

Dehydrogenation of Propane to Propylene Over Pt-Sn/Al₂O₃ Catalysts: The influence of operating conditions on product selectivity

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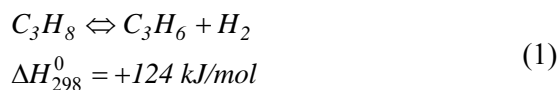
Abstract

The extent of side reactions in propane dehydrogenation over Pt-Sn/Al₂O₃ catalyst was studied. Catalytic test runs were carried out in a fixed-bed quartz reactor under different operating conditions. The results showed that the extent of side reactions strongly depends on the operating conditions. The product distribution implied that single C-C bond rupture in propane is the predominant route for break-down of propane to the lower hydrocarbons. A beneficial effect of coke formation on propylene selectivity was observed at the expense of propane conversion, which can be attributed to the dilution effect of carbonaceous deposits on platinum sites.

Keywords: Propane Dehydrogenation, Pt-Sn Catalyst, Product Selectivity, Hydrogenolysis, Cracking

1- Introduction

Propylene has been mostly produced as a by-product of refinery streams or steam crackers along with ethylene. However, due to the rapid growing demand, on-purpose production methods such propane dehydrogenation has received much attention [1].



The reaction is highly endothermic and high reaction temperatures are necessary to achieve high propane conversion. In the UOP Oleflex process, propane dehydrogenation is

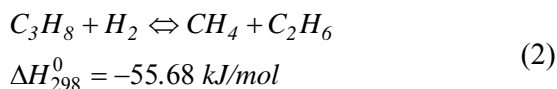
performed over a Pt-Sn/alumina catalyst in moving-bed reactors under nearly atmospheric pressure and temperatures of 580-650 °C.

Despite the simple chemistry, industrial implementation is very complicated due to side reactions such as deep dehydrogenation, hydrogenolysis, cracking, polymerization and coke formation. Side reactions impact the complexity of the process, operating costs and the purity of the products. The extent of side reactions can be controlled by catalyst formulation and operating conditions. The high reaction temperature required, for example, favors thermal cracking reactions to

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coke and light alkanes, leading to a decrease in product yield and an increase in catalyst deactivation [2]. This limits the upper bound of temperature in commercial practice.

Platinum is the primary component in many dehydrogenation catalysts due to its high activity for activating C-H bond, coupled with an inferior activity for the rupture of C-C bond, resulting in intrinsically high selectivities toward dehydrogenation. On a Pt surface, only low coordination number sites (steps, kinks) are able to catalyze the C-C bond breaking, while essentially all Pt sites catalyze the rupture of C-H bond [3, 4]. Therefore, the main side reaction over Pt is hydrogenolysis of propane, for example



At intermediate temperatures, hydrogenolysis activity can involve multiple C-C scissions initially, but the build-up of carbonaceous deposits deactivates such sites only leaving those able to support single C-C bond rupture

in propane [5]. Additionally, the acidity of the catalyst support promotes undesirable cracking and isomerization reactions [6,7].

Another undesired side reaction is coke formation. The major cause of catalyst deactivation in the dehydrogenation process is carbon deposition. Different technologies developed various methods to cope with this problem [8,9]. Some technologies utilize diluents such as steam or hydrogen to reduce coke formation.

Fig. 1 shows the thermodynamics of propane dehydrogenation and the associated side reactions. Higher temperatures favor the endothermic dehydrogenation, pyrolysis and cracking reactions, while the exothermic hydrogenolysis reaction is much less affected. One also observes that dehydrogenation reaction is energetically less favored compared to the competitive reactions. Consequently side reactions should be controlled kinetically, that is, by using appropriate catalysts and operating conditions.

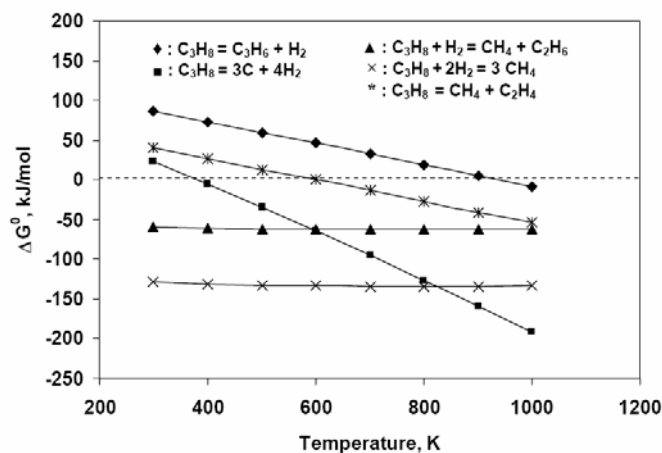


Figure 1. Thermodynamics of propane dehydrogenation reactions (free energy data from reference [10]).

