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Aging of Commercial Diesel Oxidation Catalysts: a preliminary

Structure/Reactivity Study

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Abstract

This study focuses on the catalytic behavior of the Diesel Oxidation Catalyst using different aging characteristics of road mileage 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/Al₂O₃) provided by Continental. Hydrothermal aging were performed on carrots of monolith in varying the temperature of treatment. These carrots were characterized, X-ray diffraction (XRD), transmission electron microscopy (TEM) coupled by EDS and Specific surface measurement (S_{BET}). The catalytic measurements consisted of series of temperature programmed surface reactions (TPSR). To be close to real driving conditions, our experimental setup comprised a pre-heater in which the gases were heated up to 500°C. The goal of this study is to understand the evolution of the active phase with the aging and to correlate these aging results with the corresponding overall catalytic activity and their impact on the reactions involved in the DOC with respect to CO, hydrocarbons and NO.

Keywords: NO oxidation, bimetallic DOC, hydrothermal aging, effect of the feed

1. Introduction

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In order to reduce the vehicle emissions and to reach the actual EURO VI standards, the automotive manufacturers need better understandings of the after-treatment systems. Increasingly stringed regulations for diesel engine emissions have a significant impact on the required efficiency of Diesel Oxidation Catalysts (DOC) since the after-treatment line is now composed by a DOC, a Diesel Particulate Filter (DPF) and a NO_x abatement system (NO_x trap or NH₃ SCR) [1]. Lowered DOC oxidation efficiency due to thermal aging effects influences the efficiency of the exhaust after-treatment systems downstream of the DOC [2] and mostly on SCR systems.

In this study the behavior of the Diesel Oxidation Catalysts “DOC”, composed mainly by noble metals supported on alumina [3,4] is analyzed, in order to develop improvements of the efficiency of an ammonia SCR system on a complete after-treatment line composed by a DOC + DPF + SCR. It is already known [5] that the control of the NO₂ concentration before the SCR system is pretty important, due to the so-called “FAST SCR” reactions.

In this work, the effect of hydrothermal aging on the reactivity and structure of a commercial DOC is investigated as a function of temperature in order to understand what are the chemical reactions affected by the aging versus time on road. Hydrocarbon, CO and NO oxidation reactions are assessed for catalysts aged at various temperatures and for different gaseous feeds.

2. Experimental section

The catalyst used for this study is a commercial DOC catalyst provided by Continental. The catalyst is composed by a bimetallic Pt/Pd (3/1) phase supported on alumina with a metallic loading of 80g/ft³. The first study was performed using a stabilized catalyst (750_4H). The aged catalysts are designated by "850_10H", "850_24H" and "950_4H" respectively, because the catalysts have been aged at 750°C, 850°C and 950°C under different durations (4, 10 or 24 hours) in 10%H₂O/Air. The first two aging temperatures were chosen because they were

representative of real driving cycles [5] and the last one was selected in order to lead to a severe aging of the DOC. The aging was done using temperature programmed reaction in which water (10% in volume) was injected on the catalyst in a flow of synthetic air (total flow of 19 NL.min⁻¹). These thermal agings were performed on carrot monolithic catalyst, as described elsewhere [5]. XRD data were recorded on a Bruker Advanced D8 using CuK α radiation. PXRD measurements were performed from 5 to 90° in an interval of 1° with a count time of 6s for each point. The specific surface area was obtained by using the Brunauer-Emmett-Teller (BET) method. N₂ 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 (0.2666Pa). High resolution TEM (HRTEM) was performed on a JEOL-JEM 2011 HR (LaB) microscope operating at 200 kV.

The catalytic activity studies have been conducted in a synthetic gas bench using a synthetic gas mixture representative of the exhaust gases from diesel engines. The different experimental conditions are presented in Table 1.

Tab.1. Synthetic gas bench experimental conditions

	NO ppm	NO ₂ ppm	C ₃ H ₆ ppm	CO ppm	CO ₂ (%)	O ₂ (%)	H ₂ O (%)	N ₂ (%)
Mix 1	300	-	200	300	5	10	5	Balance
Mix 2	300	100	200	300	5	10	5	Balance
Mix 3	300	100	200	-	5	10	5	Balance
Mix 4	-	100	200	300	5	10	5	Balance

The carrot (d=2.54 cm; L=2.6 cm) was placed inside a stainless steel reactor, which itself was positioned inside an oven reaching temperatures up to 500°C. Two thermocouples were available to follow the reaction temperature at the inlet and the outlet of the catalyst. The total flow was fixed at 11.8 L·min⁻¹ resulting in a gas hourly space velocity (GHSV) of 55,000 h⁻¹.

