

Mechanisms of Gas-Phase Oxidative Dehydrogenation of n-Octane

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The oxidative dehydrogenation (ODH) of alkanes, whereby hydrogen is removed to form unsaturated compounds, is an important process, particularly in the petrochemical industry. The ODH of lighter alkanes (C3–C6) is well-reported in the literature, and there are several reports on the ODH of *n*-octane (C8).

Keywords: n-octane ; oxidative dehydrogenation ; metal oxides ; oxidants

1. Introduction

1.1. Importance of Alkane Activation and Associated Products

C-H bond activation has been studied for decades with particular attention to the selective transformation of inert carbon–hydrogen bonds into other useful functional groups more recently. The conversion of long-chain and medium-chain alkanes to value-added products is an important reaction both industrially and scientifically, as the low octane number *n*-alkanes get converted into the high octane number alkenes, dienes, and aromatics ^{[1][2]}. Over the span of many years, research has shown that there is an increased demand for alkenes, aromatic compounds and functionalized alkanes, which can be derived from alkanes as feedstock. Alkenes constitute highly adaptable intermediates for the manufacture of many value-added chemicals ^[3]. Medium-chain olefins are majorly used in the synthesis of alcohols or aldehydes, the production of copolymers with short-chain olefins and the production of synthetic lubricants ^{[4][5]}. With regards to aromatics, despite the growing interest in biofuels, especially renewable hydrocarbon, the current process for hydrocarbon production still lacks a step for producing aromatics. Aromatics are important as they increase the octane rating in bio-gasoline and give solvent characteristics in the fuel ^[6]. These compounds are also useful in the improvement of the anti-knock index in petroleum fuels. **Table 1** summarizes the main uses of alkenes obtained from the oxidation of long- and medium-chain alkanes ^[7].

Table 1. Main uses of alkenes ^[7].

Ethene	Polymers (PE), ethylene oxide, vinyl acetate, vinyl chloride, styrene
Propene	Propene polymers (PP), propene oxide, acetone, butanal, plasticizer alcohols, acrylonitrile, epichlorohydrin synthesis
1-Butene	Butene polymers, solvents
Butadiene	Polymers, oligomers, adiponitrile, sulfolane, chloroprene, vinylcyclohexene, cyclododecatriene
1-Hexene	Co-monomer in PE
1-Heptene	Reagent and solvent in organic synthesis
1-Octene	Co-monomer in PE

C10-C14	Detergent alcohols
C14-C16	Sulfates and sulfonates in detergents

1.2. Conversion of Intermediate Chain Alkanes

Linear alpha olefins/1-alkenes were initially produced from paraffinic wax using thermal cracking. This process gave a large proportion of 1-alkenes as the primary products, together with alkanes [8]. Products such as detergent alcohols could be produced subsequently via the hydro formylation of mixtures of 1-alkenes and internal alkenes. C4–C8 linear alpha olefins are majorly used for producing linear aldehydes via oxosynthesis for the later production of fatty acids. This is achieved via oxidation of the intermediate aldehydes, or linear alcohols for plasticizer applications [9][10]. Industrially, alkenes are produced following dehydrogenation (cracking) of alkanes at extremely high temperatures (500–900 °C), which results in high energy consumption. However, the dehydrogenation of alkanes to olefins and hydrogen is an endothermic process limited by the thermodynamic equilibrium. There are basically two undesirable features of the dehydrogenation reaction, viz., high energy consumption and the breaking of the equilibrium while the equilibrium limitation is also broken [11]. As such, researchers have shown an interest in the conversion of alkanes using various oxidants. These reactions have shown higher conversion and low carbon deposition with a lower energy demand than the non-oxidative route [12]. While the dehydrogenation of short-chain (C2–C4) and long-chain paraffins (C10–C14) has been studied vastly, there are very limited studies on the conversion of *n*-paraffins with intermediate chain length (C6–C9) to linear olefins.

2. Oxidants

Despite molecular oxygen being the most studied oxidant in the oxidative dehydrogenation of alkanes, there are other oxidants such as CO₂, bromine, sulphur, N₂O and iodine and their compounds. These oxidants offer the advantage of high selectivity for dehydrogenation. However, halogen and sulfur gases are corrosive and are a potential environmental concern, which has deterred their commercialization [13]. N₂O and CO₂ are regarded as unconventional oxidants (as opposed to molecular oxygen). However, due to the different nature of the oxygen species they generate and their lower oxidizing power, they are used to evade the selectivity issue encountered when molecular oxygen is used [14]. Nonetheless, for the oxidative dehydrogenation of *n*-octane, the use of oxidants is mainly limited to molecular oxygen and CO₂.

