



SELECTIVE CATALYTIC REDUCTION OF NO BY C₃H₆ OVER A COMMERCIAL AUTOMOTIVE IRIIDIUM BASED CATALYST

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ABSTRACT

Ir/TiO₂ coated on cordierite monolith was investigated in the selective catalytic reduction (SCR) of NO with propene using a broad temperature range and simulated diesel exhaust gas conditions under the standard mixture (1000 vpm NO, 2000 vpm C₃H₆, 500 vpm CO, 10 vol.% O₂). The physicochemical characterization of the commercial catalyst showed that the BET surface area of the fresh and aged samples are very low (~ 5m²/g). XRD patterns revealed the presence of rutile TiO₂ and Ir metallic phases. Irreversible H₂ adsorption performed on the fresh and used catalysts indicated a very low accessibility of H₂ to metallic surface. The catalyst exhibited a significant DeNO_x performance (>80% reduction of NO into N₂ with a selectivity approaching 90% at the end of heating-up cycle (620°C)). During the cooling-down step, the NO reduction into N₂ activity was further weakly decreased (20% loss in DeNO_x activity). The commercial automotive catalyst was not stable after hydrothermal treatment (10% H₂O/N₂, 720°C). The NO-N₂ and the NO-NO₂ conversions start at a temperature close to that at which the oxidation of CO and C₃H₆ by oxygen has been already complete. N₂ forms under conditions where reductants are fully converted to CO₂.

INTRODUCTION

There have been numerous reports concerning lean NO_x selective catalytic reduction (SCR) technology categorized by reducing agent such as urea (or ammonia) [1–3], hydrocarbons(HC) [4], oxygenated hydrocarbons (OHCs) [5, 6], and hydrogen [7]. These reports show highly practical potential of lean NO_x SCR technology for application to the exhaust line of real diesel engine vehicle fleet with more than 50% NO_x conversion at relatively low temperatures similar to diesel exhaust temperatures under lean conditions. Selective catalytic reduction (SCR) of NO_x by hydrocarbons is an attractive means of limiting the NO_x emissions of diesel and lean-burn gasoline engines. Noble metal-based catalysts are effective for this reaction and can tolerate water and sulphur but their DeNO_x activity is significant within a narrow range of temperatures. Platinum was demonstrated to exhibit the highest activity of the metal based catalysts series but its operating temperature range would be 200–350°C and it suffers the production of large amounts of nitrous oxide in addition of nitrogen. Iridium-loaded solids have been proposed as active and durable catalysts [8–10].

The SCR of NO by propene over Ir/Al₂O₃ under lean-burn conditions has been previously studied in our laboratory [11, 12]. The dispersion of supported Ir catalysts was found to be an important factor influencing the activity in propene-SCR of NO. A dispersion in the 0.08–0.15 range was found to be required to obtain the best activity in NO reduction into N₂. Such a dispersion could be achieved after heating cycles in the reaction mixture up to 620°C. Highly dispersed Ir particles obtained after preparation of the fresh catalysts were found to sinter under reaction conditions, regardless of whether the catalyst was oxidised in O₂ or in situ reduced in H₂ [11] before reaction. Furthermore, it has been shown that, besides the size of Ir particles, the composition of the reaction mixture is another important factor influencing the activation of the Ir catalyst toward reduction of NO to N₂. The presence of both CO and O₂ was found to be necessary for activating Ir/Al₂O₃ while NO would not be [12]. In situ FTIR results revealed that initially fully oxidized Ir particles partially reduced in the reaction feed to form reduced Ir⁰ surface sites adsorbing CO at temperatures as high as 350–400°C [12].

In a direct connection with our previous reported studies [11, 12], the present work has been undertaken to investigate the catalytic behaviour of a coated monolith Ir supported catalysts for NO_x reduction by propene (C₃H₆) under simulated conditions of automotive engine operating taking into account the flexibility towards temperature variation, presence or absence of O₂ and the feed gas composition. The SCR runs have been conducted under the various treatments to examine their effects on the total conversion of NO and the product selectivity using catalysts



in the fresh and wet aged states. The ultimate objective is to better understand the operating mode of such catalysts in a practical DeNO_x activity operation for an improved converter design.

MATERIALS AND METHODS

Catalyst preparation

A commercial available Ir/TiO₂ powder was used as a model substance. The catalytic material was coated on a cordierite honeycomb. For the catalytic investigation, the cordierite monolith was cut into pieces of the size 3.8 cm x 1.7 cm x 1.2 cm fitting to the sample holder of the tube reactor.

