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NO_x selective catalytic reduction over supported metallic catalysts

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ABSTRACT

In this work we present the results obtained with 3 catalysts (Pt, Rh and Ag on alumina) tested in ranges of temperatures and gas hourly space velocities typical of diesel engines in real trucks. NO concentration was 500 ppm, C_3H_6 ranged between 500 and 2000 ppm, while oxygen was always 5%. All the catalysts were active and showed high conversions. Both Pt and Rh were active at low temperature (T_{50} = 200–250 °C) but had quite high selectivity towards NO_2. Silver was active at higher temperature, but showed very high selectivity towards N_2. A strong boosting effect on NO conversion was recorded if H_2 was added to the gas mixture.

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1. Introduction

In the last decades, the diesel engine emissions limits are becoming more stringent and soon in the EU the new EURO 6 emission standard will impose much more restrictive limits mainly on particulates and NO_x emissions. While for the particulate control, some technologies are already available, there exist no efficient catalysts for hydrocarbon selective reduction of NO_x (HC-SCR). This process uses a hydrocarbon as a reducing agent and a supported metallic catalyst to remove NO_x from the exhaust gas stream [1,2]. The conventional three-way catalyst (TWC) is very effective for gasoline engines, but diesel engines exhaust gas contains a large excess of oxygen and at these conditions the three-way catalysts are ineffective. A solution is represented by the reduction of NO_x with urea, but some technical issues arise as the need to include a storage tank onboard and the difficult control of the amount of urea added to the exhaust gas, depending on the working conditions of the engine [3]. HC-SCR, instead, exploits the unburned hydrocarbons already contained in the exhaust gas combined with the addition of extra diesel fuel. This would be a more suitable solution for cars and trucks. Recently work and research have been done to equip trucks with an auxiliary power unit (APU) to reduce the fuel consumption during idling periods. These units are based on fuel cells working with H_2 produced on board reforming diesel fuel [4]. With such a technology the boosting effect of H_2 noticed for silver catalysts could be exploited without the need of storing H_2 on the vehicle.

2. Experimental

All the catalyst materials were prepared by the incipient wetness technique and were 2 wt.% Ag/Al_2O_3, 2 wt.% Pt/Al_2O_3 and 2 wt.% Rh/Al_2O_3.

The alumina used was PURALOX NGa-150 supplied by Sasol Germany. Silver nitrate, tetraamineplatinum (II) nitrate solution, and rhodium (III) nitrate solution were all dissolved separately in deionised water to a total volume of 20 cm^3. Each solution was added to 20 g of γ-alumina in two steps with a drying step at 90 °C for 3 h in between. After the final impregnation step the materials were dried at 90 °C overnight. Finally the materials were calcined at 500 °C for 4 h with a temperature ramp of 10 °C/min.

The catalytic materials were coated onto ceramic monoliths made of cordierite supplied from Corning, with a cell density of 400 cpsi and a volume of 4.6 cm^3 (d = 14 mm; h = 30 mm). The support powder impregnated with active phase was added to ethanol, 95.5 vol.% (20 wt.% dry substance). The slurry was then ball-milled for 24 h in order to bring down the particle size and to obtain a homogeneous slurry suitable for dip-coating. Monoliths were immersed into the slurry and the channels of the monolith were filled with it. The residual slurry was removed by compressed air. This resulted in a layer of the solid suspended in the slurry deposited on the wall of the monolith. The monoliths were dried at 90 °C for 30 min and the dipping/drying procedure was repeated until the required catalyst loading (150 g support/catalyst volume [L]) was reached. The washcoating procedure is explained and described in Ref. [5]. The coated monoliths were then dried overnight at 90 °C followed by calcination at 500 °C for 4 h (HR = 5 °C/min). The calcination temperature was chosen after our industrial partner suggested us a temperature range of 300–500 °C for realistic applications. For Pt and Rh the highest temperature reached during the tests was always below 500 °C, while Ag

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Table 1
Surface features of the catalysts.

Catalyst	BET surface area (m^2/g)	Average pore diameter (Å)	Total pore volume (cm^3/g)
Ag/Al_2O_3	152.3	118.8	0.452
Rh/Al_2O_3	154.4	113.2	0.437
Pt/Al_2O_3	149.6	121.4	0.454

required higher temperatures to be fully characterized (up to 600 °C). Repeated tests at the same temperature, gas concentration and GHSV allowed us to verify the reproducibility of the results, meaning that the catalyst was stable also working at temperatures higher than the one chosen for calcination.

