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Reactivity of Mg-Ba catalyst in NO_x storage/reduction

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Abstract

A new catalyst for NO_x storage/reduction was prepared to improve the activity of Ba-Pt/γ-Al_2O_3 by replacing Ba with a mixture of Ba and Mg. The catalyst was prepared by impregnating 1 wt.% Pt and then the alkaline-earth metals (Mg, Ba) on commercial γ-Al_2O_3. The tests have been carried out in a wide temperature range (ca. 200–400 °C) in order to understand the role of the mixture of alkaline-earth metals as a function of temperature. The behaviour of the two catalysts was different and indicated a synergetic effect between Mg and Ba.

Keywords: NSR; NO_x storage/reduction; Alkaline-earth metal; Pt

1. Introduction

Gasoline fuel lean-burn engine is a key technology to improve the fuel efficiency of a passenger car [1]. However, lean operating conditions have been limited, since NO_x emitted under oxidizing conditions could not be purified using the conventional three-way catalysts. Recently, catalysts for selective NO_x reduction under oxidizing conditions have been widely investigated: one of the most promising solution has been proposed by Toyota researchers [2,3] and is called NO_x storage reduction concept (NSR). This catalytic system has also been studied by other research groups [4–7]; the air–fuel ratio changes between lean (oxygen excess) and rich (fuel excess) mixtures. During lean periods (1–2 min), NO_x is oxidised into NO_2 on a Pt site, and NO_2 adsorbed on BaO and $BaCO_3$ [4]. During short rich periods (3–6 s), the storage material is regenerated and the desorbed NO_x reacts with CO, hydrocarbons and H_2 (the strongest reductant, obtained by Water Gas Shift or Steam Reforming reactions) to produce CO_2, H_2O and N_2.

Researches on storage components has focused on studying single alkali and alkaline-earth metals, mainly the Ba-Pt/γ-Al_2O_3 system [3,8,9]. More recently, studies have addressed NSR catalysts that used different storage systems [10], and different interactions between the components and the support [11,12].

At present, Ba-Pt/γ-Al_2O_3 is the most widely used system for lean burn gasoline passenger cars. The aim of this research was to study with different conditions a new catalytic system in which Ba was partially replaced with Mg [13]. The adsorption capacity and the constancy behaviour of the cycles of NSR was investigated at different temperatures and compared with those of the reference 17Ba-1Pt/γ-Al_2O_3 (17/1/100, w/w). The saturation effect of active site was also analysed.

2. Experimental

The M^{2+}, Pt/γ-Al_2O_3 catalysts (1 wt.% Pt, M^{2+} = Mg and/or Ba) were prepared using a commercial γ-Al_2O_3 [Sasol (D)] incipient wetness impregnated using at first $Pt(NH_3)_2(NO_2)_2$ and then M^{2+} solutions according to literatures [9,14]. The precursors utilized for impregnation, $Ba(CH_3COO)_2$ and/or $Mg(NO_3)_2$, allows the dissolution of the storage cations in minimum amount of water. After each impregnation, the samples were dried at 90 °C overnight, and then heated to 550 °C for 12 h. The final powder was formed in 0.250–0.600 mm particles, which were then activated at 350 °C for 1 h in a 100 ml/min flow of H_2 in He (20%), followed by mild re-oxidation at 80 °C for 1 h in 100 ml/min flow of O_2 in He (20%).

XRD patterns were recorded using a Philips PW 1710 instrument with Cu Kα radiation (λ = 0.15418 nm) (40 kW, 25 mA). BET surface area and porosity were measured using a

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Table 1
Characteristics of the samples used

Catalysts	Surface area (m^2/g)	Volume of pore (cm^3/g)	Diameter of pore (nm)	Crystalline phases (XRD)	$BaCO_3$ crystal size (nm)
γ-Al_2O_3	208	0.488	7.0	γ-Al_2O_3	–
1Pt/γ-Al_2O_3	189	0.472	7.0	γ-Al_2O_3	–
1.5Mg8.5Ba-1Pt/γ-Al_2O_3	188	0.430	6.7	$BaCO_3$; BaO; γ-Al_2O_3	21
17Ba-1Pt/γ-Al_2O_3	144	0.339	6.8	$BaCO_3$; BaO; γ-Al_2O_3	20

17Ba-1Pt/γ-Al_2O_3 (17/1/100, w/w); 1.5Mg8.5Ba-1Pt/γ-Al_2O_3; (1.5/8.5/1/100, w/w).

