



## Surface Carbon Formation and its Impact on Methane Dry Reforming Kinetics on Rhodium-Based Catalysts by Operando Raman Spectroscopy

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### Significance and Relevance

A mechanism for carbon deposition and its impact on Methane Dry Reforming (MDR) kinetics using rhodium-based catalysts is presented. By integrating Raman spectroscopy with kinetic analysis in an operando-annular reactor under strict chemical conditions, we discovered that carbon deposition on a Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst follows a nucleation-growth mechanism strongly influenced by the CO<sub>2</sub>/CH<sub>4</sub> ratio and the CH<sub>4</sub> concentration. This work elucidates the spatiotemporal development of carbon aggregates on the catalyst surface and their effects on catalytic performances. Furthermore, these findings prove that CO<sub>2</sub> influence on MDR kinetics is just an indirect result of carbon accumulation.

*Preferred and 2<sup>nd</sup> choice for the topic:* 1<sup>st</sup> CO<sub>2</sub> utilization and recycling, 2<sup>nd</sup> Fundamental advances in understanding catalysis

*Preferred presentation:* Oral preferred or Short Oral

### Introduction and Motivations

Methane Dry Reforming reaction (MDR) is a promising route for biogas valorization. Nevertheless, MDR industrial scalability is constrained by catalyst deactivation due to carbon deposition, a phenomenon with mechanisms and kinetic implications still under debate.<sup>1,2</sup> In our investigation, we have combined kinetic measurements in an annular reactor, time-resolved and spatially-resolved operando Raman spectroscopy to shed light on the carbon formation pathway and its kinetic consequences during MDR over Rh-based catalysts.

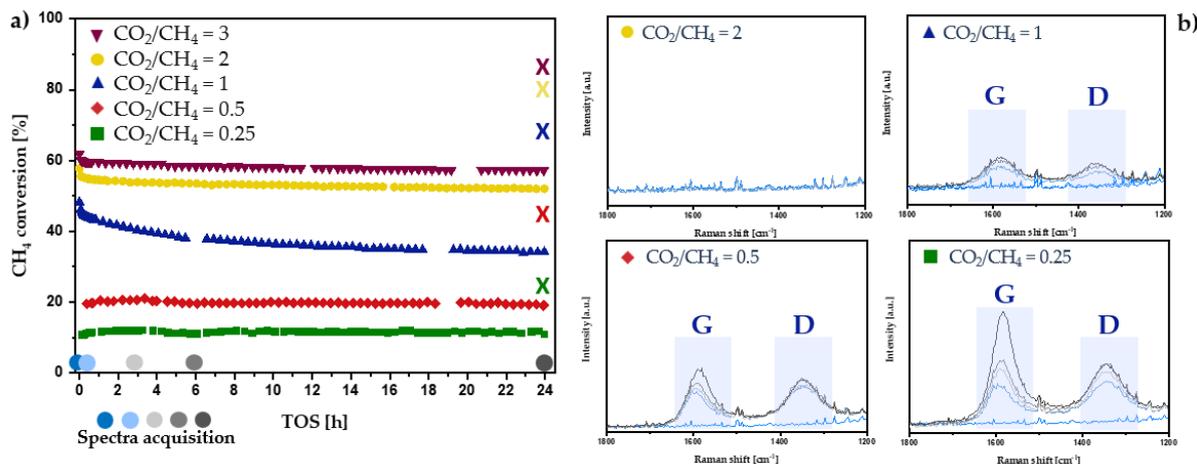
### Materials and Methods

MDR catalytic tests have been performed employing an operando-annular reactor in conjunction with Raman spectroscopy. The reactor consists of a hollow alumina tube as structural support sealed at one end and coaxially inserted in an optical-quality quartz tube. The catalyst (4 wt.% Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>), coated as a thin layer (thickness 10-30  $\mu$ m, length 20 mm) on the external surface of the alumina tube, was prepared via dry impregnation of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support with a solution of the active phase precursor (Rh(NO<sub>3</sub>)<sub>3</sub>). A sapphire window is present in correspondence to the catalytic bed to collect both time-resolved and spatially-resolved operando Raman spectra through a laser probe supported on a motorized moving stage. The Raman measurements are performed by a JASCO<sup>®</sup> NRS-4100 spectrometer equipped with a Coherent<sup>®</sup> Sapphire SF488 laser (488 nm) as an excitation source.

