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NO_x storage/reduction catalysts based in cobalt/copper hydrotalcites

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Abstract

The use of materials based on hydrotalcites as NO_x storage/reduction (NSR) catalysts has been investigated, examining their activity at low temperature and their resistance to poisons such as H_2O and SO_2. The results obtained show that catalysts derived from Mg/Al hydrotalcites containing copper or cobalt is active at low temperatures, specially the samples containing 10 or 15% of Co. The addition of 1 wt% of transition metals with redox properties such as Pt, Pd, V and Ru to the hydrotalcite increases its activity because the combination of the redox properties of these metals and the acid-base properties of the hydrotalcite. The best results were obtained with the catalyst derived from a hydrotalcite with a molar ratio Co/Mg/Al = 15/60/25 and containing 1 wt% V. This material shows a higher activity, at low temperatures and in the presence of H_2O and SO_2, than a Pt–Ba/Al_2O_3 reference catalyst.

Keywords: NO_x; Storage reduction catalysts; Hydrotalcites; Cobalt; Vanadium

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1. Introduction

One of the principal environmental concerns in air pollution is the minimization of NO_x emissions. These emissions come mainly from mobile sources and their control becomes an urgent necessity. Among the technologies envisaged, the most widely applied method is the three-way catalyst. This system gives excellent results when the air to fuel ratio is close to the stoichiometric ratio, but the efficiency diminishes in the presence of an excess of oxygen [1]. Nowadays the tendency is to use engines with better fuel efficiency, as lean-burn gasoline and diesel engines that works with an excess of oxygen over the stoichiometric ratio, i.e. lean conditions. These operation conditions strongly diminish the efficiency of the traditional three-way catalysts, for this reason the discovery of an alternative technology, which can achieve efficient NO_x, reduction at high oxygen concentrations, without increasing fuel consumption, is an imperative need.

Different alternatives have been proposed to break this challenge [2,3]. The first approach relies on the selective catalytic reduction of NO_x using ammonia, or urea, as reductants [4]. However its implementation for mobile applications requires the development of a urea distribution network and it presents the problems associated with the use of a pollutant, as ammonia. Another possibility is the use of hydrocarbons as selective reductant agents employing metal exchanged zeolites as catalysts [5,6]. These materials are quite active, but present a low hydrothermal stability resulting in a fast deactivation of the catalyst [7]. In the last years a new alternative has appeared that it is attracting much attention, this is the NO_x storage/reduction (NSR) technology [8–10]. It is based in the selective storage of the NO_x as nitrates under lean (oxidizing) conditions and their non-selective reduction under the short, rich (reducing) excursions. NSR catalysts are typically composed of at least one basic compound (alkaline or alkaline-earth oxides) and at least one precious-metal component. One of the most common formulations used is Pt and Ba supported on Al_2O_3 [2]. This catalyst works in two steps, in the first step, under lean conditions, NO is oxidised into NO_2 on the Pt active sites, and the NO_2 is adsorbed on the BaO as nitrate. In the rich conditions, the nitrates decompose and the NO_2 formed is reduced into N_2 with the hydrocarbons, CO and H_2 present in the exhaust gases. The problem of this material is its fast poisoning by sulphur compounds and its low activity at low temperatures [2,11,12]. In this work it is studied the

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possibility of using other materials, such as hydrotalcites, as the base for a NSR catalyst.

The hydrotalcite structure can be considered as a positively charged brucite-type octahedral sheets, in which a part of the Mg^{2+} is substituted by a trivalent metal like Al^{3+}, generating a partial positive charge that is compensated with carbonate anions and water molecules located in the interlayer space. Nevertheless it is possible to prepare different hydrotalcites by the partial or the total substitution of Mg^{2+} and Al^{3+} with other divalent or trivalent metals. Hydrotalcites retain the layered structure up to 400 °C, but at higher temperatures yield to high surface area metal mixed oxides. Calcined hydrotalcites are potentially useful as catalysts or catalyst precursors if the advantage of their properties of high surface areas, redox and basic character can be utilized. In this way, Mg/Al hydrotalcites with copper or cobalt in the structure have been described as active catalysts for the SO_x, NO and N_2O removal [13] and even the possibility of using hydrotalcite derived materials as NO_x storage/reduction catalysts has been studied [14–19]. The objective of this work is to combine the redox and the acid-base properties of the Co or Cu/Mg/Al hydrotalcites in order to design a NO_x storage-reduction catalyst active in lean burn conditions at low temperatures and in presence of water and SO_2.

