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Steam reforming of methane, ethane, propane, butane, and natural gas over a rhodium-based catalyst

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ABSTRACT

Steam reforming of methane, ethane, propane, butane, and a sulfur-free natural gas is studied over a rhodium-based monolithic honeycomb catalyst. The product distribution is analyzed as function of temperature (250–900 °C) and steam-to-carbon ratio (2.2–4) for two honeycomb channel densities (600 and 900 cpsi) and an uncoated monolith by gas chromatography and mass spectroscopy. The reactive flow in the single monolith channel is modeled by a two-dimensional flow field description coupled with detailed reaction mechanisms modeling surface and gas-phase kinetics. Ethane, propane, and butane are converted at much lower temperature than methane, also in natural gas mixtures. An impact of the presence of the higher hydrocarbons on methane conversion in steam reforming of natural gas is found. Steam reforming in the pure gas phase occurs only above 600 °C and the product spectrum differs from that of catalytic conversion.

1. Introduction

Steam reforming of hydrocarbons is an important chemical processes [1–3] providing synthesis gas (H_2 and CO), which can subsequently be converted to numerous valuable basic chemicals. The most prominent catalysts for the reforming of natural gas are nickel, which is the conventional catalyst in industry, and rhodium. According to literature, rhodium has been extensively studied as catalyst for steam reforming (SR) of methane [4–11] and propane [12–16], but no study has been found for SR of ethane and only one for SR of butane [17].

Modeling of catalytic SR of natural gas has mainly been based on global kinetic expressions [18–20] and thermodynamic calculations [21]. Even though, a variety of detailed multi-step surface reaction mechanisms have been published over the last years, for instance for modeling partial and total oxidation of hydrocarbons over Pt [22–26], Ni [27–31], and Rh [29–33], there is no mechanism available which covers SR of natural gas, which in fact consist of more than methane.

This article presents an experimental and modeling study on steam reforming of methane, ethane, propane, butane, and natural gas over a rhodium-based catalyst. The final objective of this study is the development of a detailed mechanism including conversion of the higher alkanes present in natural gas and potential gas-phase reactions.

Subsequently experiments using ethane, propane, and butane were performed. In natural gases alkanes higher than butane are only found as traces with concentrations less than 0.04% [34] and were not investigated as their influence is negligible.

2. Experimental set-up

In this study steam reforming of the different alkanes is investigated at temperatures ranging from 300 to 1000 °C. The experiments were carried out in a tubular flow reactor schematically depicted in Fig. 1. Distilled water for steam production was kept in a pressure reservoir at 3 bar. The flux of liquid water to the vaporizer was electronically controlled by a Bronkhorst Hi-Tec LiquiFlow. The gas compounds argon, methane, ethane, propane, butane, and natural gas were electronically controlled using mass flow controllers (Bronkhorst Hi-Tec F-201C operated with the control unit Bronkhorst Hi-Tec E-700). All gases were provided by AIR LIQUIDE Deutschland GmbH. Those gases were also fed to the homemade vaporizer, a vessel filled with discarded metal slices, which also serves as mixing chamber for fuel and steam.

The reactor itself is made out of the ceramic material Pythagoras and natural stone. The Pythagoras tube which serves as outer reactor wall is glued with silicon between two flanges. These flanges consist of stainless steel and are held at a temperature of 90 °C using ethyleneglycol pumped by a

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