Micrometrics ASAP 2020 analyser (Table 1). Catalytic tests were carried out in a quartz flow micro-reactor using 0.5 g of catalyst. An on-line mass quadrupole analyser (VG SX200) and a chemiluminescence Eco Physics (CLD 82 S h) were used for monitoring the feed composition and the reaction products. The NSR activity was studied using a series of cyclic sequences of feed changes from lean conditions (5% O_2, 1000 ppm NO, remaining He) to rich conditions (2.5% H_2, 1000 ppm NO, remaining He). The reactor temperature was changed from 200 to 300, and then to 400 °C. Each catalytic test was repeated six times at the same temperature, starting from an oxidant phase carried out until 200 ppm of NO_x at the exit of reactor was reached, and then followed by a reducing phase carried out for a time proportional to that of oxidant phase ($time_{red} = time_{ox}/8$).

3. Results and discussion

3.1. Characterization

Fig. 1 shows the X-ray diffractograms for all the catalysts, highlighting the presence of the pattern of the support (γ-Al_2O_3) and – in the Ba-containing samples – also of Ba crystalline phases (BaO < $BaCO_3$). The porosity of γ-Al_2O_3 did not decrease after impregnation with Pt, thus showing that it did not influence the volume of pore (Table 1). Also, the calcination of γ-Al_2O_3, at 550 °C for 12 h produced only a slight decrease in porosity from 0.488 to 0.461 cm^3/g. On the contrary, the addition of alkaline-earth metals lead to a progressive occlusion of pores. This occlusion could change the NSR activity because the Pt can be covered by the alkaline-earth metals decreasing the amount of noble metal for the NSR reaction. The mean crystal sizes of $BaCO_3$ were calculated by the Scherrer equation and were bigger than the dimension of the pores (Table 1). Quantitative analysis of crystalline $BaCO_3$ orthorhombic has been performed by XRD using integrated intensity of the (1 1 1) reflection ($2\theta = 24.091$).

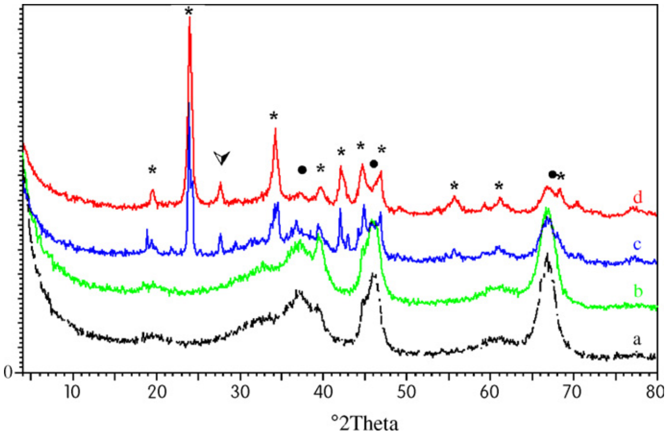

Fig. 1. X-ray diffraction patterns for: (a) γ-Al_2O_3, (b) 1Pt/γ-Al_2O_3, (c) 1.5Mg8.5Ba-1Pt/γ-Al_2O_3 and (d) 17Ba-1Pt/γ-Al_2O_3 ((●) γ-Al_2O_3, (*) $BaCO_3$ and (⮟) BaO)).

3.2. Catalytic activity in NSR

Utilizing a series of 10 cycles for each isotherm (120 s for oxidant phase and 15 s for reduction phase [13]) previously, we reported that the sample 17Ba1Pt/γ-Al_2O_3, showed a very high conversion in a very limited temperature range (200–350 °C), with a lower activity at 400 and 500 °C. Instead, the

Table 2
Quantity of products at different reaction temperatures for 17Ba-1Pt/γ-Al_2O_3 and 1.5Mg8.5Ba-1Pt/γ-Al_2O_3

