



## Direct grafting of alkoxide promoters on vanadium hydrogen phosphate precursors: Improved catalysts for the selective oxidation of *n*-butane

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### ABSTRACT

New vanadyl phosphate (VPO) catalysts for the oxidation of *n*-butane to maleic anhydride were synthesized by grafting reactive metal alkoxides onto pre-formed vanadyl phosphorus oxide precursor, VO(HPO<sub>4</sub>)<sub>1</sub>/2H<sub>2</sub>O, followed by a calcination and activation protocol. A series of precursors grafted with these alkoxides was used to generate promoted catalysts containing molybdenum and mixtures of molybdenum with main group or transition metal promoters. For many catalysts, a large increase (greater than twofold) in oxidation activity for *n*-butane was observed and the high selectivity to maleic anhydride was not compromised. For these catalysts, the N<sub>2</sub> BET surface areas do not change significantly with respect to unpromoted catalysts. Large reactivity enhancements were also obtained by contacting the alkoxides with vanadyl phosphate catalyst precursors which had been spray dried with polysilicic acid to form attrition resistant microspheres.

Promoted VPO catalysts containing molybdenum combined with other promoters such as Sn, Ti and, in catalysts without silica binder, Fe, Mn, and Zn show further performance improvements compared to the single promoter system containing molybdenum. Hence, the relative ordering of molybdenum co-promoters for VPO catalysts without silica binder is Sn > Fe > Zn > Mn ~ Bi > Co ~ Ni in order of decreasing activity. For catalysts spray dried with silica binder, the relative ordering of co-promoters is Ti > Sn > Cu > Al ~ Fe ~ Zr. The reactive grafting technique of promoters with VPO is well suited for rapid, high throughput screening methods for the preparation of materials in which a vanadyl phosphate precursor "scaffold" is used to generate the new materials. This technique may be extended to generate a variety of new catalysts.

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### 1. Introduction

Vanadyl phosphorous oxide (VPO) catalysts commercially important materials for the large-scale industrial production of maleic anhydride [1–6]. Several reviews have been published concerning the synthesis of VPO precursors as well as the role that promoters can play in improving catalytic performance [7,8].

In previous patents and publications, we have described our efforts to improve the performance of VPO catalysts by a synthetic method in which promoter cations are incorporated into the precursors by cation substitution into the VPO lattice during its synthesis. Our approach in these studies, in some cases, has been to substitute aliovalent or lower valent cations for vanadium on equivalent sites (e.g., Fe<sup>3+</sup> or Cr<sup>3+</sup> for V<sup>4+</sup>). One goal in doing so is to

increase the oxidation state of vanadium (for a stoichiometric catalyst) to improve performance. Other approaches involved using Fe<sup>3+</sup> and Sb<sup>5+</sup> or Bi<sup>3+</sup> and Mo<sup>5+</sup> to also substitute for V<sup>4+</sup> to modify the surface chemistry and reactivity of these catalysts [9,10].

In this paper, we describe novel catalysts for butane oxidation catalysis. These new catalysts for the oxidation of *n*-butane to maleic anhydride are synthesized by grafting reactive promoter alkoxides onto a pre-formed vanadyl phosphorus oxide precursor, VO(HPO<sub>4</sub>)<sub>1</sub>/2H<sub>2</sub>O. Since the VPO precursor has both water of hydration as well as hydrogen phosphate groups, it can react with alkoxides through hydrolysis or related reactions. In so doing, these alkoxides can directly graft onto the precursor surface. During a calcination and activation procedure, the promoter cations migrate into the bulk of the catalyst in varying degrees to form new microstructures with accompanying improvements in catalytic performance. In an earlier publication, we described initial studies in which VPO catalysts with combinations of bismuth and molybdenum promoters were synthesized using this

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grafting technique [11]. Now, a series of promoters have been studied to generate VPO based catalysts containing molybdenum, as well as molybdenum with other co-promoters derived from cations of several main group and transition metals. For some of these promoted catalysts, a large increase in activity was observed in microreactor evaluations, without compromising the high selectivity to maleic anhydride.

## 2. Experimental

### 2.1. Catalyst synthesis

A variation of an organic method was employed to synthesize the “base” catalyst precursors [12]. Vanadium pentoxide and anhydrous phosphoric acid, prepared by mixing  $P_2O_5$  with aqueous phosphoric acid, were refluxed in an 11:1 mixture of isobutyl alcohol and benzyl alcohol solvent under an inert atmosphere. Enough anhydrous phosphoric acid to satisfy a 1.1/1,  $P/V$  ratio was slowly added to the alcohol mixture over a period of 2 h. The solution was heated to reflux for an additional 15 h. Soluble pentavalent vanadyl species were reduced predominantly by benzyl alcohol to precipitate the blue tetravalent precursor, which in the case of pure VPO catalysts, crystallizes as  $VO(HPO_4)1/2H_2O$ . Excess phosphoric acid was washed from the blue filter cake with fresh isobutyl alcohol. The precursors were subsequently dried under vacuum at 150 °C for 18 h.