2.1. Molecular Oxygen

The oxidative dehydrogenation route to activating alkanes provides the advantage of low environmental impact and a relatively low cost of raw materials. Using molecular O₂ in the reaction allows for oxidative dehydrogenation over properly selected catalysts, which can produce oxygenated compounds [15]. In the case of molecular oxygen as an oxidant, it has been demonstrated that many metal oxides have different abilities to activate O₂, and the metal oxide's tendency to activate O₂ depends on its ability to chemisorb O₂ [16][17]. The various properties that determine the ability of metal oxide catalysts to activate oxygen include the rate and extent of reduction, the electronic properties and the surface acidity, bandgap energy of the metal oxides and O₂ activation.

Fadlalla and Friedrich studied the oxidative dehydrogenation of *n*-octane using cobalt molybdate catalysts under varying oxygen ratios. The results indicated that under dehydrogenation conditions, the catalyst demonstrated low *n*-octane conversion, which resulted in the complete segregation of the catalyst. Additionally, the introduction of oxygen showed a notable improvement in the conversion and also the selectivity to aromatics. Different C-to-O₂ ratios gave different selectivity profiles. The best carbon-to-oxygen ratio for octenes was an 8:1 C:O ratio, while for aromatics it was 8:3 [18].

2.2. Carbon Dioxide

Carbon dioxide can be used as a soft oxidant in the ODH of alkanes (CO₂-ODH). The use of CO₂ is regarded as beneficial since it can be re-used and meet the demand for olefins [19]. Using CO₂ as an oxidant is a greener alternative to the traditional dehydrogenation process [20][21][22][23]. The use of CO₂ can also be regarded as an attractive route when it comes to CO₂ mitigation via carbon capture and use [24]. Various authors have used different materials to activate CO₂ and, in some cases, indicated the role CO₂ played as an oxidant. In a study conducted by Adam et al., the role of CO₂ as an oxidant was investigated during the dehydrogenation of *n*-octane using Cr-Fe catalysts. The CO₂-ROR and EPR

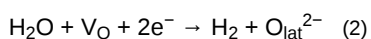
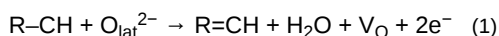
results demonstrated that CO₂ performed an oxidative role over the Cr monometallic catalyst. Adam et al. used a reaction mechanism to illustrate that the predominant mechanism over the Cr catalyst used is via the CO₂-ODH [22].

Moloi et al. [21] investigated the CO₂-assisted activation of *n*-octane over VO_x supported on anatase catalysts that showed superior interaction with CO₂ by dissociating it. This was followed by lattice oxygen replenishment by the oxygen reduced. During CO₂ dissociation, the oxygen produced may replenish lattice oxygen, which may then react with hydrogen via the reverse water gas shift reaction. Additionally, a combustion of carbon deposits may occur via the reverse Boudouard reaction. Another study conducted by Farahani et al. where mesoporous 2D NiO–Nb₂O₅–Al₂O₃ and template-free ordered mesoporous alumina were used in a CO₂-assisted dehydrogenation of an *n*-octane reaction gave more insights about the role of CO₂ in the reaction. The results obtained showed that adding Nb₂O₅ to the NiO catalyst facilitates CO₂-DH via the promotion of the RWGS and reverse Boudouard reactions. This was consistent with the findings of Moloi et al., even though the two studies employed different catalytic systems. Despite the limited use of this oxidant in the dehydrogenation of *n*-octane, previous studies on shorter chain alkanes, such as butane, and theoretical studies have demonstrated that CO₂ has a kinetic barrier, and its activation energy is higher than that of O₂ and N₂O [25][26]. An important factor to consider in the ODH of alkanes is the mechanism that describes the kinetics of the reactions, their positions and limitations.

3. Mechanisms of Alkane Oxidation

3.1. Mars and Van Krevelen

This mechanism was developed by Mars and Van Krevelen when they investigated naphthalene oxidation [27]. It was developed for oxidation reactions where the catalysts are based on transition metal oxides which are able change their oxidation states easily [28]. The mechanism is reported by Hosono et al. [29] to occur via the following reactions:



In the above reactions, O_{lat}²⁻ and V_O represent the lattice oxygens and oxygen vacancies, respectively.

3.2. Langmuir–Hinshelwood and Eley–Rideal

The Langmuir–Hinshelwood (LH) mechanism finds applications in reactions where organic substrates undergo oxidation on the catalyst surface in the presence of oxygen [30]. The mechanism assists in explaining the kinetics between two adsorbed species and assumes that the energy of interaction between the adsorbent and adsorbate is constant as the coverage increases. On the other hand, in the Eley–Rideal (ER) mechanism, one of the species is adsorbed on the catalyst surface, and the other species reacts with the chemisorbed species in the gas phase [31]. The Eley–Rideal mechanism is not as common as the Langmuir–Hinshelwood mechanism, and the majority of surface-catalyzed reactions are said to follow the latter mechanism.

It is, however, important to note that the mechanisms depend on the catalysts used.

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