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TPD and TPR Studies of Vanadyl Pyrophosphate Catalysts derived from $VOPO_4 \cdot 2H_2O$ Precursor

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Abstract

Three vanadyl pyrophosphate catalysts synthesised via $VOPO_4 \cdot 2H_2O$ have been calcined for 40, 100 and 132 hours at 673 K in a reaction flow of *n*-butane/air. These catalysts were denoted VPD40, VPD100 and VPD132. The nature of oxidants in/on these catalysts has been investigated by using temperature-programmed techniques. One peak maximum was found desorbed in O_2 temperature programmed desorption (TPD) at 992 K for VPD40 with a total amount of oxygen desorbed of 2.4×10^{20} mol×g^{-1}. However an increased of calcination duration to 100 and 132 hours produced one oxygen peak desorbed at 986 K with a total amount of oxygen desorbed doubled to 4.4×10^{20} mol×g^{-1}. Temperature programmed reduction with H_2 resulted in the removal of ~ 10 times more than the lattice oxygen which can be desorbed thermally with the development of a new low reduction peak at ~ 840 K.

Introduction

Vanadyl pyrophosphate, $(VO)_2P_2O_7$, is the main crystalline phase and well known to be the most effective catalyst for mild oxidation of *n*-butane to maleic anhydride [1]. This catalyst was normally prepared by using either organic or aqueous medium as a reductant for V_2O_5. In a study by Hutchings *et al.* [2-4], they found that the final catalyst derived from the reduction of $VOPO_4 \cdot 2H_2O$ exhibited very high activity as well as high BET surface area. Recently, we have reported the nature of oxidants in/on vanadyl pyrophosphate catalyst, which prepared in an organic medium and calcined for 6 hours in a mixture of *n*-butane/air [5] and also prolonged calcination for 40, 100 and 132 hours [6,7].

The purpose of this paper is to investigate the nature of the oxidants of $(VO)_2P_2O_7$ catalysts synthesised via the reduction of $VOPO_4 \cdot 2H_2O$ phase. This is done by oxygen temperature-programmed desorption (TPD) and hydrogen temperature-programmed reduction (TPR).

Experimental

Catalysts Preparation

The catalyst, $(VO)_2P_2O_7$ was prepared in a two steps procedure based on $VOPO_4 \cdot 2H_2O$. $VOPO_4 \cdot 2H_2O$ was prepared by reacting V_2O_5 (12 g) with 85% of *o*-H_3PO_4 (115.5 g) in water (288 ml) under reflux for 24 hours. The solid recovered by filtration (yellowish coloured) was then washed with water and dried at 110°C. This solid was confirmed as $VOPO_4 \cdot 2H_2O$ by XRD. $VOPO_4 \cdot 2H_2O$ was then refluxed with isobutanol for 20 hours (50 mol×alcohol/L×mol $VOPO_4 \cdot 2H_2O$) and the solid recovered was found similar to $VOHPO_4 \cdot 0.5H_2O$. The final catalysts were obtained by calcined the precursor at 400°C for different periods (40, 100 and 132 hours) in a mixture of *n*-butane/air (0.75% *n*-butane in air). These three catalysts obtained were denoted VPD40, VPD100 and VPD132.

The gases

The gases, O_2, He, H_2 in Ar (5% H_2) and *n*-butane

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*corresponding author. E-mail: yap@fsas.upm.edu.my in air (0.75% *n*-butane in air) (Malaysian Oxygen Berhad) were used directly from the cylinder.

The apparatus

TPD and TPR experiments were carried-out using Micromeritics 2900 TPD/TPR apparatus provided with thermal conductivity detector (TCD).

Results and Discussion

Temperature-Programmed Desorption of Oxygen

The oxygen desorption spectra shown in Fig. 1 were obtained by pretreating the catalysts by heating them to 673 K in an oxygen flow (25 cm^3×min^{-1}) and holding them under that flow at 673 K for 1 hour before cooling them to ambient temperature. The flow was then switched to helium (25 cm^3×min^{-1}) and the temperature was raised (10 K×min^{-1}) to 1100 K following the conductivity of the eluted gas.

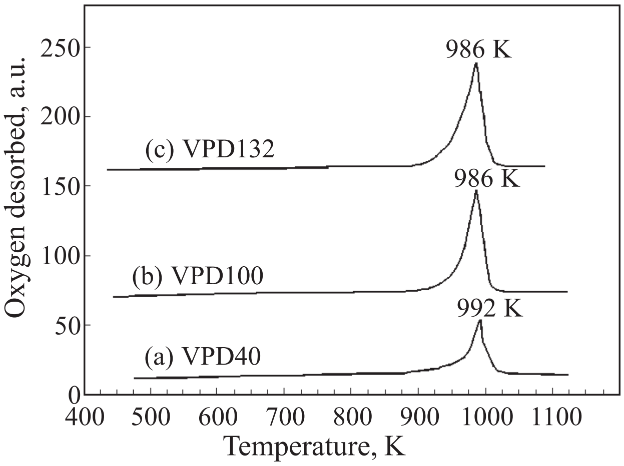

Fig. 1. Temperature-programmed desorption spectra of oxygen from VPD40, VPD100 and VPD132.

