n-Butane Oxidation to Maleic Anhydride and Furan with no Carbon Oxide Formation using a Catalyst derived from $VO(H_2PO_4)_2$

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The oxidation of *n*-butane at 390 °C over a catalyst derived from $VO(H_2PO_4)_2$ gives only maleic anhydride and furan as products and no CO or CO_2 are formed.

Maleic anhydride is obtained commercially from the oxidation of *n*-butane using vanadium phosphate catalysts[1] and this process represents one of the few highly selective processes available for the utilisation of an alkane. In previous research almost exclusive attention has been paid to catalysts formed from the catalyst precursor $VOHPO_4{\cdot}0.5H_2O$ which gives a final catalyst comprising mainly $(VO)_2P_2O_7$ after stabilisation in an air–butane reaction mixture.[2,3] For these catalysts the products that are observed for butane conversions up to 90% are mainly maleic anhydride and carbon oxides together with a trace of C_2 and C_3 acids.[1,4] The exclusive formation of partial oxidation products has not been observed with these catalysts and in general the selectivity to maleic anhydride is typically 80 mol% even at very low *n*-butane conversions (*ca.* 1–2%). A great effort has been expended in the modification of catalysts using promoters[5] but although catalyst activity has been improved by this approach, there are very few examples of selectivity enhancement and there are no reported catalysts that give no CO and CO_2, *i.e.* the products of total oxidation. Hence there is a need to significantly improve the selectivity to partial oxidation products for this reaction since the formation of any carbon oxides can represent a significant yield loss. We have now successfully addressed this problem and have found that catalysts derived from $VO(H_2PO_4)_2$ as the catalyst precursor give exclusive selectivity to the partial oxidation products of *n*-butane.

Pure $VO(H_2PO_4)_2$ was prepared by refluxing V_2O_4 (10 g) with H_3PO_4 (85%, 82 ml, *i.e.* $P/V = 10$) at 180 °C for 1 h. The solution was evaporated and the precipitate was washed with water and acetone to remove the unreacted H_3PO_4, and dried (110 °C, 15 h). Characterisation by powder X-ray diffraction confirmed the material to be $VO(H_2PO_4)_2$ and four different final catalysts were prepared from this precursor. Catalysts C1, C2 and C3 were prepared by heating the $VO(H_2PO_4)_2$ precursor at 500 °C for 24 h in air, nitrogen and 1.5% *n*-butane–air environments, respectively. Catalyst C4 was prepared by heating $VO(H_2PO_4)_2$ *in situ* in the reactor at 400 °C in 1.5% *n*-butane–air for 24 h. These catalysts were tested for *n*-butane oxidation (1.5% *n*-butane in air) using a standard laboratory microreactor and products were analysed by on-line gas chromatography. It was significant that at 390 °C only maleic anhydride and furan were formed as products and no CO or CO_2 was observed (Table 1). This result was confirmed by several repeat experiments and rigorous carbon mass balances confirmed that all carbon-containing products had been observed. For comparison catalysts derived from the standard $VOHPO_4{\cdot}0.5H_2O$ precursor were also investigated (Table 1) and the results confirm that for catalysts derived from this precursor the typical products of maleic anhydride, CO and CO_2 are observed. Although the *n*-butane conversion with catalysts derived from $VO(H_2PO_4)_2$ are low (≤8% at 390 °C) this is due to the low surface areas of the final catalysts C1–C4 (1 $m^2\ g^{-1}$) and the specific activity (mol maleic anhydride $m^{-2}\ h^{-1}$) is comparable to or higher than the catalysts derived from $VOHPO_4{\cdot}0.5H_2O$.

Characterisation of the final catalysts C1–C4 after catalyst testing using X-ray diffraction showed that the materials are not particularly crystalline and exhibit diffraction lines associated with $VO(PO_3)_2$ which is expected from the calcination of $VO(H_2PO_4)_2$.[6] X-Ray photoelectron spectroscopy indicates that the surface ratio of phosphorus and vanadium atoms of these materials before and after catalyst testing is $P/V = 4$. This is higher than the surface P/V ratio of catalysts derived from $VOHPO_4{\cdot}0.5H_2O$, for which most studies indicate a surface P/V $\leqslant 2.5$.[7]

In a separate set of experiments pure $VO(H_2PO_4)_2$ was prepared by a different method involving the reaction of $VOPO_4{\cdot}2H_2O$ with octan-3-ol[8] which was then heated *in situ* in the reactor in 1.5% *n*-butane in air for 24 h to form catalyst C5 and similar results were achieved (Table 1). In particular 100 mol% selectivity to maleic anhydride was observed at 4% *n*-butane conversion. The surface area for the final catalyst C5 was higher than C1–C4 (2.2 $m^2\ g^{-1}$) and in addition the specific activity was also enhanced. Hence it is clear that although the method of preparation of $VO(H_2PO_4)_2$ does not affect the high selectivities observed it can affect activity in a positive manner.

The absence of CO and CO_2 as products for catalysts derived from $VO(H_2PO_4)_2$ together with the formation of furan is a most significant result. In particular furan is not observed as a product of *n*-butane oxidation in oxygen-rich atmospheres for catalysts derived from $VOHPO_4{\cdot}0.5H_2O$.[4,9] It is possible that the high surface P/V ratio favours the isolation of the surface VO clusters that are considered to be the active sites for *n*-butane oxidation.[10] Alternatively it is also possible that new active sites are formed on the phosphorus-rich surface which are specific to the formation of maleic anhydride and furan. It is clear that further studies are required to fully understand these catalysts. However, it is interesting to note that a number of previous studies have shown that there is a controversy concerning the role of low levels of $VO(H_2PO_4)_2$ when present with $VOHPO_4{\cdot}0.5H_2O$ in the catalyst precursor. Some of our previous studies have shown that low concentrations of $VO(H_2PO_4)_2$ are deleterious[11] whereas more recently Morishige *et al.*[12] have indicated that $VO(H_2PO_4)_2$ can be beneficial. The present study therefore clarifies these previous findings.

Table 1 *n*-Butane conversion over catalysts derived from $VO(H_2PO_4)_2$[a]

Catalyst	T/°C	Conv./%	Product selectivity (%) MA	Furan	CO + CO_2	Specific activity/ 10^5 mol MA $m^{-2}\ h^{-1}$
C1	390	2	60	40	0	0.94
C2	390	6	80	20	0	3.80
C3	390	1	100	0	0	1.27
C4	390	8	75	25	0	2.90
	375	5	67	33	0	1.73
C5	375	4	100	0	0	2.36
VPA[b]	390	11	51	0	49	1.24
VPO[b]	390	27	52	0	48	1.35

[a] Catalyst (1 ml), 1.5% *n*-butane in air, total flow rate 1000 ml/ml catalyst h^{-1}, time on line 24 h. [b] VPA was prepared according to a standard procedure using hydrochloric acid as solvent and VPO was prepared according to a standard procedure using butan-2-ol as solvent; full details are given in ref. 13. Surface areas: VPA = 4 $m^2\ g^{-1}$, VPO = 14 $m^2\ g^{-1}$.

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