NO_x storage on barium-containing three-way catalyst in the presence of CO_2

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NO_x trapping capability of "NO_x storage–reduction" commercial catalysts (4–9 wt% Ba-containing three-way catalysts) was compared to that of bulk barium carbonate and alumina-supported barium carbonate from Rhodia (9 wt% Ba). These samples were characterized by infrared spectroscopy, X-ray diffraction, HRTEM and EDX. It was shown that bulk barium carbonate was partially converted to barium nitrate in flowing NO/O_2 mixture without CO_2. Thermodynamic calculation showed that bulk barium nitrate could not form in the presence of CO_2-containing gas exhausts. Using HRTEM and EDX, it was evidenced that barium was engaged as either large barium carbonate crystals or highly dispersed barium species on the alumina support. NO_x storage experiments using gas mixtures containing or not O_2 or CO_2, confirmed firstly that NO was stored on barium trap only via NO_2 and secondly that NO_2 and CO_2 are competing for the same barium trapping sites. The fact that no significant amount of stored NO_x could be evidenced in the bulk barium carbonate, suggested that over the catalytic surface, the well dispersed barium phase can play an important role in the NO_x trapping properties of these catalysts.

KEY WORDS: lean-burn; NO_x storage; CO_2 effect; barium nitrate formation; thermodynamic data

1. Introduction

In view of limiting the greenhouse effect originating from CO_2 emission in the atmosphere, a number of studies [1–3] have been recently devoted to the development of automotive post-combustion catalysts working in lean-burn conditions (oxygen-rich mixture) [2]. These catalysts consisted of a three-way catalyst (TWC) associated to a barium trap, able to store NO_x in lean gas mixture, and to release NO_x during a subsequent rich period, allowing their reduction by the noble metal of the three-way catalyst.

At the present time, the composition of the barium-containing phase, and the nature of the active sites efficient for NO_x trapping, at the surface of these catalysts, are still controversial. Does NO_x trapping occur on barium associated with a carbonate phase [2,4], an oxide phase [4,5], a peroxide phase [6], or still, an aluminate phase [5]? Is this phase crystallized or amorphous? Is it a surface or a bulk phase on the alumina support? The study of commercial catalysts evidences the presence of barium carbonate before and after engine ageing [4], but its contribution to NO_x storage still remains to be defined. Similarly, the nature of the interaction of NO_x with the active sites of the barium trap is still unknown. Do we have the formation of bulk barium nitrate, surface nitrate or nitrite ions [7,8], or "coordinately Ba–NO_2 species", which could result from the interaction of NO and BaO_2 [6]? For some authors, the selective formation of barium nitrate or barium carbonate could be strongly dependent on the barium environment on the alumina support [5].

So, the mechanism of NO_x storage on the barium trap is still questionable [3]. It has been observed that NO_x storage significantly decreases with the CO_2 partial pressure in the reactant gas mixture [9,10] and deduced [10] that a competitive storage of NO_x and CO_2 on a same type of barium sites could occur. Recent work also suggested that NO_x storage could be strongly dependent on the presence of both NO_2 and atomic oxygen species [9]. The limiting stage of the NO_x storage could be the interaction of NO in the gas phase and NO adsorbed or adsorbed N-containing species [7].

In the present work we tried to obtain new information concerning the nature of both the barium-containing phase, and the active sites for NO_x trapping by NOx trap catalysts working in the presence of CO_2 (10 vol%).

As it will be shown below, barium carbonate has been always evidenced at the alumina surface of the stabilized catalyst. So, in this paper, the possible contribution of this carbonate phase to the NO_x trapping activity will be considered. The conditions of formation of a bulk barium nitrate phase will be discussed using thermodynamic arguments. NO_x trapping capabilities of a bulk barium carbonate, and of a sample of barium carbonate dispersed on alumina will be compared to that of the commercial barium-containing three-way catalysts.

