



Effect of varying reflux durations on the physico-chemical and catalytic performance of vanadium phosphate catalysts synthesized via vanadyl hydrogen phosphate sesquihydrate

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ABSTRACT

A series of vanadyl pyrophosphate, $(VO)_2P_2O_7$, catalysts prepared via vanadyl hydrogen phosphate sesquihydrate precursors ($VOHPO_4 \cdot 1.5H_2O$) was calcined in a reaction flow of 0.75% *n*-butane in air mixture at 733 K for 18 h. The precursors have been synthesized by refluxing vanadyl phosphate dihydrate ($VOPO_4 \cdot 2H_2O$) with 1-butanol for different lengths of time, i.e. 8, 15 and 24 h, and the produced catalysts were denoted as VPO₅-R8, VPO₅-R15 and VPO₅-R24, respectively. X-ray diffraction (XRD) patterns of the three catalysts showed similar diffraction pattern, comprised of a well-crystallized $(VO)_2P_2O_7$ phase. Brunauer–Emmett–Teller (BET) surface area measurements showed that VPO₅-R24 has the highest specific surface area, i.e. $31 \text{ m}^2 \text{ g}^{-1}$ followed by $27 \text{ m}^2 \text{ g}^{-1}$ and $19 \text{ m}^2 \text{ g}^{-1}$ for VPO₅-R15 and VPO₅-R8, respectively. Inductively coupled plasma (ICP) analyses indicated that the P/V atomic ratios of these catalysts were in the optimum range in producing $(VO)_2P_2O_7$ phase. A small increment in the average oxidation number of the vanadium was observed as the precursor reflux duration increased. Scanning electron microscope showed the secondary structures of the catalysts with plate-like crystals in different sizes, which were agglomerated into rosette-shape clusters. The total amount of oxygen desorbed from the catalysts increased as the precursor reflux duration increased. Temperature-programmed reduction (TPR) in H_2 profiles of all the catalysts gave three reduction peaks. VPO₅-R8 gave the highest total amount of oxygen removed from V^{5+}/V^{4+} phase followed by VPO₅-R15 and VPO₅-R24. Catalytic tests revealed that the catalyst with lower precursor reflux duration exhibited higher selectivity but lower activity and vice versa.

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1. Introduction

The high environmental impact and mounting prices of benzene in the early 1970s have resulted in the finding of other feedstocks for maleic anhydride [1]. Consistent researches in both academic and industrial sectors have shed considerable light on the nature of a catalyst performing an extremely selective, 14-electron oxidative conversion of *n*-butane to maleic anhydride [2]. This industrial process is still the only commercialized alkane selective oxidation by heterogeneous gas-solid catalytic process, which is specifically based on the presence of vanadyl pyrophosphate, $(VO)_2P_2O_7$ [3,4]. $(VO)_2P_2O_7$ has been identified as the critical active phase for the selective oxidation of *n*-butane [5].

Recently, different researchers have extensively studied a variety of modifications for the preparation pathway of vanadium phosphorus oxide (VPO) catalyst such as calcination conditions [6], incorporating promoters [7] and P/V atomic ratios [8,9]. The

surface chemistry and bulk properties of the active VPO catalysts change with the time and condition of calcination were reported [10]. Also, the catalytic properties of this catalyst could be improved by the incorporation of specific promoters, which encourage higher selectivity towards maleic anhydride [11,12].

In the present study, the latest alternative route in producing $(VO)_2P_2O_7$ catalyst, which is via vanadyl hydrogen phosphate sesquihydrate precursor ($VOHPO_4 \cdot 1.5H_2O$) [13–15] has been employed. The effect of varying reflux durations in the preparation of the sesquihydrate precursors towards the physico-chemical properties and catalytic performances of the catalysts was examined.

2. Experimental

2.1. Preparation of vanadyl pyrophosphate catalysts via sesquihydrate precursors

The synthesis of $VOHPO_4 \cdot 1.5H_2O$ precursor involving vanadyl phosphate dihydrate, $VOPO_4 \cdot 2H_2O$ as an intermediate product,

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