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On the dynamic behavior of “NO_x-storage/reduction” Pt–Ba/Al_2O_3 catalyst

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Abstract

The NO_x storage and reduction functions of a Pt–Ba/Al_2O_3 “NO_x storage–reduction” catalyst has been investigated in the present work by applying the transient response and the temperature programmed reaction methods, by using propylene as the reducing agent. It is found that: (i) the storage of NO_x occurs first at BaO and then at $BaCO_3$, which are the most abundant sites following regeneration of catalyst with propylene; (ii) the overall storage process at $BaCO_3$ is slower than at BaO; (iii) CO_2 inhibits the NO_x storage at low temperatures; (iv) the amount of NO_x stored up to catalyst saturation at 350 °C corresponds to 17.6% of Ba; (v) the reduction of stored NO_x groups is fast and is limited by the concentration of propylene in the investigated T range (250–400 °C); (vi) selectivity to N_2 is almost complete at 400 °C but is significantly lower at 300 °C due to the formation of NO which can be tentatively ascribed to the presence of unselective Pt–O species. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: NO_x storage–reduction; Pt–Ba/Al_2O_3 catalyst; Temperature Programmed Surface Reaction

1. Introduction

The development of catalysts able to reduce NO_x in the presence of excess oxygen has become a topical problem nowadays [1]. Among the different solutions, the so-called NO_x storage–reduction (NSR) catalysts present interesting features [1–3]. These catalysts are constituted by a NO_x-storage component (e.g. an alkaline metal oxide), which stores NO_x under excess oxygen, and by a noble metal (Pt), which reduces the stored NO_x during a short reduction period.

In spite of the fact that these catalysts are currently used at a demonstrative scale, mechanistic and kinetic aspects of the reaction are not completely clarified yet. Accordingly, a study has been undertaken in our labs in order to investigate the NO_x storage and reduction functions of a Pt–Ba/Al_2O_3 catalyst sample by using propylene as reducing agent. The transient response method has been applied in a wide temperature range to clarify the dynamic characteristics of the process upon switching between lean (NO_x-storage) and rich (NO_x reduction) conditions. This allowed the separate analysis of the NO_x-adsorption and reduction steps, and accordingly quantitative information on the reactions involved in the storage and reduction stages could be obtained. The influence of carbon dioxide (which is typically present in the exhaust gases) on both the NO_x adsorption and reduction processes has also been investigated. Besides, the results of temperature programmed surface reaction (TPSR) experiments obtained upon storage of NO_x at different temperatures followed by reaction with propylene will be presented, aiming at a better understanding of the reaction

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sequence involved in the reduction of the stored NO_x species.

2. Experimental

A homemade Pt–Ba/Al_2O_3 (1/20/100 w/w) catalyst has been considered in this study, prepared by impregnation of a commercial γ-alumina support with Pt (first) and Ba (later) aqueous solutions (dinitrodiammine platinum and barium acetate, respectively). After each impregnation step, the catalyst powders were dried overnight at 80 °C in air and then calcined at 500 °C for 5 h. The surface area of the calcined sample is near 160 m^2/g.

XRD analysis pointed out the presence of crystalline $BaCO_3$ (orthorhombic whiterite); however a quantitative evaluation of XRD spectra indicated that less than 20% of the total Ba is present as crystalline $BaCO_3$ so that most of the Ba is actually well dispersed onto the catalyst surface. Evidence for the presence of carbonate species has also been provided by FTIR [5]. Further details on the catalyst characterization can be found elsewhere [4,5].

The NO_x storage–reduction capability of the catalyst has been investigated by transient experiments performed in a flow micro-reactor system. Rectangular step feed of NO (1000 ppm) in He + 3% (v/v) O_2 and of propylene (1000 ppm) in He have been alternatively forwarded to the reactor separated by a He purge, while continuously analyzing the gases exiting the reactor by mass spectrometry. Experiments have been performed at different temperatures in the range 250–400 °C; in each run 120 mg of catalyst (75–100 μm) were used and a total flow rate of 200 cm^3/min STP was maintained in the different phases. The experiments have been performed in the absence and in the presence of carbon dioxide (2000 ppm).