2. Experimental

2.1. Material

2.1.1. Commercial catalysts

Commercial catalysts provided by PSA Peugeot-Citroën were studied. They were monoliths of cordierite impregnated by a washcoat containing a noble metal phase (Pt and

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Rh) supported over alumina enriched by ceria, and barium additives (contents varying from 4 to 9 wt%). Before characterization and testing, the samples were submitted to a stabilization treatment for 2 h at 873 K by flowing 10 vol% H_2O and 10 vol% O_2, in nitrogen. The monolithic samples could be crushed, before characterization, using the method proposed by Salin et al. [11], to get a powder representative of both the washcoat and the cordierite. For analytical characterizations the washcoat alone was recovered from the cordierite by scraping the walls of the monolith channels.

2.1.2. Bulk barium carbonate

The barium carbonate used in this study was a RP Normapur (99.5% $BaCO_3$) of the whiterite type with orthorhombic structure. Its stability was particularly high [12]: at a temperature as high as 1573 K, it decomposed to give BaO and CO_2. At a lower temperature bulk carbonate underwent two polymorphic transformations at 1073 K (ortho ↔ hexa) and 1241 K (hexa ↔ cubic). Bulk barium carbonate could be easily identified by transmission electron microscopy from the characteristic lattice fringe (3.72 Å) of the most intense diffracting crystallographic plane (111). It was also identified by XRD (JCPDS, 45-1471,1997), or by its infrared spectrum in the 4000–500 cm^{-1} range, with characteristic bands at 1420, 857, and 692 cm^{-1} [13].

2.1.3. Barium carbonate supported on alumina

This sample provided by Rhodia, consisted of a γ-alumina (180 m^2/g) impregnated with an aqueous solution of barium nitrate. After calcination and stabilization the barium content of the sample was 9 wt%.

2.2. Techniques

2.2.1. Infrared spectroscopy (IR) analysis

Infrared spectra of the various samples were recorded using a Brucker IFS 66-V interferometer. Spectra were recorded in KBr disks at room temperature and accumulated during 128 scans. The standard resolution was 4 cm^{-1}.

2.2.2. X-ray diffraction (XRD) analysis

The samples were characterized by X-ray diffraction using a Siemens D500 automatic diffractometer. The $K\alpha$ wavelength of copper was selected by a graphite diffracted beam monochromator. Data were collected and analyzed with Socabim diffract-AT software.

2.2.3. High-resolution transmission electron microscopy (HRTEM) analysis

Samples studied by HRTEM were ground and dispersed in pure ethanol; the suspension was stirred in an ultrasonic bath and one drop was deposited on a carbon-coated grid. HRTEM images were performed with a Jeol 100 CXII apparatus equipped with a top entry device and operating at 100 kV. The X-rays EDX (energy dispersive X-ray) analysis were obtained either from large domains (600 × 800 nm^2) or from smaller domains (spot beam diameter 700 nm^2) using a LINK AN 10000 system connected to a Si–Li diode detector and a multichannel analyzer.

2.2.4. Storage and release experimental device

Storage experiments were carried out on a catalytic device described elsewhere [10]. NO_x storage was achieved in lean conditions with gas mixtures consisting of 340 ppm NO (99%), 8 vol% O_2 (99.998%), 0–10 vol% CO_2 (99.99%) in nitrogen (99.995%). Nitrogen oxides were detected at the outlet of the reactor by a chemiluminescence detector ECO physics CLD 700 Al. NO_x release was realized using a gas mixture containing 10 vol% CO_2 in nitrogen.

3. Results

3.1. Study of NOx trap catalyst, before and after NO_x storage

The washcoats of commercial catalysts were studied after stabilization treatment. The XRD pattern of the stabilized catalyst showed the well resolved peaks of the bulk barium carbonate. Let us note here that Balcon et al. [10] could not detect by XRD the presence of barium carbonate on the same samples due to the too high dilution of barium carbonate in cordierite.

