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The effects of steam on *n*-butane oxidation over VPO as studied in a riser reactor

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Abstract

The effects of steam, fed to the riser section of a laboratory recirculating solids reactor, on butane oxidation over a vanadyl pyrophosphate catalyst are reported. Gas fed to the riser was either butane in inert or butane co-fed with oxygen in inert. The catalyst regenerator-vessel was fluidized with air in all cases. It was observed that steam added to the riser competes for sites required for gas-phase oxygen activation, while catalyst lattice oxygen utilization is not affected. The competition for sites with oxygen causes a decrease in butane conversion and a corresponding increase in selectivity to maleic anhydride. The improvement in selectivity is more pronounced under anaerobic conditions, and an explanation for this result is offered. This study demonstrates the opportunity offered by a recirculating solids reactor to study various aspects of selective oxidation catalysis independent of the complicating effects of simultaneous catalyst reduction and oxidation reactions.

Keywords: Alkane oxidation; Riser reactor; Steam

1. Introduction

Despite the fact that steam is constantly present as a by-product, its effect on the butane-oxidation reaction has not received extensive attention. There are only a few systematic studies on the effects of steam reported in the scientific literature. A study conducted by Zazhigalov and Zaitsev [1] concluded that the introduction of water vapor had no effect, either on the rate of butane oxidation or on the maleic anhydride yield. More recent studies carried out by Arnold and Sundaresan [2] and Lerou and Mills [3] concluded that the addition of steam leads to an enhancement in selectivity to maleic anhydride and a simultaneous decline in activity toward butane oxidation.

All of the aforementioned studies were conducted in fixed-bed reactors with oxidation conditions characterized by low (<2%) butane concentrations and large excesses of oxygen. Lerou and Mills [3] demonstrated that while the addition of steam enhanced selectivity to maleic anhydride, as compared to an anhydrous feed at the same butane conversion, the effect was greatly diminished at high butane conversions. The results were interpreted by these authors to indicate that the addition of steam competes for sites that are responsible for the generation of non-selective products. In addition, they concluded that the increase in the selectivity was probably attributable to a decreased surface-residence time

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of maleic anhydride, thereby minimizing its subsequent degradation.

There are a number of ways in which steam can conceivably affect the butane-oxidation reaction; for example, steam may interfere with the adsorption and activation of either butane or oxygen. Another possibility is that the interaction of steam with the catalyst surface may inhibit migration of protons across the surface, a step which is likely required for the formation and desorption of by-product water. In this study, we explore the effect of steam in a re-circulating solids reactor in an attempt to better define how steam brings about the changes in catalytic performance that are observed and, specifically, what types of surface sites are affected.

The work reported here was carried out in a laboratory circulating solids reactor, schematically shown in Fig. 1. The catalyst is oxidized in a fluidized bed regenerator zone fed by air. The oxidized catalyst particles then move down the standpipe and enter the bottom of the riser reactor zone. The catalyst particles are carried upward in the riser in a stream of high velocity feed gas, containing a relatively high concentration of butane. Butane is oxidized by the catalyst in the riser. The reduced catalyst particles are separated from the product stream, stripped of any carbonaceous species and returned to the regenerator for re-oxidation. The design and the operation of this reactor take advantage of the fact that the butane-oxidation chemistry proceeds essentially by a two-step process, typically referred to as the Mars–van Krevelen mechanism [4]. The first step is the oxidation of butane by the oxidation catalyst, resulting in the formation of maleic anhydride and other oxidation by-products along with reduced catalyst. In the second step, the reduced catalyst is re-oxidized by oxygen, back to its initial state.

In fixed-bed reactors, of the type in which the earlier studies were conducted, these two reactions (catalyst reduction and catalyst oxidation) occur simultaneously. At steady state, the rates of hydrocarbon oxidation and catalyst oxidation must be equal, but this rate is frequently controlled by just one of these steps. In practice, this translates to large excesses of oxygen being used to maintain reasonable reaction rates and to maintain the catalyst near its optimum oxidation state. In the circulating bed, on the other hand, the catalyst oxidation and reduction zones are physically separated. The riser reactor zone is operated with a high butane concentration, resulting in catalyst reduction and hydrocarbon oxidation. The fluidized bed regenerator is designed solely to effect catalyst re-oxidation in the absence of any hydrocarbon chemistry. Using this type of reactor to maintain the catalyst in a transient, cyclic state permits the oxidation and reduction zones to be independently controlled and optimized. This control allows us to gain an improved understanding of butane-oxidation

