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Hysteresis effect study on diesel oxidation catalyst for a better efficiency of SCR systems

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ABSTRACT

This study focuses on the behaviour of the diesel oxidation catalyst in order to improve the efficiency of an ammonia SCR system on an after-treatment line composed by a DOC + DPF + SCR. The studied catalyst is a commercial diesel oxidation catalyst ($Pt/Pd/Al_2O_3$) provided by Renault. For this study, the catalytic phase was extracted from a monolith and different ageings in temperature were performed. The catalysts were characterized by elementary analysis, X-ray diffraction (XRD), transmission electron microscopy (TEM) coupled by EDS and X-ray photoelectrons spectroscopy (XPS). The specific surface area was also calculated using a specific apparatus. Main physicochemical properties and elementary analysis of the catalysts were performed in order to determine the noble metal contents. The catalytic measurements consisted on temperature programmed surface reaction (TPSR). The heating rate was chosen equal to $10\,^{\circ}C\,min^{-1}$. The TPSR were used to determine light off temperature of each pollutant present in the exhaust gases. To be close to industrial conditions, our experimental setup is composed by a heater where the gases are heated up to 500 °C. The goal of this study is to study the hysteresis effect with different gas composition and with different catalysts state (ageing, sample/powder).

1. Introduction

In order to reduce the vehicle emissions and reach the future EURO VI standards, the automotive manufacturers needs to develop new technologies and also gain a better understanding of the after-treatment systems. Among the different solution studied, the hybrid technology gets an increasing interest. Hybrid power technologies have already been applied successfully in vehicles [1]. With the combined use of two different powertrain technologies, the hybrid vehicles can work with high efficiency, low pollutants emission and optimized fuel consumption. An example of this application can be the hybridization between an internal combustion engine and an electric powertrain. In this case, the after-treatment system undergoes with a transitory temperature profile which leads to an hysteresis behaviour in the catalytic activity during heat-up phases and cool-down phases [2]. To reach EURO V applications, this kind of phenomena is not quite important because of low impact in term of CO and HC oxidation but this hysteresis can be a problem in the future in order to obtain a good efficiency of an EURO VI after-treatment line [3]. To illustrate this purpose, this study deals with the behaviour of the diesel oxidation catalysis, "DOC", composed mainly noble metals supported on alumina [4,5], in order to improve the efficiency of an ammonia SCR system on a complete after-treatment line composed by a DOC + DPF + SCR. It is already known [6] that the control of the NO_2 concentration before the SCR system is very important, due to the FAST SCR and in case of the hybridization of the vehicle. Moreover, this control is affected by a hysteresis effect. The most likely explanation for the hysteresis effect is a reversible oxidation at the surface of the DOC.

The formation of such surface oxides has been demonstrated by numerous of experimental techniques [7]. In these systems, the nature of the platinum oxides does not seem to be fully understood. Thus, the oxygen can be in different forms at the surface of the complex industrial catalyst [8,9]. It is possible to have the formation of a platinum oxide layer [10] or a more complete oxidation of the platinum into a bulk PtOx form [11]. In this paper we study the NO oxidation process under temperature cycles composed by a first linear increase of the temperature followed by the linear decrease of the temperature of the catalyst. The main objective of this paper is to demonstrate that even with a constant exhaust gas composition a hysteresis effect on a bimetallic Pt/Pd commercial catalyst

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can be observed. The second objective is to understand this hysteresis phenomenon in the course of the reaction. This hysteresis can be due to palladium oxide formation at the surface leading to higher NO conversion in NO in cold down conditions.

2. Experimental

2.1. Commercial diesel oxidation catalyst

The catalyst used for this study is a commercial DOC catalyst provided by Renault. The catalyst is composed by a bimetallic Pt/Pd (3/1) phase supported on alumina with a metallic loading of 80 g/ft^3. As typical commercial catalyst, this catalyst is zone-coated [12]. Thus, the first third of the catalyst (front) have 66% of the total metallic loading and the other third (rear) have the 34% left. For this reason, the characterization and the catalytic tests have been divided in two parts and are designated by “front” for the first part of the catalyst and by “rear” for the second part. In order to follow a real mileage of such catalytic system, three different ageing were used for the study. The first study was performed using a fresh catalyst that is designated by “New” in this paper. The second and the third are aged catalysts and designated by “5H750°C” and “5H800°C” because the catalysts have been aged at 750 °C or 800 °C during 5 h. These ageing temperatures were chosen because there are representative of real driving cycles. The ageing is a Renault ageing, using temperature programmed reaction in which water is injected on the catalyst in a flow of air. These thermal ageings were performed on industrial monolithic catalyst (1.2 L). For the catalytic tests, at the laboratory scale, the active phase was studied. In order to extract the active phase of the catalyst, the following process is used:

1. The catalyst is first immersed in a bath of liquid nitrogen.
2. The catalyst is then immersed in a bath of water using an ultrasound system.
3. Finally, the water is filtrated and obtained power is dried.