	1st cycle	2nd cycle	3rd cycle	4th cycle
200 °C				
1.5Mg8.5Ba-1Pt/γ-Al_2O_3				
NO adsorbed[a]	0.34	0.28	0.28	0.28
%N_2 formed[b]	88	89	88	90
%NH_3 formed[b]	8	9	9	9
17Ba-1Pt/γ-Al_2O_3				
NO adsorbed[a]	0.17	0.15	0.15	0.15
%N_2 formed[b]	102	95	98	93
%NH_3 formed[b]	9	13	13	13
300 °C				
1.5Mg8.5Ba-1Pt/γ-Al_2O_3				
NO adsorbed[a]	0.29	0.32	0.32	0.32
%N_2 formed[b]	80	84	86	85
%NH_3 formed[b]	7	7	7	7
17Ba-1Pt/γ-Al_2O_3				
NO adsorbed[a]	0.36	0.34	0.34	0.34
%N_2 formed[b]	99	95	103	90
%NH_3 formed[b]	10	12	12	11
400 °C				
1.5Mg8.5Ba-1Pt/γ-Al_2O_3				
NO adsorbed[a]	0.19	0.19	0.18	0.18
%N_2 formed[b]	87	88	90	89
%NH_3 formed[b]	9	8	8	7
17Ba-1Pt/γ-Al_2O_3				
NO adsorbed[a]	0.46	0.44	0.43	n.d.
%N_2 formed[b]	91	85	89	n.d.
%NH_3 formed[b]	12	19	19	n.d.

[a] mmol NO/mmol storage element.
[b] estimated amounts of nitrogen and ammonia.

$1.5Mg8.5Ba1Pt/\gamma\text{-}Al_2O_3$ (the number of mole of alkaline-earth metals was maintained constant to have constant number of storage sites) already exhibited very good activity at 150 °C, that remained very high until 500 °C [13].

The storage capacity of the $1.5Mg8.5Ba\text{-}1Pt/\gamma\text{-}Al_2O_3$ and the reference $17Ba\text{-}1Pt/\gamma\text{-}Al_2O_3$ catalysts are compared in Table 2 as a function of the reaction temperature. In accordance with literatures [4,11,14,15], the catalyst $17Ba\text{-}1Pt/\gamma\text{-}Al_2O_3$ showed an activity which was low at 200 °C, but increased as the temperature reached 300 and 400 °C. The sample containing Mg and Ba exhibited a good capacity with a very high adsorption between 200 and 300 °C, but slightly lower

