

Simulating Heterogeneous Catalysis with Kinetic Monte Carlo

CHE384T: Example Report

1 Introduction

Heterogeneous catalysis involves reaction between a catalyst of a different phase from the reactants and products. An important application of heterogeneous catalysis is photocatalysis, which is used for water splitting and purification. Photocatalysis involves a semiconductor, such as TiO_2 , as the catalyst. Light is incident upon the semiconductor and generates an electron-hole pair. The electron and hole then must travel to the surface to initiate a redox reaction with the surrounding water molecules. This redox reaction decomposes water into usable hydrogen and oxygen gas. In this report, a summary of simulating heterogeneous catalysis using kinetic Monte Carlo is provided.

2 Implementation of KMC

Several reactions are possible in photocatalysis. There is a rate of generating the electron-hole pair, of bulk recombination, and of the rate at which each carrier reaches the surface to react. For the simplicity of the model developed here, these reactions are neglected and it is assumed that there is always an carrier available at a site of possible reaction. Appendix B enumerates neglected reactions. This report focuses on the generation of hydrogen and oxygen gas, for which the considered reactions have of the following forms



For each species, a rate of adsorption r_{ads} , desorption r_{des} , and reaction r_{rxn} (if relevant) is considered. A possible list of events depends on the occupation of the site (and neighbors, if applicable). All possible rates for the model simulated are

$$r_{ads} = k_{ads}[A](1 - \theta) \quad (2a)$$

$$r_{des} = k_{des}\theta \quad (2b)$$

$$r_{rxn,LH} = k_{LH}\theta_A\theta_B \quad (2c)$$

$$r_{rxn,ER} = k_{ER}\theta_A[B] \quad (2d)$$

where $[A]$ and $[B]$ is the concentration of adsorbing species and θ_i is fraction of sites occupied by the i th species. The form for the rate of reaction is explained in Section 3.2. To simulate these events, a Kinetic Monte Carlo (KMC) code was constructed based off that of Ref. [1] and Ref. [2]. Figure 1 shows the decision tree for the possible events that are occupation specific. A two dimensional square lattice is used for simulations. The basic procedure is outlined below.

1. Input of initial parameters (e.g., lattice size, initial concentrations, KMC steps, reaction rate constants)
2. Find initial rates of reaction based on initial parameters and initialize lattice
3. For each KMC step, find activity of each lattice site and the corresponding total activity of the lattice. Based on the activity, for a randomly chosen lattice site
 - (a) Determine the possible M events and calculate the associated activity $A(t) = \sum_{k=1}^M r_k(t)$.
 - (b) Find probability of each event from calculated activity and select randomly a possible event to occur
 - (c) Update state of the lattice site, and relevant concentrations and fractional occupancies.
 - (d) Increment time by $\Delta t = -\frac{\ln(\mathfrak{R})}{A}$, where \mathfrak{R} is a random number uniformly distributed between 0 and 1, and A is the time and site-dependent activity.
4. Repeat the above step until all reactants have been consumed

For the empty site lattice, the corresponding activity is the sum of all species' adsorption and desorption reaction rates. Such a definition is to allow for the possibility of the lattice site to stay empty. Similarly, the activity of an occupied lattice site is the sum of the adsorption, desorption, and reaction rates for the particular adsorbed species. By similar logic, this definition of the activity allows for the possibility that the lattice site remains adsorbed or desorbs without reaction. A reaction occurs only if a nearest neighbor is occupied with the appropriate species. In simulations involving generating products, the products are allowed to stay within the system and inhibit reactions through re-adsorption. All simulations were done with a 20 x 20 square lattice with periodic boundary conditions for a minimum of 100 KMC steps.

3 Results and Discussion

3.1 Adsorption Equilibria

We begin with a summary of adsorption equilibria. In equilibrium, the rate of adsorption and desorption are equal, and an equilibrium fraction of occupied sites is achieved. No reactions occur in equilibrium. The Langmuir adsorption isotherm is followed in this report, which assumes

1. all sites are equal; that is, all species compete for the same site and all possible events can occur for each site.
2. monolayer adsorption only; adsorption beyond a single layer is not allowed.