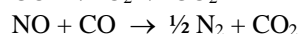
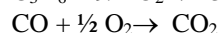
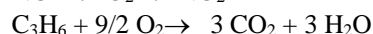
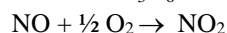
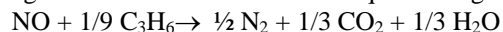
Catalyst characterization

The elemental composition was determined by inductively coupled plasma (ICP) method ($\lambda = 212.861$ nm). In order to avoid the possible loss of iridium under reaction conditions [13–15], special care was devoted to the chemical attack of the samples followed by subsequent reduction in H₂ at 400°C prior to elemental analysis, as described in a previous work [11]. The catalysts were characterized also using X-ray diffraction (XRD, Model: INEL 120) using Cu K α_1 radiation in the 2θ range of 20 – 110°. Specific surface area was determined by BET nitrogen adsorption using a Micromeritics ASAP2000. Adsorption measurements were conducted in a conventional volumetric apparatus. The catalysts were reduced overnight in situ at 400°C under flowing H₂, and then evacuated at the same temperature for 2 h. The irreversible chemisorption uptake of H₂ was measured at 25°C. The dispersion (ratio of the number of superficial Ir atoms to the total number of Ir atoms) was thus deduced from this uptake assuming a H/Ir_s = 1 stoichiometry [16, 17]. For TEM and EDX analysis, samples of reduced catalysts were exposed to air and suspended in ethanol, a drop of this suspension was deposited on a carbon-coated grid, and the specimens were examined with a high resolution Jeol 2010 electron microscope.

An ageing procedure (denoted as "wet aged") was applied to the commercial automotive Ir-based catalyst coated on cordierite using a hydrothermal treatment at 720°C in the presence of 10% water in nitrogen for 20 h.

Catalyst tests

The selective catalytic reduction activity measurements were carried out in a down flow fixed-bed quartz reactor at atmospheric pressure, as already described [18, 19]. The sample mass was introduced into the reactor under helium flowing and the catalyst was exposed to the reactant gas mixture containing 1000 vpm NO, 2000 vpm C₃H₆, 500 vpm CO, 10 vol.% O₂ and He as a carrier gas (total flow rate 10 L.h⁻¹). The activity was measured as a function of temperature at increasing and decreasing temperatures following a heating cycle under the reaction mixture. Each experiment was conducted as follows: introduction of the mixture at 25°C, heating from 25 to 620°C at a rate of 2°C.min⁻¹, plateau at 620°C for 20 min, cooling from 620 to 25°C (2°C min⁻¹). Several successive temperature cycles could also be performed. The gas hourly space velocity (GHSV = volumetric gas flow/coated monolith volume) was constantly kept at 100000 h⁻¹, which represents the flow conditions in SCR converters on board of diesel vehicles. Reactants and products (CO₂, N₂O, O₂, N₂, CO) were analysed by gas chromatography, with He as carrier gas, using a dual CTR1 column from Alltech (Porapak and molecular sieve) and a TCD detector. A Porapak column and a flame ionization detector were employed for hydrocarbons. In addition, the concentrations of NO, NO₂, N₂O and CO₂ were continuously measured on-line by means of Rosemount IR and UV analyzers. The conversions of NO into N₂, N₂O and NO₂ (in %) were $100 \times 2[\text{N}_2]/[\text{NO}_x]_i$, $100 \times 2[\text{N}_2\text{O}]/[\text{NO}_x]_i$ and $100 \times [\text{NO}_2]/[\text{NO}_x]_i$, respectively ($[\text{NO}_x]_i$ is the inlet NO_x concentration). CO was never detected. The nitrogen and carbon balances were equal to or greater than 95 %. Several reactions are considered:



Very low amounts of N₂O are formed on Ir-based catalysts and the corresponding reactions are not taken into account.

RESULTS AND DISCUSSION

Physicochemical characterization

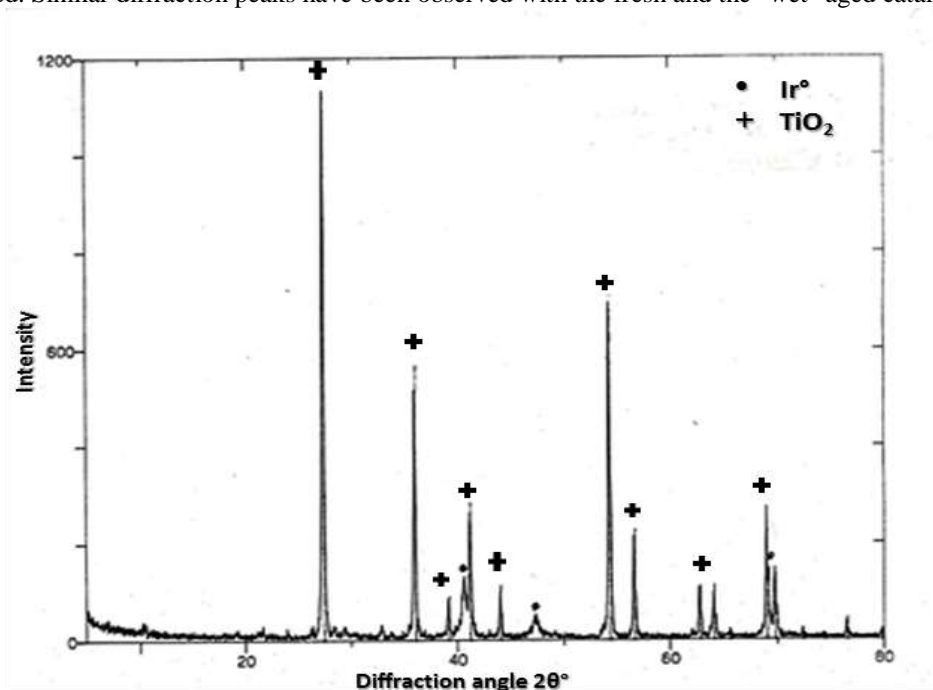
Irrespective of the treatments described above, all our samples contained 0.47–0.48 wt.% Ir. The chlorine content is less than 300 ppm. Remaining elemental analysis data can be found in Table 1.