In this work the effect of operating conditions on the selectivity of the platinum-based catalysts in dehydrogenation of propane is studied. The influence of time-on-stream on catalyst performance is also considered.

2- Experimental

The commercial Pt-Sn/Al₂O₃ catalyst sample was supplied by a European company.

The structure of catalyst support was characterized by XRD and BET techniques. X-ray diffraction (XRD) pattern of the support was obtained by a Philips Expert coupled with a copper anode tube with α_1 wavelength [Å]: 1.54056 and α_2 wavelength [Å]: 1.54439. The scanning rate was 0.02(°/s). The surface area and pore size distribution of the supports were measured by N₂ adsorption at -196 °C with a Micrometric ASAP 2010 N₂-adsorber. The elemental composition was determined by the ICP method.

The catalyst performance tests were carried

out in a fixed-bed quartz reactor (ID=15 mm) using a mixture of propane and hydrogen as the feed. For each run, 1.5 g of the catalyst was loaded. The reactor effluent was analyzed for light-hydrocarbons by an online gas chromatograph (Agilent 6890N), equipped with TCD and FID detectors. Propane conversion, and C₁-C₃ selectivities of the catalyst were calculated at different times. Depending on operating condition, the propane conversion was within the range of 25-40%. Ethane and ethylene selectivities were considered as measures of hydrogenolysis and cracking reactions, respectively.

According to operating conditions typical of commercial plants for propane dehydrogenation, temperature and space velocity were selected in the range of 580- 620 °C and 1.8-2.2 (h⁻¹) respectively. The as-received catalyst was reduced in an H₂ flow (80 ml/min) at 530 °C for 1 h in the reactor prior to feed injection. The schematic of the experimental set-up is depicted in Fig. 2.

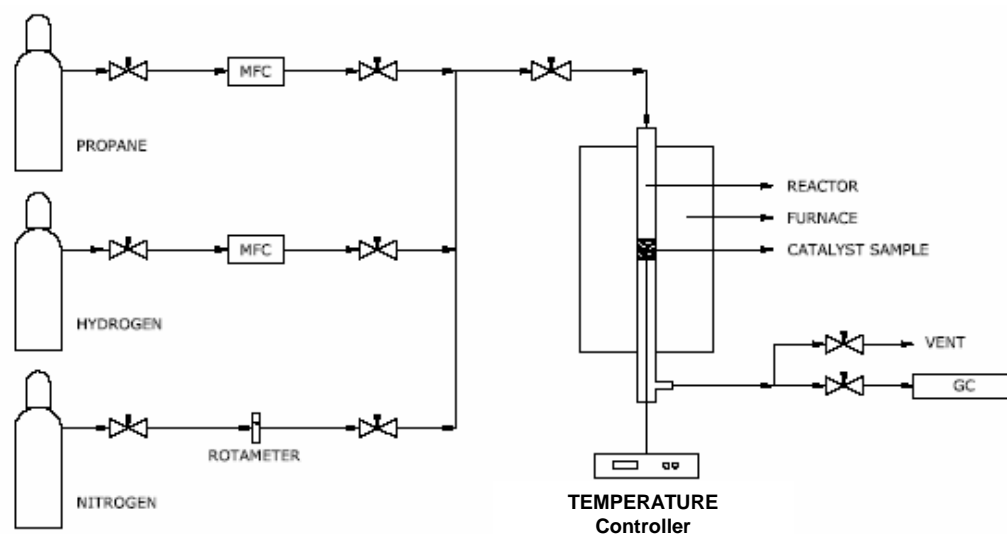


Figure 2. Schematic representation of the experimental set-up

3.-Results and discussion

3.1. Characterization results

The XRD results showed three maximum peaks at $2\theta = 35.53, 45.63, \text{ and } 66.49^\circ$ which are related to the $\gamma\text{-Al}_2\text{O}_3$ phase in the support. Elemental measurements showed a trimetallic formulation (Pt=0.5 wt%, Sn=0.7 wt%, and K=0.6 wt%) for the catalyst. The BET measurements showed a surface area of $196 \text{ m}^2/\text{g}$, which is typical of $\gamma\text{-Al}_2\text{O}_3$ phase (Table 1).

Table 1. Summary of textural test results.

