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# Role of support in lean DeNO<sub>x</sub> catalysis

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FTIR and pulse thermal analysis were applied to investigate catalysts containing Pt (1 wt%)/Ba (17 wt%) supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and ZrO<sub>2</sub>. The aim was to learn how the support material affects the thermal stability of barium carbonate and its activity in the reaction to bulk Ba(NO<sub>3</sub>)<sub>2</sub>. The lower thermal stability of BaCO<sub>3</sub> in alumina supported samples was found to influence the formation of barium nitrate during the NO<sub>x</sub> storage process. Quantification of Ba(NO<sub>3</sub>)<sub>2</sub> formed during NO<sub>x</sub> storage indicated that for alumina supported catalysts only ca. 30% of barium present in the sample is involved in the storage process. The low thermal stability found for alumina supported barium nitrite excludes its role in the formation of barium nitrate during interaction of NO<sub>x</sub> with the catalyst at 300 °C. The studies indicate that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> plays a major role in influencing the thermal stability of BaCO<sub>3</sub> and Ba(NO<sub>3</sub>)<sub>2</sub>. This finding seems to be relevant for the higher activity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported catalysts in NO<sub>x</sub> storage reduction reactions.

**KEY WORDS:** Lean DeNO<sub>x</sub>; BaCO<sub>3</sub>; Ba(NO<sub>3</sub>)<sub>2</sub> and Ba(NO<sub>2</sub>)<sub>2</sub> thermal stability; pulse thermal analysis; role of the support in NO<sub>x</sub> storage.

## 1. Introduction

Lean burn engines, working with an air/fuel ratio of about 22 (by weight), instead of the actual 14.6, have been developed mainly for improving fuel economy. Under these conditions conventional three ways catalysts (TWC) are not capable to reduce NO<sub>x</sub> species due to lack of reducing agent in the exhaust gases. Among all the proposed solutions, the most promising are the NO<sub>x</sub> storage catalysts: they trap NO<sub>x</sub> when the engine works at lean conditions, and reduce adsorbed NO<sub>x</sub> during a brief interval in which the engine runs at rich conditions.

NO<sub>x</sub> storage catalysts for mixed lean conditions containing Al<sub>2</sub>O<sub>3</sub>-supported noble and alkaline earth metals were patented by Toyota [1] in 1994. In 1996, Takahashi *et al.* [2] proposed a storage mechanism in which NO is oxidized on Pt to NO<sub>2</sub>, then stored as Ba(NO<sub>3</sub>)<sub>2</sub> and subsequently reduced by HC activated on Pt sites. The primary role of Ba as storage compound was shown in [3–5], whereas some debate is still open about the kind and amount of Ba containing species active during NO<sub>x</sub> storage. Applying TPD on activated catalysts Prinetto *et al.* [5] estimated that 50% of Ba is present as BaCO<sub>3</sub> which is subsequently decomposed by the formation of bulk Ba(NO<sub>3</sub>)<sub>2</sub>. Nova *et al.* [6] found that only 17% of Ba present in the catalyst is involved in the process of NO<sub>x</sub> storage.

*In situ* FTIR studies were performed by several authors [5–11] showing the formation of both nitrite and nitrate species during storage of NO/O<sub>2</sub>. Li *et al.* [12] stated that the higher the adsorption temperature, the higher is the concentration of nitrate compared to nitrite. Although several studies on selective catalytic

reduction of NO with SiO<sub>2</sub>, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>-supported Pt catalysts were made [13–35], relatively little attention has been given so far to the influence of the support on NO<sub>x</sub> storage behavior. It is not clear yet how the support material affects the stability and the chemical transformation of the Ba constituent. Higher dispersion and possible support interaction can lower the thermal stability of these components.

Here, we studied the influence of the support on the stability of BaCO<sub>3</sub> and on the formation of Ba(NO<sub>3</sub>)<sub>2</sub> using thermoanalytical methods and DRIFT-spectroscopy. The relative amount of Ba species which is active in the storage of NO by formation of nitrate species is determined.

## 2. Experimental

Catalysts were prepared via wet impregnation of the supports using the procedure described in [11]. Commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (BET surface area 210 m<sup>2</sup>/g), SiO<sub>2</sub> (200 m<sup>2</sup>/g) and ZrO<sub>2</sub> (60 m<sup>2</sup>/g) were impregnated with precursor solutions of Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> and Ba(CH<sub>3</sub>COO)<sub>2</sub> to a final loading of active metals of 1 wt% Pt and 17 wt% Ba. Catalysts were then dried at 80 °C for 12 h and finally calcined at 500 °C for 5 h.

XRD analysis was carried out on a Siemens D5000 powder X-ray diffractometer using the Cu -K $\alpha$  radiation in step mode between 10 and 80° 2 $\theta$ , with a step of 0.01° and 0.3 s step<sup>-1</sup>.

Thermogravimetry (TG) combined with mass spectrometry (MS) was performed on a Netzsch STA 409 thermoanalyzer which was connected to a valve device enabling pulse thermal analysis (Pulse TA<sup>®</sup>). This set-up [36] allows the injection of controlled amounts (0.5–5 mL) of probe gas into a carrier gas stream flowing through the thermoanalyzer. The composition of the gas

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phase was monitored by a Balzers QMC 420 quadrupole mass spectrometer, which was connected to the thermoanalyzer by a heated (ca. 200 °C) stainless steel capillary. The experiments were carried out with 40,0 mg samples using 5 vol% O<sub>2</sub> in He or pure He when investigating the desorbed species from samples previously exposed to NO<sub>x</sub> at 300 °C. In non-isothermal experiments the heating rate was 10 K/min.

DRIFT analysis was performed on a Bruker IFS 55 spectrometer. A Praying Mantis Diffuse Reflection attachment (DRA) coupled with a HVC-DRP2 reaction chamber (Harrick) was used. The composition of the gas phase was monitored by an Omnistar GSD 310 02 quadrupole mass spectrometer, which was connected to the DRIFT cell by a stainless steel capillary. Isothermal measurements were conducted at 300 °C while in non-

isothermal experiments the heating rate was 6.5 K/min. Sample temperature was controlled with a thermocouple directly in contact with the catalyst powder. Spectra were recorded at a resolution of 4 cm<sup>-1</sup> and bulk, KBr diluted, BaCO<sub>3</sub>, Ba(NO<sub>3</sub>)<sub>2</sub>, Ba(NO<sub>2</sub>)<sub>2</sub>, Ba(OH)<sub>2</sub> and BaO were also measured and used as reference spectra.

### 3. Results and discussion

#### 3.1. Thermal stability of barium carbonate

Temperature-programmed desorption experiments were performed with alumina, silica and zirconia-supported catalysts.

