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Re-oxidation kinetics of a VPO catalyst

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Abstract

Oxidation of vanadium pyrophosphate (VPO) to the orthophosphate was investigated by temperature programmed oxidation (TPO) and by weight gain measurements in a TGA unit as a model for the re-oxidation of a catalyst in a two-bed process in the partial oxidation of butane to maleic anhydride (MA). It was demonstrated by FTIR observations that the weight gain corresponds to the VPO oxidation. The results of separate measurements of a catalyst alternatively exposed to oxygen and to a stream containing butane should also be applicable to a VPO catalyst employed in a two-bed process. The VPO oxidation measurements demonstrate that re-oxidation of a VPO catalyst in a two-bed process should be carried out at a higher temperature than the butane partial oxidation. When this is carried out, significant performance improvements in the two-bed process are observed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Catalyst re-oxidation; Vanadium orthophosphate catalyst; Dynamic measurements of oxygen uptake; Forced unsteady state operation

1. Introduction

This paper examines the oxidation and reduction processes of a domestic vanadium pyrophosphate (VPO) catalyst that occur in either a two-step catalytic partial oxidation of butane to MA or when this partial oxidation is conducted by periodically switching between an oxygen containing stream and a stream containing both butane and oxygen. Recently, the Du Pont de Nemours Company commissioned a full scale commercial plant to make maleic anhydride (MA) in a two-bed system consisting of a riser reactor in which the catalyst along with some supplementary air oxidizes butane to MA and a fluidized bed in which the catalyst is re-oxidized [1]. Splitting up the overall reaction in two-steps requires knowledge of the kinetics of each step and models that express the kinetics. Our paper concerns the re-oxidation step.

There is a large amount of literature on butane oxidation to MA over catalysts [2–7]. Some recent papers deal with the two-step process and the work is well summarized by Golbig and Werther [5]. A simple model for the re-oxidation kinetics is presented by Golbig and Werther [5] who showed using the pulse experiments of Uihlein [8] and of Emig et al. [9] that the rate of re-oxidation may be expressed as a function of the oxygen loading in the catalyst to the 3.8 power so that the rate decreases exponentially as the catalyst takes up oxygen. The authors, however, criticized this relationship claiming that it leads to excessively high re-oxidation rates and they suggested that for short exposure duration re-oxidation is mass transfer limited. They offered, however, no experimental evidence for the mass transfer limitation and the relationship they

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Nomenclature

C_O	mols of removable oxygen/kg of the pyrophosphate catalyst (mol/kg)
E_i	activation energy for *i*th reaction (kJ/mol)
k_i	rate constant for *i*th reaction (mol/kg s)
k_i	preexponential factor for *i*th reaction follow the Arrhenius form (mol/kg s)
M_O	molecular weight of oxygen atom (kg/mol)
N_S	total concentration of active adsorbing sites (mol/kg)
N_L	total concentration of catalyst lattice sites (mol/kg)
T	temperature (°C)
W	catalyst weight (kg)
W_c	weight faction of VPO in catalyst
y_{O_2}	mole fraction of oxygen

Greek letters

θ_S	fraction of the total active adsorbing sites containing oxygen
θ_L	fraction of the total removable oxygen capacity of the catalyst

assumed. Golbig and Werther [5] followed Emig et al. [9] and assumed the re-oxidation rate to be proportional to the oxygen partial pressure to the 0.5 power. It is clear from these comments that considerably more research on the re-oxidation step is needed.

In the past, all studies have performed the partial oxidation reaction and the catalyst re-oxidation steps at a same temperature. With a two-bed process, there is no need for this restriction. In this contribution, we consider carrying out the latter step at higher temperatures. This would reduce reactor size and catalyst hold-up and, thus, may be beneficial.

Our objectives in this paper are to determine the kinetics of the re-oxidation step and to investigate the effect of temperature on this step.