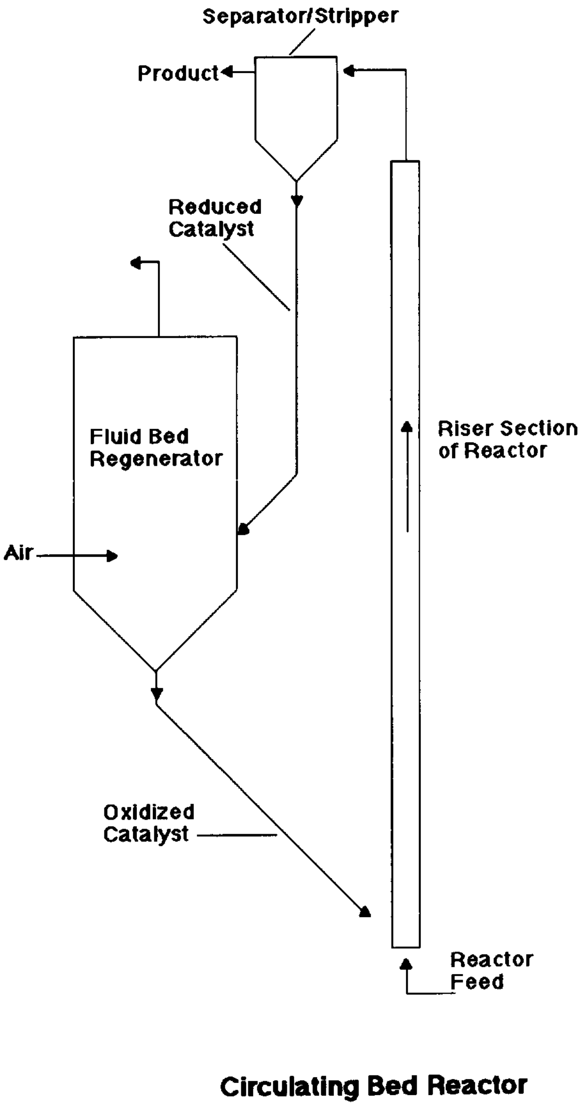


Fig. 1. Schematic diagram of the laboratory circulating bed reactor.

chemistry and study aspects of this chemistry, without the complicating effects of simultaneous catalyst reduction and oxidation reactions.

2. Experimental

The butane-oxidation catalyst used in this study was single phase $(VO)_2P_2O_7$. It was derived from $VOHPO_4 \cdot 1/2H_2O$ prepared in isobutanol:benzyl alcohol (11:1 molar ratio), as previously described [5]. The activated VPO (vanadium phosphorus oxide) was in the form of spray-dried microspheres characterized by a 70 {μ}m mean diameter. Attrition resistance was imparted to these microspheres by the 10 wt% SiO_2, which was segregated as a microporous shell, produced by spray drying the VPO precursor in an aqueous polysilicic-acid slurry [6].

All tests in the recirculating bed reactor were run at 380°C and 1 atm pressure. The gas feed to the regenerator vessel was always air. Two different types of gas feed conditions were used on the riser side of the reactor: aerobic conditions were maintained with 10% butane/5% oxygen/balance inert with either 0 or 11% steam; anaerobic conditions were maintained with 2% butane/balance inert with either 0 or 11% steam. The aerobic condition was chosen so as to result in a relatively low butane conversion. The catalyst residence time in the regenerator was set so as to insure equivalent and substantially complete oxidation of the catalyst surface for both the aerobic and the anaerobic cases. Based on the previous results of Lerou and Mills [3], the low conversion conditions were expected to clearly reveal the performance effects accompanying the presence of steam.

The feed-gas stream to the riser side of the reactor consisted of appropriate amounts of butane, oxygen and nitrogen, which were blended after having been individually metered through mass-flow controllers. The butane and oxygen concentrations in the feed-stream were independently confirmed by gas chromatography. Steam was added by metering water through an ISCO pump to a vaporizer which was connected to the feed-gas line. Product-gas composition was monitored at the riser stripper and regenerator exits by gas chromatography to detect CO, CO_2, O_2 and C_4H_{10}. Maleic anhydride production was determined by titration of the aqueous-product quench.

