

Role and distribution of different Ba-containing phases in supported Pt–Ba NSR catalysts

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Pt–Ba/MeO (where MeO = Al₂O₃, CeO₂, SiO₂ and ZrO₂) NO_x storage-reduction catalysts with Ba-loading varying from 0 wt.% to 28 wt.% were investigated concerning stability of Ba phases and NO_x storage-reduction efficiency. For Pt–Ba/Al₂O₃ three different Ba-containing phases with different thermal stability are distinguished based on their interaction with the support. The relative concentration of these phases varies with the Ba-loading and NO_x storage tests indicated that the BaCO₃ phase decomposing between 400 °C and 800 °C (LT–BaCO₃) is the most efficient Ba containing phase for NO_x storage. Similar investigations of Pt–Ba catalysts supported on CeO₂, SiO₂ and ZrO₂ showed that the relative amount of LT–BaCO₃ phase depends also on the support material. NO_x storage measurements confirmed a correlation between the concentration of LT–BaCO₃ and NO_x storage efficiency. Basicity and textural properties of the support are identified as crucial parameters for efficient NO_x storage catalysts.

KEY WORDS: NO_x storage-reduction catalysts; Pt–Ba/ceria; Pt–Ba/zirconia; Pt–Ba/silica; Pt–Ba/alumina; NO_x storage efficiency; effect of Ba-loading; stability of barium carbonates.

1. Introduction

The introduction of more efficient combustion engines operating under lean conditions stimulated the development of new catalysts for NO_x pollution control. In 1995 Toyota successfully proposed NO_x storage-reduction (NSR) catalysts for dynamic NO_x control [1]. The NSR process is based on storage of nitrogen oxides under lean conditions over an alkaline or alkaline-earth component (i.e. BaCO₃ or BaO) in the form of nitrates which are then reduced to nitrogen during a short fuel rich period [2]. The original catalyst formulation, Pt–Ba/Al₂O₃ (Ba-loading varies from 8 wt.% to 20 wt.%), prepared by wet impregnation of an alumina support with aqueous solutions of barium and platinum precursors has been extensively studied [3,4].

Recent studies evidenced the existence of different NO_x storage active sites [5–8]. Detailed characterization of Ba-containing species on the support indicated that, depending on their interaction with the support [9,10], they possess different stability and NO_x storage efficiency [11,12].

Al₂O₃, CeO₂, ZrO₂, Ce–Zr-oxides and SiO₂ are widely used in the control of combustion pollutants [13–21] and in our studies we specifically addressed the comparison of these oxides as supports in Pt–Ba based NO_x storage-reduction catalysts. Preliminary results on Pt–Ba catalysts supported on different oxides indicated different NO_x storage behavior depending on the support [9].

Here we first revisit the influence of the support-active Ba-phase interaction on the relative distribution of Ba-containing species and correlate it with the NO_x storage activity of Pt–Ba/Al₂O₃ catalysts. Then, we extend the study to corresponding Pt–Ba catalysts supported on CeO₂, SiO₂ and ZrO₂, and analyze how the distribution of Ba-containing species and the related NO_x storage activity are affected by the properties of support materials.

2. Experimental

Pt–Ba supported NO_x storage catalysts with different Ba-loading (4.5–28 wt.%) were prepared by incipient wetness method [10,11]. First, 1 wt.% of Pt was loaded by impregnation with Pt(NH₃)₂(NO₂)₂ solutions onto the supports calcined at 500 °C in air. The Pt/support samples were then dried at 80 °C for 12 h, calcined at 500 °C for 5 h in air, impregnated with differently concentrated Ba(CH₃COO)₂ solutions and then dried again at 80 °C for 12 h. The samples are designated as Pt–Ba(*x*), where *x* denotes the weight % of Ba in the sample, e.g. Pt–Ba(22). Dried samples were calcined *in situ* prior to each experiment in 20 vol.% O₂/He at 500 °C, and then allowed to cool to reaction temperature under controlled atmosphere.

XRD analysis was carried out on a Siemens D5000 powder X-ray diffractometer using the Cu-K α radiation in step mode between 10 and 80° 2 θ with a step of 0.01° and 2 s step⁻¹.

Thermogravimetry (TG) combined with mass spectrometry (MS) was performed on a Netzsch STA 409

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thermoanalyzer which was connected to a valve device enabling pulse thermal analysis (Pulse TA[®]). This set-up [22] allows the injection of controlled amounts (0.5–5 mL) of probe gas into a carrier gas stream (here fixed at 50 Ncm³ min⁻¹) flowing through the thermoanalyzer. The composition of the gas phase was monitored by a ThermoStar Pfeiffer Vacuum GSD 301 O1 mass spectrometer, which was connected to the thermoanalyzer by a heated (ca. 200 °C) stainless steel capillary.