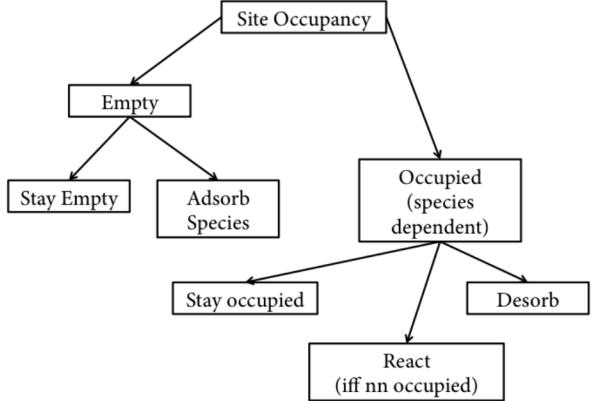


Figure 1: Decision tree for deciding upon the possible site-dependent reactions.

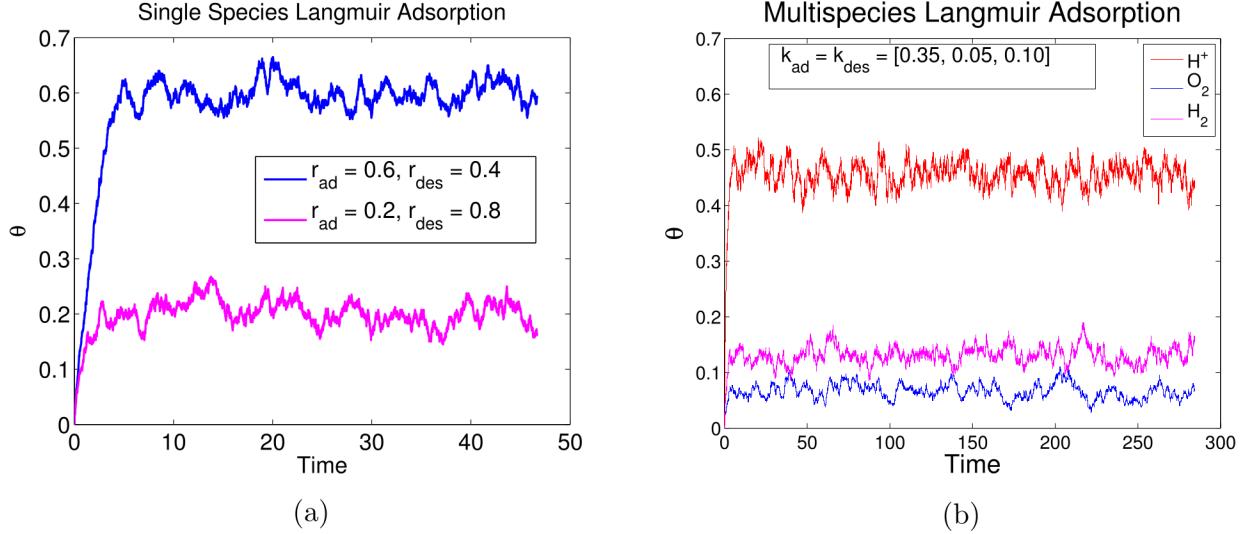


Figure 2: Langmuir adsorption isotherms for (a) single species and (b) multiple species adsorption for a set of reaction rate constants.

3. no interaction between species (except for reactions).

4. no diffusion of species; that is, once a species adsorbs, it is stuck until a desorption event.

The Langmuir adsorption isotherm is appropriate as the generation of products requires reaction with carriers that migrate to the surface, which restricts reactions to an adsorbed monolayer. The form of single-species may be easily extended to multiple species adsorption, in which the fraction of occupation of species i for N species is

$$\theta_i = \frac{K_i C_i}{1 + \sum_{j=1}^N K_j C_j}, K = \frac{k_{ads}}{k_{des}} = \frac{C_i^*}{[*]C_i} \quad (3)$$

where K is the equilibrium constant, C is the concentration of adsorbing species and $*$ indicates a surface site.

