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PRIORITY COMMUNICATION

Amorphous Vanadium Phosphate Catalysts from Supercritical Antisolvent Precipitation

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Crystalline vanadium phosphate catalysts (VPO) are the only example of a commercial heterogeneous partial oxidation catalyst for the activation of alkanes. The origin of activity is generally accepted as being associated with the crystallinity of the compounds. Here we describe a new preparative route to VPO using antisolvent precipitation with supercritical CO_2 to generate amorphous microspheroidal VPO, which produces a material with an activity per unit area comparable to those of conventional crystalline VPO catalysts. This finding throws doubt on the currently accepted view for the origin of the activity of VPO catalysts and the role of crystalline phases. © 2001 Academic Press

INTRODUCTION

Heterogeneous catalysts for selective oxidation of hydrocarbons for the most part involve oxides, phosphates, and molybdates of a range of metals. A key feature of all these materials has been the observation that well-defined crystalline phases are often associated with the selective activation of the hydrocarbon feedstock (1, 2). For example, highly crystalline bismuth molybdate phases are known to be involved in the selective oxidation and ammoxidation of propene (3), and additionally crystalline $FeSbO_4$ (4, 5) and $USbO_{10}$ (6) have been used commercially for the same reaction. The observation that crystalline materials are involved in these important surface-catalysed reactions has aided the understanding of the mechanism by which these catalysts function (1, 2, 7). It has also directed the preparation methodologies used in the design of new catalytic materials, since these may involve impregnation and coprecipitation methods (8) together with a high-temperature heat treatment step that favours crystallisation. For one particular catalyst, namely vanadium phosphate (VPO) catalysts, the preparation and evaluation of crystalline VPO phases has dominated the research since their discovery in 1968 (9). Indeed, over a thousand papers and patents have addressed this complex catalyst system, but mainly focusing on the preparation and testing of crystalline catalysts. In contrast, our studies demonstrate that amorphous VPO catalysts have comparable catalytic performance, in terms of the rate of product synthesis per unit area of catalyst surface, when compared with the previously well-characterised crystalline materials and that the key to improving catalysts in the future may focus upon optimising amorphous material.

Vanadium, phosphorus, and oxygen can form a broad range of crystalline phases and many of them have been identified in oxidation catalysis, e.g., $VOHPO_4.0.5H_2O$, α_I-$VOPO_4$, α_{II}-$VOPO_4$, β-$VOPO_4$, γ-$VOPO_4$, δ-$VOPO_4$ and $(VO)_2P_2O_7$ (10). In view of this, previous catalytic studies have concentrated on the preparation of these crystalline materials. Indeed, current industrial catalysts are based on $VOHPO_4.0.5H_2O$ as a low-temperature precursor which gives a final catalyst that comprises mainly crystalline $(VO)_2P_2O_7$ after stabilisation in an air–butane reaction mixture (11, 12). In these catalysts the transformation from the precursor to the final catalyst is known to be topotactic and this has focused attention on developing catalyst preparation methods that enable control of the crystalline precursor morphology. Early methods for the synthesis of $VOHPO_4.0.5H_2O$ utilised V_2O_5 and H_3PO_4 with HCl (9, 13) or alcohols (14) as reducing agents. Subsequently, we have shown that $VOPO_4.2H_2O$ could be transformed to $VOHPO_4.0.5H_2O$ on reaction with alcohols and the choice of alcohol governed the morphology of the material formed (15). Recently, we have shown that the three materials

