

KINETIC MODELING OF AUTOTHERMAL REFORMING OF DIMETHYL ETHER

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Summary

A global kinetic model was developed for the autothermal reforming of dimethyl ether (DME) over a Pd-Zn/Al₂O₃ catalyst on a cordierite monolith. A kinetic model consisting of five overall reactions captured the main features of experimental data. The modelling also accounted for heat transport effects in the reactor that are of importance when coupling exothermic oxidation reactions with endothermic steam reforming reactions. The modelling confirmed that oxidation reactions dominate near the inlet of the reactor, generating a local hot spot. The influence of the reactor scale and oxygen supply by air feed on the performance of the reactor was examined.

Keywords

Hydrogen production, Environmental reaction engineering

Introduction

Dimethyl ether (DME) is considered an attractive alternative diesel fuel due to low emissions of particulates, reduced engine noise emissions and well-to-wheel study indications for a strong potential for low CO₂ emissions for DME produced from renewable feedstocks.

Idling of trucks and other heavy-duty vehicles for on board power generation is an enormously inefficient use of power from a diesel engine. As a result there have been on-going efforts to develop fuel cell auxiliary power (APU) units that produce electricity efficiently with low emissions. Experimental studies concerning the production of hydrogen via reforming of diesel or surrogate diesel fuels have started to appear in the literature. But also production of hydrogen from DME either by steam reforming or autothermal reforming¹ has garnered some attention. Although experimental studies of DME reforming have been undertaken, kinetic modelling studies are sparse. Here we report on a kinetic modelling study of autothermal reforming of DME over a PdZn/γ-Al₂O₃ catalyst. The catalyst is in the form of a washcoated monolith similar to that likely to be applied in an actual APU process. The experimental data forming the basis of this modelling study is taken from a part of a previous publication¹.

Modelling Methods:

Transport Models:

Two different transport models were used with different levels of detail. A more rigorous 2D model accounted for mass and heat transport between the gas and

solid, mass transport resistance in the catalyst washcoat, as well as heat transport both radially and axially in the monolith. Convergence of this model to a solution could not be obtained for all ranges of kinetic parameters and various kinetic models. Instead for parameter optimization purposes a more robust and less computationally demanding 1D model was used. This model lumped the radial heat transport into an overall heat transport term that was determined from parallel simulations with the 2D model.

Kinetic Model:

The approach adopted with this modelling effort was to limit the kinetic model to a few key overall reactions that captured the experimental observations and yielded well-defined kinetic parameters. The kinetic model consisted of reactions for DME total oxidation, DME hydrolysis, methanol decomposition, the water-gas shift reaction as well as methane by-product formation via DME decomposition. Langmuir-Hinshelwood type rate expressions for each of the reactions were used. It was assumed that all reactions occur on a single site, where adsorption of various species was included in the rate expressions.

The goal of the modelling was to estimate the kinetic parameters based on experimental results. Parameter fitting was performed using a gradient search method with the objective function of minimizing the residual sums of squares for the measured outlet temperature as well as the

concentrations of DME, CO, CO₂, H₂O, H₂, CH₄ and methanol.

Results and Discussion

Figure 1 shows some sample results comparing the experimental and model predicted outlet DME and major product compositions for a series of experiments with varying feed oxygen concentration and feed temperature. With higher feed temperature and oxygen feed concentration the conversion of DME and outlet concentrations of major products (CO₂, CO, and H₂) increases, both according to the experiments and model predictions. It is expected that a higher feed concentration of oxygen promotes the DME oxidation reaction which in turn generates more heat that sustains the DME hydrolysis and methanol decomposition reactions. Promotion of DME hydrolysis and the water-gas shift reactions with increased oxygen feed is also indicated by the drop in the outlet water concentration. This behaviour was confirmed by the model and could be illustrated by the model predictions of temperature profiles in the monolith, where a peak temperature was predicted at the centre of the monolith close to the inlet. The oxidation reactions dominated close to the reactor inlet, creating a temperature peak. The peak temperature reached which is dependent on the feed temperature and feed concentration of oxygen, determines the extent of activation of the following endothermic reactions including DME hydrolysis and methanol decomposition. The WGS reaction was found to be close to equilibrium for conditions at higher operating temperature, as indicated in Figure 1 by the deviation of the predicted CO concentrations from the WGS equilibrium levels. The kinetic rate equations only included a water adsorption term, because higher water concentration appeared to reduce DME conversion.

