

# Propylene Synthesis

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Propylene is one of the most important feedstocks in the chemical industry, as it is used in the production of widely diffused materials such as polypropylene. Conventionally, propylene is obtained by cracking petroleum-derived naphtha and is a by-product of ethylene production. To ensure adequate propylene production, an alternative is needed, and propane dehydrogenation is considered the most interesting process.

Keywords: propane dehydrogenation ; propylene ; platinum ; catalysis

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## 1. Introduction

Propylene <sup>[1]</sup> is the feedstock of strategic materials such as acrolein, polypropylene, acetone, polyacrylonitrile, propylene oxide and other industrial products <sup>[2]</sup>. The conventional propylene production industrial processes are the fluid catalytic cracking and the naphtha and light diesel steam cracking <sup>[3]</sup>. The fast consumption of fossil fuels is making conventional propylene production methods unsuitable to meet the growing demand for propylene; therefore, the development of more efficient and economical production methods is a major concern <sup>[4]</sup>. Innovative methods to produce propylene have been proposed, including the propane dehydrogenation (PDH), the methanol–olefin process and the Fischer–Tropsch olefin process <sup>[2]</sup>. The development of shale gas <sup>[5]</sup> extraction methods has generated an abundance of light alkanes, therefore making propane dehydrogenation the best candidate for replacing conventional propylene production processes <sup>[6]</sup>. Several catalysts and propane dehydrogenation processes have been developed, whose representatives are UOP Oleflex, Lummus Catofin, Linde–BASF PDH, Uhde STA and Snamprogetti–Yarsintez FBD <sup>[2]</sup>. Currently, Lummus Catofin <sup>[7]</sup> and UOP Oleflex <sup>[8]</sup> are mainly used in industrialized devices. The Catofin process uses chromium/aluminum-based catalysts, which show good performance, assuring good stability and high propylene yield and resulting in a propylene selectivity higher than 87% <sup>[2]</sup>. However, this process has low efficiency due to frequent switching to high-temperature conditions <sup>[2]</sup>; moreover, chromium is not considered an environmentally friendly catalyst. The Oleflex process uses platinum/aluminum-based catalysts, and the hydrogen produced together with propylene can be used as fuel in the unit; furthermore, the dehydrogenation unit can be integrated with downstream conversion processes <sup>[2]</sup>. At the moment, therefore, processes using platinum-based catalysts can provide the highest propylene selectivity, high reaction rate and stability and can be considered more eco-friendly than chromium-based ones.

## 2. The Reaction

Propane dehydrogenation is an equilibrium endothermic reaction (1). The thermodynamic analysis shows that the equilibrium conversion drops exponentially with pressure, so a reduction in hydrocarbon partial pressure can be beneficial to increase the conversion <sup>[9]</sup>. To reduce the hydrocarbon partial pressure, steam or other inert gases can be used to dilute the reacting mixture; steam is preferred to compensate for the conversion decrease, but an increase in reaction temperature is necessary <sup>[9]</sup>. Therefore, to obtain high propane conversions, high operating temperatures (800–950 K) are required.



The reaction conditions therefore result in an increase in side reactions such as thermal cracking, deep dehydrogenation, coke formation and the sintering of the supported nanoparticles, limiting the average life of the catalyst <sup>[6]</sup>. To overcome the catalyst deactivation, it is therefore mandatory to employ a periodic regeneration through oxidative cycles to eliminate the coke, followed by reduction; moreover, oxygen–chlorine treatment can be carried out to partially redisperse agglomerated Pt particles <sup>[10]</sup>.

The side reactions are attributed to the persistence of propylene on the active site; therefore, the geometric and the electronic features of the catalysts play a crucial role in the suppressing of them <sup>[2]</sup>.

Moreover, the propylene formation rate and the selectivity–conversion relationships for propylene and coke formation depend on the kind of supported metal, on the loading, on the size of supported metal nanoparticles, on the presence of promoters and on the reaction temperature [11].

### 3. Polymetallic and Promoted Catalysts

Pt-Sn is one of the most promising catalytic systems, the performance of which is strongly dependent on its structure. Sn can promote the separation of multifold Pt sites and donate electrons to Pt; comparative studies between Pt/Al<sub>2</sub>O<sub>3</sub> and PtSn/Al<sub>2</sub>O<sub>3</sub> highlight, in the case of bimetallic catalyst, a significantly higher propylene selectivity and only traces of cracking products [12]. In fact, the multifold Pt (111) sites are more active towards the breaking of C–C bonds than the PtSn (102).

The Pt-Co catalysts show much higher propylene selectivity than the monometallic Pt or Co in the PDH reaction [13]. The turnover rates of Pt in the bimetallic catalysts are similar to monometallic Pt, thus suggesting that the active sites are the resulting alloys. The Co acts as a nonactive promoter, and thus the high selectivity of Pt<sub>3</sub>Co can be attributed to geometric effects, due to the presence of smaller Pt–Pt ensembles, and to the decrease in the energy of the Pt 5d orbitals compared to monometallic Pt.

Spatially resolved kinetic data were acquired during PDH over GaPt/SiO<sub>2</sub> SCALMS [14]. The results showed an enhanced deactivation of the catalyst at the end of the bed, with the deactivation front moving from the end to the beginning of the catalyst bed over the time on stream, probably due to the enhanced coking of the catalyst under high conversion.

Lanthanum was used to improve the performance of PtSn/γ-Al<sub>2</sub>O<sub>3</sub> catalyst; the parent catalyst was impregnated with different amounts of lanthanum salt precursor to obtain a loading of 0, 1.2, 2.2 or 3.2 wt% [15]. La can improve both propane conversion and propylene selectivity, and the best performance was obtained with a loading of 2.2 wt%.

### 4. Catalyst Regeneration and Coke Combustion Kinetics

An efficient regeneration is essential to carry out a PDH process, and a continuous process by the regenerator is essential to perform an efficient process. Regeneration is typically achieved by periodic coke burning to realize sustainable operation; thus, the coke combustion is a crucial aspect in the management of a propylene production plant by propane dehydrogenation.

The exact composition of the coke is, to date, the subject of study. It has been suggested that the coke formed on PtSn-based catalysts in PDH reaction mainly consists of three kinds of species: aliphatics, aromatics and pregraphite, with the aliphatic one constituting most of the deposit, with the C/H ratio of around 1.5 [16]. Raman studies on exhausted Pt-Sn/SBA-16 catalysts have shown an increase in coke crystal size from 60 to 180 min on stream and from 180 to 300 min under reaction [17]. These results are consistent with the so-called “coke migration phenomenon”, attributed to the coke movement near the particle to the support, or to the sintering of the metallic particle.

The cofeeding of hydrogen decreases the coke formation rate and increases the stability of the catalyst by removing the precursor of coke, while the cofeeding of water decreases the coke formation while increasing the activity by decreasing the apparent activation energy of propane conversion [16].

Coke burning may result in extensive active metal sintering, so alternative regeneration processes have also been proposed, which make use of ozone, hydrogen and oxychlorination. Optimal conversion recovery has been obtained by treatment of Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts, with 35% HCl, after coke burning [18]. HCl treatment seems to play a similar role as oxychlorination in redispersing the Pt particles and generating the Pt<sub>3</sub>Sn alloy.

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