This process is used several times in order to extract the washcoat. After analyses (STEM) and weight of the samples; we observed that 90% of the washcoat was extracted.

2.2. Catalyst characterization

X-ray photoelectron spectroscopy (XPS) measurements were performed with a hemispherical analyzer (PHOIBOS 100, SPECS Gmbh) using Al K (1486.6 eV) radiation. The power of the X-ray source was 400 W and the energy pass for analyzer was 10 eV. XRD data were recorded on a Bruker Advanced D8 using CuKα radiation. PXRD measurements were performed from 5° to 90° in steps of 1° with a count time of 6 s at each point. The specific surface area was obtained by using the Brunauer–Emmett–Teller (BET) equation. N_2 adsorption–desorption isotherms were measured at liquid nitrogen temperature by a Micromeritics ASAP 2010. Before the measurements, the samples were evacuated at 200 °C under vacuum (2×10^{-3} Torr). High resolution TEM (HRTEM) was performed on a JEOL-JEM 2011 HR (LaB) microscope operating at 200 kV.

2.3. Catalytic measurements

2.3.1. Active phase runs

Temperature-programmed surface reaction (TPSR) were carried, in a U-type glass reactor by using gas mixtures exposed in Table 1. The heat-up ramp is from 80 °C to 500 °C with 10 °C min^{-1} and was directly followed by cooling phase in which the same ramp of temperature from 500 °C to 100 °C is applied on the catalyst. The temperature is followed by two thermocouples, one is for the temperature of the gases at the entrance of the catalyst, and the other for the temperature of the catalyst. The total flow rate of the gas was maintained at 250 mL min^{-1} for all experiments. The goal of the study is to simulate a monolithic GHSV of 25,000 h^{-1}, corresponding to a monolithic GHSV for the front part of 75,000 h^{-1} and 50,000 h^{-1} for the rear part. The monolithic equivalent GHSV is calculated as follows:

$$VVH = \frac{Q \times \alpha}{m} \qquad (1)$$

Q is the volume flow (L/h), m is the mass of powder (g), α is the washcoat loading (g/L).

Table 1
Gas composition used for catalytic runs (active phase and monolithic catalysts).

Type of test	Ar (%)	CO_2 (%)	O_2 (%)	NO (ppm)	C3H6 (ppm)
NO oxidation	Balance	5	8	150	0
(NO + HC) oxidation	Balance	5	8	150	150

The washcoat loading is the mass of powder extracted from a known volume of monolith. For our catalyst, the washcoat loading is calculated at 57 g/L. So the mass of powder can be adjusted for reach these GHSV. The gases (NO, O_2, CO_2 and Ar) were fed from compressed cylinders provided by “Air Liquide” and adjusted with Brooks mass flow controllers (5850 TR and 5850 TE). The sample was held on plugs of quartz wool and the temperature was controlled through a EUROTHERM 2408 temperature controller, K-type thermocouple. The outflow experimental reaction was continuously monitored a variety of detectors such as: an Eco Physics CLD 700 AL chemiluminescence NO_x analyser (for NO and total NO_x) (i.e. NO + NO_2), which allowed the simultaneous detection of NO and NO_x. Two Ultramat 6 IR analysers were used to monitor N_2O, CO and CO_2. A FID detector (Fidamat 5) was used to follow the concentration of the hydrocarbons.

2.3.2. Monolithic sample activity measurements

In order to be the most representative of real mileage conditions, we have managed to use the same catalytic device but using a monolithic reactor. Thus, we used a U-type glass reactor with a sample of commercial catalyst instead of active phase. The volume of the sample was adjusted in order to run at the same GHSV as in a realistic condition. All the conditions and the analyzers are similar than those chosen for the active phase tests exposed in the previous section in order to compare the two types of tests. Prior each catalytic run, catalysts were placed in Argon at 120 °C for 30 min in order to clean the surface, then the samples were cooled down to room temperature.

3. Results and discussion

3.1. Characterization of the catalyst

The specific surface area of the different catalysts is presented in Table 2, and we can observe a decrease of the specific surface area with the evolution of the ageing.

In parallel of the study, a destructive elementary analysis was made on the catalysts by the “Centre National de Recherche Scientifique” in France. The results of this elementary analysis are

Table 2
Evolution of the specific surface of the front part of the catalysts as function of the ageing.

Sample	New (F)	5H750°C (F)	5H800°C (F)
Surface (m^2/g)	154.0	148.4	147.1
Difference vs. fresh catalyst (%)	–	3.6	4.5