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Modeling the effect of coke deposition in a heat integrated ethanol reformer

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ABSTRACT

The dynamic performance of a reformer as a incorporating the catalyst deactivation at the reactor level is modelled by accounting a theoretical coking model. This model incorporates the effect of coke deposition on catalyst activity, diffusion resistance of reactants, and subsequently catalyst pore blockage. The influence of catalyst fouling on the conversion of the product of interest has been illustrated by coupling a rate equation for the formation of coke to the continuity equation for the main products. The transient coke uptake curves are shown to have two regions of kinetics controlled and diffusion controlled through internal effectiveness factor. The implications of varying pore size on the reactor performance through such curves are discussed. It is shown that small pore size (high surface to volume ratio) is not always efficient owing to rapid plugging. The energy intensive endothermic reaction system is coupled with an exothermic reaction to improve the thermal efficiency. The effect of this coupling on the coke formation and its implications on reactor performance is discussed incorporating the switching of species flow direction (co-flow and counter-flow) in combustion section.

This modelling effort is unique is elucidating the spatial distribution of catalytic activity in a reformer, evolving owing to varying rates of local catalyst deactivation. Moreover, the simultaneous variation of catalyst activity and effective diffusivity have been modelled, which has never been investigated in the past. Conclusions from this work counter the often-maintained belief that enhanced heat transfer always enhance the reformer performance. We expect the broad conclusions of the modelling effort to direct future catalyst development.

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Introduction

Hydrogen as a source of energy has attracted significant attention for applications in fuel cell and several portable devices. For mobile applications, it has to be produced on-site in a compact device or a fuel processor, since there is a storage barrier in being able to stock large molar quantities of

hydrogen particularly on a vehicle or in mobile devices. As mostly sourced from biomass, ethanol has emerged as an attractive contender against non-renewable sources like natural gas, petroleum, and coal, for the production of hydrogen [1]. Additionally, ethanol has low toxicity, allowing ease of handling and transportation.

Steam reforming is most economical and thus widely used to produce hydrogen from ethanol [2]. In a typical steam

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reforming operation, hydrogen is extracted not only from the hydrocarbon but also from water. Even though the reaction is kinetically favourable, yet it is not a completely green process as carbon dioxide (CO₂) is produced amongst products that behaves as a greenhouse gas, which increases the environment burden. Bio-ethanol serves as a potential solution to this drawback as the produced CO₂ is consumed through photosynthesis, and thus has a closed CO₂ cycle [3]. On the other hand, ethanol steam reforming is accompanied by many undesired side reactions; some produce carbonaceous deposits that deactivate the catalyst [4]. Deactivation is known to affect the intrinsic catalyst activity and is thus detrimental for stable reactor operation even causing frequent shutdowns [5]. Forzatti and Lietti [6] have analysed the causes of deactivation and proposed a mathematical description of the phenomena in a comprehensive review on catalyst deactivation.

Over the past few decades, several investigations of catalyst deactivation have led to the development of models enabling superior stable catalyst designs and minimising the deactivation [7–9]. These studies provide a considerable impetus for understanding the underlying processes governing catalyst deactivation. Bartholomew [5] has categorized the intrinsic mechanisms of catalyst deactivation into six types: poisoning, vapour compound formation and vapour-solid or solid–solid reactions (chemical causes), fouling and attrition (mechanical causes), and thermal degradation.

In the case of steam reforming of hydrocarbons, significant formation of coke is observed that causes fouling of the catalytic bed. Thick layers of coke deposition on the catalytic surface are of considerable concern in steam reforming as it hinders hydrogen production required for compact reformers. Physical deposition of coke occurs inside the catalyst pores and blocks the active sites, thereby decreasing the catalyst activity. Further, depending on the timescales of the phenomena, this blockage might lead to a reduction in reactor voidage due to the disintegration of catalyst particles. Significant work on the mechanism of deactivation through coking is reported for steam reforming over Pt [10], Co [4,11,12] and Ni [3,10,13–16] based catalysts. Zhang et al. [17] reported superior anti-carbon deposition ability of Co, Ni and Ir catalysts supported on CeO₂ for ethanol steam reforming. Due to inherent complexities, the suitable catalyst for steam reforming of ethanol is a work still in progress.

