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Borate-assisted liquid-phase selective oxidation of *n*-pentane

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ABSTRACT

Oxidation of *n*-pentane with molecular oxygen to *sec*-pentanols was performed in the presence of a free radical initiator (di-*tert*-butyl peroxide) and a boron compound (*sec*-butyl metaborate), with *in situ* adsorption of water on molecular sieve 3 A. Kinetics of the reaction was studied in a laboratory-scale batch reactor over a broad range of conditions (130–150 °C, 20–30 bar, 5–10 vol% O_2) in order to establish the optimum parameters for maximising the selectivity and yield of *sec*-pentanols. Results show that the initiator markedly improves the rate of oxidation, and hence yield, compared to thermal oxidation without an initiator, while the boron species enhances the selectivity to *sec*-pentanols. Under the conditions investigated, maximum *sec*-pentanol selectivity is 56% with an alcohol-to-ketone ratio of 3.6:1 for the borate-assisted oxidation compared to 33% and 1.1:1, respectively, for the oxidation without borate. This work demonstrates the feasibility of oxyfunctionalization of *n*-pentane with industrially relevant selectivity and yield.

1. Introduction

Light paraffins, such as C_4 and C_5 alkanes, are abundant hydrocarbon resources that are key components of liquefied petroleum gas (LPG) and naphtha. In recent times, stricter government regulations have been introduced to minimise the evaporative emission of volatile organic compounds from motor vehicles as well as upstream and midstream gasoline vapour emissions from distribution and storage systems, which cause air pollution problems, including high ground-level ozone or smog. One approach that has been adopted is the control of Reid Vapour Pressure (RVP), which is a measure of gasoline volatility. New environmental regulations impose strict specifications on refiners for the level of light hydrocarbons which can be present in gasoline blends to meet emission targets. The drive towards low-RVP and high-octane fuels has increased the availability of C_4 and C_5 alkanes, consequently, there is considerable interest from the petrochemical industry in novel processes for the upgrading and conversion of these low-cost hydrocarbon feedstocks into chemicals of higher commercial value.

Developments in catalysis and process design has led to industrial-scale exploitation of *n*-butane for the production of maleic anhydride and acetic acid through catalytic gas-phase and liquid-phase selective oxidations, respectively [1,2]. *n*-Pentane, on the other hand, has so far not witnessed the same level of large-scale oxyfunctionalization application. Currently, *n*-pentane is mostly processed by steam cracking at high temperatures to make olefins by dehydrogenation [3]. A significant disadvantage of this process is that it is highly endothermic, requiring temperatures in the range of 500–800 °C to drive the reactions towards olefins, and is therefore very energy intensive. There are a few reported routes for the transformation of *n*-pentane *via* oxidation, as shown in Scheme 1. These include oxidative dehydrogenation to 1- and 2-pentenes [4], and selective oxidation to a mixture of phthalic and maleic anhydrides [5,6]. These two processes are gas-phase heterogeneous catalytic oxidation reactions, which take place at 350–500 °C. A third option is the direct oxidation of *n*-pentane in the liquid phase with molecular oxygen at temperatures in the range of 100–150 °C, with or without a catalyst, into oxygenated products, such as alcohols and ketones. Despite the potential economic value of these approaches, there are currently no practical industrial applications of any of these routes for the conversion of *n*-pentane.

The liquid-phase oxidation of *n*-pentane to alcohols and ketones is a significant challenge. One of the main issues with the activation of *n*-pentane, like other light alkanes, is its low reactivity [7]. Small chain alkanes are considerably more difficult to oxidise than longer-chain alkanes as shown by the rate of oxygen uptake in Table 1. Reactivity increases with decreasing C–H bond strength as chain length increases [1,8]. As a result of its relatively low reactivity compared to higher alkanes, the oxidation of *n*-pentane under typical conditions of liquid-phase reactions gives conversion that is too low for commercial exploitation.

A second issue is that the process is typically limited by poor selectivity to alcohols. Selectivity is challenging for two reasons. Liquid-

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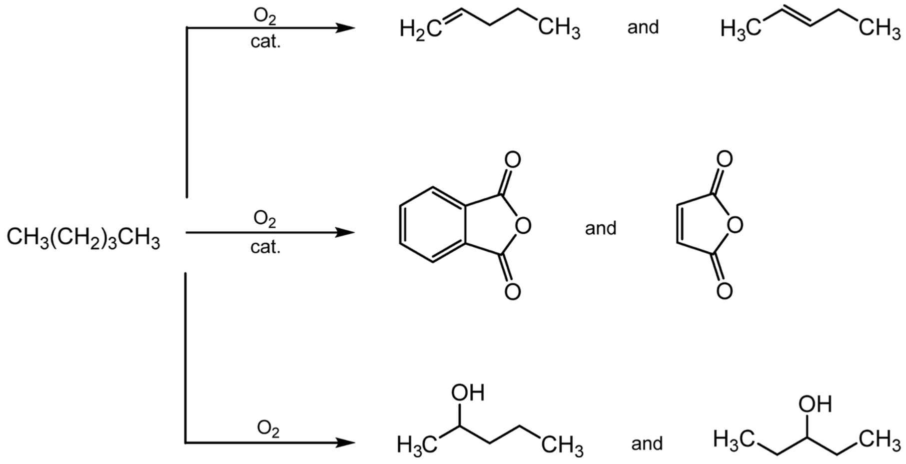
Nomenclature

