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## Research Article

# Study of the Effects of External and Internal Diffusion on the Propane Dehydrogenation Reaction over Pt-Sn/Al<sub>2</sub>O<sub>3</sub> Catalyst

<sup>1</sup> National Petrochemical Company, Research & Technology, Tehran, Iran.

<sup>2</sup> Chemical Engineering Faculty, Tehran University, Tehran, Iran.

In the study of a reaction on a heterogeneous catalyst, external and internal mass diffusion play an important role since they can have an inherent affect on the kinetics of the reaction. Therefore, in the study of intrinsic rates of reaction, the effects of external and internal mass diffusion must be eliminated or considered prior to proper kinetic studies. In this study, the effects of external and internal mass diffusion on the propane dehydrogenation reaction over a Pt/Sn catalyst were investigated. Some experiments were performed in a laboratory scale setup and the required data was gathered. The rate of reaction was considered to be first order based on propane. External diffusion was studied using Mears' criterion and internal diffusion was investigated by the Thiele Module and the Internal Effectiveness Factor, based on experimental data.

**Keywords:** Catalysis, Dehydrogenation, Diffusion, Kinetics

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## 1 Introduction

Alkenes, with the general formula C<sub>n</sub>H<sub>2n</sub>, are a group of chemical materials with widespread usage in petrochemical industries. Propylene is an important intermediate material for the production of polymers and chemicals. Steam cracking and Fluidized Catalytic Cracking (FCC) are two traditional methods for the indirect production of light alkenes which can produce a wide range of products in a nonselective manner. Due to the huge demand for light alkenes, plants based on cracking processes cannot supply enough alkenes to meet these requirements. Therefore, other direct production methods, especially catalytic dehydrogenations, have been considered since the 1980's because of their ability to selectively produce alkenes and the availability and low price of the raw materials involved (saturated hydrocarbons such as propane) [1, 2].

Catalysts, based on Pt/Sn, are used for the dehydrogenation of alkanes and exhibit a high selectivity and stability in the dehydrogenation of paraffins to olefins [3–5]. In this study, the effects of internal and external mass diffusion on the catalytic dehydrogenation of propane over a commercial Pt/Sn based catalyst are investigated.

## 2 Theory

The effects of internal and external mass diffusion on the reaction rate of heterogeneous catalytic reactions are very important. The reactants have to diffuse from the bulk of the fluid to the surface of the catalyst pellet, and subsequently, from the surface to the internal parts of the pellet. These two resistances play a major role in the transfer rate of reactants to heterogeneous catalysts, and therefore, in the study of intrinsic rates of reaction, the effects of internal and external mass diffusion have to be eliminated. Otherwise, the rate of reaction will be incorrect and contains the effects of mass transfer parameters.

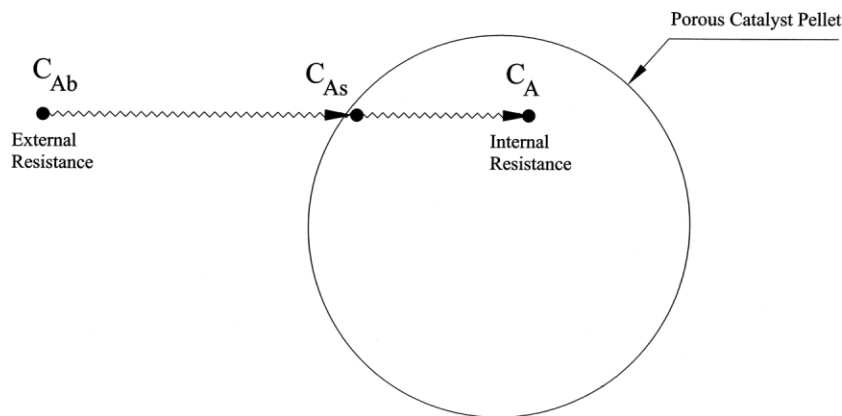
In this study, the effects of these resistances were investigated for propane dehydrogenation over a commercial Pt/Sn based catalyst.

### 2.1 External Mass Diffusion to the Surface of the Catalyst

At steady-state conditions, the diffusion rate of reactants from the bulk of the fluid to the catalyst external surface is equal to the consumption rate of reactants, both within and on the pellet, Fig. 1. In order to find the intrinsic rate of reaction, the external diffusion resistance has to be investigated, and if present, it has to be eliminated.

