Selective oxidation of butane on phosphorus-modified silica supported vanadia catalysts

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Triethylphosphate impregnation of 2.8 wt% V/SiO_2 and subsequent controlled calcination produced phosphorus-modified supported vanadium catalysts. Phosphorus modification enhanced the yield of maleic anhydride in the partial oxidation of butane. Varying the phosphorus to vanadium atomic ratio from 0 to 2.8 increased the selectivity to maleic anhydride from 0 to approximately 48%. The selectivity was nearly constant up to 20% butane conversion and for different O_2/C_4H_{10} ratios. The Raman spectra of the phosphorus-modified samples had bands at 1040 and 930 cm^{-1}, and broad unresolved bands between 580 and 540 cm^{-1}. It was concluded that the active phases in these samples were α-$VOPO_4$.

Keywords: V/SiO_2; triethylphosphate; calcination; maleic anhydride; butane oxidation

1. Introduction

Alkanes are attractive alternative feedstocks for chemical synthesis. Compared to their aromatic counterparts, alkanes are both relatively inexpensive and environmentally friendly. Unfortunately, few catalysts selectively oxidize alkanes. Some of the few successful examples in the literature include: dehydrogenation of alkanes on V–Mg oxide [1], oxidation of propane to acrolein on Bi–Ag–V–Mo oxide [2], and oxidation of butane to maleic anhydride on V–P oxide [3]. Of these examples, only V–P–O is used to functionalize an alkane commercially.

Several groups in recent years have attempted to support V–P–O catalysts on silica [4–6], alumina [7,8], titania [4,7,9] or $AlPO_4$ [10]. Research into supported materials has been driven by two factors: supports (1) improve mechanical strength and thermal stability of the catalyst, and (2) increase dispersion of the active phase and, therefore, exposure of active sites. Unfortunately, most supported V–P–O catalysts reported in the literature have relatively poor selectivities to maleic anhydride production compared to the unsupported catalysts. Martinez-Lara et al.

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added either silica or titania to a reaction mixture used to produce α-$VOPO_4$ [4,11]. The resulting catalysts showed very poor selectivity in butane oxidation. Zazhigalov et al. impregnated mixtures of $VOCl_3/CCl_4$ and $POCl_3/CCl_4$ onto silica to produce catalysts with different P : V ratios. They observed a maximum maleic anhydride selectivity of 23% at a P : V ratio of 2.9 [5]. Do and Baerns impregnated both alumina and titania with a mixture of vanadium oxalate and phosphoric acid to produce catalysts with P : V ratios of 0.78 and vanadium loadings varying from 2.8 to 11.0 wt% [7]. The highest selectivities to maleic anhydride they obtained were 12 and 31% for 5.6 wt% V/Al_2O_3 and 2.8 wt% V/TiO_2, respectively. In comparison, Kuo and Yang have reported selectivities as high as 54% for a 14 wt% $VP_{1.6}O_x/AlPO_4$ catalyst [10].

In the above mentioned studies the optimum P : V ratio for maleic anhydride production was found to be significantly greater than 1 : 1, although unsupported V–P–O catalysts traditionally have had an optimal P : V ratio close to unity. The highest selectivities reported for the unsupported samples were only about 50%, much lower than ~ 70% for the unsupported ones. Unfortunately, these studies did not provide sufficient structural characterization of the active phase in the samples to understand these differences. We report here a study of phosphorus-modified silica-supported vanadia in which the samples were characterized with Raman spectroscopy to understand the changes in the selectivities for maleic anhydride in the oxidation of butane.

2. Experimental

The 2.8 wt% V/SiO_2 (equivalent to 5 wt% V_2O_5/SiO_2) was prepared with acid washed 35–60 mesh Davisil silica grade 646 using a procedure described previously [12]. Inductively coupled plasma atomic emission spectroscopy (ICP) analysis detected only low levels of metal impurities, which included less than 100 ppm of aluminum, titanium, and sodium, approximately 120 ppm of calcium and zirconium, and 200 ppm of iron. This sample is denoted PV0.0. Phosphorus was introduced to this sample as follows. Between 0.6 and 1.0 g of PV0.0 was calcined at 500°C in vacuo and then under 1 atm O_2 for 30–45 min in a pyrex tube equipped with a quick connect fitting containing an internal check valve. The tube was cooled to room temperature and transferred to a dry bag. The calcined sample had a Raman band characteristic of an isolated form of vanadia at 1040 cm^{-1} [12–16]. An appropriate amount of triethylphosphate (TEP, Aldrich 99%) was dissolved in an amount of methanol (Fischer Scientific, 99.9%, anhydrous) equivalent to 1.05 ml/g (the pore volume of PV0.0) in an impregnation vial and then transferred to the dry bag. The calcined PV0.0 was mixed with the TEP solution and shaken until the solid flowed freely.

