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

Venkata D.B.C. Dasireddy, Sooboo Singh, Holger B. Friedrich*

School of Chemistry, University of KwaZulu-Natal, Durban 4000, South Africa

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ABSTRACT

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_2O_5 on HAp loaded catalyst. There was a marked decrease in octene selectivity and a significant increase in the formation of C8 aromatics when higher loadings of vanadium were used. At a conversion of 24% at 450 °C, the 15 wt% V_2O_5 on HAp showed a selectivity of 72% towards octenes. A maximum selectivity of 10% for C8 aromatics was obtained using the 15 wt% V_2O_5 on HAp catalyst at a conversion of 36% at 550 °C.

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 alkanes 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, $[Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}]$, $0 \leq x \leq 1$. Stoichiometric HAp has $x = 0$ to give $Ca_{10}(PO_4)_6(OH)_2$, whereas the calcium deficient non-stoichiometric hydroxyapatite has $0 \leq x \leq 1$ [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^{5+} cation (Lewis acid centre) and the oxygen-associated O^{2-} anion (basic centre). Acidity is essential, however strong acidity favours the successive formation

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* Corresponding author. Tel.: +27 31 2603107; fax: +27 31 260 3091.
E-mail address: friedric@ukzn.ac.za (H.B. Friedrich).

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of oxygenated products. In most oxidation reactions, the catalysts consist of the vanadium oxide phase which is highly dispersed on the surface of the support, as shown by Matralis et al. [27] who observed that V_2O_5 supported on TiO_2 was more active than the bulk or crystalline V_2O_5. The analysis of structure activity relationships indicates that various species, characterised by different reactivities, exist on the surface of these catalysts. There is some evidence that catalysts with vanadium species having a tetrahedral geometry are efficient for alkane oxidative dehydrogenation. There have been very few reports on the oxidative dehydrogenation of *n*-octane. These are over V–Mg–Al hydrotalcites [28], tantalum and niobium substituted hydrotalcites [29,30], and VMgO catalysts [31,32]. The effectiveness of vanadium [33–35] and hydroxyapatite [2,36] in the ODH of lower paraffins has stimulated our interest, leading to the study of the ODH of the higher paraffin, *n*-octane.

2. Experimental

2.1. Synthesis of catalysts

All the chemicals used in the preparation of the catalysts were purchased from Merck KGa, Darmstadt, Germany (99%). Hydroxyapatite was prepared using the method of Yasukawa et al. [14]. In a typical method for the preparation of HAp, aqueous NH_3 (Merck, 32%) was added to a 60 mL solution of $Ca(NO_3)_2{\cdot}4H_2O$ (6.67×10^{-2} mol) to elevate the pH to 11. The solution was then diluted to 120 mL with distilled water. A 100 mL solution of $(NH_4)_2HPO_4$ (4.00×10^{-2} mol) was also adjusted to pH 11 with the adding of aqueous NH_3 and diluted to 160 mL. The phosphate solution was added to the calcium solution drop wise over a period of 30 min at room temperature. A gelatinous precipitate formed which was stirred and boiled for 10 min. After filtration, the precipitate was washed thoroughly with distilled water and dried in an oven set at 100 °C overnight, thereafter calcined at 550 °C. Bulk V_2O_5 was prepared by the thermal decomposition of NH_4VO_3 at 450 °C for 6 h in air. The loading of 2.5, 5.0, 7.5, 10.0 and 15.0 wt% vanadia on the hydroxyapatite support, which are noted as 2.5% V-HAp, 5% V-HAp, 7.5% V-HAp, 10% V-HAp and 15% V-HAp was performed by wet impregnation. The desired amounts of V_2O_5 were suspended in 20 mL of distilled water and added to the calcium hydroxyapatite support. The water was removed by evaporation with constant stirring. The solid was dried overnight at 110 °C and later calcined at 550 °C for 6 h.

2.2. Characterization of catalysts

BET surface areas were determined using a Micrometrics Gemini 2360 multi-point BET surface area analyser. Prior to analysis, the powdered samples (~0.05 g) were degassed overnight at 200 °C using a Micromeritics FlowPrep 060 instrument.

2.2.1. Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

Inductively coupled plasma (ICP) was performed using a PerkinElmer Optical Emission Spectrometer Optima 5300 DV to determine the elemental composition of the materials. Standards (500 ppm Ca, V and P) were purchased from Fluka.

2.2.2. X-ray diffraction (XRD)

The phases of the catalysts were observed using powder X-ray diffraction conducted on a Bruker D8 Advance instrument, equipped with an Anton Paar XRK 900 reaction chamber, a TCU 750 temperature control unit and a Cu radiation source with a wavelength of 1.5406 λ. The crystallinity of the powder was estimated from the XRD data using the following equation:

$$X_c = 1 - \left(\frac{V_{112/300}}{I_{300}}\right)$$

where X_c is the degree of crystallinity, $V_{112/300}$ is the intensity of the shoulder between the (1 1 2) and (3 0 0) diffraction peaks and I_{300} is the intensity of the (3 0 0) peak [37]. The crystallite size of the powder was evaluated from the peak broadening of XRD patterns based on Scherrer's formula given as follows:

$$X_s = \frac{0.9\lambda}{\text{FWHM}\cos\theta}$$

where X_s is the crystallite size (nm), λ is the wavelength of the monochromatic X-ray beam ($\lambda = 0.15406$ nm for CuKα radiation), FWHM is the full width at half-maximum for the diffraction peak under consideration (radians) and θ is the diffraction angle (degrees).

2.2.3. Infrared spectroscopy

IR spectra were obtained using a PerkinElmer Precisely using a Universal ATR sampling accessory equipped with a diamond crystal at a pressure of 120 Gauge.

2.2.4. Temperature programmed techniques

Ammonia temperature programmed desorption (TPD) and temperature programmed reduction (TPR) were carried out using a Micromeritics 2920 Autochem II Chemisorption Analyser. Prior to the reduction of the sample in TPR, the catalyst was pretreated by heating under a stream of argon (30 mL/min) at 400 °C for 30 min and then cooled to 80 °C. Thereafter, 5% hydrogen in argon was used as a reducing agent at a flow rate of 30 mL/min. Samples were analysed from room temperature to 950 °C using a ramp rate of 20 °C/min under static air. In the TPD experiments, the catalyst was pretreated at 350 °C under the stream of helium for 60 min. The temperature was then decreased to 80 °C. A mixture of 4.1% ammonia in helium was passed over the catalyst at a flow rate of 30 mL/min for 60 min. The excess ammonia was removed by purging with helium for 30 min. The temperature was then raised gradually to 950 °C by ramping at 10 °C/min under the flow of helium and desorption data was recorded.

2.2.5. Scanning electron microscopy-energy dispersive X-ray (SEM-EDX)

The surface morphology of the catalysts was observed using a Leo 1450 Scanning Electron Microscope. Prior to SEM analysis, the samples were mounted on aluminium stubs using double-sided carbon tape and subsequently gold spluttered using the Polaron E5100 coating unit.

2.2.6. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) images were viewed using a Jeol JEM-1010 Electron Microscope and selected area electron diffraction (SAED) patterns for the catalyst samples were viewed in the adjusted diffraction mode of the JEM-1010 Electron Microscope. The images were captured and analysed using iTEM software.

2.3. Catalytic testing

Gas phase oxidation reactions were carried out in a continuous flow fixed bed reactor in down flow mode. A tubular stainless steel reactor tube with 10 mm internal diameter and 300 mm length was used to pack the catalyst. The catalyst bed (1 mL) was located at the centre of the reactor with 24-grit carborundum packed in