Table 1: Chemical analysis of the commercial automotive catalyst.

Preciousmetal	Additives
0.47–0.48 % of Ir	Fe : 0.579%
	K : 0.152%
	Ti : 4.99%
	Zr : 0.04%

The BET surface area of the fresh and "wet aged" samples, measured after desorption under vacuum at 400°C for 2 hours, are respectively of 4.5 and 3.9 m²/g. These values are low, which indicate a low level of wash coat or the presence of phases of low BET surface area.

Figure 1 shows the XRD patterns of the industrial sample. The experiments were performed on the wash coat from the fresh sample, peeled off by the N₂ liquid method. The main diffraction peaks can be directly indexed to the rutile TiO₂ and Ir metallic phases. No crystal phase of components of Ir, Fe, Zr, K emerged which indicated that all the active components were highly dispersed on the catalyst surface. Also, the cordierite phase has not been detected. Similar diffraction peaks have been observed with the fresh and the "wet" aged catalysts.

**Figure 1. XRD patterns of the commercial automotive catalyst.**

For EDX analysis, the results are similar on the two fresh and wet aged samples. In general, there is enough homogeneous coherence between the channels of the monolith and the holes corresponding typically to the cordierite containing iron. We have noted an excess of Al and Si compared to the cordierite with the presence of K and Na. There is no preferential localization for Ir and chlorine has not been detected.

Hydrogen chemisorption measurements were carried out on the two samples. For this purpose, they were reduced in hydrogen before measuring hydrogen uptakes. We assumed that the reduction at 400°C does not drastically modify the size of iridium oxide agglomerates. It is well known that these agglomerates are very difficult to redisperse and that iridium sintering can proceed under oxidising atmosphere but not in reducing media [20]. The amounts of irreversibly adsorbed H₂ on the initial reduced state of the fresh and wet aged catalysts are in the limit of detection of the device and consequently, the metal surfaces accessible to H₂ are very low.

Catalytic activity

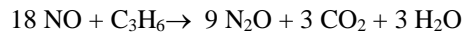
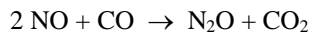
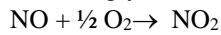
Catalytic activity under the standard (NO-C₃H₆-CO-O₂) reaction mixture

Figure 2 shows the DeNO_x performance of the catalyst during a temperature cycle (heating from 25 to 620°C and cooling from 620 to 25°C with a plateau at 620°C for 20 min) under the standard (1000 vpm NO, 2000 vpm C₃H₆,



500 ppm CO, 10% O₂ and He balance) mixture. The NO conversion of 90 % was obtained during the heating-up temperature step. The maximum NO-N₂ conversion reached 80 % at 450°C with N₂ selectivity of ~ 90 %. During the cooling-down temperature step, the NO reduction into N₂ activity was further weakly decreased. Then, the maximum NO reduction into N₂ reached 62% at 498°C with N₂ selectivity and the activity-temperature window was wide (250-600°C).

Figure 2 clearly shows that only negligible amounts of NO₂ and N₂O were formed during SCR of NO by C₃H₆ between 250 and 600°C and that no NO₂ and N₂O are formed beyond 600°C (The NO-NO₂ and NO-N₂O conversions are less than 10 %). This makes the following reactions very unlikely, which are expected to produce increasingly amounts of NO₂ and N₂O formation at higher temperatures.



Let us point out some specific features of the catalytic behaviour in the presence of selective catalytic reduction of NO_x. The NO-N₂ and the NO-NO₂ conversions start at a temperature close to that at which the oxidation of CO and C₃H₆ by oxygen has been already complete (figures 2 and 3). It is noteworthy that N₂ forms under conditions where reductants are fully converted.