Catalysts were evaluated in terms of oxidation capacity and NO conversion for temperatures ranging from 50°C to 500°C. Exhaust gas composition before and after the reactor were characterized by an environment S.A. analyzer composed of a set of modules. Among them, the TOPAZE 32M module allowed NO, NO₂ and total NO_x measurement thanks to a

chemiluminescence analyzer. A MIR2M module was composed of an IR spectrogram, for the measurement of H₂O, CO and CO₂ molar fractions, and a magnetic sensor, for the O₂ molar fraction measurement. At last, a flame ionization detector (FID), present in the GRAPHITE 52M module was used for measuring total HC.

3. Results and Discussion

3.1 Characterization of the catalysts

From TEM (Fig.1.), on both fresh and aged catalysts, only alloys of Pt-Pd are identified. HRTEM was performed, but neither Pt nor Pd was identified independently. Furthermore, EDS was performed (not shown here), on two samples: the stabilized one (740_4H) and the 950_4H, respectively. On both samples, the same Pt/Pd ratio is always observed irrespective of the targeted zones (20 nm² and higher). From the Fig.1., one also observes that the aging of these particles leads to a sintering of the initial alloy and thus to a reduction of the contact surface of the active phase, resulting in a global decrease of the specific activity of the catalyst. XRD patterns also reveal the presence of support sintering (Fig. 2.). These results are in agreement with those found in the literature [6,7]. The textural parameters for the studied catalysts are given by S_{BET} measurements and porous volume. The S_{BET} are found to be 83, 59, 54 and 51 m²·g⁻¹ for 750_4H, 850_10H, 850_24H and 950_4H respectively, which is consistent with the literature when the catalysts are aged at different high temperatures [8,9].

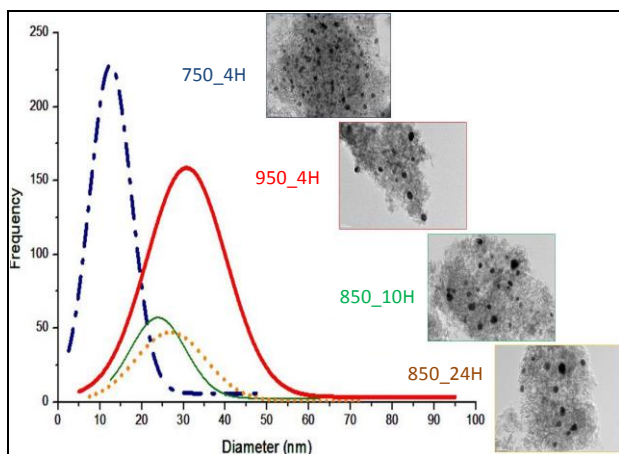


Figure 1 – Evolution of the particle distribution with aging procedures.