2. Experimental

Four different groups of experiments were done in this investigation. The first group consisted of temperature programmed oxidation (TPO) and kinetic measurements of catalyst re-oxidation process in which the variables were final temperature and oxygen partial pressure. Next, two-step reaction experiments were done in which the catalyst was exposed successively to oxygen and to a butane oxygen mixture. Our objective in these experiments was to demonstrate that catalyst oxidized at a high temperature was effective for MA formation at a lower temperature and that over oxidation of the catalyst is possible if the oxygen exposure duration is too long. Cycling experiments were undertaken in a fixed bed reactor to explore the stability of the catalyst and to show that operating the re-oxidation of the catalyst and partial oxidation steps at different temperatures can enhance catalyst performance. Finally, an infrared spectroscopic examination of the catalyst surface before and after re-oxidation was undertaken. The purpose of this examination was to show that the weight gain corresponds to a change in the composition of the catalyst.

Fig. 1 is a sketch of the thermogravimetric (TG) unit employed for the TPO and kinetic measurements. The TG unit was a Perkin-Elmer TGS-2, a fully automatic TG balance with temperature control that allowed an operation up to about 800 °C. A feed array was used equipped with a switching valve that permitted the introduction of a controllable mixture of O_2 in He, or a mixture of 4% butane (C_4) in He. It was possible with this array to make up a mixture of C_4 and O_2 in He that was used to determine the weight loss of the catalyst during the partial oxidation step.

The TPO measurement was taken with fresh VPO catalyst. A 45 mg sample was brought to 50 °C in flowing He. At time zero, a mixture of 21 vol.% O_2 in He at 20 ml/min. was introduced and the temperature was brought to 800 °C at a rate of 10 °C/min. In the kinetic experiments, the sample was first heated from room temperature to 280 °C in dry, flowing He and held at that temperature to remove adsorbed water until no further weight loss was observed. After water was removed, the sample was heated rapidly to a desired final temperature. Then, a mixture of O_2 in He was introduced.

In the two-step reaction experiments, the catalyst re-oxidized at 600 °C but with different durations of O_2 exposure was cooled in flowing He to 425 °C. Once this temperature was reached, the flowing gas was switched to a mixture of 4 vol.% C_4, 20 vol.% O_2 He. The sample was held at this condition for up to 60 min. In some experiments, the catalyst sample was

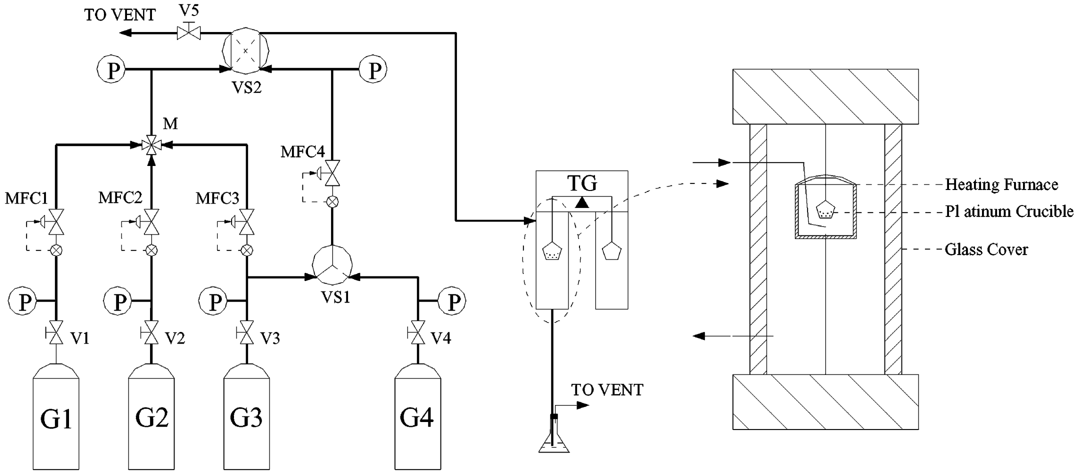

Fig. 1. Schematic diagram of the TGA experimental set-up. G1: O_2; G2: C_4/He; G3: He; G4: O_2/He; M: mixer; V1–V5: valves; MFC1–MFC4: mass flow controllers; VS1: two-position three-way valve; VS2: two-position four-way valve.

heated up to 600 °C with He flushed once again, and the weight gain was measured once after O_2 in He was re-introduced.