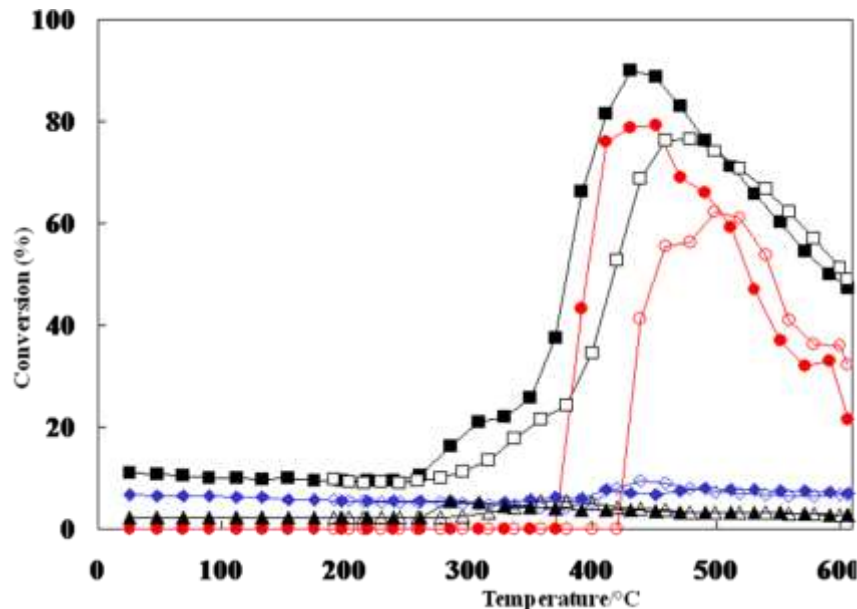


Figure 2. Fresh catalyst. Conversion of NO consumption and that of NO into NO₂, N₂ and N₂O (%) vs temperature (°C) under NO-CO-C₃H₆-O₂ mixture during a first temperature cycle with plateau at 620°C for 20 min. (■, □) Conversion of NO, (♦, ◇) NO-NO₂, (●, ○) NO-N₂ and (▲, Δ) NO-N₂O. The full symbols indicate the heating-up steps and the empty symbols the cooling-down steps.

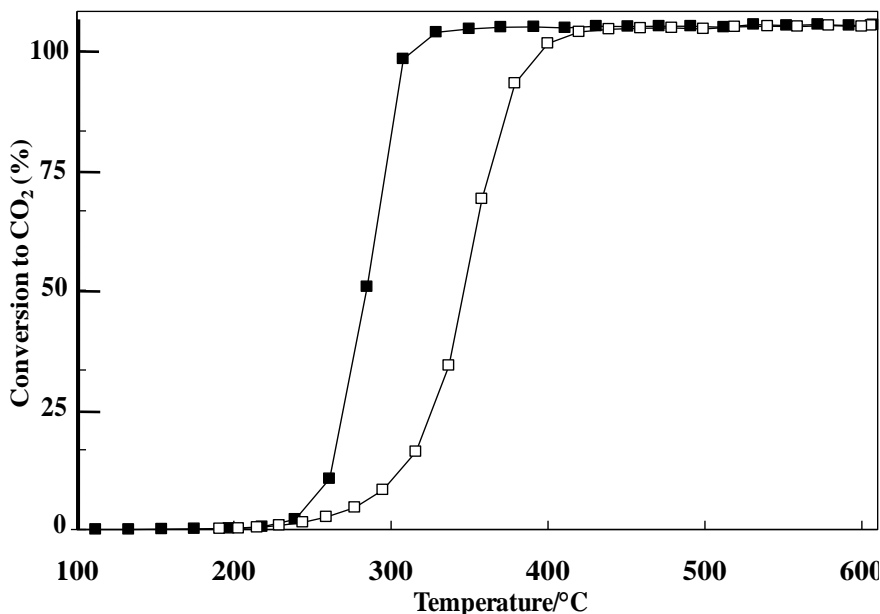


Figure 3. Fresh catalyst. Conversions of CO and C₃H₆ into CO₂ vs temperature (°C) in (NO-CO-C₃H₆-O₂) reaction mixture during a first temperature cycle with plateau at 620°C for 20 min. (■: the heating-up steps and □: the cooling-down steps).

Table 2 summaries the main catalytic activity results for various samples, pre-treated under different atmospheres and obtained upon reaction temperature cycling under the standard (NO-CO-C₃H₆-O₂) mixture.

Table 2. Catalytic activities on the commercially Ir-based catalyst pre-treated in different atmospheres with the standard (NO-CO-C₃H₆-O₂) mixture

Sample		Max conversion NO consumption (mol)	Max conversion (%) of NO to N ₂ (mol)	Max conversion of NO to NO ₂ (% mol)	Temp. of full conversion of CO and C ₃ H ₆ to CO ₂ ; T ₁₀₀ ^a (°C)
Fresh					
First cycle	Heating	90 (430°C)	80 (450°C)	~ 9 (413°C)	330
	Cooling	77 (470°C)	62 (498°C)	~ 10 (440°C)	402
"Wet" aged					
First cycle	Heating	89 (380°C)	~60 (380°C)	20 (364°C)	325
	Cooling	44 (482°C)	0	23 (471°C)	425
"Wet" aged					
Second cycle	Heating	40 (470°C)	0	26 (470°C)	413
	Cooling	33 (525°C)	0	18 (510°C)	475
^b "Wet" aged					
First cycle	Heating	60 (400°C)	0	34 (420°C)	296
	Cooling	44 (463°C)	0	27 (463°C)	403

^a Temperature (°C) at which CO and C₃H₆ conversions into CO₂ reached 100 %.

