THE INFLUENCE OF Pt INCORPORATION ON NO$_x$ STORAGE-REDUCTION CAPACITY OF NSR MONOLITH CATALYSTS

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Introduction

Diesel engines and lean burn gasoline engines operates with an excess of oxygen, i.e. lean operation. Controlling the exhaust NO$_x$ emission has been recognized as one of the most challenging aspects for lean-burn engine technology as the conventional three-way catalyts (TWC) are not effective in reducing NO$_x$ in a lean exhaust due to the high oxygen content [1]. A NO$_x$ storage/reduction (NSR) catalyst is among the most promising solutions to control NO$_x$ in lean exhaust.

The NSR concept is based on operating under lean conditions in a cyclic mode with alternating lean and rich periods. NO$_x$ is stored in the catalyst during the long lean periods as nitrites or nitrates and the catalyst is regenerated during short fuel rich periods. During regeneration NO$_x$ is released from the storage sites and reduced to N$_2$.

In the literature, there is a lack of agreement with the order of incorporation of the precious metal and the storage component onto the alumina washcoat, and subsequent mutual interactions among the platinum, the storage component and the support material, which can ultimately affect the dispersion and particle size of the active metal [2].

In the present work, we have prepared several Pt/BaO/Al$_2$O$_3$ monolith catalysts by both impregnation and adsorption from solution methods, leading to important differences in the platinum particle size, determined both by H$_2$ adsorption and transmission electron microscopy (TEM). Also scanning electron microscopy (SEM) may be helpful in determining the distribution of platinum and barium on the alumina surface [3]. The aim of the study is to find some correlation between the platinum particle size and the NO$_x$ storage-reduction capacity of the prepared monoliths.

Experimental

Four cordierite monoliths (A, B, C and D), 20 mm in length and diameter, were cut from a commercial monolith supplied by Corning, with a cell density of 400 cells per square inch. After a calcination step in air at 1000 °C to remove possible impurities, the monoliths were washcoated with γ-alumina supplied by Saint-Gobain with a BET area of 190 m^2 g^{-1}. The as received 3 mm alumina pellets were crushed in a wet ball milling step, thereby reducing the particle size. The monoliths were immersed for 10 seconds in a slurry consisting of a mixture of 10wt% of alumina in acetic acid (glacial 100%, Merck). Afterwards, the excess liquid was blown out with compressed air. Then the monoliths were dried at 110 °C for 30 minutes. This procedure was repeated until

the desired amount of alumina was washcoated. Finally, the monoliths were calcined in air at 700 °C for 4 h to anchor the alumina layer onto the monolithic support.

The platinum incorporation was carried out by wetness impregnation (monolith A) or adsorption from solution (monoliths B, C and D). The metallic precursor was tetraamine platinum (II) nitrate supplied by Alpha Aesar. For wetness impregnation, the desired amount of salt was dissolved in an amount of water equivalent to that of the alumina washcoated. After filling the channels with the aqueous solution, the sample was dried in air at 110 °C for 24 h and finally calcined in air at 500 °C for 4 h (monolith A). When the incorporation of platinum was done by adsorption, the remaining three monoliths (B, C, and D) were immersed in an aqueous solution with a specific initial concentration of platinum. The pH of solution was set at 11.6 by adding NH_4OH (ammonia 25% as NH_3, Panreac). The monoliths were maintained in contact with the aqueous solution for 24 h to reach the equilibrium. Then the excess liquid was blown out and the catalysts were dried at room temperature in horizontal position. Finally monoliths C and D were calcined in air at 500 °C and monolith B at 550 °C for 4 h.

The incorporation of the NO_x storage compound was carried out by wetness impregnation (W.I.) or dry impregnation (D.I.). For wetness impregnation, the desired amount of barium acetate was dissolved and the channels were filled with this aqueous solution (monoliths A, B and C). For dry impregnation (D.I.), the channels were filled, but the excess of liquid was blown out with compressed air (monolith D). Then the monoliths were dried at 110 °C for 24 h and finally calcined in air at 500 °C (monolith A, C and D) or at 550 °C (monolith B).

Table 1. Preparation methods for A, B, C and D monoliths.

Monolith	A	B	C	D
Pt incorporation	W.I.	A.S.	A.S.	A.S.
Ba incorporation	W.I.	W.I.	W.I.	D.I.
Calcination temp.	500°C	550°C	500°C	500°C

The resulting monolith catalyst were characterized by scanning electron microscopy (SEM, Sirion FEG) and transmission electron microscopy (TEM, Jeol JEM-2010F). The size of particle metal was measured either by HAADF-STEM and hydrogen chemisorption (Micromeritics ASAP 2010).