For catalysts VPD40, TPD showed an oxygen peak maximum at 992 K with an onset at 873 K. This is the lattice oxygen also seen in VPO catalyst prepared in an organic medium [7]. The peak maximum temperature, 992 K corresponds to a desorption activation energy of 254 kJ×mol^{-1} which is obtained by solution of the Redhead equation for an assumed value of 10^{13} s^{-1} for the pre-exponential term [8]. The total amount of oxygen desorbed for VPD40 is 2.4×10^{20} atom×g^{-1} and this is roughly the same amount as we reported for VPO catalysts prepared in an organic medium which had been calcined for 6 hours [5] and 40 hours [6]. However for both VPD100 and VPD132, the oxygen was desorbed at a slightly lower temperature at 986 K with a desorption activation energy of 252 kJ×mol^{-1}. The significance of the results of these latter two catalysts is that the amount of the oxygen which desorbed (4.4×10^{20} atom×g^{-1}) was virtually doubled that which desorbed from VPD40 and from the organically produced VPO catalyst. Furthermore this is the reverse of what was observed on prolonged calcination of the $(VO)_2P_2O_7$ catalyst prepared in the organic medium, a decrease of the amount of oxygen being noted on increased time of calcination [7].

The origin of these observations is not immediately obvious. Nevertheless the discovery of the near doubling of the amount of oxygen desorbed (remembering that we have shown that this oxygen as it desorbs is 100% selective in the partial oxidation of C_4 hydrocarbons to selective products [9]) explains the findings of Hutchings and co-workers that VPO catalysts derived from the reduction of $VOPO_4{\cdot}2H_2O$ are more active and selective [2-4].

Temperature-Programmed Reduction

More information as to the nature of the oxidizing species available from the VPO catalysts can be obtained by TPR in H_2/Ar stream (10% H_2) using a fresh sample of catalyst and raising the temperature from room temperature to 1173 K at 20 K×min^{-1} in that stream.

The reduction of the VPD40 catalyst by H_2 (Fig. 2) had an onset at ~ 773 K after which two distinct peaks maxima were observed in the rate of H_2 consumption. These occur at 1026 and 1113 K. However both VPD100 and VPD132 produced three peaks with onset of reduction at slightly lower temperature *i.e.* ~ 723 K. Peaks are observed at 841, 1009 and 1104 K for VPD100, whereas VPD132 gave peaks at higher temperatures *i.e.* 854, 1021 and 1105 K. The most interesting result from the TPR spectra is that increasing the duration of *n*-butane/air calcination from 40 to 100 and 132 hours results in the forming of a new peak which appeared at a lower temperature (~ 840 K). This has not been observed in VPD40 and other VPO catalysts [7]. It appears therefore that a new structure of the VPD100 and VPD132 catalysts is formed due to the longer thermal pretreatment. The total amount of H_2 consumed (oxygen atoms removed from the catalysts) is 2.7×10^{21} atom×g^{-1} for VPD40 which increases with the duration of calcination to 3.2×10^{21} and 3.3×10^{21} atom×g^{-1} for VPD100 and VPD132, respectively, in rough agreement with the temperature programmed desorption results. This finding suggesting that higher selective catalyst may produce by longer period of calcination.

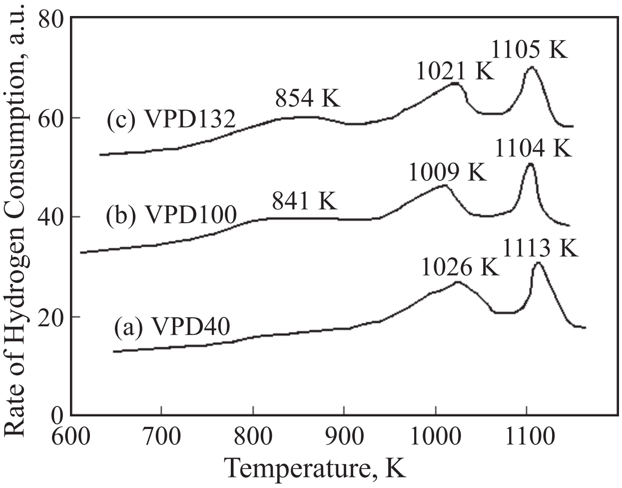

Fig. 2. Temperature-programmed reduction spectra in hydrogen from VPD40, VPD100 and VPD132.

A comparison with the thermally induced desorption shows that the reaction of the catalysts with H_2 induced the removal of a greater amount of oxygen (~ 10 times) from the lattice. The peak maximum temperature of the reduction is higher than that of the thermally induced desorption suggesting that the diffusion of oxygen through the lattice is the rate determining step.

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