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Agent-based Modeling of Visible Light-Driven Hydrogen Production

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Abstract

A two dimensional agent-based program was created based on the form of the kinetic equations for the reactions in visible light-driven hydrogen production. Programmed agents represent the chemical species involved allowing useful, though limited visual feedback on the activation energy and orientation factor estimates. The model simulates the simultaneous reactions involved and predicts the change in reactant concentrations over time. Lastly the model is used to provide insight for optimizing hydrogen production through controlling the initial concentrations of the chemical reactants.

The model has good agreement with published experiments.

Keywords: Water-splitting; Photocatalysis; Predictive Modeling; Computer Simulation

1. Introduction

Sustainable and clean energy technologies are considered relatively new, but highly important fields of research. One of the cleanest and most promising of these technologies is the utilization of hydrogen energy. Both ultraviolet light and visible light have been shown to be able to split water into its hydrogen and oxygen components in the presence of certain transition metal catalysts such as titatnia. Visible light contains 50% of solar light energy compared to the 3-4% energy in ultraviolet light [Ni *et al.*, 2007]. Visible light-driven hydrogen production is receiving a lot of attention with recent research trying to lower costs and improve efficiencies [Yu *et al.*, 2011, Rosseler *et al.*, 2010]. Photocatalytic experimentation in this field necessitates building reactors and using costly measuring equipment. Each experimental run can also take days to complete. Building a model that readily analyzes current available data will allow for simulations that would suggest the best scenarios to cover on the succeeding experiment.

An emerging approach to modeling complex systems is through rule-based modeling. Rules are used to capture the dynamics of molecular interactions. The model in this case is a computer program and agent-based computational approaches can be applied to simulate the chemical kinetics of a particular system [Chylek]. Agent-based models of elementary reactions have been able to qualitatively capture the experimental results particularly for the dimerization of the gas nitrous oxide to tetranitrogen dioxide [Stieff and Wilensky, 2001, Wilensky, 1999]. This paper is part of an ongoing work to model complex and non-elementary reactions in visible light-driven hydrogen production.

2. Agent-Based Model

The model is based on the catalyst and reactor in Tolod *et al.*, 2011. The set of reactions assumed to be occurring in the reactor are the following [Puangpetch *et al.*, 2009].

1. $2H^+ + 2e^- \rightarrow H_2$
2. $CH_3OH + H_2O + 6h^+ \rightarrow CO_2 + 6H^+$
3. $2OH^\bullet + 2h^+ \rightarrow O_2 + 2H^+$
4. $H_2O \rightarrow H^+ + OH^-$
5. $H_2O \rightarrow H^+ + OH^-$
6. $H_2O \rightarrow H^+ + OH^-$
7. $SrTiO_3 + hv \rightarrow e^- + h^+ + SrTiO_3$
8. $e^- + h^+ \rightarrow \emptyset$
9. $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
10. $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
11. $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
12. $H_2CO_3 \rightarrow H_2O + CO_2$
13. $H_2CO_3 \rightarrow H_2O + CO_2$
14. $H_2CO_3 \rightarrow H_2O + CO_2$

A popular model used for chemical reaction kinetics is the Power Law Model shown in (1). It's expanded form is (2). Z represents the frequency of collisions. Q is the orientation factor. The molecules normally need more than a collision to react. The orientation of the reactants have to be favorable for reaction as well. E_a is the activation energy. A reaction with a high activation energy

will occur with less probability than a reaction that only needs a low activation energy. R is a chemical constant. T is the temperature. $y_i^{\alpha_i}$ is the concentration of reactant i raised to the power α_i, where α_i indicates the order of reaction with respect to species i.

$$r = k \prod y_i^{\alpha_i} \quad (1)$$

$$r = Z \cdot Q \cdot e^{-\frac{E_a}{RT}} \prod y_i^{\alpha_i} \quad (2)$$

The Expanded Power Law model can be rearranged and grouped to differentiate 2 parts, first, the number of collisions between the required species, and second, the probability that the collision will yield a reaction in the manner of (3) and (4).

$$\text{rate} = (\text{Amount of collisions})\,(\text{Probability that reaction occurs during a collision}) \quad (3)$$

$$r = \left(Z \cdot \prod y_i^{\alpha_i}\right)\left(Q \cdot e^{-\frac{E_a}{RT}}\right) \quad (4)$$

The orientation factor Q and the activation energy E_a are both dependent on the chemical reaction alone. R is constant and T changes with the temperature of the solution and the reactor. In the laboratory environment that this research is trying to model, the temperature is kept fairly constant, practically isothermal. Thus, the second grouping in (4) can be considered a function of the reaction alone and may be as a group be designated as ρ_r representing the probability of a reaction proceeding based on its activation energy requirement and its likely orientation. Z is the collision frequency. Chemical concentrations are represented by y_i.