^b"Wet" aged catalyst tested under a first temperature cycle and then reduced in H₂ at 300°C.

Figure 4 shows the catalytic activities for NO reduction and CO and C₃H₆ oxidations over the "wet" aged catalyst during a first temperature cycle (heating from 25 to 620°C and cooling from 620 to 25°C with a plateau at 620°C for 20 min). The activity concerning the reduction of NO by hydrocarbons is lower in comparison to the fresh catalyst (figure 3). The production of N₂ was exclusively observed and only during the heating-up temperature step. The maximum NO-N₂ conversion reached about 60 % at 380°C with N₂ selectivity of ~ 68 % and the activity-temperature window was wide (320-620°C). However, during the cooling-down temperature step, the catalyst

was totally deactivating (conversion of NO to N₂ equal to zero in the same temperature range (figure 4). It can be noted that the maximum conversion of NO during the cooling-up temperature step obtained with the wet aged sample (44% at 482°C) is lower than that measured on the fresh solid (77% at 470°C). However, the oxidation properties of NO into NO₂ are slightly increased during the heating and the cooling-up temperature step after aging the catalyst at 720°C in the presence of 10% water in nitrogen for 20 h (table 2). The conversions of NO to N₂O are very low in the activity-temperature window (320–620°C) (The maximum of conversion NO-N₂O is not exceeding 5%). As above, the NO-N₂ and the NO-NO₂ conversions start at a temperature close to that at which the oxidation of CO and C₃H₆ by oxygen has been already complete (table 2). It is noteworthy that N₂ forms under conditions where reductants are fully converted.

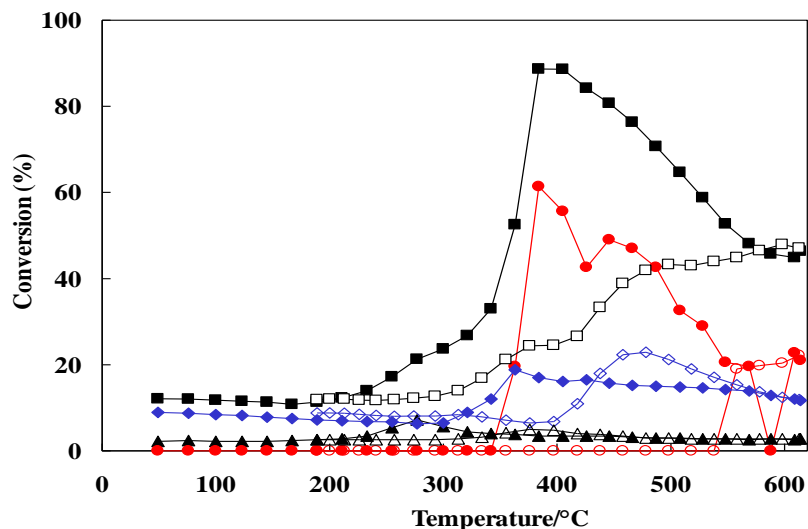


Figure 4. "Wet" aged catalyst. Conversions of NO and of NO into NO₂, N₂ and N₂O (%) vs temperature (°C) with NO-CO-C₃H₆-O₂ during a first temperature cycle with plateau at 620°C for 20 min. (■, □) Conversion of NO, (◆, ◇) NO-NO₂, (●, ○) NO-N₂ and (▲, Δ) NO-N₂O. The full symbols indicate the heating-up steps and the empty symbols the cooling-down steps.

Figure 4 shows that during cooling down-up step, no activity of reduction of NO into N₂ was observed on the aged catalyst. This deactivation process seemed to depend on the time on stream since a second heating-cooling cycle on the wet aged sample did not lead to reduction of NO into N₂ by hydrocarbons in the widening of the temperature range at which the catalyst converted NO into N₂ (figure 5). Simultaneously, the activity for NO oxidation into NO₂ is almost the same on the wet aged catalyst after one or two heating-cooling cycles (Table 2). Whenever the activity for total NO conversion is very decreased after the second cycling of temperature on the sample (89 % at 380°C and 40 % at 470°C during heating-up temperature respectively after 1 and 2 cycling temperature) (Table 2). The activity for N₂O formation remained low, the conversion of NO into N₂O being typically less than 10% compared to the 33–40% total conversion of NO at maximum activity. These results proved unambiguously that the commercial automotive catalyst deactivated completely under standard reaction mixture and did not exhibit any DeNO_x activity between 320 and 620°C without any good selectivity toward nitrogen. It can be noted that the NO-NO₂ maximum conversion was detected at temperatures (see table 2) above T₁₀₀ temperatures at which CO and C₃H₆ conversions into CO₂ reached 100 %.