3. Results

Fig. 2 shows the percentage selectivity to maleic anhydride and the percentage butane conversion vs. time with the riser, maintained under aerobic conditions. Consistent with the earlier studies of Lerou and Mills [3] and Arnold and Sundaresan [2], a small but reproducible increase (about 4%) in selectivity and corresponding, but larger percentage decrease (about −11%) in conversion are observed in the presence of steam, as compared to a dry riser feed. The effect is reversible, as shown in the figure. The change in

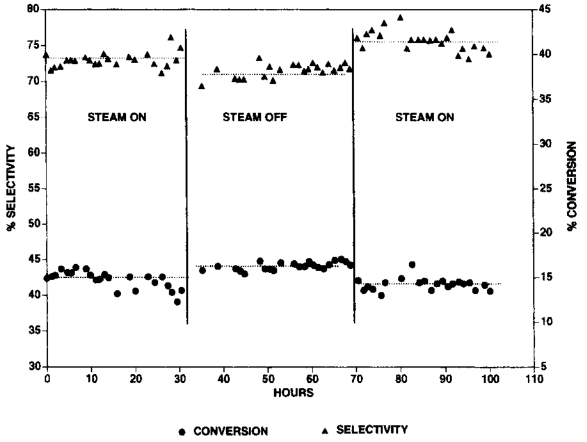


Fig. 2. The effect of steam fed to the riser on selectivity to maleic anhydride and butane conversion. Oxygen has been co-fed with butane. Dotted lines represent mean values.

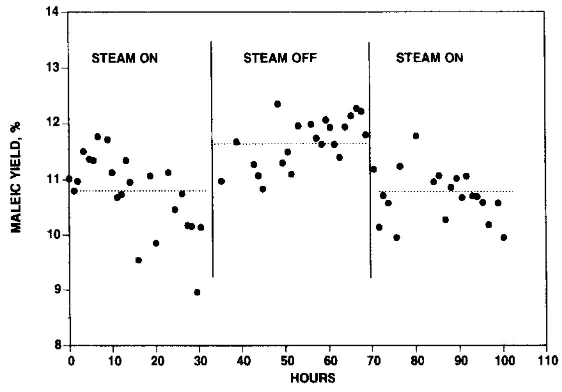


Fig. 3. The effect of steam fed to the riser on maleic anhydride yield. Oxygen has been co-fed with butane. Dotted lines represent mean values.

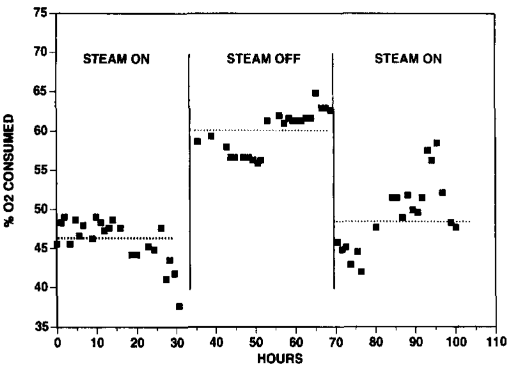


Fig. 4. The effect of steam fed to the riser on gas-phase oxygen consumption in the riser. Dotted lines represent mean values.

maleic yield, shown in Fig. 3, is dominated by the relatively larger change in butane conversion; thus, the yield is higher in dry feeds than in the presence of steam. The most striking change noted when steam is introduced to the riser feed-stream is the substantial decrease in the consumption of oxygen being fed to the riser, as evidenced in Fig. 4. In contrast, the catalyst's lattice oxygen utilization remains constant, as indicated (although not shown here) by the constant oxygen consumption on the regenerator side.

Under anaerobic conditions, an increase in selectivity to maleic anhydride in the presence of steam vs. a dry feed is again noted, but the effect, seen in Fig. 5, is much more pronounced (about 8% increase). Relatively little change in conversion is noted. Once again, the effect is reversible as is confirmed by the consistent trends in two independent tests (temperature and gas compositions were equivalent in these tests, but other experimental variables, e.g., catalyst circulation rates and residence times were not). Fig. 6 shows that, unlike the situation under aerobic conditions, the maleic-anhydride yield increases with steam, a consequence of the relatively large change in selectivity and the relatively small change in conversion. The oxygen consumed in the regenerator, as seen in Fig. 7, remains constant, independent of whether steam is fed to the riser or not. Thus, under anaerobic conditions, lattice oxygen is utilized to the same extent regardless of the steam content on the riser side.

