

Microkinetic modelling of a Pd-based three-way catalyst for stoichiometric natural gas vehicles

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Significance and Relevance

A thermodynamically consistent comprehensive microkinetic model is developed for a Pd-based three-way catalyst for stoichiometric natural gas vehicle exhaust. The model is able to predict the experimental data quite well. A sensitivity analysis is performed to identify the elementary reaction steps which govern the overall rate and the product composition. This work elucidates the detailed microkinetics and rate determining step(s) on the predominantly used Pd-based three-way catalysts, which can be helpful for further catalyst design.

Preferred and 2nd choice for the topic: Automotive and stationary emission control (preferred), Multiscale modeling and advanced simulation aspects (2nd choice)

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivation

Natural gas vehicles are a promising alternative to diesel and gasoline vehicles considering the abundant availability of natural gas reserves and lower NO_x and particulate emissions. Moreover, natural gas, which is mainly composed of methane, produces comparatively lower CO_2 emissions per unit energy produced due to the higher hydrogen to carbon ratio. However, methane being a relatively stable hydrocarbon, the abatement of unburnt methane in the vehicle exhaust poses a demanding challenge, considering the stringent emission norms throughout the world. Pd-based three-way catalysts are predominantly employed for the aftertreatment of natural gas vehicles exhausts under stoichiometric conditions due to the high activity of Pd for methane oxidation.¹

Various global reaction models have been developed to investigate and predict the catalytic activity of Pd-based three-way catalysts.² However, global reaction models use a single rate expression for each overall reaction, which does not contain information on the individual reactions occurring on the surface. Microkinetic modelling, which involves elementary reaction steps, has emerged as a promising tool to gain a deeper insight into the fundamental surface kinetics of the catalyst. Several microkinetic models for CH₄ oxidation under lean conditions and NO reduction under rich conditions on Pd-based catalysts have been developed separately. However, to the best of our knowledge, a comprehensive microkinetic model for a Pd-based three-way catalyst for natural gas vehicles involving CH₄ and NO reduction simultaneously is not available in the literature, which serves as a motivation for this work.

Materials and Methods

The individual methane oxidation and NO reduction mechanisms on Pd (111) surface, obtained from literature, were combined to develop the initial model. A total of 42 elementary steps with 21 surface species and 10 gaseous species were included. A 1D+1D single channel isothermal monolith reactor model was employed to perform the simulations. A sensitivity analysis was conducted to identify the key steps that govern the product composition. The pre-exponential factors of the key steps were obtained by fitting the experimental data from literature ³, with the parameter fitting performed using *'Isqnonlin'* function in MATLAB. During the parameter fitting, thermodynamic consistency of the reaction mechanism was ensured by comparing the standard heat of reaction (Δ H) and standard entropy change (Δ S) of the global reactions (CH₄ oxidation, CO oxidation, and NO reduction to N₂, N₂O and NH₃) obtained from the elementary reaction steps using NIST database.



Results and Discussion

During the preliminary sensitivity analysis, 8 elementary steps were identified as the key steps. A comparison of the model-predicted results and the reported conversion data is shown in Figure 1. The model was able to predict the conversion of CH₄, CO, and NO with reasonable accuracy over the entire lambda range encompassing lean and rich conditions. As shown in Table 1, Δ H and Δ S of all the global reactions were in close agreement with the corresponding values obtained from the NIST database implying that the mechanism is thermodynamically consistent. A sensitivity analysis was performed under lean as well as rich conditions to identify the rate-determining steps. The dissociative adsorption of CH₄ was the key step for CH₄ conversion whereas, the H-assisted dissociation of adsorbed NO played a key role in NO conversion.



Figure 1. Comparison of model-predicted and experimental product composition at 520 °C.

	Calculated		NIST database		% error	
Reaction	∆H (kJ/mol)	ΔS (J/mol K)	∆H (kJ/mol)	ΔS (J/mol K)	ΔН	ΔS
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	-734.3	-5.1	-802.3	-5.1	8.5	0.0
$CO + 0.5O_2 \rightarrow CO_2$	-284.6	-84.0	-283.0	-86.4	0.6	2.8
$NO + 2.5H_2 \rightarrow NH_3 + H_2O$	-345.4	-165.2	-378.1	-155.8	8.6	6.0
$2NO + H_2 \rightarrow N_2O + H_2O$	-291.4	-150.1	-340.4	-143.4	14.4	4.7
$2NO + 2H_2 \rightarrow N_2 + 2H_2O$	-605.9	-115.5	-664.2	-113.6	8.8	1.7

Table 1. Comparison of calculated ΔH and ΔS with NI	NST database
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References

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