The impregnated precursor was transferred to a reactor, and then heated to 80°C at a rate of 1°C/min under 20 ml/min of He to remove adsorbed methanol.

Subsequently, the sample was heated to 230°C at a rate of 2°C/min under 8 ml/min of O_2 and then rapidly to 425°C to decompose any remaining organic species. The catalysts were analyzed by ICP to determine the P : V ratios. Only a limited amount of phosphorus could be added in any one impregnation. Consequently, multiple impregnation–calcination cycles were required to produce catalysts with higher P : V ratios. The final compositions of the catalysts are shown in table 1.

Reaction studies were performed in a tubular, fused silica, flow microreactor with either an 88/8/4 or a 77/22/1 mixture of 2 mol% N_2 in He (Linde, high purity grade)/O_2 (Linde, extra dry grade)/C_4H_{10} (Linde, CP grade). After the final TEP impregnation, the calcined catalysts typically were exposed to 25 to 200 ml/min of the reaction mixture and were heated to the desired reaction temperature. A thermocouple housed in a thermowell inserted into the catalyst bed monitored the bed temperature. Typically 0.2–0.7 g of catalyst were used. The products were analyzed by on-line gas chromatography using columns described previously [12].

Raman spectra were collected using the 514.5 nm line of a Coherent INOVA 70-2 Ar ion laser at 25 mW power. The catalyst samples were pressed into wafers and mounted into a Raman cell. The cell was evacuated and heated at a rate of 15°C/min to 500°C whereupon 1 atm of O_2 was introduced. The samples were calcined for 30–40 min, cooled to room temperature, and analyzed by Raman spectroscopy in the O_2 atmosphere.

3. Results and discussion

The TEP impregnated 2.8 wt% V/SiO_2 sample (VP0.0) evolved methanol, small amounts of TEP, and trace amounts of acetaldehyde when purged with helium in the reactor at room temperature. Ethene was detected at about 60°C. Other organic species were detected as the sample was heated in oxygen from 80 to 230°C.

Table 1
Compositions, catalytic activities, and colors of catalysts

Catalyst	As prepared			Post-reaction			Activity[a]	Color
	wt% V	wt% P	P : V[b]	wt% V	wt% P	P : V[b]		
P/SiO_2	0.00	1.23	–	0.00	–	–	3.0	white
PV0.0	2.57	0	0	2.53	0	0	0.057	orange brown
PV0.6	2.57	0.89	0.57	2.44	0.85	0.57	0.073	brown green
PV1.4	2.69	2.36	1.45	2.39	2.08	1.44	0.085	dark green
PV2.2	2.46	3.32	2.22	2.33	3.13	2.22	0.065	dark green
PV2.8	2.09	3.54	2.78	–	–	–	0.051	dark green

[a] Rates of butane conversion at 425°C using an 88/8/4 He/oxygen/butane feed mixture, in mol C_4 converted (mol V)$^{-1}$ min^{-1}.
[b] Atomic ratios.

Between 140 and 200°C acrylic acid and acetone/propanal accounted for >15% of the organics, whereas above 200°C acetic acid accounted for 35% of the observed organics. Ethene was also detected over this temperature range, as well as some unidentified higher molecular weight species. Subsequent TEP impregnations and calcinations produced similar distributions of organic decomposition compounds.

Only a limited amount of phosphorus was retained by the catalysts in any one impregnation. In a series of experiments, sufficient TEP to produce samples with P : V ratios of 0.6, 1.0, and 2.0 was impregnated onto PV0.0. In every case the catalysts after calcination had P : V ratios of approximately 0.6. Successive impregnations were required to produce catalysts with higher P : V ratios. Phosphorus was also added to unmodified acid washed silica. A single phosphorus impregnation produced a 1.23 wt% P/SiO_2 catalyst. This would have corresponded to a P : V ratio of 0.72 had the 2.8 wt% V/SiO_2 precursor been used. The catalyst was denoted P/SiO_2.

P/SiO_2 was white whereas the PV0.0 was light yellow deepening to reddish orange on exposure to moisture. The phosphorus-modified vanadium catalysts became increasingly bluish with increasing phosphorous content and their colors were unaffected by exposure to the atmosphere. The colors of the samples are listed in table 1.