Parameter	value
Surface area (m^2/g)	196
Average pore diameter (nm)	10.6
Total pore volume (m^3/g)	0.5

3.2- Performance test results

Fig. 3 shows the selectivity of $\text{C}_1\text{-C}_3$ hydrocarbons as a function of reaction

temperature. The selectivity of methane and C_2 hydrocarbons increases with temperature, while that of propylene decreases. This can be explained by the fact that the main routes to lower hydrocarbons are pyrolysis and cracking reactions. Higher temperatures favor these reactions kinetically, and cracking reaction thermodynamically as well. The latter can occur both catalytically on acidic sites and thermally in the gas phase. In practice this reaction is suppressed by neutralizing the acidic site through incorporation of alkali promoters in the catalyst formulation.

Fig. 4 shows the influence of hydrogen to the hydrocarbon ratio on the selectivity of products. The observed increase in hydrogenolysis selectivity is consistent with the stoichiometry of equation (2).

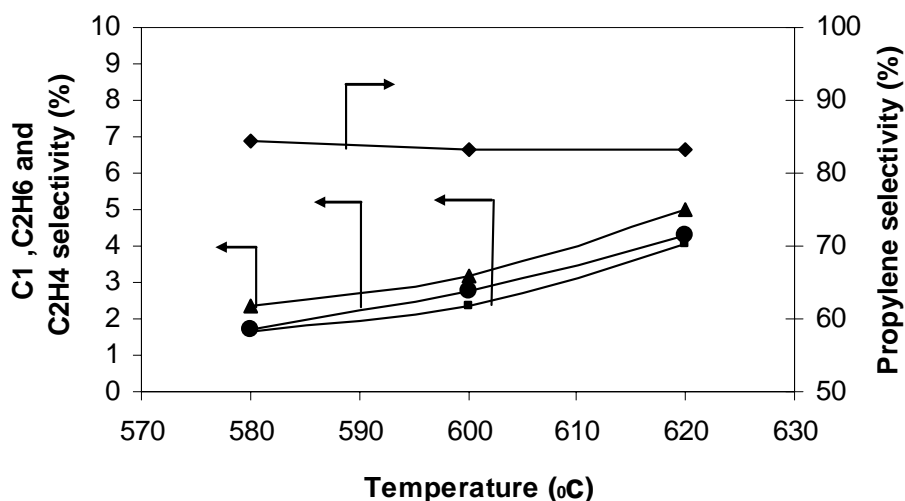


Figure 3. Influence of temperature on catalyst performance: (♦) propylene selectivity, (▲) C_1 selectivity, (■) C_2H_4 selectivity and (●) C_2H_6 selectivity (WHSV=2 h^{-1} , $\text{H}_2/\text{HC}=1$)

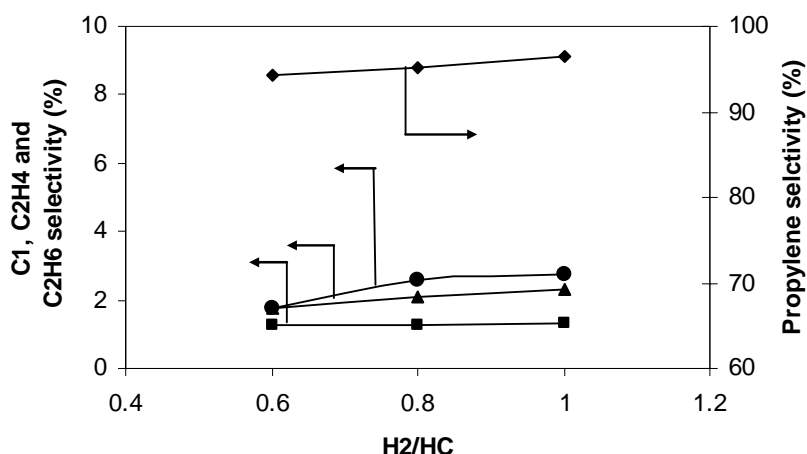


Figure 4. Influence of H₂/HC ratio on catalyst performance: (♦) propylene selectivity, (▲) C₁ selectivity, (■) C₂H₄ selectivity and (●) C₂H₆ selectivity (WHSV=2 h⁻¹ and T=600 °C).

Fig. 5 shows the effect of space-velocity on the selectivity of different products. The small decrease in propylene selectivity and the increase in hydrogenolysis products at higher space velocities might be attributed to the average higher propane concentration in the reactor at higher space velocities which

promote hydrogenolysis reaction from equation (2). The concentration of hydrogen is less strongly affected by conversion, and therefore space-velocity, as hydrogen is added to the feed in relatively high concentrations.

