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Catalytic oxidation of methane:

Modeling and simulations

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1. Introduction

Natural gas is of great interest nowadays in the effort to move towards less polluting marine fuels. Gas engines operating in lean conditions have proven to be successful in maintaining high efficiency while reducing NO_x, SO_x, CO_2, and PM emissions. However, these benefits are, in part, offset by unacceptable levels of methane emissions in the exhaust gas of lean-burn gas engines. In our previous study [1], we concluded that already 2.5% methane slip from LNG combustion negates the benefit of reduced CO_2 emissions, leading to global warming potential equal to diesel fuel. This underlines the importance of controlling methane emissions from gas engines.

A methane oxidation catalyst (MOC) is increasingly being considered as a critical component in the exhaust after-treatment architecture of lean-burn gas engines. The oxygen present in exhaust gases from lean-burn engines enables oxidation of CO and hydrocarbons (HC) over an oxidation catalyst. However, the conversion of methane remains more challenging compared to other HCs because high catalyst temperatures are necessary for the oxidation of this highly stable compound [2]. In addition, under lean-burn conditions, the oxidation reaction occurs in the presence of large quantities of water, which has a deactivating effect on catalysts. Furthermore, methane oxidation catalysts are sensitive to sulfur poisoning, even at very low sulfur levels. Sulfur present in lean-burn conditions, dominated by large excess of air, will be oxidized to SO_2, and further to SO_3, leading to the formation of sulfates and sulfites on both the noble metal active phase and the support [3]. Gremminger et al. [3] found that even <0.3 ppm amounts of sulfur species led to the accumulation of sulfur on MOC and caused rapid deactivation of the catalyst.

The ability to regain CH_4 conversion activity of deactivated catalyst via a regeneration mechanism is a critical issue for lean-burn gas engine applications. There are two ways for regenerating sulfur poisoned PGM-based catalysts. The first method is thermal regeneration. The problem with this approach is that temperatures required for regeneration are high. Studies have shown that complete regeneration is not possible even at a temperature of 650°C [2,4]. Another approach for catalyst regeneration is to change the chemistry of the exhaust gas. [4] For example, lowering the oxygen concentration in the catalyst feed gas can aid regeneration [5].

This study aimed to investigate the potential of using a simulation-based approach for predicting MOC behavior over time, i.e., deactivation and the effect of regeneration. The simulation model was created by GT-SUITE software developed by Gamma Technologies, LLC. Global kinetics was used to represent the oxidation reactions over a bimetallic Pt-Pd catalyst. To further develop the model, the SO_2 effects were added. Finally, the complete model was used to simulate catalyst regeneration by changing the temperature and exhaust gas composition.
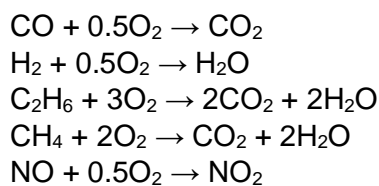
2. Materials and methods

The catalyst modeled in this study was a bimetallic Pt-Pd catalyst with the Pt/Pd weight ratio of 1:4. The noble metal loading in the catalyst was 200 g/ft^3 (7.06 g/l). Gamma alumina (γ-Al_2O_3) served as the support material.

2.1 Kinetic modeling

According to the software provider, typically two HC's in the system is sufficient and practical for modeling purposes. In general, one fast oxidizing and one slow oxidizing, or large HC, need to be modeled [6]. In our model, C_2H_6 represented the fast oxidizing HC and CH_4 the slow HC. Among alkanes, methane is the kinetically least reactive molecule [7].

The set of oxidizing reactions considered in this work was:

$CO + 0.5O_2 \rightarrow CO_2$
$H_2 + 0.5O_2 \rightarrow H_2O$
$C_2H_6 + 3O_2 \rightarrow 2CO_2 + 2H_2O$
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
$NO + 0.5O_2 \rightarrow NO_2$

2.2 Model calibration

MOC calibration means finding a set of reaction rates that best fits the measured data so that the model adequately predicts the conversion of reactants over the range of expected exhaust gas temperatures, flow rates, and species concentrations [6]. Typically, there are two rate constants for each reaction that needs to be calibrated; the frequency factor or pre-exponent multiplier, A, and the activation energy, E_a, in units of J/mol:

$$k = A \cdot exp\left(\frac{-E_a}{RT}\right),$$

where k is the rate constant, R is the universal gas constant in units of J/mol/K, and T is the temperature in units of K. The term E_a/R is also known as the activation temperature in units of K.

