



# Modeling of three-way catalytic converter performance with exhaust mixture from natural gas-fueled engines



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## ABSTRACT

The ability of a three-way catalytic converter (TWC) to treat the exhaust from a natural-gas fueled engine was evaluated by numerical simulation. A comprehensive and thermodynamically consistent surface reaction mechanism describing the surface reactions in the TWC was built by compiling elementary-step reaction kinetics involving CH<sub>4</sub>, CO, formaldehyde, NO, NH<sub>3</sub> and N<sub>2</sub>O from literature sources. The reaction parameters are taken from literatures and fitting calculations. The mechanism was implemented in a one-dimensional PFR model describing a single channel of the catalyst. The simulation results were evaluated by comparison with field data collected from a TWC operated isothermally at steady-state. The model predicted the major trends in conversion/formation of all species in the TWC over a wide range of air to fuel ratios. Sensitivity analysis was utilized to study the key reaction steps that impact the exhaust emission mole fraction. It was found that methane, NO, CO and formaldehyde are most sensitive to the corresponding adsorption steps, while NH<sub>3</sub> and N<sub>2</sub>O are sensitive to the reactions that relate to their formations, such as reactions involving surface hydrogen atoms for NH<sub>3</sub> and NO for N<sub>2</sub>O.

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## 1. Introduction

In response to stringent environmental regulations, the automotive industry has conducted a substantial amount of research into three-way catalytic converter (TWC) systems to simultaneously remove unburned hydrocarbon (HC), NO<sub>x</sub> and CO from the exhaust from gasoline-fueled engines [1]. This includes the development of TWC converter microkinetic models that comprehensively describe the catalytic chemistry on a molecular level [2,3]. Recently, there is an interest in using TWC for treating the exhaust from natural gas engines due to the New Source Performance Standards promulgated by EPA in January, 2008. In addition, natural gas is the world's fastest growing major energy source and is projected to rise into second place among energy sources by 2040 [4]. For this reason it will be increasingly important to explore catalytic processes to reduce emissions from natural gas-powered engines. The models developed for gasoline engines are insufficient for modeling a TWC for treating emissions from natural gas engines, since they lack detailed chemistry for methane.

The core of the TWC is a multi-channeled ceramic or metallic monolith. A washcoat (catalyst carrier) containing finely dispersed

noble metals (Pt, Pd, Rh) and ceria is coated on the wall of the channel, through which exhaust gases flows. The noble metals are the active sites, catalyzing both oxidation and reduction [5]. Ceria is added because of its structural properties, its reversibility of sulfur poisoning and its rapid kinetics of oxygen storage and release [6], however this effect is not considered in the current steady state model. The exhaust emission condition is quantized using the normalized air to fuel ratio as

$$\lambda = \frac{AF_{\text{realistic}}}{AF_{\text{stoichiometric}}}$$

Therefore,  $\lambda > 1$  corresponds to fuel lean conditions while  $\lambda < 1$  corresponds to fuel rich conditions. It is widely accepted that the air to fuel ratio has a great impact on the TWC ability to efficiently remove CO and NO<sub>x</sub> from the exhaust. The efficiency reaches a maximum around the stoichiometric condition ( $\lambda = 1$ ) [7]. Research on gasoline [8] and natural gas engines [9] both indicate that there is a trade-off between NO and CO conversion. Fuel-rich conditions produce high NO conversion but low CO conversion, while the opposite trend is noted at fuel-lean condition. Only at air to fuel ratios very close to the stoichiometric point can both components be reduced significantly.

Methane oxidation chemistry over noble metals, particularly platinum and palladium, has been extensively studied. Activation of the C–H bond is generally considered as the rate limiting step for methane combustion and two activation mechanism were pro-

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posed on these two metals. Burch and coworker [10] proposed that Pt activates the C–H bond of methane by dissociative adsorption of methane at vacant metal sites, fully covered with oxygen species cannot activate C–H bond. By contrast, Pd is much more effective than Pt at lean conditions, Pd<sup>2+</sup>O<sup>2-</sup> ions on PdO surface can more easily activate the C–H bond and PdO is considered as the active phase [11]. The reversible transformation between PdO and metallic Pd is well observed and a correlation has been found between this transformation and methane oxidation activity [12]. Miller and Malatpure [13] indicated that methane total oxidation is correlated to the density of PdO–Pd· (\* is an O-vacancy) site pairs: if the PdO is over-stabilized by the support (CeO<sub>2</sub>), then it cannot be partially reduced to Pd· to form the site pairs required by the reaction, and activity is decreased. Even though Pd exhibited better methane oxidation performance at lean condition, the complex transformation between metallic palladium and the metal oxide complicates the kinetic modeling of methane oxidation which should include the PdO formation [14].

Methane chemistry over platinum has been investigated for autothermal reforming [15], catalytic partial oxidation [16] and complete oxidation [17]. Burch and Loader compared the methane combustion over Pt/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub>, and showed that at higher methane conversions with stoichiometric or rich mixtures Pt/Al<sub>2</sub>O<sub>3</sub> is a more active catalyst. They also concluded that platinum can be a more effective catalyst than palladium for methane combustion under real conditions [18].

Lyubovskiy et al. studied the methane catalytic combustion over Pt-group catalyst both in fuel lean and fuel rich conditions [19]. They showed that the surface is covered with oxygen when reacting with a fuel-lean mixture, while it is covered with CO and H when reacting with a fuel-rich mixture. They suggested that the catalyst had a different state under fuel lean and fuel rich conditions, which resulted in different mechanisms for the interaction of methane with the catalyst. Buyevskaya [20] investigated the role of surface coverage on methane partial oxidation by flowing CH<sub>4</sub> over an initial O<sub>2</sub>-treated catalyst. The initial CO<sub>2</sub> selectivity was 100% but the major product produced shifted from CO<sub>2</sub> to CO as the surface oxygen was consumed, indicating that an oxygen-rich catalyst surface promoted the CO<sub>2</sub> formation, while an oxygen-lean surface leads to CO formation.

