Supported Metallic Catalysts for Hydrocarbon Selective Catalytic Reduction of NO$_x$ from Diesel Engines

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Introduction

During the last decades the number of cars and trucks increased rapidly and even more rapid was the increase in the diesel engines registered. Both in Europe and in the United States, the emissions limits are becoming more stringent and soon in the EU the new rules EURO 5 and 6 will impose much more restrictive limits mainly on particulates and NO$_x$ emissions. While for the particulate control, some technologies based on filters are already available, there exist no efficient catalysts for NO$_x$ emission control. The so called "hydrocarbon selective catalytic reduction" (HC-SCR), uses a hydrocarbon as a reducing agent and a supported metallic catalyst to remove NO$_x$ from the exhaust gas stream [1]. In this work we present original results obtained with 3 different catalysts, tested in ranges of temperature (200 - 500 °C) and gas hourly space velocity (GHSV, 10 000 – 40 000 h^{-1}) typical of diesel engines in real trucks. NO concentration was 500 ppm, C$_3$H$_6$ ranged between 500 and 2000 ppm, while oxygen was always 5%. The catalysts were also tested in the presence of steam and feeding a mixture containing CO, CO$_2$, H$_2$.

Materials and Methods

The catalysts tested were Ag, Pt and Rh supported on alumina (2% metal load). The powders prepared by incipient wetness impregnation, were washcoated on cordierite monoliths. Activity tests have been carried out in a continuous flow reactor. It consists of a quartz tube, where the catalyst was located. The reactor is centred inside an electrically heated furnace, governed by a programmable temperature controller. Reaction products and residual reactants were detected by a non-dispersive infrared detector (NDIR) for NO, NO$_2$, CO and CO$_2$; a FID was used to detect C$_3$H$_6$, while hydrogen was detected by a TCD and O$_2$ by a paramagnetic detector. Water was calculated from mass balances.

Results and Discussion

All the catalysts tested showed to be active and reached very high NO conversion (max conv ranging between 80 and 100%, see Figure 1, left) in the tests run. Some significative differences were detected between them. Silver is active between 350 and 500 °C, achieving complete conversion in a quite wide temperature range. Rh was less active than Ag (max conv. was 80%) and NO conversion showed the typical volcano shape often detected in this reaction, but it was active at lower temperatures (250 – 350 °C). Both Ag and Rh showed a decreased activity when the GHSV was increased from 10 000 to 40 000 h^{-1}. Pt was as active as Rh, but NO conversion remained above 70% in a temperature range between 180 and 300 °C. This is very important since in a truck engine, the exhaust gas temperature can be rather low (during start up or when the truck stops), so a catalyst active already at 200 – 250 °C is required. Another interesting feature of Pt was that it did not decrease its activity when the GHSV increased, though at 40 000 h^{-1} it lit up the reaction at a higher temperature (220 °C). A

drwaback common to both Pt and Rh was the low selectivity towards N$_2$, while significant amounts of NO$_2$ were detected. Silver instead converted all the NO to N$_2$ and, furthermore, also converted the small amount of NO$_2$ (few ppm) present in the NO canister. This fact can be exploited with a bimetallic catalyst, with either Pt or Rh in the first part of the monolith and silver in the second one, since certain amount of NO$_2$ are required in the so called "fast SCR". The effect of water was studied feeding 8% of steam in the gas mixture. Pt and Rh showed a lower activity and a sligtly higher light off temperature; Ag was more active with steam than without, up to 400 °C, while further increasing the temperature, caused a decrease in the conversion, with respect to the dry tests (this remaining anyway above 80 %).

Some very interesting tests feeding a mixture of H$_2$, CO, CO$_2$ and H$_2$O were run, simulating a gas mixture coming from a reforming process (Figure 1, right). On Rh a very limicted effect was observed, while on Pt the maximum NO conversion was the same as detected at the same GHSV, but the conversion was 50% already at 120 °C. Ag was the catalyst most affected by the different mixture composition, evidencing a dramatic enhancement of the conversion. It activated the reaction at 170 °C, keeping a complete NO conversion between 230 and 400 °C. This improvement is possible since H$_2$ (which does not seem to directly participate in the deNO$_x$ reaction) keeps silver in the metallic state avoiding the formation of AgNO$_3$, which, if formed, is transfered on the support surface and limits the reaction [2,3].

Significance

Testing different metals in realistic T and GHSV conditions allowed to detect their positive features that can be combined to obtain an effective catalyst for NO reduction. The hydrogen effect highleghed is a very intersting aspect that must be further investigated.
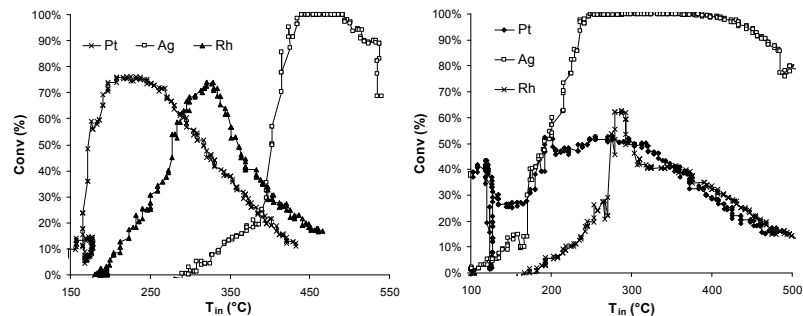

Figure 1. On the left, NO conversion detected with different metals (GHSV = 10 000 h^{-1}, NO = 500 ppm, C$_3$H$_6$ = 1000 ppm, O$_2$ = 5 %). On the right, effect of H$_2$ on the conversion at 20 000 h^{-1}; H$_2$ = 2000 ppm.

References
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