344a Methane Oxidation on Noble Metals for Hydrogen Production: a Hierarchical, Multiscale Microkinetic Modeling Approach

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Abundant feedstocks of natural gas can be used for power generation, chemical synthesis, and H_2 production for fuel cell applications. Steam reforming of methane on Ni is a well-established process for H_2 production. However, since the emergence of short contact time reactors, catalytic partial oxidation (CPOX) of methane on noble metal catalysts is extensively being explored. CPOX is a compact and low capital expenditure technology because it doesn't require heat input due to its exothermicity and is able to produce high methane conversion and syngas selectivity on noble metals. Nonetheless, commercialization of CPOX is hindered by a lack of fundamental understanding of the underlying chemistry and development of predictive models. A number of microkinetic models have been proposed in the literature for methane CPOX on various noble metals, but in most cases, their performance is limited to a narrow range of operating conditions due to tuning against a single type of experiment, lack of important reaction pathways, lack of adsorbate-adsorbate interactions, and thermodynamic inconsistency. Consequently, the underlying pathways of methane oxidation at short contact times are still unclear.

In this work, we present comprehensive elementary-like reaction mechanisms for methane oxidation on noble metals. Surface science experimental data, semi-empirical methods, and first principles techniques are efficiently integrated together for rate parameter estimation. Based on a hierarchical multiscale parameter refinement approach, important rate parameters are more accurately estimated using quantum mechanical density functional theory. Thermodynamic consistency is ensured over a wide temperature range by including temperature effects using statistical mechanics and constraints-based optimization. These mechanisms are capable of capturing the basic chemistry of CO and H_2 oxidation, the coupling between CO and H_2 fuels arising in water-gas shift and preferential oxidation of CO, as well as methane combustion, reforming, partial oxidation, and oxygenate decomposition. Our noble metals mechanisms predict a transition from methane partial and total oxidation, whose specific paths and products depend on catalyst, to reforming as a function of reactor length. Furthermore, evidence of homogeneous chemistry at high pressures is demonstrated under certain conditions. The mechanisms are rigorously validated against multiple variables including effects of composition, dilution, temperature, pressure, and flow rate. These predictions are in excellent agreement with spatially resolved experimental data. Optimal conditions of operation leading to syngas production for on-board hydrogen production will also be discussed.