Due to platinum's high activity for methane oxidation and NO reduction, detailed elementary-step mechanisms for methane catalytic partial oxidation and NO reduction have been reported on platinum. Hickman and Schmidt [21] proposed a 19-elementary-step model for methane oxidation under methane-rich conditions on Pt and Rh surfaces. The dissociative adsorption of methane was grouped into a single step and was not reversible. The mechanism indicated that the H<sub>2</sub> and CO are primary products. Deutschmann et al. have developed microkinetic models for methane oxidation on rhodium that can be used to simulate steady-state partial oxidation [22] and transient behavior of catalytic monoliths [23]. Vlachos [24] used a hybrid parameter estimation methodology, based on experimental data, semi-empirical methods and first principle density function theory to estimate reaction rate constants for various steps in methane oxidation. The activation energy was both temperature and coverage dependent via the UBI-QEP method. A comprehensive reaction mechanism including methane, CO, formaldehyde and methanol was proposed. The methane dissociative adsorption was separated into four reversible, elementary steps.

NO reduction over platinum had been extensively studied with reducing agents such as H<sub>2</sub>, CO, CH<sub>4</sub>, propane and propene [25,26]; H<sub>2</sub> was the most efficient while CH<sub>4</sub> was the least efficient. When hydrogen was used as the reducing agent, NO was reduced to NH<sub>3</sub> [27,28], N<sub>2</sub> [28], and slight amounts of N<sub>2</sub>O [27]. N<sub>2</sub>O formation is favored when NO is reduced by CO [27] and NH<sub>3</sub> [29]. The primary role of hydrogen is to keep the catalyst surface clean by react-

ing with surface oxygen [30], exposing more vacant sites for the adsorption of NO. Meanwhile, a mechanism [31] suggested that adsorbed NO dissociated to surface nitrogen N· and surface oxygen O· with the promotion of vacant Pt sites.

In this paper, we describe a microkinetic model for the TWC applied to natural gas engine exhaust. Due to the lack of microkinetic models of methane oxidation over palladium, notably a lack of a comprehensive mechanism including carbon monoxide, methanol, formaldehyde, we chose to build our TWC model on a platinum reaction mechanism. To create our model, published methane oxidation and NO reduction mechanisms on platinum were combined and modified to fit experimental data while maintaining thermodynamic consistency. The resulting mechanism was used to simulate a commercial TWC [9] applied to reducing the emissions from a natural gas engine over a wide range of air to fuel ratios.

## 2. Mathematical model

The mass balance for the adsorbed species on the solid phase are obtained by assuming competitive adsorption of all species. The adsorption of each species on the catalyst, represented here as a change in species surface coverage ( $\theta_i$ ), at steady state can be calculated as follows:

$$\frac{\partial \theta_i}{\partial t} = 0 \quad (1)$$

$$\frac{\partial \theta_i}{\partial t} = \mathfrak{R}_{\text{adsorption},i} - \mathfrak{R}_{\text{desorption},i} + \sum_j \mathfrak{R}_{\text{reaction},j} \quad (2)$$

The surface coverage of vacant sites is defined as  $\theta_v$ :

$$\theta_v = 1 - \sum \theta_i \quad (3)$$

The adsorption rate could be calculated as:

$$\mathfrak{R}_{\text{adsorption},i} = \frac{s_i}{\Gamma} \sqrt{\frac{RT}{2\pi M_i}} \left(\frac{T}{T_0}\right)^\beta \exp\left(-\frac{E_{\text{adsorption}}}{RT}\right) C_i \theta_v \quad (4)$$

where  $s$  is the sticking coefficient,  $\Gamma$  is the site density of the catalyst,  $R$  is the gas constant,  $T$  is the absolute temperature,  $T_0=300$  K,  $\beta$  is the temperature component and  $M$  is the molecular weight.

The desorption rate is formulated as follows:

$$\mathfrak{R}_{\text{desorption},i} = A_{\text{desorption},i} \left(\frac{T}{T_0}\right)^\beta \exp\left(-\frac{E_{\text{desorption},i}}{RT}\right) \theta_i \quad (5)$$

The Langmuir–Hinshelwood type rate expressions are used to describe reaction rate:

$$\mathfrak{R}_{\text{reaction},j} = A_{\text{reaction},j} \left(\frac{T}{T_0}\right)^\beta \exp\left(-\frac{E_{\text{reaction},j}}{RT}\right) \Pi \theta_i \quad (6)$$

Assuming that flow in the channel can be represented as plug flow, we can write the flowrate for each species as:

$$\frac{dF_i}{dz} = \sum_j \mathfrak{R}_{\text{reaction},j} \Gamma S_m S_{\text{cross}} \quad (7)$$

where:  $S_m$  = catalyst surface area, m<sup>2</sup>/m<sup>3</sup>,  $S_{\text{cross}}$  = channel cross section area, m<sup>2</sup>. According to the definition above, at steady state condition, the PFR model equation can be formulated as:

$$\frac{dF_i}{dz} = (\mathfrak{R}_{\text{desorption},i} - \mathfrak{R}_{\text{adsorption},i}) \Gamma S_m S_{\text{cross}} \quad (8)$$

This plug-flow reactor (PFR) model was used to model a single channel in the TWC. The effects of mass transfer limitations in the transport of species to the monolith wall and through the washcoat layer were not considered in our model. To evaluate the validity of

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