TPSR experiments were performed by saturating the catalyst with a stream of 1000 ppm NO in He + 3% O_2 (total flow rate = 200 cm^3/min STP) at a given temperature (in the range 250–400 °C). Then the catalyst was cooled to 40 °C in He + O_2 and eventually heated at 5 °C/min under flow of He + 800 ppm C_3H_6 (total flow rate = 200 cm^3/min STP). Further details on the experimental apparatus and procedures can be found elsewhere [4,5].

3. Results and discussion

3.1. NO_x adsorption

The catalyst must be conditioned before stable performances could be obtained. This has been accomplished by performing several NO_x adsorption–reduction cycles. After catalyst conditioning, a typical result obtained following a rectangular step feed of NO (NO_x storage phase) is shown in Fig. 1 for $T = 320\,^\circ C$. The outlet concentration of NO, NO_2, NO_x (=NO + NO_2) and CO_2 are displayed, along with that of the NO inlet concentration (NO_{IN}). Upon NO addition at $t = 0$ s, the NO outlet concentration shows a dead time, thus indicating that NO_x are stored on the catalyst surface. After ∼150 s the NO reactor outlet concentration increases with time, eventually reaching a steady-state value after ∼1000 s. A correspondent evolution of NO_2 is also observed, pointing out that NO is partially oxidized to NO_2. At steady-state, the NO_x concentration corresponds to the NO inlet concentration one. The area included between the NO inlet concentration trace and the outlet NO_x concentration is proportional to the amounts of NO_x stored on the catalyst surface. Values of stored NO_x near 1.84×10^{-4} mol/g_{cat} before NO_x breakthrough could be estimated from the data reported in Fig. 1, and near 5.53×10^{-4} mol/g_{cat} upon saturation. During the storage of NO_x, the evolution of CO_2 is also observed. Notably, CO_2 evolution exhibits a dead time of 50 s and occurs according to a tailing peak with maximum near 150 s.

Upon decreasing the NO inlet concentration back to zero ($t = 1200$ s), the outlet NO and NO_2 concentrations decrease showing a pronounced tail which is related to the desorption/decomposition of weakly adsorbed NO_x species.

The results herein presented suggest that the storage of NO_x involves different adsorption sites. As suggested in previous papers [4,5], NO_x adsorption may occur at BaO, $BaCO_3$ and $Ba(OH)_2$ sites. NO_x adsorption on BaO result in the formation of nitrite and nitrate species; nitrite and nitrate are also formed upon adsorption of NO_x on $BaCO_3$ and $Ba(OH)_2$, but in this case their formation is accompanied by the release of CO_2 and H_2O, respectively. Surface Ba carbonate species, which are the most abundant species under these experimental conditions, are

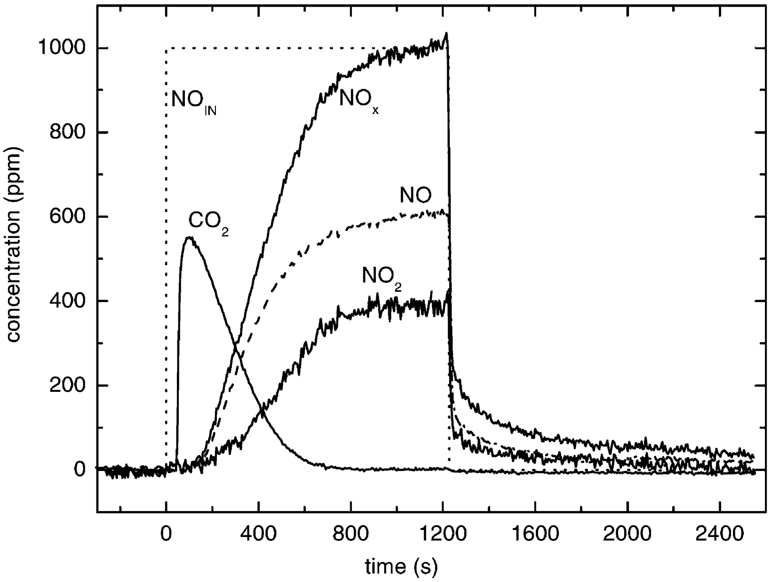

Fig. 1. Results of NO step addition (1000 ppm in He + 3% O_2) over Pt–Ba/Al_2O_3 at 320 °C. NO, NO_2, NO_x (=NO + NO_2) and CO_2 outlet concentrations with time.