### Results and Discussion

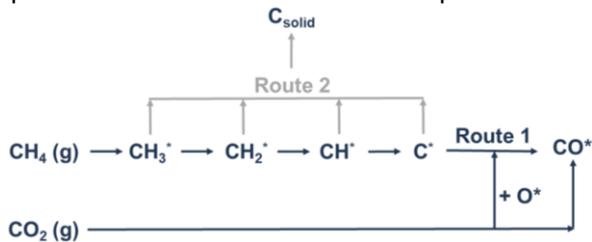
Several tests at different co-reactant-to-methane ratios (CO<sub>2</sub>/CH<sub>4</sub> between 2 and 0.25) and inlet CH<sub>4</sub> molar fractions (8 vol.% and 1 vol.%) have been performed at 600°C and atmospheric pressure to investigate the kinetic role of CO<sub>2</sub>, the mechanism of carbon formation over Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst and how these two are correlated during MDR.<sup>3</sup> The experimental evidence (Figure 1.a) shows that when CO<sub>2</sub>/CH<sub>4</sub>  $\geq$  1 methane conversion curves undergo an initial decline over time, with a slope notably influenced by the co-reactant-to-methane ratio, followed by an apparent conversion stabilization at higher times. For tests at inlet CH<sub>4</sub> 8 vol.% and ratios equal to 2 and 3 the initial slope of the curve is lower than the one observed for ratio equal to 1, while for ratios below the unity (e.g., 0.5 and 0.25) the curve is quite flat at a stationary value. As shown in Figure 1.b, Raman spectra acquired in over-stoichiometric conditions show no presence of carbon peaks (i.e. G and D peaks) over 24 h. Conversely, at stoichiometric ratio, Raman spectra revealed the formation of carbonaceous structures after 3 h of

reaction, while for sub-stoichiometric ratios Raman spectra highlight the presence of carbon peaks already after 5 minutes from the beginning of the catalytic test.



**Figure 1.** a) Experimental (symbol) and equilibrium (“X” symbol) methane conversion at different CO<sub>2</sub>/CH<sub>4</sub> ratios for MDR on 4% Rh/Al<sub>2</sub>O<sub>3</sub> catalyst at CH<sub>4</sub> = 8 vol.% during 24 h tests. T = 600°C, P = 1 atm, GHSV = 1.4x10<sup>6</sup> NL/kg<sub>cat</sub>/h; b) Raman spectra acquired before the reaction, after 5 min, 3 h, 6 h and 24 h.

Our findings indicate that the co-reactant concentration does not significantly alter the kinetics of MDR at the start of the reaction (TOS = 0 h). However, carbon deposition markedly impacts catalyst stability and activity. The deposition process, characterized by a longer timescale than the turnover rate, is strongly dependent on the CO<sub>2</sub>/CH<sub>4</sub> ratio. Specifically, at a CO<sub>2</sub>/CH<sub>4</sub> ratio of 1 or lower, carbon deposition is evident within 24 hours of operation. As proposed in Figure 2, adsorbed carbon (C\*) and CH<sub>x</sub>\* species can follow two possible routes: under CO<sub>2</sub>-rich conditions (i.e. CO<sub>2</sub>/CH<sub>4</sub> > 1), they tend to follow preferentially Route 1 leading to CO formation; instead, in a CO<sub>2</sub>-deficient environment, these species start to form solid carbon deposits via Route 2. The resulting carbon aggregates decrease the availability of Rh surface, leading to deactivation and providing an apparent kinetic dependence on CO<sub>2</sub>. Moreover, spatially-resolved operando Raman spectra has unveiled a descending trend of carbon deposits along the reactor axial coordinate, while tests performed with the addition of a small fraction of O<sub>2</sub> (0.8 vol.%) proved to inhibit carbon species deposition and growth.



**Figure 2.** Proposed pathway for C-species formation

All in all, this work highlights the pivotal role of a multi-technique approach in deepening our understanding of catalytic processes, especially when intrinsic kinetics are obscured by deactivation.

## References

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