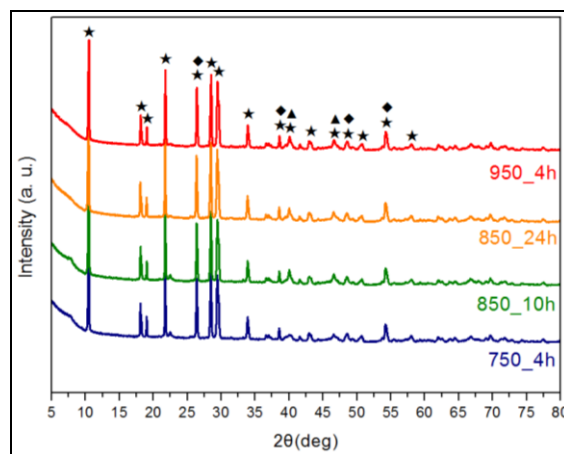


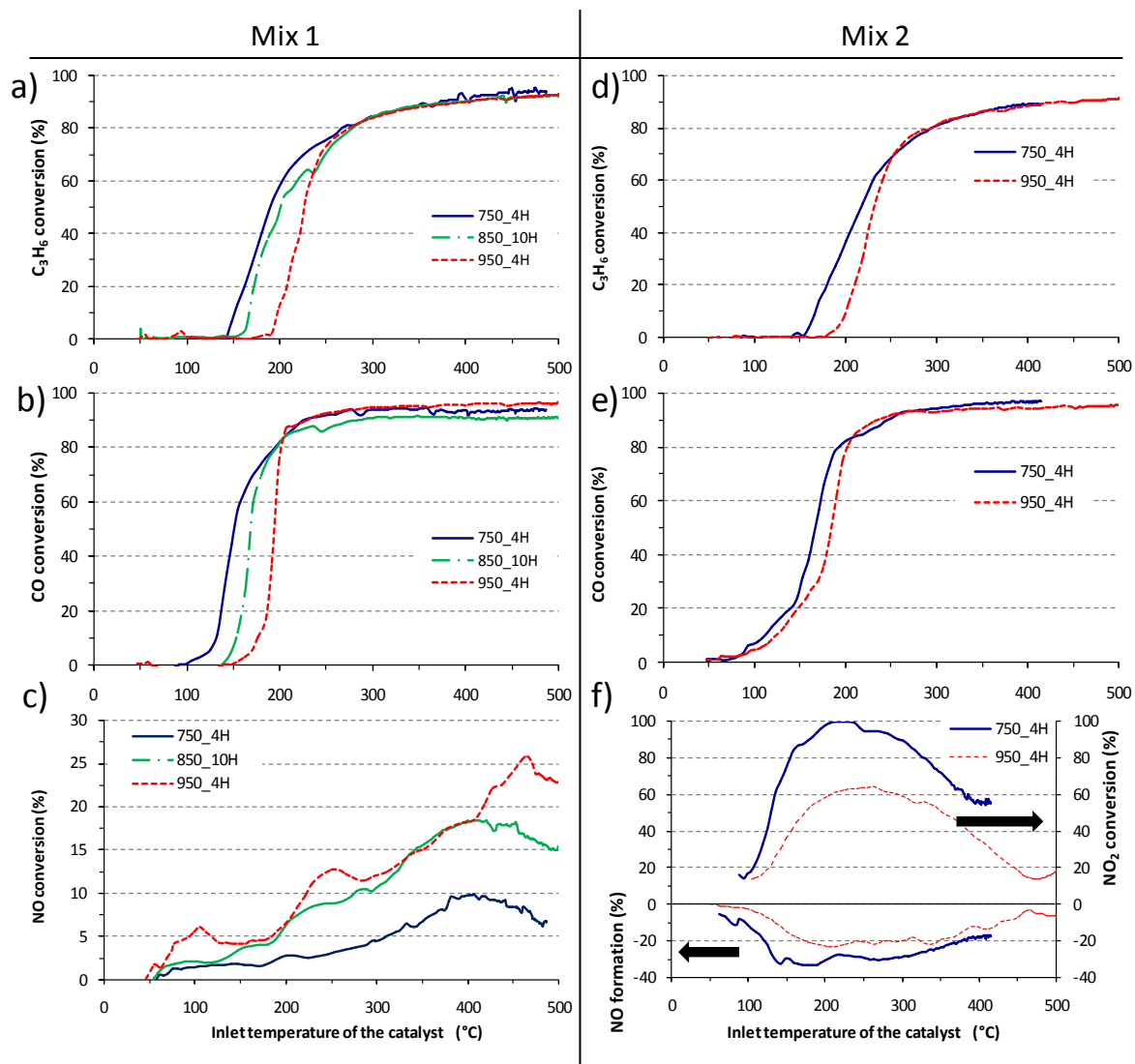
Fig.2 X-ray diffractograms of the reference catalyst and aged catalysts

* Cordierite (ICDD 00-012-0303) ▲ Pt/Pd (ICDD 01-072-28-38) ◆
Aluminum (ICDD 01-070-3319)

In conclusion, the characterizations of the catalyst show that most of the active phase is an alloy of Pt-Pd supported on alumina. The analyses of aged catalyst reveal an increase of the alloy size, a support sintering and quantified the diminution of the catalyst specific surface area.

