Surface kinetic modeling of ozone-assisted methane oxidation over Coβ catalyst: validation against experimental data under humid conditions

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Introduction

Methane is a potent greenhouse gas, but its high C–H bond stability makes catalytic oxidation challenging at low temperatures. Ozone-assisted catalysis provides a promising approach by supplying reactive oxygen species that can promote methane oxidation under mild conditions.
Co-exchanged β-zeolite (Coβ) has shown promising activity for low-temperature ozone-assisted methane oxidation [1,2]. Experimental data reported by Yasumura et al. are therefore used in this work as a reference for evaluating the surface kinetic model [2].
The aim of this work is to develop a surface kinetic description capable of reproducing the experimentally observed CH_4 conversion and providing a basis for predictive modelling of plasma-catalytic methane oxidation. Particular attention is given to methane oxidation under humid conditions, using the 10% H_2O experimental condition as the current benchmark. The model is evaluated over a broad temperature range by comparing the calculated CH_4 conversion with the corresponding experimental data.

Surface Kinetic Model

A surface kinetic mechanism was implemented in LoKI-GM [3] based on the reaction pathway proposed by Yasumura et al. The mechanism describes the formation of reactive surface oxygen species, methane activation, and the subsequent oxidation of methane-derived surface intermediates toward CO_2 formation. H_2O was explicitly included through reversible adsorption and desorption on vacant surface sites.

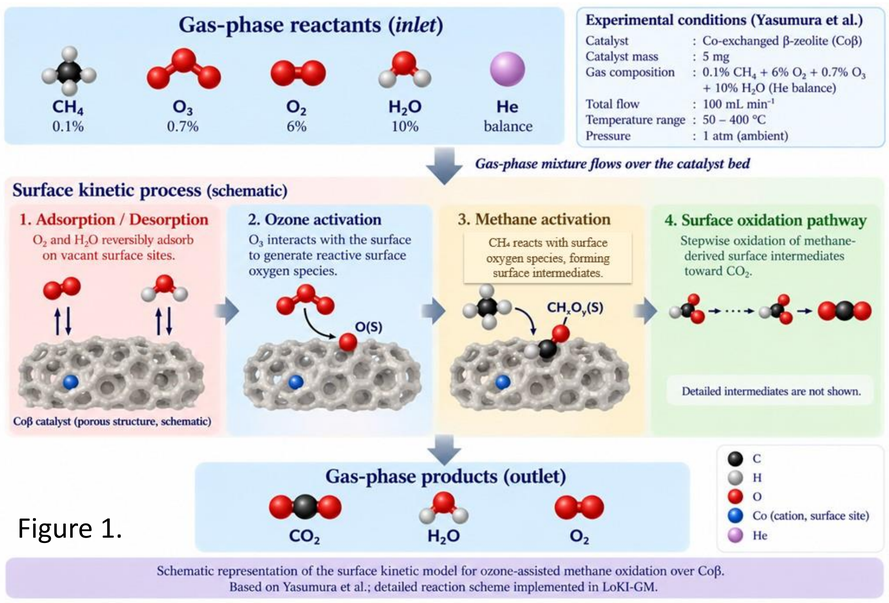

Figure 1.

Temperature-Dependent Ozone Treatment

It is well established that ozone thermally decomposes at elevated temperatures, with the extent of decomposition depending on the specific system and operating conditions. Therefore, the model inputs must reflect the appropriate O_3/O_2 ratio throughout the 50–400 °C temperature range of interest to this study.

The treatment of temperature-dependent ozone availability was initially inspired by the approach used for the So Min Jin's et al. system [1], where the O_3 fraction decreases and the O_2 fraction increases with temperature. However, because the experimental conditions of the Yasumura system are different [2], a system-specific O_3/O_2 temperature profile was required. Since a temperature-resolved inlet O_3 profile was not available for the Yasumura conditions, the O_3/O_2 inlet composition was treated as a temperature-dependent modelling assumption, following the expected decrease in ozone availability at higher temperatures. Above the conversion maximum, the temperature-dependent decrease in ozone availability becomes particularly important. Although increasing temperature can accelerate surface reaction kinetics, the simultaneous decrease in available O_3 reduces the oxidizing capacity of the system. The resulting competition between these effects is consistent with the observed decrease in CH_4 conversion at higher temperatures.