Figure 2 shows an example simulation for Langmuir adsorption for single-species and multiple species. In both instances, the equilibrium fraction of occupied sites is achieved quickly. Fluctuations exist due to the stochastic nature of the KMC method. Testing adsorption equilibria provides a check for the remainder of the project when reaction rates are introduced.

Other models of adsorption isotherms exist, depending on the set of assumptions used. For example, the BET (Brunauer-Emmett-Teller) isotherm model relaxes the monolayer adsorption assumption to include multiple layers. However, since the generation of products involves reactions with carriers at the surface, Langmuir adsorption is deemed to be most appropriate experimentally.

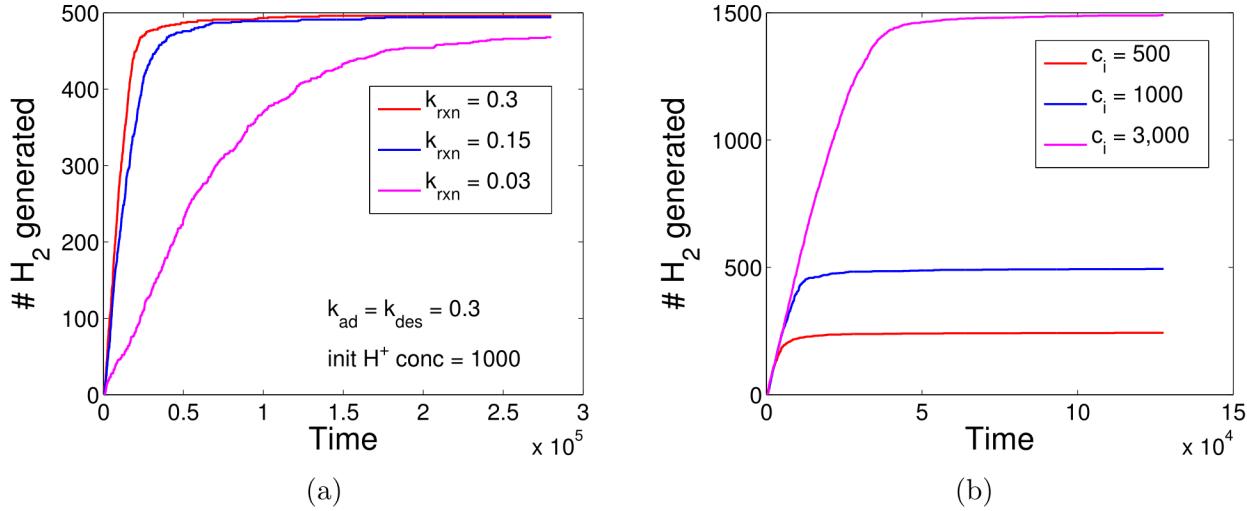


Figure 3: Trends in generation of H_2 for varying (a) reaction rate constants and (b) initial concentrations c_i of H^+ ; all other parameters are equal.

3.2 Generation of products

We now introduce rates of reactions, which is defined to occur only between nearest neighbors of like species. In heterogeneous catalysis, two mechanisms are possible. We consider only the Langmuir-Hinshelwood mechanism in which two neighboring species must be adsorbed to react. This is consistent with experiment for photocatalysis, which have observed behavior similar to Langmuir-Hinshelwood mechanisms [3-4]. More information on heterogeneous catalysis mechanisms may be found in Appendix C. To test the validity of the implementation, the rate of reaction and initial concentrations are varied for the half of the redox reactions involved hydrogen gas generation. These tests are shown in Figure 3.

As seen in Figure 3, increasing the reaction rate constant increases the rate at which H_2 is generated, indicated by the steeper slope. In contrast, varying the initial concentration does not affect the rate of generating H_2 . This is due to the method of implementation of the KMC method in which the frequency of an event is proportional to its relative magnitude to other possible events instead of its absolute magnitude regardless of the rates of other events. Nevertheless, the implemented KMC model performs as expected.

