

KINETIC ANALYSIS OF DRY REFORMING OF METHANE CATALYZED BY Rh (111)

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The dry reforming of methane (DRM) is a reaction of high interest, using two greenhouse gases, CO₂ and CH₄, to produce the valuable syngas (H₂/CO). However, it requires high temperatures and suffers from competitive reactions, such as the reverse water gas shift reaction (RWGS) and coke formation.[1] In this contribution, following our previous study on Ru(0001) [2], we combined density functional theory (DFT) calculations with kinetic Monte Carlo (*k*MCC) simulations to study the DRM reaction and its related processes on the Rh (111) surface, one of the most active monometallic catalysts for this reaction, at 700-825 K. The *k*MCC results reveal that the competitive RWGS reaction does not affect the final ideal ratio (H₂/CO = 1) between the main products of the DRM catalyzed by Rh (111) under all studied temperatures. Further, the formation of COOH* intermediate is negligible, in agreement with the DFT calculations with a most favorable CO₂ direct activation (CO₂* → CO* + O*), meaning the CO₂ activation assisted by H₂ (CO₂ + H₂ → COOH*) does not contribute at all toward the RWGS reaction. The formation of the DRM main products (H₂ and CO) proceeds mainly through the **CH* oxidation** pathway (CH* + O*), as shown in **Figure 1**, which cannot be inferred from DFT calculations. We performed the Degree of Rate Control analysis proposed by Campbell [3], which suggests the CO₂ dissociation step is the only rate-determining step of the DRM catalyzed by Rh (111). Our calculated apparent energy activation using the Arrhenius equation from simulations at five different temperatures equals 53 kJ·mol⁻¹.

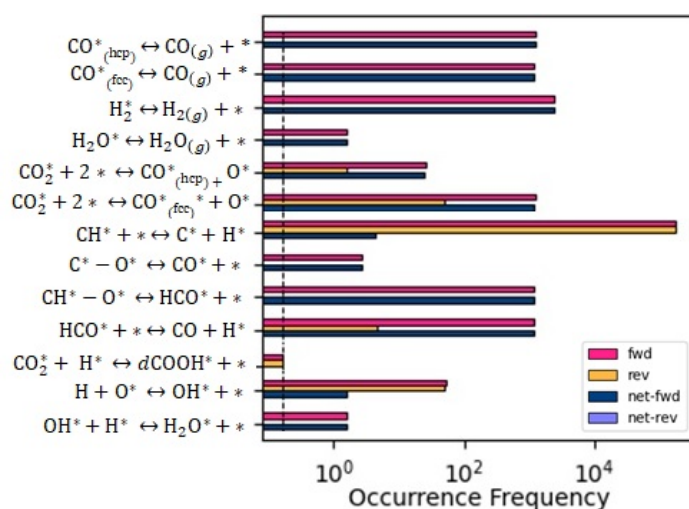


Figure 1. CO formation processes and their frequencies for the DRM on Rh (111) at $P = 1$ bar and $T = 700$ K for an initial CH₄/CO₂ ratio of 1:1.

[1] Fan, M. S.; Abdullah, A. Z. and Bhatia, S. *ChemCatChem* **2009**, *1*, 192-208.

[2] a) Campbell, C.T. *Topics Catal* **1994**, *1*, 353; b) Campbell, C.T. *ACS Catal.* **2017**, *7*, 2770– 2779.

[3] Díaz López, E. and Comas-Vives, A. *Catal. Sci. Tech.*, **2022**, *12*, 4350-4364.