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Potentialities and limitations of lean de-NO_x catalysts in reducing automotive exhaust emissions

P. Ciambelli[a,*], P. Corbo[b], F. Migliardini[b]

[a] *Dipartimento di Ingegneria Chimica ed Alimentare, Università di Salerno, Via Ponte Don Melillo, 84084 Fisciano, Salerno, Italy*
[b] *Istituto Motori-CNR, Via Marconi, 8 80125 Naples, Italy*

Abstract

The performance of Pt–γ-Al_2O_3 and CuZSM5 de-NO_x catalysts was evaluated at the exhaust of a lean-burn gasoline engine. It is shown that durability for zeolite catalysts and N_2O formation for Pt catalysts are the main limitations which have to be still overcome to successfully apply the lean de-NO_x technology. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Road vehicles significantly contribute to the atmospheric pollution in urban areas and pose a major challenge to the development of emission control technologies. Since the raw emission of passenger cars cannot be reduced as much as required by next regulations, improved after-treatment systems have to be developed.

In Table 1 the emission limits for light-duty vehicles to be met in the European Union in the next years are reported. For petrol cars the Pt/Rh based commercial catalytic converters (TWC) are very effective in complying with the current limits, but they require the air/fuel ratio to be maintained very close to the stoichiometric point. The future limits could be met by improving this technology, possibly coupled with specific devices for hydrocarbon (HC) emission control in the cold start phase. However, in order to obtain best fuel economy, together with lower CO_2 emissions, the interest of automobile industries is addressed toward lean-burn engines, operating at air/fuel ratio higher than stoichiometric. While the future limits on particulate matter (PM) emitted from diesel engines could be met by optimising the combustion efficiency (high pressure fuel injection electronically managed), the very low NO_x standards proposed for the stage 2005 require the development of novel exhaust catalytic after-treatment systems.

On the other hand, since the novel technology of gasoline direct injection (GDI) utilises lean mixtures in partial load operating conditions of spark ignition engines, novel de-NO_x catalysts are required for petrol cars too. The simultaneous removal of organic compound emissions is also required, but it should be easily accomplished due to the large excess of oxygen in the exhaust of lean-burn engines.

The selective catalytic reduction (SCR) of NO_x to N_2 by NH_3 over V_2O_5–WO_3–TiO_2 systems is the current commercial process for the treatment of flue gas from stationary sources, ammonia being a highly selective reducing agent in the presence of oxygen.

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[*] Corresponding author. Tel.: +39-089-964-151;
fax: +39-089-964-057.
E-mail address: ciambell@dica.unisa.it (P. Ciambelli)

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Table 1
European emission limits for light-duty vehicles (g/km) (Directive 98/69/EEC)

	Stage 2000		Stage 2005	
	Petrol	Diesel	Petrol	Diesel
CO	2.30	0.64	1.00	0.50
HC	0.20		0.10	
NO_x	0.15		0.08	
$HC+NO_x$		0.56		0.30
PM		0.05		0.025

Nevertheless, this technology is not suitable for automotive applications due to the engine transient conditions and the hazard related to the presence of an ammonia tank on-board.

The SCR process can be applied to lean-burn engines exhaust treatment by replacing ammonia as reducing agent of NO_x with unburned HCs present in the engine exhaust. However, the strong competition occurring between oxidation of HCs by O_2 or by NO_x must be taken into account. The following scheme shows the main reactions involved in the NO_x-SCR process at the automotive exhaust:

$$3NO + CH_2 \Rightarrow \tfrac{3}{2}N_2 + CO_2 + H_2O \quad (1)$$

$$CH_2 + \tfrac{3}{2}O_2 \Rightarrow CO_2 + H_2O \quad (2)$$

$$2CO + O_2 \Rightarrow 2CO_2 \quad (3)$$

$$CH_2 + O_2 \Rightarrow CO + H_2O \quad (4)$$

$$2NO + O_2 \Leftrightarrow 2NO_2 \quad (5)$$

$$6NO + CH_2 \Rightarrow 3N_2O + CO_2 + H_2O \quad (6)$$

Reaction (1), referred to a generic HC, is the desired one, mainly competing with the HC oxidation (2). Moreover, reaction (6) leading to N_2O formation can further on limit the efficiency of NO_x reduction to N_2, CO oxidation (3) is favoured in excess of oxygen, while HC partial oxidation to CO (4) is often detected at low catalyst activity conditions. Reaction (5) takes into account the role that NO_2 seems to play in the overall reaction mechanism, as discussed in the following. All reactions shown in the above scheme are thermodynamically favoured in the temperature range usually occurring in engine exhaust gas, except reaction (5), which is reversible in the same temperature range.