Now, the entirety of redox reactions is considered for the generation of both O_2 and H_2 gas. The system begins with only an initial concentration of water, and the reaction is allowed to proceed. For the products O_2 and H_2 , the rate of reaction is set to effectively null. The reactions are also set to occur stoichiometrically (i.e., 2 water molecules form 4 H^+ and a single O_2 molecule). An additional distinction is made between H_2 and O_2 reacted and generated. Once H_2 or O_2 is reacted, it is allowed to remain within the system and inhibit a lattice site through re-adsorption. There is also a probability that the gas reacted leaves the system to be H_2 and O_2 gas generated as a useful product for other applications. The generation of products in the system and outside the system as useful is shown in Figure 4b.

Figure 4a traces the progression of concentration of water and products of its oxidation.

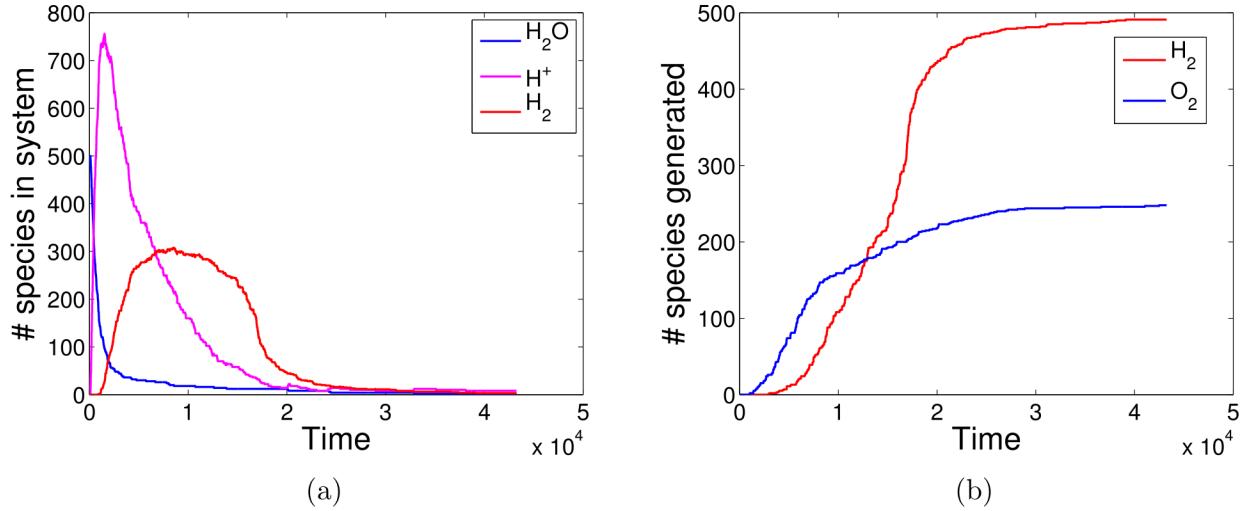


Figure 4: Progression of concentrations in the redox reaction for water splitting for (a) the system of the lattice and adsorbents, and (b) outside the system, defined as the generation of useful products that are extracted from the system for an initial concentration of 500 water molecules.

Initially, only water is present, but is quickly consumed before tailing off as rates of adsorption and reaction lessen with decreasing concentration. At the point when water is reacted, the presence of H^+ peaks. When a sufficient concentration of H^+ is generated and adsorbed on the lattice in the oxidation of water, the peak begins to drop. Simultaneous with this peak drop is an increase in the presence of H_2 that has been reacted from the H^+ . By similar logic with H^+ , at a sufficient concentration of H_2 , it becomes favorable for the H_2 to escape the system and become useful H_2 generated, which is approximately when the presence of H_2 in the system begins to drop off. The behavior of O_2 in the system is similar to that of H_2 and is not shown for clarity. The generation of useful products (i.e., O_2 and H_2) is shown in Figure 4b, which parallels the peaks and asymptotic behavior of the species in the system as the system exhausts its reactants. Notable in Figure 4b is the delay in generation of O_2 with respect to the initial time of reaction and of H_2 with respect to O_2 . This reflects the progression of redox for water splitting, particularly that water molecules must first be oxidized to produce the H^+ ions needed for reduction to occur.