2. Experimental

Cu(II)Mg(II)Al(III) and Co(II)Mg(II)Al(III) hydrotalcites were prepared by a standard co-precipitating procedure using two solutions. The first solution contained $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and $Cu(NO_3)_2 \cdot 5H_2O$ or $Co(C_2H_3O_2)_2$, having a (Al + Mg + Cu or Co) molar concentration of 1.5. The second solution contained NaOH and Na_2CO_3 in the adequate concentration to obtain the total precipitation of aluminium, magnesium and copper or cobalt in the former solution and to fix the pH at a value of 13. Both solutions were added, while vigorously stirring, at a total flow-rate of 30 cc/h for 4 h. The gel was aged under autogenous pressure conditions at 80 °C for 14 h, then filtered and washed with distilled water until the pH was 7 and carbonate was not detected in the filtrate. The hydrotalcite was calcined at 650 °C in air for 3 h before reaction, obtaining a mixed oxide. Some samples were impregnated by incipient wetness, with different salts of platinum, palladium, ruthenium and vanadium, and calcined at 550 °C for 6 h in order to prepare some catalysts based on Mg/Al/Co hydrotalcite and with a 1 wt% of Pt, Pd, Ru or V. The Pt–Ba/Al_2O_3 (1 wt% Pt, 15 wt% Ba) reference catalyst was prepared according to Toyota work [8,9].

The reaction experiments were carried out in a fixed bed, tubular reactor (2.2 cm diameter and 53 cm length). In the experiments 1 g of catalyst, as particles of 0.25–0.42 mm, was introduced in the reactor and was heated up to 450 °C under nitrogen flow. At this temperature the flow was maintained for 2 h. After that, the desired reaction temperature was set and the reaction feed admitted. This consists in 650 ml min^{-1} of a mixture composed by NO, C_3H_8, oxygen and balanced with nitrogen. Catalytic tests were set at a space velocity of 20,000 h^{-1}, using a cyclic sequence of changes in the feed composition, simulating car exhaust emissions in lean (120 s: 13% O_2, 530 ppm NO_x, 50 ppm C_3H_8, N_2 balance) and rich conditions (60 s: 8% O_2, 530 ppm NO_x, 700 ppm C_3H_8, N_2 balance). After evaluating the behaviour during a sequence of seven lean–rich cycles at a given temperature, the reactor temperature was raised to another temperature where the behaviour was further monitored over the cycles series. The influence of water and SO_2 was investigated by adding 8% water and 60 ppm of SO_2 in the gas stream. The NO_x present in the gases from the reactor were analyzed continuously by means of a chemiluminescence detector Rosemount 951A. The formation of N_2O was tested by gas chromatography with a 5 Å molecular sieve column used to separate oxygen, nitrogen and carbon monoxide and a Poraplot Q column for the separation of carbon dioxide and hydrocarbons. Nevertheless the formation of N_2O was negligible, for this reason the consideration that all the NO_x is converted into N_2 is assumed.

The surface areas of the catalysts were obtained in an ASAP 2000 apparatus, using the BET method from the nitrogen adsorption isotherms at 77 K.

X-ray diffraction patterns (XRD) of the catalysts were collected using a Phillips X'Pert-MPD diffractometer provided with a graphite monochromator, operating at 40 kV and 20 mÅ and employing nickel-filtered Cu Kα radiation ($\lambda = 0.1542$ nm).

