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Catalytic methane oxidation in the exhaust gas aftertreatment of a lean-burn natural gas engine

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HIGHLIGHTS

- Chemically-bonded energy in lean exhaust gas improves catalytic methane conversion.
- Modeling the active zone movement inside the catalyst requires multiple cells.
- The absent carbon monoxide in lean-burn engines impede the methane abatement.

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ABSTRACT

Internal combustion engines that run on compressed natural gas with lean-burn combustion instead of stoichiometric combustion have the potential to reach a high overall efficiency. However, the aftertreatment of unburnt methane in the exhaust gas is problematic. Catalytic methane oxidation is drastically impaired in lean conditions, even when the inlet exhaust gas temperature is high. In this study we link this effect to the availability of carbon monoxide in the exhaust gas. In stoichiometric operation, the exhaust gas contains a significant amount of carbon monoxide. The corresponding catalytic oxidation reaction has a low light-off temperature and the released reaction enthalpy heats the active surface of the catalyst. This heat helps to reach the significantly higher light-off temperature of the catalytic methane oxidation reaction. Lean exhaust gas, however, contains little to no carbon monoxide, and the exhaust gas temperature is not sufficient to reach light-off for the methane oxidation in many operating points of the engine. After investigating the effect experimentally, this article introduces a control-oriented model of the effect that is able to correctly predict the methane conversion efficiency under lean operation. Finally, we discuss different operating strategies in terms of energy consumption and discuss the effect of a moving active zone inside the catalyst.

1. Introduction

Today's research in the field of internal combustion engines is increasingly focused on the reduction of carbon dioxide (CO_2) emissions. Switching to alternative energy carriers like compressed natural gas (CNG) is known to be a promising approach to pursue this target. Both the high knock resistance and the low carbon-to–hydrogen ratio of methane, which is the main component of natural gas, allow for significant reductions in CO_2 emissions [1,2]. The vast majority of current CNG engines used in passenger cars are operated with a stoichiometric fuel–air equivalence ratio. However, the operation in lean-burn mode, i.e. with an excess of oxygen, has the potential to improve engine efficiency, mainly by reducing the pumping losses and the heat transfer [3].

One major issue with CNG engines is the abatement of unburnt methane in the exhaust gas. Small crevices and squish volumes in the combustion chamber are inevitable sources of unburnt methane. An additional oxidation of such methane emissions using an exhaust gas aftertreatment system is necessary, as methane is a potent greenhouse gas and the raw emissions typically are too high according to the recent pollutant legislation.

The state-of-the-art three-way catalyst (TWC) used for CNG engines is based on palladium (Pd). This type of catalyst exhibits a more effective oxidation of methane while featuring better resistance against sintering under lean-burn conditions [4,5] compared to platinum (Pt). With a lean-burn concept, NO_x reduction mechanisms are disabled. Nonetheless, the catalyst can still be used for the oxidation of unburnt hydrocarbons (HC) and carbon monoxide (CO) similar to an oxidation catalyst.

Catalysts used for stoichiometric CNG engines usually contain a

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relatively large amount of coating material as a consequence of the chemical stability of the fuel. Unburnt methane requires a higher activation energy for the oxidation process than a longer-chain HC representative of gasoline or Diesel exhaust. Typical values for the methane catalyst light-off temperature are reported to be 100 °C higher than for longer-chain HC [6].

Moreover, catalysts reportedly show a poor methane conversion under lean conditions. The explanations found in literature for this conversion drop at lean conditions are manifold. Some studies trace the conversion loss to the influence of water in the exhaust gas. In comparison to gasoline, the combustion of methane leads to a higher water concentration in the exhaust gas. This reportedly aggravates the competition between water and methane for the active sites [4,7]. In addition, the activity loss due to sulfur oxide seems to be greater when water is present [8,9]. Other studies locate the cause of the conversion drop with lean exhaust gases in the inhibiting effect of nitrogen oxide (NO) or of carbon monoxide, respectively, in the feed gas mixture [10–12]. Moreover, the formation of a metallic palladium layer is reported to decrease the methane oxidation capability [13,14].

Largely absent from the discussion on the conversion drop with lean mixtures is the influence of the reactive heat that originates from the oxidation of CO in the exhaust gas. The operation with stoichiometric mixtures comes with CO emissions, in contrast to lean operation where the CO emissions are significantly lower. With a light-off temperature of around 300 °C, carbon monoxide is oxidized in the catalyst at a lower temperature than methane [15]. At the same time, the CO oxidation is capable of releasing a significant amount of thermal energy as the CO still holds around a fifth of the original specific energy contained in methane. A related concept known from chemical process industries is the autothermal reactor [16]. In such systems, the catalyst bed is heated by an exothermic reaction such that the feed temperature can be reduced to ambient temperature. An application related to the autothermal catalysis in the automotive field is the reversing flow catalytic converter [17].

