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Analysis of the propylene epoxidation mechanism on supported gold nanoparticles

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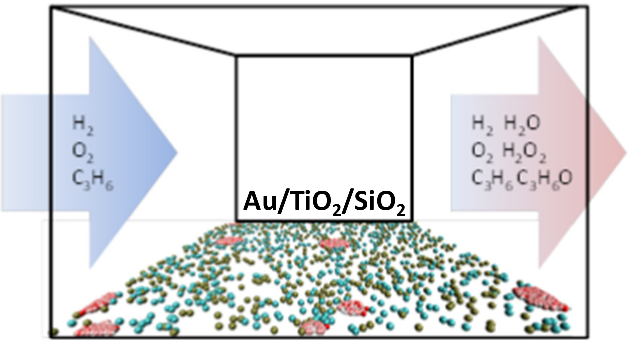
HIGHLIGHTS

- A kinetic Monte Carlo model for direct propylene epoxidation is proposed.
- The kinetic Monte Carlo surface reactions are coupled to a dynamic gas phase.
- Re-adsorption of hydrogen peroxide significantly accelerates the epoxidation.
- Experimental benchmarking tests sensitivity to reactant concentrations.

GRAPHICAL ABSTRACT



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ABSTRACT

The direct propylene epoxidation reaction has been investigated experimentally in the past by several different groups, and gold-based catalysts tend to provide high selectivity for propylene oxide, but the conversion is relatively low. Models that can connect the atomistic catalytic details to the observed experimental data are desired, in order to identify new catalyst structures and formulations. While electronic structure calculations have been used to quantify some of the key reaction steps in the direct propylene epoxidation reaction, atomistic models for translating this information into more experimentally-relevant data are needed. Here, kinetic Monte Carlo (KMC) simulations are used to bridge this gap in the modeling hierarchy. Relevant data from previous experiments and electronic structure calculations are used to parameterize a KMC model for predicting propylene oxide production from an Au/TiO_2/SiO_2 catalyst. The model connects the H_2/O_2-related reactions occurring on the Au sites with the epoxidation step on the isolated Ti surface sites. In addition, the composition in the bulk gas phase is synchronized with the dynamic reaction events occurring on the surface. The KMC model is able to adequately reproduce the experimental trends with respect to temperature and different reactant partial pressures. However, this is only achieved by considering the re-adsorption of trace amounts of the oxidant (H_2O_2) from the gas phase, versus merely assuming that desorbed species are immediately swept away in the gas stream.

1. Introduction

Propylene oxide (C_3H_6O, PO) derived from propylene (C_3H_6) is a key chemical intermediate for the production of a number of com-

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modity chemicals, including polyol, propylene glycol, and glycol ethers (Weissermel, 2003). However, current industrial methods that produce propylene oxide from propylene, namely chlorohydrin and hydroperoxide processes, pose environmental risks because of the production of chlorinated or peroxycarboxylic waste (Monnier, 2001; Nijhuis et al., 2006). Using supported gold-based catalysts to produce propylene oxide directly from propylene and molecular H_2 and O_2 provides an alternative, clean, and potentially more efficient route.

Nearly 20 years ago, Haruta and co-workers discovered that nm-sized Au catalysts on TiO_2 are active and highly selective for the direct gas-phase PO reaction (Hayashi et al., 1998; Uphade et al., 2001; Uphade et al., 2002). When propylene, oxygen, and hydrogen are co-fed, hydrogen peroxide can be readily formed on the surface of gold, and in turn, selectively oxidizes propylene molecules that are adsorbed on TiO_2 sites to propylene oxide (Nijhuis et al., 2006). Also, it has been found that Au supported by titanium silicalite (TS-1) is particularly effective at catalyzing the propylene epoxidation reaction. The isolated Ti active sites are necessary for obtaining a high selectivity towards propylene oxide (Stangland et al., 2000; Nijhuis et al., 1999; Chen et al., 2013a), since propylene oxide molecules that adsorb on adjacent Ti sites lead to catalyst deactivation and the formation of unwanted byproducts. Although the selectivity is very high (>90%), even the best catalysts found to date still suffer from multiple challenges, including low propylene conversion (<10%), poor stability and inefficient usage of H_2 (<50%). Therefore, significant improvement with regard to these issues is necessary, and this requires a more thorough understanding of the underlying chemical reaction network.

A lot of experimental effort has been focused on developing Au-based catalysts for the direct PO reaction (Nijhuis et al., 2006; Chen et al., 2013a, 2013b; Feng et al., 2016; Ferrandez et al., 2015), Also, many related studies have investigated different catalysts for direct H_2O_2 synthesis (Joshi et al., 2007; Landon et al., 2002, 2003; Edwards et al., 2009), since this is a key reaction step prior to the propylene epoxidation. Alternate catalyst formulations have been explored (including Ag, Cu, Mo, as well as photocatalysts) (Ghosh et al., 2014; Lei et al., 2010; Cheng et al., 2014; Chu et al., 2006; Vaughan et al., 2005; Song et al., 2007; Murata et al., 2003; Amano et al., 2004), but performance issues still limit economic viability.

