

Microkinetic analysis of water-promoted CO oxidation, water-gas shift, and preferential oxidation of CO on Pt for hydrogen generation

Ashish B. Mhadeshwar and Dionisios G. Vlachos

Department of Chemical Engineering and Center for Catalytic Science and Technology,
University of Delaware, Newark, DE 19716-3110, USA

Hydrogen based proton exchange membranes (PEM) fuel cells show good potential for production of electricity. However, widespread commercialization of PEM fuel cells will depend on cheap and environmentally benign production of hydrogen. Currently, hydrogen is mainly produced from syngas by the water-gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$) followed by preferential oxidation (PROX) of CO. Extensive work has been devoted to the catalytic oxidation of H_2 and CO on transition metals, and several microkinetic models, consisting of elementary reaction steps, have been proposed, especially on Pt. Yet, microkinetic models that could be used in the design of WGS and PROX are still lacking. There are several generic shortcomings of the existing microkinetic models. In particular, thermodynamic inconsistency of kinetic parameters is common in nearly all POX models of syngas. Another specific problem to these chemistries is the synergetic effects, arising from using mixtures of CO and H_2 , which have not been exploited yet as much. An example of such coupling is the production of the carboxyl (COOH), via the recombination reaction ($\text{CO} + \text{OH} \rightarrow \text{COOH}$), and its subsequent decomposition ($\text{COOH} + \text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ or $\text{COOH} \rightarrow \text{CO}_2 + \text{H}$). Recent temperature programmed reaction (TPR) results (Bergald *et al.*, Surface Science, 495, 2001, L815) have clearly shown that even minute fractions of H_2O have an autocatalytic effect on the CO oxidation by oxygen, an example of the aforementioned coupling.

In this work, we will present a comprehensive surface reaction mechanism on Pt that is capable of describing CO oxidation, H_2 oxidation, WGS, PROX of CO, and the promoting role of H_2O on the CO oxidation reasonably well. This mechanism consists of CO oxidation chemistry, a surface reaction mechanism for H_2 oxidation on Pt, and coupling reactions between the CO and H_2 chemistries included for the first time. Thermodynamic consistency, which is shown to be essential for WGS, is ensured in all steps of the entire mechanism. The CO- H_2 coupling via the $\text{CO} + \text{OH}$ reaction, which may involve the direct CO_2 formation, $\text{CO} + \text{OH} \leftrightarrow \text{CO}_2 + \text{H}$, as well as an indirect pathway via the carboxyl intermediate, is explored. The role of coupling in capturing the promoting effect of H_2O on the CO oxidation TPR experiments at low temperatures as well as the overall speed of the WGS and PROX reactions will be discussed. The relative significance of different reaction pathways will be presented.