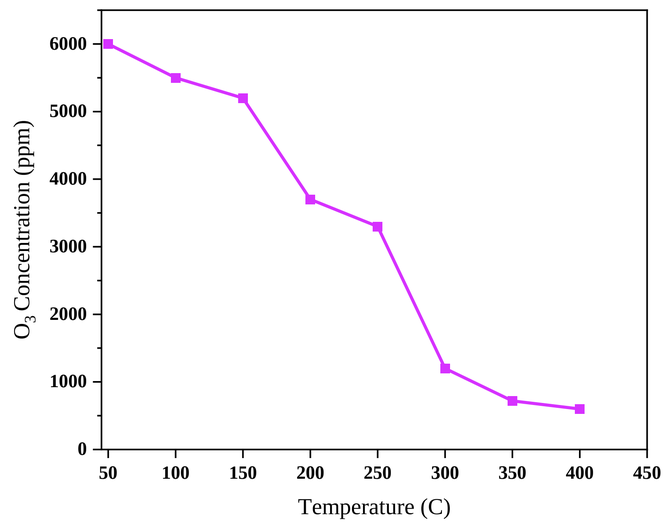

Figure 2. Temperature-dependent O_3 profile for Yasumura simulations

Results

The LoKI-GM simulations show close agreement with the experimental CH_4 conversion for the 10% H_2O condition over the investigated temperature range. The model reproduces the overall temperature-dependent trend, with CH_4 conversion increasing sharply between 100 and 200 °C, reaching a maximum of approximately 79% at 250 °C, and subsequently decreasing at higher temperatures. From 150 to 400 °C, the calculated conversions closely match the experimental values; for example, at 250 °C the simulation predicts 78.77% conversion compared with 78% experimentally. At 50–100 °C, both simulation and experiment indicate very low CH_4 conversion. The decrease in CH_4 conversion above 250 °C is consistent with the reduced O_3 availability considered at elevated temperatures in the model (Table 1 and Figure 3).

Temperature (°C)	LoKI-GM CH_4 conversion (%)	Yasumura experiment (%)
50	0.14	0
100	4.14	0
150	41.02	41
200	73.34	73
250	78.77	78
300	29.70	30
350	17.96	18
400	15.01	15

Table 1. CH_4 conversion, simulations vs experimental

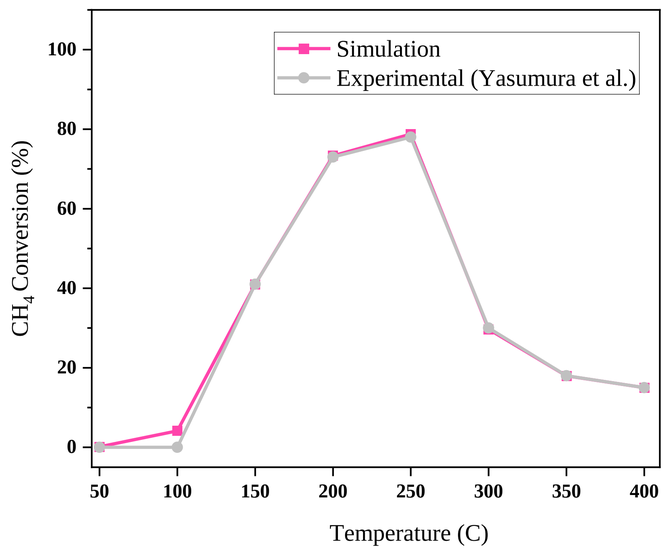

Figure 3. CH_4 conversion, simulations vs experimental

Conclusions:

- A surface kinetic model for ozone-assisted CH_4 oxidation over Coβ was implemented in LoKI-GM and evaluated for the 10% H_2O condition.
- The simulations closely reproduce the experimental CH_4 conversion reported by Yasumura et al. over the 50–400 °C temperature range, capturing both the increase up to approximately 250 °C and the subsequent decrease at higher temperatures.
- A temperature-dependent treatment of O_3 availability was incorporated to account for the reduced ozone availability at elevated temperatures.

Perspectives:

The immediate next step is to apply the same modelling framework to the other experimental humidity conditions and determine whether the same reaction mechanism and kinetic parameters remain transferable. This is a stronger test than independently tuning each water concentration.

After that, kinetic-parameter optimization and analysis can be used to identify which parameters control the observable methane conversion most strongly. The longer-term objective is a robust surface kinetic model that can support predictive plasma-catalytic methane-oxidation simulations.

References:

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