For this investigation, Mears [6] proposed a criterion, as follows: Mears' criterion, C<sub>m</sub>, is the ratio of the rate of reaction to the external diffusion rate. If this criterion is less than 0.15,

**Correspondence:** M. Mohagheghi (m.mohagheghi@npc-rt.ir), National Petrochemical Company, Research & Technology, Tehran, Iran.



**Figure 1.** Mass transfer and reaction steps for a catalyst pellet.

the external diffusion resistance is low and can be neglected, Eq. (1)<sup>1)</sup>:

$$C_m = \frac{-r'_A \rho_b R n}{k_c C_{Ab}} \ll 0.15 \quad (1)$$

where  $r'_A$  = reaction rate per unit mass of catalyst (kmol/kg s),  $n$  = reaction order,  $R$  = catalyst particle radius (m),  $\rho_b$  = bulk density of the catalyst bed (kg/m<sup>3</sup>),  $\rho_b = (1 - \varepsilon) \rho_c$ ,  $\varepsilon$  = catalyst bed porosity,  $\rho_c$  = catalyst density,  $C_{Ab}$  = bulk concentration (kmol/m<sup>3</sup>), and  $k_c$  = mass transfer coefficient (m/s).

## 2.2 Internal Mass Diffusion in the Catalyst

At steady-state conditions, the following relations can be obtained by performing a mass balance on species A, as shown in Fig. 2. In these relations, the positive direction of mass transfer is considered to be outward from the catalyst pellet [6].

- Inlet molar flow rate of A at  $r$  is  $[4\pi r^2 N_A]_r$
- Outlet molar flow rate of A at  $r + \Delta r$  is  $[4\pi r^2 N_A]_{r + \Delta r}$
- Rate of consumption of A in the element with a thickness of  $\Delta r$  is  $r'_A \rho_c 4\pi r_m^2 \Delta r$

A combination of these relationships yields the following equations, Eqs. (2) and (3):

$$[4\pi r^2 N_A]_r - [4\pi r^2 N_A]_{r + \Delta r} + r'_A \rho_c 4\pi r_m^2 \Delta r = 0 \quad (2)$$

$$\frac{d(N_A r^2)}{dr} - r'_A \rho_c r^2 = 0 \quad (3)$$

The molar flow rate of A by molecular diffusion inside the catalyst pellet is given by Eq. (4):

$$N_A = -D_e \frac{dC}{dr} \quad (4)$$

where  $D_e$  = effective diffusivity (m<sup>2</sup>/s), and is obtained from the following relation, Eq. (5):

$$D_e = \frac{D_{AB} \phi_p \sigma}{\xi} \quad (5)$$

where  $D_{AB}$  = the bulk or Kundsens diffusivity of A in B,  $\phi_p$  = pellet porosity = (Volume of void space/total volume (voids and solids)),  $\sigma$  = construction factor, and  $\xi$  = tortuosity = (actual distance a molecule travels between two points/shortest distance between those two points).

Based on values for  $\phi_p$ ,  $\xi$  and  $\sigma$  proposed in [6], the following approximate values for these parameters are used in this study:  $\phi_p = 0.4$ ,  $\xi = 3.0$  and  $\sigma = 0.8$ . For investigation of internal mass diffusion effects inside the catalyst pellet, further proposed relations are used in this study [6].

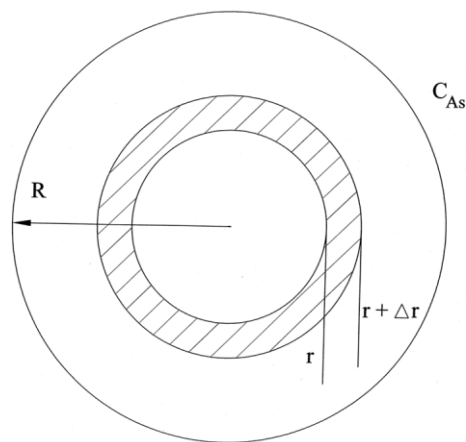
The Thiele module,  $\Phi_n$ , is the ratio of reaction rate to diffusion rate inside the catalyst pellet and is calculated by the following relations, Eq. (6):