Temperature-programmed reaction-desorption (TPRD) experiments were carried out in He with a heating rate of 10 °C min⁻¹. NO_x storage tests were performed at 300 °C in a 5 vol.% O₂/He atmosphere, with repeated 1 cm³ NO pulses injected into a carrier gas stream till saturation of active sites (maximal mass uptake) was reached.

3. Results and discussion

3.1. Influence of Ba-loading on thermal stability and NO_x storage efficiency of Pt–Ba/Al₂O₃ catalyst

Alumina-supported Pt–Ba catalysts with different Ba-loadings were investigated with respect to the stability and NO_x storage activity of different Ba-containing species formed during calcination of barium precursor Ba(Ac)₂.

The XRD analysis of freshly calcined samples indicated the presence of crystalline BaCO₃ for Ba loadings higher than 16.7 wt.% (figure 1). Both, the major, orthorhombic (whiterite) and the monoclinic phases were present, the latter being metastable and progressively disappearing with time [10,23–25].

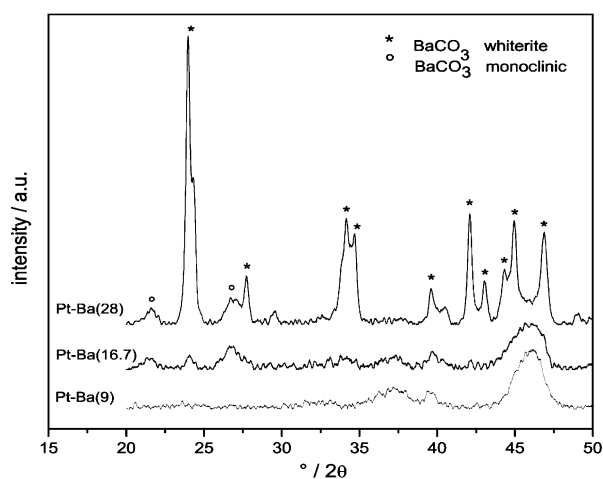


Figure 1. XRD patterns of Pt/Al₂O₃ loaded with Ba(Ac)₂ after calcination in 20 vol.% O₂/He up to 500 °C. Crystalline monoclinic and orthorhombic (whiterite) BaCO₃ could be detected for Ba loadings higher than ca. 16 wt.%. Unlabeled reflections correspond to γ -Al₂O₃. XRD analysis was carried out with freshly calcined samples, avoiding long term ambient atmosphere exposure.

Evaluation of different BaCO₃ phases formed during decomposition of Ba(Ac)₂ was achieved through quantification of evolved CO₂ according to the stoichiometry of the reaction BaCO₃ → BaO + CO₂ during TPRD experiments (figure 2). Three types of BaCO₃ with different thermal stability resulting from their different interaction with the support have been detected: (i) very unstable BaCO₃ in intimate contact with the alumina, decomposing at temperature lower than 500 °C and forming BaO, (ii) *Low-Temperature barium carbonate* (LT-BaCO₃) being in direct contact with the BaO layer and decomposing between 400 °C and 800 °C, and (iii) bulk-like, *High-Temperature barium carbonate* (HT-BaCO₃) decomposing at temperatures higher than 800 °C and being present in the form of larger aggregates that are less affected by the support influence.

The distribution of these BaCO₃ phases depends on the Ba-loading (figure 3) and on the nature of the support. The influence of the support is most prominent at low loadings, while the progressive growth of Ba-containing domains, at higher Ba-loading (> ca. 16.7 wt.%) does not contribute anymore to the Ba/support interface.

Catalysts calcined at 500 °C, containing LT- and HT-BaCO₃, were exposed to NO pulses in 5 vol.% O₂/He atmosphere till saturation of the active storage sites was achieved. Assuming that NO_x species are stored as nitrates allowed to quantify the amount of NO stored by TPRD of NO_x saturated catalysts and to derive the fraction of active Ba [9,24,26]. The NO_x storage efficiency is presented in figure 4 in terms of fraction of Ba involved in the NO_x storage process versus the total Ba loaded.