Evolution of CO<sub>2</sub> from catalysts stored at ambient conditions is shown in figure 1 for the Pt/Ba/Al<sub>2</sub>O<sub>3</sub>,

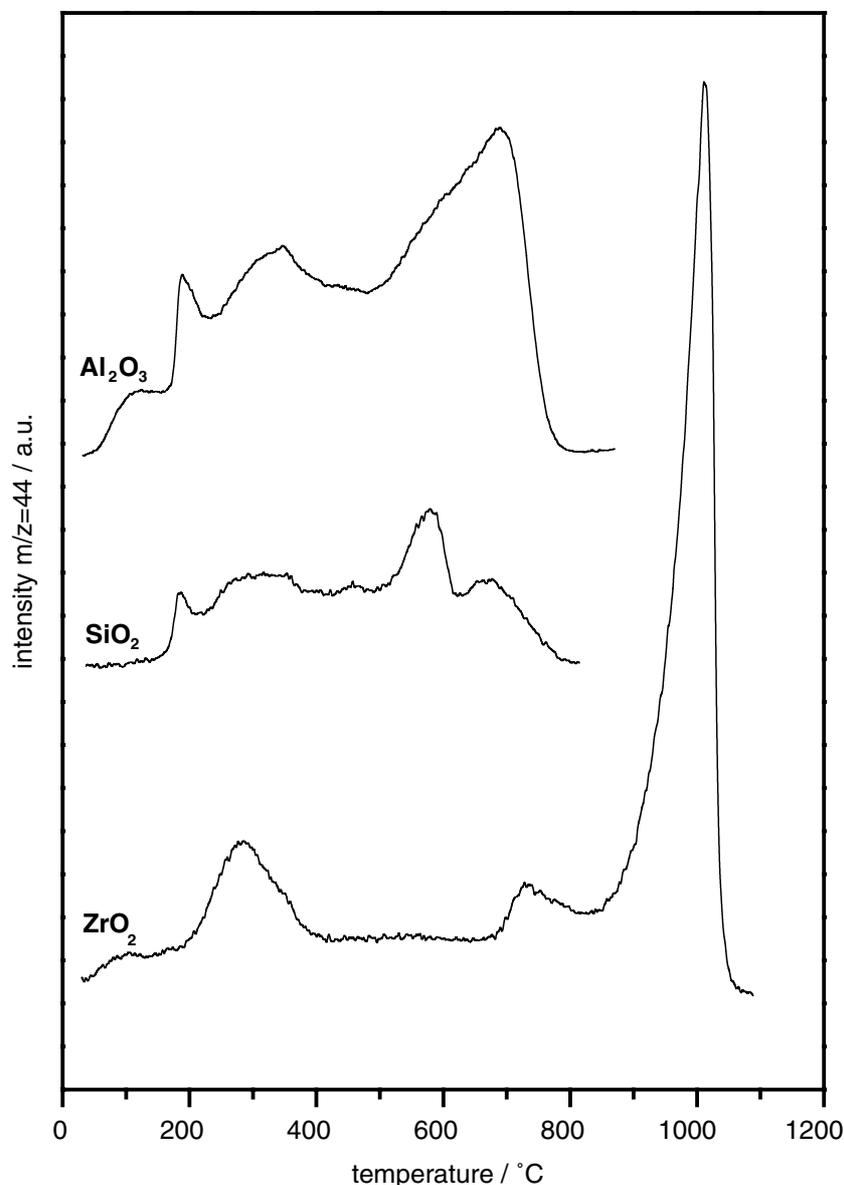


Figure 1. Evolution of CO<sub>2</sub> from catalysts containing Pt 1 wt% and Ba 17 wt% on different supports (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>) during TPD experiments carried out with TG-MS system.

Pt/Ba/SiO<sub>2</sub> and Pt/Ba/ZrO<sub>2</sub> samples. Four CO<sub>2</sub> desorption peaks can be observed for the Al<sub>2</sub>O<sub>3</sub>-supported sample appearing at ca. 100, 200, 350 and 680 °C, respectively. The first signal (around 100 °C), which appears with alumina and zirconia-supported catalysts, is due to weakly adsorbed monodentate and bidentate CO<sub>2</sub> [37] as confirmed by *in situ* DRIFT analysis (figure 2).

The sharp peak observed around 190–200 °C is very likely related to the combustion of adsorbed hydrocarbons, catalyzed by the presence of Pt. The disappearing of some peaks recorded by DRIFT related to C-H bonds starts around 150–160 °C (figure 2). The peak at 350 °C is due to evolution of CO<sub>2</sub> species more strongly bound to Al<sub>2</sub>O<sub>3</sub> [5,38] as confirmed by TPD with pure alumina (not shown) and CO<sub>2</sub> species stemming from decomposition of BaCO<sub>3</sub> which starts around 250–300 °C, as evidenced by DRIFT analysis. The rate of decomposition of BaCO<sub>3</sub> reaches its maximum around 680 °C, and rapidly decreases to zero at around 800 °C.

Note that the SiO<sub>2</sub>-supported sample behaves similarly as the Al<sub>2</sub>O<sub>3</sub>-supported one till 500 °C (figure 1), at higher temperatures CO<sub>2</sub> evolves in two peaks (at 580 and 680 °C). This is probably related to the fact that for the alumina-supported sample XRD analysis had shown a considerable amount of crystalline BaCO<sub>3</sub>, whereas in the SiO<sub>2</sub>-supported sample the amount of crystalline BaCO<sub>3</sub> was neglectable and the major part of carbonates was present in amorphous form. The coexistence of crystalline and amorphous BaCO<sub>3</sub> led probably to its decomposition in two distinct temperature regions.

For ZrO<sub>2</sub>-supported catalyst a prominent evolution of CO<sub>2</sub> occurs in the range of 820–1080 °C with a maximum at around 1000 °C. The decomposition of BaCO<sub>3</sub> is accompanied by the reaction of BaO with

ZrO<sub>2</sub> resulting in formation of BaZrO<sub>3</sub>, as corroborated by XRD analysis.

Results of DRIFT analysis of Pt/Ba/Al<sub>2</sub>O<sub>3</sub> heated with a rate of 6.5 °C/min from 30–234 °C in 5% O<sub>2</sub>/Ar are presented in figure 2.

Bands at 1660 cm<sup>-1</sup> and those at 1530, 1370 cm<sup>-1</sup> can be related to bidentate and monodentate CO<sub>2</sub>. Bands at 2852 and 2931 cm<sup>-1</sup> are assigned to C–H bonds originating from the presence of organic species which were adsorbed on the surface during exposure to air. The signal at 1660 cm<sup>-1</sup> disappears completely at 190 °C. The two peaks characteristic to C–H bonds decrease in intensity above 160 °C. The simultaneously recorded mass spectrometric signal of *m/z* = 32 (not shown) confirmed the consumption of oxygen due to oxidation of adsorbed hydrocarbons resulting in formation of the CO<sub>2</sub> signal centered at ca. 200 °C (figure 1).