The experimental validity of the implemented KMC code follows general trends in chemical reaction that may be scaled to the size of an actual chemical reaction (i.e., 10^{23} species instead of 10^3) from which physically meaningful reaction kinetic may be extracted with relevant kinetic rate constants. As demonstrated in this report, a Kinetic Monte Carlo method has been implemented for heterogeneous catalysis in water splitting applications.

[1] R. LeSar. *Introduction to Computational Materials Science*. Cambridge University Press. 2013.

[2] N. Eisenmenger. *Simulating Copolymer Synthesis Using a Kinetic Monte Carlo Method*. Matl 228 Final Project.

[3] E. Du, Y.X. Zhang, L. Zheng. *React. Kinet. Catal. Lett.* **97** (2009) 83-90.

[4] M.A. Lazar, S. Varghese, S.S. Nair. *Catalysts*. **2** (2012) 572-601.

Appendices

A Code included

The following code is included:

1. `runKMC.m` → parameters used for all runs in this report
2. `KMClangad.` → single-species Langmuir adsorption isotherm
3. `KMClangadmulti.m` → multiple species Langmuir adsorption isotherm
4. `KMClhH.m` → reduction half (i.e., generation of H_2 gas) of water splitting with Langmuir-Hinshelwood mechanism
5. `KMCerH.m` → reduction half of water splitting with Eley-Rideal mechanism
6. `KMClhHO.m` → redox of water splitting with Langmuir-Hinshelwood mechanism
7. `movieKMC.m` → from the output of `KMC*.m`, generates a movie of the configurations over time
8. `pbc.m` → periodic boundary conditions
9. `sqlatt.m` → generates coordinates of square lattice

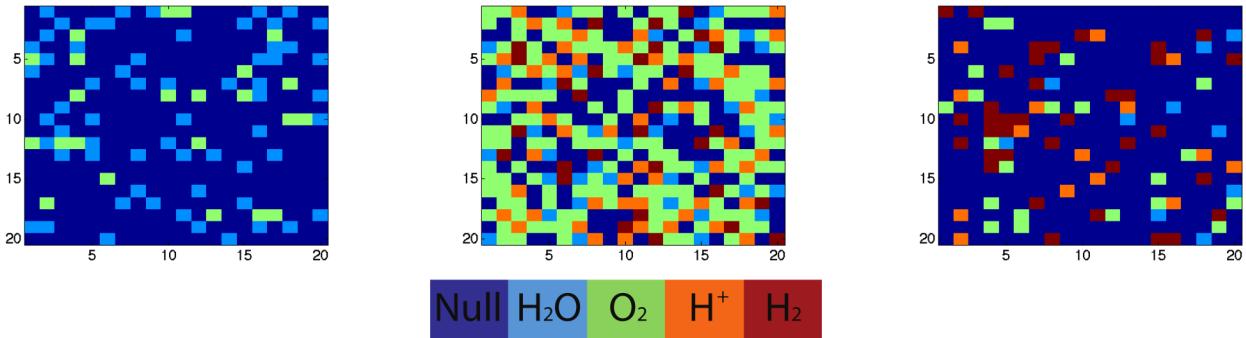


Figure 5: Screen shots of movie generated of sample configurations at initial stages (left) progressing towards the end of the reaction (right) for a particular step in KMC simulation for the generation of H_2 and O_2 gas.

For visualization is `movieKMC.m`, which is used to visualize the site occupancies during the course of the simulation. Figure 5 shows screen shots at different times of a simulation of heterogeneous catalysis using `KMClhHO.m`.

B Inaccuracies in KMC modelling

Several simplifications were made in this particular implementation of KMC for heterogeneous catalysis. The largest assumption was neglecting the excitation and transport of carriers to the surface that make redox possible. There is indeed a rate and lattice site specific factor that must be considered in real materials. It is expected that embedding these events into the KMC model will result in similar curves for generation of oxygen and hydrogen gas, though over longer time scales as more events in sequence would need to occur for a reaction to occur. This would need to be tailored to the particular material being modeled.