Prior to reaction catalytic activity, the samples were reduced with a flow of 4%H_2/N_2 at 250 °C for 20 minutes. Storage and reduction of NO_x were evaluated in a flow reactor. All the gases were fed via mass flow controllers and the total flow rate in all experiments was set at 3365 ml min^{-1}, which corresponded to a gas hourly space velocity of about 32100 h^{-1}. The inlet gas composition of the 150 s-long lean period was 370 ppm NO and 6% O_2 using N_2 as the balance gas. For the 20 s-rich period the composition was 370 ppm NO and 2.3% H_2. The outlet gases were continuously measured by using chemiluminiscence (NO_x) and paramagnetic (O_2) detectors (Rosemount Analytical).

Results and discussion

Washcoating the substrate is the first step to propose a NSR monolithic catalyst. The particle size distribution of the alumina is an important parameter to achieve a good adhesion of the layer on the monolith. The wet ball milling of the alumina resulted in an adequate particle size distribution, with a mean diameter of 1 micron to be anchored on the cordierite surface. Moreover, the incorporation of acetic acid with an optimum concentration improved the reological behavior of the slurry, thus reducing the viscosity and favoring the incorporation of the alumina on the monolith. As a result, a homogeneous coating of all the monolith channels, with a constant thickness of about 5 microns, was obtained. The adhesion test revealed a very strong adhesion with a small weight loss of 0.36 % when subjecting the monoliths to ultrasound agitation for 30 minutes. Figure 1 shows the incorporation of the alumina as a function of the number of successive immersions while Figure 2 a SEM image of the final washcoat obtained.
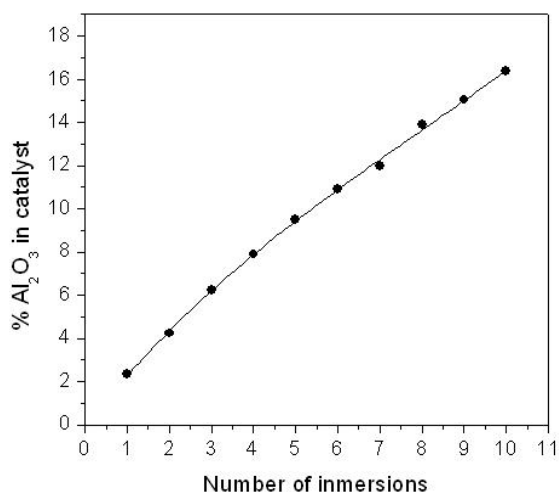

Figure 1. Alumina incorporation velocity to the monolithic support.
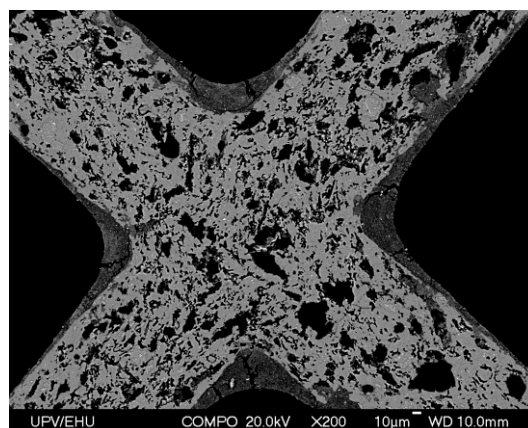

Figure 2. SEM image of the washcoated monolith.

The deposition of active metallic phases on a washcoated monolith is the last and crucial step in the preparation of monolithic catalysts [4]. Notable differences in the dispersion and distribution of the active phases over the monolithic catalyst were found. To evaluate the distribution, the monoliths were cut in several pieces and the concentrations were determined by ICP-MS. When the platinum and barium were incorporated by wetness impregnation (A) the final distribution resulted in an egg-shell type. The results showed that the concentrations of both platinum and barium in the internal side of the catalyst were considerably lower than in the outer. In order to improve the distribution of the metallic phase, the incorporation of platinum was carried out through adsorption from solution (B, C and D). The result was a more homogeneous distribution. Finally, the poor distribution obtained for barium by wetness impregnation was improved by incorporating the storage compound by dry impregnation, decreasing the difference between the inner and outer concentration of this component.

The incorporation of the active phases in the monoliths B and C was carried out through the same method, so the distribution was only measured in the monolith B assuming the same distribution for the monolith C. The internal side of the monolith refers to a internal radious of 0.8 cm, and the outer side to a 0.2 cm thick outer ring.