Over the same time period, computational chemistry approaches, mainly first-principles density-functional theory (DFT), have provided additional insights into the chemical mechanisms driving the experimentally-observed PO reaction behavior. These studies have been used to clarify energetic and structural information about the active sites most responsible for the production of PO. For instance, there are DFT reports of the $O_2 + H_2$ reaction mechanisms on Au surfaces and clusters (Wells et al., 2004a; Barton and Podkolzin, 2005), as well as comparisons of the same reactions on other transition metal surfaces (Rh, Ir, Ni, Pd, Pt, Cu, Ag) (Ford et al., 2010; Duzenli et al., 2015) and bimetallic surfaces (Li and Yoshizawa, 2015) (including extrapolations via scaling relations) (Grabow et al., 2012). Computational studies focused exclusively on the direct PO reaction mechanism are more limited, and these have mainly originated from the Thomson (Wells et al., 2004b, 2006; Joshi et al., 2006, 2007) and Corma (Pulido et al., 2012a, 2012b) groups, along with a few related studies of ethylene epoxidation (Karlsen and Schoffel, 1996; Limtrakul et al., 2004). These DFT studies provide an excellent framework for interpreting the experimental results, but due to the variability of experimental sample preparation (structural defects, catalyst particle size distributions, etc.) there can be a wide range of experimentally-observed performance (Qi et al., 2004; Feng et al., 2015a, 2015b; Huang et al., 2010; Lee et al., 2011, 2013, 2014) that is difficult to capture with computationally-expensive DFT approaches. Thus, a lot of the modeling efforts have been more empirical, in order to provide analytical expressions for the product distributions as a function of the natural experimental variables (temperature, reactant partial pressure, feed rates, catalyst loading, etc.). For instance, a series of methodical experimental kinetic tests of the propylene epoxidation performance and related reactions have previously been used to regress reaction orders and elementary reaction steps (Ferrandez et al., 2015; Barton and Podkolzin, 2005; Bravo-Suarez et al., 2008, 2007).

While the DFT-based approaches provide fundamental electronic structure information about ideal systems, and the experimentally-derived rate expressions are useful for optimizing synthesis conditions, there is a large gap between these two ends of the modeling spectrum. More predictive models are needed that can directly connect the atomistic details to the observed experimental behavior. In order to establish this connection, we have pursued a kinetic Monte Carlo (KMC) simulation approach. Fundamental DFT-based values (such as adsorption energies and transition state barriers) can be combined with information about the catalyst surface, in order to make predictions about reactivity on experimentally-relevant time scales. This approach has been pursued previously for modeling heterogeneous catalyst behavior (Hansen and Neurock, 2000; Haug and Raibeck, 2003; Mei et al., 2003, 2006, 2010; Kieken et al., 2005), as well as other activated processes, such as surface deposition (Turner et al., 2016; Jiang and Hou, 2015; Rodgers et al., 2015; Hu et al., 2009a, 2009b; Zheng et al., 2008; Drews et al., 2004; Lou and Christofides, 2004; Wadley et al., 2001), diffusion, (Van der Ven and Ceder, 2000; Greenfield and Theodorou, 2001; Krishnamurthy et al., 2004; Scarle et al., 2005; Munn et al., 2009; Neyertz and Brown, 2010) and electrochemical systems (Lau et al., 2008; Turner et al., 2015).

In the present work, KMC simulations are constructed by selecting a minimal set of systems events relevant to direct PO synthesis (adsorption, desorption, reaction, diffusion), as well as their associated rate expressions. Although the model does not capture all of the possible reactions and side products that are known to exist, it serves as a first step towards developing a stronger connection between the atomistic events and the experimental performance of the direct PO synthesis reaction. This is intended to provide the necessary insight to enable the design of efficient and economical heterogeneous catalysts in the future. In particular, our KMC model is able to adequately reproduce the experimental trends with respect to temperature and different reactant partial pressures. However, we find that this is only achieved by considering the re-adsorption of trace amounts of H_2O_2 from the gas phase, versus merely assuming that the desorbed products are immediately swept away in the gas stream. The next section describes the details of our KMC implementation, followed by our results, experimental benchmarking, and analysis. The conditions for the experimental data used for comparison correspond to a feed gas concentration of 10% H_2, 10% O_2, 10% C_3H_6, and the balance Ar at a total flowrate of 35 ml/min (additional details provided in the Supplementary Information). The coverage of TiO_2 on SiO_2 is approximately 10% and the Au deposition is 1 wt%, and the temperature ranges from 413 to 473 K.

2. Computational methods

The KMC simulation technique originated from the early contributions of Young and Elcock (1966), Cox and Miller (1965)), and Gillespie (1976). In the years following, Fichthorn and Weinberg (1991) provided an additional analysis of the method, and others (Chatterjee and Vlachos, 2007; Voter, 2005) have provided valu-