

The effect of support and promoters on the performance of Pt-based H₂-SCR catalysts for NO_x removal

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ARTICLE INFO

Keywords:

Emission control
H₂-SCR
Platinum
Ceria
Titania
Promoters

ABSTRACT

H₂-combustion engines represent a promising alternative for achieving carbon neutrality. However, to efficiently remove the resulting NO_x emissions, the current H₂-SCR technologies require a more in-depth understanding that will enable further catalyst improvements. In this context, this manuscript reports a systematic study on the effect of support and promoters on the H₂-SCR performance of Pt-based catalysts. Parameters such as catalyst pre-treatment, noble metal loading, space velocity, and gas composition were varied to elucidate their effects on the measured activity and selectivity profiles and to gain insights into the underlying reaction mechanism. A moderate interaction with the support and the formation of small Pt nanoparticles were identified as essential for NO_x conversion at low temperatures. Accordingly, TiO₂-supported catalysts were found to be superior in terms of NO_x conversion and N₂ yield compared to the CeO₂-supported samples. Highly dispersed Pt species as present on strongly interacting supports are also highly sensitive to H₂O and O₂ inhibition. Acidic promoters broaden the activity window, while basic dopants shift and narrow the NO_x conversion window toward higher temperatures. Nevertheless, the presence of basic sites on the catalyst surface improves the N₂ selectivity over the entire operating temperature window and contribute to NH₃ formation as a secondary byproduct.

1. Introduction

As the energy sector transitions from fossil fuels toward carbon neutrality, hydrogen is emerging as a promising alternative fuel for internal combustion engines. Key advantages include carbon neutrality and near-zero emissions during combustion [1,2], the feasibility of retrofitting existing engines [3], and anticipated high availability at low future costs. Growing interest in a hydrogen economy [4] has spurred predictions of rapidly declining green hydrogen production costs from electrolyzers [5], further enhancing the potential for near-zero emissions in hydrogen combustion engines. However, the combustion of hydrogen introduces a range of technical challenges that must be addressed. Due to high combustion temperatures, nitrogen oxides (NO_x) remain the predominant undesirable emission. The catalytic removal of NO_x is typically achieved via the selective catalytic reduction (SCR) reactions using ammonia (NH₃) as reducing agent, a technology also known as NH₃-SCR [6–9]. The operating temperature of such systems typically exceeds 200 °C. For H₂-combustion engines, the direct use of hydrogen for NO_x removal is regarded as a promising alternative due to its

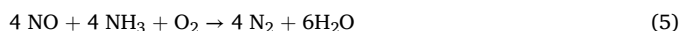
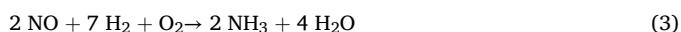
on-board availability and high chemical reduction potential. For mobile applications, this approach would eliminate the space constraints and challenges associated with urea dosing [10] and the need for additional catalysts to mitigate ammonia slip [11]. Furthermore, the direct use of hydrogen avoids extra steps associated with ammonia production via the Haber-Bosch process [12]. Finally, the development of the H₂-SCR technology could potentially supplement the NH₃-SCR catalysts during the cold start phase [13]. Particularly, in the low temperature range H₂-SCR catalysts have demonstrated promising NO_x removal activity [13–15].

H₂-SCR requires an excess of hydrogen relative to the NO_x concentration in the feed. Therefore, it is not strictly selective, yet it is frequently referred to as such within the terminology of this field. Depending on the specific study, the applied H₂:NO ratios may vary [16–18]. The main reactions occurring in excess of oxygen are described by the equations. Apart from the reduction of NO to nitrogen (1), its partial reduction can also lead to nitrous oxide formation (2), as the main byproduct. Over-reduction of NO to NH₃ may also occur (3). Finally, since both hydrogen and oxygen are present, their direct

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reaction to form water (4) must be considered as side reaction and is the main reason for overdosage of H_2 in relation to NO . Due to possible ammonia formation, NH_3 -SCR (5) of NO_x as well as unselective ammonia oxidation reactions [19] should be additionally considered. These reactions involve NO adsorption/dissociation on acidic sites and/or NO oxidation/reduction on basic sites via a dual-function mechanism [20,21]. In the pathway involving acidic sites, NO is reduced to form active ammonium species (NH_4^+) [22], which further react in an NH_3 -SCR-like reaction (similar to reaction (5)). When basic sites are involved, NO_x is stored on the catalyst surface and is subsequently reduced to nitrogen, similarly as over an NO_x storage-reduction catalyst (NSR) [23].