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prepared by three different methods, designated as VPA, VPO, and VPD, respectively, give final catalysts that have similar activity per unit surface area of catalyst even though the catalysts comprise differing relative amounts of crystalline $(VO)_2P_2O_7$ and various $VOPO_4$ polymorphs as shown by a detailed high-resolution electron microscopy study (16). This observation is surprising since the broad range of crystalline V(V) and V(IV) phases present would have been expected to give very different catalytic performances, as has been shown for the individual pure compounds (17). The identical catalytic performance could, in principle, be ascribed to a common overlayer that is stabilised on the crystalline subsurface (whether it be $(VO)_2P_2O_7$ or $VOPO_4$) by the reaction conditions (i.e., partial pressures of butane and oxygen, and temperature). Indeed detailed TEM studies of the catalysts have indicated that an amorphous layer 1–2.5 nm in thickness (Fig. 1a) exists on the surface of the crystalline $(VO)_2P_2O_7$ phase (18) although the origin of this overlayer is uncertain. *A number of previous studies (19, 20, 21, 22) have indicated that amorphous material is present in active catalysts and may play a role in the selective activation of butane. However, the catalyst in all these previous studies contained substantial quantities of crystalline phases in addition to the amorphous material, and hence it is not possible to determine the role, if any, of these amorphous compounds*. We consider that the presence of *an amorphous* overlayer on $(VO)_2P_2O_7$ (Fig. 1a) may result from a combination of one or more of the following processes: (i) exposure of the crystalline surfaces to the reaction feed producing amorphous material *in situ*, (ii) electron beam damage of the $(VO)_2P_2O_7$ crystallites (which are known to completely amorphise after 20–30 s under typical electron beam irradiation conditions in the microscope), and/or (iii) preferential beam sensitivity of crystalline surface $VOPO_4$ (which are known to completely amorphise in a matter of seconds in the electron beam of the microscope). With TEM alone we are not able to determine unequivocally whether the presence of a surface amorphous layer is simply an artefact due to beam damage or a genuine catalytically active phase. One way around these problems is to attempt to create and maintain a completely amorphous VPO catalyst which has an activity similar (if not identical) to those of standard "crystalline" catalysts.

METHODS

A solution of H_3PO_4 (1.8 g, 100%, Aldrich) in isopropanol (120 ml) was refluxed with $VOCl_3$ (1.6 ml, Aldrich) for 16 h to give a blue solution. The resulting isopropanol solution was processed using supercritical carbon dioxide to precipitate the vanadium phosphate from solution using the following methodolgy. The isopropanol solution of vanadium phosphate was pumped through a fine capillary (220 μm i.d.) into the precipitation vessel containing concurrently flowing CO_2. Carbon dioxide was pumped as a liquid by a modified HPLC pump and the system pressure was maintained by a back pressure regulator (BPR). To achieve supercritical conditions the precipitation vessel (PV) was held in a GC oven and VPO_{scp} was collected on a filter bed. The isopropanol solution was pumped at 0.1 ml/min through the capillary into excess CO_2 which was pumped at 7 ml/min. The system pressure was held constant at 110 bar and the precipitation vessel kept at 60°C.

