

Chapter 1

Steam reforming of natural gas on noble-metal based catalysts: Predictive modeling

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Steam reforming of natural gas over a noble-metal based catalyst is studied experimentally and numerically at varying reactor temperature and steam-to-carbon ratio. The catalytic monolith applied in the experiment is modeled by a two-dimensional flow field coupled with detailed reaction mechanisms for both surface and gas-phase reactions and taking the complexity of natural gas compositions into account. Steam reforming of methane, ethane, propane, and butane as single components as well as of a real gas mixture is studied to develop and evaluate a multi-step surface reaction mechanism. The model developed can now be used to predict conversion and selectivity in steam reforming of natural gas of widely varying composition.

1. Introduction

Steam reforming has been described by several groups with different rate expressions; reviews are given by Rostrup-Nielsen [1,2]. In kinetic expressions, the methane chemistry is usually applied to simplify the description of natural gas conversion [3, 4]. Since natural gas contains, aside from methane, a variety of other components, such as light alkanes and CO₂, predictive modeling of chemical conversion of natural gas needs to account for the complexity of the mixture composition. In this study, we focus on the light alkanes present in natural gas. Therefore, step-by-step the single components methane, ethane, propane, and butane are studied independently, and finally, North Sea Gas H (composition given in Table 1) as example for a real natural gas is investigated. The models developed are further evaluated by comparison of numerically predicted and experimentally observed steam-reforming of a “made up” gas composition.

CO ₂	1.87	vol-%
N ₂	0.94	vol-%
CH ₄	86.72	vol-%
C ₂ H ₆	8.10	vol-%
C ₃ H ₈	2.03	vol-%
C ₄ H ₁₀	0.44	vol-%
> C ₄	0.10	vol-%

Table 1: Composition of natural gas type ‘‘North Sea H’’ used in the present study

2. Experiment

The experimental set-up consists of the feed section, reactor, and analytical devices. Via liquid and mass flow controllers (Bronkhorst Hi-Tec) the gaseous components and the water are fed into a vaporizer which also serves as mixing-chamber. The small dimension of the reactor, heated by a surrounding furnace and made out of ceramic materials, and the argon dilution of the fuel guarantee isothermal conditions. Three cordierite monoliths with one centimeter in length are placed inside the flow reactor; only the central monolith is catalytically active by a rhodium/alumina coating. The monoliths in the middle and the back are honeycomb monoliths composed of approximately ninety rectangular channels. A foam monolith is placed in the front of the catalyst to ensure a nearly flat velocity profile at the catalyst inlet. Gas temperatures at the front and back of the catalytic monolith are monitored with Rh/Pt thermocouples type S. The temperature difference between those two points ranges from 0°C to 15°C. The reactor is operated at atmospheric pressure. The product composition is determined with a chemi-ionization mass spectrometer (AIRSENSE 500) and a gas chromatograph (Varian CP-3380). The experimental set-up is described in more detail in [5].

All experiments are carried out with a gas hourly space velocity (GHSV) of 40000 h⁻¹; as the flow consists of 75% argon, only 10000 h⁻¹ account for the potentially reactive gases. As natural gas may contain a remarkable amount of CO₂, it is also included in the feed gas and analysis. Monolithic catalysts with two different channel densities (400 and 900 channels per square inch (cpsi)) have been examined.

3. Modeling approach

Simulations are carried out using the software DETCHEM^{CHANNEL} [6], in which the reactive flow in a single cylindrical channel is simulated in two dimensions with the axial (z) and radial (r) coordinates as independent variables. Since

transport in flow direction is mainly realized by convection at the high flow rates used, axial diffusion can be neglected (radial diffusion is taken into account) leading to the well-known boundary-layer equations [7], which are solved in the computer code. The complex heat transfer between reactor and furnace overlapped by the heat consumed by the endothermic reaction is not considered due to isothermal operation. Reactions in the gas phase are modelled by a set of 757 elementary reactions among 64 chemical species, which was recently developed for combustion, partial oxidation, and reforming of light alkanes [8].

The model for the catalytic surface reactions is also based on the molecular behaviour. Here, the mean field approximation is applied, in which the adsorbed species are assumed to be randomly distributed on the surface, and the state of the catalyst is described by the locally resolved surface coverage. The temperature dependence of the rate coefficients is described by a modified Arrhenius expression:

$$k_{f_k} = A_k T^{\beta_k} \exp\left[\frac{-E_{ak}}{RT}\right] \prod_{i=1}^{N_s} \Theta_i^{\mu_{ik}} \exp\left[\frac{\varepsilon_{ik} \Theta_i}{RT}\right]$$

This expression accounts for an additional coverage dependence of the activation energy using the parameters μ_{ik} and ε_{ik} [6]. These Arrhenius coefficients were taken mainly from BOC-MP or UBI-QEB calculations following the approach of Shustorovich [9]. A surface site density (maximum number of adsorption sites) of $1.6 \cdot 10^{-9}$ mol/cm² is chosen for the rhodium catalyst. Chemisorption measurements resulted in a ratio of catalytic to geometric surface area of 143, which is an input parameter for the model coupling the surface chemistry and flow field [6].