While for gasoline engines the amount of HCs present in the exhaust gas is sufficient to achieve the complete stoichiometric reduction of NO_x (passive de-NO_x catalysts), for diesel engines an additional amount of reductant (typically about 2–3% of additional fuel) should be fed upstream of the catalyst (active de-NO_x catalysts).

The main properties required for a lean-burn de-NO_x catalyst in order to work as a TWC converter are the following:

- high activity of NO_x, HC and CO simultaneous conversion.
- high reduction selectivity to N_2.
- high durability in the severe engine exhaust conditions.

Moreover, these properties have to be exhibited in a wide range of temperatures and space velocities (SVs) imposed by the engine operating conditions.

In the last years many catalysts have been proposed, especially precious metal based systems and zeolitic materials modified with different transition metals [1–4]. In particular, CuZSM5 is very active and selective [1,3–6], but the deactivation suffered by this catalyst strongly limits the commercial application [1,5–9]. Both reaction and deactivation mechanisms are discussed in the literature [6,10–13], however they have not been completely enlightened. A FeZSM5 catalyst has been recently claimed to be more durable than CuZSM5 in wet feed, but the results should be verified in real conditions [14]. Noble metal systems exhibit better catalytic durability at the engine exhaust, but the high undesired selectivity to N_2O reduces the efficiency of NO_x removal [15–17]. Furthermore, metal oxides have been taken in consideration for their potential thermal stability and large composition variability [18].

In this paper, potentialities and limitations of de-NO_x catalysts prepared by us are analysed with reference to the three requirements indicated above. In particular, catalytic performances of Pt-based systems and Cu-modified zeolites at lean-burn engine exhaust have been investigated. For all systems the effect of metal loading and support characteristics on activity and selectivity is evaluated as a function of temperature, SV and time on stream.

2. Experimental

Platinum based catalysts were prepared (i) by dry impregnation of γ-Al_2O_3 with a platinum chloride solution and (ii) by ion exchange of HZSM5 with $Pt(NH_3)_4Cl_2$ solution. Several ZSM5 based catalysts with different copper contents were prepared by the ion-exchange method described in detail elsewhere [19].

De-NO_x catalytic performances were evaluated at the exhaust of a lean-burn SI engine (1350 cm^3 displacement, air/fuel mass ratio A/F=18, 2000 rpm, 17 kW). A fixed bed reactor, loaded with powder catalysts (200–400 μ), was fed with a fraction of the exhaust gas flow rate. Temperature programmed tests (from room temperature to 550°C) and isothermal durability tests (at 400°C) were performed.

The exhaust gas average composition for the catalytic test was the following: O_2=4%, CO_2=11%, H_2O=12%, HC (as propane)=410 ppm, NO_x=1220 ppm, CO=1310 ppm, N_2=balance. The experiments were effected at SV ranging from 30 000 to 600 000 h^{-1}. NO_x, N_2O, HC, CO and O_2 concentrations were measured by on-line analysers. An on-line gas-chromatograph equipped with an FID detector was adapted to analyse the concentration of specific HCs. Further experimental details are described in [19].

3. Performance of a commercial TWC in lean-burn conditions

Before evaluating activity and selectivity of the prepared catalysts the behaviour of a commercial Pt–Rh TWC, that allows to simultaneously remove NO_x, HC and CO at stoichiometric air/fuel ratio, was determined in lean-burn conditions.

Fig. 1a shows that in the lean mixtures range (air index>1) HC and CO oxidation is favoured, while NO_x conversion suddenly drops from 99 to 0% already at air index of 1.02. However, further on increasing the air/fuel ratio a substantial NO_x conversion is observed (15% at 300°C and air index=1.23, i.e. at O_2=4%). For higher oxygen concentration the reduction activity of the catalyst again goes to zero. The observed NO_x conversion, even if low, shows an unexpected behaviour of the TWC in lean conditions, but the results of Fig. 1b, obtained at air index=1.23, clearly show what is the main limit of these materials.

