Investigation of the nature of the oxidant (selective and unselective) in/on a vanadyl pyrophosphate catalyst

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The anaerobic oxidation of CO by a $(VO)_2P_2O_7$ catalyst has been used to investigate the nature of the oxidant (selective and unselective) in/on that material. Three peaks were observed in the rate of production of CO_2 – at 993, 1073 and 1093 K. The temperature of the maximum in the rate of production of the first CO_2 peak and the amount of oxygen associated with it are the same as that observed in the selective anaerobic oxidation of *n*-butane to butene and butadiene, but-1-ene to butadiene and furan and but-1,3-diene to dihydrofuran, furan and maleic anhydride. The interaction of CO with the $(VO)_2P_2O_7$ catalyst forming CO_2 at 993 K is therefore concluded to be with the selective oxygen. The total amount of oxygen removed by the CO from the $(VO)_2P_2O_7$ lattice (> 5 monolayers) is about six times greater than that of the selective oxygen. The higher activation energies for the removal of the unselective oxygen accounts for the high selectivities (~80%) encountered commercially for the anaerobic oxidation of *n*-butane to maleic anhydride. Re-oxidation of the CO reduced $(VO)_2P_2O_7$ by N_2O quantitatively replaces all of the lattice oxygen removed by the formation of CO_2, but does not restore the original morphology.

Keywords: selective oxidation, vanadyl pyrophosphate catalyst, lattice oxygen

1. Introduction

A previous study into the origins of the selectivity in the partial oxidation of the C_4 hydrocarbons butane, but-1-ene and but-1,3-diene over vanadyl pyrophosphate catalyst has shown that it is a specific form of the oxygen of the vanadyl pyrophosphate lattice which is responsible for the oxidation of: (i) butane to butene and butadiene, (ii) of but-1-ene to butadiene and furan and (iii) of but-1,3-diene to dihydrofuran, furan and maleic anhydride [1]. The specific form of lattice oxygen was that oxygen which evolved from the lattice in two desorption peaks at 993 and 1023 K on temperature programming. The C_4 hydrocarbons, on anaerobic oxidation, reacted with the desorbing lattice oxygen at 993 and 1023 K and were quantitatively transformed into the partial oxidation products listed above. There was complete oxygen balance between the amount of oxygen which desorbed and that which was required for the formation of the selective products [1].

The purpose of this paper is to extend this earlier work by investigating the nature of both the selective and unselective oxidants in/on vanadyl phosphate catalysts. This is done by the aerobic and anaerobic oxidation of carbon monoxide.

2. Experimental

2.1. The vanadyl pyrophosphate catalyst

The method of preparation of the vanadyl pyrophosphate catalyst (P/V = 1.07) has been described in detail previously. It had a surface area of 24 $m^2\ g^{-1}$ and was shown by X-ray diffraction to be pure $(VO)_2P_2O_7$.

2.2. The gases

The gases, O_2 and He (British Oxygen Company), CO in He (10% CO) and N_2O in He (5% N_2O) Electrochem were all 99.9995% pure and were used direct from the cylinder. The CO in O_2 mixture (10% CO) was produced by mixing flows.

2.3. The apparatus

The microreactor system with on-line mass spectral analysis of products has been described in detail previously [4].

2.4. The anaerobic temperature-programmed oxidation of CO over the $(VO)_2P_2O_7$ catalyst

The $(VO)_2P_2O_7$ catalyst (0.5 g) was pre-treated by holding it under an oxygen flow (1 bar, 25 $cm^3\ min^{-1}$) at 673 K for 1 h. The catalyst was then cooled to ambient in the oxygen flow at which point the flow was switched to a CO/He stream (10% CO, 1 bar 25 $cm^3\ min^{-1}$) and the temperature was raised from ambient to 1100 K at 10 K min^{-1} following CO ($m/z = 28$) and CO_2 ($m/z = 44$) on the mass spectrometer. The temperature-programmed oxidation profile of CO to CO_2 is shown in figure 1.

