Enhancement of 3-way CNG catalyst performance at high temperature due to the presence of water in the feed: on the role of steam reforming of methane

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Introduction

Rigorously regulated automotive exhaust gas emissions according to standards as Euro 4 (in effect since January 1, 2005) or Euro 5 (September 1, 2009), demands the employment of efficient strategies for emission reduction. Natural Gas (NG), primarily composed by methane, is regarded as one of the most promising alternative fuels: natural gas engines produce lower PM than diesel and for NG combustion lower combustion temperatures are required which leads to a decrease of NOx emissions [1]. However, methane is the major hydrocarbon exhaust component and the most difficult to catalytically oxidize. Three-way catalysts, which are known as effective for simultaneous NOx, CO and HC removal by their interaction with noble metals as Rh, Pt and Pd. Moreover, palladium has gained especial attention particularly for CNG vehicles applications due to its high performance for methane abatement. In the last years, authors essentially focused on the understanding of mechanism and kinetic of the reactions CO+O_2, CO+NO and HC+ NO separately. However, exhaust gas is not only composed by the three major pollutants and has been observed that for a gasoline 3-way catalyst, water presence in the exhaust gas (up to 10%) play a very important role as oxidant of unburned hydrocarbons [2]. The aim of this work is to understand the role of water on the methane oxidation at high temperatures during the exhaust gas treatment using a commercial 3-way CNG catalyst.

Materials and Methods

2.1. Materials

The catalytic tests were performed on two commercial CNG catalysts (named A and B) in a monolith form which dimensions are 1 inch diameter x 1,9 inches length. These catalytic converters correspond to an active phase coated on a ceramic honeycomb monolith.

2.2 Catalysts characterization and catalytic runs

The metal contents of the two catalysts tested were obtained by ICP (Induced Coupled Plasma) elemental analysis. Catalytic tests were performed on a Synthetic Gas Bench (SGB) which reaction mixture was composed by: 0.25% NO, 0,17% CH_4, 0,48% of O_2, 9,25% CO_2, 0,47% CO, 0,34% H_2 and 18% H_2O. This conditions lead to a richness of R=1,005.
A second tests was performed in the presence of 0,17% CH_4 and 18% H_2O. The GHSV was of $40000h^{-1}$.

Results and Discussion

3.1 Catalyst characterization

According to ICP elemental analyses these catalysts present a very different composition:

Table 1 : Noble metal content of A and B catalyst

% wt	A	B
Pd	2,55	0,7
Rh	0,18	0,08
Pt	0,07	0,00

No Pt loading was detected on catalyst B. This catalyst is essentially constituted by Pd, however its content is 3.5 times lower than the one detected on catalyst A.

3.2 Catalytic runs

After a temperature programmed reaction with the complete reaction mixture it was possible to observe with catalyst A which is the most active, a total conversion of methane in CO_2. The catalyst B, in comparing the noble metals contents of both catalysts, also leads to very interesting results for NOx and CO elimination (Tlo_A.= Tlo_B + 30°C). However, after total conversion of NO in N_2, the CH_4 conversion stops and at 500°C reaches a maximum of 60% conversion. Thus, a second experiment was performed in order to study only the reaction between methane and water over the two catalysts.

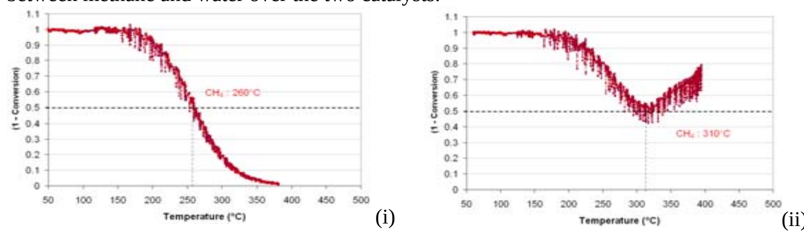

Figure 1. CH_4 profile during temperature programmed reaction in the presence of 0,17% of methane and 18% of H_2O with catalyst A (i) and B (ii)

According to Fig.1, with catalyst A methane starts interacting with water from 170°C and at 350°C all the amount of HC supplied is reacting with water. The reaction occurring is the steam reforming of methane: $CH_4 + H_2O = CO + 2H_2$.Catalyst B, however, is not active for the reaction of steam reforming of methane, with a maximum conversion of 50% reached at 310°C. The presence of water in the exhaust CNG vehicles seems to have a major importance for the abatement of methane in rich conditions at high temperatures. The low methane conversion obtained with catalyst B leads us to conclude that the presence of Pd is necessary not only for the reaction between NO and methane but also for the steam reforming reaction that is essential for the total consumption of methane in rich atmospheres.

Significance

Due to the decrease of oil reserves in the future years, the natural gas could be a good alternative as fuel. Already 7 millions CNG vehicles are in use all around the world. However, actual commercial catalysts present problems of durability and the loadings in noble metal should be decreased for sustainable processes.

References

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