By assuming that the changes in concentration of each chemical species are governed by the chemical rate constant k, the vector of concentrations of the different reactant species, $\mathbb{Y}$, the numerical coefficients of the stoichiometry of the reactant species, α, and the frequency of collision Z, for relatively short intervals, Δt, we can write probabilities for one-step change of system state. The rules for the agent-based model is shown as in (5).

$$\begin{aligned} p^+(Y_i) &= \left[\sum_{m=1}^{M} \min\left[\mathbb{Y}/\alpha_{mj}\right](Z_m)(k_m)\right]\Delta t \\ p^-(Y_i) &= \left[\sum_{n=1}^{N} \min\left[\mathbb{Y}/\alpha_{nj}\right](Z_n)(k_n)\right]\Delta t \end{aligned} \quad (5)$$

$p^+(Y_i)$ is the probability of one-step increase of chemical species due to reactions wherein Y_i is a product and $p^-(Y_i)$ is the probability of a one-step decrease due to reactions where Y_i is consumed. Simulated collisions of agents representing chemical molecules provide estimates for the collision rates. The probability of reaction given collision is taken using the kinetic rate constants computed using the Eyring equation, which is based on the Gibbs free energy of the reactions found in the system. The method used was adapted from [Stieff and Wilensky, 2001].

3. Results and Discussion

Figure 1 shows the user interface of the resulting agent-based model program. Chemical reaction kinetic quantities such as the frequency of collision, the orientation factor and the activation energy are incorporated within the model under isothermal laboratory conditions. The relative physical dimensions of the reactor as well as the relative concentrations of the different reactant species in the said experimental work are also incorporated. Options such as light intensity, initial concentrations of reactants and catalyst are controlled through sliders. Non-spatial dependent reaction factors such as the orientation factor and the activation energy for each of the reactions are set as probabilities conditioned on the event that the required species collide in the reactor. The concentrations of the different species are monitored as well as shown though animation.

Plots of species concentration against time were generated based on experimental and simulated runs and were used as input for the optimization process. Analysis of the plots easily produce an input

matrix where each row comprised of the concentration of each of the species and the number of time steps it took for such a combination of concentrations to produce hydrogen.

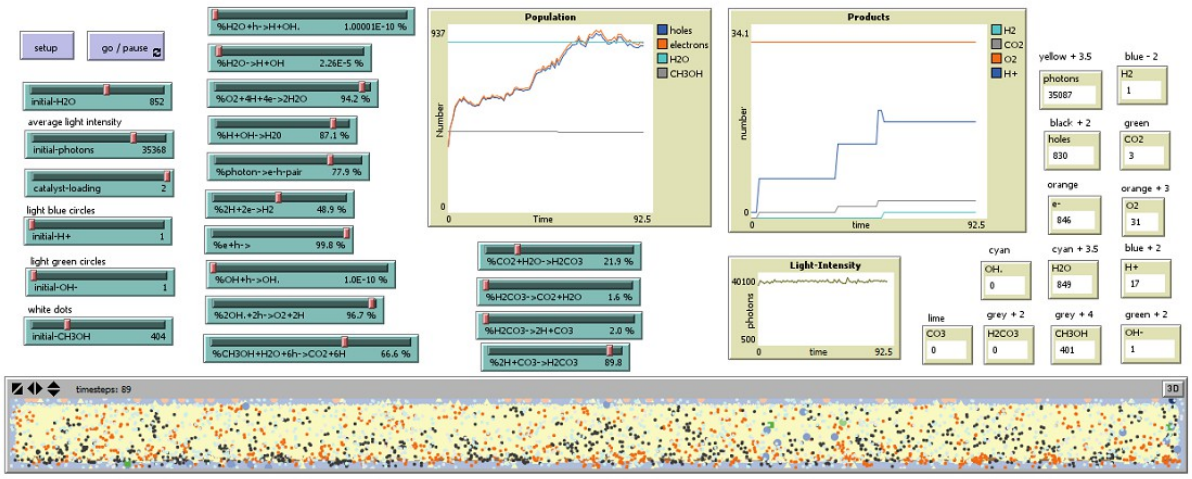

Figure 1: Interface of the agent-based simulator for visible light-driven hydrogen production

Figure 2 shows the plot of the simulated hydrogen production. It shows good qualitative agreement with the experimental hydrogen production results in [Rosseler *et al.*, 2010, Alenzi *et al.*, 2010, Xu *et al.*, 2010].

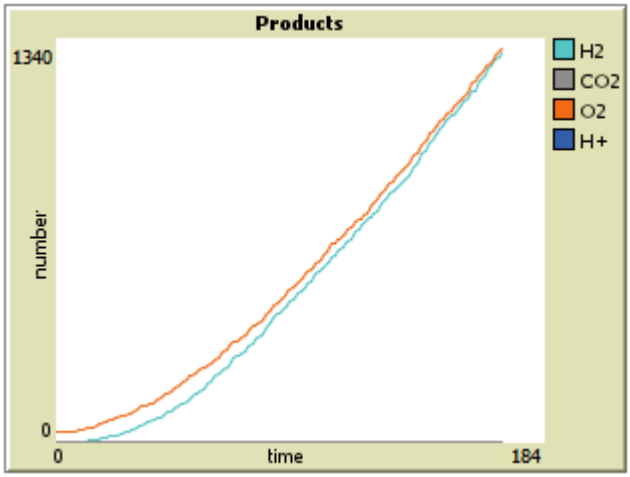

Figure 2: Plot of simulated hydrogen production at timestep 169

4. Conclusion

The created model of visible light-driven hydrogen production kinetics using a rules based approach qualitatively match the experimental results found in literature.

Further experiments will be done to compare plots of oxygen and carbon dioxide evolution with those predicted by the model. The program and experiments will also be adjusted to remove the need for an isothermal assumption.

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