

Microkinetic Modeling of Catalytic Polyol Thermal Decomposition and Reforming on Platinum

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Introduction

There has been increasing interest in the utilization of biomass for renewable energy and chemical production. Abundant biomass resources consist of oxygenated hydrocarbon building blocks. Successful conversion of oxygenated hydrocarbons to synthesis gas will result in better utilization of renewable biomass resources for energy and chemical production. Small-scale catalytic reforming technologies can increase distribution of synthesis gas production and increase reaction rates over current large-scale enzymatic technologies. Distributed synthesis gas can be used for production of methanol, ammonia, liquid fuels (Fischer-Tropsch process) or hydrogen. Current small-scale reforming technologies, including autothermal reforming [1] and aqueous phase reforming [2], have shown high conversion and selectivity toward desired products for small oxygenates (e.g., methanol, ethylene glycol, glycerol). For full and efficient biomass utilization to become a reality, these successes of current technologies must be extended to larger polyols.

Microkinetic models can provide great insight into the surface reaction mechanisms of polyol thermal decomposition and reforming. These models can be applied to reactor design and catalyst optimization for conversion of polyols to syngas. The focus of this study is the development of a thermodynamically consistent microkinetic model that describes the detailed mechanisms for thermal decomposition and reforming of methanol and ethylene glycol, as well as the extension of this model to larger polyols (e.g., glycerol).

Materials and Methods

The microkinetic model in this study was developed using the constraint of thermodynamic consistency [3]. Thermochemical properties of reaction intermediates were estimated using G3B3 level [4] quantum mechanical calculations and statistical mechanics for temperature dependent properties. Enthalpy of formation for previously unstudied reaction intermediates were calculated using a methodology involving isodesmic reactions described by Wang et al. [5]. Binding energies for reaction species and activation energies for individual reactions from periodic DFT studies in literature were used in the model. Order of magnitude estimates of pre-exponential factors were tuned to published experimental data.

Results and Discussion

A complete microkinetic model has been developed to describe thermal decomposition and reforming of polyols on Pt. The surface mechanism includes 244 irreversible elementary reactions of the following classifications: adsorption/desorption, hydrogen extraction, carbon-carbon bond cleavage, hydrogen oxidation, carbon monoxide oxidation, and hydrogen and carbon monoxide coupling reactions via the carboxyl intermediate through an OH intermediate formed by H oxidation.

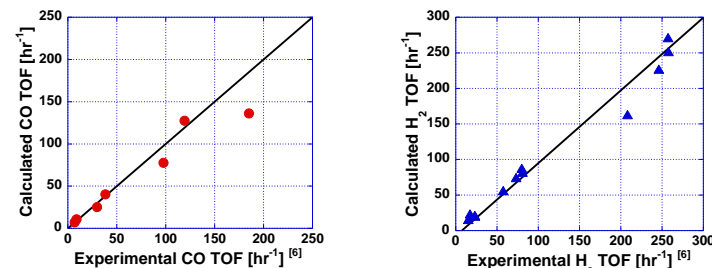


Figure 1. Comparison of microkinetic model results to published experimental results for methanol thermal decomposition

The model accurately describes experimental data for polyol thermal decomposition in a plug flow reactor at temperatures under 500 K with varying polyol inlet concentrations (<10% by mole). In the case of methanol, this comparison is depicted in the two parity graphs of Figure 1. Similar accuracy is seen when comparing the model results to ethylene glycol experimental data. Analysis shows that characteristics of the methanol surface mechanism are in good agreement with previously published microkinetic models and experimental observations. Reaction path analysis of the ethylene glycol processes indicates that ethylene glycol undergoes several hydrogen extraction reactions to form the HOCCO surface intermediate. From this intermediate, C-C bond cleavage takes place, followed by water-gas shift chemistry to yield the products observed in experimental studies.

Along with analysis of the ethylene glycol mechanism, this work also highlights the methodology and results of extending this microkinetic model to larger polyols, specifically glycerol. Aside from thermal decomposition, the microkinetic model is capable of describing reforming data under steam and partial oxidation modes.

Significance

This work presents the first thermodynamically consistent, full microkinetic model of small polyol thermal decomposition and reforming on platinum. It also introduces a methodology for extending this model to larger polyols. This work provides new strategies for the modeling of biomass reforming mechanisms that can give great insights into future reactor design and catalyst optimization for biomass reforming technologies.

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