displaced by NO_x with formation of nitrites/nitrates likely due to the higher acidity of NO_x species with respect to CO_2. It has been reported that the NO_x storage occurs preferentially in the order at BaO, $Ba(OH)_2$ and $BaCO_3$ [5]: the NO_x adsorption data presented in Fig. 1 further confirm this picture, with NO_x adsorbing at BaO sites first (no release of CO_2 or water) and at $BaCO_3$ sites later (accompanied by the release of CO_2 with a dead time of ~50 s). This order of reactivity is likely related to the greater basicity of BaO with respect to $BaCO_3$ and $Ba(OH)_2$. The lack of water evolution may indicate the absence of relevant amounts of $Ba(OH)_2$ after catalyst regeneration with propylene (see below). As a matter of facts, upon catalyst regeneration with hydrogen [5], water but not CO_2 desorption has been observed upon NO_x adsorption because H_2O instead of CO_2 was produced during catalyst regeneration, hence leading to the formation of $Ba(OH)_2$ instead of $BaCO_3$.

NO_x adsorption experiments have also been performed at different temperatures, in the range 250–400 °C. On increasing the catalyst temperature, an increase in the dead time of the NO_x concentration and in the system response after the dead time is observed. This behavior can be explained by considering that the NO_x adsorption process is activated and/or that temperature affects the BaO/$BaCO_3$ ratio. This leads to an increase of the amount of NO_x accumulated on the catalyst surface before the NO_x breakthrough, i.e. from 1.01×10^{-4} mol/g_{cat} at 250 °C to 3.17×10^{-4} mol/g_{cat} at 400 °C. Also, an increase in the dead time of CO_2 evolution is observed, suggesting an increase of the amounts of BaO species with respect to $BaCO_3$. Notably, the amounts of NO_x desorbed upon decreasing the inlet NO concentration at the end of the NO step also increases with temperature. As a result, the net amounts of NO_x stored onto the catalyst surface shows a maximum of 4.3×10^{-4} mol/g_{cat}, at 350 °C, corresponding to 17.6% of Ba involved in the form of Ba nitrite or nitrate. These data well compare with literature indications [6], and are lower if compared with those obtained measured when H_2 is used as a reducing agent. This is possibly due to the fact that storage at $BaCO_3$ is less favored than at BaO/$Ba(OH)_2$.

3.2. NO_x reduction

The reduction of the stored NO_x (i.e. catalyst regeneration) has been carried out by imposing a C_3H_6

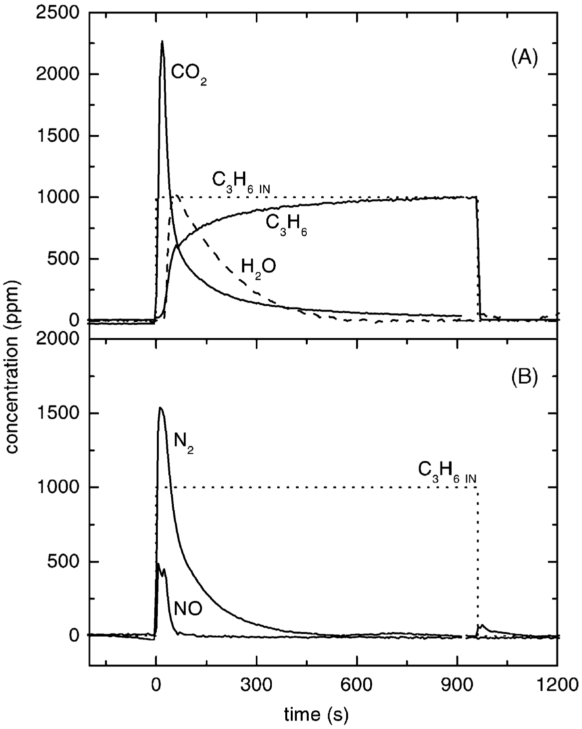

Fig. 2. Results of C_3H_6 step addition (1000 ppm in He) over Pt–Ba/Al_2O_3 at 320 °C. (A) C_3H_6, CO_2 and H_2O reactor outlet concentrations with time; (B) NO and N_2 reactor outlet concentrations with time.