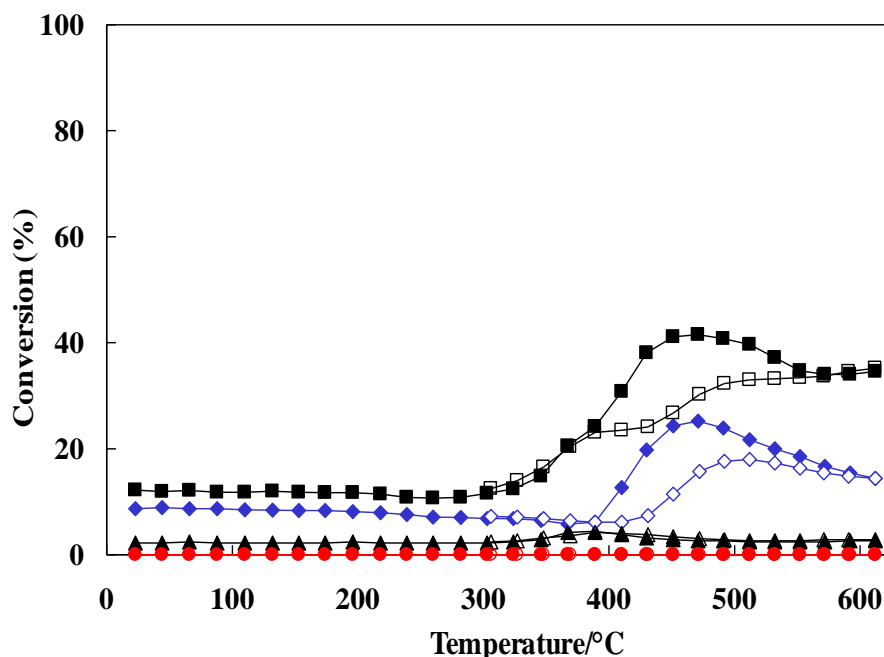


Figure 5. "Wet" aged catalyst. Conversions of NO and of NO into NO_2 , N_2 and N_2O (%) vs temperature ($^{\circ}\text{C}$) with NO-CO- C_3H_6 - O_2 during second temperature cycle with plateau at 620°C for 20 min. (■, □) Conversion of NO, (♦, ◇) NO- NO_2 , (●, ○) NO- N_2 and (▲, △) NO- N_2O . The full symbols indicate the heating-up steps and the empty symbols the cooling-down steps.

In another part, we have performed some experiments on the wet aged catalyst which has worked under a first heating-cooling cycle under the standard mixture (NO- C_3H_6 -CO- O_2) in order to restore the activity for NO reduction into N_2 . The sample was in situ reduced at 300°C for 2 hours under flowing hydrogen, and then the reactor was switched to pure helium ($10 \text{ L}\cdot\text{h}^{-1}$). The solid was cooled in He to room temperature and it was tested in SCR of NO by C_3H_6 in the same conditions as above. Figure 6 shows the De NO_x performance of the aged and reduced catalyst during a temperature cycle under the standard (NO- C_3H_6 -CO- O_2) mixture. The results summarized in table 2 are similar to those required on the catalyst without reduction in H_2 with little differences. After reduction, the maximum total conversion of NO and the maximum conversion of NO to NO_2 are slightly increased during the heating-up temperature. During the cooling-down temperature, the behaviour of the solid was analogue to the aged sample which was not contacted with hydrogen at 300°C . It can be concluded from these results that the regeneration under flowing hydrogen of the catalytic performance of the wet aged solid having worked under a first temperature cycling has no effect on the activity for the reduction of NO into N_2 .