Based on the model, the performance of the monolith reactor was examined, if it were operated with air feed to supply oxygen and scaled-up to produce sufficient hydrogen to power a 5 kW fuel cell. It was found that at operating conditions giving a high conversion of DME (>95%), the model predicted an outlet H₂ concentration greater than 40 mol%. According to the model the reactor can be operated with varying total feed concentrations of the reactants with only small changes in the temperature profile, however the reactor scale strongly influences the heat transport behaviour of the reactor and as a result the temperature profile. A catalyst support material with higher thermal conductivity, may be advantageously used in a larger scale reactor to improve the heat transport behaviour and moderate operating temperatures in an APU system.

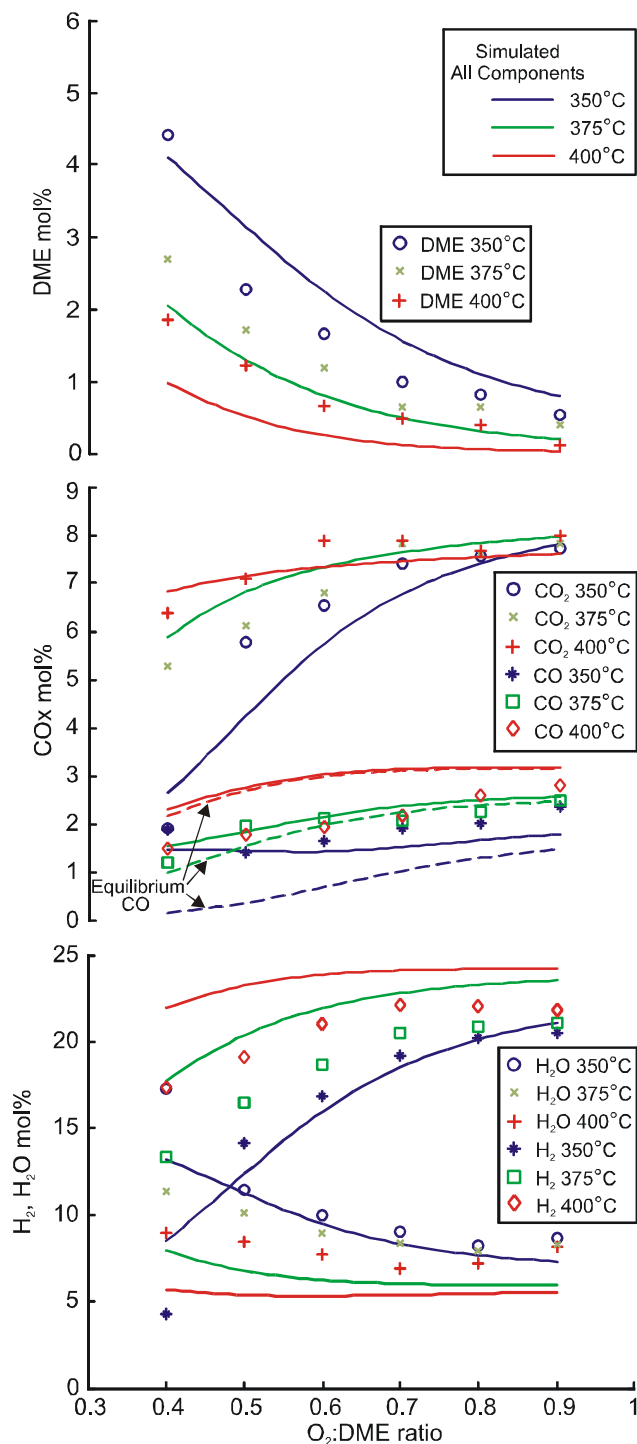


Figure 1. Outlet concentrations of DME, H₂O and major products as a function of O₂:DME molar feed ratio and feed temperature. Symbols are experimental results and curves are simulated.

References

- (1) Nilsson, M., Jozsa, P., Pettersson, L.J. Evaluation of Pd-based catalysts and the influence of operating conditions for autothermal reforming of dimethyl ether. *Applied Catalysis B: Environmental* **2007**, 76, 42.