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Hierarchical, multiscale surface reaction mechanism development: CO and H_2 oxidation, water–gas shift, and preferential oxidation of CO on Rh

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Abstract

A hierarchical multiscale parameter refinement approach was used to develop microkinetic models for CO and H_2 oxidation, and CO–H_2 coupling for water–gas shift (WGS) and preferential oxidation (PROX) of CO on Rh. The rate parameters were estimated with a combination of quantum mechanical density functional theory (DFT), the semi empirical unity bond index-quadratic exponential potential method, and transition-state theory. To improve the predictive ability, selected pre-factors of the CO and H_2 oxidation reaction mechanisms were optimized against multiple experimental data sets, such as ignition, molecular beam, and laser-induced fluorescence. Thermodynamic consistency of rate parameters was ensured over a wide temperature range by a combination of statistical mechanics and constraints-based optimization. DFT calculations were used to estimate cross adsorbate–adsorbate CO–H interactions. It is shown that the coupling between the two fuels arising from these interactions is essential for PROX of CO. Important reaction pathways in the WGS and PROX chemistries are discussed. For example, it is shown that the oxidation of CO by OH via the carboxyl intermediate, and not by O, is the dominant path in PROX. Thus, hydrogen acts as a "catalyst" for CO combustion under certain conditions. Finally, the mechanisms are validated against additional sets of redundant experimental data.

Keywords: Microkinetic modeling; Hierarchical parameter refinement; Fuel processing; Carbon monoxide; Hydrogen; Catalytic combustion; Water–gas shift; Preferential oxidation; Thermodynamic consistency; Rhodium

1. Introduction

Fuel-cell technology is of recent interest for generating electricity because of its potential widespread applications, ranging from small-scale portable devices to stationary power generation and automobiles. Compared with conventional lithium batteries, fuel cells offer far higher energy densities, and they are less polluting and could be more efficient than internal combustion engines. H_2 acts as the fuel in proton exchange membrane (PEM) fuel cells. However, H_2 storage and transportation are a major problem in the widespread commercialization of PEM fuel cells. Furthermore, even minute amounts of CO in the H_2 fuel can poison the fuel-cell catalyst. Catalytic partial oxidation (CPOX) of natural gas on various transition metals can be used to produce syngas. Syngas produced by various means typically undergoes water–gas shift (WGS) reaction to convert CO to H_2

$$CO + H_2O \leftrightarrow CO_2 + H_2. \tag{1}$$

To minimize the remaining CO content in the H_2 stream in order to avoid poisoning of the fuel-cell catalyst, preferential oxidation (PROX) of CO is typically carried out

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \quad \text{and} \quad H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O. \tag{2}$$

All of these processes encompass the same fundamental chemistries of CO and H_2 adsorption, desorption, and combustion, as well as synergetic effects arising from using multiple fuels. This synergism was referred to in Ref. [1] as

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CO–H_2 *coupling* (see Section 3 for a more detailed discussion).

Microkinetic modeling [2] offers an efficient approach to understanding the underlying chemistry and eventually design fuel processors used upstream of a PEM fuel cell. Obviously, the uniqueness of kinetic parameters that can explain certain experimental features still remains a problem under certain conditions. For example, we have found examples where even small changes in parameters can change the rate-determining step [1]. A number of microkinetic models have previously been proposed for natural gas CPOX and its subsets on Pt and Rh [3–10]. However, all of these mechanisms have some inherent limitations, as outlined in [11–14]. A primary reason for the lack of a single comprehensive predictive reaction mechanism is that most of these mechanisms are optimized against a single type of experimental data. A limited number of fundamental density functional theory (DFT)-based microkinetic models [15,16], for PROX and WGS on various transition metals, established the foundations for first-principles modeling but do not account for CO–H_2 coupling steps, adsorbate–adsorbate interactions, and catalyst heterogeneity. Most fitted mechanisms lack thermodynamic consistency, an essential feature for ensuring correct rate calculations, equilibrium composition, energy balance, and temperature profiles [17]. This becomes an essential issue when equilibrium limited reactions, such as WGS, are modeled at high temperatures.

