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A Thermodynamic Investigation of the Redox Properties of VPO Catalysts

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Abstract The redox properties of a vanadium phosphorus oxide (VPO) catalyst with a V:P ratio of one were investigated using Coulometric Titration at 873 K. Equilibrium between $(VO)_2P_2O_7$ and $VOPO_4$ exists at a $P(O_2)$ of 3×10^{-4} atm, corresponding to ΔG of -60 kJ/mol O_2. This value for VPO is significantly lower than that measured with other vanadium-containing catalysts that have been studied. Furthermore, compared to other vanadium catalysts, V^{+4} was stabilized against further reduction at lower $P(O_2)$. These redox thermodynamics may help to explain the unique catalytic properties of VPO catalysts for partial oxidation of butane to maleic anhydride.

Keywords Maleic anhydride · Oxidation of butane · Oxidation thermodynamics · VPO catalysts

1 Introduction

Maleic anhydride is an important feedstock for the manufacture of a wide range of products, from unsaturated polyester resins to lubricating oil additives and other chemicals [1]. The majority of it is produced by the partial oxidation of n-butane over vanadium-phosphorus oxide (VPO), a material that is reported to be the only active and selective catalyst for this reaction [1]. Although the catalyst is sensitive to the synthesis and pretreatment conditions, the primary phase present in active catalysts is $(VO)_2P_2O_7$ [2–4]. The formal oxidation state for the vanadium atoms in $(VO)_2P_2O_7$ is +4 but the oxidation states of surface vanadiums in a working VPO catalyst are believed to be a combination of +4 and +5 [1]. At least one process for maleic anhydride manufacture converts n-butane over an oxidized catalyst in the absence of air [5], demonstrating that lattice oxygen from VPO is involved in the reaction.

The unique properties of VPO compared to other vanadium catalysts are due in part to the geometry of the sites and in part to the redox properties of the VPO catalyst. Focusing on the redox properties, it is interesting to notice that the energetics for oxidation of vanadium in various mixed oxides differs by almost 250 kJ/mol O_2 [6], depending on the composition of the second oxide. Although supported vanadates do not appear to be so strongly dependent on the nature of the underlying oxide [7] the case of VPO appears to be more analogous to that of mixed oxides since product can be formed in a circulating bed [5]. Therefore, it is of interest to measure the redox properties of VPO and compare its oxidation and reduction energetics to that of other mixed oxides.

Unfortunately, measurement of oxygen binding strengths is difficult. While Temperature Programmed Reduction (TPR) is commonly used for this purpose, TPR really just measures the temperature at which the solid reacts with H_2 at a significant rate and this may or may not be related to oxygen binding in the sample. A simple demonstration that TPR is not a good measure of oxygen binding in the solid is shown by the fact that the addition of dopant levels of a catalytic metal to a reducible oxide (e.g. addition of Rh to ceria) can reduce the reduction temperature of the oxide by hundreds of degrees, even when most of the oxide is not in contact with metal [8]. A more quantitative measure of oxygen binding involves measuring the thermodynamic, equilibrium properties of the oxide. For example, if VO_2 and V_2O_5 are in equilibrium with each other and with the gas phase

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($2VO_2 + ½O_2 = V_2O_5$), the measured $P(O_2)$ directly provides ΔG of oxidation for this reaction, since $K = P(O_2)^{-½} = \exp\{-\Delta G/RT\}$.

Measurement of the equilibrium constants for the oxidation of solids can be accomplished using Coulometric Titration, an electrochemical method based on the same operating principles used in the oxygen sensor in automotive exhaust applications [9]. In this experiment, the sample is placed in a sealed container in which at least part of the container wall is a yttria-stabilized zirconia (YSZ) electrolyte with electrodes on either side. YSZ is an oxygen-ion conductor and known amounts of oxygen can be pumped in and out of the sealed container by applying a current across the electrodes. At open circuit, the electrical potential across the electrodes can be used to calculate the $P(O_2)$ within the container via the Nernst equation. A more detailed description of this technique, along with a demonstration of its accuracy, can be found in several of our previous publications [10–12].

In this paper, we will show that the VPO catalyst cycles between V^{+4} and V^{+5} at a well defined $P(O_2)$ that is significantly higher than that required for equilibrium in bulk vanadia. Although the kinetics of oxidation and reduction were sluggish based on the long times required for the samples to reach equilibrium, the magnitude of ΔG of oxidation for the VPO catalyst is lower than that of bulk vanadia or of any mixed oxide that we have studied previously [6].