Two distinct peak maxima are observed in the rate of production of CO_2. These occur at 993 and 1093 K. A

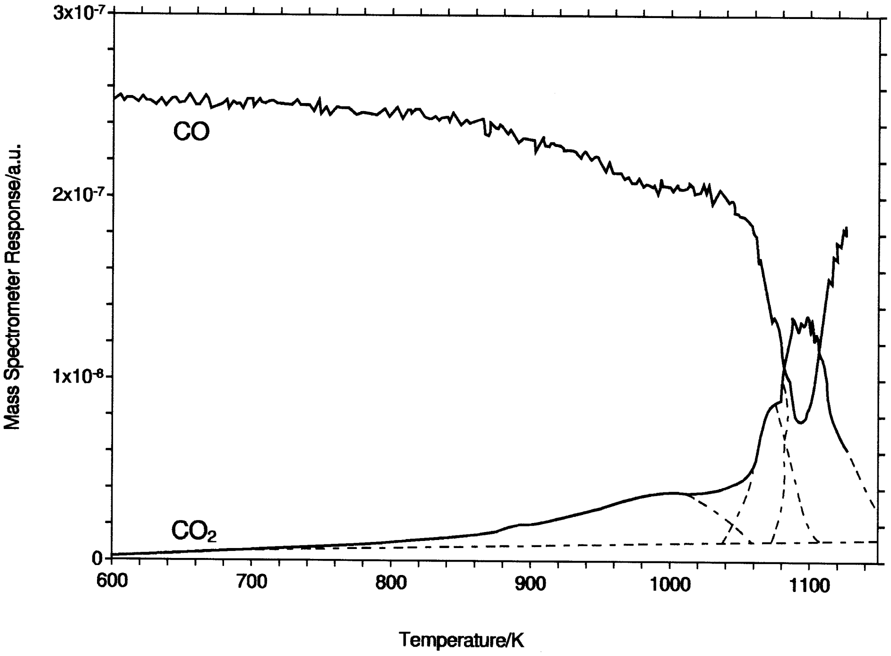

Figure 1. The anaerobic temperature-programmed oxidation of CO by the fresh $(VO)_2P_2O_7$ catalyst.

shoulder, at 1073 K, is also observed in the rate of production of CO_2. These peaks in the rate of CO_2 production are exactly mirrored by troughs in the CO signal on the mass spectrometer. The oxygen which is thermally induced to desorb from this $(VO)_2P_2O_7$ catalyst does so with peak maxima of 993 and 1023 K [1] and so, the 993 K maximum which occurs in the rate of CO_2 production could result from the CO reacting with this oxygen which is thermally evolving from the lattice at this temperature.

A rough estimate of the amount of CO_2 produced (oxygen atoms removed from the lattice) at the three separate maxima 993, 1073 and 1093 K was made by deconvoluting the peaks by hand as shown in figure 1. The amounts of oxygen atoms removed are: (i) 2.2×10^{20} atom g^{-1} for the 993 K CO_2 peak, (ii) 9.2×10^{19} atom g^{-1} for the 1073 K shoulder and (iii) 8.6×10^{20} atom g^{-1} for the 1093 K peak. These are listed in table 1.

The amount of oxygen atoms removed from the $(VO)_2P_2O_7$ lattice by CO to form CO_2 at 993 K is exactly the same as the total amount of oxygen which has been found to desorb from the lattice at the same temperature by thermal instigation [1] (table 1). These therefore appear to be the same oxygen. The rate-determining step in the oxidation of CO to CO_2 appears to be diffusion of the oxygen from the bulk of the lattice to the surface. Additionally since the carbon monoxide coverage of the catalyst at 993 K is likely to be vanishingly small, the reaction mechanism is probably impulsive with the CO molecule removing oxygen from the catalyst upon collision with the surface i.e. the Rideal–Eley mechanism.

This oxygen which desorbs at 993 K and which reacts quantitatively with the CO at this temperature has been

Table 1
Total number of oxygen atoms removed from the catalyst [a] by reduction in CO/He

Peak	T_{max} (K)	Reduction activation energy, E (kJ mol^{-1})	Oxygen atom removed from the catalyst		Notional oxygen coverage [b] (atom cm^{-2})	Monolayers of oxygen removed [c]
			(mol (g-cat)$^{-1}$)	(atom (g-cat)$^{-1}$)		
1	993	172	3.6×10^{-4}	2.2×10^{20}	0.9×10^{15}	1.3
2	1073	189	1.5×10^{-4}	9.2×10^{19}	0.4×10^{15}	0.6
3	1093	186	1.4×10^{-3}	8.6×10^{20}	3.6×10^{15}	5
total oxygen atom removed			1.9×10^{-3}	1.2×10^{21}	4.9×10^{15}	6.9

[a] Surface area = 24 $m^2 g^{-1}$. Weight of catalyst 0.5 g.