Figs. 8 and 9, respectively, show that the product CO/CO_2 ratio is unaffected by the presence of steam in the riser feed gas under aerobic conditions, while

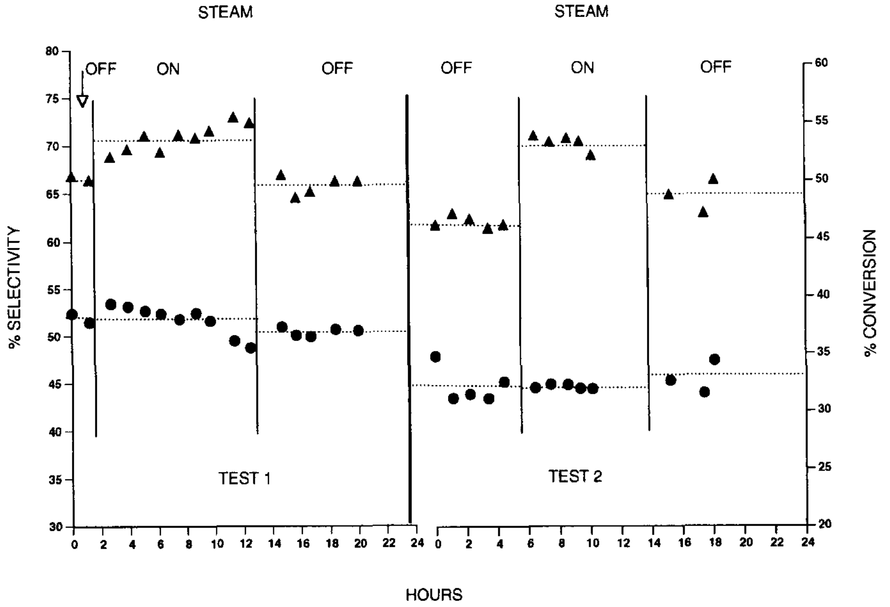


Fig. 5. The effect of steam fed to the riser on selectivity to maleic anhydride and butane conversion. No gas phase oxygen has been fed to the riser. Dotted lines represent mean values.

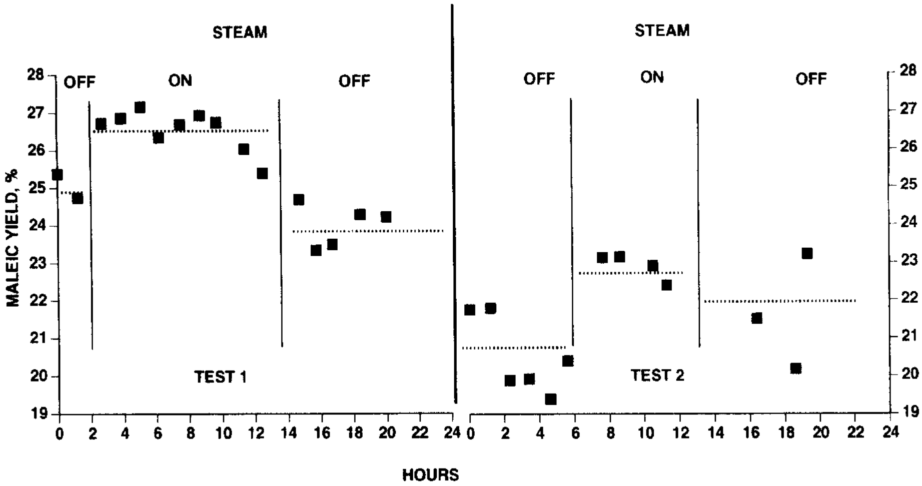


Fig. 6. The effect of steam fed to the riser on maleic anhydride yield. No gas-phase oxygen has been fed to the riser. Dotted lines represent mean values.