For the cyclic experiments, the gas-mixing array shown in Fig. 1 was still used, but the TG unit was replaced by a fixed bed micro-reactor contained in a temperature controlled furnace. The reactor diameter was 4.7 mm, length was 302 mm and the bed was filled with 0.6 ml of catalyst. Off gas leaving the reactor was collected in a gas-bag and the time average mixture was analyzed by a gas chromatograph using FID and TCD detectors.

Fresh catalyst was employed for the cyclic experiments. The sample was heated to the re-oxidation temperature in flowing He. When this temperature was reached the flow was switched to 21% O_2 in He and held for 5 min. Following the time limited re-oxidation, the catalyst was cooled to 416 °C in He and then exposed to 1.5% C_4 and 20% O_2 for 10 min. A whole cycle took about 120 min. Measurements were taken in the second cycle. It is of course not certain that a cycling invariant state was reached in these limited experiments, as laboratory facilities made longer runs impossible.

Two cyclic experiments were performed. In the first, both partial oxidation of C_4 to MA and re-oxidation of the catalyst were carried out at 416 °C. This temperature is typically used in full scale plants. In the second experiment, re-oxidation was done at 580 °C. Our purpose in these experiments was limited to demonstrate that carrying out the two-steps at different temperatures, respectively would give significantly better results. The butane concentration used in the partial oxidation step follows industrial practice.

The VPO catalyst was obtained from Beijing Research Institute of Chemical Technology. XRD and XPS measurements showed that the fresh catalyst was primarily $(VO)_2P_2O_7$. The other component was the orthophosphate, $VOPO_4$. The mean vanadium valence was 4.1. The catalyst as received was crushed and sieved to give a fraction between 40 and 60 US mesh, but not otherwise pretreated.

FTIR spectra of the fresh catalyst, the catalyst after re-oxidation and the catalyst after cycling were determined by using a Nicolet 60 SXB FTIR.

3. Experimental results and discussions

3.1. Temperature programmed oxidation experiment

Exposure of fresh catalyst at 50 °C to 21% O_2 in He in a TGA cell generated the response on temperature ramping at 10 °C/min as shown in Fig. 2. Ait-Lachgar et al. did the same experiment and the result was similar [10].

Initially the sample lost water and the weight decreased until about 280 °C. The weight increased

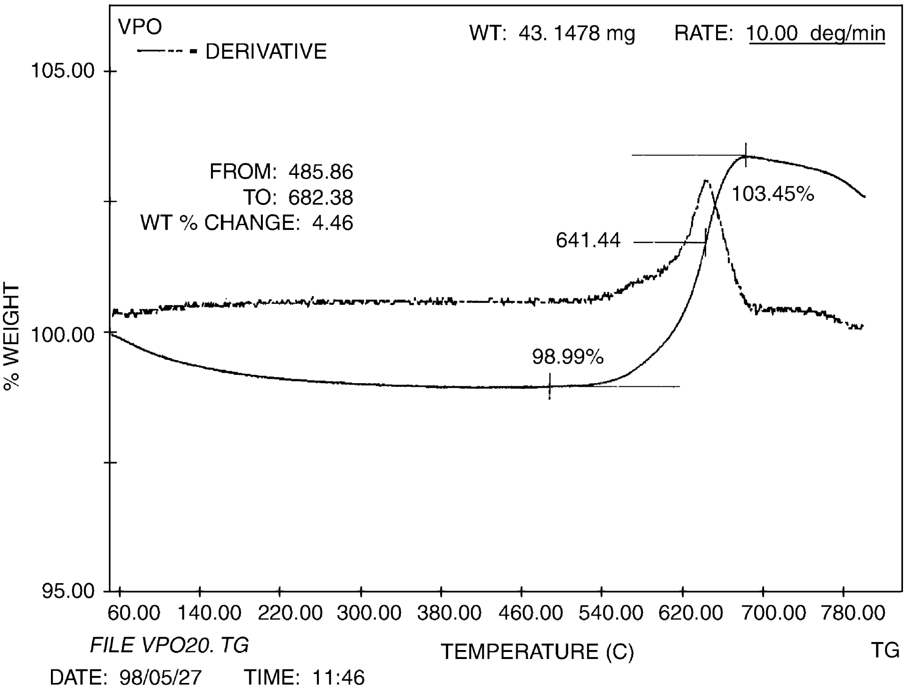

Fig. 2. TGA curves as a function of temperature in a flowing mixture of oxygen with He.