All of the PV catalysts were catalytically active for the oxidation of butane, whereas P/SiO_2 was not. Phosphorus modification of PV0.0 changed the product selectivity significantly. Table 2 shows the product distributions for each sample at two butane conversions for reactions at 425°C with 88/8/4 mixtures of $He/O_2/C_4$. The product distributions at other conversions followed the trends shown in the table. In addition to the products listed, small amounts of propene,

Table 2
Product distribution in butane oxidation at 425°C. He/oxygen/butane = 88/8/4

Sample	catalyst wt (g)	Total flow	Butane % conv.	% Selectivities [a]					
				MA	C_3O	CO	CO_2	other	TDS
P/SiO_2	0.301	103	0.0	0.0	0.0	0.0	0.0	0.0	0.0
PV0.0	0.259	99	4.5	0.0	6.2	12.7	17.2	9.1	54.9
	0.602	50	16.2	4.2	5.6	37.1	35.5	7.7	10.0
PV0.6	0.490	217	5.0	23.0	0.8	50.5	22.3	2.5	1.3
	0.490	50	18.7	21.1	0.2	50.9	24.8	3.0	0.0
PV1.4	0.508	200	6.8	39.6	0.6	40.1	16.9	2.7	0.0
	0.508	50	20.0	35.2	0.2	43.0	19.8	1.8	0.0
PV2.2	0.258	101	4.7	45.7	1.7	34.6	13.8	4.2	0.0
	0.690	33	16.5	48.7	0.5	33.7	14.9	2.2	0.0
PV2.8	0.297	100	3.7	46.4	0.0	37.8	15.8	0.0	0.0

[a] MA = maleic anhydride; C_3O = acetone/propionaldehyde; TDS = total dehydrogenation = sum of 1-butene, trans-2-butene, cis-2-butene, and 1,3-butadiene; others = sum of acetic acid, acrylic acid, and propene.

acrylic acid, and acetic acid were detected. All carbon balances were consistently satisfied within 2%.

At low conversions, PV0.0 produced primarily a mixture of 1-butene, trans-2-butene, cis-2-butene, and 1,3-butadiene but very little maleic anhydride [12]. At higher conversions, carbon oxides dominated. In comparison, all phosphorus-modified catalysts had higher selectivities for maleic anhydride. Although unsupported V–P–O has the greatest selectivity for maleic anhydride at a P : V ratio of approximately unity, the selectivity for maleic anhydride for the supported catalysts increased from 23 to 48% with a corresponding increase in the P : V ratio from 0.6 to about 2.8. Furthermore, the maleic anhydride selectivity remained constant for butane conversions up to 20%, the highest conversion studied. Another sample of a P : V ratio of 3.2 was also prepared. It was much less active than the other PV samples, although its selectivity for maleic anhydride remained at approximately 48% for a butane conversion of 2%.

The effect of O_2 : butane ratio in the feed was investigated with the PV2.8 sample. Under steady state conditions, a more oxidizing reaction mixture of 77/22/1 $He/O_2/C_4$ produced slightly lower activity and maleic anhydride selectivity, being 36.8%, than if the feed was an 88/8/4 $He/O_2/C_4$ mixture.

The activation energies for butane consumption on the phosphorus-modified catalysts also differed from that of PV0.0. They were calculated from data obtained between 400 and 450°C at less than 8% butane conversion. The values were $115 \pm 15, 97 \pm 10, 97 \pm 18, 97 \pm 12$, and 96 ± 13 kJ/mol for samples PV0.0, PV0.6, PV1.4, PV2.2, and PV2.8, respectively. Thus, within experimental error, the phosphorus containing samples had the same activation energy that was lower than that of V/SiO_2. The activities of the catalysts, expressed as moles of butane converted per mole of vanadium per minute, are shown in table 1. For most samples, the rates were within a factor of two.

The change in the catalytic properties of V/SiO_2 upon phosphorus modification suggested interaction between phosphorus and vanadia. Unfortunately, useful X-ray patterns were not collected with these samples, indicating that any vanadium phosphorus compounds formed were very small crystallites. However, changes in the samples could be observed with Raman spectroscopy. Fig. 1 shows the Raman spectra of the samples. Spectra of both silica and phosphorus-modified silica were featureless. The spectrum of a fresh sample of PV0.0 had a band at 1040 cm^{-1}, characteristic of a tetrahedrally coordinated isolated vanadyl species [13–17]. After reaction, bands characteristic of crystalline V_2O_5 at 998, 706, 408, 309, and 285 cm^{-1} appeared (fig. 1b). This agglomeration of isolated vanadia under butane oxidation conditions has been observed on high loading vanadia samples [12]. Both fresh and used samples of all of the PV catalysts retained the band at 1040 cm^{-1}. The spectra of samples PV1.4, PV2.2, and PV2.8 (figs. 1e, 1f, and 1g) had strong bands at about 1040 and 930 cm^{-1}, a weak band at about 980 cm^{-1}, and unresolved bands between 580 and 540 cm^{-1}. The spectra did not change after the samples were used in reaction. These spectra compared well with those of α_1-

