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VPO transient lattice oxygen contribution

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Abstract

n-Butane partial oxidation to maleic anhydride is practiced commercially in several reactor types with vanadium phosphorous oxide (VPO) catalyst. DuPont operated a Circulating Fluidized Bed facility in which catalyst was shuttled between a net reducing zone (a transport bed) to a net oxidizing zone (air regenerator). Several advantages have been cited for this technology but the role of oxygen is hotly debated and different models have been proposed to characterize the complicated $14e^-$ exchange. To examine the role of surface lattice oxygen, we carried out transient experiments in which catalyst was subjected to high concentrations of butane followed by an extensive re-oxidation treatment. Carbon accumulates on the surface lattice surface thereby contributing to a reduction in reaction rates and the quantity increases with the butane/oxygen ratio. This carbon reacts in the presence of molecular O_2 during the regeneration step. The surface lattice is capable of storing significant amounts of oxygen and when the catalyst is highly oxidized, both selectivity and activity are higher.

Keywords: Butane oxidation; Maleic anhydride; Commercial VPO catalyst; Lattice oxygen

1. Introduction

Throughout the last decade several multi-national conglomerates have devoted significant research efforts to commercialize breakthrough technology related to oxidative catalysis. These processes are generally based on C_1–C_4 hydrocarbons (alkanes and alcohols) as a feedstock since they are the most abundant and cheapest raw material source. Both fixed and fluid bed processes are employed and the general trend to improve yields has been to increase hydrocarbon partial pressures. However, the upper feed concentration limits may often be constrained by the hazards associated with mixing a combustible gas and molecular oxygen. Fixed bed reactors are further constrained by heat transfer and hot spots that may volatilize active species in the catalyst. A possible remedy to reduce feed oxygen concentrations is to use the catalyst lattice oxygen. This technology, commercialized by DuPont, involves oxidizing the catalyst with air in a regenerator and then shuttling the catalyst to a zone rich in hydrocarbon. Together with reducing the safety hazards an additional advantage often cited is that productivity and selectivity are higher versus conventional reactor designs. However, to adequately model this reactor system requires a detailed knowledge of both the transient reduction and oxidation kinetics. Several models have been proposed to describe the transient oxygen reaction kinetics [1–6] but there has been no consensus with respect to the form of the oxygen – surface, bulk or adsorbed – or the reaction kinetics.

2. Experimental set-up

In order to evaluate the lattice oxygen contribution of VPO catalyst, we carried out experiments in a fluid bed under both steady and unsteady state conditions. It was 41 mm in diameter and 790 mm in height. The reactor was loaded with 200 g of catalyst (withdrawn from DuPont's commercial reactor after 116 days of operation) and it was immersed in a heated fluid bed to maintain isothermal conditions. The non-condensable gases were analyzed by a Hewlett Packard 5890 GC, an Oxymat 5F Paramagnetic oxygen analyzer and two ABB 501 B IR analyzers for CO and butane. Condensable gases were

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accumulated in a water scrubber and the conductivity was monitored on-line and in real-time [5].

The focus of this work was to compare maleic anhydride and CO_x evolution and oxygen reaction under highly oxidizing and reducing conditions. The protocol involved [5] feeding a mixture of butane/nitrogen/air to the catalyst for a period of 40 min (reduction step) followed by 10 min of nitrogen (purge), 40 min of air/nitrogen mixtures (oxidation), 10 min of nitrogen (purge) and then a final oxygen treatment (re-oxidation step). The reduction step was conducted with butane concentrations between 2% and 9% with 0–10% oxygen. The oxidation step was run with oxygen concentrations varying between 2% and 20% and pressures of up to 3 bar.