Thiele modulus for  $n^{\text{th}}$  order reaction :

$$\Phi_n = \frac{\text{a surface reaction rate}}{\text{a diffusion rate}} \quad \text{and} \quad \Phi_n^2 = \frac{k C_{As}^{n-1} \rho_c S_a R^2}{D_e} \quad (6)$$

where

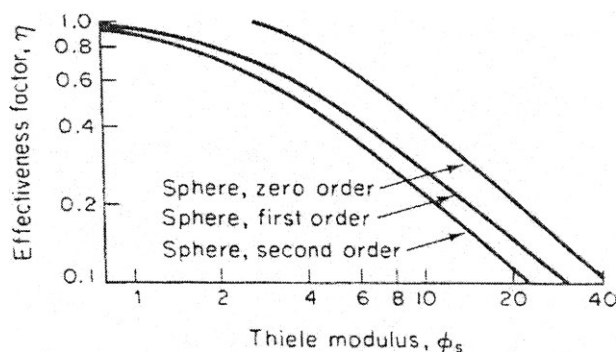
$k'$  = rate constant  $\left(\frac{\text{mol}}{\text{m}^3}\right)^{(1-n)} \left(\frac{\text{m}}{\text{s}}\right)$ ,  $C_{As}$  = concentration of A at the catalyst surface (mol/m<sup>3</sup>),  $\rho_c$  = catalyst density (kg/m<sup>3</sup>),  $S_a$  = catalyst surface area (m<sup>2</sup>/kg catalyst),  $R$  = radius of catalyst particle (m), and  $D_e$  = effective diffusivity (m<sup>2</sup>/s). In the case of high values of the Thiele module, Eq. (6) represents the situation where mass diffusion is the rate limiting step and in the case of low values of the Thiele module, the reaction on the catalyst surface is the rate limiting step. In addition, the internal effectiveness factor,  $\eta$ , which is a criterion for the importance of internal mass diffusion resistance, can be used in this regard.  $\eta$  is calculated by the following relation:



**Figure 2.** Shell balance on a catalyst pellet.

1) List of symbols at the end of the paper.

$$\eta = \frac{\text{actual overall rate of reaction}}{\text{rate of reaction that would result if entire interior surface were exposed to the external pellet surface conditions } C_{As}, T_s}$$



**Figure 3.** Variation of  $\eta$  with Thiele module for a spherical shaped catalyst.

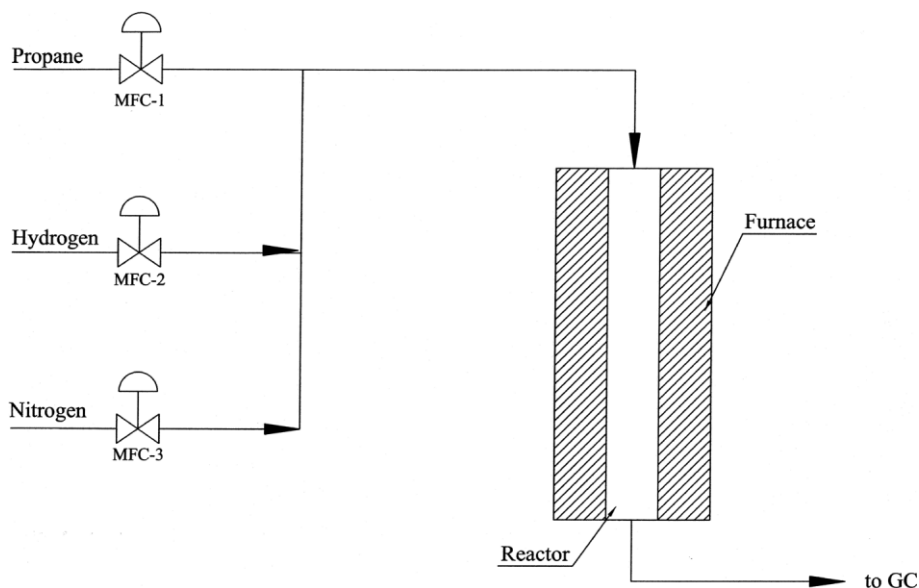
$\eta$  is a function of the reaction order and catalyst shape. For a first order reaction on a spherical catalyst,  $\eta$  is obtained by Eq. (7):

$$\eta = \frac{3}{\Phi_1^2} (\Phi_1 \coth \Phi_1 - 1) \quad (7)$$

Fig. 3, represents the variation of  $\eta$  with  $\Phi$  and also, the relationship of these two parameters with the rate limiting step [6]. When  $\eta \rightarrow 1$ , the internal mass diffusion inside the catalyst pellet has no resistance and the reaction on the catalyst surface is the rate limiting step, i.e. surface reaction limited. In contrast, when  $\eta \rightarrow 0$ , internal mass diffusion inside the catalyst pellet is the rate limiting step, i.e., internal diffusion limited.