Comparison between Kubelka–Munk transformed DRIFT spectra of Ba/Al<sub>2</sub>O<sub>3</sub> samples taken before and after the TPD at 300 °C (not reported) showed a decrease in intensity of bands due to BaCO<sub>3</sub> indicating the decomposition of carbonates. Decomposition of BaCO<sub>3</sub> species sets in between 200 and 300 °C.

In figure 3 a comparison of thermal stability between bulk BaCO<sub>3</sub> and BaCO<sub>3</sub> supported on Pt/Al<sub>2</sub>O<sub>3</sub> is presented. Note that, on Pt/Al<sub>2</sub>O<sub>3</sub>, BaCO<sub>3</sub> starts to decompose at a much lower temperature than unsupported pure BaCO<sub>3</sub>, which is stable till 800 °C. The same behavior was observed for the Pt/SiO<sub>2</sub>-supported BaCO<sub>3</sub>, whereas BaCO<sub>3</sub> on Pt/ZrO<sub>2</sub> starts to decompose at about 700 °C. Also in this case, BaCO<sub>3</sub> decomposition is completed much earlier than for bulk BaCO<sub>3</sub> (1080 and 1380 °C, respectively), because BaO formed during decomposition reacts immediately with ZrO<sub>2</sub>

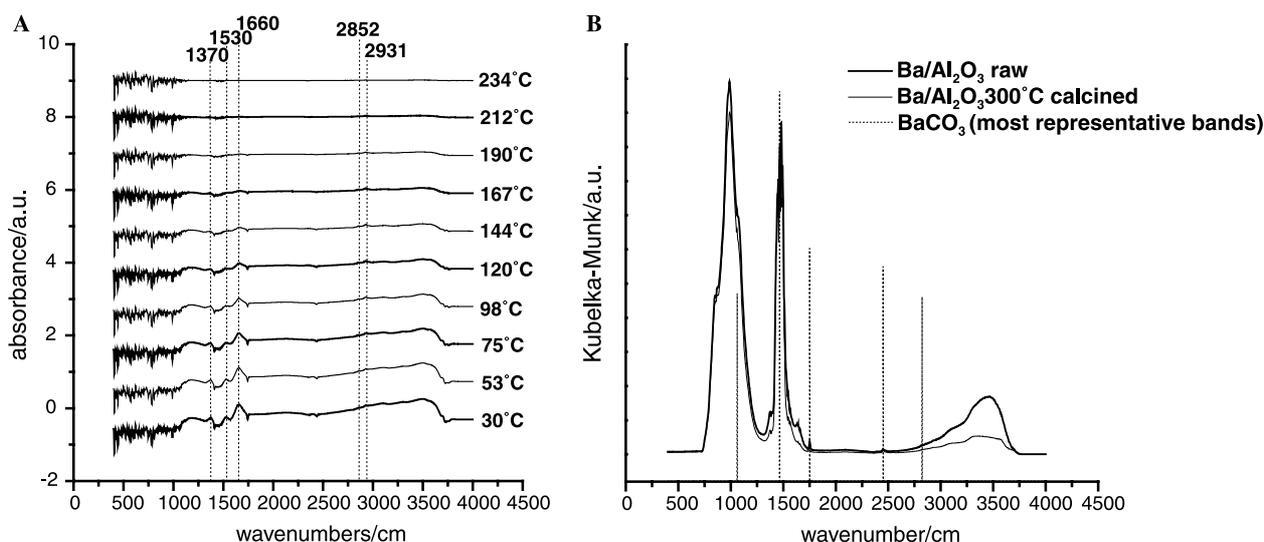


Figure 2. *In situ* DRIFT analysis of Pt/Ba/Al<sub>2</sub>O<sub>3</sub>. A. Spectra taken at different temperatures during TPD. Assignment of the bands: 1660 cm<sup>-1</sup> bidentate CO<sub>2</sub>, 1530 and 1370 cm<sup>-1</sup> monodentate CO<sub>2</sub>, and 2852 and 2931 cm<sup>-1</sup> C–H bond. B. TPD of Ba/Al<sub>2</sub>O<sub>3</sub>. Note the decrease in the intensity of the Kubelka–Munk transformed signal characteristic for BaCO<sub>3</sub>. Band 3000–3750 cm<sup>-1</sup> is due to OH-groups and therefore is related to evolution of water.