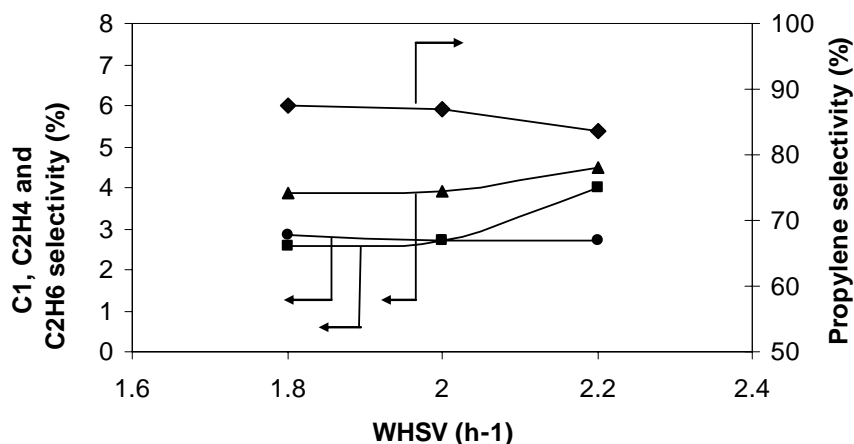


Figure 5. Effect of space velocity on: (♦) propylene selectivity, (●) C₂H₆ selectivity, (■) C₂H₄ selectivity and (▲) C₁ selectivity (when T=600°C; H₂/HC:1.0)

Fig. 6 shows the influence of time-on-stream on the selectivities in a long-term run. One observes the selectivities are rather constant with a small increase in the selectivity of propylene along with a small decrease in the selectivity of hydrogenolysis products with time. Since both hydrogenolysis and coke formation are more sensitive to the support structure than is dehydrogenation [3], any impurity or inactive species on the surface may act as a site diluent and should increase the selectivity toward dehydrogenation.

Finally, the fact that the selectivity to C₂ hydrocarbons is typically twice that of methane in most runs implies that the single C-C bond rupture in propane is the predominant route for production of lower hydrocarbons as by-products. Since multiple C-C scissions are thermodynamically more

favorable under reaction conditions, one concludes that the side reactions are controlled kinetically.

4- Conclusions

Operating conditions affect the selectivity of dehydrogenation and side reactions over platinum-based catalysts. Lower reaction temperatures and higher hydrogen to hydrocarbon ratios result in higher propylene selectivity at the expense of lower propane conversions. Similarly, longer times-on-stream result in higher propylene selectivity, which is due to the dilution effects of coke on platinum sites. Single C-C rupture is the main route for the conversion of propane to lower hydrocarbons under conditions typical of commercial operation.

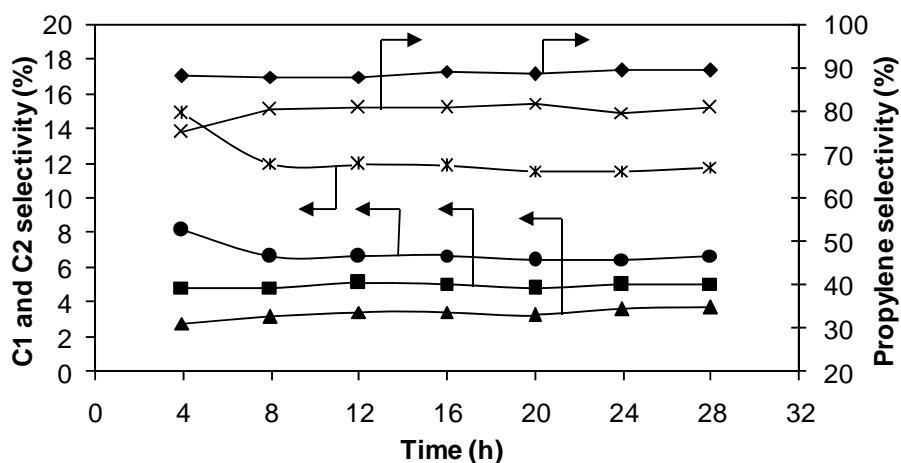


Figure 6. Results of catalyst stability tests: (◆) selectivity of propylene at $T=600\text{ }^{\circ}\text{C}$, (×) selectivity of propylene at $T=620\text{ }^{\circ}\text{C}$, (*) selectivity of C₂ at $T=620\text{ }^{\circ}\text{C}$, (●) selectivity of C₁ at $T=620\text{ }^{\circ}\text{C}$, (■) selectivity of C₂ at $T=600\text{ }^{\circ}\text{C}$, (▲) selectivity of C₁ at $T=600\text{ }^{\circ}\text{C}$ (WHSV=2 h⁻¹, H₂/HC=1).

5- Nomenclature

ΔH	enthalpy, kJ/mol
H ₂ /HC	molar ratio of hydrogen to hydrocarbons, mol/mol
T	temperature, °C
WHSV	weight hourly space velocity, h ⁻¹

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