step in He. The results are shown in Fig. 2, in terms of C_3H_6, H_2O, CO_2 (Fig. 2A) and N_2, NO (Fig. 2B) outlet concentrations with time for $T = 320\,^{\circ}C$, along with that of the C_3H_6 inlet concentration ($C_3H_{6\,in}$).

Upon C_3H_6 admission ($t = 0$ s), the reduction reaction starts and consumes the NO_x previously adsorbed onto the catalyst surface; accordingly the C_3H_6 outlet concentration profile shows a dead time during which it is completely consumed by the reaction; then it slowly increases up to the inlet concentration value. A correspondent evolution of N_2, H_2O and CO_2, major products of the reduction, is observed. A sharp NO desorption peak is also observed, along with minor quantities of N_2O detected by gas chromatography (not reported in the figure). A NO desorption peak upon switching from lean to rich conditions as also been observed by Fridell et al. [7]. The reaction appears to be very fast, fairly selective to molecular nitrogen (≈96%) and limited by the propylene gaseous concentration.

Reduction of stored nitrites and nitrates occurs according to the following stoichiometries:

$$3Ba(NO_2)_2 + C_3H_6 \rightarrow 3N_2 + 3CO_2 + 3H_2O + 3BaO \quad (1)$$

$$9Ba(NO_3)_2 + 5C_3H_6 \rightarrow 9N_2 + 15CO_2 + 15H_2O + 9BaO \quad (2)$$

The ratio between the amounts of CO_2 and of N_2 evolved during the reduction phase is in the range expected for reactions (1) and (2). Assuming that the most abundant species are nitrates [5], the evolved CO_2 is lower than that expected for reaction (2): this is likely due to the carbonation of BaO sites made available following the reduction of surface nitrites/nitrates:

$$BaO + CO_2 \rightarrow BaCO_3 \quad (3)$$

This result is also consistent with the observed evolution of CO_2 during the NO_x adsorption phase.

Along similar lines, the time delay (30 s) monitored for water can be explained by considering that it is involved in adsorption processes onto the catalyst surface, possibly onto BaO sites (either available at the catalytic surface before reduction or restored upon reduction of nitrates/nitrite species to form $Ba(OH)_2$) and/or onto the alumina support. It is noted that water desorption still continues when the carbon dioxide concentration level is restored to the background value (above 500 s in Fig. 2); this fact may indicate that at the end of the reduction period $Ba(OH)_2$ species are transformed to BaO species with release of water.

Similar results have been obtained at the other investigated temperatures; notably, the higher the temperature, the smaller the NO desorption peak detected upon the C_3H_6 switch (200 ppm at 400 °C vs. 1100 ppm at 300 °C). This feature can be related with the reduction of Pt–O species to metal Pt and with the lower efficiency of the oxidized Pt species in the NO_x reduction if compared to the metal Pt, as discussed in the following.

3.3. *Carbon dioxide effect on the storage–reduction of NO_x*

Transient experiments have been also performed in presence of CO_2 (≈2000 ppm) to investigate its