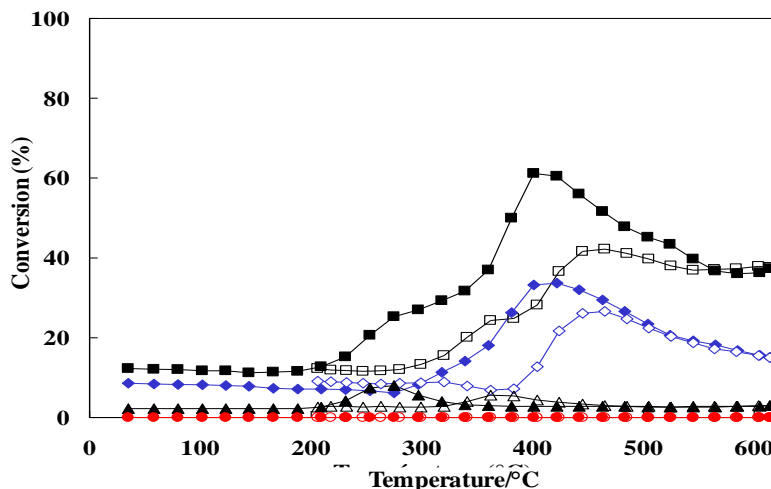


Figure 6. "Wet" aged catalyst tested under a first temperature cycle and reduced in H_2 à $300^\circ C$. Conversions of NO and of NO into NO_2 , N_2 and N_2O (%) vs temperature ($^\circ C$) with $NO-CO-C_3H_6-O_2$ during a first temperature cycle with plateau at $620^\circ C$ for 20 min. (■, □) Conversion of NO, (♦, ◇) $NO-NO_2$, (●, ○) $NO-N_2$ and (▲, Δ) $NO-N_2O$. The full symbols indicate the heating-up steps and the empty symbols the cooling-down steps.

Evolution of the catalytic activity in ($NO-C_3H_6-CO$) reaction mixture

In order to identify which part of the each component C_3H_6 or CO as reductant is implied in the SCR of NO over the commercial automotive catalyst, we have performed some experiments where the activity was measured with ($NO-C_3H_6-CO$) mixture on either the fresh and the wet aged solids for $DeNO_x$ properties with reaction composition: 1000 vpm NO , 2000 vpm C_3H_6 , 500 ppm CO and balance He ; the total flow rate is $10 L.h^{-1}$. Figure 7 showed the conversions of NO into N_2 , NO into N_2O and the conversions of CO and C_3H_6 into CO_2 during heating-cooling up temperature cycling on the catalyst in the fresh state. It can be seen that similar curves of different conversions can be observed on both catalysts (curves for aged catalyst not shown). The key point was that treating the catalysts in the ($NO-C_3H_6-CO$) mixture up to $600^\circ C$ shows that NO was exclusively reduced into N_2 and the formation of N_2 starts at low temperature ($250^\circ C$) in the same time of the oxidation of CO and C_3H_6 into CO_2 and the conversion $NO-N_2O$. However, the NO reduction into N_2 by the reductants of the commercial catalyst was always kept around 80 % over the broadened temperature window ($250 - 620^\circ C$) (figure 7).

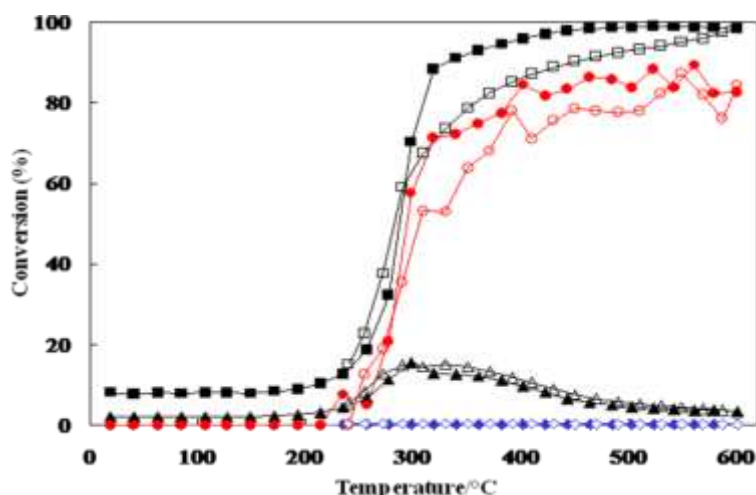
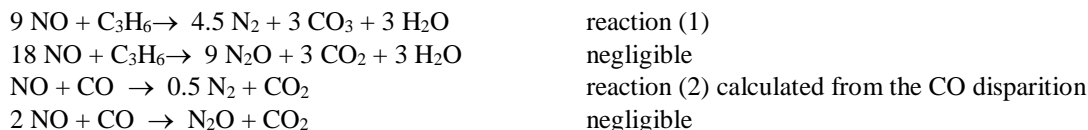


Figure 7. Conversions of C_3H_6 into CO_2 and of NO into N_2 and N_2O vs. temperature under ($NO-C_3H_6-O_2$) over the fresh catalyst. (■, □) Conversion of NO, (♦, ◇) $NO-NO_2$, (●, ○) $NO-N_2$ and (▲, Δ) $NO-N_2O$. The full symbols indicate the heating-up steps and the empty symbols the cooling-down steps.