There were notable differences between the nominal (1.2% Pt and 15% BaO) and actual concentration of the active phases into the catalyst (Table 2). The incorporation of platinum through wetness impregnation showed the higher deviation. On the other hand, when depositing barium by dry impregnation, it was assumed that the volume of barium acetate solution remaining in the catalyst after blowing out the excess, would be equivalent to the pore volume of the alumina. It can be concluded that the volume remaining in the catalyst is higher, thereby the percentage of barium deposited is much higher than the nominal.

Table 2. Distribution of the active phases in the monolithic catalysts. The concentration is given as weight percentage of active phase in washcoat.

Monolith	Pt incorp.	BaO incorp.	% Pt			% BaO		
			average	outer	inner	average	outer	inner
A	W.I.	W.I.	0.72	1.18	0.46	13.1	23.5	7.11
B	A.S.	W.I.	1.34	1.60	1.17	13.3	22.5	7.42
D	A.S.	D.I.	1.14	1.33	1.03	25.2	33.1	20.6

To evaluate the dispersion of the platinum, transmision electron microscopy and hydrogen chemisorption were used. The wet impregnation resulted in a low dispersion with a particle size up to 100 nm, determined by TEM. When the incorporation method employed was adsorption from solution (A.S.) the platinum precursor was dissolved and the pH was turned basic, over the point of zero charge of the alumina. Under these conditions, the cation $((NH_3)_4Pt)^{2+}$ was attracted by electrostatic forces to the negatively charge alumina surface, so the incorporation was selective, leading to a finely dispersed platinum, with a mean particle diameter of 1.3 nm (Figure 3).
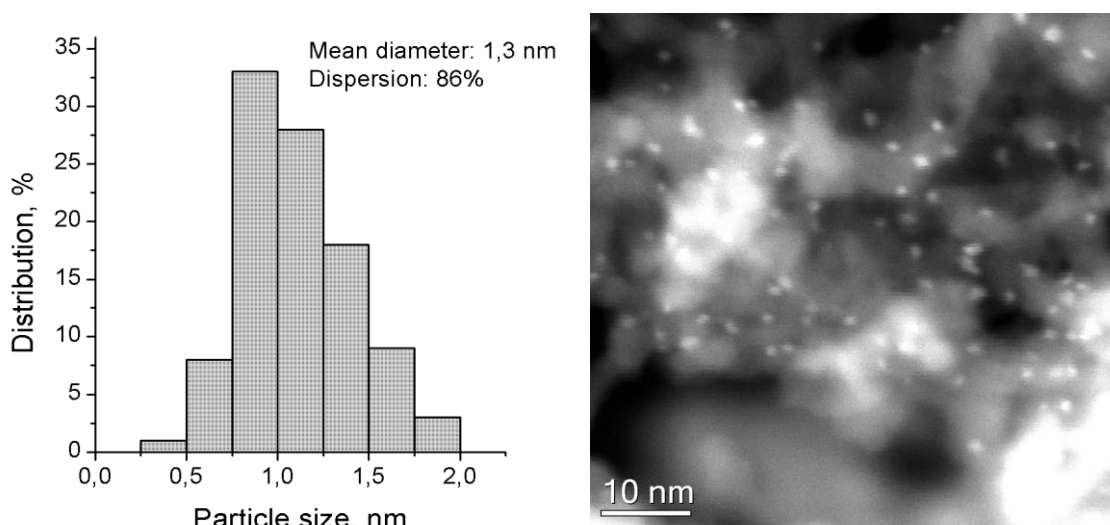

Figure 3. Particle size distribution and HAADF-STEM image, for a Pt/Al_2O_3 monolithic sample prepared by adsorption from solution, calcined at 500°C.

Another key step in the performance of a Pt/BaO/Al$_2$O$_3$ monolithic catalyst is the calcination temperature. Pt dispersion was determined by hydrogen chemisorption and TEM analysis for samples calcined at 450, 500 and 550 °C. Hydrogen chemisorption experiments were carried out in powder, whereas TEM experiments were done over the alumina previously scrapped from the monolith. No big difference were observed in the dispersion of catalysts calcined up to 500°C,which resulted higher than 90% by both analysis methods. However, higher calcinations temperature, i.e. 550 °C decreased the platinum dispersion around 50%.

It could be concluded that a calcination step at 500°C was suitable for achieving both a high Pt dispersion and an appropriate thermal stabilization of the monolith, thereby preventing structural changes during reactions.