2 Experimental Techniques

The Coulometric Titration apparatus has been described in more detail elsewhere [12]. It consists of a YSZ tube, 1 cm in diameter and 20 cm long, with Ag electrodes painted both on the inside and outside of the tube. The sample to be characterized was then placed in an alumina crucible and inserted into the YSZ tube, which was in turn inserted into a tube furnace with both ends protruding. Ultra-Torr fittings were attached to both ends of the YSZ tube to allow flowing gases to be passed over the sample, after which glass plugs were inserted into the fittings to seal the contents from the outside air. After adding or removing known amounts of oxygen by passing a current across the electrodes using a Gamry Instruments potentiostat, the open-circuit potential across the electrodes was measured in order to determine the equilibrium $P(O_2)$ within the tube using the Nernst Equation. Equilibrium was assumed to have been reached when the potential varied less than 0.1 mV/h, a rate typically achieved after 5 to 10 days.

The sample size in these measurements was chosen so as to have 230 μmol of vanadium. Before sealing the YSZ tube with the glass plugs, the catalyst was heated in flowing air at a rate of 1.75 K min^{-1} to 873 K. As an additional check that equilibrium was achieved in these measurements, one set of experiments was conducted starting from the oxidized catalyst and one starting from the reduced catalyst. For the experiments with the oxidized sample, air was simply flushed from the YSZ tube with a mixture of 2.5 % O_2, 50 % CO_2, and 47.5 % Ar prior to beginning the measurements. This specific composition was chosen so as to simultaneously maintain the sample in its oxidized state, while minimizing the amount of gas-phase oxygen that would need to be pumped from the cell. The high CO_2 concentration was chosen in order maximize the rate at which equilibrium was attained at low $P(O_2)$, since this is established by equilibrium with CO and CO_2. For the reduced sample, the VPO precursor was first exposed to a gas mixture of 7 % CO, 28 % CO_2, and 65 % He for 1 h to initially reduce the sample and provide a buffer for maintaining $P(O_2)$ (7 % CO, 28 % CO_2).

The vanadyl hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5\ H_2O$) sample used in this study was prepared in our laboratory using a method described elsewhere [13]. Specifically, 5.4 g of vanadium (V) oxide (Aldrich, 99.6+ %) was refluxed in 125 mL of 2-butanol (Aldrich, 99 %) and 4.5 mL of H_3PO_4 (Fisher, 85 %) at 373 K for 16 h. The precipitate was subsequently washed with 200 mL of 2-butanol and 150 mL of ethanol until the filtrate was clear. The residue was then dried at 338 K for 72 h.

The X-Ray Diffraction (XRD) measurements were performed with a Rigaku Giegerflex-D diffractometer with a Cu Kα radiation source ($\lambda = 0.15405$ nm). XRD data was collected at a 2° 2θ min^{-1} rate with 0.002° step size in 2θ. BET surface areas were measured using N_2 adsorption at 78 K.

3 Results and Discussion

Figure 1 shows the XRD powder patterns for angles between 10 and 35° 2θ of the VPO sample after various pretreatments. The pattern of the as-prepared *v*anadyl hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5\ H_2O$) precursor is shown in Fig. 1a; it matches the pattern reported in the literature for this composition [13–15] and agrees well with JCPDS File No. 84-0761. Figure 1b is the XRD pattern obtained from this sample after it was oxidized in flowing air at 873 K for 1 h, then quenched to room temperature. This pattern corresponds to a decomposed ω-$VOPO_4$ [16], JCPDS File No. 37-0809. The formal oxidation state of the V for this material is +5. Finally, when the sample was reduced at 873 K in a flowing mixture of 3 % CO, 12 % CO_2, and 85 % He for 1 h, then quenched to room temperature, its XRD pattern became