In ethanol steam reforming operations, coke is formed by a complex scheme of reactions: ethanol dehydration followed by polymerization along with several side reactions like Boudouard reaction, reverse carbon gasification, and methane decomposition [18]. Conditions like temperature, H₂/CO or H₂O/C molar ratios and nature of the catalyst (metal and support) influence the extent of each reaction. Trane-Restrup et al. [19,20] predicted enhanced ethanol conversion and hydrogen yield with increase in S/C molar ratio. Also, the carbon deposition and hydrocarbon yield decreased when Ni based catalyst was used. They compared the activity of Ni catalyst for various supports and promoting the catalyst with K and CeO₂ gave promising results of higher conversion and lower carbon deposition. Wu and Liu [21] showed higher carbon content in range of temperature (575–900 °C) when m-cresol was steam reformed over Ni/MgO catalyst. Thus, carbon deposition occurs either at very high operating

temperatures (>500 °C), or when steam to carbon ratio is below a certain critical level (for a given temperature and feed). Bartholomew [22] suggested a possibility for deactivation to be linked to reaction conditions and composition of the reaction mixture. However, there seems to be no agreement while relating deactivation rate to the amount of carbon on the catalyst. Several studies have reported the formation of multiple layers of fine carbon particles that were suspected to hinder access of reactants to active metal sites as their path becomes more tortuous [23]. This leads to an enhancement of internal mass transfer resistance (affecting effective diffusivity), thus reducing catalyst activity. Richardson [24] measured the diffusivity of Ar/He mixture in a fouled Nalco 471 catalyst through chromatography method. It was noticed that the bulk diffusion coefficients of freshly prepared catalyst was 0.0546 cm² s⁻¹ and pore radius was >1000 Å at 25 °C while in the case of a fouled catalyst it was 0.0281 cm² s⁻¹ with 19.9% carbon deposited and pore radius reduced to 15–35 Å. They concluded that fouling leads to enhancement of the dominating role of Knudsen diffusion in the micropores. Froment [25] has briefly discussed effects of coke formation at multiple scales (the active site, the catalyst particle and the reactor), wherein it was claimed that at the active site level, information on the interaction of deactivating agents with the sites is required.

Prior studies on deactivation models have primarily focused on the active sites and at particle level [23,26,27]. Gottifredi and Froment [27] developed concentration profiles in the catalyst particle accounting internal diffusion limitations at a given position in the reactor. The extent of coking in steam reforming have been extensively studied experimentally [11,28–30], but relatively lesser attention has been directed to theoretical analysis of coking [3,25,31]. The studies have been done to control coking by examining the coke formation mechanisms and composition of catalysts [32]. Moreover, even fewer studies have been extended to reactor level explanations on effects of coking limited for practical purposes [23,33]. Beyne and Froment [23] investigated the parallel and consecutive coking in an isothermal reactor maintaining the plug flow condition.

With this backdrop, we present an integral reactor level analysis of the steam reforming of ethanol. In our modeling considerations, which are at an integral reactor level, we assess how the carbon deposition profiles and associated diminishing of the local catalyst activity affect the overall reactor performance, as a whole. A pseudo-homogeneous modeling framework for unsteady operation in a fixed bed reactor under adiabatic conditions is proposed, incorporating the phenomenon of fouling from coke formation into consideration. The catalyst fouling phenomenon is addressed through an activity parameter and effective diffusivity, which includes the deterioration of catalyst and thus internal mass transport resistance. Species flow through the bed with a flow pattern is assumed to be plug flow. An effectiveness factor quantifies the internal mass transfer resistance within the catalyst. Further, the endothermic reforming reaction system is coupled with ethanol combustion externally to have an energy efficient process targeting an autothermal state. This arrangement of coupling permits regulating the operating conditions of two sections independently.

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