

Conversion of Hydrocarbon Fuels over Rhodium: Towards a Better Understanding of Coking of Catalyst

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Introduction

In conversion of hydrocarbon fuels in high temperature processes coking is a significant process leading to deactivation of the catalyst [1]. The carbon deposition occurs by chemisorption or physisorption of hydrocarbon intermediates from the gas phase and decomposition on the catalyst surface, which may lead to formation of carbonaceous over layers and even encapsulation of the catalyst particles. In order to minimize and even avoid coking, the hydrocarbon conversion and carbon deposition have to be understood in detail. The final objective is the development of coking models than can be coupled with elementary step reaction mechanisms describing hydrocarbon conversion [2-4] to numerically simulate the reactor behavior at a wide range of varying operating conditions. To reach this goal, several new efforts have been started to investigate coking in hydrocarbon conversion in detail. One step in this direction consists in a better understanding of the roles and interaction of support and catalyst during carbon deposition. In this study we exemplarily focused on hydrocarbon conversion over rhodium, because Rh is a very active but expensive catalyst widely used in reduction of pollutant emissions, fuel reformers, and chemical reactors, for instance for the production of NO from ammonia, and hydrogen from fossil and alternative feed stocks.

Materials and Methods

For our investigations we used Rh/alumina coated monoliths and thin discs. The catalysts were coked in flow reactors either heated by a furnace for steam-reforming (SR) of the fuel or autothermal operation for partial oxidation (CPOX) of the fuel. The following conditions were chosen:

- i) CPOX of several logistic fuels and fuel surrogates was carried out at gas-hourly space velocities (GHSV) of 85.000 h⁻¹ and C/O ratios between 0.8 and 1.3.
- ii) Undiluted SR of natural gas "Nordsee H" (Airliquide) was carried at GHSV of 17.000 h⁻¹ and steam-to-carbon (S/C) ratio of unity.
- iii) Additionally, selective coking of the same catalyst was performed by pyrolysis of different hydrocarbons such as propylene and methane.

The product composition during the coking experiments was analyzed by mass spectroscopy, gas-chromatography, and Fourier-transformed infra-red spectroscopy (FTIR). The coked catalysts were burned off by temperature programmed oxidation in a flow of 20 Vol% O₂ and 80 Vol% N₂; maximum temperature was 700°C. The amount of deposited carbon was determined by analyzing the product gas flow concerning the concentration of CO and CO₂ by FTIR. The coked Rh/alumina foils were additionally analyzed by Atomic Forced Microscopy (AFM) and Transmission Electron Microscopy (TEM) as well as SEM and EDX.

Results and Discussion

In SR of natural gas, formation of coke on the catalyst was detected depending on S/C ratio and temperatures [4]. Three different deposition rates were identified depending on temperature. At temperatures above 800°C, gas-phase reactions become significant accelerating catalyst deactivation, which can be described by a recently published mechanism [5].

In catalytic partial oxidation of i-octane, coking occurs in the downstream section of the catalyst for any C/O ratios above unity. The transition to coking conditions in the reactor occurs at the location where no oxygen is available at the catalyst (may differ from the gas-phase concentration), which could also be numerically predicted by a 2d flow field description coupled with a detailed reaction scheme of over 7000 reactions in the gas-phase and 70 surface reactions.

AFM measurements were carried out using thin α -alumina discs covered with well-defined Rh particles after SR of natural gas over that disc. The samples were analyzed by the recently developed Chemical-Contrast-Imaging AFM-mode [6] to determine the initial carbon deposition by friction measurements.

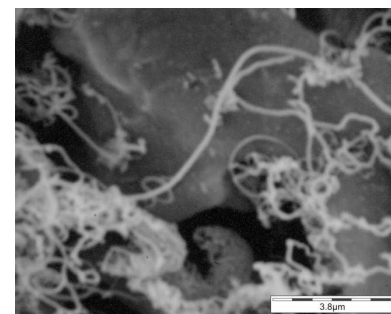


Figure 1 SEM micrograph of a catalyst surface coked during pyrolysis of propylene at T = 750°C

References

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