Research article

Methane steam reforming at low steam to carbon ratios over alumina and yttria-stabilized-zirconia supported nickel-spinel catalyst: Experimental study and optimization of microkinetic model

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A B S T R A C T

An experimental work to acquire reaction kinetic data of methane steam reforming (MSR) to produce syngas was carried out over alumina and yttria-stabilized-zirconia (YSZ) supported nickel-spinel catalyst (Ni-spinel). With the aim of making MSR more energy efficient, the catalyst was tested at 1.25 and 1.50 steam to carbon (SC) ratios, slightly higher than the stoichiometric ratio of 1.0 but far less than normally considered 3.0. The experiments were conducted at isothermal plug-flow conditions and at near atmospheric pressure in a laboratory scale quartz reactor for five different space times (STP) between 55 ms and 277 ms at three different temperatures of 973 K, 1073 K, and 1123 K. Reaction kinetic data of MSR over Ni-spinel catalyst are presented in terms of methane conversion and products yield or selectivity. To simulate measured kinetic data in a 1D plug-flow reactor model, a surface microkinetic model of MSR over nickel based catalyst was adopted from the literature and validated by optimizing the kinetic parameters of the most influential elementary reaction steps. A stepwise approach based on a partial equilibrium analysis and a local sensitivity analysis was implemented to scrutinize the most influential elementary reaction steps. With the adjustment of only 12 parameters out of 78, the optimized microkinetic model predicted the exit flow rates of chemical species accurately for the entire operating space. Adsorption of H_2O, desorption of $H_2(s)$, and reaction pairs of surface dehydrogenation of $CH_4(s)$ and $CH_2(s)$ were found to be the most influential reaction steps for the studied operating conditions. Surface coverages of $H(s)$, $CO(s)$ and $H_2O(s)$ were increased in the case of optimized microkinetic model of Ni-spinel catalyst compared to the original microkinetic model. Increased surface coverage of $H_2O(s)$ in the case of optimized microkinetic model supports the experimental finding in the literature that the introduction of yttria to zirconia increases the activity of the oxygen pumping component.

1. Introduction

Syngas (H_2 + CO) plays a significant role in various catalytic processes such as Fisher-Tropsch synthesis, methanol synthesis, and hydroformylation. Hydrogen from syngas is widely used in the production of ammonia, hydrogenation processes in petroleum industry and as a clean energy carrier in fuel cells. In 2015, the global hydrogen production was amounted between 61 and 65 million metric tons and is expected to grow further [1]. Prediction suggested that hydrogen usage for sectors other than the petroleum and chemicals will grow to nearly 3.5 billion kg by 2030 [2]. Increased demand of energy due to population growth and the pressure of decarbonizing the earth's atmosphere demands the deployment of more clean energy sources such as fuel cell. It is expected that fuel cell will play a key role in combating against global pollution while transition from carbon economy to low-carbon

economy takes place. Thus, the demand of fuel cells will continue to increase along with other clean energy sources. Consequently, the demand for hydrogen, the most important fuel for fuel cells and now emerging as a universal energy carrier with energy security, will also continue to rise. Though hydrogen is considered as the most abundant fuel in the universe, pure hydrogen exists in a very limited amount on our planet. Therefore, to fulfill the demand, various methods are developed to produce hydrogen from its primary sources. Two methods are commonly in use to produce hydrogen: (1) reformation and (2) electrolysis. Reformation involves hydrogen separation from water and carbon compounds such as methane; whereas, electrolysis separates hydrogen from oxygen in water [3]. Production of hydrogen by electrolysis is not a viable choice because it requires electricity to produce hydrogen.

To produce hydrogen via reformation, methane is the desired fuel of

choice for the most fuel cells due to its lowest carbon content [4]. Recent discoveries of vast reserves of shale gas have strengthen the choice of methane as the desired fuel. Generally, the production of hydrogen rich syngas from methane is carried out by three major processes: (1) steam reforming (SR), (2) autothermal reforming (ATR) and (3) partial oxidation (POX). Among these three major processes, SR provides maximum hydrogen yield. Traditionally, the production of hydrogen is carried out over nickel (Ni) based catalysts via MSR with steam to carbon (SC) ratio of three or above to avoid carbon formation [5–10]. The SC ratio of three or above is very high compared to the reforming reaction stoichiometric ratio of one. High SC ratio dilutes the syngas content and is energetically unfavorable due to the requirements of more energy to produce excess steam in a boiler at the reactor upstream and to condense unreacted steam in a condenser at the reactor downstream. Noble metals such as rhodium and ruthenium based catalysts are more resistant than the traditional nickel based catalysts to carbon formation. However, due to excessive cost and limited availability of noble metals, it is more profitable to develop nickel based catalysts which can be more resistant to carbon accumulation and can exhibit long term stability at low SC ratios [11].

It is well established fact that supports play an equally significant role in coordination with the active metal component in the performance of catalysts. Due to the chemical bonding between a support and an active metal, the reactivity of an active metal component can be affected significantly by the choice of supports [12]. Support in catalysts provides stability and high active surface area with its porous structure, which results in a longer stability and lifespan of catalysts. Research work has identified that carbon formation on nickel based catalysts is sensitive to the acidic and the basic nature of the support. For example, support such as zirconium dioxide (ZrO_2) with strong Lewis basicity has shown a strong interaction with an active nickel which has eventually led to the formation of small nickel crystallites and suppress the carbon formation [13–17]. Support such as alumina increases acidic nature of catalysts [18]. The acidic support promotes cracking of methane and thus produce carbon [12]. Lahousse et al. [19] have reported that addition of support with basic nature to a catalyst plays a crucial role in catalyst performance by balancing Lewis acidity and hence the formation of carbon.