C	Concentration (mol%, vol%, mol L^{-1})
DTBP	Di-*tert*-butyl peroxide
ΔH_r^o	Standard enthalpy of reaction (kJ mol^{-1})
LOC	Limiting oxygen concentration (vol%)
P	Total pressure (bar)
PeO	Pentanones
RH	Alkane
ROOH	Alkyl hydroperoxide
S	Selectivity (%)
s-BuMB	*sec*-Butyl metaborate
s-PeOH	*sec*-Pentanol
T	Temperature (°C)
T*i*PrB	Triisopropyl borate
Y	Yield (%)



Scheme 1. Potential routes for the conversion of *n*-pentane to petrochemicals.

phase oxidations are free radical reactions, which are indiscriminate, with oxidative attack on all reactive C—H groups in the alkane molecule. Consequently, for alkanes with more than four carbon atoms such as *n*-pentane, a complex mixture of oxygenated products is formed, including hydroperoxides, alcohols, ketones, carboxylic acids, and esters with all possible isomers. Furthermore, the desired alcohols are more reactive than the starting alkane, and are thus more readily over-oxidised into ketones and acids. Hence, the oxidation process offers little control over alcohol selectivity [9,10].

A number of studies have been published in the literature on the liquid-phase oxidation of *n*-pentane, largely involving the application of transition metal-based homogeneous and heterogeneous catalysts [12–15]. Despite these attempts, however, none of the reported studies has attained pentane conversion and selectivity to alcohols that are high enough for industrial exploitation. It is evident, therefore, that the direct oxidation of *n*-pentane to alcohols with high selectivity and yield continues to be a challenge.

There are a number of strategies for enhancing the selectivity of partial oxidation reactions [16]. One concept that has been reported for improving alcohol selectivity in alkane oxidations is the Bashkirov process, which involves the use of boron compounds such as boric acid, boric oxide and borate esters [17–19]. These boron species function as Lewis acids which direct the oxidation towards the formation of alcohols, and subsequently trap the alcohols in the form of borate esters to protect them from over-oxidation [20–24]. This idea formed the basis of several industrial-scale processes for the oxidation of cyclohexane to cyclohexanol/cyclohexanone, used as intermediate for the production of nylon-6, oxidation of cyclododecane to cyclododecanol/cyclododecanone used as intermediates for nylon-12, as well as the oxidation of C_{10} – C_{20} alkanes for the synthesis of higher aliphatic alcohols used in the manufacture of detergents and surfactants [20,25,26]. The borate-assisted oxidation process allows higher selectivity to be achieved at relatively high feed conversions compared to typical autoxidations, which are normally carried out at low conversions in order to keep selectivity at an acceptable level. For example, during cyclohexane oxidation in the presence of boric acid, conversion of 10–15% can be achieved with a combined alcohol and ketone selectivity of 90% and alcohol to ketone ratio of up to 10:1. In the absence of boric acid, the combined selectivity to cyclohexanol and cyclohexanone is 60–70% with alcohol-to-ketone ratio of 1:1 and 4–5% conversion [17,21].

Table 1
Relative oxidation rates of different linear alkanes [1,11].

n-Alkane	Relative oxidation rate $\left(\text{oxidation rate}=\frac{\text{mol } O_2}{(\text{mol alkane})\times\text{time}}\right)$
Ethane	0.001
Propane	0.1
Butane	0.5
Pentane	1.0
Hexane	7.5
Octane	200
Decane	1380

Although borate-assisted alkane oxidation was performed commercially for high boiling alkanes, this concept has so far not been successfully applied to light alkanes such as *n*-pentane. One of the main constraints is removal of the water formed under reaction conditions, given the high susceptibility of borate esters to hydrolysis in the presence of moisture. Thus, to achieve high selectivity there is a need for effective removal of water from the reaction zone under elevated pressure [27–29]. A second issue is the fact that the low reactivity of light alkanes coupled with the inhibiting action of boron on the oxidation through a reduction in the concentration of free radicals, may result in a substantially lower yield of products.

In this study, we addressed the issue of low reactivity of alkanes and removal of water in the successful attempt to develop a process for selective oxidation of *n*-pentane.

2. Mechanism of liquid-phase oxidation of *n*-pentane

The liquid-phase oxidation of hydrocarbons is a free radical reaction