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Effect of different calcination environments on the vanadium phosphate catalysts for selective oxidation of propane and *n*-butane

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Abstract

Vanadium phosphate catalysts were synthesized via $VOPO_4{\cdot}2H_2O$ and were calcined in two different hydrocarbon reaction environments, *i.e.* *n*-butane/air and propane/air. Both catalysts are denoted VPDB and VPDP, respectively. Both catalysts exhibited a good crystalline with characteristic peaks of pyrophosphate phase. However, the peaks for VPDP are shown to be more prominent than those of VPDB. BET surface area showed that VPDB gave higher surface area (23 $m^2\ g^{-1}$) compared to VPDP (18 $m^2\ g^{-1}$). The average V valence state for VPDP is 4.08 and the higher V valence state for VPDB is 4.26 due to higher amount of V^V for VPDB. Furthermore 14.2% of V^{III} was found for VPDP but none for VPDB. SEM micrographs clearly revealed that the morphologies of both catalysts composed of plate-like crystallite that was arranged into the characteristic of rosette cluster. However, the catalyst calcined in *n*-butane/air environment (VPDB) resulted in an increment of the amount of plate-like crystal formed in the rosette rosebud agglomerates. TPR in H_2 profiles of both catalysts gave two reduction peaks corresponding to two kinetically different oxygen species which were associated with V^V and V^{IV} phases, respectively. VPDB removed larger amount of active oxygen species linked to V^{IV} phase which eventually caused a higher conversion rate in the selective oxidation of *n*-butane and propane to maleic anhydride and acrylic acid, respectively.

Keywords: VPO; *n*-Butane oxidation; Propane oxidation; Maleic anhydride; Acrylic acid

1. Introduction

The most active phase of VPO catalysts for synthesis of MA is made up of a well-crystallized $(VO)_2P_2O_7$ which is considered to possess unique structural and surface features to allow the activation of alkane [1,2]. This phase is generally generated by a long-term calcination of the precursor, $VOHPO_4{\cdot}0.5H_2O$ prepared via reduction of $VOPO_4{\cdot}2H_2O$ using isobutanol as reducing agent followed by treatment in a reaction environment. Transformation of precursor to active phase can be affected by the temperature, time and atmosphere of treatment [1].

The surface chemistry and bulk properties of the active VPO catalysts change with the time of calcination and with the calcination condition [4]. The composition of the VPO surface is complex as crystalline phases other than the main phase vanadyl pyrophosphate are often observed and disordered phases are also found. The capability of VPO system to form different phases with similar structures often leads to a multiphase system and all these phases can be transformed easily into each other enhanced the complexity of the VPO catalysts. Different phases showed different catalytic performance in selective oxidation of *n*-butane. A number of previous studies [2,5] suggested that a combination of vanadyl pyrophosphate along with patches of $VOPO_4$ phases play an important role in the selective oxidation of *n*-butane. However, very little has been reported concerning the catalyst active phases or active sites of the VPO catalyst in selective oxidation of propane. Therefore, the nature of the active sites, the preferred composition of the catalyst and the role of the V^V and V^{III} phases remain to be a fascinating topic for study.

In the present study, we investigate the influence of calcination agents (*n*-butane/air and propane/air) on the catalytic performance of the VPO catalysts prepared from $VOPO_4{\cdot}2H_2O$ for partial oxidation of *n*-butane and propane. The changes in the physical and chemical properties of the VPO catalysts calcined in

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two different conditions are systematically observed by X-ray diffraction, redox titration, ICP-AES, N_2 adsorption–desorption isotherms, scanning electron microscopy (SEM) and H_2-TPR. Furthermore, their catalytic performances are discussed in relation to the reactivity of the lattice oxygen and the vanadium species present in the samples.

2. Experimental

2.1. Catalysts—preparation

The catalysts were prepared via dihydrate method. Vanadium pentoxide, V_2O_5 (15.0 g from Fluka), was suspended by rapid stirring into a mixture of *o*-H_3PO_4 60 mL, 85% from Merck (71.75 cm^3) and water (360 cm^3). The vanadium oxide–acid mixture was stirred and refluxed for 24 h at 393 K. The mixture was then cooled to room temperature. The yellow solid was recovered by filtration, washed sparingly with water and oven dried at 383 K for 24 h. $VOPO_4{\cdot}2H_2O$ was then refluxed with isobutanol (1 g/20 mL) for 21 h and the solid product was recovered by filtration and oven dried at 383 K for 21 h to obtain the precursor, $VOHPO_4{\cdot}0.5H_2O$, denoted VPDpre. The resulting precursor, which was shown to be a well-crystallized $VOHPO_4{\cdot}0.5H_2O$ by XRD analysis, was then calcined under a flow of propane/air mixture (1% propane in air) at 673 K for 36 h (denoted VPDP) and under a flow of *n*-butane/air (0.75% *n*-butane in air) for 75 h (denoted VPDB).