### 3 Experimental and Results

The laboratory scale setup used for undertaking the propane dehydrogenation experiments is shown in Fig. 4. The inside diameter of the reactor in this setup is 12 mm and 3 g of catalyst was loaded in the reactor. The specification of the catalyst studied, is shown in Tab. 1. In these experiments, mixtures of propane and hydrogen with a molar ratio of 0.7 and different flow rates were passed over the catalyst bed at 630 °C and atmospheric pressure. The outlet stream of the reactor was analyzed online by gas chromatography (model PERICHROM 2100, Packed column, SS316, 6 m, 1/8 in, 28 % DC200 on Chromsorb PAW 60/80, ENRO 3015) and the conversion of propane was calculated for each



**Figure 4.** Sketch of propane dehydrogenation setup.

**Table 1.** Specification of propane dehydrogenation catalyst.

2 mm	Diameter
0.65 g/cm <sup>3</sup>	Bulk Density, ( $\rho_b$ )
1.12 g/cm <sup>3</sup>	Catalyst Density, ( $\rho_c$ )
200 m <sup>2</sup> /g	Catalyst Surface Area, ( $S_a$ )

**Table 2.** Results of experiments.

$X_A$	$\frac{W}{F_{A0}} \left( \frac{\text{kg s}}{\text{mol}} \right)$	Run
0.59	237.6	1
0.55	168.1	2

experiment. The results of these experiments are shown in Tab. 2.

It can be shown that the reaction rate equations suggested in reference [7] (it should be noted that these equations were acquired based on some supposed mechanisms) convert to Eq. (8), at high temperatures and low pressures:

$$-r_A = k' \left[ P_{C_3H_8} - \frac{P_{C_3H_6} P_{H_2}}{K_{eq}} \right] \quad (8)$$

The elimination of the adsorption terms in the denominator of above mentioned rate equations is due to the decrease of surface coverage on the surface catalyst at high temperatures and low pressures. In addition, the rate equation, Eq. (8) can be written as follows:

$$-r_A = k'P_{C_3H_8}\gamma \quad (9)$$

where

$$\gamma = 1 - \frac{P_{C_3H_8}P_{H_2}}{K_{eq}P_{C_3H_8}} \quad (10)$$

In the above rate equation,  $\gamma$  is a criterion of the proximity level of the reaction to thermodynamic equilibrium.  $\gamma$  varies from 0–1 ( $0 < \gamma < 1$ ), and at  $\gamma = 0$ , the reaction is at thermodynamic equilibrium and the reaction rate is zero. As  $\gamma \rightarrow 1$ , the reaction rate increases, and therefore, according to Eqs. (6) and (7), in case of external mass transfer, the Thiele module will increase and  $\eta$  will decrease. In the case of internal mass transfer, Mears' criterion will increase. Therefore, if in case of  $\gamma = 1$ , the mass transfer resistance is negligible, certainly the mass transfer resistance will be negligible when  $\gamma < 1$ . Therefore, in this study  $\gamma$  is assumed to be unity, although in the experiments performed, the conversion of the reaction is approximately equal to the equilibrium conversion and  $\gamma$  actually still has a small value.

### 3.1 Study on External Mass Transfer

In order to determine the external mass transfer effects, the calculation of  $k_c$  and  $D_{AB}$  (the diffusion coefficient of propane in hydrogen) is required, based on Mears' criterion. The Wilke-Lee equation [8] is used for the calculation of  $D_{AB}$  and the equation presented in reference [9], is used for the calculation of  $k_c$ .

$$Re = \frac{uR}{3\psi\nu(1-\varepsilon)} \quad (11)$$

where  $u$  = superficial velocity (m/s),  $\nu$  = kinematic velocity ( $m^2/s$ ),  $\psi$  is a shape factor (0.91 for spherical particles), and:

$$Sh = 0.91\psi Re^{0.49} Sc^{0.33} = \frac{2k_c P_{B,M} R}{P_t D_{AB}} \quad (12)$$

The results of the calculations are detailed in Tab. 3.  $C_m$  was calculated at the outlet concentration of propane, which is the worst case scenario for  $C_m$ , as shown in Eq. (1). According to Tab. 3, Mears' criterion is smaller than 0.15.

**Table 3.** Calculation results for external mass transfer effects.

0.84	Re
0.0106 m/s	$k_c$
0.0017 mol/kg s	$-r'_A$
0.00029 $m^2/s$	$D_{AB}$
0.0108	$C_m$

### 3.2 Study on Internal Mass Transfer

The Thiele module for a first order reaction on spherical shape catalysts is as follows, Eq. (13):

$$\Phi_1 = R \sqrt{\frac{k' C_{As} \rho_c S_a}{D_e C_{As}}} \quad (13)$$

In addition,  $\eta$  is calculated from Eq. (7) and the results of the calculations are presented in Tab. 4. Due to negligible external mass transfer resistance, one can suppose that  $C_{As} = C_{Ab}$  in internal mass transfer calculations.