[b] The "notional oxygen coverage" is calculated by dividing the number of oxygen atoms removed from the lattice by the total surface area.

[c] The "monolayers of oxygen removed" is calculated by dividing the "notional oxygen coverage" by 7×10^{14} atom cm^{-2} – the stoichiometric value of monolayer oxygen coverage.

shown previously to be completely selective in the oxidation of butane, but-1-ene and but-1,3-diene [1]. The oxygen atoms which react with the CO at 1073 and 1093 K must therefore be unselective oxidants; their quantity (1×10^{20} atoms g^{-1} (1073 K peak), and 2.2×10^{20} atoms g^{-1} (1093 K peak), catalyst area $24\ m^2\ g^{-1}$) shows them to involve more than five monolayers of the oxide lattice (table 1). They are therefore lattice oxygen atoms. It is apparent, however, that the top five monolayers of lattice oxygen will not be completely depleted of oxygen. There will be a distribution of defects from the surface into the bulk, with the concentration of defects decreasing on moving further into the bulk. The defects will therefore penetrate ten or more layers into the bulk.

The fact that unselective lattice oxygen ions react with the CO molecules at higher temperatures than the selective oxidant suggests that they have either a higher activation energy for diffusion through the lattice or a higher activation energy for the CO/O(s) reaction. It is reasonable to suppose that the same relative ordering of kinetics obtains for the selective and unselective anaerobic oxidation of C_4 hydrocarbons over this catalyst a rationale which would account for the high selectivity (~80%) observed industrially for the anaerobic oxidation of butane to maleic anhydride [2,3]. Industrially, the reaction is carried out at long contact times at ~400°C and so the selective oxidative pathway by dint of its lower activation energy will always be favoured over the unselective route.

The total amount of oxygen removed from the lattice by reaction with carbon monoxide nevertheless remains small (1.2×10^{21} atom g^{-1} or ~5% of the total) and so the peaks observed in the rate of production of carbon dioxide are in no way related to those observed by Koranne et al. [5] and by Bosch et al. [6] in the temperature-programmed reduction of V_2O_5 which they ascribed to the

$$V_2O_5 \rightarrow V_6O_{13} \rightarrow V_2O_4 \rightarrow V_2O_3$$

transformations. Indeed the $V_2O_5 \rightarrow V_6O_{13}$ transformation alone accounts for 13% of the total oxygen. The amount of oxygen removed in the CO_2 peaks observed here, being less, suggests that it derives from the formation of extended surface and bulk defects, similar to those described by Gai and Kourtakis who, using in situ high-resolution electron microscopy, observed two sets of symmetry related extended defects producing glide planes on the surface of a $(VO)_2P_2O_7$ catalyst after reaction with *n*-butane or H_2 [7].

2.5. *Temperature-programmed reduction of nitrous oxide by a CO reduced vanadyl pyrophosphate catalyst*

The vanadyl pyrophosphate which had been reduced to the extent described in table 1 by temperature programming to 1100 K in a CO/He stream, was re-oxidised by temperature programming ($10\ K\ min^{-1}$) to 1100 K in N_2O/He stream (5% N_2O, 1 bar, 25 $cm^3\ min^{-1}$), following the N_2O ($m/z = 44$) and the N_2 ($m/z = 28$) signals continuously on the mass spectrometer. The temperature dependence of the reduction of the N_2O is shown in figure 2. Nitrogen evolution occurs as a