Physical characterization of the catalysts has been done with a Micromeritics ASAP 2000 analyzer. Table 1 summarizes the results obtained.

Since the active materials have been deposited on the same alumina support, all the surface features are very similar.

XRD patterns were obtained with a Siemens D5000 diffractometer with a Cu Kα monochromatic radiation and a scanning range 2θ between 10 and 90°.

In all the analyses $(Al_2O_3)_{1.333}$ and also tetragonal Al_2O_3 is detected. Concerning the metals, in all the samples different oxides are detected. The metallic form is also detected for Pt and Rh (See Table 2).

Catalysts were characterized by repeated temperature-programmed reduction (TPR) and oxidation (TPO) in sequence, i.e. a TPR followed by a TPO. The analysis was repeated twice. The reduction was performed with a 5% H_2 flow in argon, while the oxidation was done with a 5% O_2 flow in helium.

In all the analyses the intensity of the TCD signal (that is the H_2 adsorbed during the reduction or the O_2 adsorbed during the oxidation) is very low, indicating the catalysts are rather hard to reduce and oxidize. This should result in a good stability of the catalyst during the tests. For silver a broad peak (between 150 and 350 °C) was detected. It corresponds to the reduction of different Ag oxides, while the reduction of Ag_2O gives a peak at 450 °C [7,8].

Rh TPR gave a peak centered around 100 °C, assigned to the reduction of RhO_x species according to the reaction: $RhO_x + xH_2 \rightarrow Rh + xH_2O$ [9].

Pt TPR gives a peak with maximum at $T = 200$ °C with a shoulder at around 100 °C, that might correspond to the reduction of PtO_2 to metallic Pt [10].

3. Results and discussion

All the samples have been widely tested ranging the experimental conditions between the values typical of a real diesel engine. Tests have been run feeding 500 ppm of NO and a variable concentration of C_3H_6 resulting in a C/N ratio ranging between 3 and 12. A large excess of oxygen (5%) was always fed. The gas hourly space velocity (GHSV) ranged between 10,000 and 40,000 h^{-1}. The temperature ranged between 40 and 600 °C, with a constant heating rate of 10 °C/min. Some tests feeding steam has also been run, setting a steam concentration of 7.4%. Finally, every catalyst was evaluated feeding a mixture of H_2, CO, CO_2 and H_2O simulating the composition of a gas obtained by reforming of diesel fuel. N_2 was used as balance gas in all the tests. The values of temperature, concentration and space velocities have been chosen according to realistic values from heavy duty trucks. The gas analyzer used detects NO and NO_2 and it was assumed that NO was converted to NO_2 (when detected) and to N_2. Some N_2O might have been formed, but since it was not possible to detect it, nothing can be stated about that compound.

Table 2
Metallic phases detected on the catalysts.

Catalyst	Metallic phases detected
01 Ag/Al_2O_3	Ag_2O_2, Ag_3O_4, Ag_3O, AgO, Ag_2O
02 Rh/Al_2O_3	Rh_2O_3, RhO_2, Rh
03 Pt/Al_2O_3	Pt_3O_4, PtO, PtO_2, Pt

3.1. Effect of the C/N ratio

All the catalysts showed a limited dependence on the C/N ratio.

In every condition investigated, propene conversion was always complete with the production of CO_2 as well, this increasing with the hydrocarbon concentration indicating that the compound was combusted during the tests. Fig. 1 shows NO conversion detected feeding 500 ppm of NO, 5% O_2 and a propene concentration ranging between 500 and 1500 ppm. The space velocity (10,000 h^{-1}) was the lowest investigated, that is the longest residence time for the gases. There is rather a big difference between the trends with C/N = 3 and the highest ratios, both for the temperature at which the catalyst starts being active (400 °C vs. 300–350 °C) and for the maximum conversion (80% vs. 100%). The temperature interval within which the catalyst is very active is much wider when the propene concentration is higher than 500 ppm. In the chart the classic volcano shape is easily detectable with the conversion increasing to the maximum value and then decreasing while the temperature still goes up. This is due to the fact that propene starts being combusted at a certain temperature, so it is not available anymore for the reduction reaction in the nominal concentration set. The same trend was detected at the other space velocities tested (20,000 and 40,000 h^{-1}). Pt and Rh, instead, (Fig. 2), gave the same conversion at every C/N investigated, with very small differences between the trends detected. Such behaviour is very desirable, since it means that the catalysts are active in every working regime of the engine (concerning the flow rate of the exhaust gas).

