

Experimental study of the intrinsic kinetics of steam methane reforming on a thin Ni coating

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Highlights

- New Ni-based shapeable catalyst for structured reactors
- Experimental study of intrinsic kinetics in a specifically designed micro-reactor
- Intrinsic kinetics of methane steam reforming and water-gas shift reactions determined

1. Introduction

Steam methane reforming is the most widely practiced industrial process for the production of hydrogen and syngas from methane. The reactions are endothermic and conventionally carried out in packed bed reactors suspended in a furnace. The reactor performance is limited by heat transfer, pressure drop and intra-particle diffusion limitations. Structured catalytic reactors are a promising technology in order to intensify the process. When properly designed, the structure provides increased heat transfer efficiency and reduced pressure drop [1-2]. The use of a thin catalyst coating allows increased catalyst effectiveness factors, but the application of such a coating that is expected to be stable under severe operating conditions is challenging. Alloy Surfaces Co. Inc. developed an intrinsically bound thin-layered catalyst adhered on a metal substrate. The material has a uniform coating thickness which allows physical structuring into the desired geometry and avoiding a posteriori washcoating. The intrinsic kinetics of steam methane reforming and water-gas shift reactions were experimentally studied on this new catalyst and a comparison with the kinetics of a conventional SMR catalyst was made. Finally, intra-particle diffusion limitations were studied to estimate an optimal coating thickness.

2. Methods

The kinetics was studied in an experimental tubular packed bed micro-reactor. The reactor was specifically designed and operating conditions selected to have plug flow, isothermal operation, negligible pressure drop and negligible interfacial and intra-particle transport limitations [3]. Methane steam reforming experiments were carried out at temperatures ranging from 450 and 600°C, pressure between 1 and 25 bars and steam-to-carbon ratios between 3 and 5. Hydrogen was co-fed and the catalyst bed diluted to guarantee isothermal operation. Methanation and water-gas shift experiments were performed at temperatures between 300 and 450°C and pressure between 1 and 25 bars.

Different reaction mechanisms with potential rate determining steps were proposed and rate equations were derived following the Langmuir-Hinshelwood-Hougen-Watson approach. The integral method of kinetic analysis was applied. Discrimination between the models and estimation of the rate parameters followed from regression and statistical and physicochemical testing [4-5].

3. Results and discussion

Among 35 sets of rate equations based on assumed reaction mechanisms and rate determining steps, only six were thermodynamically consistent. Based on F-test and R^2 value, the reaction mechanism and rate determining steps and corresponding rate expressions found for the conventional SMR catalyst by Xu and Froment (1989) were confirmed [6]. Figure 1 shows a comparison of experimental and predicted curves of methane (a) and carbon dioxide (b) molar conversions versus the space time. Comparison of the activity of the thin-layered ASC catalyst and conventional SMR catalyst shown significantly increased activity of the thin-layered catalyst (per kg catalyst basis), partially explained by its higher Ni-content. Under typical

commercial operating conditions, a 10 to 20 micron coating is optimal, a thicker coating leading to significantly lower catalyst effectiveness factors.

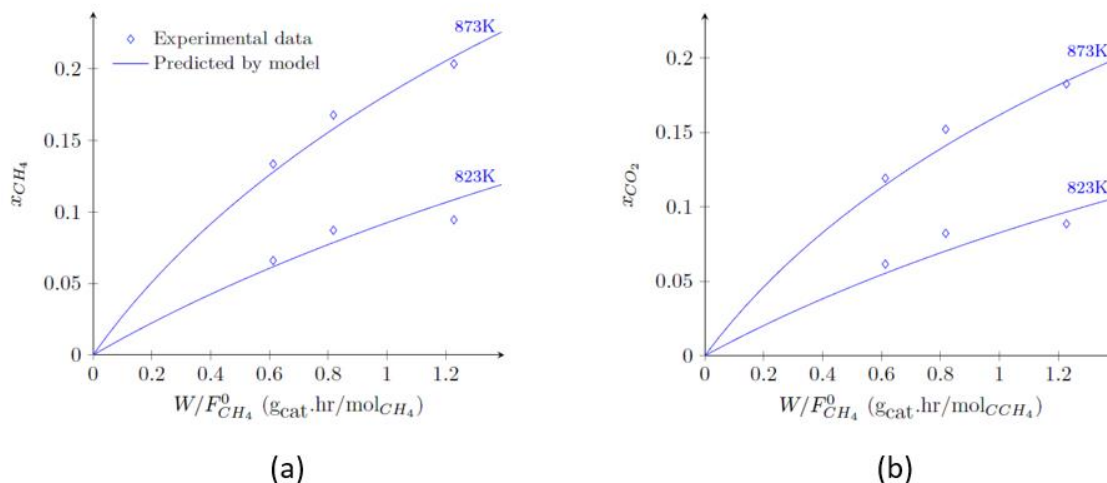


Figure 1. Molar conversions of CH₄ (a) and CO₂ (b) versus space time, at $p_t = 3$ bar and steam to methane molar ratio = 3,5.

4. Conclusions

An experimental study of steam methane reforming on an adherent nickel-based coating on a metal substrate developed by ASC was carried out. An experimental fixed bed reactor was designed and operating conditions selected to allow measurements of the intrinsic reaction kinetics. Discrimination between different kinetic models and the corresponding sets of rate equations followed from physicochemical and statistical testing. The retained model confirms the mechanism and rate determining steps found by Xu and Froment (1989) for a conventional SMR catalyst. The thin-layered ASC catalyst is shown to be significantly more active than the conventional SMR catalyst, with an optimal catalyst coating thickness of 10 to 20 micron.

References

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Keywords

Thin layered catalyst ; Structured catalytic reactor ; Steam methane reforming ; Intrinsic reaction kinetics