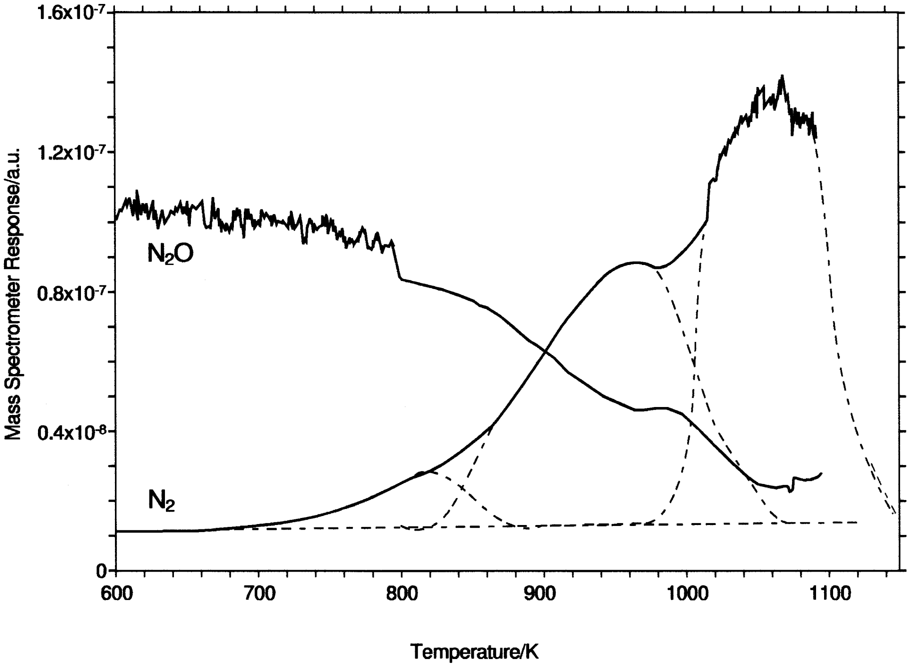

Figure 2. Temperature-programmed reduction of N_2O by a CO reduced $(VO)_2P_2O_7$ catalyst.

result of the nitrous oxide adsorbing and decomposing on the oxygen vacancies according to the following reaction

$$N_2O + \square \rightarrow N_2 + O(s)$$

where $\square$ is the oxygen vacancy and O(s) is lattice oxygen.

The figure shows that there are two distinct peak maxima in the rate of the nitrogen evolution (973 and 1073 K) and a shoulder at 813 K. These derive from three distinct kinetic regimes for the re-oxidation of the vanadyl pyrophosphate. A rough estimate of the amount of oxygen to be taken up by the catalyst in each of the temperature regimes can be made by curve fitting the peaks. The results of the curve fitting are shown in dotted lines on figure 2 and the amounts are listed in table 2.

It can be seen by comparison of table 2 with table 1 that the total oxygen taken up by the catalyst by oxidation by N_2O is exactly the same as the amount removed by CO reduction. All of the anion vacancies produced by CO reduction have therefore been healed by oxidation by N_2O. However, there is no correspondence between the amount of oxygen taken up at 813, 973 and 1073 K by N_2O oxidation with that removed at 993, 1073 and 1093 K by CO reduction. Therefore, while the activation energies of re-oxidation of the CO reduced vanadyl pyrophosphate are lower than the reduction activation energies, the different extents of oxidation in the three temperature regimes suggest that the re-oxidised catalyst is not the same, morphologically, as the initial state.

This suggests that whereas the oxygen may have healed specific isolated anion vacancies in the lattice, the glide plane structures produced by the extended defects have not been affected by the re-oxidation.

2.6. *The anaerobic temperature-programmed oxidation of CO over the N_2O re-oxidised $(VO)_2P_2O_7$ catalyst*

Corroborative evidence for the conclusion that N_2O re-oxidation of the $(VO)_2P_2O_7$ catalyst does restore the catalyst to its original morphology is to be found in the anaerobic oxidation of CO by the re-oxidised catalyst.

Figure 3 is the temperature-programmed reduction profile obtained by passing a carbon monoxide/helium stream (10% CO, 1 bar, 25 cm^3 min^{-1}) over the N_2O re-oxidised vanadyl pyrophosphate catalyst raising the temperature at 10 K min^{-1} and following the CO_2 ($m/z = 44$) and CO ($m/z = 28$) signals on the mass spectrometer. This temperature-programmed reduction profile is considerably different from that shown in figure 1 which is the TPR profile for CO reduction of fresh vanadyl pyrophosphate. While the temperature of the onset of reductions is the same, only one peak at ~893 K is observed for the CO reduction of the N_2O re-oxidised material. Therefore the activation energy for the anaerobic oxidation of CO by the lattice oxygen $(VO)_2P_2O_7$ catalyst is lowered on N_2O re-oxidation. Additionally, the amount of oxygen capable of being removed from the N_2O re-oxidised material by the carbon monoxide ($\sim 5.2 \times 10^{20}$ atom g^{-1}) is 1/2 that of the fresh catalyst.