3. Catalyst reduction

Directly preceding the reduction step, the VPO catalyst was oxidized for a period of at least 70 min. At the end of this pre-treatment step, the oxygen concentration exiting the reactor reached a steady value. Fig. 1 illustrates both CO and maleic acid (MAC) evolution during the reduction step for experiments conducted with 10% oxygen and 9%, 5% and 2% butane (balance N_2). The instantaneous production rate of MAC was calculated by differentiating the conductivity measurements and the CO concentration was measured by IR. The CO peak height is delayed versus the MAC by approximately 1 min due to the additional residence time between the reactor and gas phase analysers: maleic anhydride is immediately hydrolyzed in the quench at the exit of the reactor whereas the non-condensable gases pass through the quench and an ice trap before reaching the IR and paramagnetic analyzers. Both the CO and MAC concentrations rise rapidly during the first 2 min to a maximum and then they drop more slowly. The CO concentration approaches a steady value within about 10 min after starting butane while it appears that it takes somewhat longer for the MAC to attain a constant value. The absolute overshoot for both CO and MAC are substantially the same regardless of the molecular oxygen concentration. The overshoot in the CO evolution is on the order of 1% on an absolute basis. For example, the steady state CO concentration with 9% butane is 1.5% and the maximum recorded value is 2.5%. The MAC peak height is approximately proportional to the butane feed concentration. That is, the maleic production rate with 9% butane is about double the rate at 5% which is double that at 2%. In addition to the peak height, the peak width becomes narrower with increasing butane concentration. However, all of the three MAC traces converge to the same production rate at about 5 min of operation and continue to decline to a steady value after 25 min. This result is very surprising since the gas phase oxygen conversion increases with butane concentration.

Together with overshoots in MAC and CO, at 2% butane and 10% oxygen, there is a slight overshoot in the oxygen concentration. The overshoot in oxygen indicates that the surface is highly oxidized and the butane concentration is insufficient to reduce the catalyst enough to create vacant sites. However, increasing the partial pressure of oxygen (at constant %butane) increases both the MA and CO production rates proportionately.

The rate at which the lattice oxygen reacts with butane increases with butane concentration, and we assume that it is only the first several surface layers that participate. Bulk diffusion rates would be presumably too low to account for a three-fold increase in the maleic production rate versus the steady state value. Contractor et al. showed that the time frame to oxidize the bulk lattice was on the order of hours [7]. Furthermore, Kleimenov et al. [8] demonstrated that only 1 nm of the surface lattice participates in the reaction. However, the rate at which the surface lattice reacts decreases as the molecular oxygen partial pressure increases. In the conditions with 10% oxygen in the feed it takes approximately 30 min to reach a steady MAC production rate. With lower concentration of oxygen the steady rate is on the order of 5–10 min.

While MA production was essentially independent of butane concentration, CO evolution was slightly lower when the feed gas contained 2% butane and increased with increasing butane. This trend is consistent with the model of Lorences et al. [5] that includes a reaction step in which butane chemisorbs on to vacant sites.

Fig. 2 illustrates the change in butane conversion with respect to time for experiments run at 380 °C with varying

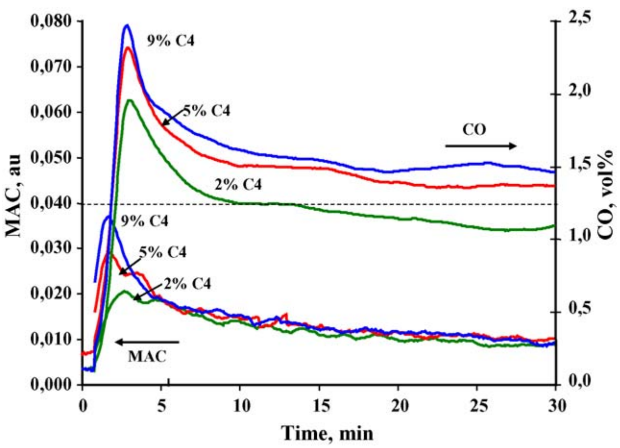

Fig. 1. MA and CO evolution during the reduction step (10% O_2).