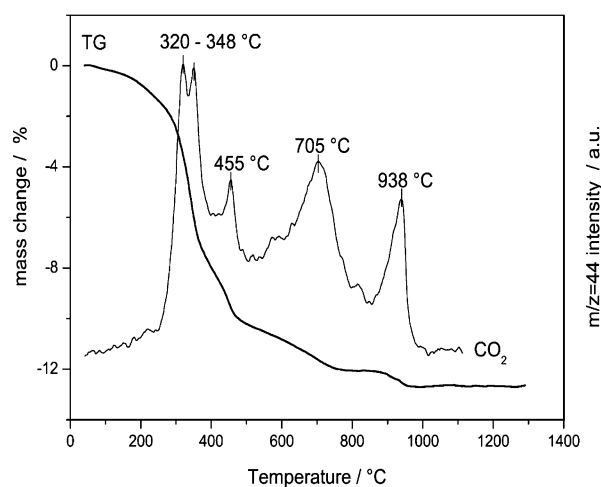


Figure 2. TPRD in He atmosphere of Pt–Ba(22)/Al₂O₃ catalyst. Thermogravimetric (TG) curve and mass spectrometric signal $m/z = 44$ tracing the mass changes and CO₂ evolution resulting from the decomposition of Ba(Ac)₂ followed by the decomposition of formed BaCO₃.

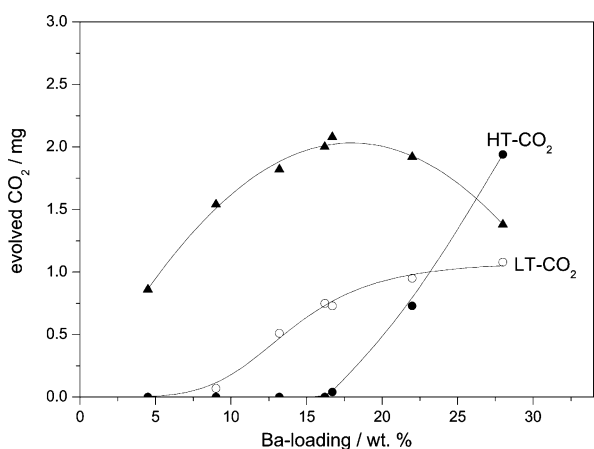


Figure 3. Influence of Ba-loading on amount of CO_2 evolved during decomposition of BaCO_3 phases, formed during calcination of $\text{Ba}(\text{Ac})_2$ deposited on $\text{Pt}/\text{Al}_2\text{O}_3$, (\blacktriangle) up to 400°C ; (\circ) between 400°C and 800°C (Low Temperature BaCO_3); (\bullet) at temperatures above 800°C (High Temperature BaCO_3).

The volcano shaped curve clearly indicates that the storage efficiency is affected by the Ba-loading [27], particularly a correlation can be found with the relative concentration of LT- and HT- BaCO_3 phases. At low Ba-loading the NO_x storage efficiency curve grows parallel with the increase of the concentration of LT- BaCO_3 , indicating that this phase contributes mainly to the storage activity. At higher Ba-loading, once the HT- BaCO_3 phase starts to form, the NO_x storage efficiency decreases, indicating that HT- BaCO_3 shows a poor NO_x storage activity, comparable to that of bulk BaCO_3 (not shown) and is affected by diffusional limitation [28–30].

3.2. Influence of support on Ba-containing species stability and NO_x storage efficiency

Series of Pt–Ba supported on CeO_2 , SiO_2 and ZrO_2 were prepared varying the Ba content from 4.5 wt.% to

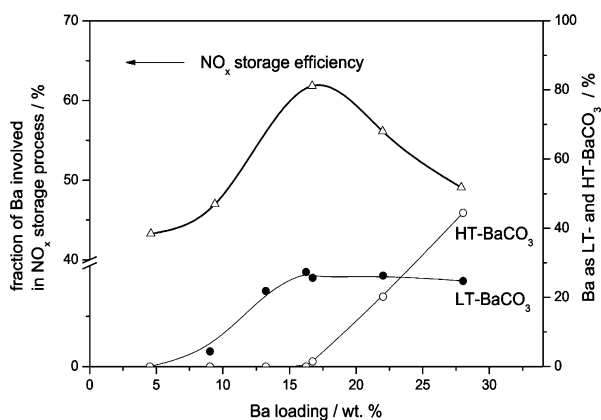


Figure 4. NO_x storage efficiency as a function of Ba-loading and BaCO_3 distribution. Note that the volcano shaped efficiency curve can be addressed to the concentrations of more active LT- BaCO_3 and less active HT- BaCO_3 phase.