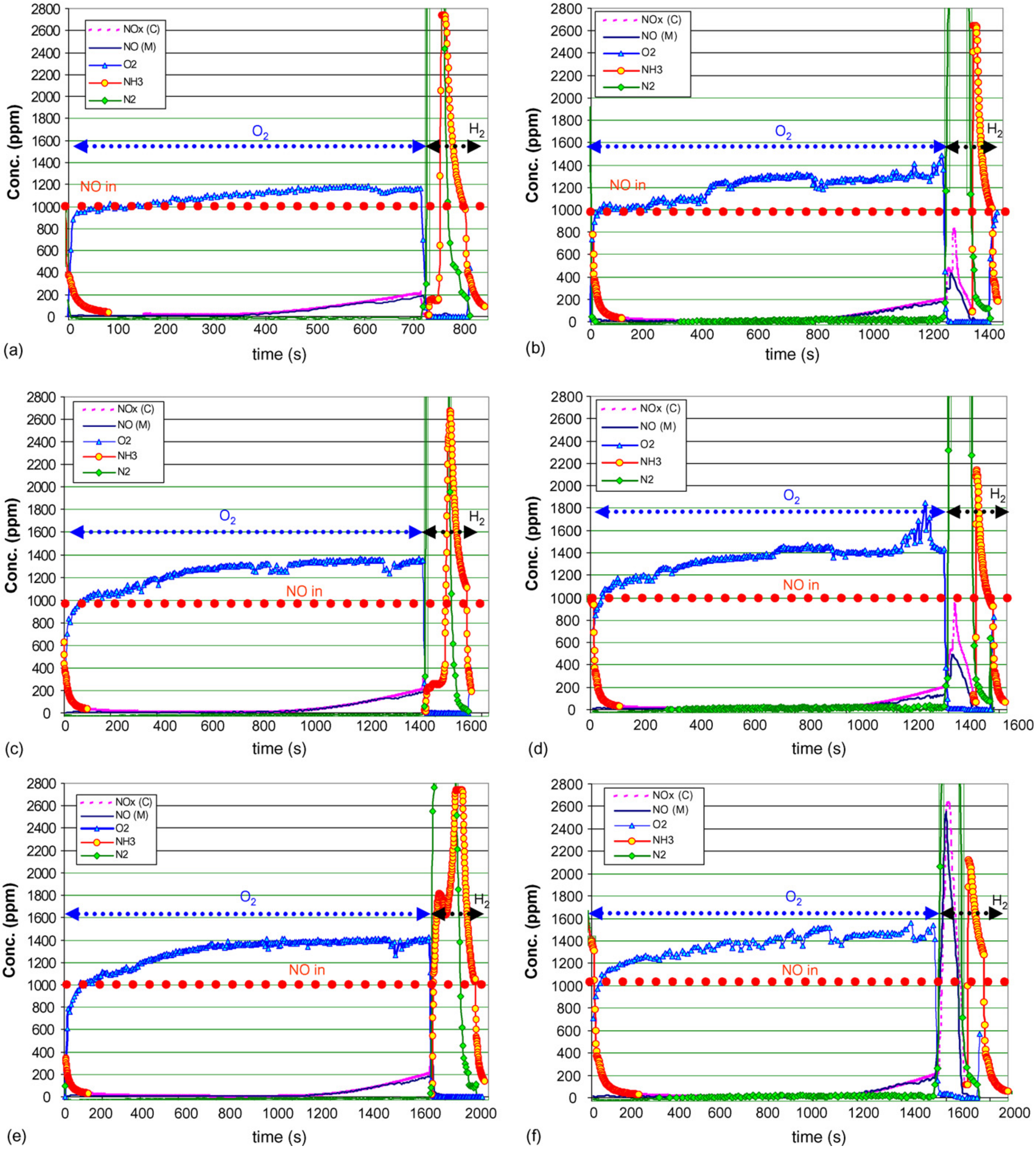

Fig. 2. Comparison of the NSR activity at different reaction temperatures for $17Ba\text{-}1Pt/\gamma\text{-}Al_2O_3$ ((a) 200 °C, (c) 300 °C and (e) 400 °C) and $1.5Mg8.5Ba\text{-}1Pt/\gamma\text{-}Al_2O_3$ ((b) 200 °C, (d) 300 °C and (f) 400 °C). Concentration of NO ((—) NO measured with spectrometer mass, M), NO_x ((- - -) NO_x measured with chemiluminescence, C), O_2 (—△—), NH_3 (—○—) and N_2 (—◇—) during the last cycle for all isotherms.

adsorption at 400 °C. The high capacity at temperature ≤ 300 °C could be used to produce catalysts with interesting property for emissions from gasoline engine (cold start) and from light-duty diesel engines, since for a large part of the time the emissions are at low temperature, typically in the 100–300 °C range [16,17].

Only a small variation of the NO adsorption has been noted between the 1st and 2nd cycle, while it remained constant in the following cycles.

The results obtained for the last storage/reduction cycles at 200, 300 and 400 °C for the 17Ba-1Pt/γ-Al_2O_3 and 1.5Mg8.5Ba-1Pt/γ-Al_2O_3 catalysts are shown in Fig. 2 (a, c and e) and Fig. 2 (b, d and f), respectively. The NO, NO_x, O_2, N_2 and NH_3 concentration curves are reported as a function of time and temperature. Unlike previous reports [15,18], in all samples and all temperatures during the oxidant phase, NO_2 was not detected as a product, probably because the NO_2 produced remained adsorbed on the surface and its presence can only be revealed after a large induction time [18].

The mechanism of the NO_x adsorption has not been clarified. Although many authors suggest that the storage process involves at first the NO oxidation to NO_2 on Pt sites, and then its adsorption on the nearest sites of the storage component [14,15,19], also an NO adsorption far from the noble metal on strong basic sites may also be possible [14,19,20].

From Table 2, it is possible to evaluate the fraction of storage elements in the storage process. The amounts of "active sites" of storage elements ($M(NO_3)_2$) change on increasing the temperature, from 15 to 34%, and 44% for the catalyst 17Ba-1Pt/γ-Al_2O_3 and from 28 to 32%, and 19% for the sample 1.5Mg8.5Ba-1Pt/γ-Al_2O_3. These values are similar to the data reported in literature [18] and demonstrate that the decrease of porosity does not change the catalytic activity. In our conditions, the active sites of 17Ba-1Pt/γ-Al_2O_3 increase linearly on increasing the temperature, while those of 1.5Mg8.5Ba-1Pt/γ-Al_2O_3 have their maximum at 300 °C and then decrease at 400 °C.