4. Results and Discussion

First, steam reforming of CH₄ is studied in a temperature range of 450°C to 850°C at six different steam-to-carbon (S/C) ratios ranging from 2.2 to 4. Conversion starting at 400°C is complete at temperatures above 800°C. The 900 cpsi catalyst exhibits slightly higher conversion. CO is barely formed at low temperatures, the selectivity then increases to 50% at 800°C. A detailed multi-step surface reaction mechanism consisting of 42 reactions among 12 surface and 6 gas-phase species is derived from these experiments and the previously developed mechanism of Schwiedernoch et al. [3, 4] for modeling catalytic partial oxidation of methane over rhodium. Several additional reactions proposed by Hei et al. [10] and Lin et al. [11] are added.

Steam-reforming of ethane, propane, and butane starts between 350°C and 400°C, followed by a steep increase in conversion. Complete conversion is

already achieved between 550°C and 600°C. Compared to the conversion with S/C 2.5 the conversion with S/C 4 reaches the same value at approximately 25°C lower temperature. Steam-reforming reactions on rhodium are modeled by an extension of the initial methane mechanism, in which the higher alkanes are assumed to adsorb dissociatively.

Exemplarily for a real natural gas composition, steam reforming of the natural gas type “North Sea H” was studied. The conversion of the alkanes occurs in two temperature ranges: From 350°C to 400°C ethane (60%), propane (80%), and butane (85%) are already highly converted. When conversion of methane starts, the conversion of the higher alkanes has already reached nearly 100%. The experimental results are then used to validate the multi-step mechanism.

Even though conversion in the gas phase can be neglected in the catalytic system used, the gas-phase kinetics was evaluated in additional experiments without catalytic coating. In particular for increasing C_{2+} contents in the feed and at higher temperature as well as outside the catalytic section, gas phase conversion may matter.

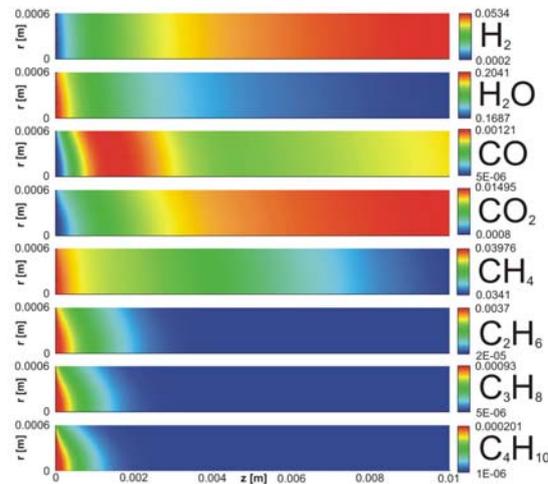


Fig. 1: Species profiles along the channel axis (flow from left to right; channel centerline at the bottom, catalytic surface at the top) for SR of gas “North Sea H” at 430°C and S/C 4.

5. Predictive Modeling

By the detailed models, the two-dimensional distributions of the gas phase species, shown in Fig. 1, and profiles of the surface coverage are calculated (not

shown). The main conversion is exhibited to occur within the first millimeters of the catalytic section of the reactor.

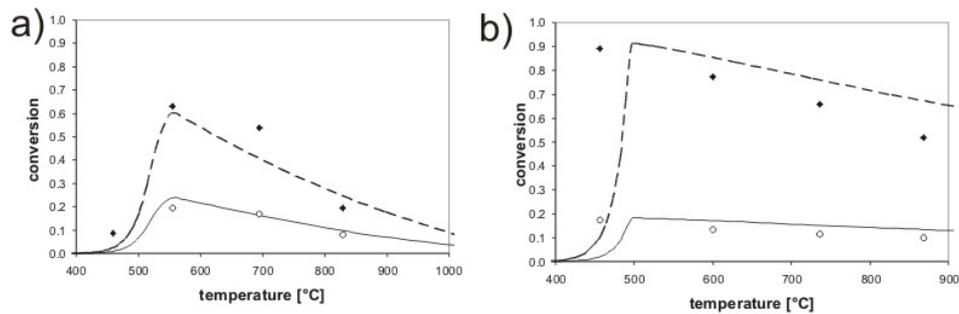


Fig. 2: Conversion for CO/CO₂/H₂O mixtures a) with and b) without hydrogen — CO simulation, ● CO experiment, — water simulation, ○ water experiment

