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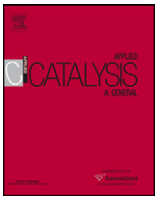

Microkinetic modeling of Pt-catalyzed ethylene glycol steam reforming

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ABSTRACT

A predictive mean-field microkinetic model is developed for steam reforming of ethylene glycol over a Pt catalyst using a hierarchical multiscale modeling approach. The model's predictive capabilities are assessed by comparison to experimental data under kinetically controlled conditions. It is found that early dehydrogenation reaction steps control the reaction rate, highlighting a kinetic analogy between ethylene glycol steam reforming and CH_4 steam reforming on Pt catalysts.

1. Introduction

Interest in the production of biomass-derived fuels and chemicals continues to grow, spurred on by a number of different drivers [1,2]. Recent work on the catalytic steam reforming of oxygenated hydrocarbons and sugars demonstrates that such compounds can be used to produce H_2 [3,4], which in turn can be used in fuel cells, feedstock upgrade, desulfurization, hydrogenation, and other processes. Obtaining a fundamental understanding of the mechanistic pathways of oxygenate reforming persists as a vital step towards fully utilizing these discoveries. Over the last 20 years, the development of microkinetic modeling has enabled successful replication of experimentally observed reaction kinetics over heterogeneous catalysts [5,6]. More recently, models have been integrated with first principles-based values of rate constants, providing a theoretical basis for model parameters and offering valuable insights into reaction mechanisms [6]. While a considerable number of microkinetic models have been developed, only a limited number have been reported for oxygenate chemistries, focused principally on thermal decomposition. Under steady-state reactor conditions over a Pt catalyst, Kandoi et al. demonstrated that initial C–H bond scission is rate-determining in methanol decomposition [7], similar to methane decomposition [8]. On the other hand, in ethane hydrogenolysis [9,10], C–C bond scission is kinetically controlling. In contrast, Salciccioli and Vlachos reported that early C–H and O–H bond scissions are rate-determining in ethylene glycol thermal decomposition on Pt [11]. Thus, it is not always clear when mechanistic analogies may be drawn between hydrocarbons and oxygenates containing equal numbers of carbon atoms.

Thermal decomposition often leads to catalyst deactivation. Co-reactants, such as H_2O, can limit deactivation. Therefore, understanding the influence of a co-reactant on the mechanism is also important. For example, Wei and Iglesia have elucidated experimentally that co-reactants (either H_2O or CO_2) have no detectable kinetic influence on C–H bond scission in methane reforming over Pt [8]. In the context of catalytic conversion of biomass-derived oxygenates to synthesis gas, water is a typical co-reactant because of its presence in biomass. A reduced, lumped model with parameters fitted to experimental kinetic data has been reported for steam reforming of ethylene glycol [12], but mechanistic details are still lacking. For example, ethylene glycol steam reforming may proceed as thermal decomposition of ethylene glycol to CO and H_2, as shown in reaction (R1), followed by a shift to CO_2 and H_2, as shown in reaction (R2):

$$C_2H_6O_2 \leftrightarrow 2CO + 3H_2 \qquad \text{(R1)}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \text{(R2)}$$

(R2) maynot only change the product distribution but also free up catalyst sites from adsorbed CO and thus speed up (R1). Furthermore, water-derived OH^*, formed according to reaction (R3), may also directly promote decomposition of oxygenates (such as

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ethylene glycol) by catalyzing C–H or O–H bond scission as shown in reaction (R4):

$$H_2O^* + {}^* \leftrightarrow OH^* + H^* \quad (R3)$$

$$C_xH_yO_z{}^* + OH^* \leftrightarrow C_xH_{y-1}O_z{}^* + H_2O^* \quad (R4)$$

To date, no detailed kinetic model has been reported for ethylene glycol steam reforming that includes reactions like (R4). Yet, previous work has shown that barriers for OH-assisted reactions with oxygenates are similar to or lower than the corresponding simple dehydrogenation steps [13,14], and are likely contributing steps in the overall mechanism [14]. As an example, Davis and co-workers demonstrated that ethanol and glycerol oxidation to the corresponding acids occurs on Au at high pH (whereas Au is inactive at neutral conditions), and attributed the activity to dehydrogenation reactions mediated by both solvent- and surface-OH [14].

Here we apply a hierarchical multiscale modeling approach [6,15] to develop a predictive mean-field microkinetic model for steam reforming of ethylene glycol over Pt. Model predictions are compared to experimental data, and subsequent model analysis offers insights into the ethylene glycol reforming mechanism. Finally, a kinetic analogy is drawn between ethylene glycol and CH_4 steam reforming over Pt catalysts.

2. Model development

The ethylene glycol steam reforming model consists of 147 reversible reactions (listed in Supplementary Information), which may be divided into several reaction subgroups. Ethylene glycol decomposition includes all possible C–H, O–H, and C–C bond cleaving reactions of $C_2H_6O_2$ for the formation of CO and H_2; C–O bond scission is neglected due to low selectivity over Pt [16]. Methanol decomposition is made up of an analogous set of elementary steps (except for C–C bond scission). Water–gas shift (WGS) includes water activation (R3) as well as pathways for CO_2 formation from CO, either directly or via carboxyl or formate intermediates (depicted as an overall reaction (R2)). Finally, because of the presence of H_2O as a co-reactant, oxidative dehydrogenation pathways are considered in which adsorbed OH intermediates mediate C–H and O–H scission in both C1 and C2 compounds (R4).

