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Effects of heat and mass transfer on the kinetics of CO oxidation over RuO_2(1 1 0) catalyst

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ABSTRACT

Combining first-principles kinetic Monte Carlo (KMC) simulation with a finite difference continuum model, a hybrid computational model was developed to study the effects of heat and mass transfer on the heterogeneous reaction kinetics. The integrated computational framework consists of a surface phase where catalytic surface reactions occur and a gas-phase boundary layer imposed on the catalyst surface where the fluctuating temperature and pressure gradients exist. The surface phase domain is modeled by the site-explicit first-principles KMC simulation. The gas-phase boundary layer domain is described using the second-order grid-based Crank–Nicolson method. To simplify the model, the flow and gas-phase reactions are excluded. The temperature and pressure gradients in the gas-phase boundary layer are the consequence of thermal and molecular diffusions of reactants and products under nominal reaction conditions. Different from previous hybrid multiscale models, the heat and mass fluxes between two domains are directly coupled by the varying boundary conditions at each simulation timestep from the unsteady state reaction regime to the steady state reaction regime in the present model. At the steady-state reaction regime, the activity, the surface coverages of reaction intermediates, along with the temperature and pressure gradient profiles in the gas-phase boundary layer are statistically constant with very small fluctuations. As an illustration example, we studied the effects of heat and mass transfer on the reaction kinetics of CO oxidation over the RuO_2(1 1 0) catalysts. We assume the heat from CO oxidation is exclusively dissipated into the gas-phase via thermal diffusion. By varying the thickness of RuO_2(1 1 0) catalysts, the surface temperature changes correspondingly with the heat produced by occurring surface reactions, resulting in the pronounced temperature and pressure gradients in the gas-phase boundary layer. Our simulation results indicate that the limitation of heat and mass transfer in the surrounding environment over the catalyst could dramatically affect the observed macroscopic reaction kinetics under presumed operating reaction conditions. To fully elucidate the complex heterogeneous catalytic system, proper physical description of fluid phase that imposed on the catalyst and its effect on the surface kinetics should be integrated with current surface computational models.

1. Introduction

Computational modeling plays an increasingly important role in the characterization and understanding of a broad range of elementary chemical transformations relevant to heterogeneous catalytic processes. It remains, however, a formidable challenge to computational models with a predictive capability that describe complex heterogeneous processes involving the intrinsic reaction kinetics and transport of momentum, mass and heat [1,2]. The fluctuating temperature and pressure (or concentrations) gradients in the fluid phase over catalysts in either industrial reactors or small-scale laboratory reactive equipments give rise to the inhomogeneous nature that dramatically complicates the observed macroscopic reaction kinetics. To model chemical transformation processes in such complex heterogeneous environment thus requires a computational approach or framework that includes the transport of reactants, reaction intermediates, and products, the addition or removal of reaction heat along with the accurate surface reaction model on the solid catalyst. In the past decade, a number of multiscale hybrid models have been developed to meet this requirement. These hybrid multiscale models generally combined molecular-level surface reaction models for the catalysts phase and macroscopic continuum models for the fluid phase. A common bottom-up approach was adopted, i.e., passing the information of thermodynamic, kinetics and transport properties at atomic or discrete scale to the continuum scale. For example, Vlachos et al. developed a hierarchical reactor model that coupled coarse-grained kinetic Monte Carlo (KMC) simulation with computational fluid

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dynamics (CFD) [3–6]. They have applied this multiscale model to study the macroscopic kinetics of various catalytic systems such as preferential CO oxidation, water–gas shift, and ammonia decomposition on metal catalysts in plug-flow type reactors [7–9]. Majumder and Broadbelt also proposed a multiscale model that combined KMC with a finite difference (FD) solver to study the steady-state reaction kinetics in a two-dimensional flow reactor [10]. In those multiscale models, the entire catalytic heterogeneous reaction system is decomposed into two domains: the catalyst surface phase and the flow fluid phase. The catalyst surface domain is described by molecular-level microscopic kinetic models such as coarse-grained lattice KMC simulations. The thermodynamic and kinetic parameters database for elementary surface processes including adsorption, reaction, desorption and diffusion, which is required by KMC simulation as the input, are either obtained from experiments [10] or from first-principles density functional theory (DFT) calculations combined with unity bond index quadratic exponential potential (UBI-QEP) method [7,8,11,12]. For the fluid phase domain, a continuum model such as FD and CFD that describes the mass and heat transfer is used.

