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Controlling the selectivity to N_2O over $Pt/Ba/Al_2O_3$ NO_X storage/reduction catalysts

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ABSTRACT

N_2O formation during the reduction process over NSR catalysts is analysed in this paper. The effect of catalyst characteristics and different operation parameters (chemical nature of the reductant, temperature and cycle timing) are addressed and discussed in terms of N_2O selectivity.

1. Introduction

The need of controlling CO_2 emissions has stimulated the increase in combustion efficiency in transport applications using lean-burn gasoline or diesel engines. However, the abatement of NO_X in the oxygen-rich exhaust created by these engines is a key challenge that must be tackled in order to meet the emission regulations. In this context, NO_X storage/reduction (NSR) catalytic technology merges as a promising solution for removal of NO_X from these engines.

Specific NSR catalyst formulations allow NO_X storage over the alkaline component under lean conditions mainly in the form of nitrates. The catalyst operation requires periodically imposed rich events, when the stored NO_X are reduced by H_2, CO, or hydrocarbons. During this reduction process several products are obtained, such as N_2, N_2O and NH_3 [1,2].

In particular, N_2O plays an important role in the destruction of the ozone layer in the stratosphere and also contributes to the greenhouse effect. Even though specific emission levels for N_2O in automobiles have not been approved in the EU, fleet-average CO_2 emission targets must be reached by 2015. For stricter legislations (e.g., California, USA) N_2O contribution to greenhouse gas emissions is also considered and the standards are defined in grams per mile of CO_2-equivalent, using a factor equal to 296 for the N_2O emitted. Up-to-date information about these standards can be found on the Internet [3].

This work deals with the reduction process of stored NO_X over model $Pt/Ba/Al_2O_3$ catalysts focusing on the selectivity of the process. The performance of different types of reductants such as hydrocarbons, CO, and H_2 has been compared by many groups, resulting H_2 the most effective regeneration agent [4,5]. Most attention has been devoted to the effect of different operation parameters on NH_3 formation process, which is the main by-product when H_2 is used as reductant [6,7]. In this context, a scenario with generated NH_3 acting as an reductant intermediate has been described [8,9]. In contrast, fewer studies are available regarding the formation of N_2O. In order to gain further insight into the generation of N_2O, the influence of the experimental conditions (temperature, cycle timing and chemical nature of the reductant) and the catalyst structure was investigated in this study.

2. Experimental part

The $Pt(1.3\%)/Ba(13\%)/Al_2O_3$ catalysts used in this study were prepared by wetness impregnation of γ-Al_2O_3, previously sized (0.3–0.5 mm), with aqueous solutions of $Ba(CH_3COO)_2$ and $Pt(NH_3)_4(NO_3)_2$. After each impregnation, samples were dried and then calcined at 650 °C for 4 h. Two catalysts, hereafter defined

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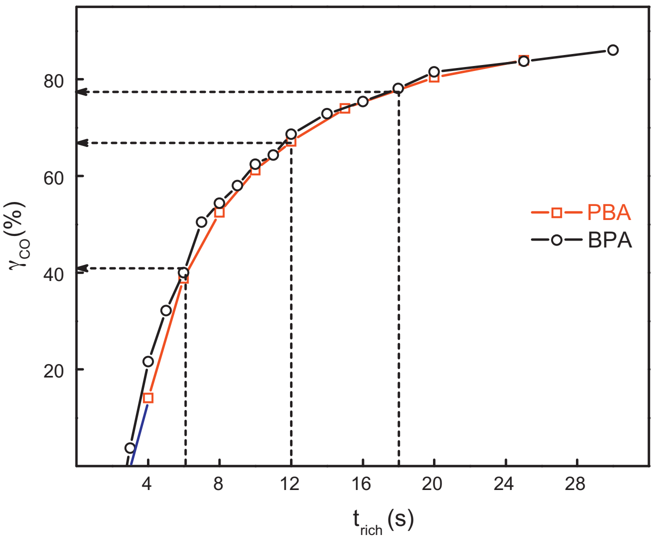

Fig. 1. CO availability (γ_{CO}) as a function of time under rich conditions for PBA and BPA catalysts.