Diffuse reflectance (DR) spectra in the UV–vis region of the cobalt catalysts were collected with a Shimazdu UV-2010 PC spectrophotometer equipped with a reflectance attachment.

The chemical composition of the samples was measured by atomic absorption with a Varian EspectrAA-10 plus system.

3. Results and discussion

The chemical composition and surface areas of the calcined hydrotalcites are comparatively shown in Table 1. It can be seen that all the catalysts tested have a surface areas between 140 and 210 m^2/g. The highest surface areas correspond with the catalysts with the lowest copper or cobalt content, decreasing the surface area when the quantity of the transition metal increases as bigger crystallites are formed [18]. The impregnation of a 1 wt% of another metal on the hydrotalcite results in a slight decrease of the surface areas.

Before calcination, the samples show the typical X-ray diffractogram (Fig. 1A) of a hydrotalcite with the peaks at $2\theta = 11.3°$, 22.8° and 34.6°, corresponding to the (0 0 3), (0 0 6)

Table 1
Chemical composition and textural characteristics of the samples

Sample	Composition (molar ratio)	Surface area ($m^2\,g^{-1}$)
5 Cu–HT	Mg/Al/Cu = 65/29/6	208
5 Co–Ht	Mg/Al/Co = 64/30/6	193
10 Co–Ht	Mg/Al/Co = 69/20/11	170
15 Co–Ht	Mg/Al/Co = 69/15/16	152
Pt 15 Co–Ht	Mg/Al/Co/Pt = 59.86/24.9/15/0.24	147
Pd 15 Co–Ht	Mg/Al/Co/Pd = 59.66/24.9/15/0.44	143

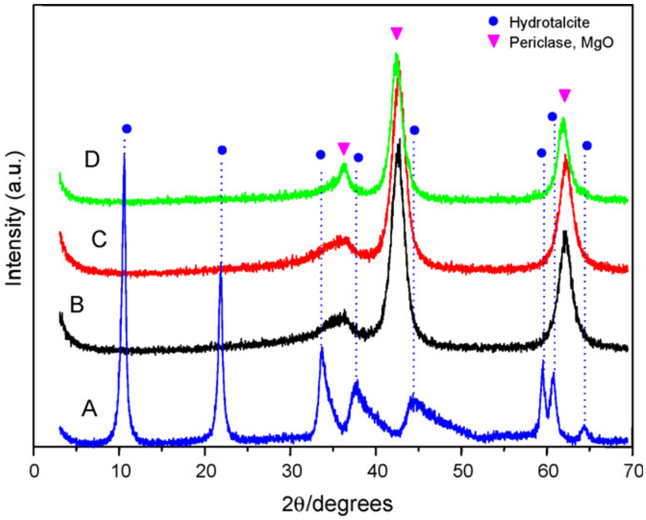

Fig. 1. X-ray diffraction patterns of the catalysts based on Mg/Al hydrotalcite with different cobalt content: (A) hydrotalcite 15 Co–Ht before calcination, (B) hydrotalcite 5 Co–Ht after calcination at 650 °C, (C) hydrotalcite 10 Co–Ht after calcination at 650 °C and (D) hydrotalcite 15 Co–Ht after calcination at 650 °C.

and (0 0 9) crystal planes, indicating relatively well-formed crystalline layered structures with rhombohedral symmetry [20]. On the other hand the broad diffraction peaks at 38° and 45° attributable to the (0 1 2) and (0 1 8) crystal planes are characteristic of poly-type $3R_1$ hydrotalcites [21]. The well defined (1 1 0) and (1 1 3) diffraction peaks at 59.8° and 61.9° reveal a quite good dispersion of metal ions in the hydroxide layers. After calcination at 650 °C, it can be observed the formation of a cubic magnesium oxide poorly crystalline with peaks at $2\theta = 36.9°$, 42.9° and 62.3° (Fig. 1B–D). These peaks are shifted to higher angles if compared with a pure magnesium oxide. This is consequence of the incorporation of aluminium in the framework of the MgO, resulting in the formation of a mixed oxide [22]. Independently of the cobalt content, no peaks assigned to the transition metal oxide are observed, indicating a better dispersion of the cobalt in the matrix. After impregnation with a 1% of other metals and calcination, the XRD patterns do not evidence significant changes neither the presence of another phase. This suggests that the crystallite size of the cubic mixed oxides is the same and that there is a good dispersion of the metal on the catalyst surface.

