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Autothermal reforming of methane on rhodium catalysts: Microkinetic analysis for model reduction

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ABSTRACT

Methane autothermal reforming has been studied using comprehensive, detailed microkinetic mechanisms, and a hierarchically reduced rate expression has been derived without apriori assumptions. The microkinetic mechanism is adapted from literature and has been validated with reported experimental results. Rate determining steps are elicited by reaction path analysis, partial equilibrium analysis and sensitivity analysis. Results show that methane activation occurs via dissociative adsorption to pyrolysis, while oxidation of the carbon occurs by O(s). Further, the mechanism is reduced through information obtained from the reaction path analysis, which is further substantiated by principal component analysis. A 33% reduction from the full microkinetic mechanism is obtained. One-step rate equation is further derived from the reduced microkinetic mechanism. The results show that this rate equation accurately predicts conversions as well as outlet mole fraction for a wide range of inlet compositions.

1. Introduction

Hydrogen as an energy carrier (U.S.E.I. Administration, 2015), and fuel cells as energy conversion device (Neef, 2009) have gained traction recently in the context of the shift toward more efficient and less carbon-intensive energy solutions (Ramachandran, 1998; Stambouli and Traversa, 2002; Leo Hudson et al., 2009). This has renewed the interest in localized hydrogen generation with a focus on hydrocarbon reforming process (Takehira, 2004; Choudhary et al., 2005; Nagaoka et al., 2005; Dauenhauer et al., 2006; Horn et al., 2007; Hou et al., 2007; Miletić et al., 2015; Silva et al., 2013), and methane is one of the prime sources of hydrocarbon based hydrogen (Takehira, 2004; Choudhary et al., 2005; Horn et al., 2007; Hou et al., 2007; Miletić et al., 2015; Dixit et al., 2015). Autothermal reforming as a means of hydrogen production has been gaining academic and research interest due to its thermodynamically neutral nature and feasible operating conditions (Khila et al., 2013; Chaubey et al., 2013; Holladay et al., 2009; Subramani and Song, 2007; Song, 2002; Tippawan and Arpornwichanop, 2014; Navarro et al., 2007; Martin and Wörner, 2011).

In the past, much attention has been focused on the design and development of catalysts and the evaluation of the process and equipment with relatively little work being done on the numerical modeling, kinetics and mechanism of the reaction. Methane reforming is a system, where multiple reaction are simultaneously in equilibrium, and hence several routes to the desired products and by-products exist (Christian Enger et al., 2008). Thus, to optimize the reactor performance a fundamental understanding of the underlying surface catalytic phenomenon is required, which is provided by a detailed microkinetic mechanism (Salciccioli et al., 2011a). A detailed microkinetic mechanism is further useful to accurately model the reaction over a wide range of reactor conditions (Deshmukh and Vlachos, 2007). A few groups such as Maestri et al. (2008) and Deutschmann et al. (2001) have worked on the development of microkinetic mechanisms for steam reforming (SR), dry reforming (DR) and partial oxidation of Methane (POx) respectively using first principle methodologies such as UBI-QEP, DFT techniques and have validated these mechanisms with experimental findings.

Salciccioli et al. (2011a,b) reviewed various modeling strategies for metal-catalysed reactions. Apart from detailed microkinetics, two kinds of empirical rate models have been observed in literature: (1) power-law kinetics and (2) Langmuir–Hinshelwood–Hougen–Watson models. The former are still commonly used in reactor and process design despite their fundamental limitations and lack of predictive power since they involve a small number of parameters that can easily be regressed to a limited number of experimental data. The latter assumes a reaction mechanism and builds the rate model around

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Nomenclature

φ	Partial equilibrium factor
θ_i	Surface coverage
C_i	Species concentration (mol cm^{-3})
r_i	Rate of reaction ‘i’ (mol cm^{-3} s^{-1})
S	Sensitivity matrix
$S_{i,j}$	Sensitivity coefficient
k_i	Reaction constant (reaction specific)
S/C	Steam-to-carbon ratio
O/C	Oxygen-to-carbon ratio

Acronyms

ATR	Autothermal reforming
CFD	Computational fluid dynamics
DFT	Density functional theory
DR	Dry reforming
PE	Partial equilibrium
POx	Preferential oxidation
RDS	Rate determining step
RPA	Reaction path analysis
SA	Sensitivity analysis
SR	Steam reforming
UBI-QEP	Unity bond index-quadratic exponential potential

this mechanism. Assumptions are also made about fast and slow processes, and a closed-form rate expression is developed. This iterative process is followed until an accurate match with experimental data is obtained. While this model may be able to predict the experimental data in a limited parametric window, it cannot predict reactor response much outside the parametric window.