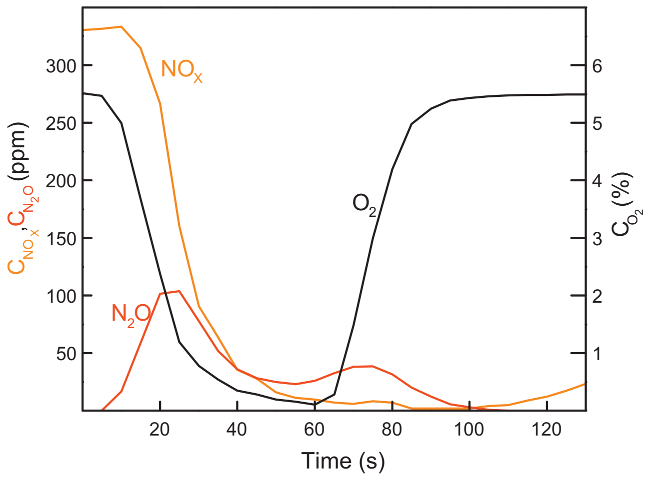

Fig. 2. NO_X, N_2O and O_2 time concentration profiles at 150 °C registered during the rich period. The gas mixture contained 300 ppm NO, 8.0%CO_2, 8.0%H_2O and 5.0%O_2 during lean conditions (30 min) and 325 ppm NO, 8.4%CO_2, 8.4%H_2O, 2.0%H_2 during rich conditions (60 s).

as PBA and BPA, were prepared as a function of the precursor incorporation order. For PBA sample the Ba-precursor was firstly incorporated. Then, Pt was added to the sample. The inverse order was adopted for BPA. The catalysts have been extensively characterised and the results can be found elsewhere [10]. Briefly, a general morphological scheme of PBA and BPA catalysts was defined, with the Al_2O_3 support almost fully covered by Ba phase in both samples and showing a similar contribution of the potentially deactivating $BaAl_2O_4$ phase. In contrast, the preparation strategy resulted in different Pt particles morphologies with mean diameters of approx. 10 and 15 nm for PBA and BPA catalysts, respectively. Moreover, and due to pore plugging and overlapping processes during Ba deposition, most of the Pt sites of BPA catalyst were isolated by the Ba phase. Then, although both components coexisted on the same support, the degree of close contact between Pt and Ba (and subsequently the Pt/Ba interface) on BPA catalyst resulted lower and mainly ascribed to non-superficial positions.

Transient reactor studies were performed as a function of temperature (150–450 °C), rich/lean cycle timing (6/62, 12/200 and 18/345 s/s) and the type of reductant (H_2 or CO). The tests consisted of cycling the gas feed between lean (300 ppm NO, 8.0% CO_2, 8.0% H_2O, 5.0% O_2 and a balance of N_2) and rich (325 ppm NO, 8.4% CO_2, 8.4% H_2O, 2.0% H_2/CO and a balance of N_2) compositions. Details concerning the reactor configuration and product analysis system can be found elsewhere [11].

Cycle timing modification has been carried out ensuring a constant amount of reductant agent for the reduction of the adsorbed NO_X species. A previous set of NSR runs as a function of cycle timing was performed in order to fix stoichiometric operation by means of t_{rich} and t_{lean} modification. Moreover, in agreement with the results reported previously by Elizundia et al. [11] the extent of the parallel reaction of the reductant agent with O_2 is dependant on cycle timing. CO availability (γ_{CO}) tests as a function of t_{rich}, Fig. 1, were performed in order to establish the aforementioned cycle timings. These tests consisted on transient runs conducted in absence of NO_X and H_2O over a fully regenerated catalyst. CO outlet concentration profiles were obtained during a series of transitions for different t_{rich} values up to 50 s. Time integration of these CO profiles, Eq. (1), provided the amount defined as γ_{CO} which is representative of the amount of CO that did not react with O_2 during the rich events.

$$\gamma_{CO} = 100 \cdot \frac{[CO]_{out}}{[CO]_{in}} = 100 \cdot \frac{\int C_{CO}(t)dt}{[CO]_{in}} \tag{1}$$

Results indicated that, regardless of the catalyst characteristics, within the $t_{rich} < 20$ s range reductions of this parameter promoted notable decays for γ_{CO}, leading to total CO depletion for $t_{rich} < 3$ s. Since stoichiometric operation was sought, the observed drop in γ_{CO}, i.e., the increase of the reductant agent involved in the parallel reaction with O_2 with decreasing t_{rich} was compensated by varying the t_{lean} accordingly to Eq. (2).

$$\gamma_{CO} \cdot \frac{t_{lean}}{t_{rich}} = \text{constant} \tag{2}$$

3. Results and discussion

Fig. 2 shows the NO_X, N_2O and O_2 concentration profiles obtained for the PBA catalyst during the rich period of transient storage–reduction tests at 150 °C using a t_{rich} of 60 s after NO_X adsites saturation during a lean period of 30 min. For this specific test the resulting values of NO_X storage and NO_X storage and reduction capacities were equal to 143 and 37 $\mu mol_{NOx}\,g^{-1}{}_{CAT}$, respectively [10]. In particular, the N_2O concentration profile revealed the presence of two events per cycle. Moreover, those N_2O peaks were ascribed to the lean-to-rich and rich-to-lean transitions as defined by the evolutions of O_2 concentration. This very storage–reduction run, i.e., using a reduction period of 60 s, was selected since the use of a relatively long t_{rich} allowed the dissipation of the mixing process that takes place during feed transitions which masked the existence of two N_2O concentration evolutions.