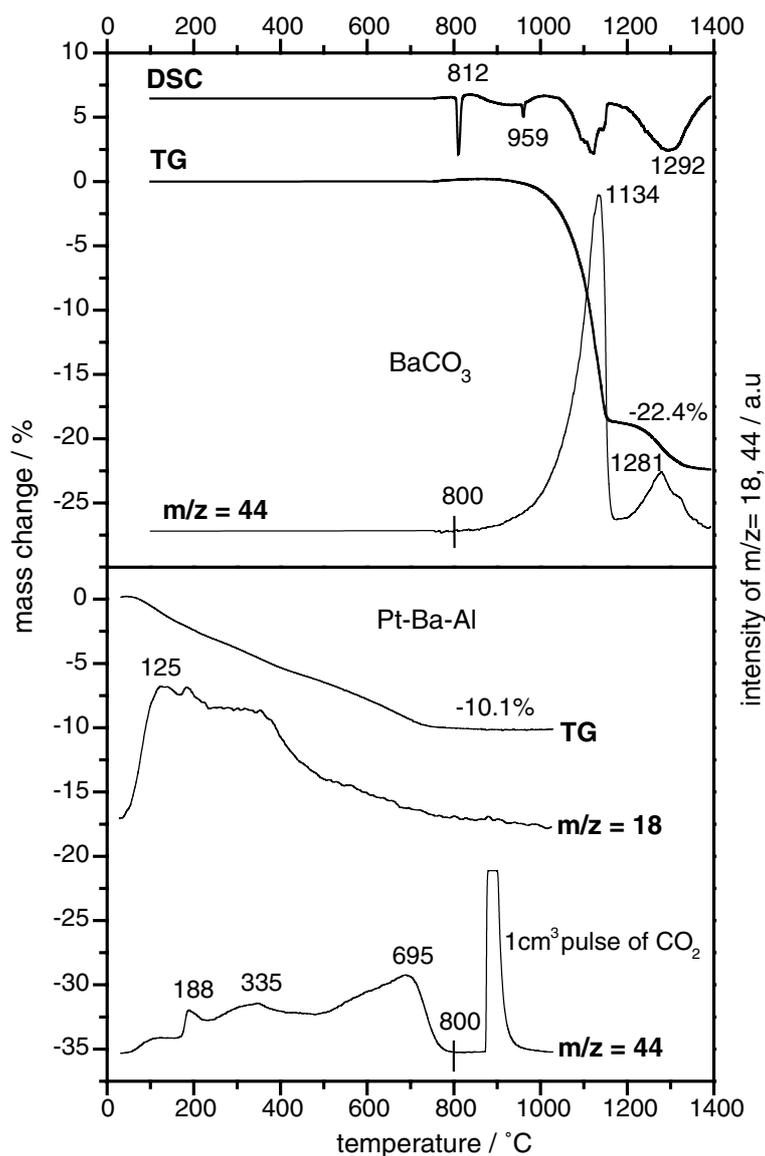


Figure 3. Comparison of decomposition of pure unsupported (top) and Pt/Al<sub>2</sub>O<sub>3</sub> supported (bottom) BaCO<sub>3</sub> investigated by TA-MS. Changes of the mass (TG), thermal effects (DSC) and mass spectrometric signals of water ( $m/z = 18$ ) and CO<sub>2</sub> ( $m/z = 44$ ) are recorded during calcinations. The amount of CO<sub>2</sub> evolved from supported sample was quantified by PulseTA technique by injection of 1 cm<sup>3</sup> of CO<sub>2</sub> after decomposition.

forming BaZrO<sub>3</sub>. The equilibrium of the decomposition reaction is consequently shifted and the decomposition is enhanced.

Table 1 lists the overall amount of CO<sub>2</sub> evolved from the raw catalysts during TPD experiments. The amount of CO<sub>2</sub> was determined using the PulseTA [36] technique by comparing the integral intensity of the CO<sub>2</sub> signal evolved during decomposition with the intensity of injected calibration pulses (1 cm<sup>3</sup>) of CO<sub>2</sub>. Quantitative analysis of Ba present as BaCO<sub>3</sub> based on the evolution of CO<sub>2</sub> during TPD experiments has been applied in another study [5]. In most cases, these analyses were performed with samples pretreated at 500 °C. Our results indicate that supported BaCO<sub>3</sub> starts to decompose at lower temperatures, around 250–300 °C. Thus it seems likely that previously reported

Table 1  
CO<sub>2</sub> content in 40.00 mg samples of tested catalysts (in mg) determined by TA-MS

Support	Supported metal	Ba-doped supported metal	Ba-doped support
Al <sub>2</sub> O <sub>3</sub>	Pt/Al <sub>2</sub> O <sub>3</sub>	Pt/Ba/Al <sub>2</sub> O <sub>3</sub>	Ba/Al <sub>2</sub> O <sub>3</sub>
0.19	1.73	2.18	2.46
SiO <sub>2</sub>	Pt/SiO <sub>2</sub>	Pt/Ba/SiO <sub>2</sub>	–
0.14	0.70	0.82	–
ZrO <sub>2</sub>	Pt/ZrO <sub>2</sub>	Pt/Ba/ZrO <sub>2</sub>	–
0.29	0.25	2.23	–

BaCO<sub>3</sub> contents [5] are affected by the surprisingly low thermal stability of this material when supported on alumina and silica.

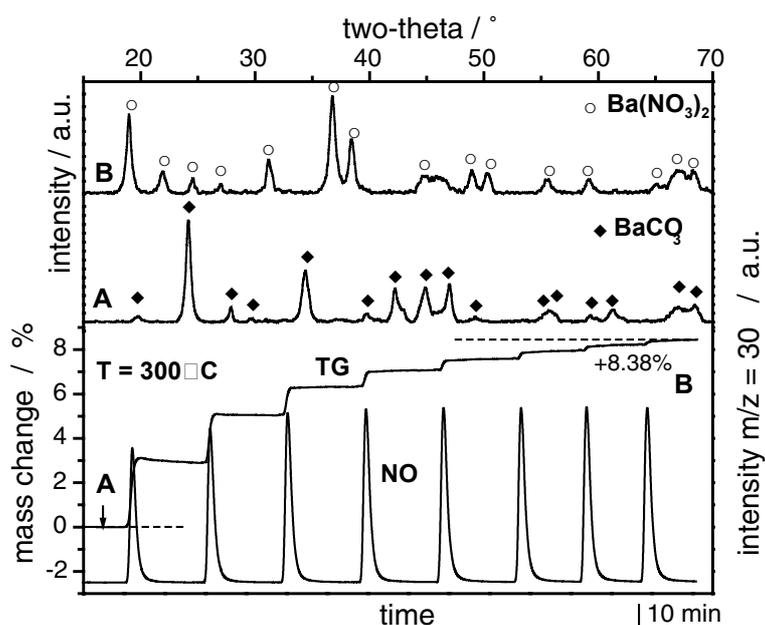


Figure 4. NO adsorption studied by PulseTA. Pulses of NO in 5% O<sub>2</sub>/He were passed over alumina supported Pt/Ba catalyst at 300 °C resulting in formation of Ba(NO<sub>3</sub>)<sub>2</sub> (B) from BaCO<sub>3</sub> (A).

### 3.2. Interaction of NO with the catalysts

The interaction of NO with the catalysts based on different supports was investigated using the PulseTA method. Pulses of NO (1 cm<sup>3</sup>) in 5% O<sub>2</sub>/He carrier gas were passed over the supported Pt/Ba catalysts at 300 °C. A representative experiment performed with Pt/Ba/Al<sub>2</sub>O<sub>3</sub> is presented in figure 4. XRD analysis of the raw catalysts (figure 4, patterns A) revealed the presence of crystalline BaCO<sub>3</sub> in line with TEM analysis, which showed clusters of BaCO<sub>3</sub> up to 60 nm in size. Pulses of NO led to mass gain of the sample.

XRD analysis of the Pt/Ba/Al<sub>2</sub>O<sub>3</sub> sample after exposure to NO pulses (figure 4, patterns B), corroborated the complete disappearance of BaCO<sub>3</sub> and the formation of crystalline Ba(NO<sub>3</sub>)<sub>2</sub>. BaCO<sub>3</sub> decomposition was also confirmed by evolution of CO<sub>2</sub> (*m/z* = 44) during the NO pulses (not shown).

The same experiments were performed with SiO<sub>2</sub> and ZrO<sub>2</sub>-supported Pt/Ba (figure. 5(a)). Both samples showed a lower activity in NO<sub>x</sub> storage reaction compared to the Al<sub>2</sub>O<sub>3</sub>-supported catalyst. This behavior indicates that less Ba containing species are active in NO storage in the silica and zirconia supported catalysts. It reveals that the support, beside the thermal stability, also affects the activity of BaCO<sub>3</sub> in the NO<sub>x</sub> storage reaction. For Pt/Ba/ZrO<sub>2</sub> it can not be excluded that surface zirconium nitrate species can be formed [26].