To create the new grafted promoted vanadyl phosphate catalyst, the reactive alkoxides were contacted with the vanadyl hydrogen phosphate hemihydrate precursor. Mixed alkoxides were prepared using the corresponding metal chlorides together with molybdenum pentachloride. The metal chlorides, when reacted with ethanol, formed a soluble mixed alkoxide complex which is different from a simple mixture of monocationic alkoxy species. For instance, bismuth alkoxide is insoluble in the absence of the molybdenum species, suggesting that a soluble alcohol complex has formed containing both bismuth and molybdenum. The mixed alkoxide, dissolved in alcohol, can be reactively grafted onto the pre-formed vanadyl phosphate precursor. The catalysts in these experiments contain only 1 mole% bismuth and 1 mole% molybdenum (based on vanadium) grafted onto  $VOHPO_41/2H_2O$ . It is likely that the alkoxides of bismuth and molybdenum react with the hemihydrate of the precursor or the hydroxyl groups associated with the hydrogen phosphate, thereby forming covalent linkages of the alkoxy species with the vanadyl hydrogen phosphate. This metallated precursor complex is then heated to yield the final, promoted catalyst. Catalyst samples (60 g) were calcined and activated in a small, 3.5 cm fluidized bed. The samples were heated in air at 390 °C for 1 h, then at 460 °C for 18 h under an atmosphere of 1.5% butane/air. The relatively high temperature of 460 °C ensured rapid equilibration of the catalysts.

A similar grafting procedure was employed on vanadyl hydrogen phosphate precursor which had been spray dried, in combination with polysilicic acid, to form attrition resistant microspheres. The VPO precursor was spray dried with polysilicic acid for attrition resistance [13]. During the spray drying operation the polysilicic acid forms a silica rich cell surrounding the catalyst microspheres. The spheres range in size from 15  $\mu\text{m}$  to approximately 100  $\mu\text{m}$ . Therefore, the attrition resistant microspheres are composed of aggregates of vanadyl hydrogen phosphate hemihydrate (typically 1–5  $\mu\text{m}$  in size) with polysilicic acid. We have discovered that the attrition resistant microspheres can be subsequently contacted with the reactive alkoxides described above, and then converted into an active catalyst by activation in a small fluidized bed microreactor using a procedure similar to that which was used for the catalyst powders.

### 2.2. Catalyst characterization

All samples were characterized by powder X-ray diffraction. Vanadium oxidation state measurements for the activated catalysts, as determined by redox titrimetry, do not show significant changes for the promoted catalysts with respect to the controls. Large differences in  $N_2/BET$  surface areas are not observed between the various promoted catalysts, or between the promoted catalysts and the unpromoted controls. This suggests that the increased *n*-butane oxidation activity is due to modification of active sites or an increase in the site density (sites/ $\text{m}^2$ ) of the catalyst surface.

To probe the catalyst microstructure, morphology and composition, electron microscopy instrumentation and techniques were used as previously described [11]. High resolution TEM, scanning TEM (STEM) with electron diffraction and electron stimulated energy dispersive X-ray spectroscopy (EDX) for chemical analysis were carried out using a high resolution CM 200 field emission (FE)–(S)TEM system operating at 200 keV. Surface topography of catalysts was investigated using a high resolution low voltage SEM (LVSEM) using an advanced Hitachi SP5000 [14]. The (S)TEM and the SEM systems were fitted with energy dispersive X-ray spectrometers (EDX) and were used for composition analyses of the catalysts.

Both as-received powders and cross-sectioned samples were used to determine the compositional depth profile in the samples. Analyses were performed on surfaces of the as-received powders, by performing experiments at different electron accelerating voltages in the LVSEM, from the same regions to understand the differences in their surface and bulk composition. The data were confirmed by analyses conducted on samples in which the catalyst particles were cross-sectioned to gain access to both the surface and the interior (core). EDX compositional analyses, of the surface of the cross-sectioned catalyst particles were then repeated at high resolution in the STEM using electron nanoprobe. The electron nanoprobe was moved gradually from the surface to the core of the particle. Analysis spectra were recorded from several dozen particles. The spectra were calibrated using well-characterized  $\text{Bi}_2\text{MoO}_6$  standards. The analyses provide high spatial resolution and increased chemical sensitivity from localized regions, thus enabling the extent of penetration of the promoters into the bulk of the catalyst to be quantified.

### 2.3. Microreactor evaluations

A fixed bed microreactor was used for catalytic evaluations. The microreactor consisted of a 40.64 cm by 0.64 cm stainless steel tube enclosed by an aluminum sheath (3.12 cm thick, to assist in minimizing thermal gradients) which itself was enclosed in a tube furnace. The reactor was mounted vertically with the direction of the gas flow from top to bottom. Pressure gauges were mounted near both the entrance and exit of the reactor to monitor pressure changes. A bypass valve installed near the reactor entrance allowed the entering gas stream to pass through either the reactor or to bypass the reactor and pass directly to the sampling valve system, allowing analysis of the reactor feed gases prior to reaction. Also, a tee connection at the top of the reactor allowed a thermocouple to be mounted for monitoring the temperature at the entrance to the packed catalyst bed. Commercially available mass flowmeters (Tylan Model FC-260) of ranges 0–100 and 0–10  $\text{cm}^3/\text{min}$ , respectively, were used at the reactor feed. The heated exit gas stream (200 °C) passed through a heated sampling valve allowing the selection of a gas sample (250  $\mu\text{l}$ ) of the stream for analysis by gas–liquid chromatography (GLC), using commercially available instruments (Gow-Mac Series 740P FID GLC). The GLC was used to analyze for butane and for reaction products, including maleic anhydride, acetic acid, and acrylic acid.

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