According to Arrhenius reaction kinetics:

$$Rate = k[A]^a[B]^b$$

Extending this to surface reactions involving coverages, the full rate becomes:

$$Rate = A \cdot exp\left(\frac{-E_a}{RT}\right)[concentration_{term}]^{order}(reactant\ coverages)(inhibition\ functions)$$

$$Rate = A \cdot exp\left(\frac{-E_a}{RT}\right)[C_i]^j(\theta_i)(G_i)$$

2.3 Experimental data

The experimental data were obtained from the catalyst developer. It included HC and CO light-off performance tests on both fresh and sulfur-poisoned catalysts. The sulfur-poisoned catalyst was first aged hydrothermally at 700°C for 20 h (10% H_2O in air) and then treated for 20 h at 400°C with a sulfur-containing gas having a concentration of 25 ppm SO_2. The exact inlet gas compositions are tabulated in Table 1.

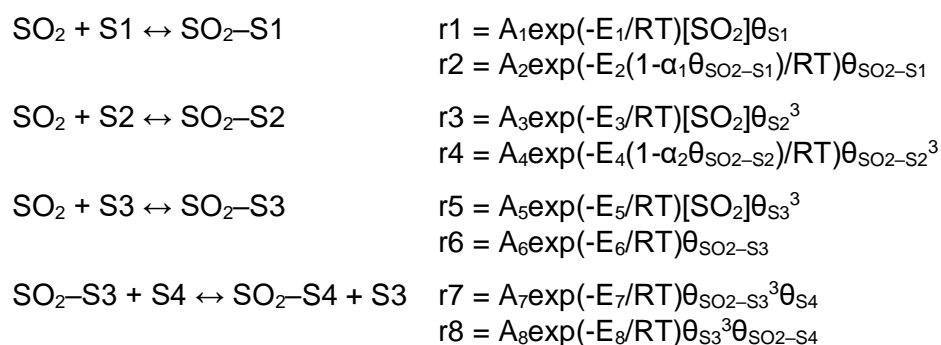**Table 1.** Simulated exhaust gas and SO_2 poisoning mixtures.

	Simulated exhaust gas	SO_2 poisoning mixture
CH_4	1500 ppm	–
C_2H_6	300 ppm	
C_3H_8	100 ppm	–
C_2H_4O	150 ppm	
NO	500 ppm	–
CO	1200 ppm	0.05%
H_2O	8%	10%
CO_2	7.5%	10%
O_2	10%	6.5%
SO_2		25 ppm
N_2	Bal.	Bal.
GHSV	50 000 h^{-1}	

2.4 Sulfur deactivation

To further develop the model, the SO_2 effects were added to the model. The sulfur poisoning model used in this study is based on the work of Gayatri [8]. In this 4-site reaction mechanism each site represents a different surface species:

- S1: Loosely bound SO_2 on PGM-site. This desorbs at low temperatures.
- S2: Surface sulfite. Present at typical MOC operating temperatures. Affect the active sites on PGM.
- S3: Surface sulfate. Present at typical MOC operating temperatures. Affect the active sites on PGM.
- S4: (Bulk) Sulfate on Alumina. SO_2 adsorbed on S4 site involves the bulk alumina and should not affect PGM active sites.