H_2O can affect the rate of ethylene glycol decomposition in at least two kinetically interesting ways. First, H_2O can remove CO via the water–gas shift reaction to free up sites (blocking of sites via CO is observed under thermal decomposition conditions [11]). In this case, steam reforming can be thought of – in a simplistic manner – as the ‘addition’ of reactions (R1) and (R2). Second, H_2O^* can dissociate to OH^* (R3), which can carry out oxidative dehydrogenation steps as shown generically in reaction (R4); these steps are absent under thermal decomposition conditions. If these elementary reactions are important, then steam reforming of polyols is the result of strong chemical coupling that goes beyond availability of free sites. Inclusion of all these elementary steps permits a direct assessment of whether, and to what extent, H_2O catalyzes ethylene glycol dehydrogenation.

To parameterize the mean-field microkinetic model, in addition to values computed as part of this work, previously reported DFT-based thermochemical and kinetic parameters for reactions involving $C_2H_xO_2$, CH_xO, and WGS intermediates were utilized. A CHEMKIN^{TM} [17,18] THERMDAT file containing NASA polynomial coefficients is provided as Supplementary Information, with entries that describe the thermochemistry of all gas and surface intermediates of this model. All entries for gas-phase intermediates were the same as in Salciccioli and Vlachos [11], except the entries for CO_2 and H_2O which were obtained from the GRI mechanism (v.3.0) [19]. Data from Salciccioli and Vlachos [11] were also used for $C_2H_xO_2{}^*$ and CH_xO^* intermediates, including HCO^* and CO^*. The entry for H^* was similar to Salciccioli and Vlachos [11]. In [11] the entropy of H^* was based on the assumption of a 2D surface fluid (i.e., loss of only 1 gas-phase translational degree of freedom), while in this work the entropy is calculated by assuming that all gas-phase translational degrees of freedom are converted to vibrational degrees of freedom. The thermochemistry for WGS surface intermediates is based on results from Stamatakis et al. [20], except for $CO_2{}^*$ which in that work was assumed to instantaneously desorb. In this work, $CO_2{}^*$ was treated using 2 translational degrees of freedom and 7 vibrational degrees of freedom (i.e., a 2D surface fluid assumption). $H_{f,298}$ of $CO_2{}^*$ is referenced from $HCOOH_{(g)}$ and H^* adsorbed on separate slabs, in order to be consistent with the reference states for the other intermediates [11]. Finally, lateral repulsive adsorbate interactions that affect the thermochemistry of intermediates were used [11], except for the effect of CO^* on the H^* binding energy. Versions of the models were considered that both included and neglected cross lateral repulsive interactions of CO^* and H^*, using a value of 5 kcal (mole ML)$^{-1}$ for both parameters. It was observed that results were qualitatively identical and quantitatively very similar; consequently, we chose to neglect those parameters to minimize model complexity.

To ensure thermodynamic consistency (i.e., closure of thermodynamic cycles) in a DFT-based surface microkinetic model, adjustment of DFT-computed thermochemical properties of at least some elementary steps involving surface species (either adsorption, reaction, or both) is required. This is because of differences between values of experimental and DFT-computed thermochemistry. Previously published methods for thermochemical parameterization offer in-depth discussion of this point [6,21]. In this work an approach is adopted in which the DFT-computed surface thermochemistry is preserved while adsorption thermochemistry is adjusted to ensure closure of thermodynamic cycles (note that the experimentally-based thermochemistry of gas phase compounds is taken to be ‘correct’ and is not adjusted). The premise of this approach is that the surface reaction thermochemistry is likely more accurate than adsorption thermochemistry because of cancellation of errors. The focus of the study is to understand the surface reaction pathways, so an approach was adopted that preserved that information from DFT.

For the kinetic parameterization, each forward reaction rate constant was defined according to one of the following expressions:

$$k_{i,f} = A_i\, e^{(-E_{a,i}/k_BT)} \quad (1)$$

$$k_{i,f} = \frac{k_BT}{h} e^{(-\Delta G_i^{\ddagger}/k_BT)} \quad (2)$$

$$k_{i,f} = \frac{s_j}{C_T{}^n}\sqrt{\frac{k_BT}{2\pi M_w}} \quad (3)$$

Surface elementary steps involving CH_xO^* intermediates were parameterized according to Eq. (1) to conform to a previous publication [7]; oxidative dehydrogenation pathways were also parameterized according to Eq. (1). Adsorption steps were parameterized according to collision theory following Eq. (3), where s_j is the sticking coefficient of reactant j, C_T is the area density of surface sites, n is the number of sites onto which the reactant adsorbs, k_B is the Boltzmann constant, T is the temperature, and M_w is the molecular weight of the adsorbing reactant. To ensure thermodynamic consistency of rate constants, reverse rate constants were calculated from the forward rate constants and the equilibrium constant, according to Eq. (4):

$$K_{eq,i} = e^{(-\Delta G_{rxn,i}/k_BT)} = \frac{k_{i,f}}{k_{i,r}} \quad (4)$$