Mass uptakes due to NO pulses (2 cm<sup>3</sup>) at 300 °C in 5% O<sub>2</sub>/He are presented in figure. 5(b). Ba containing samples showed a much higher NO<sub>x</sub> uptake, whereas some adsorption can be observed also on Pt/Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> samples. It is interesting to note that under the

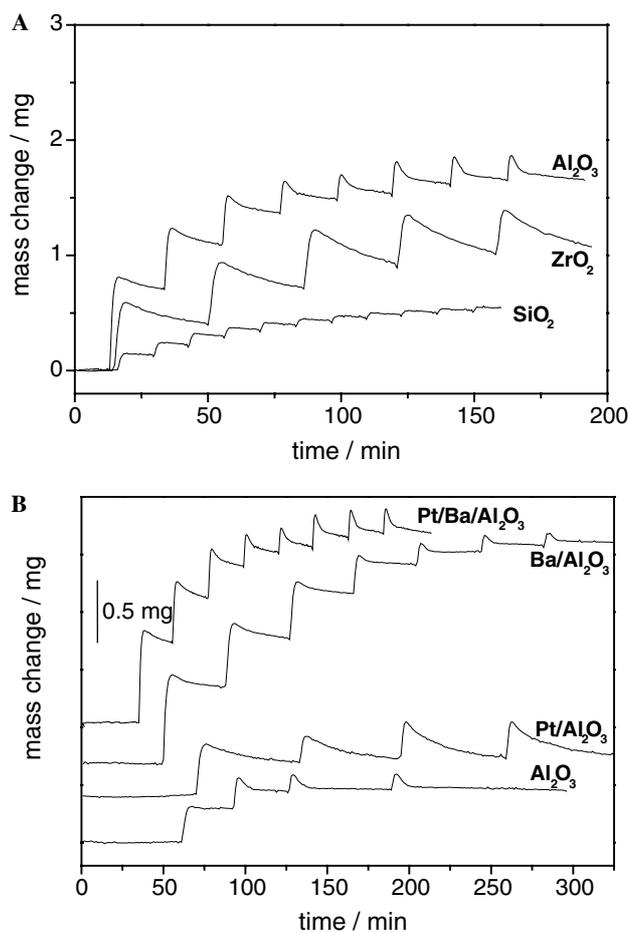


Figure 5. Pulses of NO in 5% O<sub>2</sub>/He at 300 °C: A. Pt/Ba supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and ZrO<sub>2</sub>; B. Al<sub>2</sub>O<sub>3</sub>-supported samples: Pt/Ba, Ba, Pt and pure support.

applied experimental conditions platinum had no significant influence on the NO<sub>x</sub> storage behavior of the barium containing catalysts. This could be attributed to the high temporary concentration of NO, which reached a maximum after injection of ca. 10,000 ppm. Additionally, due to the high surface area of the catalysts (ca. 180 m<sup>2</sup>/g) and relatively high reaction temperature (300 °C) we observed a high yield of NO oxidation, and thus NO<sub>2</sub> storage, even in the absence of Pt.

The catalysts after exposure to NO pulses in 5% O<sub>2</sub>/He at 300 °C were analyzed by DRIFT-spectroscopy

(figure 6(a) and 6(b)). Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> samples (figure 6(a)) contained carbonate species of various types (bands at 1300–1600 cm<sup>-1</sup>), whereas Ba containing samples showed bands characteristic for bulk BaCO<sub>3</sub> (1:1 KBr diluted, figure 6(a) dotted lines). After NO + O<sub>2</sub> exposure at 300 °C, the Ba containing samples showed absorbance bands matching those of bulk Ba(NO<sub>3</sub>)<sub>2</sub> (1:1 KBr diluted, figure 6(b) dotted lines) confirming the BaCO<sub>3</sub> → Ba(NO<sub>3</sub>)<sub>2</sub> conversion. Bands at 1343 and 1404 cm<sup>-1</sup>, observed on Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> samples can be attributed to hyponitrite