28 wt.%. Depending on the support, calcination of the samples loaded with $\text{Ba}(\text{Ac})_2$ precursor resulted in different relative amount of barium carbonate. Figure 5 shows the influence of the support and Ba-loading on the relative amount of BaCO_3 formed. SiO_2 supported $\text{Ba}(\text{Ac})_2$ decomposed completely to BaO and only a minimal amount of carbonates formed by $\text{Ba}(\text{Ac})_2$ decomposition is stable at very high Ba-loading. In contrast, on CeO_2 and ZrO_2 , a substantial amount of stable carbonates formed during $\text{Ba}(\text{Ac})_2$ decomposition. The distribution of LT- and HT- BaCO_3 phases as a function of Ba-loading and kind of support is presented in figure 6A and B, respectively. Note that the concentration of LT- BaCO_3 at low Ba-loading depends strongly on the support (figure 6A). CeO_2 and ZrO_2 seem to better stabilize the carbonates formed during precursor decomposition than Al_2O_3 which results in significantly higher concentration of LT- BaCO_3 on these supports at lower Ba-loadings. On the other hand, the concentration of HT- BaCO_3 is rather independent of the kind of support, even if the higher stability of BaCO_3 in CeO_2 and ZrO_2 samples leads to the formation of bulk-like carbonates at significantly lower Ba loadings (figure 6B).

The ability of the different supports to stabilize the carbonates formed from the $\text{Ba}(\text{Ac})_2$ decomposition decreases in the order $\text{CeO}_2 \cong \text{ZrO}_2 > \text{Al}_2\text{O}_3 > \text{SiO}_2$. Interestingly, according to Martin and Duprez [31] the basicity order of the investigated supports in terms of CO_2 chemisorption is similar: $\text{CeO}_2 > \text{ZrO}_2 > > \text{Al}_2\text{O}_3 > \text{SiO}_2$ indicating that CO_2 chemisorbs best on CeO_2 . This suggests that the observed effect of the supports on the stability of the Ba-containing species can be traced to their different basicity. CO_2 chemisorption is

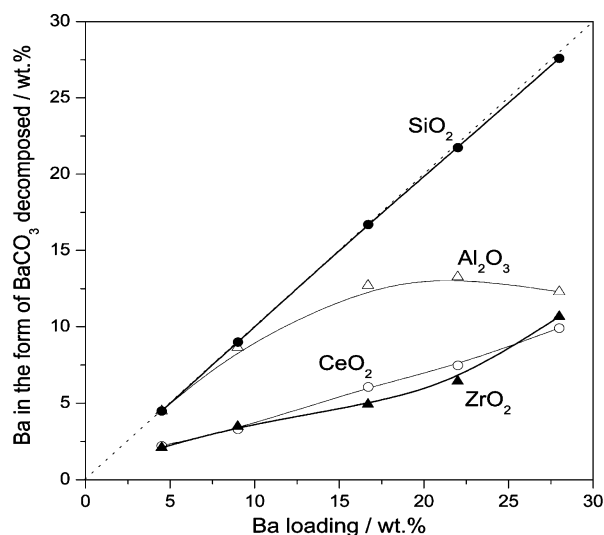


Figure 5. Influence of the support and Ba-loading on the stability of BaCO_3 formed during decomposition of $\text{Ba}(\text{Ac})_2$ supported on different oxides. In silica supported samples BaCO_3 fully decomposes during calcination.