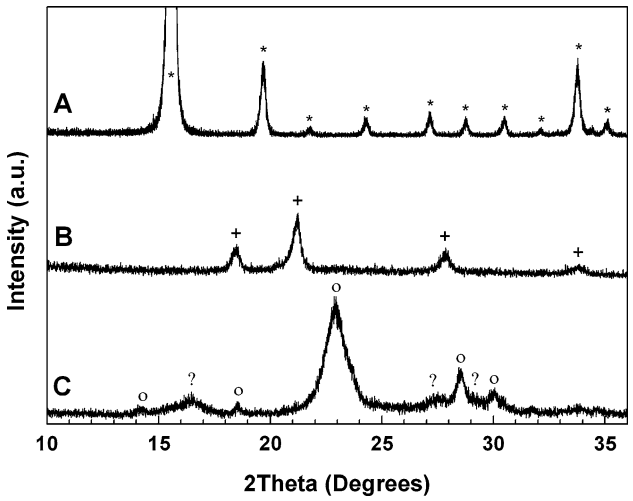

Fig. 1 XRD patterns for *a* $VOHPO_4{\cdot}0.5\ H_2O$ *b* $VOPO_4$ (magnified three-fold), and *c* $(VO)_2P_2O_7$ (magnified three-fold). The symbols indicate the following phases: (*asterisks*) $VOHPO_4{\cdot}0.5\ H_2O$; (*plus*) $VOPO_4$; (*open circle*) $(VO)_2P_2O_7$; and (*question mark*) unidentified phases

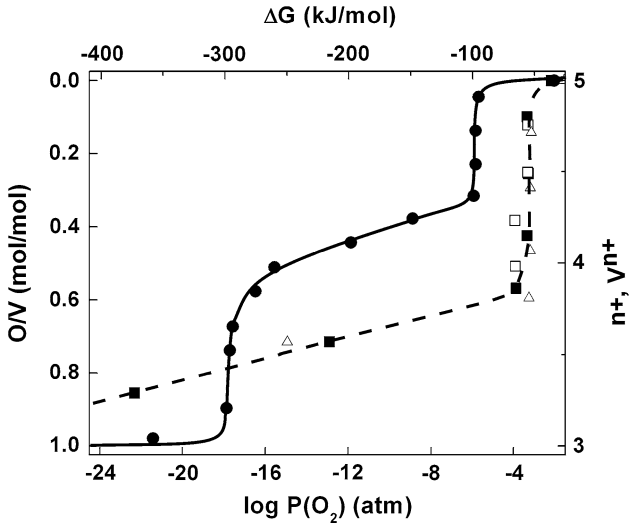

Fig. 2 Coulometric titration, equilibrium data for V_2O_5 (*filled circle*) [18] and for the VPO catalyst at 873 K. For the VPO catalyst, the data designated by (*open triangle*) were obtained starting with an oxidized sample. For the data shown as (*filled square*), the sample was first reduced in a flowing mixture of CO and CO_2. After the sample had been oxidized, the isotherm was again measured by pumping oxygen out (*open square*), demonstrating that the sample did not change over the course of acquiring the data

that shown in Fig. 1c. Most of the peaks can be assigned to $(VO)_2P_2O_7$ [13, 14, 17] (JCPDS File No. 83-2388), although unidentified peaks were also observed at 16.5, 27.3, and 30.0° 2θ. It is noteworthy that the unidentified peaks in Fig. 1c do not correspond to V_2O_3 and that all of the peaks in this the reduced sample are broad, suggesting the formation of small crystallites upon reduction of the VPO precursor. BET surface areas for the samples shown in Fig. 1a, c were found to be 37 and 95 m^2/g, respectively, providing further evidence that reduction resulted in smaller crystallite sizes.

Coulometric Titration data at 873 K for the VPO catalyst are shown in Fig. 2, along with results reported previously for bulk V_2O_5 at this temperature. The amounts of oxygen that were added or removed from the samples, relative to their vanadium contents, are reported on the left ordinate axis, while the equilibrium $P(O_2)$ are plotted on the lower abscissa. Because $\Delta G = -RT\ \ln\{P(O_2)\}$, the Gibbs Free Energies for the oxidation reaction per mole of O_2 can be related to the equilibrium $P(O_2)$ and are shown at the top of the plot. Assuming that the vanadium atoms exist in the +5 oxidation state in the sample exposed to flowing air at 873 K, the average oxidation state of the vanadium in the samples can be calculated as a function of $P(O_2)$. These values are reported on the right ordinate.

The data for bulk vanadia have been discussed in detail elsewhere [18]. Over the $P(O_2)$ range from 10^{-2} to 10^{-24} atm, precisely one mole of O is removed for every V, indicating that vanadia is initially in the form of V_2O_5 at 10^{-2} atm and is reduced to V_2O_3 at 10^{-24} atm. The reduction occurs in two steps, at 5.5×10^{-6} and at 3×10^{-19} atm, corresponding to equilibria between V_2O_5 and VO_2 and between VO_2 and V_2O_3. Because there are mixed valance compounds at intermediate $P(O_2)$, the transition in the O/V stoichiometry over the pressure region from 5.5×10^{-6} to 3×10^{-19} atm is gradual. Oxides that do not exhibit mixed-valance compounds show a much sharper transition [6].

