Modeling of TWC converter performance with exhaust mixture from natural gas-fueled engines

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Introduction
Extensive research has gone into developing and modeling the three-way catalyst (TWC) to reduce the emissions of hydrocarbons, NO, and CO from gasoline-fueled engines level [1]. However, much less has been done to model the use of the three-way catalyst to treat exhaust from natural gas-fueled engines. This is a significant issue because natural gas will be the world’s fastest growing major energy source through 2040 and by 2025 and it is expected to overtake coal as the second-largest energy source. In addition, the New Source Performance Standards promulgated by EPA in January, 2008, may require operators of natural gas engines to tightly control their emissions. This paper address this gap in the literature by developing a detailed surface reaction mechanism for platinum based on elementary-step reactions. The surface reaction mechanism is used to simulate the performance of a commercial TWC for a range of natural gas-engine exhaust compositions, and the results are compared to experimental data [2].

Method
A reaction mechanism consisting of 24 species and 114 elementary reactions was constructed from literature values. Elementary kinetics for reactions of methane oxidation were obtained from [3] while reactions for N-O chemistry were obtained from [4-6]. All reaction parameters were used as found in the literature sources except for eight steps (methane adsorption, CO desorption, formaldehyde dissociation, NO dissociation, nitrous oxide formation and ammonia formation) which were modified to model the TWC to the experimental data. The TWC was simulated as a one-dimension, isothermal plug flow reactor (PFR) The ordinary differential equations (ODEs) for the PFR model plus algebraic equations for steady state surface reaction are coupled as differential algebraic equations (DAEs) and solved by Matlab.

Results and Discussion
The simulation results and experimental results plotted as a function of normalized air fuel ratio ($\lambda$) are showed in Figure 1. In general, the simulation captures all experimental trends except that nitrous oxide is under predicted in the transition from rich ($\lambda<1$) to lean ($\lambda>1$) compositions. Methane conversion is low at fuel rich condition and higher at lean condition because excessive oxygen can react with unburned methane at fuel lean condition. NO exhibited the opposite trend due to enhanced reduction in a reducing environment, where methane, CO and H$_2$ are the potential reducing agent to convert the NO to N$_2$ and NH$_3$. The formaldehyde conversion is consistently high at all conditions, while CO conversion is a little over predicted at rich conditions. As the NO conversion rate decreased, NH$_3$ formation decreased simultaneously, which indicated that NH$_3$ formed from precursor NO and this reaction occurred in the TWC converter, not in the combustion engine [7]. Results showed that NH$_3$ formation increased, as the surface coverage of H atoms increased, suggesting that a hydrogen source is necessary to produce NH$_3$ over the TWC.

Significance
This work described a method to quantitatively simulate the natural gas TWC converter performance, providing a deep understanding of the surface chemistry in the converter. This work can further be applied industrially to improve converter design.

References