2.2. Catalysts—characterization

The total surface area of the catalysts was measured by BET (Brunauer–Emmer–Teller) method using N_2 adsorption at 77 K. This was done by using ThermoFinnigan Sorptomatic 1990 nitrogen adsorption–desorption analyzer.

The average oxidation states of vanadium in all the samples were determined by the method described by Niwa and Murakami [6].

The X-ray diffraction (XRD) analyses were carried out using a Shimadzu diffractometer model XRD 6000 employing Cu Kα radiation to generate diffraction patterns from powder crystalline samples at ambient temperature.

The bulk chemical composition was determined by using a sequential scanning inductively coupled plasma-atomic emission spectrometer (ICP-AES) Perkin-Elmer Emission Spectrometer model Plasma 1000.

SEM was done using a Jeol JSM-6400 electron microscope. The samples were coated with gold using a sputter coater.

TPR (temperature-programmed reduction) analysis was done using a ThermoFinigan TPDRO 1110 apparatus utilizing a thermal conductivity detector (TCD).

2.3. Catalytic oxidation of propane to acrylic acid

The oxidation of propane to acrylic acid was carried out at 673 K in a fixed bed multitubular reactor with a standard volume of catalyst (0.5 mL). A feedstock containing propane, oxygen, nitrogen and steam (ratio = 1/2/18/9) with GHSV = 1200 h^{-1} was introduced to the reactor. The products were then fed via heated lines to an on-line gas chromatography for analysis.

2.4. Catalytic oxidation of n-butane to maleic anhydride

The oxidation of *n*-butane was carried out in a microreactor with a standard mass of catalyst (250 mg). The gases *n*-butane and air were fed to the reactor via calibrated mass flow controllers to give a feedstock composition of 1.5% *n*-butane in air. The products were then fed via heated lines to an on-line gas chromatograph for analysis. The reactor comprised a stainless steel tube with the catalyst held in place by plugs of quartz wool. A thermocouple was located in the centre of the catalyst bed and temperature control was typically ±1 °C. Carbon mass balances of ≥97% were typically observed.

3. Results and discussion

3.1. X-ray diffraction (XRD) analysis

The XRD pattern of the precursor, VPDpre (Fig. 1) only shows the characteristic reflections of vanadyl hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5H_2O$), with peaks at $2\theta = 15.5^\circ$, 19.6°, 24.14°, 27.0° and 30.4° [12]. The peaks at $2\theta = 15.5^\circ$ and 30.4° corresponds to (0 0 1) and (1 3 0) reflections, respectively, and the (1 3 0) reflection was the dominant feature in the precursor which is the characteristic for the precursor prepared by using dihydrate method [7].

For VPDP and VPDB catalysts, the XRD patterns (Fig. 1) show similar diffraction pattern composed of a well-crystallized $(VO)_2P_2O_7$ phase with three main characteristic peaks appeared at $2\theta = 22.8^\circ$, 28.4° and 29.8°, which correspond to (0 2 0), (2 0 4) and (2 2 1) planes, respectively.

All three peaks for the catalyst calcined in propane/air condition for VPDP are shown to be more prominent as compared to the 75 h *n*-butane/air calcined counterpart VPDB. In fact, catalyst calcined under *n*-butane/air is less crystalline compared with the catalyst calcined under propane/air stream. The development of the crystalline structure and/or

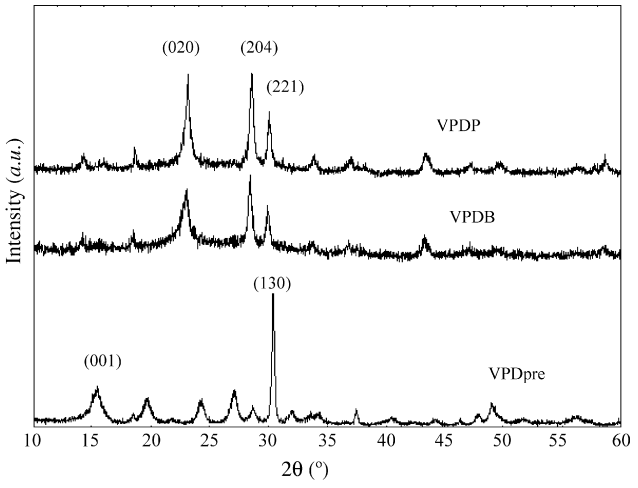

Fig. 1. XRD patterns of VPDpre, VPDB and VPDP.