The study of these materials by HRTEM and EDX shows the presence of large barium carbonate crystals (200 Å–0.2 μm) at the alumina surface, concomitantly with barium in a well dispersed state: a (Ba/(Al + Ba)) ratio equal to 0.05 was determined on the support of the stabilized catalyst. The presence of infrared bands due to carbonate ions (1440 and 858 cm^{-1}) and the absence of the band at 1385 cm^{-1} characteristic of the NO_3^- ion, in the IR spectra of the stabilized sample, confirm the XRD observations showing the omnipresence of bulk barium carbonate and the absence of bulk barium nitrate. Results by XRD are necessary to clearly conform the absence of $Ba(NO_3)_2$, because the infrared band at 1385 cm^{-1} cannot be necessarily attributed to bulk barium nitrate.

The NO_x storage properties of the stabilized commercial catalyst were studied using a reagent mixture consisting of 340 ppm NO, 8 vol% O_2 and 10 vol% CO_2 in nitrogen. Table 1 gives the corresponding values of the NO_x amount stored per gram of barium in the sample.

These data evidence the substantial activity of these catalysts as regards to NO_x storage by barium trap. Suppression

Table 1
Comparison of the NO_x storage capability of the commercial catalyst and $BaCO_3/Al_2O_3$ material at 673 K.[a]

Sample	P_{CO_2} (%)	NO_x amount stored (mol/g_{Ba})
Commercial catalyst	10	0.49
Commercial catalyst	0	2.9
$BaCO_3/Al_2O_3$ catalyst	10	0.34
$BaCO_3$	10	Not measured

[a] Gas mixture composition: 340 ppm NO, 8 vol% O_2.

of CO_2 in the gas mixture significantly increases the NO_x storage capability of the catalyst (table 1), in good agreement with the mechanism proposed previously by Balcon et al. [10] suggesting that NO_x and CO_2 interact competitively with the same barium sites.

3.2. Bulk barium nitrate formation by interaction of bulk barium carbonate and NO_x

3.2.1. NO effect

A sample of bulk barium carbonate was treated at 773 K for 2 h in flowing nitrogen containing 340–3000 ppm of NO, in the absence of CO_2 and O_2. In no case NO_x storages were observed. After this treatment, the XRD pattern and IR spectra of these samples were still those of the bulk barium carbonate. It appeared that no interaction between NO and $BaCO_3$ could occur under these conditions. In fact, the NOx trap catalyst works in the presence of a reagent mixture containing both NO and O_2, which at the surface of the noble metal of the three-way catalyst reacts and yields NO_2. If, as often suggested in the literature [2,6–9], NO_x cannot interact with the sites of the barium trap, unless as NO_2, one could understand the inertness of bulk carbonate as regards to NO alone. The effect of NO_2 on this solid has now to be studied.

3.2.2. NO_2 effect

In order to verify whether the unsupported bulk barium carbonate can react with NO_2, a reagent mixture consisting of 3000 ppm NO, 8 vol% O_2 in nitrogen was sent at 673 K for 4 h over two successive beds, consisting respectively of Pt/SiO_2 for catalyst generating NO_2, and bulk barium carbonates. So, the bulk barium carbonate was submitted to a flowing NO_2 partial pressure in the absence of CO_2. After such a treatment the XRD pattern and infrared spectrum of the bulk carbonate were carried out. The presence of bulk barium nitrate was unambiguously evidenced by XRD (figure 1(b)). The NO_3^- ion was also clearly identified by the presence of the 1385 cm^{-1} infrared band (figure 2(b)). One can deduce that, in the experimental conditions used, the bulk barium carbonate has reacted with NO_2 to form bulk barium nitrate in sufficient quantity to be detected by XRD. An additional thermal treatment in flowing CO_2 can destroy this bulk barium nitrate, as shown by the disappearance of the XRD lines of $Ba(NO_3)_2$ (figure 1(c)), and the strong decrease of the intensity of the 1385 cm^{-1} IR band (figure 2(c)).