Figure 2 also shows oxygen isotherms for the VPO catalyst at 873 K. To ensure that equilibrium had been achieved and that the sample did not change during the course of the measurements, the isotherms were measured three times on two samples. First, the isotherm was measured starting from the oxidized sample by pumping oxygen out. In a second measurement of the isotherm, a different sample was initially reduced in a flowing mixture of 7 % CO, 28 % CO_2, and 65 % He, after which the isotherm was obtained while pumping oxygen into the system. Finally, to ensure that the sample did not change over the course of an experiment, the isotherm was measured again while pumping oxygen out of the system. The data from all three runs were identical within the uncertainty of the measurements. It is noteworthy that the oxidation and reduction kinetics for the VPO catalyst were slow compared to what was observed on other vanadia catalysts. In order to reach equilibrium with the VPO catalyst, it was necessary to wait between 5 and 10 days for each point, so that each isotherm required between 6 and 8 weeks.

Assuming that all of the vanadium in the initial, oxidized VPO catalyst exists in the +5 oxidation state, reduction to V^{+4} occurred at a well defined $P(O_2)$ of 3×10^{-4} atm, implying that there is an equilibrium

between the oxidized material ($VOPO_4$) and the reduced material ($(VO)_2P_2O_7$) at this $P(O_2)$. There is some additional reduction, with approximately 0.3 O/V being removed from the catalyst when $P(O_2)$ is further lowered to 10^{-22} atm; however, there are no well defined steps in the isotherm that would indicate formation of compounds with lower valence state. The equilibrium $P(O_2)$ associated with the oxidation of $(VO)_2P_2O_7$ to $VOPO_4$ can be used to calculate ΔG for this reaction, -60 kJ/mol O_2.

It is interesting to compare these results on the VPO catalyst to those obtained in our laboratory for bulk vanadia and other vanadium mixed oxides. Materials that were investigated in previous studies include the following [6, 7]: $CeVO_4$, $LaVO_4$, ZrV_2O_7, $Mg_3(VO_4)_2$, $CrVO_4$, and $AlVO_4$, along with isolated vanadates on alumina, titania, and zirconia. First, the vanadium in all of the materials investigated in previous studies was completely reduced to the +3 oxidation state at a $P(O_2)$ of 10^{-24} atm at 873 K. By contrast, the V^{+4} appears to have increased stability in the VPO catalyst. Second, the magnitude of ΔG for oxidation of $(VO)_2P_2O_7$ to $VOPO_4$ is lower than that obtained for any of the other vanadium oxides that were studied. As shown in Fig. 2, ΔG for oxidation of VO_2 to V_2O_5 at 873 K is -100 kJ/mol O_2. ΔG for oxidation of reduced ZrV_2O_7 is similar to that for V_2O_5 but the magnitude for ΔG of oxidation is significantly higher on all of the other oxides. For example, ΔG for oxidation of $CeVO_3$ to $CeVO_4$ is -370 kJ/mol O_2 at 873 K; and ΔG for oxidation of isolated vanadates on titania, zirconia, and alumina is -300 kJ/mol O_2 at 748 K.

It is certain that redox energetics are not the only factors governing the catalytic properties of VPO catalysts. Indeed, in the case of methanol oxidation [11], it has already been demonstrated that there is no clear relationship between oxygen binding strength and reaction rates. Clearly, site geometry and rates of reduction will also be critically important; and it is intriguing that, unlike the case for other vanadium mixed oxides that have been studied in our laboratory, the VPO catalyst is not easily reduced to V^{+3}. That suggests the active oxygens in VPO are spacially better separated than in other vanadia catalysts and this may prevent over-oxidation of the butane. Clearly, it is very interesting that the VPO catalyst studied here showed such unique redox properties and it is likely that these are at least partially responsible for the unique catalytic properties observed with this material.

4 Conclusions

The thermodynamic, redox properties of VPO catalysts are different from that of most other vanadium containing oxides in that V^{+4} is stabilized to lower $P(O_2)$ in VPO catalysts. Furthermore, equilibrium between the oxidized and reduced forms of the VPO catalyst exists at a higher $P(O_2)$, implying that reduction is energetically easy. These redox properties may help explain the unique catalytic properties of VPO catalysts for oxidation of butane to maleic anhydride.

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