In fact only a small fraction of converted NO_x is reduced to N_2 (about 5%), because the remaining part (10%) is transformed into N_2O. Therefore, the performance of the commercial converter, already unsatisfactory in terms of NO_x conversion in lean conditions, becomes scarcely significant if also the selectivity to N_2 is considered.

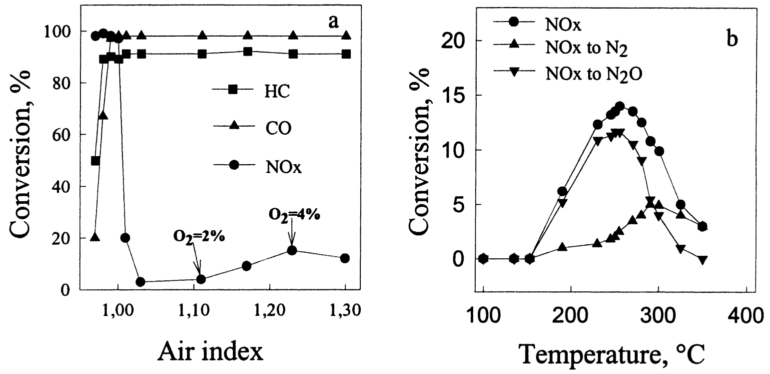

Fig. 1. Performance of a commercial "three-way" converter at the exhaust of a lean-burn engine. (a) Conversion of NO_x, HC and CO versus air index (air/fuel ratio in the test/stoichiometric ratio). T=270–300°C. (b) NO_x overall conversion and NO_x conversion to N_2 and N_2O at air index=1.23. For (a) and (b) SV=30 000 h^{-1}.

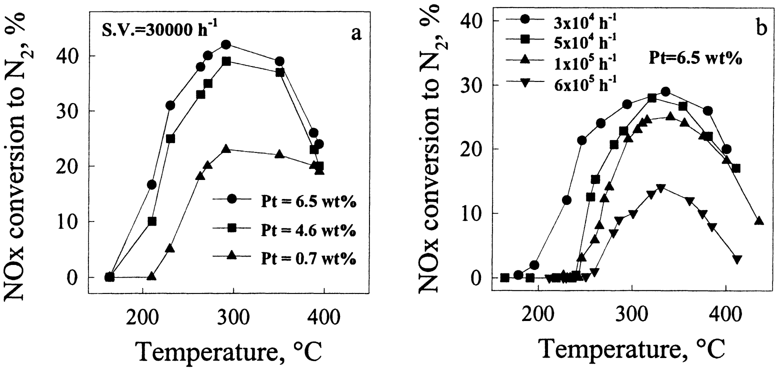

Fig. 2. Effect of platinum loading (a) and SV (b) on initial conversion to N_2 versus reaction temperature for Pt–γ-Al_2O_3 catalysts. Exhaust composition reported under Section 2.

4. Reduction activity and selectivity of Pt–γ-Al_2O_3 catalysts at engine exhaust

The main results obtained with Pt–γ-Al_2O_3 catalysts are reported in Figs. 2 and 3. The effect of metal loading and SV on NO_x reduction to N_2 is shown in Fig. 2a and b, respectively. A maximum NO_x conversion was observed at 300°C with all samples, while at higher temperatures the HCs tended to be oxidised almost exclusively by oxygen.

The conversion to N_2 increased with the metal content up to 6.5 wt.% Pt, reaching 42% at 300°C and SV=30 000 h^{-1} on the fresh sample. At 400°C the catalytic activity decreased with time on stream, reaching a constant activity level after about 10 h. The effect of SV on the performance after 10 h of 6.5 wt.% Pt catalyst is presented in Fig. 2b versus reaction temperature. The maximum conversion to N_2 remained practically unchanged up to 100 000 h^{-1}, while a significant decrease of conversion was observed only at 600 000 h^{-1} (Fig. 2b). It should be noted that these values of SV, calculated for powder catalyst in fixed bed, are comparable to those occurring for automotive catalytic converters.