The reduction of the stored NO_x (i.e. catalyst regeneration) was carried out with H_2. From the analysis of the concentration curves reported in Fig. 2, it clearly appears that in the first half of the reduction phase, the NO_x adsorbed species were readily reduced to N_2 (Table 2) and H_2O (not reported), and then in the remaining part of the phase, NH_3 appeared and began to increase (Table 2).

During the reduction process, the formation of N_2 was very fast and depended on the amount of NO_x stored. However, upon the termination of N_2 production, the formation of NH_3 was observed, thus suggesting that two phases can be distinguished:

$$M(NO_3)_2 + 5H_2 \rightarrow N_2 + 5H_2O + MO \quad (1)$$

$$M(NO_3)_2 + 8H_2 \rightarrow 2NH_3 + 5H_2O + MO \quad (2)$$

(M = Mg and/or Ba) in accordance with literature [18]. However, in this case, the behaviour did not depend only on the amount of storage component, but more on the amount of stored NO.

A saturation effect of active sites with a more constant behaviour has been recently described and reached after several cycles [21]; with our test, it is possible to reach both these results after one or two cycles.

The reduction of NO by H_2 with platinum and formation of NH_3 is known [18,22–24]; the reaction over platinum metal surfaces and oxide support could be explained by the fact that, at higher temperatures ($T \geq 300$ °C), NO can adsorb on the Pt sites and dissociate easily into atomic oxygen and nitrogen, then can react with the H_2, present in high concentration [24,25], to form N_2 and NH_3. At lower temperatures ($T \leq 200$ °C), the NO dissociation is not favoured, thus a part of it will be released directly as NO [24].

The catalysts showed a different behaviour during the reduction phase:

- 17Ba-1Pt/γ-Al_2O_3 adsorbed the NO fed [15,19] also in presence of H_2, and the formation of NH_3 began before the end of the production of N_2. The quantity of formed NH_3 increased on increasing the reaction temperature due to the higher quantity of NO_x stored. The selectivity in N_2 or NH_3 should be related to the Pt–Ba interaction [18].
- The storage capacity for the 1.5Mg8.5Ba-1Pt/γ-Al_2O_3 decreased as the temperature increased. Indeed, at 400 °C, at the beginning of the reduced phase, the curves of NO and NO_x concentration were higher than the value of NO in the feed. This could be attributed to a less efficient reduction (Pt–Mg interaction) and/or to a desorption of NO from Mg sites far from Pt in the absence of O_2. At the end of the reduction, when the production of N_2 is over, the catalyst readsorbed NO also in absence of O_2 [15,19], the adsorption of NO continued also in the presence of NH_3 formation. Finally, this sample produced a lower amount NH_3 with respect to 17Ba-1Pt/γ-Al_2O_3 sample also in cycles in which the amount of NO stored was higher.

The reduction process does not depend only on the composition and properties of the catalysts [18], but also on the amount of NO stored. For the samples 1.5Mg8.5Ba-1Pt/γ-Al_2O_3, a synergetic effect of the storage elements was evident, which significantly increased the "storage-reduction" capacity with respect to the reference. This effect was very high from 200 to 300 °C and also influenced the reduction activity, which leads to a lower production of NH_3.

4. Conclusions

The effect of the composition of a new catalytic system for NO_x storage/reduction with respect to Ba-Pt/γ-Al_2O_3 in which Ba was replaced partially with Mg was investigated. During preparation, the addition of alkaline-earth metals leads to a progressive occlusion of pores. The storage capacity is different for the two catalysts but a good stability is reached. The storage capacity of the reference sample increases with the temperature, while the Mg-Ba-catalyst shows a good activity between 200 and 300 °C, but in both cases NO_2 was not detected. The increase in the NO_x adsorption leads to different products during the reduction process for the 17Ba-1Pt/γ-Al_2O_3 sample, N_2 and also NH_3 being produced, while for the 1.5Mg8.5Ba-1Pt/γ-Al_2O_3, NH_3 is produced only when the formation of N_2 is over. This behaviour could allow the reduction time to be calibrated and therefore the rich period to be stopped before NH_3 is formed. A comprehensive and detailed mechanism of the reduction process has not yet been suggested in the literature and, therefore, we are going to concentrate our future studies on this aspect.

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