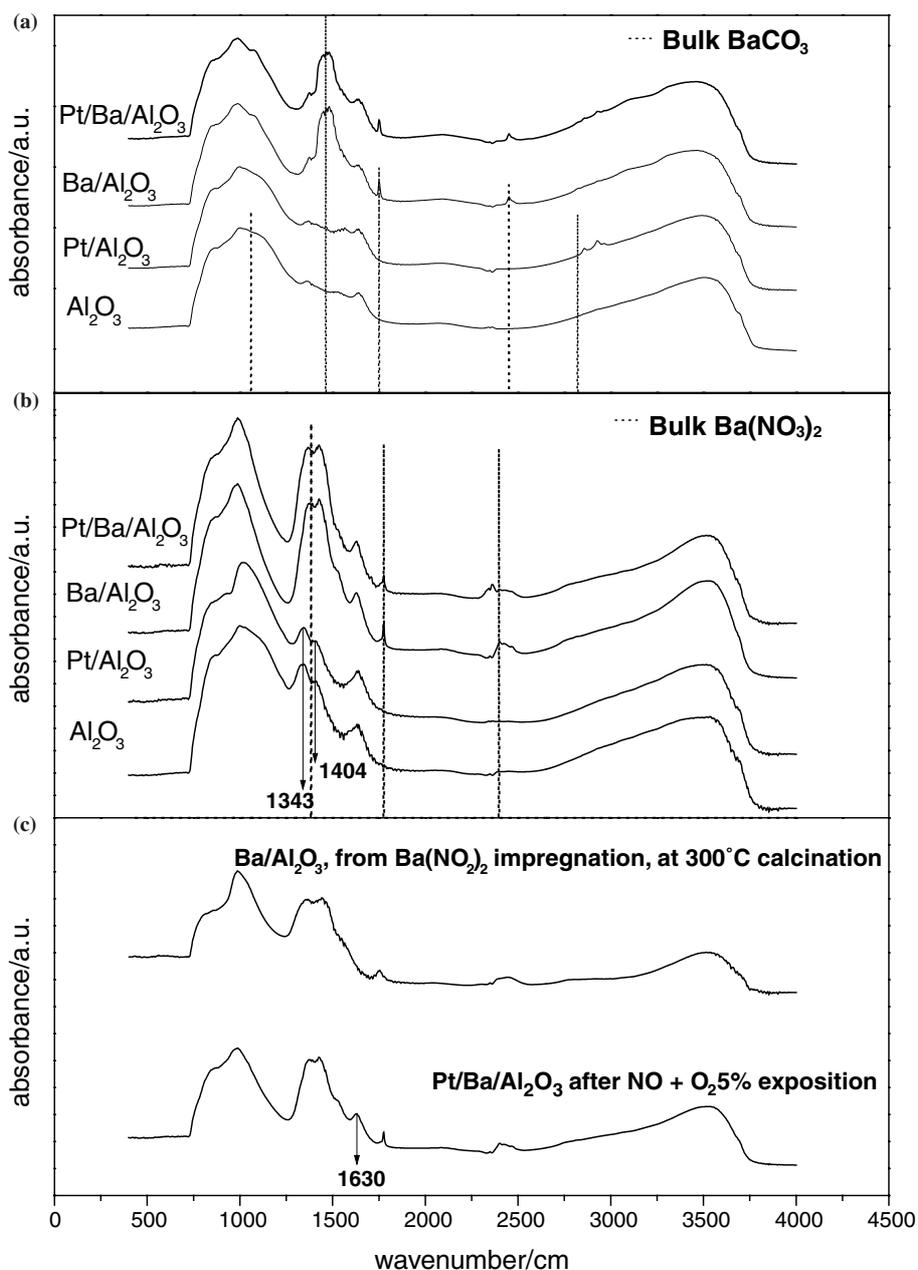


Figure 6. DRIFT analysis of Pt/Ba/Al<sub>2</sub>O<sub>3</sub> catalyst at 35 °C: (a) Fresh samples; (b) Samples exposed to NO + 5% O<sub>2</sub>/He at 300 °C: signals at 1343 cm<sup>-1</sup> refer to hyponitrite (Al<sup>+</sup>NO<sup>-</sup>) and at 1404 cm<sup>-1</sup> to nitrates species (Al<sup>+</sup>NO<sub>3</sub><sup>-</sup>) [8]; (c) DRIFT analysis of Al<sub>2</sub>O<sub>3</sub> supported Ba(NO<sub>2</sub>)<sub>2</sub> calcined in air at 300 °C and Pt/Ba/Al<sub>2</sub>O<sub>3</sub> after exposure to NO + 5%O<sub>2</sub>/He at 300 °C. Band at 1630 cm<sup>-1</sup> refers to some carbonates adsorbed on the surface due to air exposure.

(Al<sup>+</sup>NO<sup>-</sup>) and to nitrates (Al<sup>+</sup>NO<sub>3</sub><sup>-</sup>) species, respectively [8]. A comparison between Al<sub>2</sub>O<sub>3</sub>-supported Ba(NO<sub>2</sub>)<sub>2</sub> calcined in air at 300 ° and Pt/Ba/Al<sub>2</sub>O<sub>3</sub> exposed to NO + O<sub>2</sub> at 300 °C is shown in figure 6(c). The close agreement of these two spectra indicates that nitrite is not stable at 300 °C, because in both samples only bands characteristic for nitrate species are present.

### 3.3. Thermal stability of NO adsorbed on different catalysts

Temperature-programmed desorption experiments were performed with alumina-, silica- and zirconia-supported catalysts after NO pulses at 300 °C.

Evolution of NO from Pt/Ba/Al<sub>2</sub>O<sub>3</sub>, Pt/Ba/SiO<sub>2</sub> and Pt/Ba/ZrO<sub>2</sub> is shown in figure 7(a). NO desorption from the Al<sub>2</sub>O<sub>3</sub>-supported sample occurs from 230 to 730 °C with maximum at 470 °C. Desorption of NO from the SiO<sub>2</sub>-supported sample begins at 230 °C with a neglectable NO evolution. The main NO evolution occurs in the range 380 °C to 650 °C with a peak centered at around 530 °C. For the ZrO<sub>2</sub>-supported catalyst a small evolution of NO is observed between 130 and 230 °C, before the main desorption peak smoothly starts. Around 500 °C a sharp and very intense peak shows up and NO evolution continues till ca. 800 °C.

Similar TPD experiments were also performed on Al<sub>2</sub>O<sub>3</sub>-supported Pt and Ba samples: mass spectrometric signals  $m/z = 30$  (NO) and  $m/z = 32$  (O<sub>2</sub>) are presented

in figure 7(b). Both Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> show a small NO evolution centered at about 130 and 160 °C, respectively. A shoulder at 350 °C for Al<sub>2</sub>O<sub>3</sub> and at 300 °C for Pt/Al<sub>2</sub>O<sub>3</sub> is not accompanied by the evolution of O<sub>2</sub>, whereas in both cases the main NO desorption peaks (at 460 and 380 °C) are associated with O<sub>2</sub> evolution due to the decomposition of nitrate species (figure 7(b)). For both Ba containing samples, the evolution of NO alone is related to a small shoulder on the desorption curves between 350 and 400 °C, while again decomposition of Ba(NO<sub>3</sub>)<sub>2</sub> is corroborated by evolution of NO and O<sub>2</sub> that reached a maximum at 550 °C for Ba/Al<sub>2</sub>O<sub>3</sub> and at 490 °C for Pt/Ba/Al<sub>2</sub>O<sub>3</sub>. The amount of NO evolved from supported samples was quantified by PulseTA by injection of 1 cm<sup>3</sup> of NO after decomposition. Quantification of the NO resulting from the decomposition of Ba(NO<sub>3</sub>)<sub>2</sub> allowed to estimate its amount formed during interaction of the sample with NO at 300 °C. This comparison revealed that only about 30% of the barium present in the sample was involved in the NO<sub>x</sub> storage process. Some differences become apparent when comparing our results to previous investigations where the exposure of the catalysts to NO + O<sub>2</sub> was performed at 40 °C [5]. NO and O<sub>2</sub> evolution centered at around 550 – 600 °C was also observed but a distinct NO evolution around 300 °C was found only in case of low temperature exposure to NO + O<sub>2</sub>. The authors attributed this evolution to decomposition of some nitrite species.