The reaction steps and rate expressions for SO_2 adsorption on and desorption from the catalyst are as follows:

$$SO_2 + S1 \leftrightarrow SO_2\text{–}S1 \qquad r1 = A_1 exp(-E_1/RT)[SO_2]\theta_{S1}$$
$$r2 = A_2 exp(-E_2(1-\alpha_1\theta_{SO2\text{–}S1})/RT)\theta_{SO2\text{–}S1}$$

$$SO_2 + S2 \leftrightarrow SO_2\text{–}S2 \qquad r3 = A_3 exp(-E_3/RT)[SO_2]\theta_{S2}^3$$
$$r4 = A_4 exp(-E_4(1-\alpha_2\theta_{SO2\text{–}S2})/RT)\theta_{SO2\text{–}S2}^3$$

$$SO_2 + S3 \leftrightarrow SO_2\text{–}S3 \qquad r5 = A_5 exp(-E_5/RT)[SO_2]\theta_{S3}^3$$
$$r6 = A_6 exp(-E_6/RT)\theta_{SO2\text{–}S3}$$

$$SO_2\text{–}S3 + S4 \leftrightarrow SO_2\text{–}S4 + S3 \qquad r7 = A_7 exp(-E_7/RT)\theta_{SO2\text{–}S3}^3\theta_{S4}$$
$$r8 = A_8 exp(-E_8/RT)\theta_{S3}^3\theta_{SO2\text{–}S4}$$

3. Results and discussion

The kinetic parameters for CH_4, C_2H_6 and CO to best fit the experimental data were first calibrated without sulfur effect. Thus, light-off experiments with the fresh catalyst were used as a basis for calibration. Inhibition functions were adopted from the DOC_Sampara and Bisset model in the GT-Suite library.

Table 2 summarizes the temperatures for 50% and 90% conversions, frequency factors, and activation energies for CH_4, C_2H_6 and CO after calibration. A more detailed description of conversion curves for CH_4 is presented in Fig. 1.

Table 2. $T_{50\%}$ and $T_{90\%}$, frequency factors and activation energies for CH_4, C_2H_6 and CO.

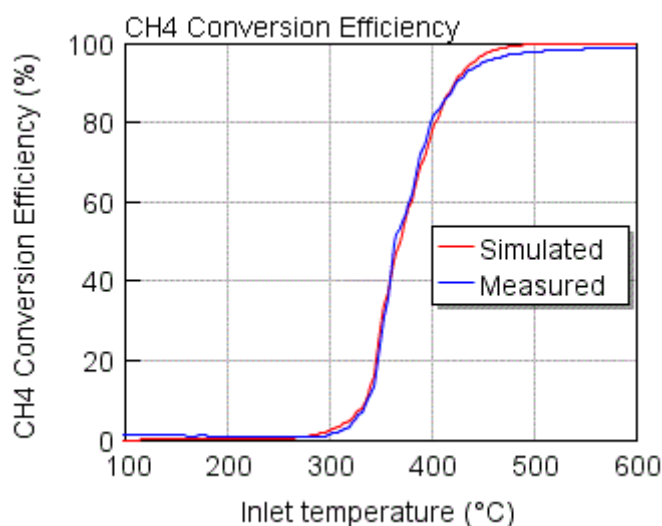|	$T_{50\%}$ (°C)		$T_{90\%}$ (°C)		A	E_a (J/mol)
	measured	simulated	measured	simulated		
CH_4	366	369	425	425	2.614E+06	88898
C_2H_6	348	348	389	393	3.692E+05	69525
CO	165	165	189	185	9.828E+04	24960

Figure 1. Measured and predicted conversion curves for CH_4 after calibration.