The preceding characterizations confirm that bulk barium carbonate interacts with NO_2 to form $Ba(NO_3)_2$, *in the absence of CO_2*. When submitted to a mixture containing CO_2 (340 ppm NO, 10 vol% O_2, 10 vol% CO_2) the bulk $BaCO_3$, as well as the large carbonate crystals identified on the support of the commercial catalyst, did not transform to bulk barium nitrate. In comparison to the commercial catalyst, pure bulk $BaCO_3$ does not store NO_x significantly, probably due to its too small surface area and subsequent poor reactivity.

3.3. NO_x storage properties of barium carbonate supported on alumina

The HRTEM study and EDX analysis of the sample of barium carbonate supported on alumina reveal two kinds of barium species on the support. Some large crystals of barium carbonate were observed ($Ba/(Ba + Al) = 0.25$), and a majority of well dispersed "barium" on the alumina surface was evidenced by EDX ($Ba/(Ba + Al) = 0.06$).

The NO_x storage properties of the barium carbonate supported on alumina were tested using the 340 ppm NO/8 vol% O_2/10 vol% CO_2/N_2 mixture as a second catalytic bed after the conversion of NO to NO_2 on a previous Pt/SiO_2 catalyst at 673 K. In contrast to the unsupported bulk barium carbonate, $BaCO_3/Al_2O_3$ has a NO_x storage capability of the same order but smaller than that of the commercial catalyst (table 1). The difference in NO_x storage activity for the two samples could be due to the fact that barium dispersion is different or to the fact that for the commercial sample the centers generating NO_2 (Pt, Rh) are intimately mixed with

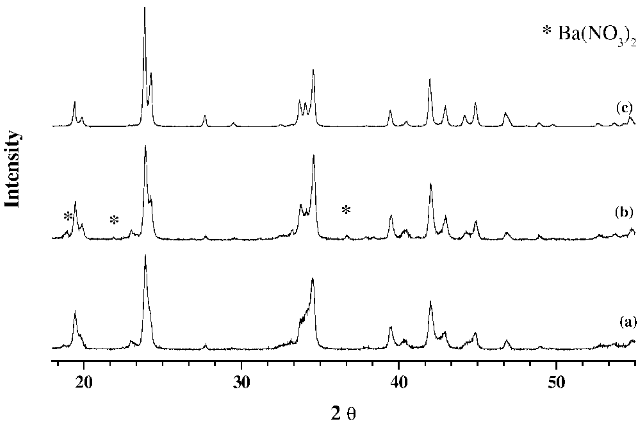

Figure 1. X-ray diffraction pattern of: (a) pure barium carbonate, (b) pure barium carbonate after NO_2 interaction at 673 K, (c) pure barium carbonate after NO_2 interaction at 673 K and thermal treatment at 823 K in CO_2.

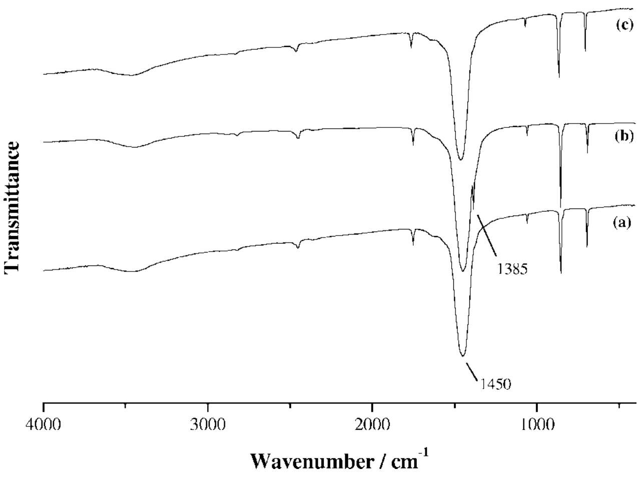

Figure 2. Infrared spectra in the 4000–500 cm^{-1} region of: (a) pure barium carbonate, (b) pure barium carbonate after NO_2 interaction at 673 K, (c) pure barium carbonate after NO_2 interaction at 673 K and thermal treatment at 823 K in CO_2.

