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Insights into the effect of catalyst loading on methane steam reforming and controlling regime for metallic catalytic monoliths

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ABSTRACT

The influence of Ru/La–Al₂O₃ catalyst loading (100–200 mg) was investigated over high cell density Fecralloy[®] monoliths (461 cpsi, 1367 cpsi) for methane steam reforming (SMR). A uniform and well-attached catalyst layer was developed by in-situ washcoating method and the developed catalysts were analyzed by using various physico-chemical characterization techniques. The results confirmed the impact of catalyst loading on the geometric and hydraulic properties of monoliths, and methane conversion was improved by increasing both the catalyst loading and cell density. As per characteristic time analysis, no external and washcoat diffusion regimes were observed and SMR was found to be in kinetic controlling regime. The methane conversion was still limited by the amount of catalyst (200 mg) deposited onto the monoliths (40.9 μm for 461 cpsi, 26.9 μm for 1367 cpsi) which demonstrated the potential to deposit more catalyst up to the transition point of washcoat diffusion limitations. For same washcoat thickness of ~20.6 μm, the higher cell density 1367 cpsi monolith showed better catalytic activity towards SMR as compared to 461 cpsi monolith and this improvement is more prominent at lower temperature with a value of 13.6% higher methane conversion at 600 °C, WHSV = 55 NL h⁻¹ g_{cat}⁻¹ and S/C = 3.0.

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Introduction

Hydrogen energy is expected to play an important role in sustainable energy future by addressing the issues of

pollution, climate change, and energy supply [1–4]. In a transition towards hydrogen economy, water electrolysis and methane steam reforming (SMR) are the most feasible technologies for supplying hydrogen and building hydrogen infrastructure [5,6]. In realization of economic water

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electrolysis, the main barriers are intermittent renewable electricity supply, higher capital cost, and uncertainty in future cost and efficiency improvements [7]. However, SMR is the most economical and efficient industrial process which is a feasible option for small scale onsite hydrogen production [8–10]. In chemical and petrochemical sectors, SMR is the main process for 48% hydrogen supply worldwide [11], using packed bed tubular reformers operating at 500–950 °C and 5–25 bar over Ni based pellet catalysts [12–14].

For methane steam reforming, noble metals are more active and stable than Ni catalyst with a relative activity sequence of Rh ~ Ru > Ir > Pt ~ Pd [15–17]. Considering process economics, Ru washcoated monoliths are the most economically viable for small scale reformers if the noble metal recovery is factored in along with ability to operate at higher space velocity, structural stability, lower pressure drop, stability, and duty cycle requirement. However in the presence of oxygen, ruthenium oxidizes to solid RuO₂ at ~400 °C and further forms toxic volatile oxides (RuO₄ and RuO₃) at higher temperature > 720 °C [18], which require a special care with control strategy [19]. This also makes Ru less attractive for combustion and oxidative steam reforming. Additionally, upstream desulfurizer is required because of its sensitivity towards sulfur poisoning. Nevertheless, Ru is extensively being studied [20–22] for methane steam reforming. Berman et al. [23] studied the kinetics of SMR reaction over 2% Ru/ α -Al₂O₃ promoted with MnO₂ to develop solar reformers operating at higher temperatures (1000–1100 °C), and found stable catalytic activity even after thermal stability at 1100 °C for 100 h. Noble metal catalysts are resistant to carbon formation [15] as compared to Ni catalyst under the same operating conditions, and the reformer can be operated at lower S/C ratio [24], which makes the process economics even more feasible. The activity, selectivity and stability of a catalyst depends strongly on the thermal stability of support material [25]. γ -Al₂O₃ is an important catalyst support with high surface area, favorable pore volume, and wide pore structure for fast transport of gaseous species. On the other hand it undergoes sintering and phase transformation at higher temperature (>800 °C) to low surface area alumina (δ -Al₂O₃ → θ -Al₂O₃ → α -Al₂O₃) [26–28]. The stability of alumina can be enhanced by the incorporation of lanthanum oxide which inhibits thermal sintering (<1050 °C) even in the presence of steam and also shifts the phase transformation temperature by 100 °C by the nucleation of cubic lanthanum aluminate (LaAlO₃) on alumina surface [29–32].