Neglected Reactions	
$\text{Semiconductor} + h\nu \rightleftharpoons e^- + h^+$	excitation, bulk recombination
$e^- + \cdot \rightarrow e^{-\cdot}$	transport to surface site
$h^+ + \cdot \rightarrow h^{+\cdot}$	transport to surface site
$H_2O \rightleftharpoons H^+ + OH^-$	dissociation of water
$e^{-\cdot} + h^{+\cdot} \rightarrow \text{Semiconductor} + h\nu$	surface recombination

In neglecting the dissociation of water, any reactions involving radicals (typically reported for photocatalytic decomposition of organic pollutants) is ignored. Examples may be found in Ref. [5]. It is also assumed that rate of adsorption and desorption is the same for all sites for each species. This is a large simplification of the Langmuir adsorption model that does not distinguish between site types. In real materials, the structure of the surface has significant implications on the rate of the adsorption and desorption [6]. For example, it is well known that the prototypical semiconductor for photocatalysis, TiO_2 , has several adsorption rates for H_2O that is dependent on surface morphology.

[5] C.S. Turchi and D.F. Ollis. *J. Catal.* **122** (1990) 178-192.

[6] A.L. Linsebigler, L. Guangquan, J.T. Yates. *Chem. Rev.* **95** (1995) 735-758.

C Other considerations

C.1 Mechanisms of Heterogeneous Catalysis

The Eley-Rideal mechanism involves the adsorption of only one species that can then react with a non-adsorbed species. Alternatively, with the Langmuir-Hinshelwood mechanism, all species involved in the reaction must be adsorbed onto the surface before reacting. Figure 6 shows the difference in generating H_2 gas when considering only the second half the redox reaction for the two aforementioned mechanisms in heterogeneous catalysis. As expected, under the Eley-Rideal (ER) mechanism, the reaction proceeds faster than that of the Langmuir-Hinshelwood (LH) mechanism, since the ER mechanism does not require two adsorption events to happen.

C.2 Tuning other parameters: a sampling

There are several knobs that are adjustable in the simulation. Here some examples are presented to illustrate basic trends that the KMC simulation can make. The first example is tuning the rate of reaction for water. Figure 7 shows an example of how tuning the rate of reaction for water affects the remaining generation of other products. A decrease in reaction rate constant of water subsequently slows the generation of all following products, as the peaks of subsequent products is broader and shallower.

An alternate trend may be found through adjusting the rate of adsorption and desorption. An example of this is shown in Figure 8, in which increasing the rate of desorption lead to faster generation of H_2 . This matches chemical intuition in that the H_2 is able to immediately escape the system upon being reacted, whereas the generation of O_2 remains largely unaffected, indicating that the the oxidation of water remains the same in comparison.