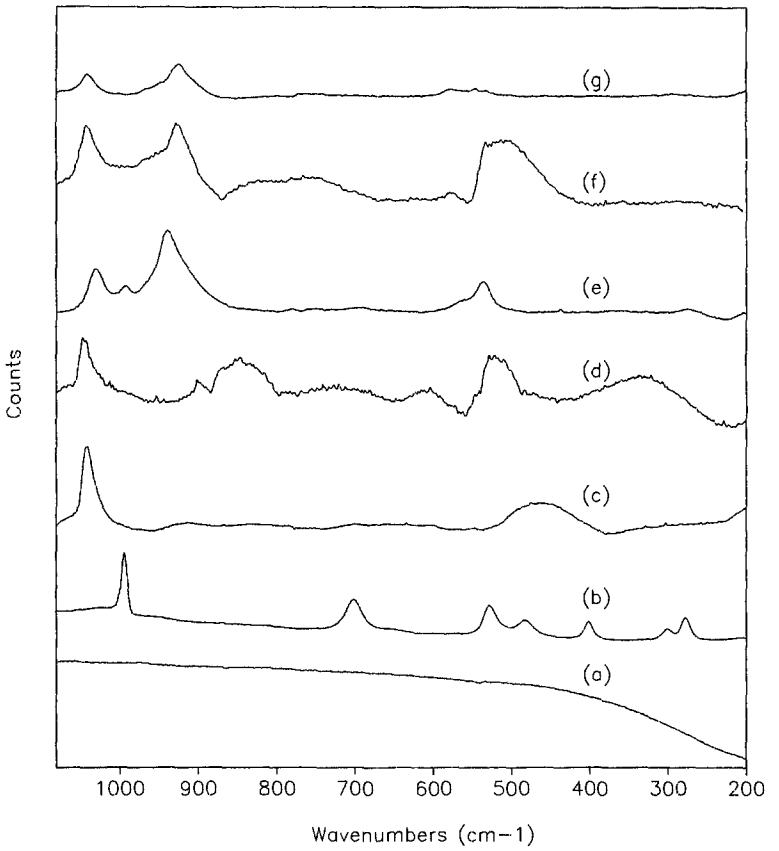

Fig. 1. Raman spectra of fresh treated: (a) silica, (b) V_2O_5, (c) PV0.0, (d) PV0.6, (e) PV1.4, (f) PV2.2 and (g) PV2.8.

$VOPO_4$ and its hydrate, $VOPO_4 \cdot 2H_2O$ [18]. Similarly Deo and Wachs have observed broad Raman bands at 1035 and 923 cm^{-1} for H_3PO_4 modified 0.56 wt% V/TiO_2 (P : V of 3.8) and have assigned them to α_1-$VOPO_4$ [9].

Thus, treatment of 2.8 wt% V/SiO_2 with triethylphosphate resulted in the formation of α_1-$VOPO_4$, which was hydrated to $VOPO_4 \cdot 2H_2O$ upon exposure to moisture. This is consistent with the catalytic results. It has been reported that over unsupported α-$VOPO_4$, butane is oxidized to maleic anhydride with a selectivity of about 50% [19], a value observed with samples PV2.4, PV2.8 and PV3.2. The formation of $VOPO_4$ instead of $(VO)_2P_2O_7$ was a result of the preparation procedure. After phosphorus impregnation, the samples were calcined in oxygen, which would oxidize the vanadium ions to the 5+ state. Phosphorus to vanadium ratios greater than the stoichiometric amount required to form $VOPO_4$ were expected because, in the impregnation procedure, phosphorus could coordinate either to the vanadia or to the silica support. A phosphorus distribution across the catalyst could yield an overall P : V ratio greater than unity, but a local P : V ratio close to

that of $VOPO_4$. Therefore, the poor selectivity for maleic anhydride reported in the literature for supported V–P–O catalysts probably is because some of the vanadium ions in those samples did not form vanadyl pyrophosphate or vanadyl phosphate due to deposition of some of the phosphorus on the support.

In conclusion, phosphorus modification of vanadia supported on purified silica enhanced the selectivity of butane oxidation to maleic anhydride. It resulted in the formation of very small crystallites of $VOPO_4 \cdot H_2O$ and α_1-$VOPO_4$, the catalytic properties of which were similar to the unsupported oxides. From these results, one would expect that if the samples were prepared in a reducing atmosphere, fine crystallites of supported $(VO)_2P_2O_7$ could be produced with catalytic properties similar to the unsupported samples.

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