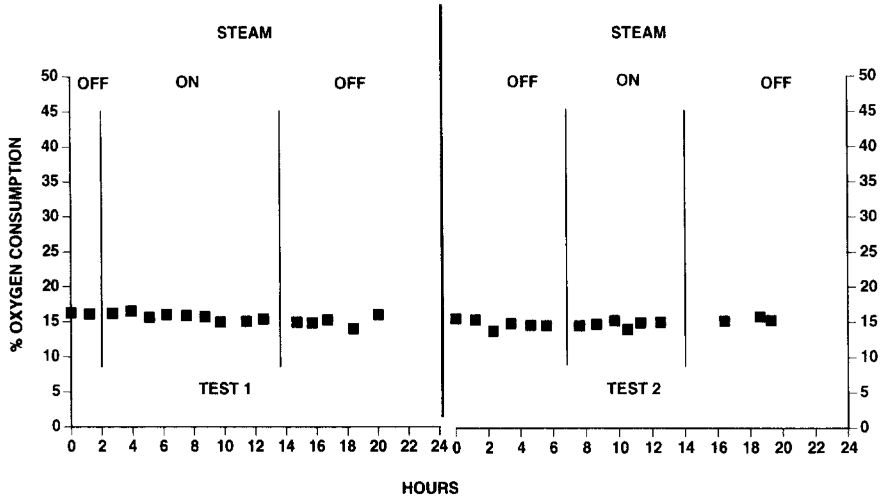


Fig. 7. The effect of steam fed to the riser on gas-phase oxygen consumption in the regenerator. No gas phase oxygen has been fed to the riser. Dotted lines represent mean values.

under anaerobic conditions, the ratio is decreased with the addition of steam.

Samples were recovered at regular intervals during the recirculating bed-reactor tests and characterized by X-ray diffraction. The catalyst remained single-phase vanadyl pyrophosphate throughout the tests, with no obvious changes in crystallinity being detected.

4. Discussion

The most prominent effect of steam addition to the riser side is a substantial reduction of the utilization of gas-phase oxygen in the riser (Fig. 4). Because of this competitive adsorption between steam and oxygen, fewer sites are available for oxygen activation, and the contribution of gas-phase oxygen to maleic-anhydride

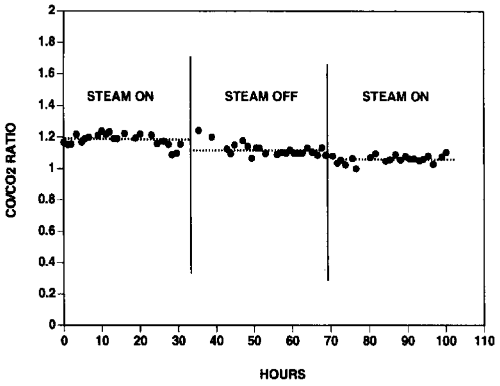
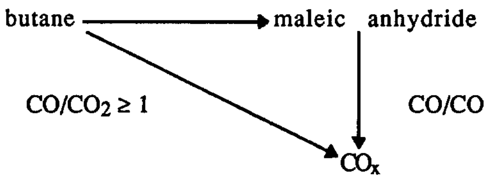


Fig. 8. The effect of steam fed to the riser on the CO/CO_2 ratio of the oxidation product. Oxygen has been co-fed with butane. Dotted lines represent mean values.

production is suppressed. In contrast, lattice-oxygen utilization is not adversely affected by steam, regardless of whether oxygen is co-fed to the riser or not. Consistent with previous studies [2,3], selectivity to maleic anhydride was improved by the addition of steam to the reactor.

The observation noted in this study, that the selectivity improvement is more pronounced under anaerobic conditions, was somewhat surprising to us. Our prior experience with butane oxidation, carried out in a recirculating bed reactor, has generally indicated [7] that the utilization of lattice oxygen leads to more favorable selectivity while molecular oxygen is a somewhat less-selective oxidant. Thus, an improvement in selectivity, accompanying the blocking of sites required for molecular-oxygen adsorption, is a very reasonable and predictable result. By the same reasoning, it would seem, at first thought, that the steam-induced selectivity improvements would be limited to the situation where oxygen is co-fed with butane to the riser, or at least more pronounced than in the anaerobic case; and yet, just the opposite is observed. Examination of the CO/CO_2 production helps reconcile this apparent anomaly.