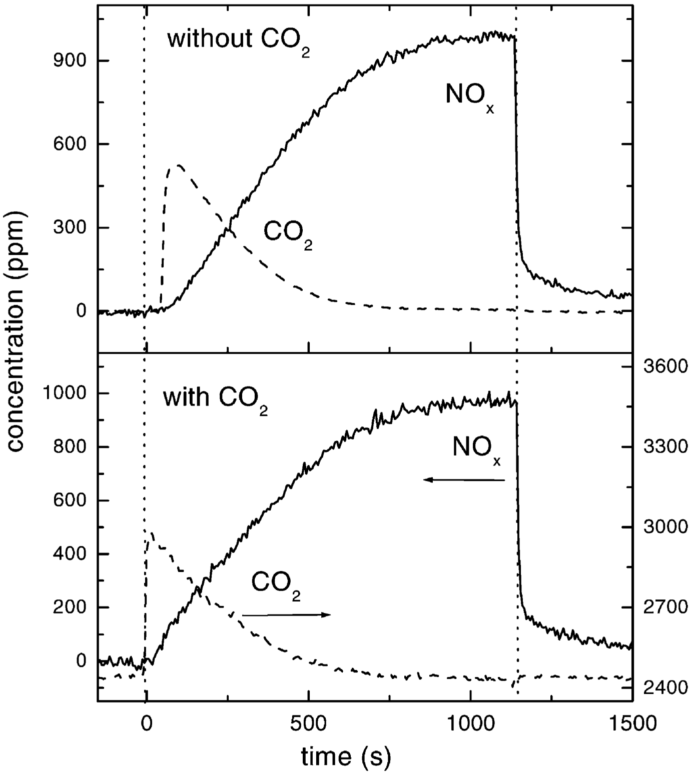

Fig. 3. Comparison between the results of NO step addition performed at 300 °C in the presence and the absence of CO_2 in the feed stream.

role on both the NO_x adsorption and reduction processes. Fig. 3 presents a comparison between the NO_x storage processes performed at $T = 300\,^{\circ}C$ in the presence and in the absence of CO_2 in the feed stream. By comparing the NO_x outlet concentration traces it appears that the presence of carbon dioxide significantly reduces the time for NO_x breakthrough and affects the rate of the adsorption process. This results in a smaller NO_x storage capability of the catalyst, which at 300 °C is reduced by more than 20% (3.2×10^{-4} vs. $4.1 \times 10^{-4}\,mol/g_{cat}$). Similar results have been collected with 2% CO_2, which indicates that the storage behavior is not much modified on increasing the CO_2 content above 0.2%. Notably, in the presence of gas-phase CO_2, the carbon dioxide outlet concentration does not present any dead time upon NO admission to the reactor, and is consistent with the stoichiometry of the formation of Ba nitrite/nitrate from $BaCO_3$. Similar results have also been reported on the literature [8]. Accordingly, it is speculated that in this case the adsorption of NO_x involves almost exclusively $BaCO_3$ species due to the complete conversion of BaO and $Ba(OH)_2$ into $BaCO_3$ in the presence of CO_2 in the gas phase.

Similar results have been obtained at different temperatures; however it has been observed that the higher the temperature, the lower is the effect of CO_2 if compared to the CO_2-free environment. This is likely related to a kinetic effect on the Ba carbonate–nitrate exchange reaction.

The effect of CO_2 on the reduction phase has also been analyzed. The results, here not reported, indicated a negligible effect of gas-phase CO_2 on the reduction of the stored NO_x: indeed also in this case the reaction is fast and is limited by the concentration of C_3H_6. The reduction of NO_x leads to the formation of N_2 as the major reaction product, along with CO_2 and H_2O. Also in this case, in addition to N_2, non-negligible amounts of NO are measured, particularly at low temperature.