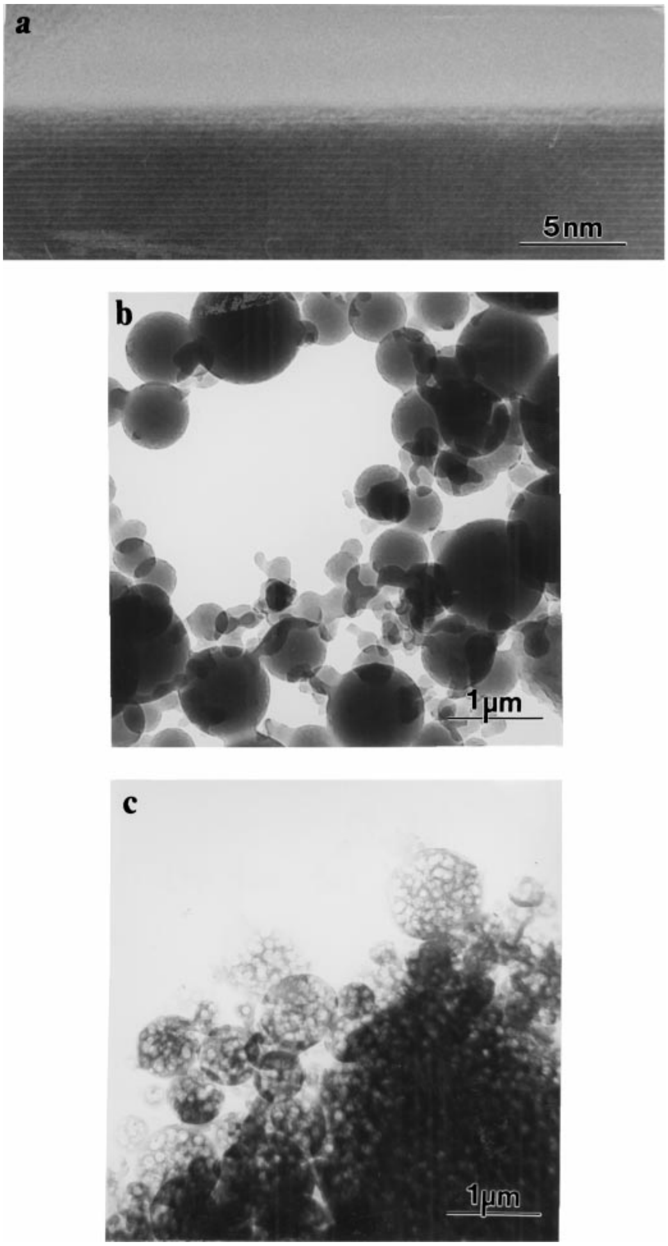

FIG. 1. (a) TEM micrograph showing the "amorphous" overlayer observed commonly on $(VO)_2P_2O_7$ crystallites in activated VPO catalysts. Electron micrographs of (b) the VPO_{scp} precursor and (c) the VPO_{scc} activated catalyst.

The evaluation of catalyst performance was carried out using a standard laboratory-scale fixed-bed microreactor apparatus fitted with on-line gas chromatographic analysis. Mass flow controllers were used to control the flow of reactant gases to the catalyst bed and satisfactory carbon mass balances were obtained for all the data collected (97–103%). Typically the mass of catalyst used was 0.500 g and the concentration of butane in air was 1.5% by volume. A gas hourly space velocity (GHSV) of 2400 h^{-1} was used during these tests. Activation of the precursor was achieved by heating the sample from room temperature to 400°C at 3°C/min under the reaction mixture. Analysis of the reactor feedstream proceeded during this activation step and for a further 72 h after a temperature of 400°C was attained.

RESULTS AND DISCUSSION

VPO_{scp} was evaluated as a catalyst for the partial oxidation of butane to maleic anhydride in a standard laboratory microreactor and the results are shown in Table 1 and Fig. 2. For comparison the results for typical catalysts prepared by standard VPA, VPO, and VPD procedures are also shown in Table 1 and Fig. 2. The data presented are normalized for surface area, which was 40 $m^2\,g^{-1}$ for the VPO_{scp} precursor and 6 $m^2\,g^{-1}$ for the used catalyst, VPO_{scc}, to show the intrinsic activities of the catalyst surfaces, since it is well known that differences in catalyst performance can be easily manipulated by changing the surface area (10). From these results it is clear that the new vanadium phosphate catalyst (VPO_{scc}) prepared using supercritical precipitation offers two distinct advantages over previous catalyst preparation methods. First, and most interestingly, VPO_{scc} does not require an extensive pretreatment time in the reactor. Stable catalytic performance is attained (and maintained for over 100 h) as soon as the catalyst reaches the required operating temperature. In contrast, the catalysts based on the industry standard precursor, $VOHPO_4.0.5H_2O$, always require 24–72 h in the microreactor to achieve stable catalytic performance. During this period the topotactic transformation of $VOHPO_4.0.5H_2O$ to crystalline $(VO)_2P_2O_7$ and $VOPO_4$ phases occurs (11) and the active sites on the catalyst surface are formed. Second, the new VPO_{scc} is apparently more active for maleic anhydride production than the standard vanadium phosphate catalysts *despite the GHSV being twice that used for the conventional VPA/VPO/VPD catalysts*. This shows for the first time that wholly amorphous VPO acts as an effective catalyst.

TABLE 1

The Yield of Maleic Anhydride (mol/h · m^2) for the VPA, VPO, VPD, and VPO_{sc} Catalysts under Steady-State Conditions

Preparation route	*n*-Butane conversion (%)	Selectivity (%)	Surface area ($m^2\,g^{-1}$)	Specific activity (mol MA $m^{-2}\,h^{-1}$)
VPA	11	51	4	1.24×10^{-5}
VPO	27	52	14	1.35×10^{-5}
VPD	62	64	43	1.19×10^{-5}
VPO_{scc}	24	48	6	2.2×10^{-5}

Note. GHSV = 1200 h^{-1} for the VPO, VPD, and VPA catalysts; GHSV = 2400 h^{-1} for the VPO_{sc} catalyst. The reaction temperature was 400°C and the concentration of butane in air was 1.5% by volume for all catalysts.