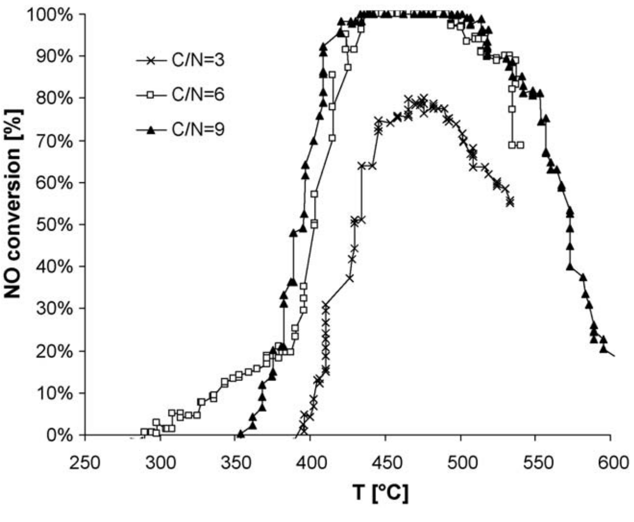

Fig. 1. NO conversion as a function of the catalyst inlet temperature obtained with Ag catalyst feeding different C_3H_6 concentrations. GHSV = 10,000 h^{-1}.

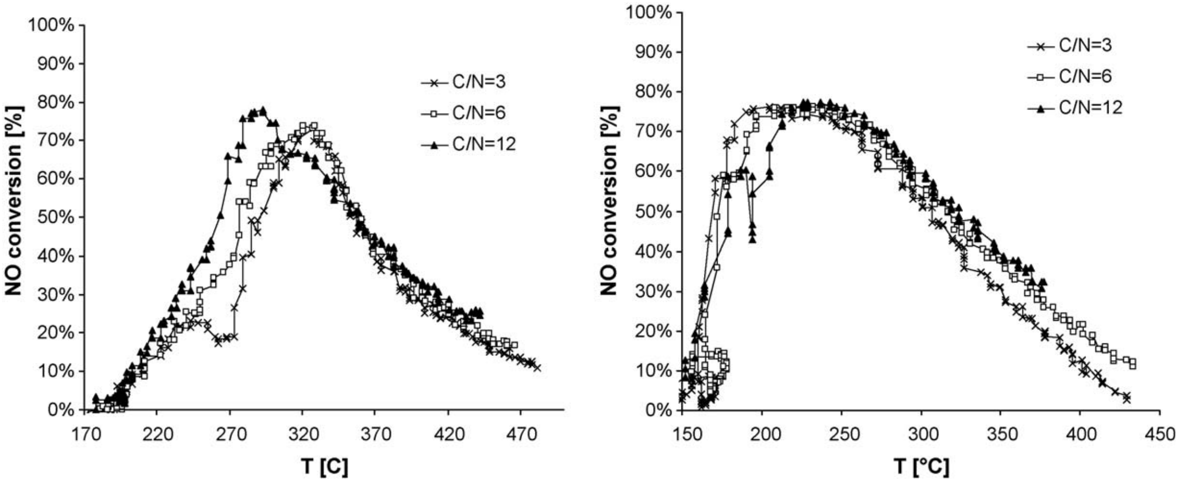

Fig. 2. NO conversion obtained with Rh (on the left) and Pt (on the right) catalysts feeding different C_3H_6 concentrations. GHSV = 10,000 h^{-1}.

Rh and Pt seem to be more selective for NO reduction than Ag and they are consequently more effective in reducing NO at low hydrocarbon concentrations. All the catalysts, indeed, are also active in propene combustion, but rhodium and platinum clearly favor the reduction of NO, this resulting in a good activity already at the lower C/N ratios.