Mulla et al. [12] showed that the steady-state selectivity to N_2O during NO_X reduction over Pt sites was strongly enhanced by increasing the [NO]/[H_2] ratio. On the other hand, previously reported results [11] characterised the real-flow behaviour in the reactor used in this study in terms of an axial dispersion modulus equal to 0.03, which was representative of a relatively high mixing degree upstream from the catalytic bed. As a result, the temporal evolution of O_2 and reductant concentrations was simulated. In this context, it was evidenced that reaction between O_2 and the reductant occurred during those transitions resulting in a cushioned evolution of the reductant concentration and, therefore in low reductant concentration at the initial and final stage of the rich period. Thus, those stages were most likely responsible for generating high [NO]/[H_2] ratios, resulting in turn in an enhanced promotion of N_2O production. In addition, the contribution of adsorbed NO_X species to the formation of N_2O was evidenced by the larger extent of the first event (during lean-to-rich

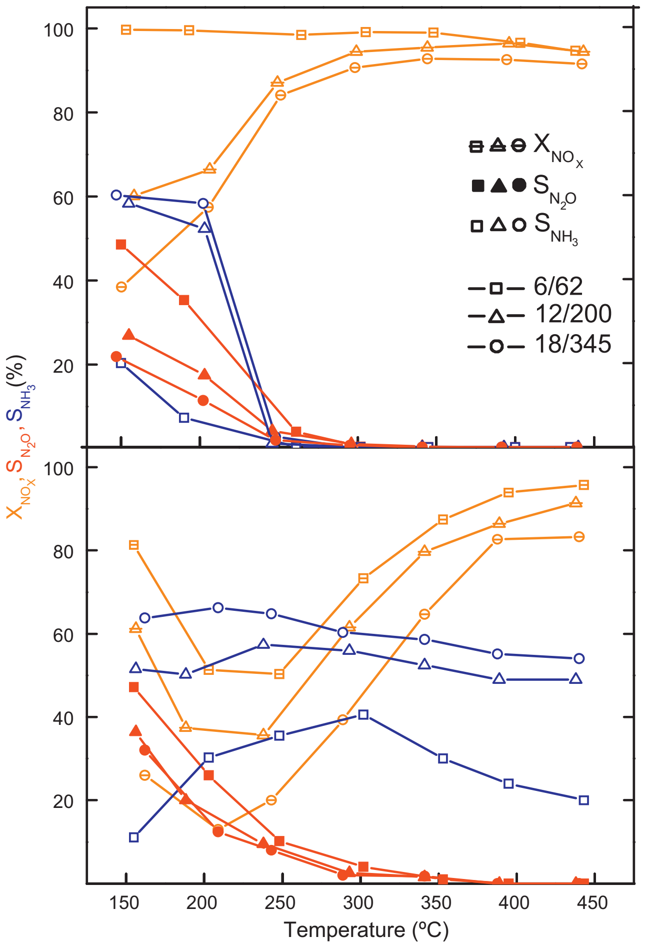

Fig. 3. NO_X conversion and selectivity to NH_3 and N_2O as a function of temperature and cycle timing (t_{rich} (s)/t_{lean} (s)) for PBA (top figure) and BPA (bottom figure) catalyst when H_2 is used as reductant.

transition) when the catalyst was closer to NO_X ad-sites saturation.

Cycle-averaged NO_X conversions and product selectivities as a function of temperature and cycle timing are shown in Fig. 3 for PBA and BPA catalysts. It can be observed the presence of NO_X conversion trends with temperature for both samples. However, measurements clearly show that the preparation procedure and consequently the catalyst characteristics influenced the activity of NO_X storage and reduction catalysts. At temperatures below 300 °C (where kinetic limitations start to control the process) the NO_X conversion achieved over PBA catalyst resulted much higher. These results evidenced the need to enhance the Pt/Ba interface which assists both storage and reduction processes. In particular, during the lean period it has been proved that the interaction of those components allows the spillover of oxidising species and NO_X from Pt to Ba sites assisting the required oxidation steps to form NO_2^- and NO_3^- species [13,14]. For the rich periods, the key role of this interaction also relays on surface diffusion processes. Possible mechanisms are the spillover of activated H_2 from Pt sites [15] and reverse spillover of NO_X ad-species with the reduction taking place at the Pt/Ba interface [14,16].

Significant amounts of NH_3 and N_2O were also observed as reduction by-products. Without going further insight in the discussion with respect to NH_3 selectivity (which will be addressed elsewhere) it was proved that NH_3 production was dependant on catalyst structure leading to a high selectivity with the BPA catalyst (lower Pt dispersion) even at high temperatures, which is in concordance with the results presented by Clayton et al. [17].