The effect of metal loading and SV on selectivity of Pt–γ-Al_2O_3 catalysts to N_2O is shown in Fig. 3. The selectivity of the sample containing 0.7 wt.% of Pt was 28% at 200°C and 30 000 h^{-1}, but rapidly decreased

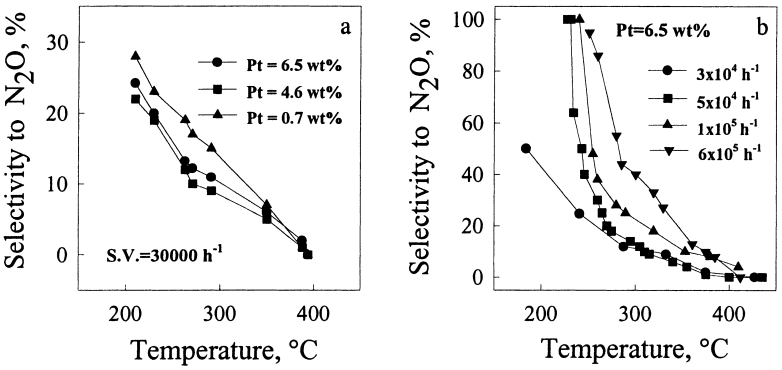

Fig. 3. Effect of metal loading (a) and SV (b) on selectivity to N_2O versus reaction temperature for Pt–γ-Al_2O_3 catalysts. Selectivity to N_2O=2 (N_2O formed/NO_x reacted). Exhaust composition reported under Section 2.

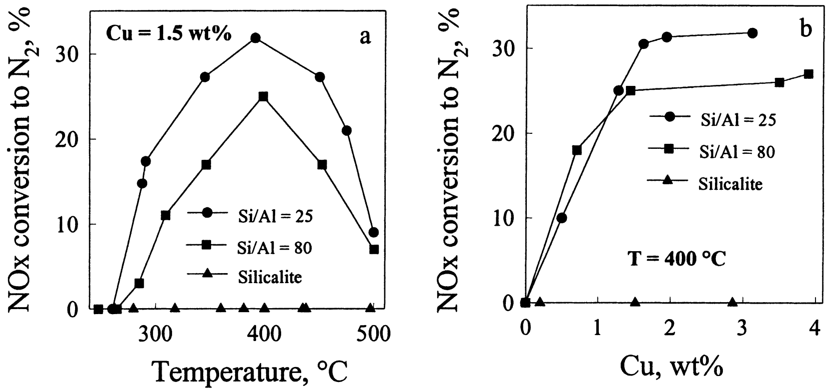

Fig. 4. Effect of Al and Cu contents of CuZSM5 catalysts on NO_x conversion at SV=30 000 h^{-1}. Exhaust composition reported under Section 2.

raising the temperature up to 400°C. Moreover, the N_2O formation was strongly dependent on platinum content (Fig. 3a).

As shown in Fig. 3b, the undesired selectivity to N_2O increased with the SV, and reached almost 100% under 300°C.

A more complex formulation of noble metal systems (Pt–Rh–Ir) has been claimed to improve catalyst selectivity to N_2 [20]. Moreover, a remarkable effect of sodium promoter on activity and selectivity of Pt–γ-Al_2O_3 in NO/propene reaction has been evidenced [21].

5. Reduction activity and selectivity of CuZSM5 catalysts at engine exhaust

In Fig. 4 the results of programmed temperature tests effected on ZSM5 based catalysts for different aluminium and copper contents are reported. On Cu-silicalite (Cu=1.5 wt.%), which has the same crystalline framework of ZSM5 but does not contain aluminium, NO_x conversion was zero at all temperatures (Fig. 4a).

NO_x conversion profiles obtained with CuZSM5 (Cu=1.5 wt.%) having two different Si/Al ratios showed a maximum value at about 400°C (33% conversion for Si/Al=25 in Fig. 4a). The effect of copper content on the maximum NO_x conversion at 400°C is shown in Fig. 4b. It is worth noting that copper percentage higher than 1.6 for Si/Al=25 and 0.65 for Si/Al=80 corresponds to over-exchanged samples (apparent ion-exchange percentage higher than 100%) [22]. The maximum NO_x conversion (33%) was reached with CuZSM5(25) at about 100% of ion exchange, and remained unchanged up to 166% of exchange level. No N_2O was detected on all Cu loaded samples. The absence of activity of Cu-silicalite toward NO_x reduction seems to be associated to the absence of framework aluminium.