3.2. *Effect of the gas space velocity*

GHSV affected all the catalysts causing a decrease of the activity as the space velocity increases. Generally the difference was not very marked switching from 10,000 to 20,000 h^{-1}, while a bigger difference was observed working at 40,000 h^{-1}. For Ag the maximum conversion decreased from 100% to 90% and 60%, respectively, while the light off temperature increased from 320 to 370 °C and 420 °C. Interestingly above 530 °C conversions overlay at every space velocity. The same trend was detected for Rh (see Fig. 3) that showed almost overlapping trends at 10,000 and 20,000 h^{-1}, though maximum conversion decreased from 75% to 60%. The ignition temperature was in both cases 200 °C, while at 40,000 h^{-1} it was 280 °C and the maximum conversion was 42%.

Again at the highest temperatures tested (above 370 °C) the conversion trends overlapped. Pt was the catalyst least affected by the gas space velocity, as shown in Fig. 4.

The qualitative trend is similar to that of the other catalysts, but the differences in the maximum conversion and in the ignition temperature are smaller in this case. It can be noted that at 20,000 h^{-1} the max conversion increases from 75% to 82% compared to that at 10,000 h^{-1}, while at 40,000 h^{-1} it keeps a rather high value of 72%. In the latter case the ignition temperature is 180 °C, while it was about 150 °C at the other space velocities. Surprisingly above 280 °C the conversion increases with the GHSV. A possible reason is the higher reaction rate at higher temperatures and the increase of the linear velocity and thereby the increase in the mass transfer coefficient at higher space velocities. Though the residence time decreases as the temperature goes up, the overall effect is a higher conversion as the GHSV increases.

Above 250 °C both O_2 conversion and CO_2 yield decrease and the decrease is proportional to the GSHV, while propene is still completely consumed. This means that the catalyst becomes more selective towards NO reduction and propene combustion is less favored. Concerning the catalysts selectivity, in all the tests described (also those in Section 3.1), Ag does not convert any NO to NO_2. On the contrary, it also converts a small amount of NO_2 contained in the gas tube (few ppm). With Rh and Pt, instead, the yield of NO_2 is in some instances usually considerable, ranging between 20% and 40% for Rh and between 30% and 70% with Pt. NO_2 is more reactive than NO and can react faster on the surface of the catalyst, probably originating from reaction intermediates that favor the overall reduction reaction, also with hydrocarbons. This can be one of the reasons why both these metal are active at lower temperatures compared to silver. On the other hand there is the drawback that NO_2 is also dangerous.

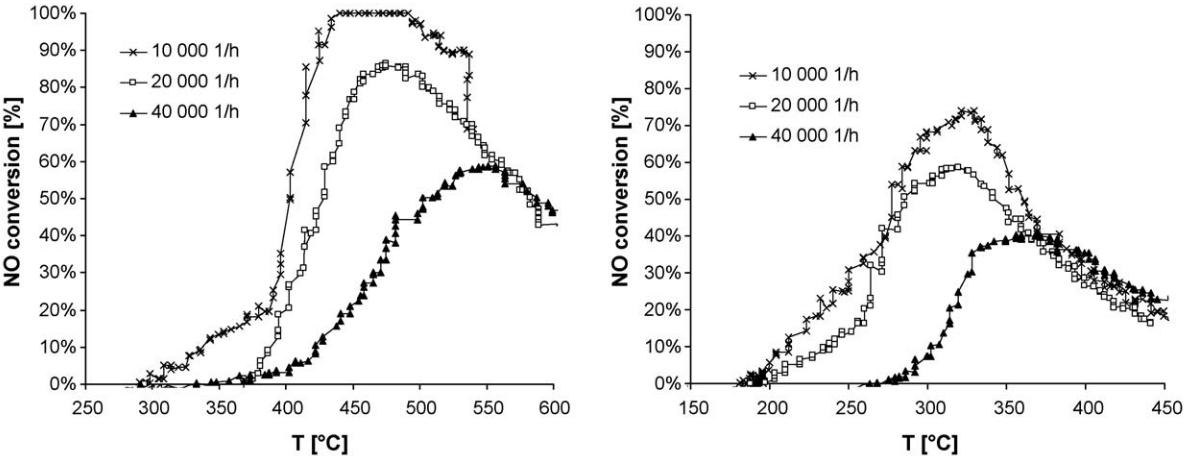

Fig. 3. Effect of the GHSV on the NO conversion with Ag (on the left) and Rh (on the right). C/N = 6.

