

FIRST PRINCIPLES INSIGHTS INTO THE WATER-GAS-SHIFT REACTION ON RHODIUM

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Summary

Guided by a previous UBI-QEP based microkinetic analysis we perform a density-functional theory study of the water-gas shift reaction on Rh surfaces. We explore the energetics of the elementary steps at different surface coverages and compare with the predictions from the semi-empirical UBI-QEP method. On the one hand, this enables a rational refinement of the microkinetic model. On the other hand, it is the knowledge from the latter that identifies the critical points and helps to focus the first-principles calculations.

Keywords

Reaction Path Analysis, Multiscale Analysis, Computational Catalysis, Hydrogen Production

Reforming technologies on noble metals are at the heart of converting fuels and biofuels to syngas and hydrogen for energy applications. Among these technologies, catalytic partial oxidation (CPO) is particularly appealing due to the compactness of the reactors that are ideally suited for decentralized energy production units. Particularly crucial for the technology development and design is the understanding of the catalytic surface chemistry¹.

Recent works, both experimental^{2,3} and theoretical^{4,5}, have highlighted the main reaction pathways involved in this process. In particular, a UBI-QEP based modeling of the surface kinetics^{4,6} predicts that the partial oxidation of CH₄ does not occur at the molecular level. Rather CPO turns out to be the result of different chemical processes in different regimes, giving rise to up to three reaction zones⁴: a deep combustion of methane, followed by a zone where direct formation of syngas in parallel with catalytic combustion occurs, and finally a steam reforming (SR) and water-gas-shift reaction (WGS) zone, when oxygen is no longer available.

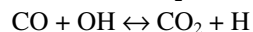
Despite this progress, a complete understanding of the catalytic mechanism has not yet been achieved. In particular, a challenging open issue is related to the kinetic role of CO₂ in CPO, that is ultimately related to role of the WGS in the process^{5,7,8}. These aspects are very relevant for applications that involve the utilization of CO₂ in CPO. In particular, in the field of power generation, interest has recently grown to conduct CH₄ CPO in catalytic burners under ultra-diluted, O₂-lean conditions^{9,10} in the presence of large amounts of H₂O and CO₂ recycled from exhaust streams. Similar recycling may also take place in solid

oxide fuel cells with direct internal reforming, where CPO can be exploited for the start-up and sustained in the presence of CO₂ and H₂O during low-power operations¹¹.

Main questions and points of discussion concerning the mechanism are related to the involved elementary steps and to the assessment of the energetics/reaction rates at different operating conditions. Corresponding issues are all suitably addressed at the level of first-principles calculations, with density-functional theory (DFT) presently offering the best compromise between accuracy and computational cost for studies at extended metal surfaces.

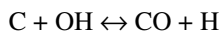
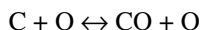
In this contribution, starting from the previous knowledge of the UBI-QEP based analysis^{4,5}, we perform a systematic first-principles investigation of the identified key-issues to allow for a fundamental understanding of the surface chemistry and a rational refinement of the semi-empirical microkinetic model through the possible insertion of features identified by the first-principles modeling.

Specifically, we perform a periodic DFT-based investigation of the key-elementary steps involved in the WGS reaction on Rh surfaces. As a first step, we consider low index planes (111), (110), (100) as the most abundant surfaces of fcc nanoparticles. Our attention is focused on the assessment of the different oxidation mechanisms of CO and C, both via OH and via O, namely:



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and



Employing differently sized surface unit-cells, the energetics of these elementary steps is explored at different surface coverages. Apart from gaining a fundamental understanding of the minimum energy pathways and the involved transition states, this enables a systematic first-principles check of the predictions from the preceding semi-empirical UBI-QEP based approach. The significance of this study stands therefore in the combination of the global knowledge from the microkinetic model (useful for identifying the critical points associated to that description) with a systematic first-principles DFT-based investigation, bridging between methodologies that are hitherto still rather disjointly developed and applied. In particular, this study provides an example of how within a multiscale-hierarchical approach, DFT studies can be effectively focused on narrowly defined aspects and specific steps of the overall mechanism.

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