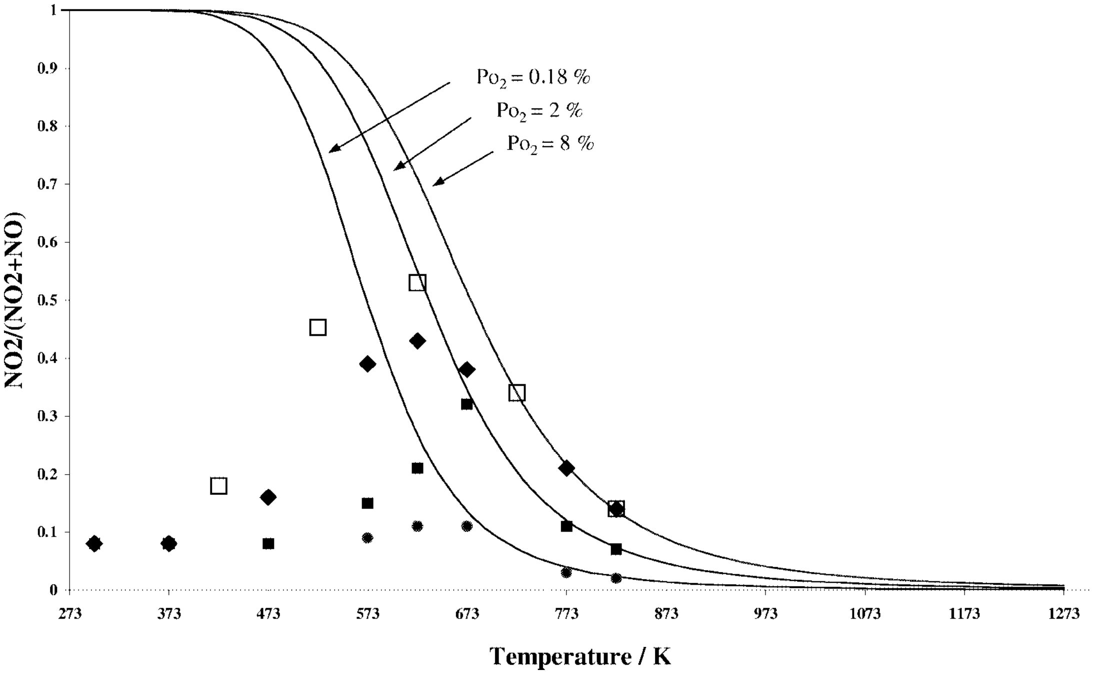

Figure 3. NO conversion into NO_2 as a function of temperature. *Theoretical thermodynamic curves* (solid lines) for three given values of the oxygen vol% in the gas mixtures: 8, 2, and 0.18%. Experimental curves for: (a) a Pt–SiO_2 (0.3 wt% Pt) catalyst with 340 ppm NO and O_2 vol% = 8 (◆), 2 (■), and 0.18 (•), (b) the commercial catalyst with 340 ppm NO and O_2 vol% = 8 (□).

the sites trapping NO_x (barium sites), which is not the case for $BaCO_3/Al_2O_3$ for which supported noble metals and barium are located in two separate beds. Some authors [9] consider that the NO_x storage mechanism involves the presence of both NO_2 and atomic oxygen. This could justify the lower trapping activity of the $BaCO_3/Al_2O_3$ on a separate catalytic bed.

It was previously shown that bulk barium nitrate could form *in the absence of CO_2*, by interaction of bulk barium carbonate and $NO_2/O_2/N_2$ mixture. It is now interesting to determine the thermodynamic conditions allowing the formation of bulk barium nitrate by interaction of bulk barium carbonate and a real reagent mixture containing 10 vol% CO_2.

3.4. Thermodynamic studies

3.4.1. Importance of the NO + $\frac{1}{2}O_2 \rightarrow NO_2$ reaction step

The reaction of oxidation of NO by O_2 to form NO_2 obviously represents an important step for NO_x storage by the barium compound since it is now well established that NO_x are trapped as NO_2,

$$NO + \tfrac{1}{2}O_2 \rightleftharpoons NO_2 \qquad (1)$$

The conversion (τ) of this reaction can be expressed as follows:

$$\tau = \frac{P_{NO_2}}{P_{NO} + P_{NO_2}} = \left[1 + \frac{1}{P_{O_2}^{1/2}\exp(-\Delta_r G^0_{(1)}/RT)}\right]^{-1},$$

where $\Delta_r G^0$ is the Gibbs energy of equilibrium (1).