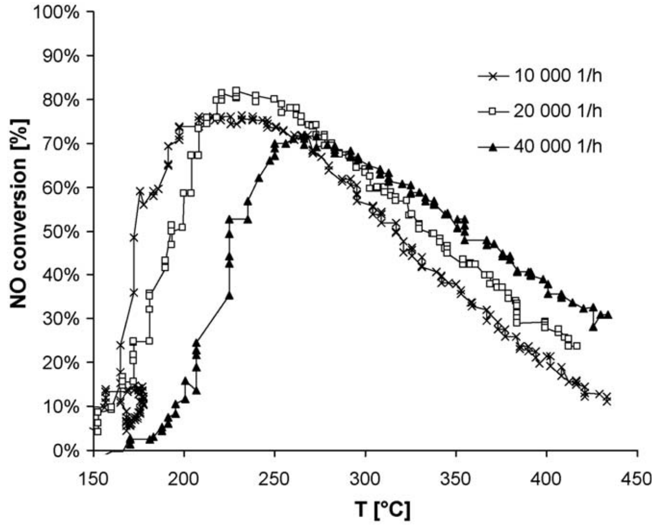

Fig. 4. NO conversion of Pt as a function of the GHSV. C/N = 6.

3.3. *Effect of steam*

On a real diesel engine exhaust gas stream, steam reaches concentration up to 10% and it is known to affect the catalysts' activity. Therefore some tests have been run adding about 7.5% of steam to the gas mixture fed to the reactor. For silver water improves the performances of the catalyst at low temperature, mainly at low C/N ratios (Fig. 5) while at higher temperatures NO conversion decreases by about 15%.

For Rh feeding steam to the reactor resulted in a marked conversion decrease in almost all the temperature ranges (max conversion decreasing from 80% to 50%), but giving the same values as without water above 380 °C.

Pt catalyst exhibits a different behaviour depending on the propene concentration. When C/N ratio is 3, the performances are strongly affected by water while when the C/N ratio is increased to 12 (Fig. 6), water slightly worsens the catalyst performance up to 220 °C, while improves them a little above that temperature.

To understand the effect of steam on the catalyst performances two different factors have to be considered. Water indeed competes with reactants in the adsorption on the active sites. When this happens the effect will be a decrease in rate of the desired reaction due to the lower number of active sites available. The other factor is that steam counteracts the formation of carbonaceous deposits that block the adsorption sites on the catalyst surface. The competitive adsorption between water and the reactants fed explains why at low C/N ratios, NO conversion is rather lowered both for Rh and Pt, mainly at low temperature. As the C/N ratio increases, this effect is limited by the higher concentration of propene. Indeed both for Rh and Pt the difference

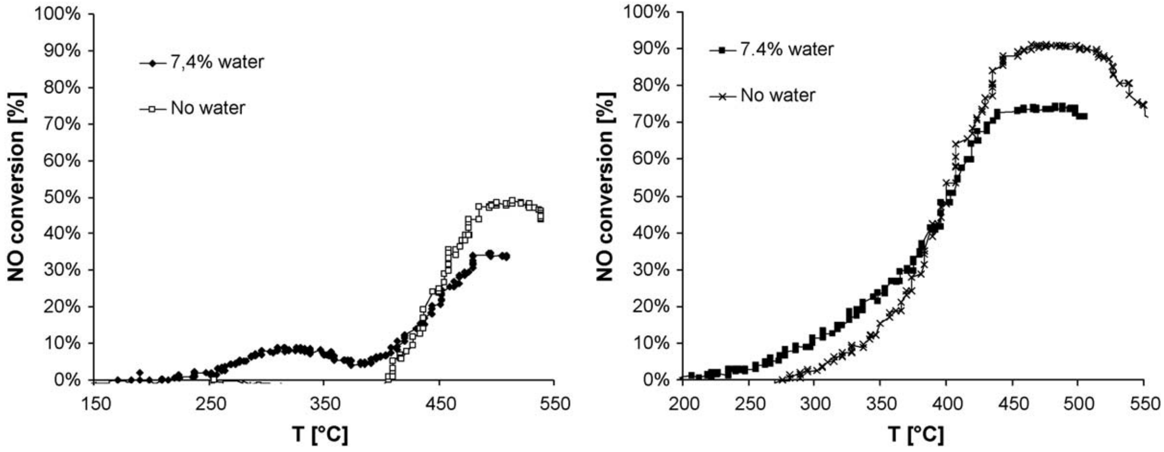

Fig. 5. Effect of steam on silver catalyst at different C/N ratios: C/N = 3 on the left and C/N = 12 on the right.