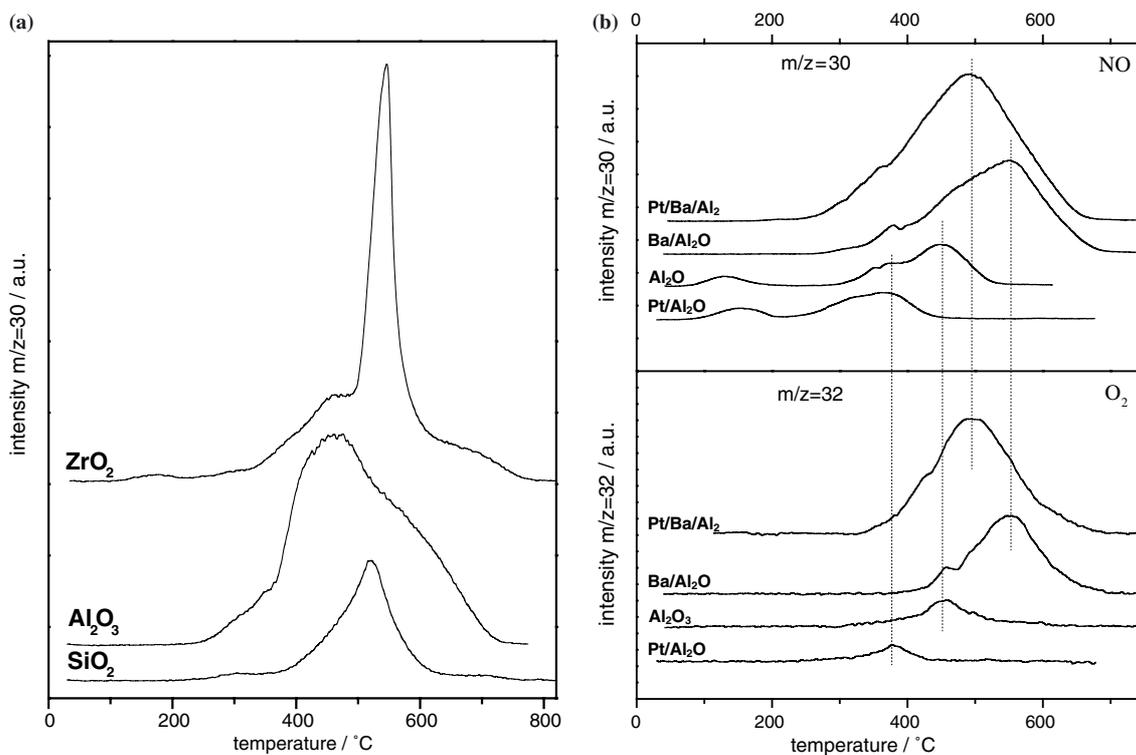


Figure 7. (a) Evolution of NO from Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and ZrO<sub>2</sub> supported Pt/Ba catalysts after prior adsorption at 300 °C in 5% O<sub>2</sub>/He flow. (b) Evolution of NO and O<sub>2</sub> from alumina-supported catalysts after prior adsorption at 300 °C in 5% O<sub>2</sub>/He flow.

To better understand these results, we prepared Al<sub>2</sub>O<sub>3</sub>-supported Ba(NO<sub>3</sub>)<sub>2</sub> and Ba(NO<sub>2</sub>)<sub>2</sub> via wet impregnation of the corresponding salts on alumina. Temperature-programmed decomposition/desorption experiments were performed with these two samples and with bulk Ba(NO<sub>3</sub>)<sub>2</sub>. In figure 8 (top) the decomposition/desorption curves of bulk Ba(NO<sub>3</sub>)<sub>2</sub> (A), Ba(NO<sub>3</sub>)<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (B) and Pt/Ba/Al<sub>2</sub>O<sub>3</sub> after NO + O<sub>2</sub> exposure at 300 °C (C) are presented. Note that nitrate formed during NO<sub>x</sub> storage reaction on Pt/Ba/Al<sub>2</sub>O<sub>3</sub> starts to decompose at a much lower temperature.

In figure 8 (bottom), mass spectrometric signals  $m/z = 30$  (NO) and  $m/z = 32$  (O<sub>2</sub>) recorded during TPD of Ba(NO<sub>3</sub>)<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and Ba(NO<sub>2</sub>)<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> are shown. Barium nitrite decomposition is characterized by a wide  $m/z = 30$  peak centered at around 210 °C, while Ba nitrate starts decomposing at higher temperatures, with a NO peak centered at around 580 °C. Due to very low stability of supported Ba(NO<sub>2</sub>)<sub>2</sub> (figure 8, bottom) which starts to decompose already below 100 °C, it is

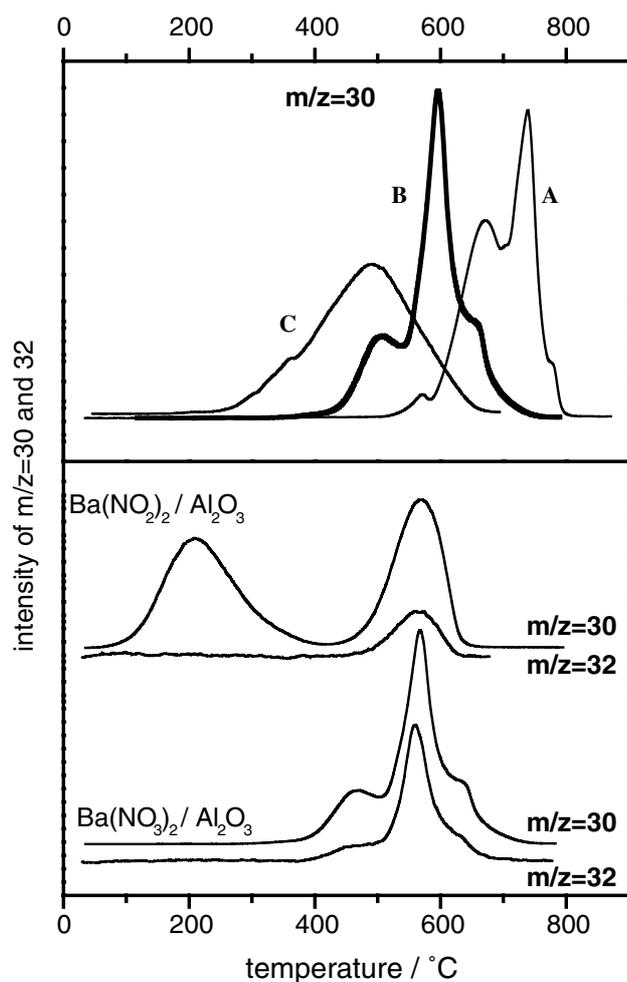


Figure 8. Thermal stability of Ba(NO<sub>3</sub>)<sub>2</sub>: (a) pure unsupported sample, (b) supported on Al<sub>2</sub>O<sub>3</sub> prepared by wet impregnation, (c) supported on Pt/Al<sub>2</sub>O<sub>3</sub> formed during injection of NO at 300 °C in 5% O<sub>2</sub>/He (Top). Thermal stability of Ba(NO<sub>2</sub>)<sub>2</sub> and Ba(NO<sub>3</sub>)<sub>2</sub> supported on Al<sub>2</sub>O<sub>3</sub> prepared by wet impregnation (Bottom).

possible that the drying of the sample at 80 °C for 10 h resulted in the formation of traces of Ba(NO<sub>3</sub>)<sub>2</sub> detected by DRIFT. DRIFT analysis of Ba(NO<sub>2</sub>)<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> during TPD in the range of RT – 300 °C is shown in figure 9. As confirmed by the reference spectra of bulk Ba(NO<sub>2</sub>)<sub>2</sub> and Ba(NO<sub>3</sub>)<sub>2</sub>, the characteristic band at 1250 cm<sup>-1</sup> present in barium nitrite disappears during calcination. This confirms that NO evolution centered at 210 °C is related to Ba(NO<sub>2</sub>)<sub>2</sub> decomposition.

