	1	71	0.084
6	$NbPMo_{12}$pyr	380	32:16:32:40	15[b]	100	5	3	1	90	0.840
7	$NbPMo_{12}$pyr	340	32:16:32:40	14	91	6	4	1	89	0.840
8	$PMo_{11}V$	380	4:2:4:5	0.5	9	31	17	–	50	1.6×10^{-3}
9	$NbPMo_{11}V$	380	4:2:4:5	0.4	9	42	19	4	25	6.3×10^{-4}
10	$PMo_{11}V$pyr	380	4:2:4:5	13.5	90	5	3	1	90	0.11
11	$PMo_{11}V$pyr	340	4:2:4:5	2	29	16	4	1	78	0.013
12	$NbPMo_{11}V$pyr	380	4:2:4:5	15[b]	100	16	5	2	76	0.090
13	$NbPMo_{11}V$pyr	380	32:16:32:40	14	95	9	5	3	80	0.760
14	$NbPMo_{11}V$pyr	340	32:16:32:40	13	83	26	10	4	59	0.560

[a] *n*-Butane:oxygen:helium:water. [b] Theoretical maximum conversion. [c] Abbreviations: C_4: *n*-butane; CO_x: carbon oxides; Ac: acetic acid; AA: acrylic acid; MA: maleic acid. [d] Space time yield of maleic acid [mmol min^{-1} g^{-1} of catalyst].

(entries 3, 4, 10 and 11, Table 1). Although the niobium content may vary, Nb/P ratios nearer to 0.25 gave higher activities. The presence of vanadium appears to have little influence on the reactivity of *n*-butane.

Table 2 compares the reactivity of *n*-butane over the new catalysts reported here to several of those given in the literature. The new catalysts exhibit substantially higher productivities (STY, entries 3 and 4, Table 2) and at least comparable selectivities, as well as the ability to operate at lower temperatures (300 °C; entry 5, Table 2). In addition to the hydrocarbon-rich conditions reported in Table 1, the new catalysts perform well in more typically studied hydrocarbon-lean environments ($C_4/O_2 = 1/10$; entry 6, Table 2).

Unlike most previous examples, these new catalysts are effective for more than one reactant: propane is also selectively oxidized to a variety of partially oxidized products (see Table 3). As with *n*-butane, the catalyst precursor that contains both niobium and pyridine gives the most active catalyst (entry 4, Table 3). Interestingly, in addition to forming acrylic and acetic acids, the new catalyst produces substantial amounts of maleic acid. Results using propene, 1,5-hexadiene, and ^{13}C-labeled propane in individual experiments as feed hydrocarbons suggest that maleic acid is formed by the reaction sequence shown in Scheme 1.

Table 4 compares the reactivity results from the new catalyst to some of the more selective propane oxidation catalysts that have been reported. Since the literature data are at different reaction conditions, for example, propane/O_2, propane concentration, temperature, residence time, etc., it is difficult to compare, but it is clear that while the catalyst reported here is not the most selective, it has exceptional productivity for acrylic acid (AA STY).

Tabelle 2. Reactivity of *n*-butane over various catalysts.

Entry	Catalyst	T [°C]	Flow rate [mL min^{-1}][a]	Conversion [%]		Selectivity [%]				
				C_4	O_2	CO_x	Ac	AA	MA	STY[c]
1	MoO_3	380	4:2:4:5	0.7	20	95	2.4	–	–	–
2	PMo_{12}	380	4:2:4:5	0.2	7	64	34	2	–	–
3	$NbPMo_{12}$pyr	380	32:16:32:40	15[b]	100	5	3	1	90	0.840
4	$NbPMo_{11}V$pyr	380	32:16:32:40	14	95	9	5	3	80	0.760
5	$NbPMo_{11}V$pyr	300	4:2:4:5	9	75	26	12	2	60	0.033
6	$NbPMo_{11}V$pyr	340	1:10:35:5	62	61	50	3.8	0.8	46	0.019
7	VPO[8]	380	4:6:26:0	30	–	8	–	–	80	0.067
8	$BiPMo_{12}O_{40} + 2\,VO^{2+}$[9]	360	6.3:58:218:34	31.8	–	37	17	14	32	0.001
9	$H_5PMo_{10}V_2O_{40}$[10]	340	0.6:5.4:24:0	90	–	–	–	–	38	0.003

[a] *n*-Butane:oxygen:helium:water. [b] Theoretical maximum conversion. [c] Space time yield of maleic acid [mmol min^{-1} g^{-1} of catalyst].

Tabelle 3. Reactivity of propane at 380 °C.[a]

Entry	Catalyst	Conversion [%]		Selectivity [%][d]						Yield [%] AA	STY[e] AA
		C_3	O_2	CO_x	$C_2^=$	$C_3^=$	Ac	AA	MA		
1	$PMo_{11}V$[b]	0.4	3.4	30	12	54	4	–	–	–	–
2	$NbPMo_{11}V$[b]	1.4	5.7	22	6	44	16	10	–	0.1	1.39×10^{-3}
3	$PMo_{11}V$pyr[b]	3.4	10.1	10	4	37	30	17	–	0.6	5.55×10^{-3}
4	$NbPMo_{11}V$pyr[c]	20.9	68.7	8	–	–	24	50	16	10.5	0.623

[a] $C_3/O_2/He/H_2O = 4:2:4:5$ (mol %). [b] Total flow rate = 15 mL min^{-1}; residence time = 0.42 s; total gas hourly space velocity (GHSV) = 9000 h^{-1}. [c] Total flow rate = 120 mL min^{-1}; residence time = 0.10 s; total GHSV = 36000 h^{-1}. [d] Abbreviations: C_3: propane; CO_x: carbon oxides; $C_2^=$: ethene; $C_3^=$: propene; Ac: acetic acid; AA: acrylic acid; MA: maleic acid. [e] STY = mmol acrylic acid min^{-1} g^{-1} of catalyst.