Recent research has focused on developing methods to employ information derived from first principles based studies to complex reactor scale simulations by various means that reduce the computational complexity (Neurock and Hansen, 1998; Vlachos et al., 2006; Corbetta et al., 2014; Sjöblom and Creaser, 2008; Sjöblom and Creaser, 2007). While a microkinetic model enables quantification of the interaction between gas-phase and surface chemistry, it is also computationally expensive, especially when employed as part of CFD simulations, (Maestri and Cuoci, 2013). Hence it becomes essential to hierarchically reduce the detailed microkinetic mechanism to mechanisms that include only the major pathways of reforming. It can be further reduced to single-step or two-step rate equations that reduce the complex mathematical interpretation of the microkinetic models to simple algebraic equations (Kumar et al., 2011; Salciccioli et al., 2011b; Mhadeshwar and Vlachos, 2005a; Maestri et al., 2014). As compared to full microkinetic models, this formulation has a few limitations. Since the model reduction is carried out over a range of temperatures, the accuracy of the reduced model depends on the actual reactor temperature. We have found that this mechanism is progressively less accurate as temperature increases beyond 700–800 °C. Maestri et al. (2008) have proposed a two-step overall rate expression for SR and DR of methane, by performing a top down hierarchical model reduction. Partial oxidation of lean hydrocarbons were studied in detail by Deshmukh and Vlachos (2007). However, a top-down hierarchical model reduction for methane autothermal reforming on rhodium catalyst is not seen in the literature.

In this paper, we adapt a microkinetic mechanism from Deutschmann et al. (2001), and derive a single step rate equation for autothermal reforming of methane. Section two describes the analysis done on the full microkinetic model: comparison with experimental data, reaction path analysis (RPA), partial equilibrium analysis (PEA) and sensitivity analysis (SA) on the mechanism to determine the rate determining steps (RDS) and most abundant reaction intermediates (MARI). Section three details the proposed one-step overall rate expression for CH_4 ATR over Rh. We see good agreement of the reduced rate expression with the full microkinetic mechanism.

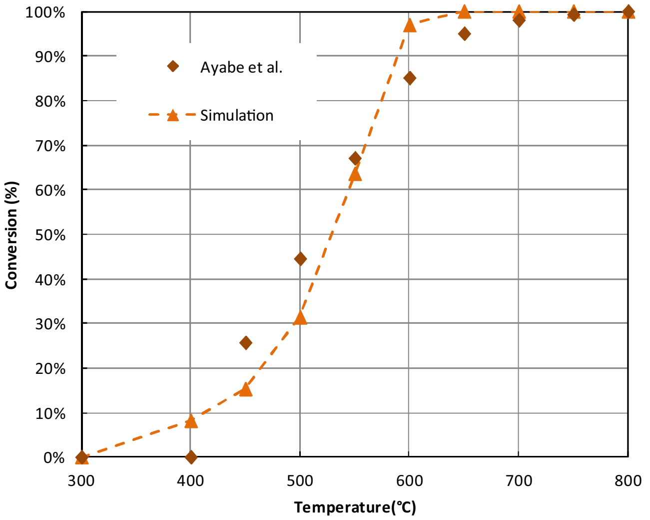

Fig. 1. Methane conversions with respect to temperature. The mole fractions of reactants are CH_4:O_2:H_2O:N_2 = 0.167:0.017:0.416:0.4.

2. Analysis of the full microkinetic mechanism

2.1. Comparison with experimental result

For an initial analysis, we adapted the microkinetic mechanism developed by Deutschmann et al. (2001) for partial oxidation of methane on Rh catalyst comprising of 7 gas phase species, 12 surface species and 40 elementary like reactions (Schwiedernoch et al., 2003). The microkinetic mechanism employed is listed in Table 1. The thermo-kinetic calculator toolbox Cantera (Goodwin et al., 2015) was used to solve the plug flow model for autothermal reforming of methane on Rh catalyst. This analysis divides the reaction zone into a set of continuously stirred tank reactors (CSTRs), assuming plug flow conditions with inifinite radial diffusion and negligible axial diffusion. Further, steady state operation under isothermal conditions and negligible pressure-drop conditions are assumed. It is also assumed that no interphase and intraparticle mass transfer limitations occur. Such models have been extensively used to model catalytic systems (Weilenmann, 2012; Larson et al., 2012; Kočí et al., 2010). The conditions simulated mirrored those of experiments conducted by Ayabe et al. (2003) (the reactant mixture consisted of 16.7% CH_4, 0–40.0% H_2O, 1.7–16.7% O_2, and balance N_2 (balance); the reactor dimensions and velocities were assumed to a space velocity of 7200 h^{-1}).

The experiments were carried out in a fixed bed reactor with 2 wt.% Rh/Al_2O_3 catalyst isothermally over a temperature range of 300–800 °C. Fig. 1 shows a comparison of methane conversion over this temperature range between experimental and modeling results. It is evident that the results obtained from microkinetic model are in good agreement with experimental results.

2.2. Reaction path analysis and rate determining step

A reaction path analysis helps identifying the main reaction paths involved in the process leading from reactants to products based on the net production rates of each surface species involved in the microkinetic mechanism (Mhadeshwar and Vlachos, 2005b).