Finally, the catalytic activity of the prepared monoliths was evaluated in lean and rich periods. Two consecutive storage-reduction cycles are shown in Figure 4 for monoliths C and D. The shape of the cycles for monoliths A, B and C was similar. A slightly increasing capacity in the NO$_x$ storage was observed in this order C>B>A; a joint effect of amount and dispersion of platinum should be considered. On the other hand, the monolith D maintained a high dispersion of platinum but with the barium more homogenously distributed. Some differences could be noticed between the shapes of the cycles for monolith C, where the barium oxide was incorporated by W.I., and for monolith D, where the barium oxide was incorporated by D.I.

As for the storage step it was noticed that the capacity of monolith C was substantially lower (260 ppm of NO$_x$ emitted at the end of the lean period) due to its non homogeneous distribution of barium. However, since a fraction of Pt particles were not blocked and remained accessible the reduction behavior was excellent (virtually all NO$_x$ fed in the rich period was reduced). In contrast, monolith D with a more homogeneous distribution of barium and a higher loading exhibited a storage capacity (190 ppm of NO$_x$ released at the end of the lean period) at the cost of a less efficient reduction of stored species.
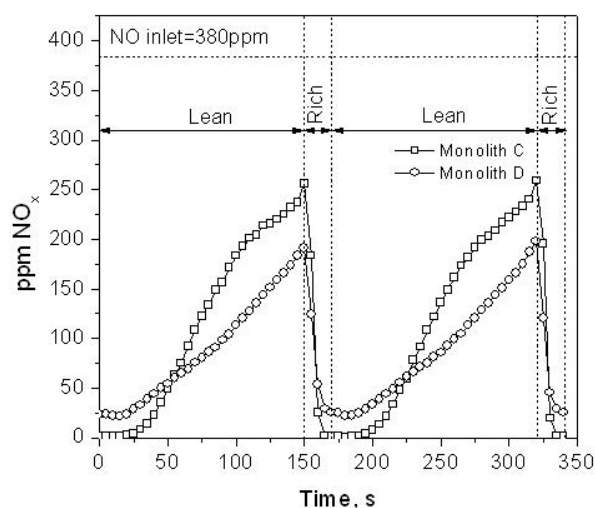

Figure 4. Outlet NO$_x$ concentration for two lean/rich cycles over the Pt/BaO/Al$_2$O$_3$ monolith C and D, at 300 °C.
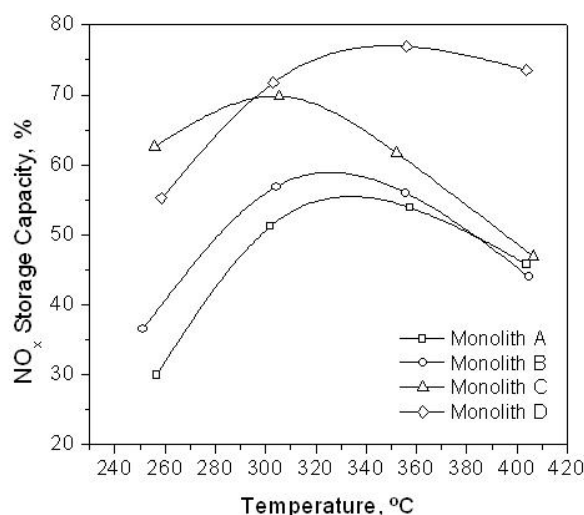
Figure 5. Comparison of catalytic performance of the Pt/BaO/Al$_2$O$_3$ monoliths A, B, C and D.

The NOx storage-reduction behavior of the prepared monoliths was evaluated through the storage ratio defined as:

$$NO_x \ StorageRatio = \int_0^t \frac{F_{NO}^0 - F_{NO_x}(t)}{F_{NO}^0} dt \qquad (1)$$

where F_{NO}^0 is the feed molar flow rate of NO, and F_{NOx} is the outlet molar flow rate of NOx. Figure 4 shows the NOx storage capacity (Equation 1) obtained with Pt/BaO/Al₂O₃ monoliths A, B, C and D under the operating conditions above mentioned at various temperatures from 250 to 400 °C in step of 50 °C. Several conclusions can be deduced from Figure 5:

i)   For all four samples, there is an optimal reaction temperature at which NOx storage is maximum.