Taking into account that the oxygen pressure is in comparison to that of NO, one can consider P_{O_2} as a constant. The $\tau = f(T)$ curve can be plotted for different values of oxygen pressure (figure 3). It clearly appears that (i) this reaction is thermodynamically limited for temperatures higher than 673 K, and (ii) for a given temperature, the conversion strongly depends on the value of oxygen pressure (figure 3). The $\tau = f(T)$ curve corresponding to the NO/O_2 reaction carried out on a 0.3 wt% Pt /SiO_2 catalyst, and the commercial catalyst were also recorded in figure 3. All these curves present a maximum of conversion for a temperature depending on the oxygen pressure. The catalytic effect of the metal as regards to the conversion is then thermodynamically limited.

So, for an oxygen pressure corresponding to lean-burn conditions (in our case 8 vol%), the higher NO_x conversion to NO_2 will be obtained in the 623–673 K temperature range.

3.4.2. The formation of bulk barium nitrate by interaction of bulk barium carbonate and $NO_2/O_2/CO_2/N_2$ mixture

The conditions for which reaction (2) can occur, can be determined by calculating $(\partial G/\partial\xi)_{T,P}$ (with ξ extent of reaction) of the reaction:

$$\begin{aligned} &BaCO_{3\ \mathrm{solid}} + 2NO_{2\ \mathrm{gas}} + \tfrac{1}{2}O_{2\ \mathrm{gas}} \\ &\quad \rightleftharpoons Ba(NO_3)_{2\ \mathrm{solid}} + CO_{2\ \mathrm{gas}} \end{aligned} \qquad (2)$$

$$\begin{aligned} \Delta_r G_{T,P} &= \left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta_r G^0_T \\ &\quad + RT\left[\ln\left(\frac{P_{CO_2}}{P_{O_2}^{1/2}}\right) - 2\ln P_{NO_2}\right]. \end{aligned} \qquad (3)$$

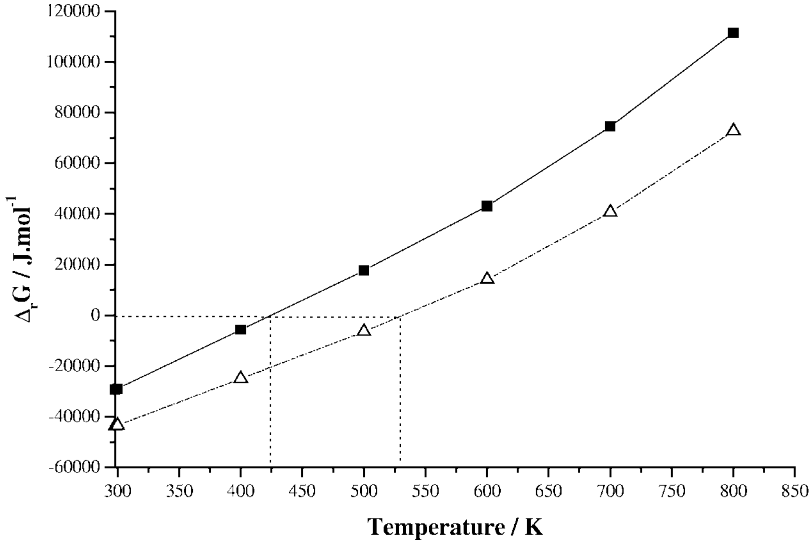

Figure 4. $(\partial G/\partial \xi)_{T,P}$ versus temperature, for the "barium carbonate → barium nitrate" reaction. $P_{O_2} = 0.08$ bar and $P_{NO_x} = 340 \times 10^{-6}$ bar. $P_{CO_2} = 0.1$ (■) and 3×10^{-4} (△) bar.

