

Thermodynamic model for reforming and oxidation of methane over nickel catalyst

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1 Abstract

Attempts have been made to develop a thermodynamic model for the steam reforming, dry reforming and oxidative reforming reactions over nickel catalyst with the help of a one-dimensional model, LOGEcat. These reforming processes have been investigated using kinetic models in literature whereas the thermodynamic models are not explored much due to the unavailable thermochemistry of the intermediate species. However, for gas-phase chemistry, a vast number of thermodynamic models are available as the thermochemistry of the gas-phase species is extensively validated and available. Whereas, in case of surface chemistry, the kinetic models are more prominent which uses all forward reactions by providing Arrhenius parameters explicitly. This is because of the fact that the thermochemistry of the intermediate species is not available. The main aim of this work is not only to develop a thermodynamic model by performing the sensitivity analysis on thermochemistry of the intermediate species but also to compare the reaction pathways for thermodynamic and kinetic model. For these models, the differences in sensitivity analysis have been observed and it provides a useful insight into the key rate determining steps.

2 Introduction

In the chemical industry, the reforming of light hydrocarbons to produce synthesis gas, H₂ and CO, is an important intermediate for manufacturing valuable basic chemicals and synthesis fuels [1]. The most common catalytic technologies to get these synthesis gases from methane are steam reforming (SR), partial oxidation (POX), autothermal reforming (ATR), and dry reforming (DR) processes [2]. Each of the process have some merits and demerits with it. For instance, the reactions in SR process are highly endothermic which demands an efficient external energy supply and the efficiency of this process is critically affected by the catalyst deactivation due to carbon formation which is also a limitation in DR of methane over nickel [2,3]. The alternative to these reforming processes is the POX of methane, however, different pre-treatment conditions affect the state of the catalyst surface which might change the reaction mechanism making the process complicated along with coke formation at elevated temperatures and pressures [4–7].

To develop a coke-resistant catalyst, a better understanding of the catalytic oxidation and reforming of methane at molecular level is needed along with the deactivation kinetics of coke formation. There are

numerous kinetic models proposed to study the reforming and oxidation of methane using several techniques [1, 8–13]. These kinetic mechanisms contains explicit pairs of forward and backward reactions employing an admittedly complicated protocol for adjusting their kinetic expression to ensure thermodynamic consistency. The present work adopts the forward reactions with their kinetic expressions from literature but the reverse rate expressions are derived from the thermochemistry of the intermediates involved, i.e., from the equilibrium constants for individual reactions. Since the thermochemistry of the surface bound intermediates is not well known, the thermochemical data is taken from different sources and adjusted according to the experimental results by performing sensitivity analysis on individual surface species.

Our previous work [14] forms the basis for this investigation. However, in [14], the surface reaction mechanism was limited for steam reforming process whereas, the mechanism developed in this work is applicable for the modeling of partial oxidation, dry reforming as well as steam reforming of methane over nickel catalyst. The main aim of this investigation is not only providing the thermodynamic data of intermediate species involved in the reaction mechanism but also to present a detailed sensitivity analysis of the reactions and reaction pathways for the new surface reaction mechanism which considers only reversible reactions. This will provide a useful insight into the key rate determining steps and will help us to understand the influence of utilization of thermochemistry of the surface bound species.

3 Reaction Mechanism and Set-up

For the considered reforming processes, the natural gas is converted into a mixture of hydrogen, carbon monoxide, and carbon dioxide via different molecular paths represented as a combination of the overall/global reactions. These global reactions are used to develop a kinetic scheme for an elementary-step detailed surface reaction mechanism consisting of 52 reactions with 6 gas-phase and 14 surface species [15]. This kinetic scheme served as basis for our study. So we used the 26 reversible reactions from [15] along with their kinetic expressions and the reverse kinetic expressions are then calculated by using the thermochemistry of the 14 surface species.

The above information is used to perform the simulations using a 1D model, LOGEcat [16]. The model is based on the single-channel 1D catalyst model where the channel is divided into a finite number of cells and each cell is treated as a perfectly stirred reactor (PSR). The model has been successfully used in past for several investigations. In this work, the model is used to perform sensitivity analysis for a new developed kinetically consistent surface reaction mechanism in order to understand the key differences between this new mechanism and the kinetic scheme available in literature [15].

The reactor used for the simulations is a circular catalyst with 5 mm radius and 27 mm length where the reactions are happening. The surface site density for Ni is 2.6×10^{-5} mol/m² and nitrogen dilution is 96%. The simulations are performed at 4 slpm (standard liters per minute) by varying the reactions temperature in a range from 400-1200 K for several reactor conditions. The catalyst parameters and inlet gas composition is used same as given in the reference paper [15]. The simulation results are shown next.

4 Results

The mechanism developed in this work is validated against experiments and simulations from literature [15] for steam reforming of methane over a nickel catalyst at constant pressure as well as fuel composition over a wide range of temperature (400-1200 K) shown in Figure 1 for methane concentration computed with our model. The mechanism is valid for dry as well as oxidative reforming of

methane over nickel, however, in this paper we limit ourselves to the steam reforming case. The simulations are inline with the experiments. The start of the methane consumption is observed around 600 K and a full consumption is noted around 1000 K.

