Oxidative dehydrogenation of $n$-octane using vanadium pentoxide-supported hydroxyapatite catalysts

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A B S T R A C T

Vanadium pentoxide, with loadings varying from 2.5 to 15 wt%, was supported on hydroxyapatite (HAp) by the wet impregnation technique. The materials were characterised by techniques such as X-ray diffraction (XRD), inductively coupled plasma-optical emission spectroscopy (ICP-OES), BET, FTIR, SEM, transmission electron microscopy (TEM), temperature programmed reduction (TPR) and temperature programmed desorption (TPD). From XRD and IR analyses, vanadium is found in the vanadium pentoxide phase for the lower loadings, whereas for weight loadings in excess of 10%, an additional pyrovanadate phase exists. Electron microscopy provides evidence of a homogenous distribution of the vanadium species on the hydroxyapatite. Oxidative dehydrogenation reactions carried out in a continuous flow fixed bed reactor showed that selectivity towards desired products was dependent on the vanadium concentration and the phase composition of the catalyst. Good selectivity towards octenes was achieved using the 2.5 wt% V$_2$O$_5$ on HAp loaded catalyst. There was a marked decrease in octene selectivity and a significant increase in the formation of C$_8$ aromatics when higher loadings of vanadium were used. At a conversion of 24% at 450°C, the 15 wt% V$_2$O$_5$ on HAp showed a selectivity of 72% towards octenes. A maximum selectivity of 10% for C$_8$ aromatics was obtained using the 15 wt% V$_2$O$_5$ on HAp catalyst at a conversion of 36% at 550°C.

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1. Introduction

Alkenes are important raw materials in a wide range of applications in the petrochemical industry due to their low cost and ability to be functionalised easily. However, it has been envisaged that the future of the petrochemical industry leans towards the direct use of alkenes as starting material, since they are a much more economical raw material and can be easily sourced from petroleum by-products [1]. For over sixty years and until recently, most of the commercial production of alkenes was through the dehydrogenation of alkanes in the absence of oxygen. These reactions are endothermic and operate at temperatures ranging from 450 to 550°C, but low conversions due to limitations associated with the thermodynamic equilibrium are obtained [2]. Also, alkene selectivity is low and carbon deposition on the active sites of the catalyst is favoured. The introduction of oxygen renders the reaction exothermic, eliminates most limitations imposed by thermodynamics and reduces carbon deposits on the catalyst [3–5]. As a result, oxidative dehydrogenation (ODH) of alkanes is now preferred and plays a growing role in the petrochemical industry [6–8].

Catalytic performance relies on the acid–base properties of the material or the isolated cations capable of activating C–H bonds [9–12], therefore the use of supports with acid–base characteristics is advantageous. Hydroxyapatite (HAp) as support offers high stability and various substitutions are allowed by the apatite structure [13,14]. Hydroxyapatite has the general formula, [Ca$_{10-x}$(PO$_4$)$_6$(OH)$_{2-x}$]$_2$OH, 0 ≤ x ≤ 1. Stoichiometric HAp has x = 0 to give Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, whereas the calcium deficient non-stoichiometric hydroxyapatite has 0 ≤ x ≤ 1 [15]. Various transition metal cations, which have potential as catalytic active centres, can be readily accommodated into the apatite framework based on the large cation exchange ability of HAp [16–19]. The OH group within the phosphate frame-work leads to the formation of active oxygen species which are essential for ODH reactions [20].

Among the transition metal oxide catalysts, the supported vanadium oxides find a variety of applications in heterogeneous catalytic oxidation reactions [21,22]. Indeed vanadium serves as an important component in oxidation catalysts for both chemical and biochemical systems [23–25]. The utility of vanadium stems from the facile inter-conversion of the vanadium ion among its higher oxidation states and the ability to activate molecular oxygen [26]. The abstraction of two hydrogens from the alkane is possible by the presence of an acid–base pair, the V$^+$ cation (Lewis acid centre) and the oxygen-associated O$^{2-}$ anion (basic centre). Acidity is essential, however strong acidity favours the successive formation