Among the different catalyst compositions, platinum- or palladium-based systems are known as the most promising. While palladium shows high selectivity toward nitrogen formation, the activity of such catalysts is lower than that of platinum-based counterparts, which on the other hand exhibit reduced selectivity [20,24,25]. As a result, considerable efforts continue to be directed toward increasing the N_2 selectivity of Pt-based catalysts. Previous studies have shown that the catalyst activity and selectivity directly depend on the state of Pt, which can be tuned by adding various promoters or by varying the used support [17,18,24,26–28]. As catalyst supports, various metal oxides/mixed oxides and zeolites have been tested, with the aim to vary the interaction with the noble metal or the acidic/basic properties of the catalyst [24]. For instance, Li et al. [29] found that the metallic state of Pt is promoted on HZSM-5 while the interaction with MgO and Al_2O_3 leads to the formation of smaller noble metal particles, which are more prone to oxidation. A pronounced interplay was also found for TiO_2 and CeO_2 supported catalysts. In the first case, the electron transfer from TiO_2 to Pt was reported by Liu et al. [30], which leads to the formation of Pt^0 . Titania is a widely applied support for the SCR of NO_x with NH_3 [31]. On the other hand, the interaction with CeO_2 prevents the sintering of Pt and enables its redispersion under oxidizing conditions [32]. However, the rather poor activity of the Pt/ CeO_2 system requires the addition of promoters, as demonstrated by several authors [18,23,27,28,33–35]. In this regard, the use of magnesium, zirconium, titanium, vanadium, lanthanum and tungsten oxides has been investigated in recent years [17,22,24,36]. Väliheikki et al. [37] reported on the H_2 -SCR activity of a WO_x -promoted $Ce_zZr_{1-z}O_2$ catalyst that is able to convert NO despite the noble metal absence. The addition on WO_3 to a Pt/ TiO_2 catalyst was studied by Liu et al. [38], who observed a notable increase in both the NO_x conversion and the N_2 selectivity. An improvement of the H_2 -SCR activity was assigned by Komatsubara et al. [39] to the presence of Nb_2O_5 on an alumina support. Generally, Nb_2O_5 presence is known to increase the catalyst surface acidity, which promotes NH_3 -SCR reactions [6–8,40,41] and the resistance towards SO_2 , hydrothermal and alkali deactivation [42–44]. At the same time, Costa et al. [18,23] studied the effect of basic promoters on the activity of Pt-based H_2 -SCR catalysts. The authors found that NO_x intermediates are formed at the interface between Pt nanoparticles and support surface in Pt-Mg/ CeO_2 catalysts, which are reduced via H_2 -spillover from the active metal species. Another regularly applied basic promoter is Ba, which is also used in NSR catalysts. In such systems, NO_x is initially stored as nitrates/nitrites, which are subsequently reduced to nitrogen [45]. As demonstrated by Costa et al. [18,23], an analogous reduction step can also occur during the H_2 -SCR process.

Although different trends in the activity and selectivity of H_2 -SCR

catalysts have been reported, the number of systematic investigations is limited for this class of catalysts. Moreover, most studies have focused on complex catalyst formulations, making it difficult to correlate the observed activity trends with specific structural features [17,46–49]. This is further complicated by the intricate reaction network involving numerous by-products. In this context, we report a comprehensive study on the effect of catalyst support and dopants on the H_2 -SCR activity of Pt-based catalysts. Catalysts supported on two different supports, i.e. TiO_2 and CeO_2 , in combination with acidic (WO_3 and Nb_2O_5) and basic (MgO , BaO) dopants were thoroughly tested under different reaction conditions. These included changes in the noble metal loading, gas composition and gas hourly space velocity. Additionally, the influence of catalyst pre-treatment was systematically investigated using oxidative as well as mild and harsh reductive steps. The obtained results are corroborated with complementary catalyst characterization using BET; XRD, HAADF-STEM, ICP-OES, XAS and TPD experiments.

2. Methods/experimental

2.1. Catalyst synthesis

Four different promoters - Mg, Ba, W, and Nb - were added to ceria and titania supports to achieve a promoter loading of 10 wt%. The promoted ceria supports were synthesized via the facile shock coprecipitation method. For this purpose, the Mg, Ba, and W precursors listed in Table SI 1 were dissolved in appropriate amounts of water to achieve a total molar concentration of 0.2 M. This solution was added dropwise into a stirred 2 M solution of ammonia. The generated precipitate was filtered and washed with water to remove residual ammonia. For the barium promoter, 2 eq. of ammonium carbonate ($(NH_4)_2CO_3$) were added to the ammonia solution to precipitate barium as barium carbonate. Due to the air and humidity sensitivity of the niobium precursor (niobium ethoxide), the dissolution process was conducted under inert argon atmosphere in a Schlenk line. The precursor was dissolved in dry ethanol, and the resulting solution was dropped into a 2 M solution of ammonia. After drying and calcination in static air at 500 °C for five hours, the noble metal precursor (Tetraaminplatin nitrate) was added to the resulting powders by incipient wetness impregnation to achieve a 0.5 wt% loading of Pt. Additionally, a reference catalyst on commercial ceria with a specific surface area of $110 \text{ m}^2 \text{ g}^{-1}$ (Solvay) was prepared with the same platinum loading.