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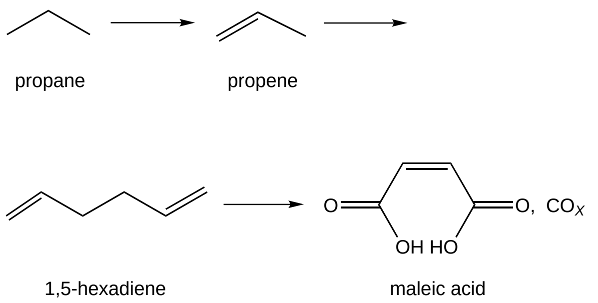
Tabelle 4. Reactivity of propane over various catalysts.

Entry	Catalyst	C_3:O_2:inert:H_2O [mL min^{-1}]	Residence time [s]	C_3 Conv. [%]	AA sel. [%]	AA yield [%]	AA STY [mmol min^{-1} g^{-1}]	Ref.
1	PMo_{12}	10:5:25:10	3.6	8	29	2	2.70×10^{-3}	6
2	$MoSbVNbO_x$	2.0:3.2:11.8:28.0	2.0	31	30	9	4.86×10^{-3}	4
3	$MoVNbTeO_x$	0.6:2.0:7.4:8.8	1.9	80	61	49	0.018	3b
4	$CsFe(PMo_{11}VO_{40})$	4.5:7.5:3.0:0	4.0	47	28	13	0.024	11
5	$NbPMo_{11}Vpyr$	32:16:32:40	0.1	21	50	11	0.623	this work



Scheme 1. Proposed sequence for the conversion of propane to maleic acid by the new catalysts.

At this time the nature of the active sites in these highly active catalysts is unknown. All the pyridine is removed by heating in helium to 420 °C. The pyridine acts as a reductant to lower the average oxidation states of vanadium (if present), molybdenum, and niobium (ascertained by using EPR, NMR, UV/Vis, and XANES studies). Heating under oxidizing conditions up to 420 °C renders the solids catalytically inactive; thus, reducing pretreatment conditions are necessary. Other amines can be used as reductants, but pyridine is the best found thus far. Exposure to temperatures above approximately 420 °C even in inert environments causes phase transitions ultimately leading to crystalline molybdenum oxides (from X-ray powder diffraction) that are not active catalysts.

The excellent performance in terms of yield and (especially) productivity, the versatility with respect to alkane feedstock, and the synthesis from precursors that are not only of well-defined composition and structure but also are amenable to a number of potentially informative spectroscopic and other methods for characterization, all strongly indicate that these new materials offer great promise towards the important goal of developing improved catalysts for selective oxidation. Further work towards extending the scope of catalytic reactivity, optimizing performance, and understanding the mechanism is ongoing.

Experimental Section

Preparation of $NbPMo_{11}Vpyr$: Sodium hydrogen phosphate (7.098 g, 50 mmol) was dissolved in water (100 mL) at room temperature and sodium metavanadate (6.097 g, 50 mmol) was dissolved in water (100 mL) at 80 °C. The two solutions were combined at room temperature and the mixture was acidified with concentrated sulfuric acid (5 mL), which led to a dark red solution. Sodium molybdate dihydrate (133.1 g, 550 mmol) was dissolved in water (200 mL) at room temperature and the solutions were combined. Concentrated sulfuric acid (85 mL) was added to the solution over 90 min (exotherm) with vigorous stirring. This generated a clear bright red solution that was added to diethyl ether (200 mL) in a separating funnel and shaken. This resulted in three phases, from which the dark red layer was decanted and retained. The aqueous layer was extracted twice, and the ethereal fractions were combined. The diethyl ether was removed resulting in a thick red syrup that was dissolved in water and recrystallized. The orange crystals of $PMo_{11}V$ were dried at 100 °C overnight. Niobium pentachloride (1.210 g, 4.48 mmol) was dissolved in water (10 mL) and the solution basified by using ammonium hydroxide (0.5 mL). The white precipitate was removed by filtration and dissolved in oxalic acid (1.008 g, 11.2 mmol in 20 mL water). The niobium oxalate solution was then slowly added to 11-molybdo-1-vandanophosphoric acid ($PMo_{11}V$; 20 g) dissolved in water (40 mL). The mixture was stirred and heated to 80 °C until the liquid had evaporated. An aqueous solution of pyridine (1.645 g, 20.8 mmol in 10 mL water) was slowly added to a slurry of the niobium polyoxometalate $NbPMo_{11}V$ (5.260 g) in water (30 mL) to form an immediate precipitate. The mixture was stirred and evaporated to dryness at 80 °C.

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