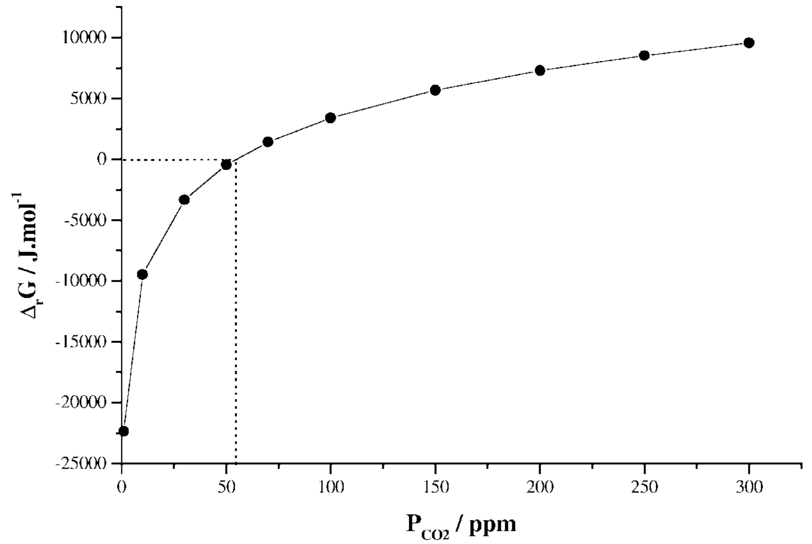

Figure 5. $(\partial G/\partial \xi)_{T,P}$ versus the CO_2 pressure at 673 K, for the "barium carbonate → barium nitrate" reaction. $P_{O_2} = 0.08$ bar and $P_{NO_x} = 1350 \times 10^{-4}$ bar.

Referring to thermodynamic data published by Kobayashi et al. [3], one can first calculate the value of $\Delta_r H^0 = -98535\ \mathrm{J\,mol^{-1}}$ and then $\Delta_r G_T^0$ versus temperature:

$$\begin{aligned}\Delta_r G_T^0 &= -RT \ln K \\ &= -RT(-11851.7)\left(\frac{1}{573} - \frac{1}{T}\right) + 7.72. \qquad (4)\end{aligned}$$

P_{NO_2} can then be expressed as a function of temperature, (equilibrium (1)):

$$P_{NO_2} = P_{NO_x}\left[1 + \frac{1}{P_{O_2}^{1/2} \exp(-\Delta_r G_{(1)}^0 / RT)}\right]^{-1},$$

where $\Delta_r G_{(1)}^0$ of the reaction is being calculated using the table of compound formations in [14].

Finally, it is possible to calculate $(\partial G/\partial \xi)_{T,P}$ versus temperature for reaction (2) (equation (3)).

In the experimental conditions used in this work, the reagent mixture contained 0.08 bar of oxygen, 3.4×10^{-4} bar of NO_x and 0.1 bar of CO_2 in nitrogen. The corresponding experimental curve representative of $(\partial G/\partial \xi)_{T,P}$ versus temperature is reported in figure 4. It is clear that the formation of bulk barium nitrate can only occur at a temperature less than 420 K. At 673 K, temperature at which NO conversion to NO_2 is known to be maximum, for the commercial catalyst working with 8 vol% O_2, one can plot the theoretical $(\partial G/\partial \xi)_{T,P}$ for the barium nitrate formation versus the CO_2 pressure in the reagent mixture. One can see (figure 5) that the formation of barium nitrate can only take place at very low partial pressure of CO_2, less than 54×10^{-6} bar.