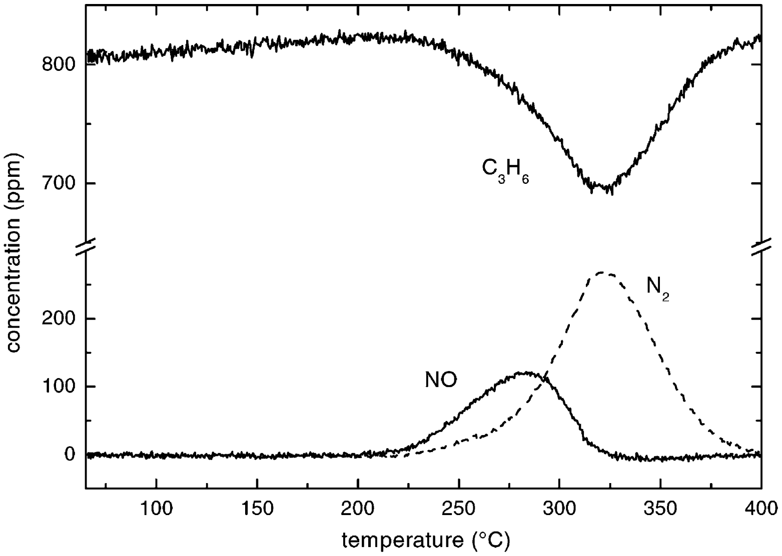

Fig. 4. Results of TPSR runs obtained after saturation with NO + 3% O_2 in He of the Pt–Ba/Al_2O_3 catalyst at 300°, C_3H_6, NO and N_2 concentration profiles as a function of temperature.

3.4. TPSR experiments

Finally, TPSR experiments following NO_x storage at different temperatures (in the range 250–400 °C) have been carried out to address the reactivity of propylene in the reduction of the stored NO_x species. Fig. 4 shows the results of TPSR runs obtained after saturation at $T = 300\,^{\circ}C$ in terms of C_3H_6, NO and N_2 concentration profiles with temperature. Upon heating, the temperature threshold for propylene consumption is observed near 225 °C. From the same temperature evolution of nitrogen, NO, CO_2 and water (these last two species not reported in the figure) is also monitored.

As shown in the figure, the stored NO_x group are primarily reduced to N_2, but significant amounts of NO are also formed. Notably, the NO evolution is observed at lower temperatures if compared to nitrogen, and at temperatures well below those corresponding to the NO_x storage (225 vs. 300 °C). Accordingly, it can be argued that NO formation is not related to a desorption–decomposition process involving the surface nitrite and/or nitrate species, but more likely derives from the unselective reduction of the stored NO_x species. It is speculated that the NO formation is associated with the presence of Pt–O species, which are reduced by propylene during the heating ramp into more selective Pt species. Accordingly, once the Pt–O surface species have been reduced to Pt, the reaction selectively proceeds towards the formation of nitrogen. A similar hypothesis may be invoked to explain the NO peak observed upon catalyst regeneration during the NO adsorption–reduction cycles previously described.

Similar results have also been obtained changing the NO_x storage temperature. The temperature onset for propylene consumption is always evident near 200–230 °C, whereas by increasing the adsorption temperature the N_2/NO ratio in the reaction products increases, thus indicating an increase of the process selectivity. This is possibly related to the higher rate of the Pt–O reduction to metal Pt, which favors the selective reduction of the adsorbed NO_x.

4. Conclusions

The results of our work can be summarized as follows:

- The storage of NO_x occurs at BaO, $BaCO_3$ and $Ba(OH)_2$ species. $BaCO_3$ is most abundant under the experimental conditions employed in this work and is partially restored upon reduction of the stored

NO_x by propylene; only minor amounts of BaO and negligible quantity of $Ba(OH)_2$ are formed upon catalyst regeneration.

- NO_x storage over BaO directly results in the formation of adsorbed nitrite/nitrate species whereas over $BaCO_3$ it leads to the additional evolution of CO_2.
- The storage of NO_x occurs at BaO first and then at $BaCO_3$.
- CO_2 inhibits the NO_x storage, particularly at low temperatures; the CO_2 inhibition tends to vanish at high temperatures.
- The overall amount of NO_x stored on the catalyst is considerable, and corresponds to 17.1% of Ba as Ba nitrite or nitrate.
- The reduction of stored NO_x groups is fast, and is limited by the concentration of C_3H_6 in the 250–400 °C temperature range. Indeed TPSR runs confirmed that the temperature onset of propylene consumption is around 200–230 °C, depending on the NO_x storage temperature.
- The selectivity of the reduction process is high, being close to 99% at 400 °C. Major unselective reaction product is NO; only minor amounts of N_2O have been determined.
- The formation of NO observed during the reduction process is ascribed primarily to the presence of Pt–O since the selectivity of the process increases for all the conditions favoring the transformation of Pt–O to Pt metal.

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