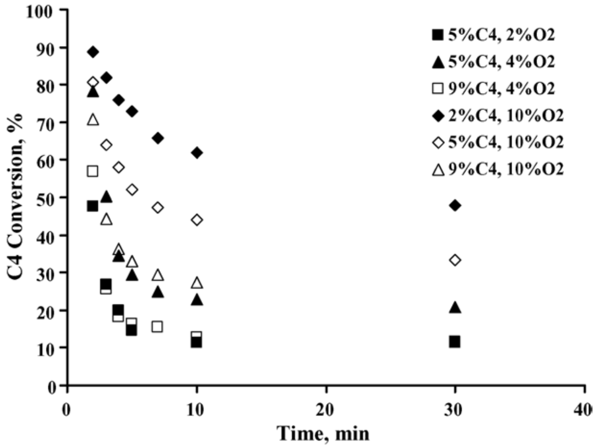

Fig. 2. Butane conversion vs. reduction time.

concentrations of butane and oxygen. The steady state conversion is shown at 30 min and in all cases is significantly lower than the initial conversion at 2 min. The drop in conversion may be a result of two factors including the reduction in the available oxygen on the surface as well as coverage of active sites by carbon (which will be demonstrated in Fig. 4). The rate at which the surface oxygen lattice is consumed depends on the severity of the reducing atmosphere. The data at 2% butane and 10% oxygen illustrate this point: at 3 min, the conversion was 82% and it dropped to 62% at 10 min. With 5% butane and 10% oxygen the conversion dropped by the same amount in only 1 min. Clearly, maintaining the near surface layers oxygenated (and a correspondingly low concentration of carbonaceous species) is essential to maintain high production rates. Finally, the butane conversion is equal for conditions with the same inlet C_4/O_2 ratio. For example, butane conversion with 5% C_4 2% O_2 equals that with 9% C_4 and 4% O_2.

4. Catalyst re-oxidation

In DuPont's commercial process for butane oxidation, the VPO catalyst was reduced in a transport bed reactor than passed through a vessel in which interstitial gas and catalyst were separated using air. Finally, the surface lattice oxygen was restored in the regenerator with air and at the same time adsorbed carbon species react in this vessel. The principal operating parameters available to increase regeneration rates include oxygen concentration, total pressure, temperature, residence time as well as the degree of reduction (this is largely determined by the butane and oxygen partial pressure in the transport bed). In this study, we report on the effect of two parameters: oxygen partial pressure during regeneration and butane partial pressure during reduction.

Fig. 3 illustrates the oxygen uptake during the first re-oxidation step after the catalyst was exposed to four different 40 min reduction steps: (i) 9% butane, (ii) 5% butane, (iii) 2% butane and (iv) 2% butane + 10% oxygen. The curves represent the difference between the oxygen concentration during the first re-oxidation step and the second step. Low values suggest that little molecular oxygen reacts, which is the case for condition (iv). The other three experiments were run in ''redox'' mode in which only butane and nitrogen were fed to the catalyst during the reduction step. Molecular oxygen conversion (as well as CO evolution) is significantly higher when catalyst is operated in the redox mode. In all four experiments, the oxygen pick-up increased rapidly during the first 5 min, reached a maximum and then approached zero after 15 min. When the data are normalized with respect to the peak height, they collapse to a single curve. Note that both the total oxygen uptake and CO evolution (which is approximately proportional to the quantity of ''adsorbed'' carbon released from the catalyst) increase with an increase in the butane partial pressure during the reduction step. However, neither the regeneration rate nor the desorption rate depend on the reduction conditions. Thus, in commercial operation, high oxygen partial pressures are preferred to accelerate the CO_x desorption rate as well as the re-oxidation rate. Oxygen conversion in the regenerator increases with the severity of the reduction step but the regeneration rate is independent of the reduction step.

Fig. 4 illustrates the evolution of CO with time and the trend is similar to the oxygen uptake: with increasing oxygen concentration, both the reaction rate and peak heights are higher and the curve is shifted to the left. The CO concentration approaches zero after 10 min with air but significantly longer times are required with 2% oxygen. Several measurements of the gas phase composition were conducted by GC to assess the CO_2 concentration. The data suggested that the CO/CO_2 ratio was similar to the concentration during the reduction step: the ratio varied somewhat with time but was close to 1.