The supported nitrate and nitrite species behave in a very different way compared to the corresponding bulk materials. Preparation and characterization of Al<sub>2</sub>O<sub>3</sub>-supported samples helped in determining the thermal stability of NO<sub>x</sub> species on the catalysts. The low thermal stability of 17 wt% Ba(NO<sub>2</sub>)<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> does rule out the possibility that at 300 °C some nitrites could be present among stored NO<sub>x</sub> species on Al<sub>2</sub>O<sub>3</sub>-supported Pt and Ba catalysts.

#### 4. Conclusions

The influence of the support on the stability of BaCO<sub>3</sub> and formation of Ba(NO<sub>3</sub>)<sub>2</sub> was investigated by TPD, DRIFT-spectroscopy and Pulse Thermal Analysis on Pt and Ba containing catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and ZrO<sub>2</sub>.

Experimental results confirmed the relationship between the stability of Ba containing species and their activity towards NO<sub>x</sub> storage. The thermal stability of BaCO<sub>3</sub> was found to be distinctly influenced by the support which in turn affects the activity of BaCO<sub>3</sub> in NO<sub>x</sub> storage reactions. The lower efficiency of SiO<sub>2</sub> and ZrO<sub>2</sub> supported samples for storing NO<sub>x</sub> species can be related to their deficiency in active Ba sites, i.e. to the lower amount of thermally less stable BaCO<sub>3</sub> present in these systems.

DRIFT-spectroscopy revealed that BaCO<sub>3</sub> in Pt/Ba/Al<sub>2</sub>O<sub>3</sub> starts decomposing between 250 and 300 °C, that is at much lower temperature than required for bulk BaCO<sub>3</sub> (ca. 800 °C).

Pt/Ba catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and ZrO<sub>2</sub> exposed to NO pulses in 5% O<sub>2</sub>/He atmosphere showed complete disappearance of BaCO<sub>3</sub> and formation of crystalline Ba(NO<sub>3</sub>)<sub>2</sub> as confirmed by XRD. Absence of Pt in Ba/Al<sub>2</sub>O<sub>3</sub> sample did not influence significantly the NO<sub>x</sub> storage. This behavior can be traced to the special conditions used in the pulse experiments, affording substantial production of NO<sub>2</sub>, even in the absence of Pt. The presence of hyponitrite and nitrate species was confirmed on Pt/Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>.

TPD experiments on pre-exposed catalysts confirmed that Ba(NO<sub>3</sub>)<sub>2</sub> formed on Pt/Ba/Al<sub>2</sub>O<sub>3</sub> is even less thermally stable than nitrate deposited through wet impregnation of Al<sub>2</sub>O<sub>3</sub> with a Ba(NO<sub>3</sub>)<sub>2</sub> solution. Both supported nitrates were less stable than bulk Ba(NO<sub>3</sub>)<sub>2</sub>. Quantification of the amount of NO evolved during

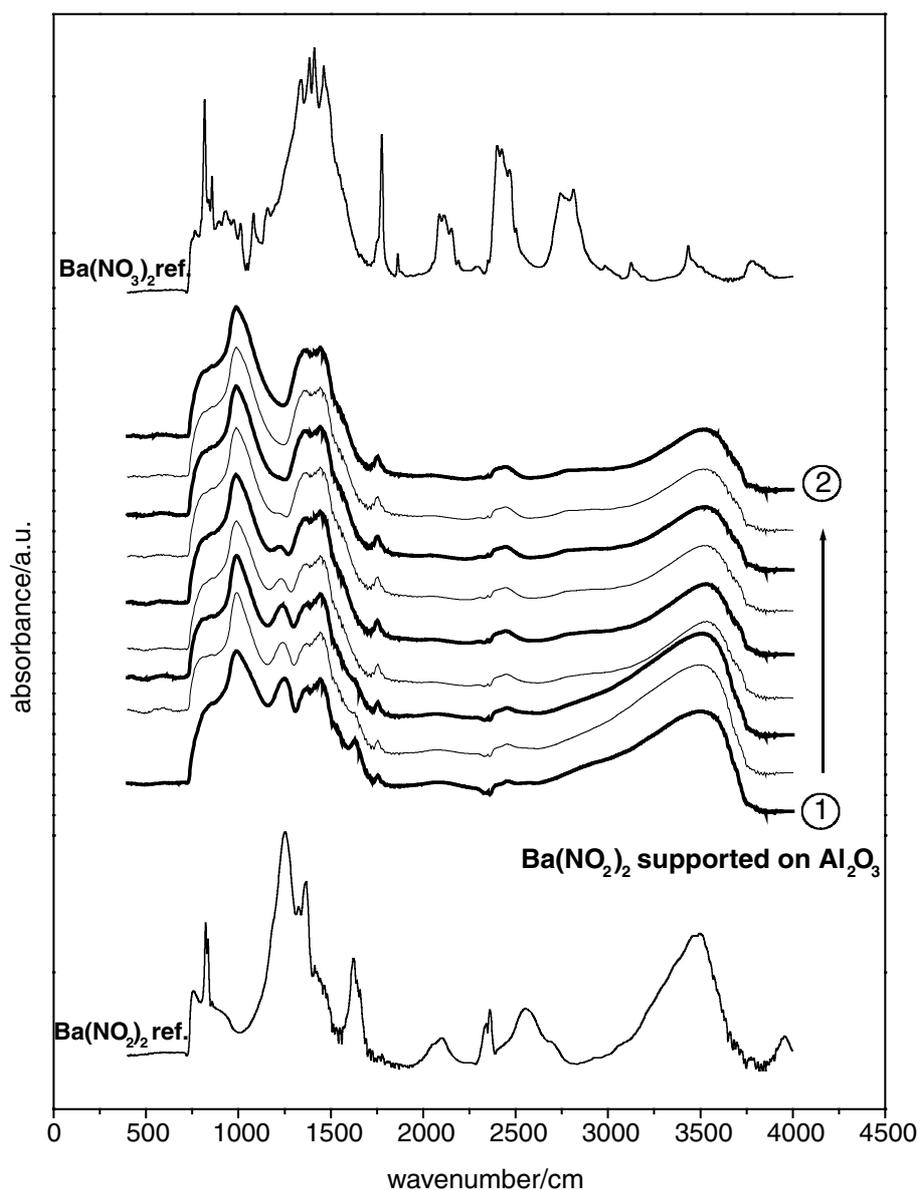


Figure 9. DRIFT analysis during TPD at different temperatures of Ba(NO<sub>2</sub>)<sub>2</sub> supported on Al<sub>2</sub>O<sub>3</sub> prepared by wet impregnation: 1. RT; 2. 300 °C, step 35 °C.

decomposition of barium nitrate formed during NO<sub>x</sub> storage indicated that only 30% of the loaded Ba is involved in the NO<sub>x</sub> storage process.

Finally, the low stability of supported barium nitrite, prepared by wet impregnation of alumina, questions whether formation of nitrates at 300 °C during NO<sub>x</sub> storage proceeds via nitrite intermediates.

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