It is generally recognized that CO_x by-products can be produced during the oxidation of butane by both series and parallel paths, as indicated schematically below. Non-selective products can be the result of the direct oxidation of butane or the subsequent oxidation of previously formed maleic anhydride. The latter, or series-path, generally results in CO/CO_2 ratios <1 while the former, or parallel-path oxidation, exhibits CO/CO_2 ratios of 1 or slightly higher [7].



One can imagine steam, leading to an improvement in maleic-anhydride selectivity in one of at least two different ways:

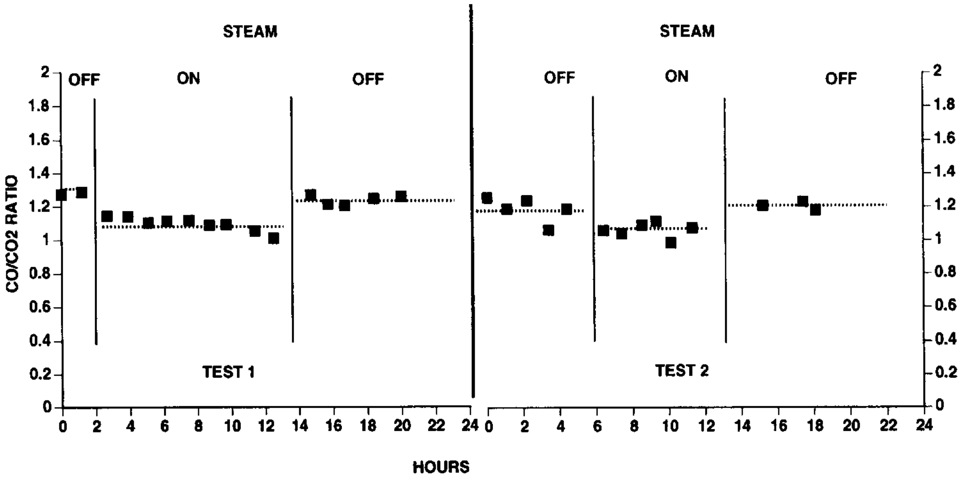


Fig. 9. The effect of steam fed to the riser on the CO/CO_2 ratio of the oxidation product. No gas-phase oxygen has been fed to the riser. Dotted lines represent mean values.

1. Steam may aid the desorption of maleic anhydride from the VPO surface and thereby prevent its further decomposition, as suggested by Lerou and Mills [3]. It is likely that this mechanism is operative in both the aerobic and the anaerobic cases.
2. Steam may be effective in stripping non-selective, low binding-energy oxygen species from the VPO surface.

With regard to the second mechanism, it has been suggested in several theoretical and experimental studies [7,8] that there are a series of equilibria established between oxygen in the gas-phase and various adsorbed oxygen species on the VPO catalyst surface, as indicated below:

$$O_2 \leftrightarrow O_{2(ads)} \leftrightarrow O^-_{2(ads)^*} \leftrightarrow 2O^-_{(ads)^*} \rightarrow 2O^{2-}_{(lattice)}$$

As the equilibria are shifted to the right, the oxygen species are gradually enriched with electrons by interaction with the substrate until conversion to lattice oxygen is ultimately achieved. The partially reduced, low binding oxygen species (denoted by the asterisks, in the equation) are thought to be highly active and non-selective [7,8] and, thereby, quite effective in promoting the parallel oxidation path.

The decrease in the CO/CO_2 ratio with steam, observed under anaerobic conditions, suggests that the parallel oxidation path is preferentially suppressed. The explanation that we offer for this behavior is that the adsorbed oxygen species, including the very non-selective, low binding ones are stripped from the VPO surface as the catalyst exits the regenerator and enters the riser. With no gas-phase oxygen present in the riser, the reservoir from which additional non-selective, low binding-energy oxygen species are generated is effectively removed. This result is consistent with previously published experimental data, suggesting that the non-selective oxygen species react rapidly with butane to produce mostly CO [7]. Previous studies [9] have shown that the effects of butane conversion over VPO on selectivity to maleic anhydride in the 10–50% conversion range are minimal. Therefore, the observations noted in this study with regard to selectivity can be confidently attributed to the influence of steam.

We believe that the ability of the recirculating bed reactor to separate the hydrocarbon oxidation and catalyst re-oxidation steps makes it a particularly valuable tool for developing a more detailed understanding of butane-oxidation chemistry and other selective-oxidation chemistries as well.

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