after 500 °C indicating oxidation. The weight gain was rapid and continued to about 680 °C where a change weakened the structure and spalling probably occurred which led to weight loss. These observations indicate that the catalyst must be dried to 280 °C before kinetics can be determined. The partial oxidation of butane to MA on the $VOPO_4$ catalyst occurs at about 410 °C; consequently, the rate of re-oxidation at the reaction temperature is extremely slow so that this step is certainly rate controlling. A temperature of at least 500 °C is needed for the oxidation process to proceed rapidly. A recent US Patent [11] describing a circulating fluidized bed process suggests maintaining the same temperature in the regenerator in which the catalyst is re-oxidized as in the partial oxidation reactor. Fig. 2 shows that for the $VOPO_4$ catalyst this is not a suitable policy.

3.2. Kinetic experiments

Kinetic experiments of the re-oxidation step were conducted as described in Section 3.1. The effect of O_2 concentration, expressed as vol.% in the gas at 101.3 kPa, on the weight gain at a constant temperature of 580 °C is shown in Fig. 3. The O_2 concentration has a strong effect on the oxidation rate up to 20 vol.%. The oxidation rate continues to increase at higher O_2 partial pressures but more slowly. At 580 °C, the catalyst is not completely oxidized even exposed under 100% O_2 for 30 min. In a second set of experiments, the O_2 vol.% was kept at 21%, but the oxidation temperature was varied. Weight gain measurements are given in Fig. 4. It is evident that oxidation goes to completion in 30 min only for temperatures above 620 °C. The figure also shows that the oxidation process is quite slow up to 500 °C. These experiments were used to derive the parameters of our re-oxidation model as discussed in the following sections.

3.3. Two-step experiments

In a further experiment, a VPO sample was heated from 280 to 600 °C in He during 5 min, then switched to a mixture of 21 vol.% O_2 with He and held at 600 °C for an additional 24 min. The sample was flushed with He and cooled to 425 °C during 9 min then exposed

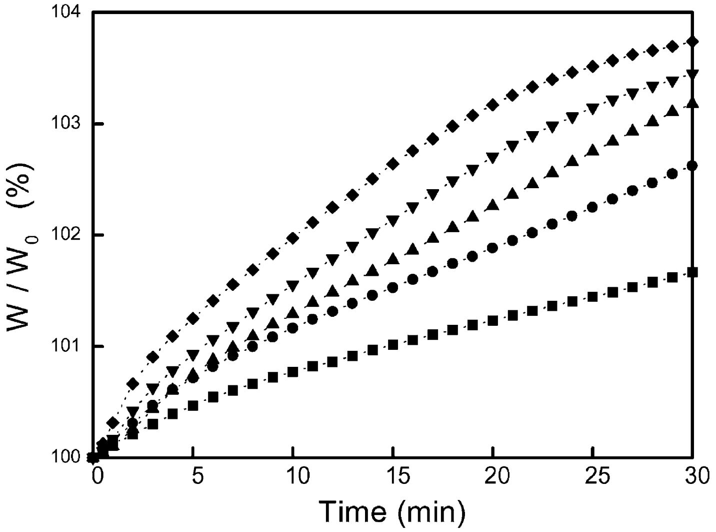

Fig. 3. The effect of O_2 concentration on catalyst re-oxidation (580 °C). Oxygen concentration: (■) 10%; (●) 20%; (▲) 40%; (▼) 60%; (◆) 100%.

to 4 vol.% $C_4 + 20$ vol.% in He at this temperature for 22 min. The trace of weight change shown in Fig. 5 shows a behavior identical to that indicated in Fig. 4 for the oxidation step. In the flushing and cooling stage, some weight gain was observed. This results from the transport and mixing lags in the system. O_2, consequently, cannot be cleared instantly from the TGA cell. In the final stage, marked with IV in the figure, there is no weight loss in the partial oxidation step suggesting that this sample is inactive. This experiment demonstrates that over oxidation or sintering of the catalyst can occur.