**Table 4.** Calculation results for internal mass transfer effects.

$D_e$	$C_{As}$	$\Phi_1$	$\eta$
0.00003 $m^2/s$	9.9 mol/ $m^3$	0.017	0.9999

## 4 Discussion

In this study, the effects of external and internal mass diffusion were investigated for the propane dehydrogenation reaction over a Pt/Sn catalyst. The value of Mears' criterion shows the importance of external mass transfer resistance over a catalyst. If this criterion is smaller than 0.15, then the external mass transfer resistance will be negligible. With regard to the results for the Pt/Sn catalyst in propane dehydrogenation with  $C_m = 0.0108$ , the external mass transfer resistance is negligible at the operating conditions, i.e.,  $P = 1$  bar and  $T = 550$ – $630$  °C.

For the study of internal mass transfer effects, the Thiele module and  $\eta$  were studied. Small values of the Thiele module over a catalyst, i.e., internal mass transfer effects can be neglected. In addition, internal mass transfer effects can be studied by using the internal effectiveness factor,  $\eta$ . As  $\eta \rightarrow 1$ , the internal mass transfer resistance will be small. In this study, the value of  $\eta = 0.9999$  calculated, shows that the internal mass transfer resistance can be neglected. In general, according to the results for the Thiele module and  $\eta$ , the internal mass transfer resistance for the propane dehydrogenation reaction over Pt/Sn catalyst is negligible and its effect on the reaction kinetics can be eliminated.

The results presented in reference [10] for the propane dehydrogenation reaction over Pt/Sn catalyst show that the value of  $E/R'$  at  $600$  °C is equal to  $9550$  K. Since the variation of the reaction rate constant with temperature is in exponential function form and the variation of the diffusion coefficient is in power function form (exponent = 1.5), the calculations show that the Thiele module will increase with increasing temperature. The temperature range that is used in industry for the propane dehydrogenation reaction is  $550$ – $630$  °C. Therefore, since the reaction temperature in this study was  $630$  °C, it can be concluded that the internal mass transfer resistance is also negligible at lower temperatures, due to decreases in the Thiele module.

## Acknowledgement

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## Symbols used

$C_{Ab}$	[kmol/m <sup>3</sup> ]	bulk concentration for component A
$C_{As}$	[kmol/m <sup>3</sup> ]	surface concentration for component A
$C_m$	[–]	Mears' criterion
$D_e$	[m <sup>2</sup> /s]	effective diffusivity
$D_{AB}$	[m <sup>2</sup> /s]	bulk or Kundsens diffusivity of A in B
$E$	[J/mol]	activation energy
$F_{A0}$	[mol/s]	molar flow rate of component A
$k_c$	[m/s]	mass transfer coefficient
$k'$	[–]	rate constant
$K_{eq}$	[–]	equilibrium constant of reaction
$n$	[–]	reaction order
$N_A$	[–]	molar flow rate of component A by molecular diffusion
$P_i$	[Pa]	partial pressure of component $i$
$P_t$	[Pa]	total pressure
$R$	[m]	catalyst particle radius
$r'_A$	[kmol/kg s]	reaction rate per unit mass of catalyst
$r_A$	[kmol/m <sup>3</sup> s]	reaction rate per unit volume
$Re$	[–]	Reynolds number
$R'$	[J/mol K]	gas constant, (8.314 J/mol K)
$S_a$	[m <sup>2</sup> /kg of catalyst]	catalyst external surface area
$Sh$	[–]	Sherwood number
$Sc$	[–]	Schmidt number
$T$	[K]	temperature
$u$	[m/s]	superficial velocity

$W$	[kg]	mass of catalyst
$X_A$	[–]	conversion of component A
$\rho_b$	[kg/m <sup>3</sup> ]	bulk density of catalyst bed
$\rho_c$	[kg/m <sup>3</sup> ]	catalyst density
$\varepsilon$	[–]	catalyst bed porosity
$\phi_p$	[–]	pellet porosity
$\sigma$	[–]	construction factor
$\zeta$	[–]	tortuosity
$\Phi_n$	[–]	Thiele modulus for $n^{\text{th}}$ order reaction
$\eta$	[–]	internal effectiveness factor
$\gamma$	[–]	criterion for proximity level of reaction to thermodynamic equilibrium
$\nu$	[m <sup>2</sup> /s]	kinematic viscosity
$\psi$	[–]	shape factor

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