Over the past few years, we have been developing techniques that overcome the above limitations [13,14,17] to describe CO oxidation [18,19], H_2 oxidation [1,13,14], and CO–H_2 coupling for WGS and PROX [1,20] on Pt. More recently, we have introduced a hierarchical multiscale approach [21] that combines quantum mechanical DFT with semiempirical methods to improve predictive capabilities with minimal computational cost. In brief, the approach is *hierarchical* in nature, since we start with simple theoretical tools (e.g., semiempirical estimation methods, mean field approximation, simple reactor models) to identify the important parameters, followed by refinement (iterative, if necessary) of these parameters only, with the use of advanced theoretical and computational tools (e.g., first-principles quantum mechanics, kinetic Monte Carlo, molecular dynamics, computational fluid dynamics). Our approach is *multiscale*, since tools and phenomena span a broad range of length and time scales, from the quantum to the reactor. Reviews of multiscale simulation can be found in [22,23]. Note that in conventional bottom-up multiscale simulation, nearly all tools are coupled. However, for complex systems, such as catalytic reactions on polycrystalline and supported catalysts, we advocate that only some of these higher-level theoretical tools should be used whenever judged necessary. Consequently, the hierarchical approach makes simulations feasible in reasonable computational times.

In this paper, we develop microkinetic models for CO and H_2 oxidation and for the WGS and PROX on Rh, using the hierarchical approach. The paper is organized as follows. The development of CO and H_2 catalytic oxidation mechanisms is discussed in Section 2 with pre-factor refinement against *targeted* experiments, which we identify via sensitivity analysis (SA) in Appendix A, and by ensuring thermodynamic consistency. These reaction mechanisms serve as building blocks for the more complex WGS and PROX reactions and to illustrate some elements of the reaction mechanism development. Section 3 is devoted to the development of a CO–H_2 coupling mechanism, along with an analysis of the important reaction pathways in WGS and PROX. Finally, further validation of the reaction mechanisms is presented in Appendix B.

2. CO and H_2 oxidation mechanisms on Rh

2.1. *Experimental data on CO oxidation and H_2 oxidation on Rh*

Sant and Wolf [24] carried out atmospheric pressure ignition experiments on a Rh/SiO_2 wafer with a mixture of CO, O_2, and N_2. The ignition temperature of CO/O_2 mixtures was found to increase with the inlet CO composition (Fig. 1). Molecular beam experiments were carried out by Gopinath and Zaera [25] on a Rh(111) single crystal to investigate the effects of temperature and inlet composition on the rate of CO_2 production (Figs. 2 and B.1). The CO_2 production rate versus temperature shows a maximum for all compositions. Coulston and Haller [26] studied the effect of temperature on the rate of CO_2 production on a Rh foil with molecular beam experiments. The CO_2 production rate exhibited a maximum (Fig. B.2). CO TPD (Fig. B.3), O_2 TPD, and CO–O_2 TPR (Fig. B.4) experiments on Rh(111) and Rh(100)

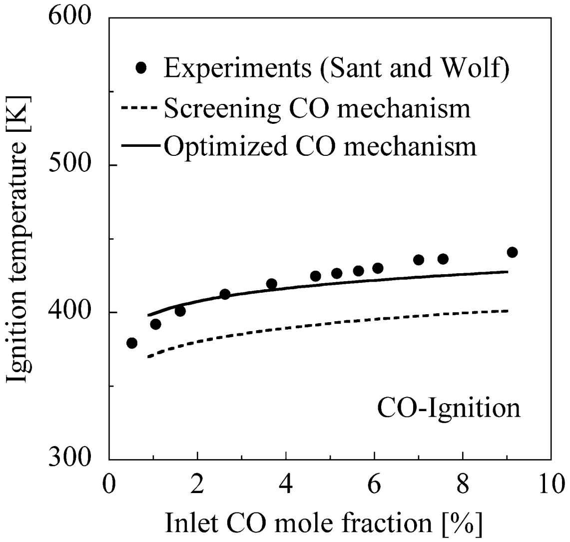

Fig. 1. Performance of the screening and optimized CO mechanisms against the CO-ignition experimental data of [24] at atmospheric pressure. Other operating conditions include a catalyst area of 5.67 cm^2, a reactor volume of 6 cm^3, and a residence time of ~1.9 s.