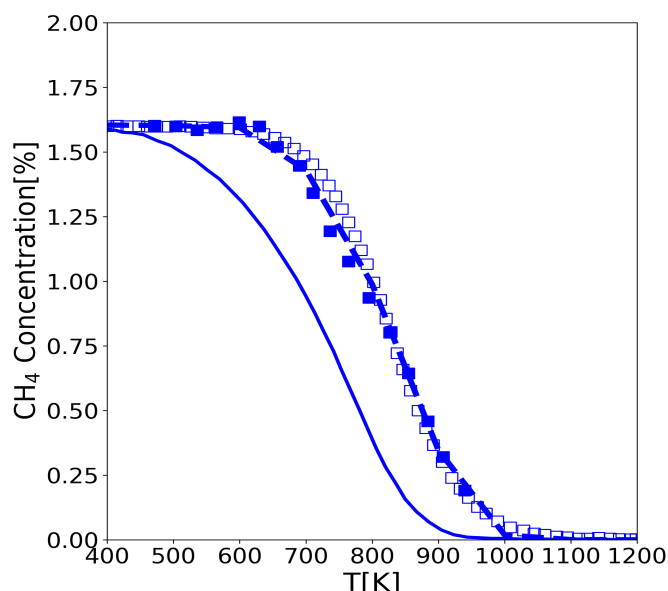


Figure 1: The concentration of methane is shown as a function of temperature with constant fuel composition along with the reference data from [15]. The unfilled squares represents reference simulations, filled squares: reference experiments, solid lines: reference equilibrium calculations and dash lines: LOGEcat calculations with the new mechanism.

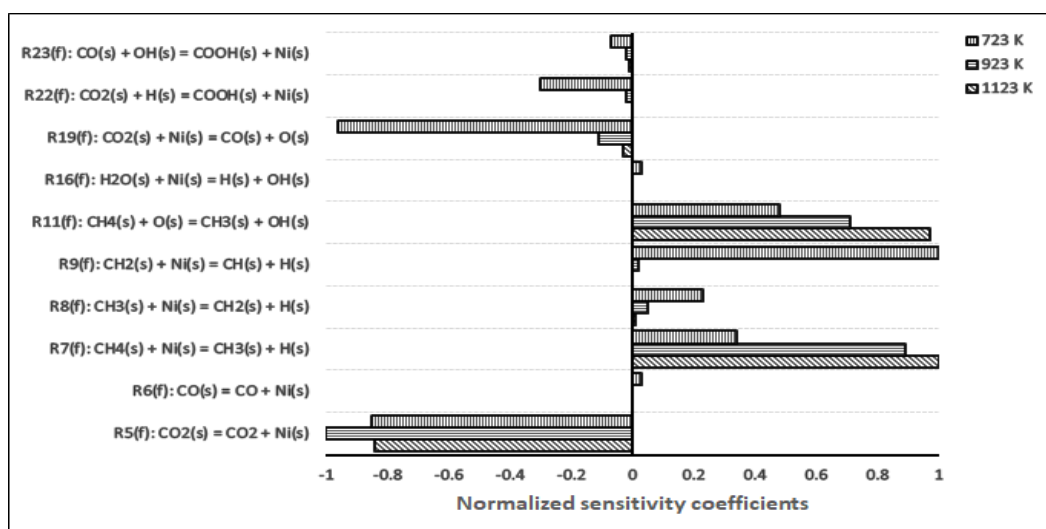


Figure 2: Sensitivity analysis of CO gas-phase concentration for steam reforming methane at different temperatures for constant fuel ratio and pressure.

After a successful validation of the mechanism, the normalized sensitivity coefficients of the CO yield at 3 different temperatures is shown next in Figure 2. The sensitivity analysis is performed at the same conditions as done in [15] in order to make a comparison between the kinetic and thermodynamic model. A different set of reactions are sensitive in the thermodynamic model as compared to the kinetic scheme given in [15]. The desorption of CO, methane dehydrogenation, and oxygen assisted methane

dehydrogenation are highly sensitive for the new mechanism at all the temperatures considered for the simulations. At 723 K, the methane dehydrogenation, carbon formation from adsorbed CO species through CO(s) dissociation and the oxidation of CO through the surface intermediate carboxyl formed from CO(s) are sensitive to the CO yield.

5 Conclusions

A thermodynamic model is developed for processes such as steam, dry, and oxidative reforming of methane over nickel catalyst using LOGEcat. In this approach, the forward reactions with their kinetic expressions are taken from literature and the reverse rate expressions are then derived from the thermochemistry of the intermediates involved, contrasting from the kinetic mechanism available in literature where the explicit pairs of forward and reverse reactions with their kinetic expressions are used to ensure thermodynamic consistency. This is interesting because the optimum method to achieve thermodynamic equilibrium would be to use the correct thermochemistry of the species and the kinetic expressions are more accurate to define the speed of the reactions instead of establishing the equilibrium. The study illustrates major differences in reaction pathways for kinetic and thermodynamic model. A further investigation is needed to understand the origin of these differences which might improve the mechanism and can also help to understand the influence of thermochemistry towards coke formations in various reforming processes.

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