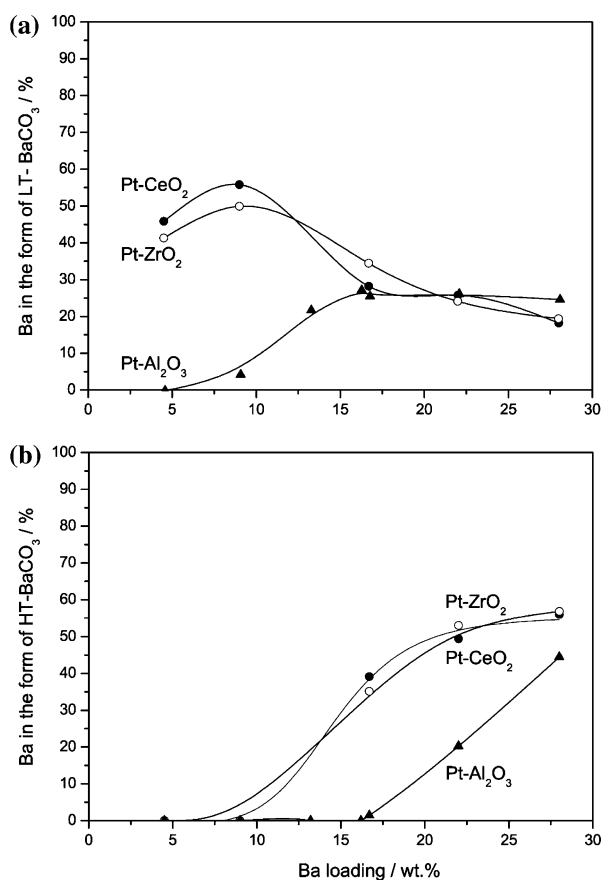


Figure 6. Distribution of BaCO₃ phases over different supports as a function of Ba-loading: (a) LT-BaCO₃ and (b) HT-BaCO₃.

favoured on basic supports, resulting in the formation of stable BaCO₃. The ability of surface active sites to interact with CO₂ species affording the formation of stable carbonates [32] is thus a major factor for explaining the influence of the support on the distribution of Ba-containing phases. CO₂ strongly chemisorbed on CeO₂ and ZrO₂ is in close contact with BaO, which results in formation of the BaCO₃ phases. In contrast, when CO₂ does not, or only weakly chemisorbs on the support, as in the case of SiO₂, BaCO₃ formed during Ba(Ac)₂ decomposition is unstable and decomposes to BaO at low temperature. Only at high Ba-loading the formed BaO covers the support allowing CO₂ chemisorption and, in turn, the formation of BaCO₃ phases.

Although, silica is an unfavorable support to stabilize barium carbonate its intrinsically high surface area could be advantageous when covered with basic oxides, like CeO₂ and ZrO₂, which favor the formation of the most active LT-BaCO₃.

NO_x storage tests confirmed the correlation between the presence of active LT-BaCO₃ and NO_x storage efficiency (figure 7). At low Ba-loading CeO₂ and ZrO₂ exhibit a higher concentration of Ba active sites consistently with their higher concentration of LT-BaCO₃, whereas at higher Ba-loading the decreasing support

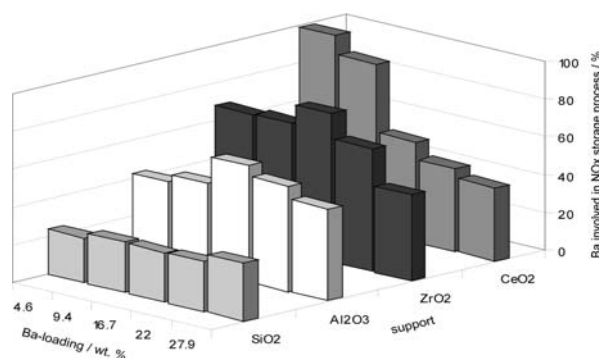


Figure 7. NO_x storage efficiency expressed in terms of percentage of Ba active in NO_x storage: influence of the Ba-loading and the support.

effect somehow equalizes the storage performance of Al₂O₃, CeO₂ and ZrO₂ supported catalysts. However, morphological differences of the supports will also affect the storage performance. The almost complete absence of carbonates over SiO₂ renders silica an unsuitable interface for accommodating barium carbonate.

4. Conclusions

In standard NSR Pt–Ba/Al₂O₃ catalysts with 1 wt.% of Pt and Ba-loading varying from 4.5 wt.% to 28 wt.% three different Ba-containing phases can be distinguished in calcined catalysts: (i) very unstable BaCO₃ decomposing to BaO at $T < 500$ °C, (ii) LT-BaCO₃ being in intimate contact with BaO and decomposing between 400 °C and 800 °C, and (iii) high temperature BaCO₃ (HT-BaCO₃) decomposing at $T > 800$ °C. Relative concentrations of these phases depend on the Ba-loading. The NO_x storage efficiency is strongly related to the concentration of the LT-BaCO₃ phase. Highest population density of active Ba sites is achieved at ca. 16 wt.% of Ba.

Investigations of Pt–Ba catalysts supported on CeO₂, SiO₂ and ZrO₂ revealed that the relative distribution of the Ba-containing phases depends on the chemical and structural properties of the supports. Basic supports as CeO₂ and ZrO₂ show highest relative concentration of LT-BaCO₃ at low Ba-loading due to their ability to stabilize carbonates. As a consequence, CeO₂ and ZrO₂ supported catalysts are the most efficient catalysts at low Ba-loading. SiO₂ supported catalysts show poor NO_x storage capacity due to very low stability of barium carbonate on this support. Consequently, the barium component should not be located at the silica interface in silica-containing storage catalysts.

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