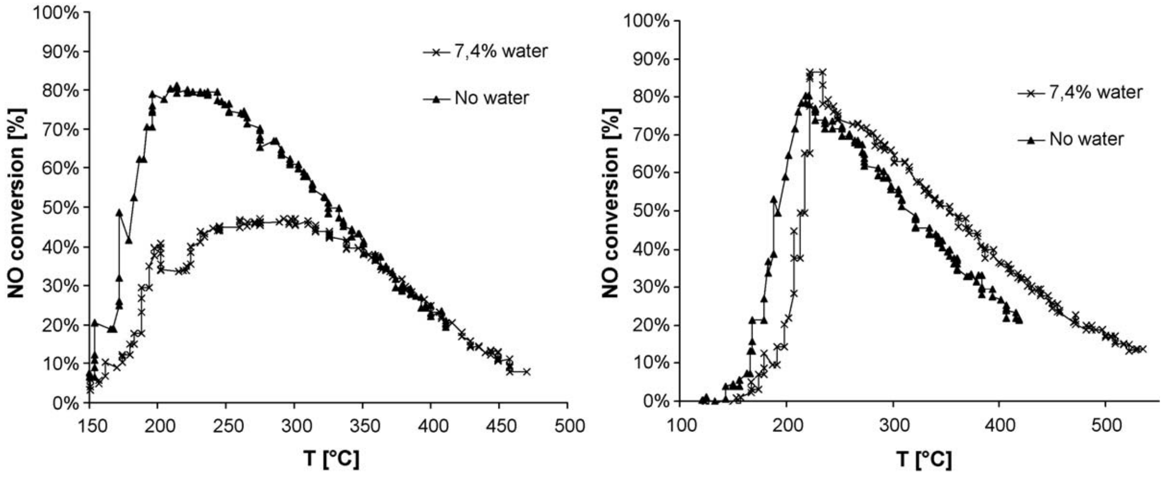

Fig. 6. NO conversion detected with Pt without steam and adding 7.4% of steam in the gas stream. C/N = 3 (on the left), C/N = 12 (on the right).

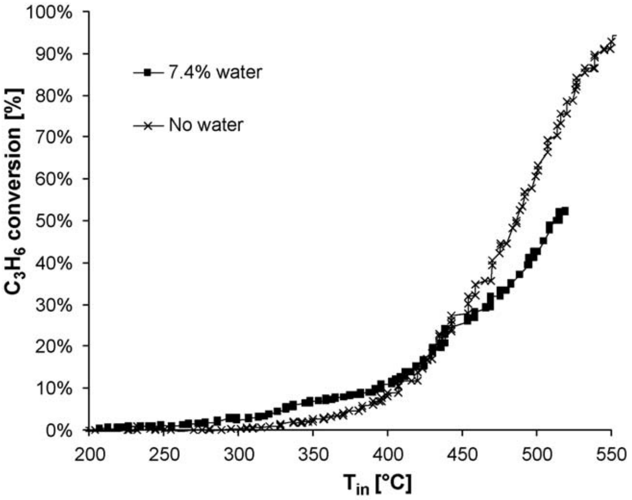

Fig. 7. Propene conversion detected with and without steam with C/N = 12 (same test shown in Fig. 6 right).

in the performances with and without water decreases at high C/N ratios. Furthermore at relatively high temperatures and at the highest C/N ratio, NO conversion seems to benefit of the presence of steam that, as mentioned before, counteracts the formation of carbonaceous deposits that is obviously favored by the higher hydrocarbon concentration. While similar trends are detected for Rh and Pt, silver is instead an exception and reveals slightly better performances at low temperatures and some limitations at high temperatures. Looking at the charts of C_3H_6 conversion (see Fig. 7) it can be noted that when water is fed and NO conversion is higher, also propene conversion is higher, this meaning that in that temperature range, water favors the reaction between NO and the hydrocarbon. Starting from about 450 °C, the lines cross each other and the trend is inverted both in NO and propene conversion.