6. Durability test of the catalysts at engine exhaust

The results of isothermal durability tests, carried out at the engine exhaust at 400°C and SV=30 000 h^{-1}, are presented in Fig. 5 in terms of NO_x conversion

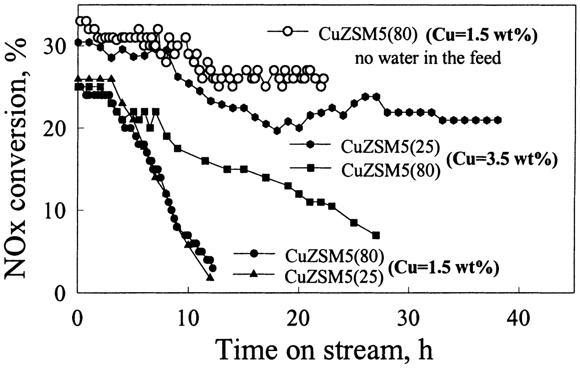

Fig. 5. Durability tests at 400°C and SV of 30 000 h^{-1} on CuZSM5 catalysts. Exhaust composition reported under Section 2.

versus time on stream. Increasing copper loading of CuZSM5 resulted in improved durability performance at both Si/Al=80 and 25. In particular, while the initial activity was totally depressed in about 12 h on CuZSM5(80) with Cu 1.5%, the deactivation rate of the sample containing Cu 3.5% was much lower. A similar trend was exhibited by CuZSM5(25). From Fig. 5, a beneficial effect of aluminium content on catalyst durability was also recognised. In fact, the ZSM5(25) sample loaded with Cu 3.5% (corresponding to 166% of theoretical ion exchange) resulted to be the most stable between those tested. The major role of water present in the exhaust in the deactivation process is demonstrated by the results obtained with the sample CuZSM5(80) at Cu 1.5% after separation of water from the exhaust gas before feeding the reactor (Fig. 5). In this case the activity remained stable at about 27% after 10 h.

Catalyst characterisation by XRD, DRS, XPS, performed in order to detect eventual modifications occurred during the test [22], indicated a correlation between the segregation of small clusters of CuO inside the zeolite channels and the activity loss, suggesting that deactivation is mainly due to sintering of copper, initially well dispersed in the fresh catalyst. This hypothesis is supported by DRS spectra shown in Fig. 6, which refer to the most stable CuZSM5 sample (Si/Al=25, Cu=3.5 wt.%). The fresh catalyst (curve b) showed the characteristic absorption (650–1000 nm) due to d–d transitions expected for Cu^{2+} in octahedral environment of O-containing ligands [23]. After durability test of 40 h at 400°C, this sample retained about 60% of initial activity (Fig. 5), and its spectrum presented a strong absorption edge between 450 and 650 nm, attributed to segregation of CuO particles (curve c). As XRD spectra did not show any signal from bulk CuO, the particles evidenced by DRS should not be larger than 30–40 Å. This absorption became very intense at larger time on stream (60 h, curve d), when a further activity decrease was observed. XPS analysis confirmed the formation of such small particles [24].

Durability tests were also performed with Pt–γ-Al_2O_3 catalysts at 400°C at the engine exhaust. After few hours of operation, during which a 25% decrease of the initial activity was observed, the NO_x conversion remained unchanged. A different result was obtained with a PtZSM5 sample, for which NO_x conversion underwent a progressive decrease with time on stream.

The behaviour of the two catalysts is compared in Fig. 7, where the NO_x conversion, determined at 300°C during a durability isotherm test at 400°C and 30 000 h^{-1} with engine exhaust gas is reported versus time on stream. The result indicates that, at least for platinum catalysts, γ-Al_2O_3 stabilises the active phase more effectively than the zeolitic support.

In lean-burn conditions oxidation of HC and CO is expected to be favoured by the larger oxygen concentration at the exhaust with respect to stoichiometric conditions. This was confirmed for all catalysts tested. In particular, CO resulted to be more reactive than HC, being totally converted before the occurrence of NO_x reduction. Concerning HC conversion,

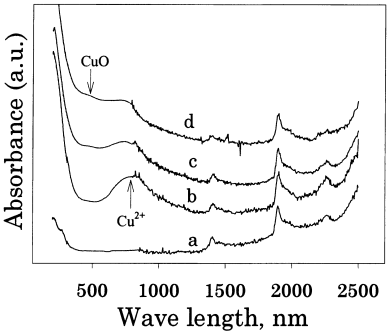

Fig. 6. DRS spectra for CuZSM5 catalyst at Si/Al=25 and 3.5 wt.% of Cu; (a) HZSM5 starting zeolite; (b) fresh CuZSM5 catalyst; (c) CuZSM5 after durability test of 40 h at 400°C; (d) CuZSM5 after durability test of 60 h at 400°C.