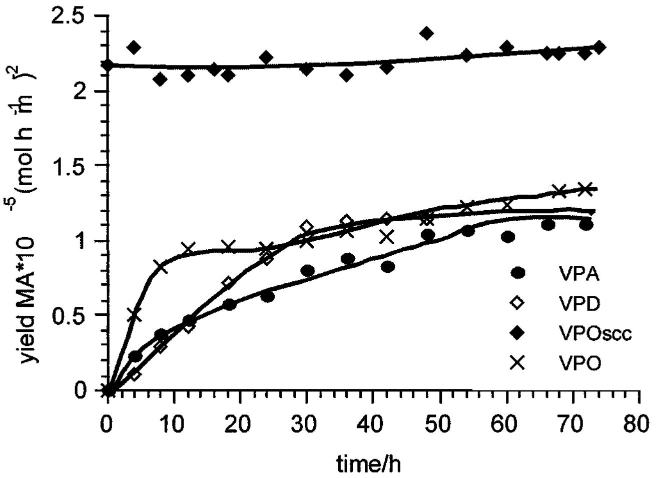

FIG. 2. The yield of maleic anhydride (mol/h · m^2) with time on stream for the VPA, VPO, VPD, and VPO_{sc} catalysts. GHSV = 1200 h^{-1} for the VPO, VPD, and VPA catalysts; GHSV = 2400 h^{-1} for the VPO_{sc} catalyst. The reaction temperature was 400°C and the concentration of butane in air was 1.5% by volume for all catalysts.

TEM images of the precursor and activated VPO_{sc} material are shown in Figs. 1b and 1c, respectively. The precursor material (VPO_{scp}) consists of discrete spherical particles ranging between 75 nm and 5 μm in size, although most lie between 75 nm and 1 μm in diameter. These particles show no diffraction contrast (only thickness contrast) and are very prone to electron beam damage. The 50 h activated catalyst (VPO_{scc}) comprises agglomerated spherical particles which show the initial signs of sintering. Several spherical voids, *ca.* 0.2 nm in diameter, are usually seen within each particle, arising presumbly from the loss of water during activation. Low-dose, high-resolution electron microscopy (HREM) imaging experiments on both the presursor and activated catalyst show no sign of lattice fringes; only amorphous speckle contrast is seen. Powder X-ray diffraction and selected area electron diffraction analysis of the VPO_{sc} material in both the precursor and activated forms show them both to be amorphous. This is also consistent with the fact that the particles show no crystallographic faceting and adopt a minimum surface area (i.e., spherical) morphology. In other VPA/VPO/VPD preparations, an equivalent activation procedure would always generate a considerable fraction of crystalline $(VO)_2P_2O_7$ and often some $VOPO_4$ polymorphs (16) (which are easily identifiable by HREM and electron diffraction) Our material, activated at 400°C for 50 h, seems to comprise a stable mixed P_2O_5– V_2O_5 glassy phase. This is entirely feasible since both P_2O_5 and V_2O_5 satisfy Zachariasen's rules for glass formation (23) and are completely miscible. In fact, even heating VPO_{scp} in pure N_2 at 750°C for 6 h resulted in the formation of only a very minor amount of nanocrystalline $(VO)_2P_2O_7$, whereas a similar treatment for VPA/VPO/VPD material would result in complete crystallisation to $(VO)_2P_2O_7$.

Our results give the first clear and definitive demonstration that a noncrystalline vanadium phosphate catalyst may be the preferred material for the selective oxidation of butane to maleic anhydride. Given the flexibility of the supercritical preparation method, i.e., the range of organic solvents that can be used together with the various experimental CO_2 parameters for this preparation methodology, we consider that VPO_{sc} could represent a new future for commercial amorphous vanadium phosphate catalysts, a field previously dominated by highly crystalline materials derived from $VOHPO_4.0.5H_2O$. Indeed, our studies show that the crystalline material, that has been the object of study for over 30 years, may only be an elegant support for an amorphous active surface layer. Furthermore, our studies show that this amorphous material can be more effectively prepared using techniques alternative to those outlined before. This observation challenges perceived ideas concerning the synthesis and design of industrial heterogeneous oxide catalysts, and hence the discovery outlined in this paper can be expected to redefine the future preparation methodology for many heterogeneous catalysts.

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