3.4. Effect of hydrogen

The catalysts' activity has been evaluated adding a mixture simulating the composition of a gas obtained by reforming of gasoline to the conventional gas stream. This means approximately a ratio $H_2/CO/CO_2/H_2O/N_2$ equal to 3/1/1.5/1/3.5 (v/v). Once added to the gas stream, the H_2 concentrations fed was 2000 ppm, the others varying proportionally.

For silver, if this gas mixture was fed without propene, no NO conversion was detected, while once the hydrocarbon was added, the catalyst performance was boosted. As shown in Fig. 8, without hydrogen the catalyst starts being active around 400 °C and the maximum conversion reaches 93%, while with H_2 the catalyst show some activity already at 100 °C and reaches and keeps complete conversion between 250 and 400 °C. According to literature [6] this might be due to the reduction of the silver nitrate formed during the process. The reaction mechanism was not investigated in this work, but there are several papers dealing with it. Ref. [1], for example, is a very interesting review. It is generally accepted that the first step of the reaction involves the formation of strongly bonded nitrites and nitrates (detected in studies made with FTIR). The formation of these species strongly adsorbed on the catalyst surface acts as a poison for the catalyst, so when H_2 is fed and helps keeping silver in its metallic state, with no other species adsorbed on it, the number of active sites is higher and NO reduction is favored. According to this explanation, H_2 does not take part directly in the NO reduction, but helps the process by providing more active Ag sites. This fact is confirmed by observing the conversion of C_3H_6 (Fig. 8, right) and O_2 (not reported), which have the same trend. Another very recent work [11], deals with the hydrogen effect showing that the concentration of the surface nitrates is lowered when H_2 is fed.

Indeed, when H_2 is also fed, C_3H_6 consumption starts already at 100 °C and is much higher at every temperature than without H_2. Such a trend indicates that more active sites are available for the reaction, causing an increase in the reaction rate at low temperatures.

The Rh catalyst does not seem to be affected by feeding the same mixture described above. On the contrary, NO conversion is a little higher when H_2 is not fed. On the other hand, when C_3H_6 is not fed at all, H_2 itself gives some conversion, this reaching 40%. In contrast with what happened with the silver catalyst, in this case H_2 actively participates in the reaction instead of acting on the catalyst oxidation/reduction state.

On platinum, H_2 has a large effect at low temperature. As shown in Fig. 9, when fed with propene, it is active in converting NO already starting from 50 °C. The boosting effect of H_2 lasts up to 170 °C, with NO conversion swinging around 50% between 100 and 220 °C. Above this temperature the conversion line almost overlaps that of the test without H_2.

Interestingly the higher NO conversion detected at low temperature is not followed by an increase of NO_2 production in the same T range. H_2 catalyzes the reaction following a different mechanism that does not lead to NO_2.

