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Oxidative steam reforming of ethanol on rhodium catalyst – I: Spatially resolved steady-state experiments and microkinetic modeling

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ABSTRACT

Oxidative steam reforming of ethanol is an important process for on board production of hydrogen in fuel cell based auxiliary power systems. Although the process has been extensively studied from a catalyst perspective, accurate models that capture species and temperature information required by model-based control algorithms during operation have not yet been developed adequately. In this work, we develop a reduced micro-kinetic model for ethanol oxidative steam reforming, which can be used in computational fluid dynamics (CFD) studies and subsequently to develop model-based control strategies. We experimentally study cordierite monolith based reactors in which Rh/CeO_2 catalysts are prepared by the solution-combustion method. The catalyst system is characterized by X-ray diffraction (XRD), Scanning Electron Microscope (SEM), temperature programmed reduction and temperature programmed desorption analyses. The experimental reformer design enables measurement of species concentrations at various points along the reactor length, along with radial temperature profiles. A micro-kinetic model is adapted from the literature and validated against these experiments, with good agreement. The model results suggest a linear activation pathway for ethanol over rhodium catalysts by forming ethoxide, acetyl and acetate intermediates. After formation of single carbon species, the methane reforming pathway is followed. We expect that these studies, when coupled with transient studies will help in formulating model-based control strategies for ethanol reformers in complex fuel cell systems.

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Introduction

Decarbonisation has been seen as an emerging trend in recent years with the renewable-hydrogen-electricity pathway being critical to achieve this goal [1]. In this context, fuel cells have seen a rapid growth in interest due to their ability to generate electricity efficiently [2]. Typical commercial methods of producing hydrogen for fuel cells are reforming of hydrocarbons,

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Nomenclature

h	height of the reactor, mm
H_2/C	ratio of moles of hydrogen and moles of carbon products
l	length of the reactor, mm
O/C	ratio of molar flow rate of O_2 to ethanol
S/C	ratio of molar flow rate of H_2O to ethanol
S_i	selectivity of species 'i'
T_i	temperature, °C
w	width of the reactor, mm
$X_{i,in}$	mole fractions of species 'i' at inlet
Y_i	mole fraction of species 'i'
S_v	Surface area to volume ratio, m^{-1}
$\dot{s}$	Net production rate of species, kmol m^2 s^{-1}
h_i	Species enthalpy, J $kmol^{-1}$
ρ	Gas density, kg m^{-3}
v	Inlet velocity, m s^{-1}
$\dot{m}$	Mass flow rate, kg s^{-1}
A_{cross}	Cross Sectional Area, m^2
$L_{reactor}$	Reactor Length, m
$V_{reactor}$	Reactor Volume, m^3
ε	Porosity

Acronyms

ATR	autothermal reforming
BET	Braunner-Emmet-Teller
CFD	computational fluid dynamics
GHSV	gas hourly space velocity
OSRE	oxidative steam reforming of ethanol
SEM	scanning electron microscope
TCD	thermal conductivity detector
TPR	temperature programmed reduction
WGS	water gas shift
XRD	x-ray diffraction

water electrolysis and gasification [3]. Of these methods, hydrocarbon reforming has seen the most research and is responsible for the majority of commercially produced hydrogen [4,5]. However, to further increase the sustainability of using H_2 as an energy carrier, new methods of H_2 production from renewable sources must be implemented [6].

Fuel cell systems have deep penetration potentials in the market with key application being its use as a stand-alone off-grid power source [7,8]. Conversion of locally available bio-ethanol to hydrogen for these systems has numerous economic and technical advantages [9,10], and has therefore been the focus of many studies worldwide [11,12]. Particularly, ethanol reforming has been studied widely due to its increasing availability and non-toxic nature [13–15]. However, most of these studies focus on steam reforming of ethanol for a variety of different catalysts [16–19]. Oxidative steam reforming of ethanol (OSRE) has seen sustained research interest in recent years because of the obvious advantages of autothermal reforming [17,20–26].

Pereira et al. studied OSRE over K promoted Co–Rh/CeO_2–ZrO_2 catalysts [27]. They studied the catalysts under variable water/ethanol (S/C) and O_2/ethanol (O/C) ratios in a fixed bed reactor. They studied the effect of Rh addition on Co catalysts as well as the effect of regeneration on catalyst performance. Morales et al. conducted a similar study using $La_xSr_{1-x}CoO_3$ perovskite catalysts while Rh–Ni/CeO_2–ZrO_2 catalysts have been studied by Mondal et al. [28,29]. $La_{1-x}Ca_xFe_{1-x}Co_xO_3$ has been reported as a stable catalyst for OSRE by Wang et al. [30]. Fierro et al. studied Ni and noble metal catalysts for OSRE as a hydrogen source for on-board hydrogen production for hybrid vehicle [31]. Pirez et al. very recently studied cerium nickel based oxyhydride catalysts in a comparative study of the three reforming pathways for ethanol [32].

The research groups of Mhadeshwar, Vlachos, Deutschmann and Maestri have been developing detailed microkinetics from first principles, semi-empirical and experimental studies for a large variety of processes and fuels [33–43]. Recently, Graschinsky et al. developed rate models for steam reforming and oxidative steam reforming of ethanol on Rh catalysts [44,45]. In a recent work, we have developed a one-step rate equation for a microkinetic mechanism for methane autothermal reforming on Rh catalyst [46]. Ethanol reforming (in particular autothermal reforming) have been reviewed extensively by Hou et al. as well as by the authors [47,48]. These reviews point out that the current research focus is only on detailed catalyst characterization and performance. While the Rh/CeO_2 system has been previously studied for OSRE, a detailed insight into the chemical kinetics and validated microkinetic models are missing.

In this work, we used Rh/CeO_2 coated ceramic monoliths for OSRE. Effect of variation of S/C and O/C on reactor performance is studied. Further, leveraging the novel reactor design, we are able to measure temperatures and gas composition along the reactor length. This gives us an insight into the reaction mechanism followed and the kinetics of OSRE. The information derived from these studies is used to develop a microkinetic mechanism. The proposed microkinetic mechanism has 14 gas phase species, 51 surface species and 56 reversible reactions, and shows good agreement with experiments.

Section Experimental studies details the experimental strategies employed such as catalyst synthesis and characterization, reactor geometry and reaction conditions. Section Results and discussion presents selected results and discussions for the experimental studies. Section Microkinetic model details the microkinetic model formulating strategy and its results.

Experimental studies

Catalyst synthesis

The catalysts were simultaneously coated and synthesized on the cordierite monoliths by the so called "dip and fire" solution combustion method; this method is widely used to synthesize simple and doped metal oxide catalysts because it is a quick process that yields a relatively large quantity of the final product [49–51]. For preparing 1%Rh/CeO_2, 5 g of ceric ammonium nitrate ($(NH_4)_2Ce(NO_3)_6$) and 2.43 ml of 1% rhodium chloride solution ($RhCl_3 \cdot 3H_2O$) were dissolved in

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