1.1. Contributions

With this article, we contribute to the general understanding of the catalytic oxidation of methane for the aftertreatment of lean-burn CNG engines. In an experimental study, we reproduce the effect of a methane conversion drop as the engine is operated in lean conditions, and show that the effect cannot be explained by the changing exhaust gas temperature or mass-flow. We demonstrate that the reactive heat released by the catalytic oxidation of carbon monoxide contained in stoichiometric exhaust gas plays a crucial role in reaching the light-off temperature for the methane oxidation reaction. As the engine is operated with excess oxygen, the exhaust gas does not contain any significant amount of carbon monoxide and therefore the methane conversion efficiency also drops. We validate our explanation using both an external injection of carbon monoxide upstream of the catalyst, or late Diesel post-injections that introduce a significant amount of unburnt hydrocarbons to the exhaust gas. With both methods, the methane oxidation efficiency of the catalyst can be restored, despite an exhaust-gas temperature below the corresponding light-off temperature. We then move on to establish, parametrize and validate a dynamic control-oriented model based on physical first principles that is able to reproduce the effect and correctly predict the methane emissions downstream of the catalyst under lean operation. In a final discussion, we i), show that the successful oxidation of unburnt methane can be reached both via increasing the exhaust gas temperature or by introducing reactive heat to the catalyst surface, we ii), demonstrate that the active area where the methane oxidation takes place can move inside the catalyst, and iii), we use the given setup to compare the overall efficiency of the engine system reachable under various thermal management strategies.

1.2. Catalyst model

A large part of the research effort to model the physical effects in three-way catalytic converters (TWC) was focused on the operation within a small range of gas compositions around stoichiometry. The main focus of the research was to reproduce the oxygen storage capability of the catalyst. In this field, both phenomenological models as well as simplified physical–chemical models [18–22] for full-sized catalysts can be found in literature. Other studies on catalysts use high-fidelity chemical models that are often validated under laboratory conditions or with real exhaust gases. These models are directly derived from first physical and chemical principles and typically cover the detailed processes in a monolith channel, such as heat and mass transfer [23,24]. Such detailed models require a lot of computational effort and are therefore not suitable for real-time applications. To the best of our knowledge, versions with reduced dimensionality are rare; one is found in [25], for instance.

1.3. Limitations of this study

A fundamental limitation of this study is the fact that in all experimental data the required light-off temperature for CO and any non-methane HC (NMHC) was reached. Thus, NMHC and CO pollutants were converted completely in all experiments. The presented model in this study cannot reproduce the catalyst behavior under cold start conditions. Furthermore, the effects related to aging of the catalytic converter are not treated. Finally, the conversion of NO_x is not considered mainly due to the impaired reduction mechanisms at lean conditions. Efficient lean NO_x abatement systems are known from series production, as for example the selective catalytic reduction (SCR) or the lean NO_x trap.

1.4. Structure

The remainder of this paper is organized as follows: First, the experimental setup for this study is presented in Section 2. An experimental analysis follows in Section 3 and the model description in Section 4. Further, a parameter identification as well as a model validation are introduced in Sections 5 and 6, respectively. Finally, a discussion of the results can be found in Section 7, while the principal conclusions are drawn in Section 8.

2. Experimental setup

The experimental setup used for this study comprises an internal combustion engine (ICE) and a TWC. An overview of the setup is given in Fig. 1. This section presents details about the hardware components and measurement equipment used.

2.1. Hardware

The ICE used in this study is not a conventional CNG engine. The ignition of the mixture is not based on a spark plug, but on a small amount of Diesel. The natural gas (mass flow $\dot{m}_g$) is injected into the intake ports, while the Diesel (mass flow $\dot{m}_D$) is injected directly into the cylinders providing ignition centers for the premixed air-gas mixture. The engine is based on a production type 2-liter Diesel engine. The TWC is a palladium-coated ceramic catalyst, originally designed for a stoichiometric CNG engine with 2-liter displacement. The geometrical data of the engine and the precious metal loading (PML) of the catalyst are specified in Table 1.

2.2. Measurement conditions

Table 2 outlines all measured variables that are relevant for this study.

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