

Operando-Raman Kinetic Analysis of Surface Carbon Formation and Its Kinetic Consequences on Methane Dry Reforming Kinetics on Rh-Based Catalysts

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Highlights

- CO₂/CH₄ ratio and inlet CH₄ molar fraction strongly affect carbon deposition
- Apparent CO₂ kinetic dependence is explained in terms of carbon formation
- Microkinetic modeling effectively predicts the loss of available Rh surface

1. Introduction

Climate change, a challenging task of the current century, has lately stimulated interest in the sustainable production of chemicals and fuels. In this scenario, the industrial application of Methane Dry Reforming reaction (MDR) offers a promising route for the valorization of biogas and CO₂-rich natural gas. Notwithstanding all the promising advantages of MDR, its scalability is constrained by the deactivation process due to carbon deposition, a phenomenon whose mechanisms and kinetic implications are still under debate [1-2]. This study aims to unravel the relationship between operational conditions, the rate and structure of carbon deposition, and catalyst activity. In our investigation, we have applied a hierarchical multiscale approach that combines precise kinetic measurements, operando spectroscopy and structure-dependent microkinetic modeling to shed light on the carbon formation pathways during MDR over Rh-based catalysts.

2. 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/ α -Al₂O₃), coated as a thin layer (thickness 10-30 μ m, length 20 mm) on the external surface of the alumina tube, was prepared via dry impregnation of the α -Al₂O₃ with a solution of the active phase precursor (Rh(NO₃)₃). 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 @ NRS-4100 spectrometer equipped with a Coherent@ Sapphire SF488 laser as an excitation source (laser wavelength: 488 nm).

The microkinetic analysis of MDR reacting system was carried out employing a C1 single-site microkinetic model [3]. It includes 80 elementary steps and 13 surface species, and it is based on a hierarchical approach that combines semi-empirical (UBI-QEP) and first-principles (DFT) methods. Due to the peculiar features of the annular reactor, the system is simulated using a steady-state isothermal 1D pseudo-homogeneous PFR.

3. Results and discussion

Several tests at different co-reactant-to-methane ratios (CO₂/CH₄ between 2 and 0.25) and inlet CH₄ molar fractions (8 vol.% and 1 vol.%) have been performed at 600°C and atmospheric pressure to investigate the kinetic role of CO₂, the mechanism of carbon formation over Rh/ α -Al₂O₃ catalyst and how these two are correlated during MDR.

The experimental evidence (Figure 1.a) shows that when CO₂/CH₄ \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 CH₄ 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.

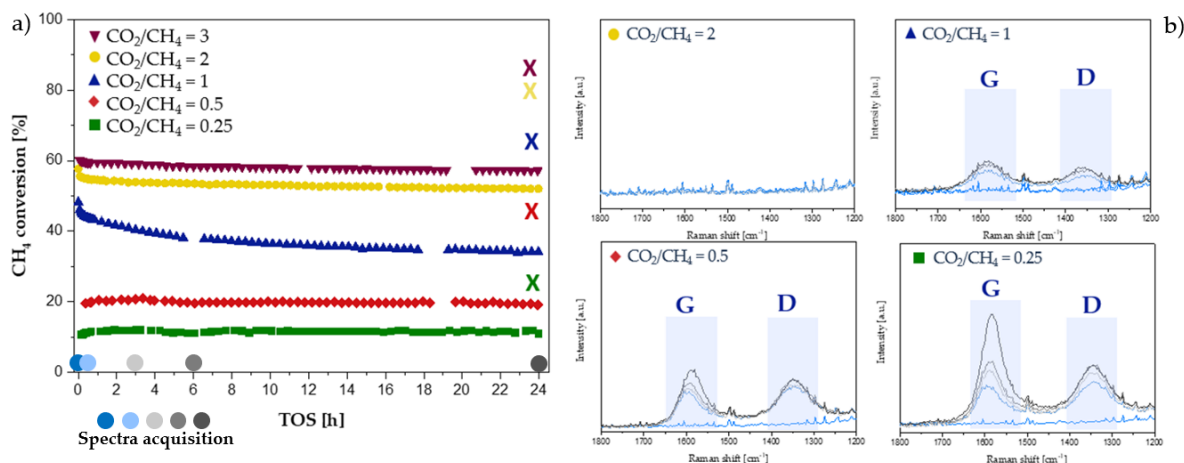


Figure 1. a) Experimental (symbol) and equilibrium (“X” symbol) methane conversion at different CO₂/CH₄ ratios for MDR on 4% Rh/Al₂O₃ catalyst at [CH₄] = 8 vol.% during 24 h tests. T = 600°C, P = 1 atm, GHSV = 1.4x10⁶ NL/kg_{cat}/h; b) Raman spectra acquired before the reaction, after 5 min, 3 h, 6 h 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 CO₂/CH₄ ratio. Specifically, at a CO₂/CH₄ ratio of 1 or lower, carbon deposition is evident within 24 hours of operation. As proposed in Figure 2, adsorbed carbon (C*) can follow two possible routes: under CO₂-rich conditions (i.e. CO₂/CH₄ > 1), adsorbed C* species tend to follow preferentially Route 1; instead, in a CO₂-deficient environment, C* 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 CO₂. Additionally, our

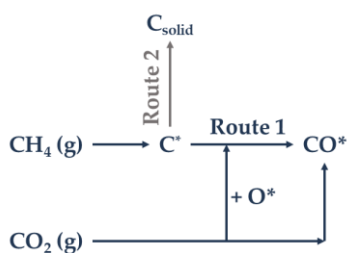


Figure 2. Possible pathways for C* adsorbed species

operando-Raman data has unveiled the evolution of G and D peaks at the catalyst surface, which follow different dynamics: notably, the G peak becomes more dominant over time, indicating the formation of less reactive carbon aggregates that contribute to the permanent catalyst deactivation.

In addition, a structure-dependent microkinetic analysis of Figure 1 data and additional experimental tests performed at lower CH₄ inlet concentration (1 vol.%) provided a quantitative estimation of the reduction of Rh surface availability due to carbon deposition. As the CO₂/CH₄ ratio decreases the predicted availability of active surface decreases as well for all the operating conditions investigated, which is coherent with the enhancement of carbon formation expected at lower co-reactant-to-reactant ratio. Moreover, at a fixed ratio, the available Rh surface is always higher for 1 vol.% tests, due to the lower number of carbon precursors fed to the reactor. Significantly, for the test performed at CO₂/CH₄ = 2 and inlet CH₄ 1 vol.% the model predicts that the fraction of active sites covered by carbon is negligible. These results are in full agreement with the kinetic and spectroscopic evidence from the experimental campaign.

4. Conclusion

Employing a multi-technique approach, the apparent CO₂ kinetic dependence of MDR reacting system was explained in terms of a catalyst surface dynamic due to carbon deposition. In addition, the resulting decrease of available Rh-surface was quantitatively studied through a microkinetic analysis.

References

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Keywords

“Methane dry reforming”, “Carbon deposition”, “Operando-Raman spectroscopy”, “Microkinetic modeling”