Commercial titania from Tronox (DT-51D, $86 \text{ m}^2 \text{ g}^{-1}$) calcined at 700 °C for five hours was used as a second carrier material, alongside the ceria carriers. Also, in this case, 10 wt% promoter loading was obtained by incipient wetness impregnation, using the precursors listed in Table SI 1. The resulting samples were dried and calcined in static air at 500 °C, as described above. Only for obtaining the 0.5 wt% Pt- WO_3/TiO_2 catalyst, a commercially available WO_3/TiO_2 support from Tronox (DT-52) was used after calcination at 700 °C for five hours. The calcined and promoted supports were loaded with noble metal (0.5 wt%) as stated above for the ceria-based catalysts. Analogous to the ceria-based catalyst series, a reference sample supported on unpromoted titania (DT-51D) was prepared with the same platinum loading.

To study the influence of noble metal loading, corresponding catalysts containing 1 wt% Pt were additionally prepared. Catalyst nomenclature follows the Pt-M-Sup format, where M and Sup represent the promoter and support, respectively.

2.2. Characterization methods

N_2 -physisorption measurements were performed for catalyst powders on a BELSORP-mini II instrument (BEL Japan). For removal of moisture, sample degassing for 2 h at 300 °C was executed. On the basis of the obtained adsorption-desorption curves at -196 °C, the surface area as well as the total pore volume of the catalyst was determined using the Brunauer-Emmett-Teller (BET) method [50].

Elemental analysis was achieved by applying inductively coupled plasma-optical emission spectroscopy (ICP-OES, iCAP 7600 DUO, Thermo Fischer Scientific). Before spectral analysis the sample was dissolved in 3 mL H₃PO₄, 3 mL H₂SO₄, 1 mL H₂O, 1 mL HF heated to a maximum of 250 °C for two hours. All measurements were conducted three times to validate the results.

X-ray diffraction (XRD) measurements were performed at room temperature using a D8 Discover diffractometer (Bruker-AXS) with Bragg-Brentano configuration, Cu K α radiation and a VANTEC-1 detector (Bruker). Diffractograms were recorded from 10 to 120° at a step size of 0.0165° and an integration time of 3 s per step. The diffractograms were analyzed using the EVA (Bruker AXS, Version 15.0.0.0) software to correct for the Cu K α signal, and a background correction was performed. The powder diffraction patterns were compared to reference diffractograms of the inorganic crystal structures database (ICSD).

Electron microscopy measurements were conducted by applying a diluted, aqueous suspension of the sample on a commercial, amorphous, ultrathin carbon film (3 nm) supported onto a 400 μ m Cu grid (Plano 01824). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images combined with energy dispersive X-ray spectroscopy (EDXS) elemental maps were acquired using a FEI OSIRIS ChemiSTEM microscope operated at 200 keV electron energy, which is equipped with a Super-X EDXS system comprising four silicon drift detectors. EDXS elemental maps of Pt (Pt-L α line), Ce (Ce-L α line), W (W-L α line), Ba (Ba-L α line), Nb (Nb-K α line), Mg (Mg-K α line) and Ti (Ti-K α line) are recorded and used to investigate their distribution within sample areas of interest. The maps are analysed by using the ESPRIT software (version 1.9, Bruker).

Particle diameters (d_i) were derived using the ImageJ software [51]. Average diameters d_m were calculated either fitting a Gauss function to the histograms or calculating the surface-averaged particle diameter d_{NP} according to formula (6) [52,53], where n_i is the number of particles with a specific diameter d_i .

$$d_{NP} = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} \quad (6)$$

Ex situ X-ray absorption spectroscopy (XAS) measurements at the Pt L₃ edge (11564 eV) in fluorescence mode were performed at beamline BM23 of the European Synchrotron Radiation Facility (ESRF). Catalyst powders were placed into quartz capillaries of 1.5 mm diameter and fixed using quartz wool [54]. Beamline configuration details were analogous to those reported by Mathon et al. [55]. For the evaluation of the acquired data, XAS spectra were calibrated for energy and normalized using Athena from the Demeter software package (version 0.9.26) [56].