3.2. Aging effect on DOC catalyst

Four different light-off experiments are performed on 750_4H, 850_10H, 850_24H and 950_4H catalysts respectively. Compared to Mix 2, which is a representative mixture (with NO/NO₂=3) of the exhaust gases prior to the DOC in the specific DOC/DPF/SCR technology, the Mix 1 contains only NO in terms of NO_x. The results are presented in Fig. 3. From Mix 1 and Mix 2, it can be noted that the aging has a negative effect on both hydrocarbon (Figs. 3a & 3d) and CO oxidation (Figs. 3b & 3e). From Fig 3a and 3b, one can conclude that the light off temperatures of hydrocarbon shifts to higher temperature with the aging severity which is agreement with the literature [9]. This result can be explained by the sintering of the particles of the aged catalysts, hindering optimal catalytic activity [10].



Fig

Figure 3: Evolution of concentration of C_3H_6 , CO, NO and NO_2 for Mix 1 and Mix 2 versus temperature for fresh and aged catalysts.

Indeed the average particle size was 12 nm for 750_4H, 24 nm for 850_10H and 31 nm for 950_4H. An opposite result is found for NO oxidation (Fig. 3c) which increases with the aging effect. This result is in agreement with the literature, since bigger Pt/Pd particles favor NO oxidation [11], However, when only NO as NO_x is present in the feed an opposite trend is observed [12,13]. Moreover for both fresh and aged catalysts, in Mix 1, NO_2 is not detected at low temperature until CO is oxidized. Schmeisser et al. [14] found that reducing agents in the lean feed such as CO and C_3H_6 hindered NO_2 formation as long as they were present. Similar results have been also found in a DPNR in lean gas conditions [15].

On Fig. 3f, both NO and NO₂ conversion are presented. In these conditions NO₂ is reduced in NO, through reactions implying CO (see part 3.3). Reactions between C₃H₆ and NO_x are not clearly identified in our experiments. Above 250°C, where the contribution of O₂ in CO oxidation is more important, the NO₂ conversion is reduced and the NO₂/NO ratio is increasing while keeping very low values (below 15%) with a view to optimal SCR activity (Figure not shown). In Fig 3f, the positive effect of aging on NO oxidation in representative mixture is quite clear. This might be principally due to the improved NO oxidation by O₂, favored by bigger Pt/Pd particles.

3.3 On the effect of the feed composition and aging on the catalytic performance of DOC

In order to elucidate the effect of gas composition on the catalytic activity of DOC, Mix 3 and Mix 4 are added to the analysis process (Tab.1.). In Mix 3, CO is removed from the feed and in Mix 4, NO is removed (Fig 4). As expected, the aging negatively affects the catalyst performance on the oxidation of C₃H₆ and CO. However, an improvement of the NO oxidation performance with the aging is observed when only NO is used in the feed (Mix 1). These behaviors are directly linked with the sintering of the Pt/Pd particles as already discussed above. In Fig. 4b and 4e, the conversion of CO is presented as a function of temperature and for different mixtures for 750_4H and 950_4H, respectively. One can see that both for fresh and aged samples, the CO conversion is enhanced when NO₂ is present in the feed (Mix 2 and Mix 4) due to an interaction which was already described in the literature [14, 15]. The reaction is limited by the concentration of NO₂, nearly totally converted (see fig. 3.f) when 30% of CO is converted (i.e., 100 ppm of reactant transformed). The comparison of NO transformation between Mix 2 and Mix 3 (same mixture with and without CO, respectively), from Figs. 4c and 4f (fresh and aged catalyst, respectively), leads to the conclusion that NO formation is enhanced below 150°C when NO₂ is reacting with CO.