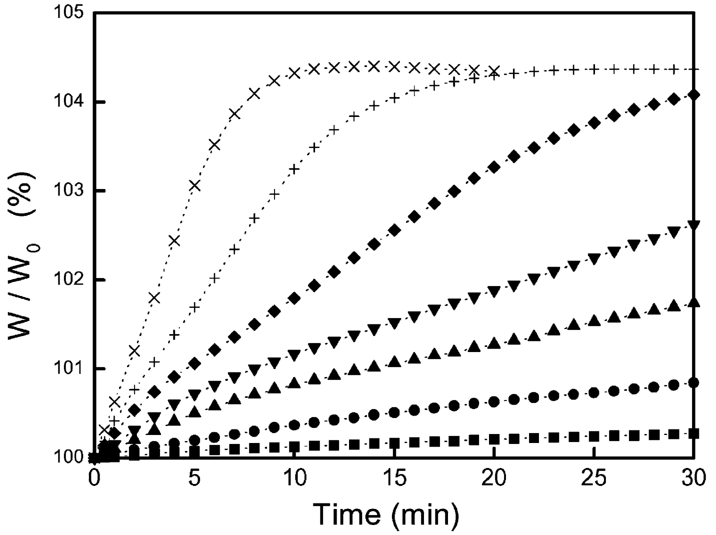

Fig. 4. The effect of temperature on catalyst re-oxidation (20% O_2). Re-oxidation temperature: (■) 500 °C; (●) 540 °C; (▲) 560 °C; (▼) 580 °C; (◆) 600 °C; (+) 620 °C; (×) 650 °C.

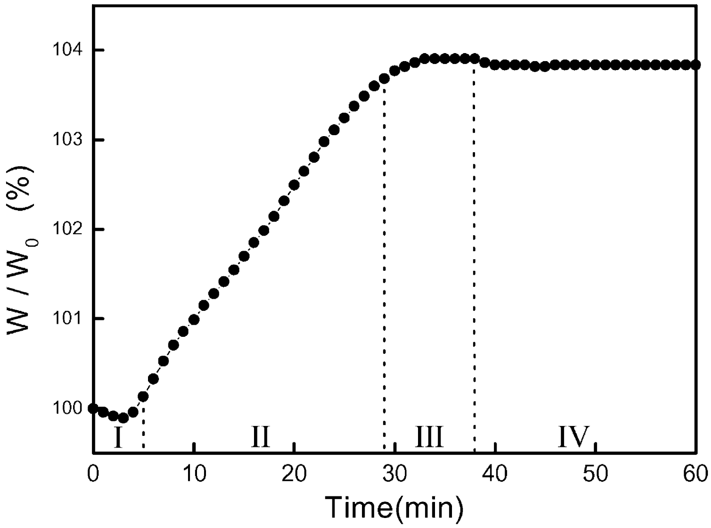

Fig. 5. Catalysis cycling ($\Delta W/W_0 = 4\%$). I: 0–5 min, 280–600 °C, He; II: 5–29 min, 600 °C, 21% O_2 + He; III: 29–38 min, 600–425 °C, He; IV: 38–60 min, 425 °C, 4% C_4 + 20% O_2 + He.

When the experiment just discussed is repeated with only 5 min exposure to O_2 instead of 24 min, the weight change behavior given in Fig. 6 is observed too. The experiment has been modified somewhat: the cooling duration from 600 to 425 °C in He has been shortened to 4 min and the exposure to the butane containing stream has been increased to 55 min. With a 5 min oxidation stage, the catalyst is not completely oxidized according to Fig. 4 and the weight loss in the partial oxidation stage shows the catalyst is now active. Indeed, the rapid weight loss in the first several minutes just after composition switching suggests a