The species profiles in the channel at lower temperatures (415 - 500 K) first show fast formation of CO which is then rapidly re-adsorbed and further reacted to CO₂. This result enforces the conclusion that water-gas shift dominates the process as also shown by additional experiments, in which the feed consisted of equal amounts of hydrogen, carbon dioxide, and carbon monoxide, and a surplus of steam. The results show a maximum in CO conversion and CO₂ formation at almost the expected temperatures (Fig. 2). Since the production of hydrogen is still low around 420°C the experiment is repeated without hydrogen. Now the temperature of the first occurrence of the water-gas-shift moves up by 50 – 100°C, which agrees with the expectation from the two-dimensional profiles (Fig. 1).

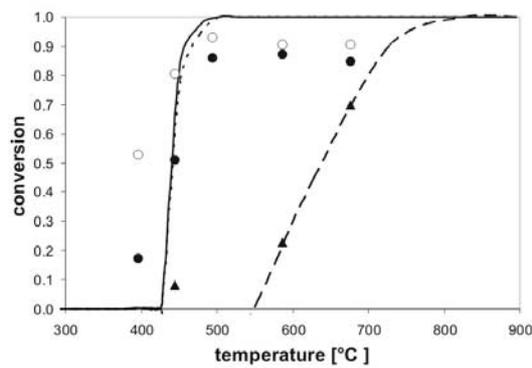


Fig. 3: Conversion in steam-reforming of the fictive “natural gas” mixture at S/C 2.5; CH₄: — model, ▲ experiment; C₂H₆: ··· model, ● experiment; C₃H₈: — model, ○ experiment.

Since all experimental observations agreed well with the predictions, eventually, an arbitrary mixed “natural gas” was studied numerically, i.e. a

mixture of 70% methane, 21% ethane, and 9% propane. The reported conversion (Fig. 3) reveal that the model developed is able to predict steam-reforming of natural gas in a general way over the rhodium catalyst applied.

6. Conclusions

The study reveals that for understanding and quantitative prediction of conversion and selectivity in steam reforming of natural gas all hydrocarbon components need to be considered. All the experimentally observed conversion and selectivity data can be well-predicted by the detailed model developed for surface and gas-phase reactions. The simulation also provides a much deeper insight into the interactions of the alkanes during the reaction. The mechanisms developed with defined experiments and theoretical data can now be used to predict the conversion and selectivity of any natural gas like hydrocarbon mixture as function of temperature over the studied catalyst without any additional parameter fitting.

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References

1. J.R. Rostrup-Nielsen, J. Sehested, J. K. Nørskov, *Advances in Catalysis* 47 (2002) 65
2. J.R. Rostrup-Nielsen, *Catalytic Steam Reforming*, Springer, 1984
3. O. Deutschmann, R. Schwiedernoch, L. Maier, D. Chatterjee, in *Natural Gas Conversion VI, Studies in Surface Science and Catalysis* 136, E. Iglesia, J.J. Spivey, T.H. Fleisch (eds.), p. 215-258, Elsevier, 2001
4. R. Schwiedernoch, S. Tischer, C. Correa, O. Deutschmann, *Chemical Engineering Science* 58 (2003) 633
5. B.T. Schädel, *Untersuchung von Reformierungsprozessen von Methan an Rhodium- und Nickelkatalysatoren* (Diploma thesis). Fakultät für Chemie und Biowissenschaften, Universität Karlsruhe (TH), Karlsruhe, Germany, 2005
6. S. Tischer, O. Deutschmann. *Catalysis Today* 105 (2005) 407; www.detchem.com
7. L. L. Raja, R. J. Kee, O. Deutschmann, J. Warnatz, L.D. Schmidt, *Catalysis Today* 59 (2000) 47
8. R. Quinceno, J. Perez-Ramirez, J. Warnatz, O. Deutschmann, *Applied Catalysis, A: General* 303 (2006) 166
9. E. Shustorovich, H. Sellers, *Surface Science Reports* 31 (1998) 1
10. M.J. Hei M. J. Hei, H. B. Chen, J. Yi, Y.J. Lin, Y. Z. Lin, G. Wei, D. W. Liao, *Surface Science* 417 (1998) 82
11. Y.-Z. Lin, J. Sun, J. Yi, J.-D. Lin, H.-B. Chen, D.W. Liao, *Theochem* 587 (2002) 63