ii) The activity is ranked as follows: D>C>B>A. Firstly, the better behavior of the monolith B compared to the monolith A could be assigned to the better distribution and higher platinum content. Secondly, the better dispersion of platinum is responsible for the improvement in the catalytic activity of the monolith C with respect to monolith B. Finally, the largest storage capacity corresponds to the monolith D. The concentration of barium is also higher in this sample but in literature it is well known that the optimum loading of barium is around 15%, and higher loadings are not beneficial for the reaction, so the improvement in the activity is related to the better distribution of barium.

iii) The conversion maximum is shifted to lower temperatures (300-320 °C) for monoliths A, B and C being their difference related to the dispersion of platinum with a similar distribution of barium. The deviation in the tendency of the monolith D is assigned to the higher activation temperatures required for the platinum sites covered by barium (360 °C).

iv) The best performance corresponds to a storage capacity of 75% attained with the monolith D, i.e. prepared by adsorption from solution and calcined at 500 °C for the noble metal, and dry impregnation for the storage component, when the reaction was carried out around 300 °C. This optimal behavior was correlated to the higher dispersion of platinum and more homogeneous distribution of both platinum and barium oxide.
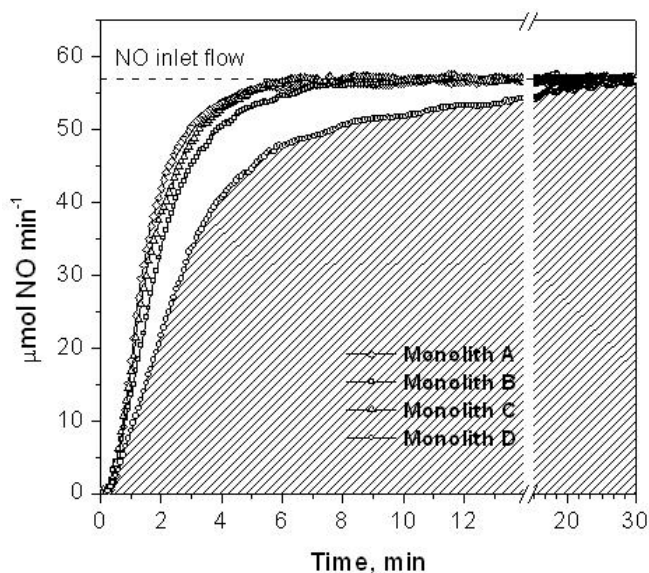
Table 3. Total amount of NOx stored.

Monolith	NOx stored, µmol
A	97.95
B	101.91
C	126.75
D	232.77

Figure 6. NOx outlet concentration until the saturation of the monoliths at 300°C.

The catalytic activity of the monoliths could be evaluated from the total amount of NO_x stored, extending the lean cycle until saturation, Figure 6. The lean-rich cycles allowed us to observe the behavior of the monoliths in real conditions, but there are several parameter that can have influence on the storage capacity, e.g. the length of the cycles. We concluded that the reduction activity of the monolith C was higher due to the superficial position of the platinum, so if the ratio between the length of the lean and rich periods (t_L/t_R) was low, the storage capacity of the monolith C was larger than the storage capacity of the monolith D. A low (t_L/t_R) would improve the catalytic behavior but it would penalize the fuel consumption, and the objective in practice is to reach the largest storage capacity with the minimum length rich period to reduce or regenerate the storage sites, so (t_L/t_R) must be high. Increasing the length of the lean cycle up to 100 s the storage capacity was the same for two monoliths. For a further increase, the storage capacity of the monolith D was larger due to the better distribution of barium.

In sum, when (t_L/t_R) is low the importance of the reduction step is higher, and this step is favored by the superficial position of the platinum. Hence, for increasing values the importance of the storage capacity increase, as well favored by the adequate distribution of barium.

The saturation experiments allowed us to calculate the total amount of NO_x stored. It could be noted that monolith D exhibited the largest storage capacity (Table 3). Monoliths A, B and C were saturated with a lean cycle of about 7 minutes, while 30 minutes were required for monolith D saturation.

Conclusions

The dispersion and distribution of the active phases are key parameters in the preparation of NSR monolithic catalyst. The active phases must be well distributed and dispersed and close from each other for the improvement of the storage capacity.

The wetness impregnation resulted in a non homogeneous distribution and poor dispersion of the active phases. The best distribution and dispersion of platinum was achieved by adsorption from solution and calcination at 500 °C. On the other hand, the distribution of the NO_x storage compound was improved by dry impregnation.

The distribution and dispersion of the active phases were correlated to the catalytic activity. The best catalytic behavior was related to the best dispersion and distribution of both platinum and barium oxide. It was found that a superficial position of the platinum favored the reducing stage and the adequate distribution of barium improved the storage capacity.

References

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