In order to study the nature of the cobalt species, these samples were studied by diffuse reflectance spectroscopy. The diffuse reflectance spectra in the UV–vis region of the cobalt hydrotalcites (no shown) presents bands at 650 and 259 nm related with the presence of tetrahedral Co^{2+} [23], in addition there is a double shoulder at 347 nm, assigned to an electronic transition of Co^{3+} in a tetrahedral disordered environment [24]. From the characterization results, it can be concluded that Co–Mg–Al oxide derived from hydrotalcites, are catalysts with high surface area, where cobalt is mainly as tetrahedral Co^{2+} although some Co^{+3} is also present, being the cobalt not only as isolated and well dispersed ions, but also as some kind of very small Co-containing particles.

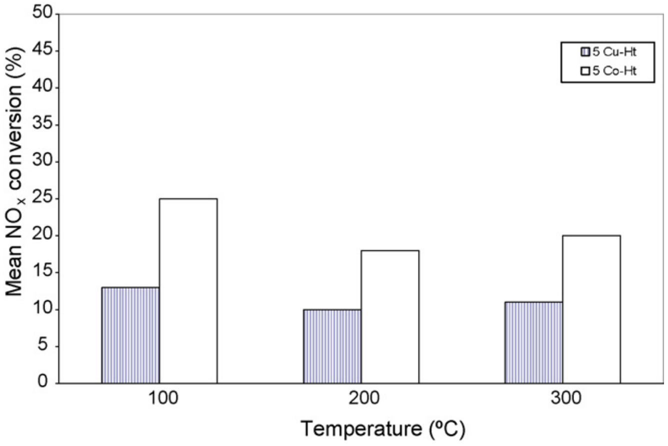

Fig. 2. Mean NO_x conversion (over seven cycles) at different temperatures on a Mg/Al hydrotalcite with 5% copper and 5% cobalt in the structure.

The mean NO conversion of seven lean + rich cycles, obtained with the copper and cobalt hydrotalcites, was compared at different temperatures and the results are shown in Fig. 2. As it can be seen, even without the presence of a noble metal, the catalysts present some activity for the NO_x removal. The NO is efficiently removed during the first lean period, adsorbing the NO_x as nitrates, but the activity falls during the rich period, without recovering the initial activity in the successive cycles. This shows that in this cycle it is no possible to desorb/reduce the NO stored in the lean cycle. Comparing the mean NO conversion of the different catalysts, it can be observed that the best results are obtained at 100 °C, probably because although at low temperatures there is a low rate of NO to NO_2 oxidation, the NO_x stored as nitrates at this temperature do no decompose, as it occurs at higher temperatures [18]. In all the range of the temperatures tested, the activity of the catalyst derived from the hydrotalcite with cobalt was better than that of the copper hydrotalcite, for this reason, the Co/Mg/Al catalyst derived from hydrotalcite was chosen as the basis for the adequate catalyst.

The activity of the catalysts based in hydrotalcites with different cobalt content was studied at different temperatures and the mean results of seven lean–rich cycles are shown in Fig. 3. In the first lean–rich cycle, the NO is efficiently removed during the lean period, adsorbing the NO_x as nitrates, nevertheless in the rich cycle the activity slightly falls because some of the nitrates desorbed are not reduced. The same behaviour is observed in the successive lean–rich cycles, observing a decrease in the maximum conversion compared with the first cycle, but stabilizing the conversion after three lean–rich cycles. The samples with higher cobalt content show the best activity in all the range of the temperatures tested, obtaining the maximum conversion at 100 °C. In this way the best activity was observed for the sample containing 15% cobalt that presents at this temperature a mean NO_x conversion of 47%. The reason of the higher activity of the catalyst when increasing the cobalt content up to 15% is related with the improvement of its oxidation capacity. In this way the NO is more easily oxidised to nitrites and nitrates that move to adjacent Mg/Al oxide to be stored. Nevertheless, an additional