4. Conclusion

In this work, we have shown that bulk barium carbonate can be partially transformed to bulk barium nitrate at 673 K, when submitted to a ($NO_x/O_2/N_2$) gas mixture. The bulk barium nitrate forms only in the presence of NO_2 and in the absence of CO_2. Barium carbonate was always identified on the surface of alumina of the stabilized catalyst. These post-combustion catalysts work at high temperatures (673 K) in the presence of gas exhausts containing high CO_2 contents (about 10 vol%). Thermodynamic calculations have evidenced that in these experimental conditions, bulk barium nitrate cannot form from the interaction of bulk barium carbonate and reagent mixture ($NO_x/O_2/CO_2/N_2$). The NO_3^- species evidenced by infrared spectroscopy concomitantly with the absence of XRD lines ascribable to bulk barium nitrate, could originate from the interaction of NO_2 with oxygen ions at the surface of the barium compounds dispersed on alumina. Note that the contribution of NO_3^- ions formed on the ceria additive or on alumina cannot be excluded [15].

In summary, it appears that for commercial catalysts with barium trap working in the presence of O_2 and CO_2: (i) NO contained in the gas exhaust has to be oxidized to NO_2 on the noble metal surface of the TWC, to be trapped over the barium compound; (ii) NO_2 and CO_2 compete for the same barium trapping sites. These sites can be either on the surface defects of the barium carbonate crystallites supported on alumina, or oxidic sites located in the vicinity of barium ions well dispersed on this support; (iii) the inertness of large crystallites of $BaCO_3$, presenting a low specific surface area for NO_x storage brings to the conclusion that the well dispersed barium phase over the alumina is probably the NO_x trapping sites.

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References

[1] N. Takahashi, H. Shinjoh, T. Iijima, T. Suzuki, K. Yamazaki, K. Yokota, H. Suzuki, N. Miyoshi, S. Matsumoto, T. Tanizawa, T. Tanaka, S. Takeishi and K. Kasahara, Catal. Today 27 (1996) 63.

[2] W. Bögner, M. Krämer, M. Krutzsch, B. Pischinger, D. Voigtländer, G. Wenninger, F. Wirbeleit, M.S. Brogan, R.J. Brisley and D.E. Webster, Appl. Catal. B 7 (1995) 153.

[3] T. Kobayashi, T. Yamada and K. Kayano, SAE Techn. paper, Ser. 970745 (1997).

[4] N. Fekete, M. Kemmler, D. Voitlander, B. Krutzsch, E. Zimmer, G. Wenninger, W. Strehlau, J.A.A. van den Tillaart, J. Leyrer, E.S. Lox and W. Müller, SAE Techn. paper, Ser. 970746 (1997).

[5] S. Hodjati, P. Bernardt, C. Petit, V. Pitchon and A. Kiennemann, Appl. Catal. B 19 (1998) 209.

[6] G. Mestl, S. Xie, M.P. Rosynek and J.H. Lunsford, J. Phys. Chem. B 101 (1997) 9329.

[7] S. Xie, M.P. Rosynek and J.H. Lunsford, J. Catal. 188 (1999) 24.

[8] E. Fridell, H. Persson, B. Westerberg, L. Olson and M. Skoglundh, Catal. Lett. 66 (2000) 71.

[9] E. Fridell, M. Skoglundh, B. Westerberg, S. Johansson and G. Smedler, J. Catal. 183 (1999) 196.

[10] S. Balcon, C. Potvin, L. Salin, J.-F. Tempère and G. Djéga-Mariadassou, Catal. Lett. 60 (1999) 39.

[11] L. Salin, C. Potvin, J.F. Tempère, M. Boudart and G. Djéga-Mariadassou, Ind. Eng. Chem. Res. 37 (1998) 469.

[12] P. Pascal, *Nouveau Traité de Chimie Minérale*, Vol. IV (Masson, Paris, 1956) p. 746.

[13] F.A. Miller and C.H. Wilkins, Anal. Chem. 24 (1952) 1253.

[14] D.R. Lide, ed., *Handbook of Chemistry and Physics* (CRC Press, Boca Raton, FL, 1996).

[15] R. Cataluna, A. Arcoya, X.L. Seoane, A. Martinez-Arias, J.M. Coronado, J.C. Conesa, J. Soria and L.A. Petrov, Stud. Surf. Sci. Catal. 96 (1995) 215.