Very recently, Matera and Reuter proposed an multiscale computational model that integrates first-principles KMC simulations with a CFD solver for studying the effects of heat and mass transfer on the surface reaction kinetics of CO oxidation over $RuO_2(1\,1\,0)$ catalyst [13,14]. The fluid phase domain above the catalyst surface was modeled by a stagnant flow geometry that mimics the experimental surface science setup. They found that the limitations of heat and mass transfer significantly mask the measured CO oxidation kinetics. To avoid the possible instability of the algorithms used in the continuum model, Matera and Reuter decoupled the interdependence of first-principles KMC simulations with a continuum model [13,14]. In their approach, a series of first-principles KMC simulations were performed in a wide range of temperature and (partial) pressure conditions, to generate a grid map of catalytic activities at the steady-state conditions as the functions of temperatures and (partial) pressures. Those simulation data, which also included the data by interpolation, then provided the continuum model as the boundary conditions. In such a way, the averaged thermodynamic and kinetic variables at the steady-state conditions obtained from KMC simulations are then communicated with the continuum model in an iterative feed-response mode. The fluctuations of thermodynamic and kinetics information from stochastic KMC simulations are not considered. Furthermore, the important information of the unsteady-state surface reaction, which may affect the ultimate steady-state intrinsic kinetics if the surrounding fluid phase conditions change correspondingly, is also not communicated with the fluid phase. Instead of truly coupling the surface and the fluid phase models, the multiscale heterogeneous reaction model proposed by Matera and Reuter is implemented in the separate mode. The variations of the surrounding reaction environment imposed on the catalyst are not taken into account in the *real-time* fashion. Only the averaged, steady-state KMC simulation results were used as the boundary conditions for the continuum models.

The methodology and the spirit proposed by Matera and Reuter actually intrigued the present work. Herein we propose a heterogeneous reaction model that directly couples first-principles KMC simulation with a finite difference continuum model in a real-time dynamical mode. The changes in the temperature and partial pressures obtained from heat and mass transfer in gas phase are taken into account before the steady-state reaction condition for the entire catalytic system is reached. At each time step, the surface temperature and the concentrations (or partial pressures) of reactants and products obtained from KMC simulation are directly used as the *in situ* boundary conditions for the continuum model. The temperature and the concentrations of the nearest adjacent gas phase layer, that are obtained from the continuum model simulation are used as the *in situ* reaction condition for KMC simulation in the next time step. As such, our proposed reaction model captures the inhomogeneous dynamical nature in both the gas phase and the surface phase domains simultaneously. CO oxidation on $RuO_2(1\,1\,0)$ catalyst has been well studied both experimentally and theoretically [12,13,15–20]. To compare with the results of Matera and Reuter [13,14], we choose the same reaction system, as the benchmark reaction system to demonstrate the proposed model. For simplicity, the heat and mass transfer in the stagnant boundary layer above the $RuO_2(1\,1\,0)$ catalyst surface are only described by thermal and molecular diffusions. Since CO oxidation on the $RuO_2(1\,1\,0)$ catalyst is exothermic, the degree of increase for the surface temperature caused by CO oxidation occurring on the surface varies with the thickness of the catalyst. The variations of the surface temperature corresponding to different catalyst thicknesses eventually affect the intrinsic surface kinetics even though the nominal invariant operating conditions that set in the bulk fluid phase are the same. In this work, we focus on the effect of the catalyst thickness on the intrinsic reaction kinetics of CO oxidation on the $RuO_2(1\,1\,0)$ catalyst.

2. Methodology

Similar to the previous multiscale models [5,10], the entire heterogeneous catalytic reaction system is decomposed into the catalyst surface phase domain and the stagnant gas-phase boundary layer domain. As shown in Fig. 1, the nominal operating reaction condition such as the temperature ($T^{(n)}$) and the partial pressures $\left(P_{CO}^{(n)} \text{ and } P_{O_2}^{(n)}\right)$ beyond the boundary layer are constant. The gas-phase boundary layer is assumed as the stagnant gas phase without bulk flow. Only the molecular diffusions of reactants (CO and O_2) and the product (CO_2) are considered (mass transfer). The heat transfer in the boundary layer is described as the thermal diffusion process. The first-principles KMC simulation and second-order Crank–Nicolson method are used for the surface phase and the gas-phase boundary layer domains, respectively.

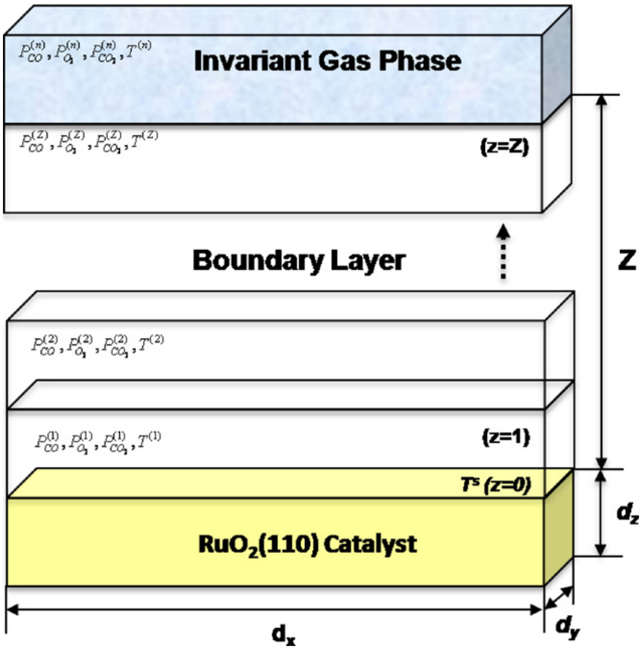

Fig. 1. Schematic diagram of the multiscale model.