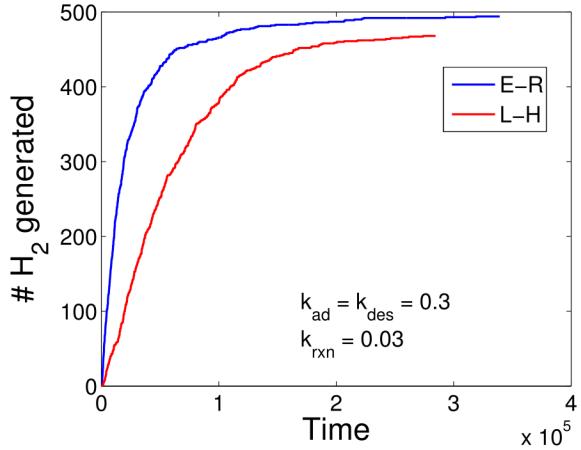
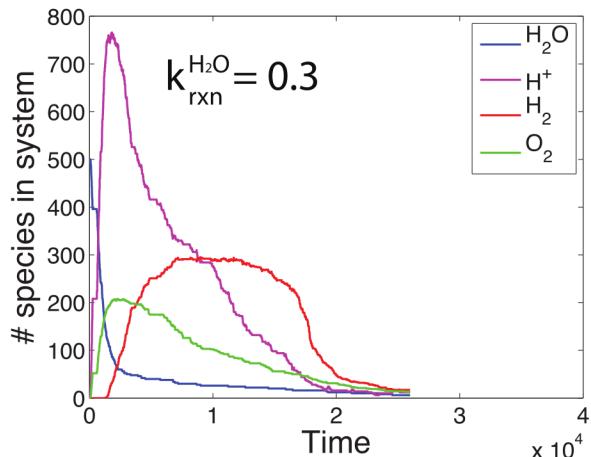
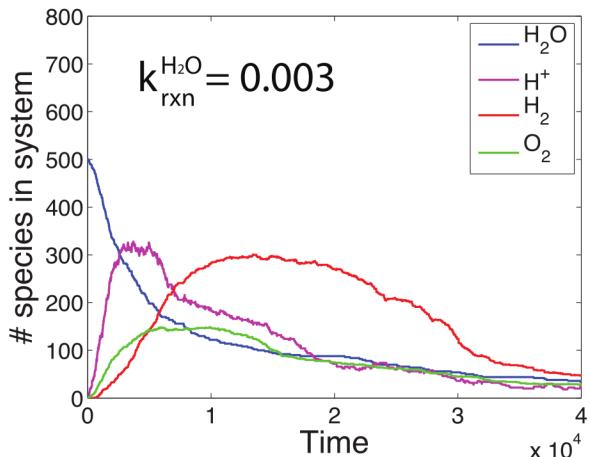


Figure 6: Comparison of Langmuir-Hinshelwood (LH) and Eley-Rideal (ER) mechanisms in heterogeneous catalysis via measurement of H_2 generated in the reactions.

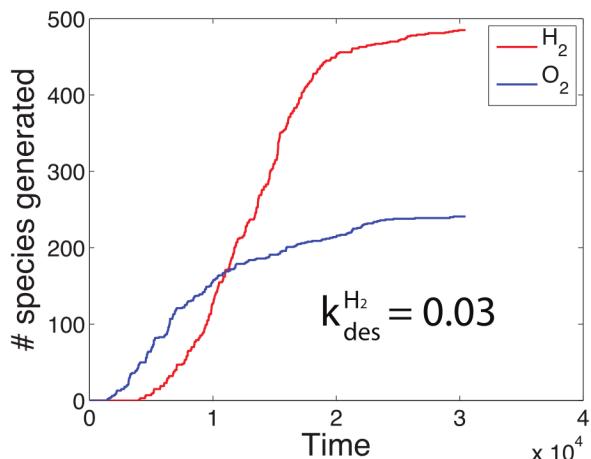


(a)

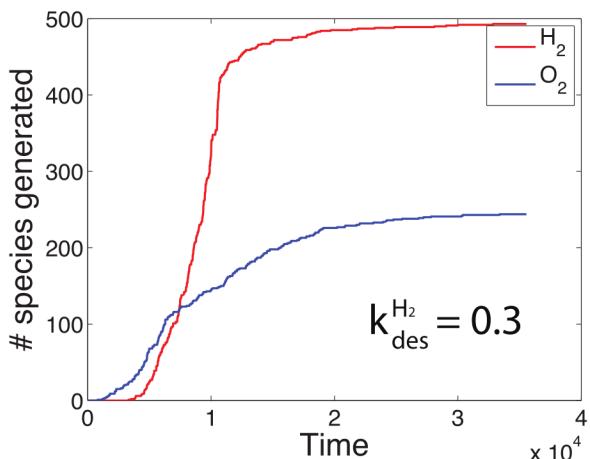


(b)

Figure 7: Progression of concentrations in the redox reaction for water splitting for different reaction rate constants for water over the same time period. A smaller reaction rate constant leads to longer reaction times.



(a)



(b)

Figure 8: Progression of products generated in the redox reaction for water splitting for different desorption rate constants for H_2 over the same time period. A larger rate of desorption for H_2 , while leaving the rest of the reaction unaffected.