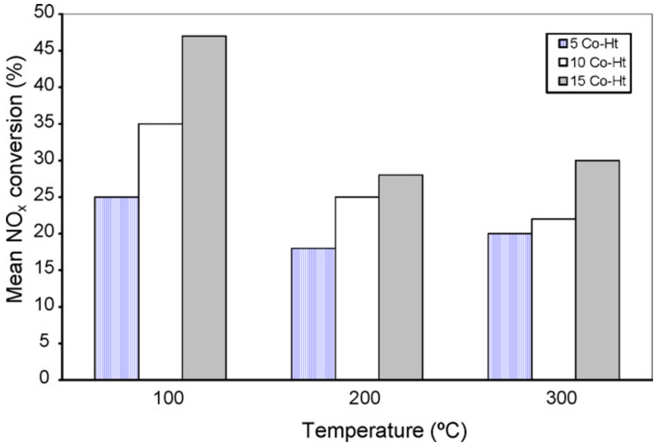

Fig. 3. Influence of the cobalt content in the mean NO_x conversion (over seven cycles) of the catalysts based on Co/Mg/Al hydrotalcites at different temperatures.

increase in the cobalt content, leads to the formation of different phases in the material resulting in a decrease of the activity.

The influence of the catalyst activation was studied with the hydrotalcite containing 15% cobalt. As it can be seen in Fig. 4, the activity of the catalyst increases significantly when the catalyst is activated at 450 °C with hydrogen instead of nitrogen, being the improvement specially significant when the reaction is carried out at 300 °C. The higher activity of the catalyst activated with hydrogen could be related with the presence of different cobalt sites. In this way, at 450 °C, hydrogen reduces the surface cobalt, but it does not reduce the bulky Co(III) or Co(II) [18], obtaining cobalt active sites with different oxidation states that show better redox properties.

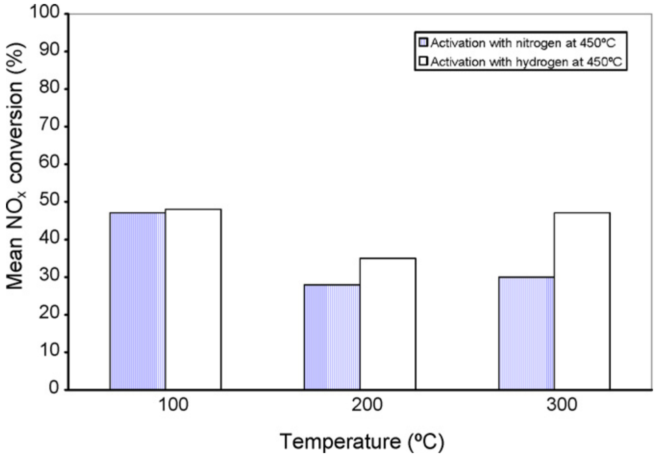

Fig. 4. Influence of the activation procedure of a Co/Mg/Al hydrotalcite, with 15% cobalt, in the mean NO_x conversion (over seven cycles) at different temperatures.