Therefore, whereas the N_2O oxidation has healed all of the anion vacancies produced by CO reduction, the final crystallography of the N_2O re-oxidised material is significantly different from that of the original material.

2.7. *Temperature-programmed reaction (TPRn) of a carbon monoxide/oxygen stream over the $(VO)_2P_2O_7$ catalyst*

Figure 4 is the temperature-programmed reaction profile obtained by passing a CO/O_2 stream (10% CO, 90% O_2, 1 bar, 25 cm^3 min^{-1}) over a fresh oxidised sample of $(VO)_2P_2O_7$ raising the temperature from ambient to 873 K at 10 K min^{-1}, following the CO ($m/z = 28$) and CO_2 ($m/z = 44$) signals on the mass spectrometer.

It can be seen from the figure that the temperature dependence of the rate of production of CO_2 is considerably different from that of CO reduction of fresh or N_2O

Table 2
Total number of oxygen atoms taken up by the CO reduced $(VO)_2P_2O_7$ [a] by TPO in N_2O

Peak	T_{max} (K)	Oxygen atom supplied to the catalyst		Notional oxygen coverage [b] (atom cm^{-2})	Monolayers of oxygen replaced [c]
		(mol $(g\text{-}cat)^{-1}$)	(atom $(g\text{-}cat)^{-1}$)		
1	813	2.0×10^{-4}	1.4×10^{20}	0.6×10^{15}	0.9
2	973	5.8×10^{-4}	3.4×10^{20}	1.4×10^{15}	2
3	1073	1.3×10^{-3}	7.4×10^{20}	3.1×10^{15}	4.4
total oxygen atom supplied		2.0×10^{-3}	1.2×10^{21}	5.1×10^{15}	7.3

[a] Surface area = 24 m^2 g^{-1}. Weight of catalyst 0.5 g.

[b] The "notional oxygen coverage" is calculated by dividing the number of oxygen atoms given to the lattice by N_2O decomposition by the total surface area.

[c] The "monolayers of oxygen replaced" is calculated by dividing the "notional oxygen coverage" by 7×10^{14} atom cm^{-2} – the stoichiometric value of monolayer oxygen coverage.

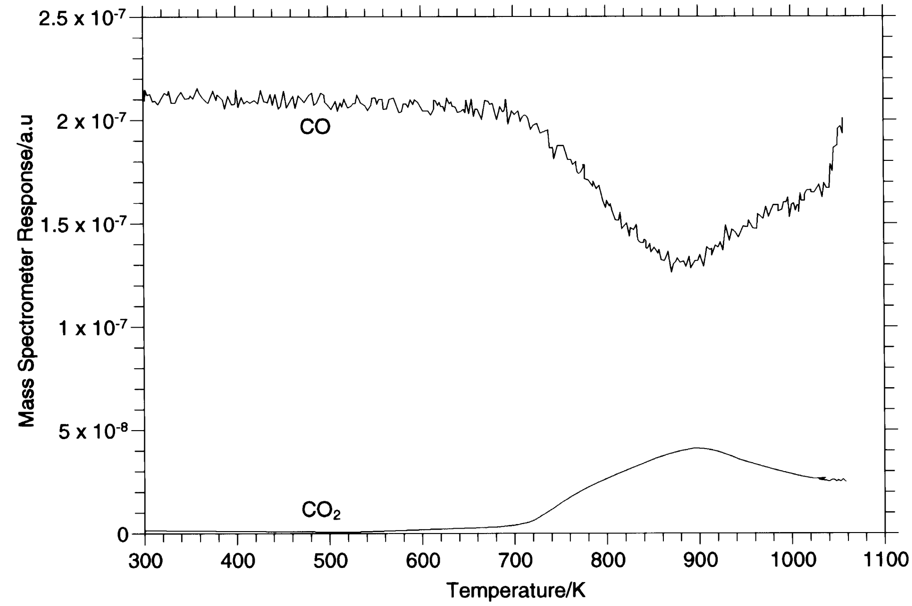

Figure 3. The anaerobic temperature-programmed oxidation of CO by a N_2O re-oxidised $(VO)_2P_2O_7$ catalyst.

re-oxidised $(VO)_2P_2O_7$. The important point to note is that the temperature of the onset of significant rates of CO_2 production from the CO/O_2 reaction (~530 K) is roughly 150 K lower than that of CO reduction of fresh or N_2O re-oxidised material.

