



Kinetic study of propane dehydrogenation and side reactions over Pt–Sn/Al₂O₃ catalyst

Saeed Sahebdehfar, Maryam Takht Ravanchi*, Farnaz Tahriri Zangeneh, Shokoufeh Mehrmazma, Soheila Rajabi

Catalyst Research Group, Petrochemical Research and Technology Company, National Petrochemical Company, No. 27, Sarv Alley, Shirazi-south, Mollasadra, P.O. Box 14358-84711, Tehran, Iran

ABSTRACT

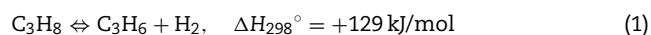
The kinetics of reactions involved in dehydrogenation of propane to propylene over Pt–Sn/Al₂O₃ catalyst was studied. The simultaneous deactivation of individual dehydrogenation, hydrogenolysis and cracking sites was also studied. A model was developed to obtain the transient conversion of propane, product selectivity and catalytic site activity. The dehydrogenation reaction was considered as the main reaction governing propane and hydrogen concentrations along the reactor. Catalytic test runs were performed in a fixed-bed quartz reactor. The kinetic expressions developed for the main and side reactions were verified by integral and a combination of integral–differential analysis of reactor data, respectively, and the kinetic parameters were obtained. The deactivation of the active sites for the three reactions was found to follow a first-order independent decay law. The rate constants of deactivation were found to decrease in the order of dehydrogenation, hydrogenolysis and cracking. Noncatalytic thermal cracking was found to be comparable to the catalytic route resulting in a very low apparent deactivation rate constant for cracking reaction.

© 2011 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

Keywords: Propane dehydrogenation; Pt–Sn catalysts; Cracking; Hydrogenolysis; Catalyst deactivation; Kinetics

1. Introduction

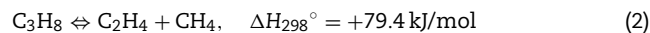
Propylene is an important feedstock for producing a variety of petrochemicals such as polypropylene, acrolein and acrylic acid. Due to ever-increasing demand and insufficient supply by crackers, alternative production methods such as propane dehydrogenation (PDH) has received attention (Heinritz-Adrian et al., 2008):



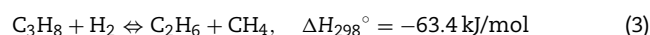
The reaction is highly endothermic and equilibrium-limited; therefore, higher temperatures and lower pressures are necessary to achieve acceptable conversions. Unfortunately, these conditions favor side reactions and accelerate catalyst deactivation as well.

In commercial practice both chromia (Arora, 2004; Miracca and Piovesan, 1999; Weckhuysen and Schoonheydt, 1999) and platinum (Bricker et al., 1990; Heinritz-Adrian et al., 2003; Pujado and Vora, 1990) based catalysts have been employed

for paraffin dehydrogenation. Platinum exhibits high catalytic activity in dehydrogenation of paraffins. To achieve high platinum dispersions, high-surface area supports are commonly used. Acidic sites on the support promote cracking (reaction (2)) and coke formation reactions. These sites are effectively neutralized by application of alkaline promoters (Bai et al., 2009; Bhasin et al., 2001; Padmavathi et al., 2005; Sanfilippo and Miracca, 2006; Yu et al., 2006; Zhang et al., 2006a)



Dehydrogenation virtually occurs on all platinum sites, while hydrogenolysis (reaction (3)) occurs on low coordination sites (steps and kinks) (Resasco, 2003)



In commercial catalysts, Sn is used as promoter to suppress hydrogenolysis reaction through reduction of surface Pt ensemble size by dividing Pt surface to smaller ensembles

* Corresponding author. Tel.: +98 21 44580100; fax: +98 21 44580505.

E-mail addresses: m.ravanchi@npc-rt.ir, maryamravanchi@gmail.com (M.T. Ravanchi).

Received 15 April 2011; Received in revised form 20 October 2011; Accepted 4 November 2011

0263-8762/\$ – see front matter © 2011 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

doi:10.1016/j.cherd.2011.11.004