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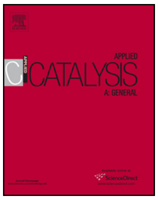

Propane dehydrogenation kinetics on supported Pt catalyst

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ABSTRACT

A kinetic model of propane dehydrogenation on a Pt,Sn/Mg(Al)O is presented, accounting for product distribution due to main and side reactions, for deactivation rates and for diffusion resistance. Parameters were estimated from steady state experiments at varying pressure and from temperature-programmed experiments, and are compared with previous models on similar catalysts and with published computed results. Steam was added to slow coke formation, leading to some steam reforming. The rate of deactivation was shown to correlate with carbon build up on the surface, which was determined from the selectivity to carbon.

Application of the model to design a Pd-membrane reactor suggests that pressure should be kept below 5 bar and steam around 10% in feed, while pellet size affects mainly the selectivity while the effect on conversion is small. While the main reaction is fast, side reactions are not negligible, especially under conditions of a membrane reactor, but selectivity to propane can be maintained about 95%.

1. Introduction

Light alkenes (olefins), which are among the most important intermediate products in chemical industry, are currently commonly obtained by steam cracking (SC) [1] and fluid catalytic cracking (FCC) [2] of light oil fractions. For example, most propylene is produced as co-product in steam crackers (> 55%) and as by-product in FCC units (~35%), while only small fraction (< 10%) is produced by alternative technologies, such as propane dehydrogenation [3]. As both SC and FCC require high temperatures, coking and side reactions are among major drawbacks [4,5]. Catalytic dehydrogenation (DH) of light alkanes suffers from several common limitations: (i) Thermodynamic restrictions on conversion, which imply high temperatures to obtain reasonable conversions [6]; (ii) Strong endothermicity, which requires heat supply. (iii) Side reactions like thermal cracking, isomerization, which become important at high residence times [7,8]; (iv) Coke formation due to the high temperatures, which is still extremely fast (less than several hours in industrial applications [6,9] and about 1 h under conditions expected in membrane reactors [10,11]). As a result, catalytic reactors have to be regenerated often, to burn off the deposited carbon.

Successful implementation of membrane reactors has a potential of replacing the currently used periodically-regenerated fixed bed reactors. Continuous removal of hydrogen by membrane separation should increase the DH conversion for a given temperature and this in turn will allow to operate at lower temperatures, therefore reducing the coke formation and side reactions. On the other hand, using H_2 selective membrane may results in extremely low H_2 partial pressures in the reaction mixture, leading to even larger deactivation rates. Therefore, introduction of H_2 separation membranes into DH process should be supported by a detailed analysis and process optimization. That in turn requires a detailed model of reaction kinetics.

The purpose of this article is to present a detailed experimental program and a model of PDH activity, selectivity and stability on supported Pt catalysts, mainly for a design of membrane reactor for PDH. Results are compared with published PDH studies on similar Pt-based catalysts. PDH membrane reactors are characterized by several features: (i) Hydrogen removal from the process stream allows for operating at lower temperatures than those of regular catalytic reactors. (ii) In order to mitigate deactivation by coking we study the process at low temperatures, at relatively low pressures with some steam and all these effects should be studied. (iii) Membrane reactors should benefit from operating at higher pressure, since the separation driving force is larger and with hydrogen separation high pressure does not inhibit equilibrium; higher pressures, however, accelerates deactivation. (iv) Selectivity is poorer in a membrane reactor since the required contact times are larger.

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Table 1
Properties of the catalysts used in this work.

Catalyst	Manufacturer	Geometry	Dimensions	Used in sections:
A	SINTEF	Powder	Diameter: 180–355 μm	2. Kinetic model: pressure effect 3.1 Catalyst deactivation 4. Pellet diffusion effect
B	Johnson Matthey	Powder	Diameter: 180–355 μm	2. Reaction Kinetics: temperature effect 3.2 Coke coverage and effect on activity 4. Pellet diffusion effect
C		Cylindrical 2 mm	Diameter: 2.5 mm Length: 2.5 mm	4. Pellet diffusion effect
D		Cylindrical 5 mm	Diameter: 4.6 mm Length: 4.4 mm	

The rate expression of the main reaction

$$C_3H_8 \rightleftharpoons C_3H_6 + H_2 \Delta H^{\circ}_{298} = 124\frac{kJ}{mol} \quad (1)$$

is expressed by a driving force for the reaction, that is the distance from equilibrium, and an inhibition due to competitive adsorption. Literature studies differ in the identity of the adsorbed of species that inhibit the catalytic active sites [12–14]. (Table 2, Section 3.1). Propylene and hydrogen are often included as inhibitors. Propylene is an obvious inhibitor, and it also acts the precursor for coking.The main reaction is accompanied by cracking to methane and ethylene with possible hydrogenation of the latter.