Following this, the SO_2 reactions were calibrated and added to the model. The completed model was then run at three different temperatures, 400°C, 450°C and 500°C. These temperatures are typical in lean operating natural gas engines [9]. Overall, the simulation indicated a fast deactivation of the catalyst in the presence of SO_2. At 400°C, a dramatic drop of the CH_4 conversion could be observed, resulting in less than 10% methane conversion after 20 h exposure time on SO_2 containing (25 ppm) stream. Similarly, at 450°C and 500°C the CH_4 conversion decreased rapidly during the first 4 h, eventually leading to CH_4 conversion of 30% and 70% after 20 h time on SO_2 containing stream (Fig. 2).
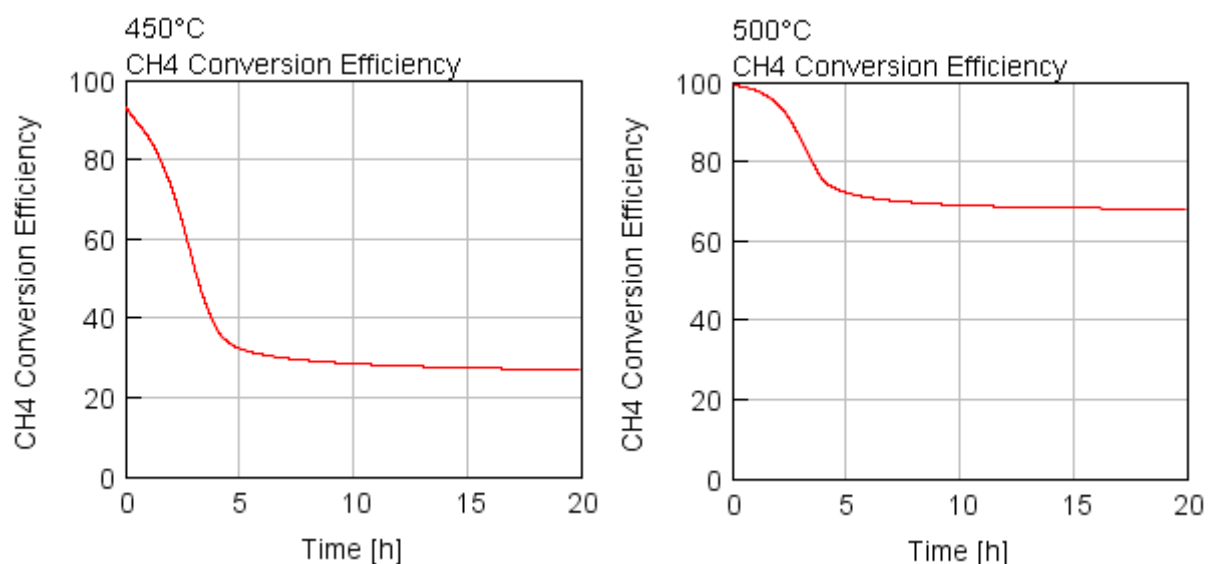
Figure 2. CH_4 conversion as function of time on SO_2 containing stream at two different temperatures.

After 20 hours exposure on SO_2 containing stream, CO $T_{90\%}$ increased from 189°C to 224°C, and C_2H_6 $T_{90\%}$ from 389°C to 492°C, respectively.

Finally, the model was run to predict the effect of the regeneration process. In the simulations both the air-fuel ratio and the temperature were changed/varied. The choice of this approach was based on Gremminger et al. [3]. They found that regeneration by reductive treatment combined with temperatures above 500°C was the most efficient for catalyst regeneration.

Results from the simulation are depicted in Figure 3. The first 5 hours demonstrates the deactivation of a fresh catalyst at 450°C with

- 25 ppm SO_2
- 1500 ppm CH_4
- 300 ppm C_2H_6
- 100 ppm C_3H_8
- 500 ppm NO
- 1200 ppm CO
- 10% O_2
- 8% H_2O
- 7.5% CO_2

in N_2. The model predicted a CH_4 conversion decrease from over 90% in fresh state to 35% in SO_2-poisoned state. After 5 hours, the regeneration period takes place. To regenerate the SO_2-poisoned catalyst, a 30 min reductive treatment is applied at 550°C. The regeneration mixture consisted of