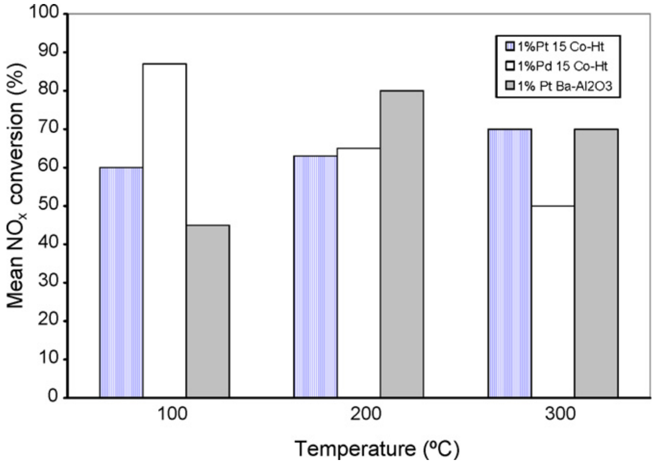

Fig. 5. Influence of a 1 wt% Pt and 1 wt% Pd addition in the activity, at different temperatures, of a Co/Mg/Al hydrotalcite (15% cobalt) and their comparison with that of a reference $Pt–Ba/Al_2O_3$ sample.

Although the results obtained at low temperatures with the hydrotalcites containing cobalt are quite interesting, the conversion obtained is no so high and the activity at higher temperatures is lower than that obtained with catalysts based in $Pt–Ba/Al_2O_3$. In order to improve the activity of the catalyst based in Co/Mg/Al hydrotalcite, the addition of 1 wt% of Pt or Pd to the hydrotalcite with 15% cobalt was studied and their activity was compared with that of a reference catalyst Toyota type (1% Pt–15% $Ba–Al_2O_3$). These samples were previously activated with hydrogen at 450° and the mean results after seven lean–rich cycles are shown in Fig. 5. In this case, the NO is efficiently removed during all the lean periods, decreasing the activity during the rich periods because in the short rich period no all the NO_x previously adsorbed as nitrates can be reduced. As in the previously reported results, the maximum activity is achieved in the first cycle, decreasing afterwards, but stabilizing after the third lean–rich cycle. Comparing these results with those shown in Fig. 4, it is observed that the presence of Pd and Pt improves the activity of the Co-hydrotalcite in all the temperatures range tested, being the most active catalysts, that one containing palladium at 100 °C and the catalyst with Pt at 300 °C. Comparing the activity at 100 °C of these catalysts with that of a reference catalyst Toyota-type, it can be observed that catalysts based on hydrotalcites with cobalt show a higher activity than the reference catalyst, obtaining with the 1 wt% Pd catalyst, a mean conversion of 87%, double than the conversion obtained with the reference catalyst. The improvement of the Co-hydrotalcite activity when adding a noble metal is due to the increase of the oxidation rate of NO to NO_2 that will be stored as nitrates in the Mg–Al sites. On the other hand, the higher activity of the hydrotalcite samples compared with that of the Pt–Ba catalyst, can be explained because the different basicity of the magnesium and barium. Barium is more basic than magnesium resulting in the formation of more stable nitrates, but also in a higher inhibition of the noble metal, due to the strong electronic interaction, being this more evident at low temperatures. On the contrary, the presence of cobalt favours, as it occurs with copper [15], the stabilization of the noble metal by a Pt/Pd–Co interaction improving its dispersion on the catalyst surface.

Although the use of catalysts based on Pt or Pd supported on cobalt hydrotalcites results in a better activity at low temperatures, the presence of water and SO_2 deactivates the catalyst, as it occurs with the $Pt–Ba/Al_2O_3$ reference catalyst. This is due to the sorption of the sulphur species on the catalyst surface and to the subsequent poisoning of the noble metals