A small deactivation was observed during the cooling step. The $NO-N_2O$ conversions versus temperature are very low and its maximum (12%) was observed at a temperature close to that at which the conversion of CO and C_3H_6



into CO₂ reached 100%. The oxidation of NO into NO₂ was never observed on the catalysts. This makes the following reactions very likely, which are expected to produce increasingly amounts of N₂ at higher temperatures:



Overall results presented so far concord about high DeNO_x activity of the commercial automotive converter, the catalyst based on Ir/TiO₂ supported on a cordierite monolith and doped with K, Fe and trace amounts of Zr exhibits over 80% reduction of NO into N₂ from 250 to 650°C at very good selectivity during a thermal treatment cycle (heating from 25 to 620°C and cooling from 620 to 25°C with a plateau at 620°C for 20 min. After aging the catalyst in 10% H₂O/N₂ mixture at 720°C for 20 hours, the NO conversion into N₂ are still higher and reached 60% at 380°C with N₂ selectivity of 68 % in the temperature window range 320 – 620°C. However, during the cooling-down step, the solid was totally deactivated (figure 3) as well as after a second temperature cycle on the fresh solid (results not shown). This deactivation process seemed to depend on the time on stream since a second heating-cooling cycle on the catalyst in the fresh and wet aged state did not lead to reduction of NO into N₂ by hydrocarbons in the widening of the temperature range. The commercial automotive catalyst was not stable after hydrothermal ageing at 720°C in the presence of 10% water in nitrogen. The mechanism of catalyst deactivation is typically divided into three classes, namely poisoning, coking and sintering. Other reasons for deactivation include masking and loss of active elements by volatilization, erosion and attrition [21, 22]. In this work, it seems that the surface area do not play a crucial role since the catalyst could perform well despite a poor initial surface area (~ 5 m²/g) indicating that the stability performance may be affected by chemical deactivation of the SCR catalysts rather than a sintering of its active surface particles. It is known that the deactivation of commercial automotive catalysts is due to chemical constraints. The presence of components such as sulfur, phosphorus, zinc, barium, etc, in the fuels and lubricants poison these catalysts according to several mechanisms: (a) competitive adsorption on the active surface sites by Pb and P adatoms [23], (b) reaction with the catalytic converter: in the presence of sulfur [24] and (c) the blockage of the porous structure of catalytic converters including by deposit of compounds based on phosphorus and zinc [25]. It is noteworthy that the catalyst here studied contains several additives among them K (see table 1). It is not yet clarified if the potassium additive would play only the role of a promoting agent for the SCR activity since the decrease of the SCR activity of TiO₂ supported catalysts after doping with potassium has been proposed by several authors [26–29]. Lietti et al. [30] also found that adding amounts higher than 0.5 wt% potassium to the 3.56 wt% V₂O₅/TiO₂ significantly deactivated the catalyst.

Currently, control of catalytic performance of industrial catalysts after deactivation is achieved in tests based on the extent of their catalytic activity. This measurement is carried out on benches engines. But, these measurements are costly and do not provide any information on the exact nature of active centers and their evolution during the operation of the catalytic activities. Therefore, more attention should be paid towards mechanistic investigation of such complex materials taking into account the effect of iridium particle size, role of support, effect of promoters, effect of reducing agent, and sulfur and water tolerance.

Under HC-SCR reaction conditions, iridium is generally present as a mixture of Ir⁰ and IrO₂. The presence of metallic Ir is essential for high DeNO_x activity [30]. The ratio of Ir⁰/IrO₂ depends mainly on the exhaust gas composition and the iridium particle size [30, 31]. This is consistent with our observations on Ir/TiO₂ coated on cordierite monolith showing the NO-N₂ and the NO-NO₂ conversions start-up at a temperature close to that at which the reducing gas (CO and C₃H₆) are fully converted into CO₂; implying a switch in active site(s) distribution on the surface of catalyst. Moreover, our results from surface area and H₂ chemisorption measurements clearly indicate the contribution of metallic Ir with larger crystallite size regardless of pretreatment or gas mixture composition. Large iridium crystallites can only be fully oxidized in air at very high temperatures, whereas small crystallites are easily oxidized and favor NO oxidation to NO₂ as well as oxidation of reducing reactants. This has been consistently observed for unsupported [31] as well as supported iridium catalysts [10, 30].

CONCLUSION

Ir/TiO₂ coated on cordierite monolith investigated in the selective catalytic reduction (SCR) of NO with propene under lean-burn conditions shows high DeNO_x activity (>80% reduction of NO into N₂ with a selectivity approaching 90% at the end of heating-up cycle (600°C)). Low values of BET surface area and Ir dispersion



determined by H₂ chemisorption were found regardless of treatment procedure of the DeNO_x-SCR catalyst. The catalyst exhibits however higher NO reduction by C₃H₆ activity either in the fresh and the wet aged states. This activity seemed to decrease with time on stream. The commercial automotive catalyst was not stable after hydrothermal treatment (10% H₂O/N₂, 720°C). The NO-N₂ and the NO-NO₂ conversions start at a temperature close to that at which the oxidation of CO and C₃H₆ by oxygen has been already complete and N₂ forms under conditions where reductants are fully converted to CO₂ implying a change in active site(s) distribution on the surface of catalyst. More deep analysis of catalyst evolution during SCR of NO_x with reductants of different types will be addressed in future investigations using in-situ operando techniques.

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