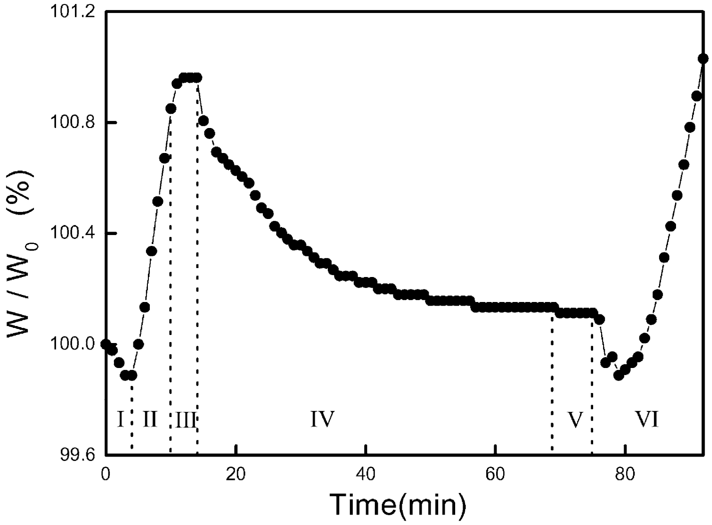

Fig. 6. Catalysis cycling ($\Delta W/W_0 = 1\%$). I: 0–5 min, 280–600 °C, He; II: 5–10 min, 600 °C, 21% O_2 + He; III: 10–14 min, 600–425 °C, He; IV: 14–69 min, 425 °C, 4% C_4 + 20% O_2 + He; V: 69–76 min, 425–600 °C, He; VI: 76–92 min, 600 °C, 21% O_2 + He.

highly active catalyst in which oxygen from the lattice is transported to the surface and consumed for butane partial oxidation.

Fig. 6 shows that weight change after exposure to 4 vol.% C_4 in O_2 and He for 55 min was halted and the catalyst was reheated up to 600 °C in He and then re-oxidized in 21 vol.% O_2 with He. Weight gain during the re-oxidation is rapid and the transient trace after 76 min almost reproduces the initial weight change shown in stage II. This indicates that the re-oxidation step is virtually the same as the initial oxidation of $(VO)_2P_2O_7$. It seems that the irreversible change in oxidation state of the catalyst was not observed, at least in the experimental duration. This is a premise of our cyclic experiments. The sharp weight loss following a switch to He and reheating of the catalyst can be attributed to desorption of strongly bound butane or C_4 intermediates, or more probably to oxidation of these species by oxygen in the catalyst lattice once there is no more O_2 in the gas feed to the TGA cell.

3.4. Cyclic experiment

In addition to obtaining kinetics of catalyst re-oxidation, an objective of our investigation was to investigate the temperature that should be used for the re-oxidation step and its effect on the performances of two-step process. The TPO and TGA measurements discussed in Section 3.3 demonstrated that this temperature should be greater than 500 °C for the catalyst used in this work, but should probably not exceed about 620 °C. The effect of temperature on the performance of the two-bed MA process was investigated in a simple two-step experiment described in Section 2. In the first experiment, the partial oxidation of butane was carried out at 416 °C in a micro fixed bed reactor and the catalyst was re-oxidized in the same bed at this temperature. In the second experiment, heating and cooling steps in the presence of flowing He were introduced and the catalyst was re-oxidized at 580 °C. Table 1 shows the conversion, selectivity and MA yield in each experiment. There is a remarkable improvement in all three parameters. A new patent based on this idea has been presented [12].

The duration of the cooling and heating steps reduce the reactor throughput for a fixed bed reactor. However, this drawback disappears in a two-bed process with catalyst circulation between beds. Optimization of the temperatures of the two-steps is possible so that the performance can be certainly further improved. Only two cycles were used in these experiments and the results were measured in the second cycle. The TGA experiment shown in Fig. 6 suggests that a reproducible cyclic operation is possible after the second cycle. This, however, was not tested, strictly. Further observation should be made so as to probe whether small but continuing long-term changes in the performance of the catalyst will occur during cyclic operation.

3.5. FTIR analysis of catalyst samples

These experiments were undertaken to show that the weight gains measured on oxidation correspond to a composition and crystal structure change in the catalyst. Fig. 7 shows a comparison between the FTIR transmission spectra for a fresh catalyst (a), a slightly

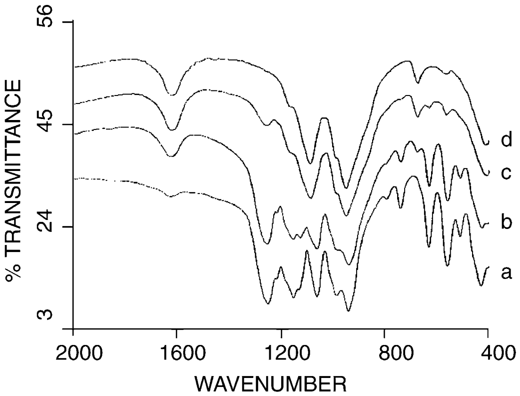

Fig. 7. FTIR spectra of VPO catalyst.