Operating at high oxygen partial pressures would be preferred in a commercial plant in order to accelerate the CO_x desorption rate and thereby minimize the catalyst inventory in the regeneration step. However, due to environmental constraints related to discharging CO to the atmosphere, it would be preferable to drive off the carbonaceous species before the regenerator. Data published by Waugh and Taufiq-Yap [9] would suggest the carbon is dehydrogenated butane and this desorbs anaerobically to butane and butadiene at high

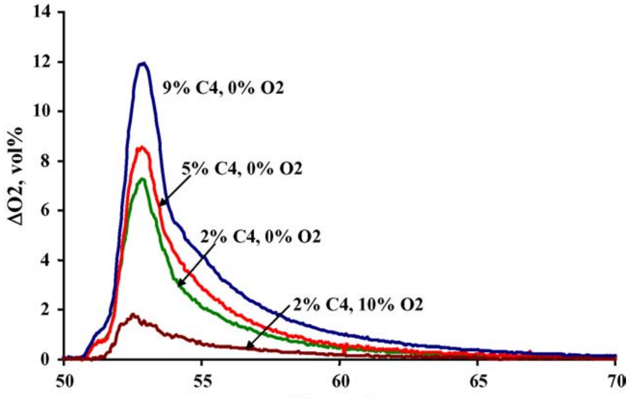

Fig. 3. Differential O_2 uptake during catalyst re-oxidation under various C_4/O_2 concentrations in the reduction step.

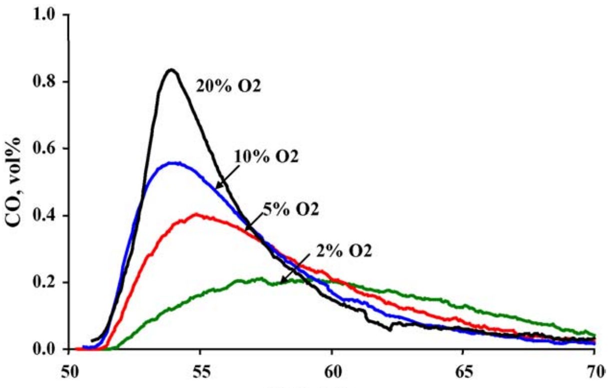

Fig. 4. CO evolution during catalyst re-oxidation at different O_2 concentrations (reduction step: 5% C_4, balance N_2).

temperatures. Typically, this is accomplished with a stripper that would have two functions: The first would be to separate the catalyst from interstitial and intraparticle gas and the second would be to react any adsorbed carbon on the lattice surface. During the desorption process, the catalyst would ultimately regenerate to some degree.

Carbon build-up on the surface is greatest under redox operation. However, under conditions with oxygen co-feed, carbon species may accumulate on the surface lattice at C_4/O_2 ratios less than 1. The accumulation increases as the gas environment becomes more reducing and therefore, the quantity of oxygen required to react this adsorbed carbon also increases. The maximum oxygen pick-up for the selective oxidation of butane is on the order of 50 mmol O_2/kg catalyst. The maximum oxygen consumed to react adsorbed carbon species reaches 50 mmol O_2/kg catalyst under redox operation.

5. Conclusions

Transient experiments were conducted in a laboratory scale fluid bed reactor with sufficient instrumentation to measure product gases and acids in real time. The focus of this study has been to examine the effect of both the reduction conditions and re-oxidation conditions on the kinetics of the re-oxidation rate. The data imply that the active species is the surface lattice oxygen and that the contribution of either the surface adsorbed oxygen or the bulk lattice oxygen is negligible. A 70 min air pre-treatment saturates the surface lattice with enough oxygen to increase maleic anhydride yields by as much as four times more than the steady state values. The increased yield is mostly due to higher conversion but selectivity also appears to be improved. The surface lattice oxygen is quickly consumed when the gas phase composition is highly reducing but under oxidizing conditions, increased maleic yields may be maintained for longer periods of times. Highly reducing conditions not only consume the surface oxygen species quickly they also cause carbon to build-up. This adsorbed carbon is most likely a contributing factor to the lower reaction rates and maleic yield. Furthermore, the data presented imply that the percent butane conversion appears to depend on the butane/oxygen ratio (at the same temperature, pressure and contact time).

The mass of carbon adsorbed on the catalyst surface was measured by monitoring the CO evolution during the re-oxidation step. It increases with butane partial pressure even in the redox mode and decreases substantially when oxygen is co-fed together with butane. The CO desorption rate appears to be independent of the mass adsorbed. The regeneration rates are also highly dependent on oxygen partial pressure.

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