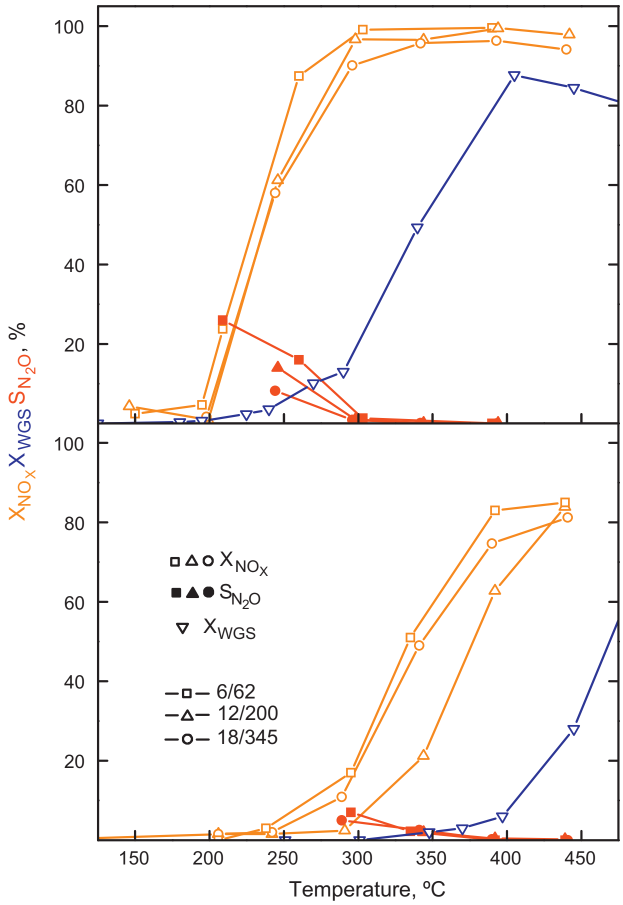

Fig. 4. NO_X conversion and selectivity N_2O as a function of temperature and cycle timing (t_{rich} (s)/t_{lean} (s)) for PBA (top figure) and BPA (bottom figure) catalyst when CO is used as reductant. WGS conversion data as a function of temperature in steady state rich conditions and in absence of NO_X.

On the other hand, for both catalysts, N_2O selectivity decreased with increasing temperature. This behaviour was in fairly good agreement with the results reported by Larson et al. [18] showing a maximum N_2O production in the 100–150 °C temperature range when fixed [NO]/[H_2] ratios were used in steady-state conditions. Although some residual N_2O production was detected for BPA catalyst at temperatures higher than 250 °C, N_2O selectivity did not show a marked dependence on NSR catalyst characteristics. However, it was found that cycle frequency strongly affected not only NO_X conversion but also by-products generation. In particular, Fig. 3 shows that an increase in cycle frequency at low temperatures promoted the N_2O production while NH_3 production was inhibited. It should be pointed out that, in spite of the fact that constant amounts of H_2 for the reduction of the adsorbed NO_X species were used, an increase in cycle frequency led to an increase in the number of lean-to-rich and rich-to-lean transitions per time unit and consequently the number of high [NO]/[H_2] ratio stages. Then, and in concordance with the concentration profiles shown in Fig. 2, the reported cycle frequency effect on N_2O selectivity could be expected.

Fig. 4 shows the dependence on temperature and cycle-timing of NSR conversions and product selectivities when CO was used as reductant. In addition, WGS process conversion as a function of temperature, obtained under steady-state conditions, is included. Results indicate that the use of CO instead of H_2 caused a marked drop in NSR activity for low temperatures. This effect can been related to the generation of a dense adsorption CO layer over Pt sites that inhibits NO_X reduction [19,20]. However, despite they were lost due to null activity at low temperatures, a similar influence of cycle length on N_2O yield was noticed. Once again, catalyst characteristics did not noticeably affect N_2O production. Moreover, NH_3 was not detected as reduction by-product. Since reduction was conducted under wet conditions, WGS reaction contribution to H_2 formation could be expected. Consistently, the study of PBA and BPA catalyst activity towards WGS reaction indicated that this process was not kinetically favoured when comparing to NO_X reduction with CO.

4. Conclusions

The results of the present paper indicated that the selectivity to N_2O strongly depends on cycle frequency and temperature. Catalyst characteristics (Pt dispersion and Pt/Ba interface) and reductant nature (H_2 or CO) showed a minor effect. For NO_X reduction at low temperature N_2O formation was detected. Its formation was noticed during lean-to-rich and rich-to-lean transitions. This finding has been related to the real gas flow behaviour which provokes high [NO]/[H_2] ratios during these stages. Accordingly, at low temperatures, those typically achieved during the cold start of the engine, N_2O emissions can be reduced by tuning the cycle length and improving the gas flow behaviour in the system (i.e., reducing mixing processes).

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