Table 1
A comparison of performance at different regeneration temperatures

Partial oxidation temperature (°C)	Re-oxidation temperature (°C)	Butane conversion (%)	Selectivity to MA (%)	Yield of maleic anhydride (%)
416	416	80.7	60.7	49.0
416	580	90.2	67.8	61.1

oxidized catalyst with a gain of 0.7 wt.% (b), a highly oxidized catalyst with a gain of 3 wt.% (c) and a fully oxidized catalyst with a 4 wt.% gain (d).

Wave numbers showing strong and very strong absorption for $(VO)_2P_2O_7$ and the β form of $VOPO_4$ were obtained from [13–15]. Strong absorption for the β form of $VOPO_4$ were found at 951, 1001 (very strong), 1055 and 1163, while for $(VO)_2P_2O_7$ they were at 430, 442, 561, 928, 941 (very strong), 991, 1063, 1151 (very strong), 1254 and 1267. In Fig. 7, which presents a plot of transmission rather than absorption, most of these $(VO)_2P_2O_7$ wave numbers are prominent in (a). There is relatively little change from (a) to (b), however, the peak near 942 has become much deeper suggesting a contribution from a form of $VOPO_4$. In (c), the valleys at 1151 and 1254 have shrunk and the characteristic peaks at 951 and 1093 have become prominent. Consequently, we believe the change at 941–951 and 1093 indicates the appearance of $VOPO_4$. There are small valleys between 500 and 680 and also one at 1254 that also appear in (a) with much stronger absorption. Thus, some $(VO)_2P_2O_7$ remains. In (d), these small valleys are missing. Otherwise, the transmission spectra is very similar to (c). Consequently, the catalyst has been virtually completely converted to the orthophosphate.

4. Modeling

It's generally considered that a series of equilibria with oxygen in the gas phase are established in which different kinds of adsorbed oxygen and lattice oxygen may form. Here, experiments described above have been modeled by using a simplified scheme proposed by Arnold and Sundaresan [16,17]:

$$O_2 + 2(S) \xrightarrow{k_1} 2O(S) \tag{1}$$

$$O(S) + (L) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O(L) + (S) \tag{2}$$

where (S) is a surface site and (L) represents an oxygen vacancy in the catalyst lattice. The transient re-oxidation model can be written as

$$r_1 = k_1 y_{O_2}(1-\theta_S)^2 \tag{3}$$

$$r_2 = k_2(1-\theta_L)\theta_S - k_2'\theta_L(1-\theta_S) \tag{4}$$

$$N_S \frac{d}{dt}\theta_S = 2r_1 - r_2 \tag{5}$$

$$N_L \frac{d}{dt}\theta_L = r_2 \tag{6}$$

$$\Delta W = (N_S(\theta_S - \theta_S^0) + N_L(\theta_L - \theta_L^0))M_O \tag{7}$$

$$N_L = W_c C_O \tag{8}$$

In the above model, θ_S is the fraction of the total active adsorbing sites containing oxygen, θ_L the fraction of the total removable oxygen capacity of the catalyst, while N_S represents the total concentration of active adsorbing sites, and N_L represents the total concentration of catalyst lattice. W_c is the mols of VPO per weight of catalyst, while C_O the mols of removable oxygen per weight of the pyrophosphate catalyst. M_O is the molecular weight of oxygen atom. $\Delta W/W_0$ is the fractional weight change of the catalyst sample. It was further assumed that the rate constants follow the Arrhenius expression.

Catalyst properties were calculated and/or measured from the composition: $M_O = 0.016$ kg/mol, and $W_c C_O = 3.247$ mol O/kg catalyst.