$$C_3H_8 \rightleftharpoons C_2H_4 + CH_4 \quad (2)$$

Cracking kinetics was modeled on several works, some presented in Table 3, Section 3.2. As the gas-phase C—C bond is weaker then C—H bond (about 246 kJ/molmol^{-1} compared to about 363 kJ/molmol^{-1}) dehydrogenation cannot be performed thermally due strong thermal cracking. With an appropriate catalyst, such as platinum and chromia, this can be overcome and good selectivity can be achieved. Note that the catalytic cracking has a higher activation energy than the main reaction implying that selectivity will diminish with higher temperatures. Note also that although the rate constant of cracking at working conditions is 3 orders of magnitude smaller than that of main reaction, the main reaction is limited by equilibrium and at high residence times, as is the situation in an integrated membrane reactor, the selectivity to cracking becomes significant. All cited works agreed on cracking being first order w.r.t. propane.

Some of the ethylene produced can be hydrogenated

$$C_2H_4 + H_2 \rightleftharpoons C_2H_6 \quad (3)$$

Most PDH models do not include ethylene hydrogenation kinetics as its effect is expected to be negligible. The reason for this is that the ethylene reactant for this reaction is produced only by cracking which, being an undesired side reaction by itself, is mitigated by catalytic formulation and reactor operation conditions. The relatively higher activation energy can also be a factor. A kinetic expression was suggested [12].

Steam will be used in the catalytic PDH process both as a diluent as well as a coke regenerator, being able to gasify coke into CO without significantly effecting the overall reaction and design [15].The suppressive effect of steam on coke formation over Pt catalysts was reported in several works [16]. However, adding steam to the PDH process may lead to steam reforming (SR) of propane and propylene

$$\begin{aligned} &C_3H_8 + 3H_2O \leftrightarrow 3CO + 7H_2 \\ &C_3H_6 + 3H_2O \leftrightarrow 3CO + 6H_2 \end{aligned} \quad (4)$$

along with water-gas shift of the products,

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

Propane steam reforming was reported to occur on several metals used for industrial hydrogen production such as platinum, rhodium, ruthenium, and more [17,18]. The reaction mechanism is likely to involve both the active metal sites, which provide the hydrocarbon dissociative chemisorption, and the support (usually Al_2O_3 or CeO_2), which provides sites for water activation into hydroxyl groups. Even though the support used in the catalysts studied here is aluminum-containing MgO, or Mg(Al)O, which is a novel material and as such is not yet tested in this aspect, the presence of both Pt as the active metal and Mg/Al oxide as the support was suspected to enable steam reforming.

Rate expressions of C_3H_8/C_3H_6 steam reforming seem to be scarce in the literature, and none were found to include distinction between steam reforming of propane to that of propylene and of the effect of side reactions of steam reforming such as water-gas shift and additional SR of side products such as methane. An example for SR kinetics which distinguish between CO and CO_2 products of SR was suggested by Barghi et al. [16].

The kinetics of propane dehydrogenation and cracking over PtSn catalyst was a topic for first principle calculations [19]. Increasing Sn content in the catalyst leads to weaker bonding of propyl and propylene to the catalyst; it lowers also the energy barrier for propylene desorption, from −0.97 eV on Pt(111) to −0.50 on Pt_3Sn (hence improving selectivity) and simultaneously increases the barrier for propylene dehydrogenation. This also leads to lower coking rates. The energy barrier for C—C bond cleavage was predicted to vary from 1.6 eV for Pt(1 1 1) to 2.02 for Pt_3Sn. The reaction involves two steps, propane to propyl and propyl to propene, having similar activation energies on Pt(1 1 1) (−0.70 eV), implying that the latter is rate determining step. Adsorption energies of propane were predicted to be weak, in the rage −0.02 to −0.08 eV (~ -2 to -8 kJ/molmol^{-1}e), while those of propene were predicted to be −0.42 to −0.61 on Pt_3Sn or Pt_2Sn compared with −0.99 on Pt(1 1 1).

1.1. *Catalyst deactivation*

Catalyst deactivation tends to be very fast on the industrial catalytic PDH process, requiring very frequent regeneration cycles, usually in a cycle of several hours [20,21]. High operation temperatures increases the rate of the cracking side reaction, which lead to lower selectivity toward propylene and to catalyst deactivation due to fast coke formation on the catalyst surface. Sintering, is naturally also encouraged. Regeneration is usually performed by oxidation in air. The need for regeneration cycles leads to higher process complexity and operation costs.

Pt catalysts, which are commonly used for PDH process, are well known to undergo rapid deactivation [22]. Addition of promoters such as Sn and K, which selectively weaken the Pt-propylene interaction without affecting Pt-propane interaction, thus lowering selectivity to coking, inhibit the coking rate. Two kinds of coke were identified in an experimental TPO study of coke formation on Pt-Sn/Al_2O_3 during propane hydrogenation [23], and were attributed to coke on the metal and coke on the support. The former, which is relevant to this study, is weakly dependent on propene and hydrogen pressure but increasing with propane pressure. The