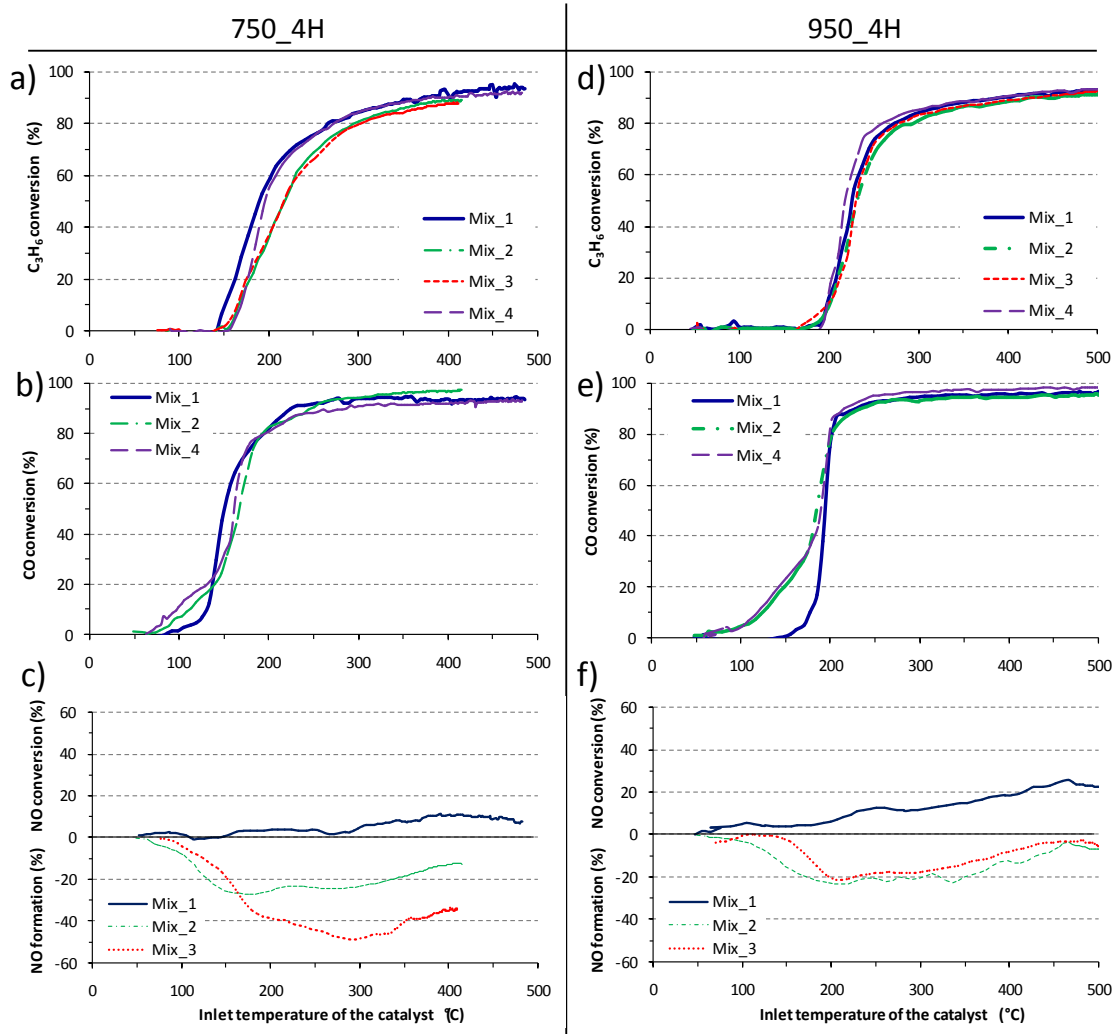


Figure 4: Effect of gas composition on the evolution of CO, C₃H₆, NO and NO₂ for fresh (750_4H) (a, b, c) and aged catalysts (950_4H) (d, e, f)

The C₃H₆ conversion is presented in Figs. 4a and 4d. Results show, for 750_4H catalyst, an inhibiting effect, already observed in previous studies [15], when NO and/or NO₂ are present in the feed. This latter is attributed by competition between NO, NO₂ and C₃H₆ for oxidation sites [11,17]. The difference between the inhibiting effect caused by NO₂ and NO additions (Mix 1/Mix 4) suggest a stronger adsorption of NO₂ than NO around 150°C. These conclusions are not so clear for 950_4H catalyst, because of the sintering of the particles sizes and then the decrease of active sites number leading to a shift of about 30°C on the start of the light off curve. However, above 250°C there is almost no difference for both CO and C₃H₆ conversion since there are still enough active sites. From Figs. 4c and 4f, one can conclude that whereas the NO

oxidation is favored with 950_4H catalyst because of the sintering when only NO is present in the feed (Mix 1), the NO formation is lowered due less lower reactivity of NO₂ with CO when the catalysts are aged.

4. Conclusion

In this work, a structure reactivity study of fresh and aged DO catalysts in changing the pollutants in feed was presented. It clearly showed that thermal aging pronouncedly impacted the overall oxidation activities of the catalysts. The decrease in activity was very large at low temperature (<200°C) whereas almost no difference was observed at high temperatures. The thermal aging was more important for NO oxidation than for CO or hydrocarbon oxidation at low temperature leading then to a low production of NO₂ and a lower SCR efficiency. Thus, this justified the development of new DOC systems in order to meet the future regulations on pollutants.

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