Parameters for the Arrhenius expressions for k_1, k_2 and k_2' were estimated from experimental data of TGA measurements. The measurements spanned the range of O_2 concentrations and temperatures used in our study. A minimum of residual sum of squares was searched using a distributed hybrid genetics algorithm implemented with MATLAB. The algorithm combines a genetic scheme with the Marquardt method and is described by Huang [18]. The values obtained are summarized in Table 2. It was assumed that the zero heat of reaction measured by Arnold and Sundaresan [17] for a vanadia catalyst for the transfer of oxygen from the catalyst surface and oxidation of the lattice apply to the VPO–orthophosphate system. Consequently, we assumed that the activation energy for the reverse step in Eq. (2) is the same as that determined for the forward step.

Table 2
Estimated kinetic parameters for catalyst re-oxidation

E_1 (kJ/mol)	157.4
E_2 (kJ/mol)	199.4
k_1 (mol/kg s)	8.85×10^7
k_2 (mol/kg s)	3.73×10^9
k_2' (mol/kg s)	1.63×10^5
N_S (mol/kg)	4.98×10^{-2}

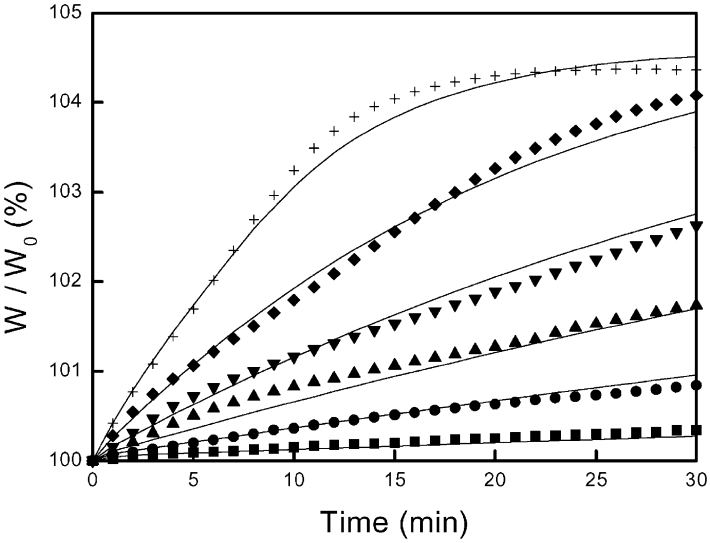

Fig. 8. A comparison between experimental data and results simulated with dissociative adsorbed model. Symbols: experimental data; lines: simulation results. Re-oxidation temperature: (■) 500 °C; (●) 540 °C; (▲) 560 °C; (▼) 580 °C; (◆) 600 °C; (+) 620 °C.

The activation energy found for the dissociative adsorption step (Eq. (1)) agreed well with the activation energy obtained directly from the TGA data. Our value is higher than the activation energy reported by Arnold and Sundaresan [17] for a vanadia catalyst and close to the value reported by Golbig and Werther [5] for a VPO catalyst. Activation energies for the transport and oxidation steps are high for a reaction that is probably diffusion controlled at least at the higher temperatures used by us. Arnold and Sundaresan [16] used a zero activation energy for this step.

The model was verified by integrating Eqs. (3)–(7) and comparing predicted weight gains with experimental data. Fig. 8 shows the comparison. The effect of temperature on the oxidation rate is closely predicted. It appears, then, that the calculation of activation energy for transport of oxygen and oxidation of the catalyst lattice is valid as well as the assumption that it is equal to the activation energy for the reverse step.

5. Conclusions

The experiments demonstrate that re-oxidation of the catalyst in a two-bed process for MA from butane should be carried out at a higher temperature than the butane partial oxidation step. For the studied VPO catalyst, this temperature should be greater than 500 °C, but less than 620 °C. Cyclic experiments show that when the two-steps are carried out at 416 and 580 °C rather than both at 416 °C, a significant improvement in butane conversion, selectivity to MA and MA yield is observed.

The catalyst re-oxidation model developed over the last several years by Arnold and Sundaresan [17], Emig et al. [9] and Golbig and Werther [5] has been successfully applied to the oxidation of VPO to the orthophosphate and the re-oxidation of VPO catalysts in a two-step process of butane to MA. The assumption of equal activation energy for the forward and backward of the lumped oxidation of the lattice and transport of oxygen from the surface to the catalyst interior appears to be valid. The fact that the participation of oxygen in the re-oxidation is proportional to the square root of its partial pressure has also been confirmed.

Acknowledgements

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