The use of stable support such as ZrO_2 increases thermal stability and oxygen vacancies in nickel based catalysts [20]. Along with its strong Lewis basicity, ZrO_2 is also characterized by high chemical resistance and its stable crystalline structure at wide range of operating temperature. It is found that the stability range of ZrO_2 support can be further enhanced by introducing ions of lower valence than $4+$, such as Y^{3+}, La^{3+}, Mg^{2+} and Ca^{2+} into the ZrO_2 lattice [21]. The replacement of Zr^{4+} cation with lower positive charge leads to a negative overall charge that is compensated by an increased number of oxygen vacancies. These modifications in the ZrO_2 support can activate the gaseous oxygen-producing O^{2-} or O^- species [22], for example, an adsorption of H_2O (steam in MSR). Bellido and Assaf [23] have carried out a comparative study of methane dry reforming over 5% Ni catalyst supported on ZrO_2 and 5% Ni catalyst supported on $ZrO_2 + Y_2O_3$. They have reported that modification of ZrO_2 support with the addition of Y_2O_3 has increased the specific surface area and surface oxygen vacancies. Surface oxygen vacancies could provide the active sites required for obtaining more energetic oxygen radicals and thus reduce the rate of carbon formation [23]. The Ni-spinel catalyst supported by YSZ and alumina employed in this study has been developed by Fauteux-Lefebvre et al. [24] at the Université de Sherbrooke, Québec, Canada. The Ni-spinel catalyst has shown promising potential to implement for diesel steam reforming [25], methane dry reforming [26] and naphthalene reforming [27]. The use of such catalyst in reformers provides flexibility in selecting wide range of fuels that are available at various locations to generate hydrogen and hence can further increase the usage of fuel cells.

To evaluate the performance of catalytic reactor designs, quantitative and sufficiently accurate information about the catalytic reaction rates are required based on the underlying physical and chemical phenomena. With increasing computer power, it is now possible to use first principle approach of multi-step microkinetic model to understand the catalytic reactions in terms of elementary steps and their relationships with each other [28]. Chemical reaction rates can also be evaluated by applying a global kinetic approach [5,7]. In the global kinetic approach, kinetic parameters are determined based on experiments carried out at specific operating conditions and with prior knowledge of a rate determining step (RDS) [29]. Hence, the applicability of the kinetic parameters obtained via global kinetic approach is valid within those conditions only. In reality, all chemical reactions proceed via many elementary reaction steps, e.g. MSR involves: (1) adsorption of methane (CH_4) and steam (H_2O) at the catalyst surface from the gas-phase, (2) surface reactions of the adsorbed species; resulting surface species may participate further into intermediate surface reactions and (3) desorption of final products hydrogen (H_2) and carbon monoxide (CO) from the catalyst surface to the gas-phase. Therefore, all chemical reactions can be studied by elementary reaction steps. MSR involves many intermediate reaction steps, where multiple reactions can be in equilibrium at the same time and hence it is possible that several paths to the desired product formation can exist [30]. Existence of several possible paths to the product formation makes it difficult to decide a single rate determining step (RDS) even for catalysts prepared using the same active metal component. For the development of reaction rate expressions using global kinetic approach, a knowledge of RDS is prerequisite. Hence, different global rate expressions are required to predict the performance of MSR over catalysts that are prepared using the same active metal component. Whereas, microkinetic approach does not require priori knowledge of the RDS and hence it may be implemented to predict the performance of MSR carried out over different catalysts that are prepared using the same active metal component after optimizing the kinetic parameters of the most sensitive reaction steps.

The objectives of this work were to obtain effective kinetic data of methane steam reforming (MSR) for low SC ratios at different temperatures over the Ni-spinel catalyst and to optimize the kinetic parameters of a microkinetic model. To simplify the kinetic model development stage and optimization procedure, a surface microkinetic model of MSR over a nickel-alumina (Ni/Al_2O_3) catalyst, developed by Maier et al. [31] was adopted. The surface microkinetic model of Maier et al. [31] was validated against the experimental data of MSR over the Ni-spinel catalyst by optimizing the kinetic parameters of the most influential elementary reaction steps that were scrutinized based on a partial equilibrium analysis (PEA) and a local sensitivity analysis (LSA).

2. Experimental

2.1. Ni-spinel catalyst

The Ni-spinel catalyst for which the reaction kinetic data collected in this work was developed and supplied by Fauteux-Lefebvre et al. [24,25] from the Université de Sherbrooke, Québec, Canada. Fauteux-Lefebvre et al. [25] prepared the catalyst by the wet impregnation method. Al_2O_3 (50%) and YSZ (50%) ($Y_2O_3(7\%) + ZrO_2$) support was prepared by mixing the two powders mechanically. Mean powder size of Al_2O_3 was 40 µm and YSZ powder size distribution had an upper limit of 20 µm. The Al_2O_3 and YSZ powder was impregnated with a hexahydrate nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) aqueous solution (for 5% weight nickel (Ni) load in the final formulation) [24]. The mixture was stirred for 90 min at room temperature followed by heating for 60 min at 368.15 K to vaporize the water. The resulting impregnated powder was dried overnight at 378 K. The impregnated powder was crushed-comminuted and calcined at 1173.15 K for 6 h to form the Ni-spinel ($NiAl_2O_4$). The final objective of this work in future is to apply a thin coating of the Ni-spinel catalyst on the surface of a fecralloy plate to