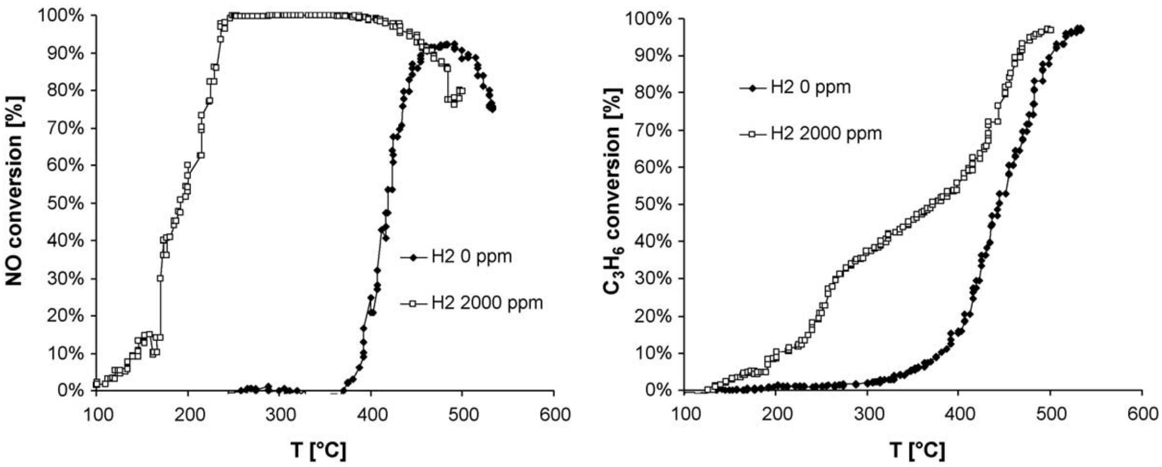

Fig. 8. NO (on the left) and C_3H_6 (on the right) conversion detected with and without H_2 with Ag catalyst. C/N = 9, GHSV = 20,000 h^{-1}.

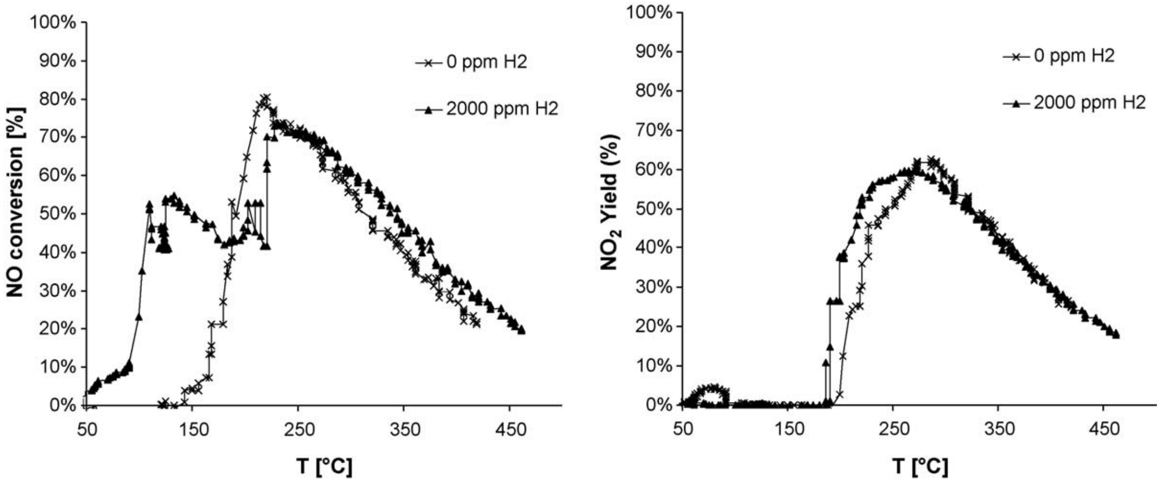

Fig. 9. NO conversion (on the left) and NO_2 yield (on the right) detected with Pt adding H_2 to the gas mixture fed. C/N = 9, GHSV = 20,000 h^{-1}.

4. Conclusions

All the catalysts tested were very active in the conversion of NO and exhibited different behaviours. Silver gave the highest conversions, these being at least 50% in the least favorable conditions (high GHSV and low C_3H_6 concentration) and between 80% and 100% in the other conditions tested. No NO_2 production was evidenced. The catalyst was active between 350 and 600 °C (the maximum *T* tested), usually showing conversion higher than 80% between 400 and 550 °C. At the highest temperatures the combustion of propene reduced the amount of reducing agent available for the reaction, this leading to the typical "volcano shape" of the conversion usually detected in the NO reduction process. This feature is common to the other catalysts tested. Steam had a limited effect, while H_2 boosted the reaction increasing the conversion at low temperatures.

Rhodium and platinum gave slightly lower conversions than Ag, but they were active at lower temperature (between 200 and 400 °C). Rh is strongly affected by steam, while Pt exhibits different performances depending on the C_3H_6 concentration, keeping a high activity at the highest C/N ratios.

For Rh the tests with hydrogen showed that H_2 itself is active in converting NO when no propene is fed, while there is a slight decrease of the performances once C_3H_6 is added to the gas mixture. With Pt, instead, there is a similar effect to that detected with silver but only up to 150 °C, while above this temperature there is not a big difference in NO conversion.

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