In industrial reformers, the reaction is controlled by significant heat and mass transfer limitations with catalyst effectiveness factor of less than 5% [33] thus not optimal for scaling down [34,35]. Noble metal washcoated monoliths demonstrated a potential of 10 times reduction in reactor size as compared to Ni based conventional packed bed reformer [19] by allowing tremendous heat and mass transfer rates [36–39]. The higher cell density monolith provides a high geometric surface area to deposit higher catalyst loading in the form of thin catalyst layer with 1–2 order of lower diffusion length, which decreased the reaction time from seconds to milliseconds [40–43]. For strongly endothermic SMR reaction, metallic monolith is the preferred substrate choice because of good thermal conductivity, higher cell density, lower pressure drop, ease of manufacturing, and possibility of

complex flow patterns. FeCrAl alloy is the most feasible Al containing ferritic steel with compositions of 70–90% Fe, 10–25% Cr, 4–5% Al and <1% minor components (Y, Ti, Zr, Ce and Hf). Under high temperature oxidation treatment, aluminum in FeCrAl alloy migrates to the surface and forms a thin, rough and adherent α -Al₂O₃ whiskers which serves as protective layer to avoid further oxidation and also as intermediate layer for mechanical anchoring of catalyst layer [44–46].

The catalyst layer is coated onto the monolith surface and active metal is distributed throughout the catalyst support. For a given reaction, various controlling regimes (kinetic, washcoat diffusion, and external mass transfer) may be observed which depend upon fluid properties, operating conditions, catalyst layer characteristics, and geometric properties [47,48]. The characteristic time analysis [49–51] is very helpful to study the influence of catalyst loadings on the transport and chemical processes involved in coated monoliths. The total flow time of reaction mixture through the channel in axial direction is called as characteristic residence time (t_c) [52]. Whereas the reactants also diffuse through the bulk fluid in transverse direction to the washcoat surface and the transfer time is described as characteristic external mass transfer time (t_{ext}) [53]. Then the reactants diffuse inside the washcoat to reach the catalyst surface and the diffusion time is defined as characteristic washcoat diffusion time (t_{wd}). After reaching the catalyst surface, the speed of reaction is described by the characteristic reaction time (t_r) [54].

The optimization of expensive catalyst loading and cell density of monolith is necessary for high throughput per unit volume. For small scale reformers, the catalyst layer thickness of ~200 μ m over structured catalysts [55,56] provides higher activity per unit volume [57] but with certain loss in catalyst productivity. At the same time, a thicker layer (>10 μ m) might induce internal mass transfer limitation and lower the global or observed rate of reaction [58]. Therefore the optimization of expensive catalyst loading and structure geometry is necessary along with the knowledge of space velocity [59] to describe conversion of hydrocarbon fuels. In a modelling study, Stutz and Poulikakos et al. [60], have demonstrated the existence of an optimum washcoat thickness and its effect on methane partial oxidation over Rh based catalyst for syngas production. In another modelling study, Cao et al. [61] carried out a numerical analysis to study the effect of washcoat properties on SMR and found out that higher catalyst loadings (washcoat thickness < 75 μ m) considerably increased reactor throughput but at the expense of certain loss in productivity due to internal mass transfer limitations. In our previous experimental study [62], the impact of catalyst loading (100–250 mg) and cell density (100 cpsi and 170 cpsi of alumina monolith) was investigated for methane steam reforming which confirmed their influence on catalytic, geometric, and hydraulic properties along with the controlling regimes of kinetic limiting, washcoat diffusion limiting and the availability of less contact time. The optimum values of washcoat thickness were found to be 58.5 μ m and 78.9 μ m with 100 mg and 150 mg of catalyst loadings over 100 cpsi and 170 cpsi monoliths, respectively. For the development of smaller reformer, the catalyst loading per unit volume can be increased by using a high cell density monolith with higher geometric surface while maintaining a thin catalyst layer. As

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