- 9800 ppm CH_4
- 200 ppm C_2H_6
- 2.02% O_2 (λ=1)

in N_2. The model now predicted a CH_4 conversion increase from 35% in SO_2-poisoned state (at 450°C) to 95% in regenerated state (at 550°C). The result is in line with the experimental data, which showed a 95% conversion at 550°C after 30 min regeneration by reductive treatment. The decrease

in CH_4 conversion during the regeneration process is due to lack of excess O_2 in the reaction gas feed [10]. Figure 3 also illustrates the release of SO_2 from the catalyst during the regeneration procedure.
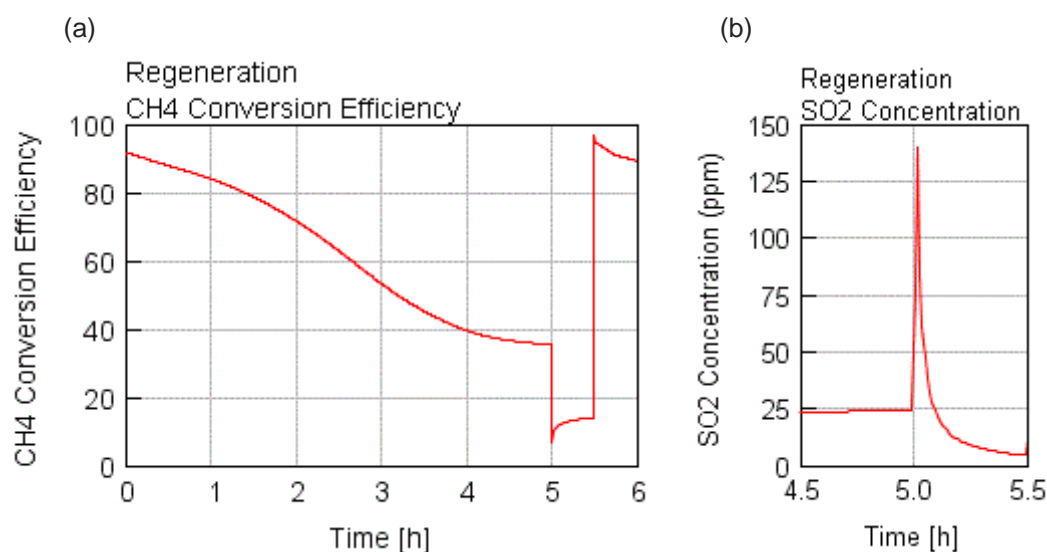

Figure 3. a) CH_4 conversion during aging and regeneration, and b) SO_2 release during regeneration.

To further elaborate the model, more detailed modeling of the reactions that may occur during regeneration could be incorporated. For example, in wet conditions, steam reforming and possibly water–gas shift reactions may take place during reductive treatment, providing hydrogen gas for low-temperature sulfate decomposition [10].

The accuracy level of the model created in this study is limited due to the limited experimental data available. To achieve reasonable confidence in a predictive after-treatment model, the test protocol should be designed in a way that it enables accurate calibration. At first, the user should be able to verify the thermal properties with confidence before moving on to calibrating kinetics. Therefore, a stand-alone experiment to characterize the thermal behavior of the reactor should be performed before attempting to calibrate reaction kinetics. To be capable of simulating changes occurring under transient conditions, the set of experiments should cover a wide range of expected inlet conditions in terms of space velocity and gas temperature [6]. Furthermore, varying the concentrations of gas-phase components (CH_4, NO, SO_2, O_2, and H_2O) in the inlet stream would benefit, e.g., tuning the inhibition terms [11].

4. Conclusions

The objective of this study was to explore the feasibility of using a simulation-based approach to predict MOC behavior over time, i.e., deactivation and the effect of regeneration. The catalyst simulation model was created with GT-SUITE software. The model was calibrated against experimental data collected from light-off performance tests on fresh, aged, and regenerated catalysts.

The main conclusions were:

1. For the fresh catalyst, the model agreement with the experimental observations was good.

2. Catalyst deactivation due to sulfur poisoning was successfully modeled by linking the CH$_4$ oxidation reaction dependent on the empty PGM-site coverages.

3. The catalyst model, and its underlying kinetic parameter set, predicted catalyst regeneration by varying the temperature and exhaust composition reasonably. The accuracy of the model under transient conditions could be improved by fine-tuning it further against varying inlet concentrations and flow rates.

4. To ensure the reliability of a predictive after-treatment model, a very careful test protocol design is required.

Acknowledgments

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