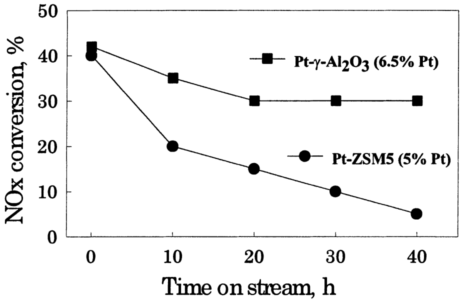

Fig. 7. Maximum NO_x conversion evaluated at 300°C versus time on stream of the durability test at 400°C and 30 000 h^{-1}. Exhaust composition reported under Section 2.

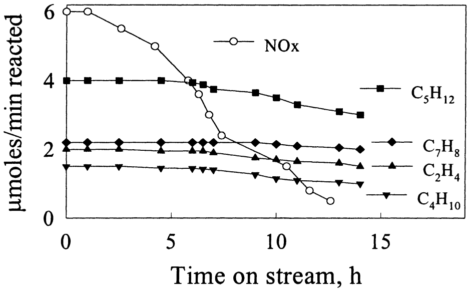

Fig. 8. Reaction rate of NO_x and selective HCs versus time on stream on CuZSM5 (Si/Al=80, Cu=1.5 wt.%). T=400°C, SV=30 000 h^{-1}. Exhaust composition reported under Section 2.

the on-line gas-chromatographic analysis allowed to determine a scale of reactivity of the different HCs present in the engine exhaust gas. The HCs not completely converted at the initial temperature of NO_x reduction were assumed as selective reductants for NO_x [22].

In Fig. 8 the reaction rate of NO_x is reported versus time on stream together with the reaction rate of some selective HCs present in significant concentration in the exhaust (ethylene, C_4–C_5 alkanes, toluene). It can be observed that the strong reduction of NO_x reaction rate is not coupled to an equivalent decrease for HCs rate, as they are easily oxidised by oxygen also when the catalyst is deactivated with respect to NO_x reduction. Therefore, any significant activity loss for CO and HC conversion was not observed with all Pt and Cu catalysts.

7. Catalytic activity of NO to NO_2

As remarked under reaction (5) in Section 1, i.e. the oxidation of NO to NO_2 is supposed to play a significant role in the overall mechanism of NO reduction to N_2 by HCs [12,22,25–27]. In particular, experiments performed by us with synthetic NO/O_2 mixtures, at the same concentrations as in the engine exhaust, have shown that all catalysts examined above exhibit a strong parallelism between activity of NO_x reduction and NO to NO_2 oxidation. Therefore, NO_2 could be the real oxidative agent for the HCs, in competition with oxygen. The correlation between NO_x conversion in SCR de-NO_x test and NO conversion to NO_2 is shown in Fig. 9.

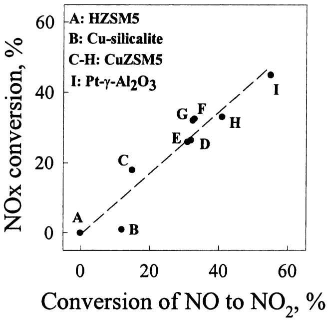

Fig. 9. Maximum NO_x conversion obtained in real conditions versus maximum NO conversion to NO_2 obtained at the same temperature with synthetic mixtures (NO=1200 ppm, O_2=4%, N_2=balance) for Cu and Pt catalytic systems at 30 000 h^{-1}.

8. Conclusions

The results presented in this paper show potentialities and limitations of different catalytic systems in the control of emissions at the exhaust of lean-burn engines. In particular, the following indications can be drawn:

- Pt based catalysts are capable of reducing NO_x in lean conditions at low temperatures, show good durability if supported on γ-Al_2O_3, but N_2O formation has to be minimised.
- High NO_x reduction and 100% N_2 selectivity are shown by CuZSM5 catalysts also in real conditions, but durability problems have to be solved.
- The optimum Al content, and the effect of other cations into ZSM5, should be deeply investigated in order to enhance the durability of zeolitic catalysts.

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