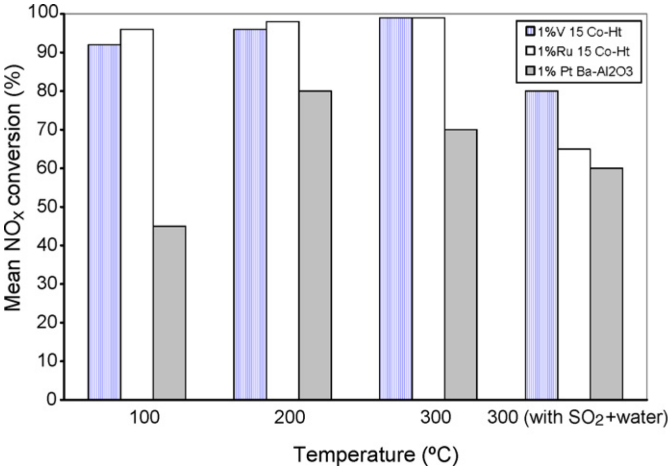

Fig. 6. Influence of the addition of 1 wt% Ru and 1 wt% V in the activity, at different temperatures and in presence of 8% water and 60 ppm SO_2 at 300 °C, of a Co/Mg/Al hydrotalcite (15% cobalt) and their comparison with that of a reference Pt–Ba/Al_2O_3 sample.

[2,11]. For this reason, the addition of other non-noble metals with redox properties and more resistant to sulphur was studied. The results are shown in Fig. 6 where it is observed that the catalysts containing 1 wt% of Ru or V show a higher activity at low temperature than those catalysts containing noble metals. These catalysts present a mean NO conversion, after seven lean–rich reaction cycles, of almost 100% at 300 °C, obtaining a mean conversion of 90–95% at 100 °C. The behaviour of the catalyst with vanadium in the different lean–rich cycles at 100 °C is shown in Fig. 7. As it is observed, the catalyst is very stable, showing the best activity during the lean cycles with a slight decrease of the activity in the rich cycle, but stabilizing the conversion in both cycles after three lean–rich cycles. Nevertheless the most interesting results are related with the activity of the catalysts in presence of 60 ppm of SO_2 and 8% water, shown in Fig. 6. The presence of water and SO_2 at 300 °C results in a small decrease of the activity in all the samples tested, but this is less important in the vanadium catalysts than in the others, showing this catalyst a mean NO conversion of 75% after the seven lean–rich cycles. Longer stability tests were made with this catalyst in these conditions, obtaining after 4 h of reaction a stable and mean conversion of 70%. From these results, it seems that this catalyst is more stable and more resistant to deactivation than the reference catalyst based in Pt–Ba/Al_2O_3. This is probably due to the low SO_3 capture rate of the magnesium sites that are less basic than the barium sites and to the highest resistance to poisoning of the vanadium compared to that of the noble metals. Nevertheless more studies and longer tests are still necessary to determine the role and the stability of the active sites in the catalyst.

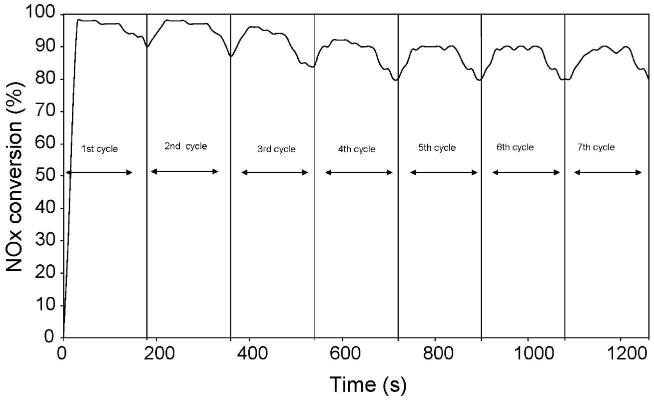

Fig. 7. Dynamic evolution of the NO_x conversion during seven cycles lean–rich (120 s lean–60 s rich) at 100 °C with the 1 wt% V–Co/Mg/Al hydrotalcite.

4. Conclusions

The results obtained from this work, suggest that catalysts based in hydrotalcites are a feasible option for NO_x storage/reduction catalyst, being the most prospective catalysts those based in Mg/Al hydrotalcites with 10 or 15% cobalt in their composition. In order to improve the redox characteristics of these materials is convenient to add 1 wt% of a transition metal with redox properties, as Pt, Pd, Ru or V, obtaining the best results with the catalyst containing 1% vanadium. This catalyst shows a high conversion even in presence of SO_2 and water. This is due to the adequate combination of the vanadium redox properties and the hydrotalcite basic properties, together with the sulphur tolerance of this material.

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