



# Kinetics and reactor modeling of a Pd-Ag/Al<sub>2</sub>O<sub>3</sub> catalyst during selective hydrogenation of ethyne

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## ABSTRACT

The selective hydrogenation of ethyne is one process to remove traces of ethyne from steam cracker cuts during the production of ethene. Even though Pd-Ag/Al<sub>2</sub>O<sub>3</sub> catalysts are predominantly used in industrial C<sub>2</sub>-tail end-selective hydrogenation reactors, a detailed kinetic study with this catalyst type has not yet been published in the open literature. For this reason, kinetic measurements were carried out on a Pd-Ag/Al<sub>2</sub>O<sub>3</sub> catalyst in an integral fixed bed reactor at different process conditions for the selective hydrogenation of ethyne. The results of these measurements were fitted on different kinetic models ranging from a classical Hougen–Watson, Langmuir–Hinshelwood and Rideal–Eley approach up to simple power law equations. The kinetic model with the best fit was found by statistical and thermodynamical evaluations of all models and their respective kinetic parameters. This model is based on a Langmuir–Hinshelwood reaction mechanism involving two different active sites for the hydrogenation of ethyne and ethene. The kinetic measurements were not dependent on mass and heat transfer as demonstrated by using the criteria from Mears and the Weisz–Prater as well as for the Damkoehler numbers in 3rd and 4th order. Finally the performance of a bypass reactor, running in parallel to an industrial C<sub>2</sub>-tail end-selective hydrogenation reactor, was successfully calculated with a reactor model.

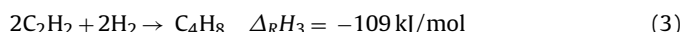
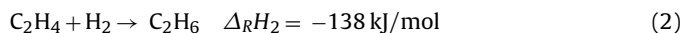
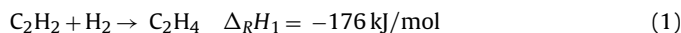
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## 1. Introduction

Ethene is mainly produced by steam cracking of naphtha [1]. This cracking process produces also impurities e.g. ethyne that causes an irreversible damage of the catalysts used in downstream processes of the steam cracker (for example Ziegler–Natta catalysts in the polymerization of ethene). The ethyne content has to be reduced to concentrations lower than 1 ppmv to avoid this damage [2]. The removal of ethyne is carried out by selective hydrogenation to ethene. Thereby an ethene gain of the steam cracker is achievable which has got additional economic value [3]. The amount of this ethene gain is linked with the selectivity of the ethyne hydrogenation catalyst. Originally nickel, iron and cobalt containing catalysts were used in the selective hydrogenation of ethyne but sulfur compounds had to be added to minimize ethene losses. Furthermore an undesired polymerization of ethyne is taking place resulting in an agglomeration of the catalyst and thus regenerations have to be performed regularly [4]. In the 1950s Bond et al. proved palladium to be the most active and selective metal in the hydrogenation of ethyne [5]. About 20 years later a new catalyst type was

commercially used containing 0.04 wt.% palladium impregnated on Al<sub>2</sub>O<sub>3</sub> pellets [4]. Another ten years later bimetallic catalyst systems and especially Pd-Ag/Al<sub>2</sub>O<sub>3</sub> catalysts were established in the industry and are still used by today [6,7]. These catalysts are characterized by an egg shell distribution of palladium and silver over the catalyst pellet to reduce the influence of mass transfer resistance on the reactions [8].

The type of catalyst, investigated in this article, is used in a process called C<sub>2</sub>-tail end-selective hydrogenation. A requirement of this process is the separation of the C<sub>2</sub>-hydrocarbons ethyne, ethene and ethane from the cracked gas of the steam cracker. As described by Borodzinski and Bond [9], the necessary hydrogen for the removal of ethyne is added into the reactor where the following three reactions are taking place:



The selective hydrogenation of ethyne to ethene in Eq. (1) is the desired reaction. Simultaneously ethene is hydrogenated to ethane according to Eq. (2). Furthermore ethyne is, as shown in Eq. (3), hydroooligomerized to butenes (1-butene, cis-2-butene and trans-2-butene).

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