However, careful examination of the temperature reduction profiles of figures 1 and 3 shows a small increase in the rate of CO_2 production at ~500 K. This will produce a small number of anion vacancies with trapped electrons on the surface of the vanadyl pyrophosphate. Adsorption of oxygen on these sites will produce O_2^- species and ultimately O^- species [8] which will react rapidly with the CO upon its collision with the surface. Many CO/O^- turnovers can occur, accounting for the markedly higher rate of production of CO_2 in the CO/O_2 mixture. These O^- species are usually regarded as being responsible for the unselective oxidation of hydrocarbons to CO and CO_2 and as such are probably

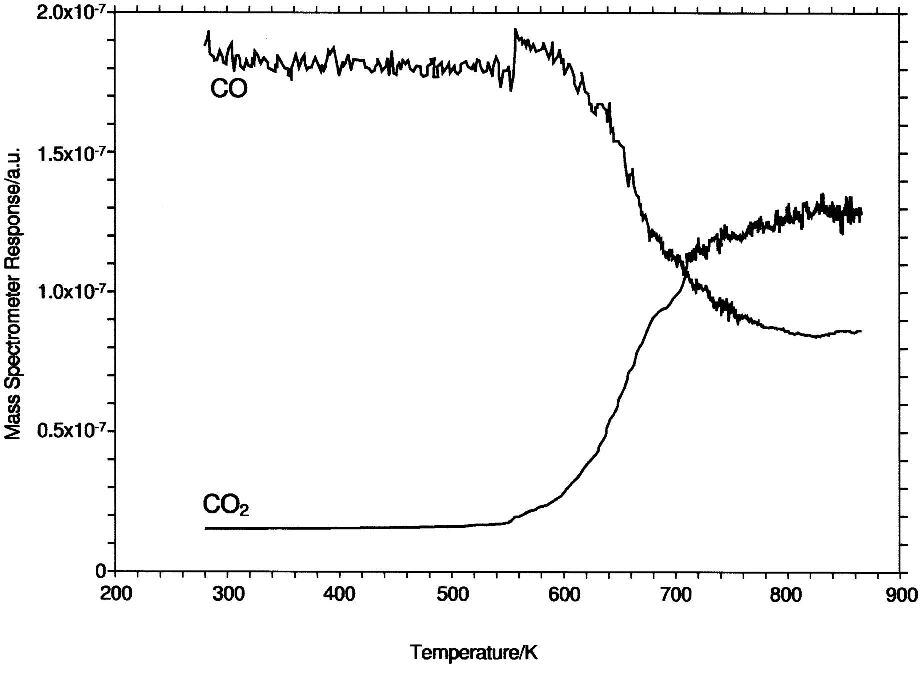

Figure 4. Temperature-programmed reaction of a CO/O_2 stream over a fresh $(VO)_2P_2O_7$.

uniquely different from the oxygen evolving at the surface from the lattice.

This suggestion has resonance in our observation of a completely unselective oxidation of *n*-butane when reacted with oxygen (0.75% n-C_4H_{10}, 20% O_2, 79.25% He) in a temperature-programmed mode over the $(VO)_2P_2O_7$ catalyst [1].

3. Conclusions

(1) The anaerobic oxidation of CO by $(VO)_2P_2O_7$ occurs at and above the temperatures at which oxygen thermally desorbs from the $(VO)_2P_2O_7$ lattice [1]. The lowest temperature peak in the rate of production of CO_2 is consistent with the CO reacting with the selective lattice oxygen. The two higher temperature CO_2 peaks are CO reaching with unselective lattice oxygen.

(2) The higher activation energy for the removal of unselective lattice oxygen accounts for the high selectivity (~80%) found commercially for the anaerobic oxidation of butane to maleic anhydride [2,3].

(3) Reoxidation of the CO reduced $(VO)_2P_2O_7$ catalyst by N_2O does not reproduce the original morphology of the catalyst. Both the kinetics of CO oxidation and the total quantitiy of oxygen available from $(VO)_2P_2O_7$ lattice are changed. This has implications for the long-term operation of the commercial $(VO)_2P_2O_7$ catalyst.

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