2.3. Catalytic activity tests

Catalytic tests were conducted on a laboratory test bench using a quartz plug-flow reactor with outer and inner diameters of 10 and 8 mm, respectively. The granulated (125 – 250 μ m) catalyst was diluted with silicon carbide (SiC) of similar grain size before loading a catalyst bed of ~13 mm into the reactor between two quartz wool plugs. Synthetic gas mixtures (Air Liquide) were dosed by individual mass flow controllers (MFC, Bronkhorst), which were previously calibrated using a gas flow measurement device (DryCal Definer 220-L, Hersteller: BIOS). All stainless-steel tubing of the test bench downstream water introduction was maintained at 150 °C to prevent condensation. The gas temperature was measured by two K-type thermocouples located directly in front of and behind the catalyst bed. The maximum difference between the inlet and outlet temperatures was 20 °C, primarily due to the reaction exothermicity. The analysis of the gas stream was carried out by a Fourier transform infrared spectrometer (FTIR, Multi-gas 2030, MKS Instruments).

Prior to activity tests, the catalysts were exposed for 1 h at 350 °C to

10 % O₂ in N₂ (heating ramp of 10 K*min⁻¹). Afterwards three consecutive transient heating and cooling cycles (light-off and light-out) were conducted in a reaction gas mixture containing 1000 ppm NO, 5000 ppm H₂, 8 % O₂, 5 % H₂O in N₂ between 50 – 300 °C with a heating ramp of 5 K*min⁻¹ (catalyst amounts and flow were adjusted to reach a weight hourly space velocity (WHSV) of 90,000 or 60,000 L* (h*g_{Pt})⁻¹). Catalyst pre-reductive treatments, were performed in 2 % H₂ in N₂ during heating and cooling (ramp rate of 10 K*min⁻¹) as well as holding for one hour at 300 °C or 500 °C for soft reduction (sR) or harsh reduction (hR), respectively. These treatments were followed by light-off/light-out activity tests. The applied measurement schemes are shown in Figure SI 1.

The equations used for the calculations of NO_x and H₂ conversion as well as for the selectivity on NO_x towards N₂O, NH₃, and N₂ are listed in (7)–(11). For the conversion of hydrogen, as it is non-IR active, the generated water and ammonia amounts were used during the calculation for most experiments. For the calculation of the selectivity of NO_x towards nitrogen, which is also non-IR active, a total selectivity of 100 % was assumed for N₂, N₂O and NH₃. In all cases, the selectivity was only calculated when the conversion of NO_x exceeded 5 % to circumvent error propagation.

$$X(NO_x) = 1 - \left(\frac{NO_{x \text{ out}}}{NO_{x \text{ in}}} \right) \quad (7)$$

$$X(H_2) = \left(\frac{H_2O_{out} - H_2O_{in} + 1.5 * (NH_3_{out} - NH_3_{in})}{H_2_{in}} \right) \quad (8)$$

$$S(N_2O, NO_x) = 2 * \left(\frac{N_2O_{out} - N_2O_{in}}{NO_{x \text{ in}} - NO_{x \text{ out}}} \right) \quad (9)$$

$$S(NH_3, NO_x) = \left(\frac{NH_3_{out} - NH_3_{in}}{NO_{x \text{ in}} - NO_{x \text{ out}}} \right) \quad (10)$$

$$S(N_2, NO_x) = 1 - (S(NH_3, NO_x) + S(N_2O, NO_x)) \quad (11)$$

2.4. Temperature-programmed reaction/adsorption/desorption tests

To elucidate details of the H₂-SCR reaction mechanism, additional light-off/light-out activity tests were conducted in the absence of oxygen (noO; 1000 ppm NO, 5000 ppm H₂, 5 % H₂O in N₂, WHSV of 60,000 L* (h*g_{Pt})⁻¹). These were followed by temperature-programmed desorption (TPD) treatments up to 500 °C (ramp rate of 4 K*min⁻¹) in inert nitrogen atmosphere.

In a next step, the NO and NH₃ storage capacities of the investigated catalysts was evaluated (Figure SI 1c). Prior to the adsorption experiments, all samples were exposed to 10 % O₂ in N₂ at 500 °C, with a holding time of 1 h. NO_x adsorption was conducted for 1 h at 50 °C (1000 ppm NO, 8 % O₂, 5 % H₂O in N₂), followed by flushing in N₂ for another hour. Afterward, the catalyst bed was heated up to 500 °C with a ramp rate of 4 K*min⁻¹ to observe the NO_x desorption profile. Afterwards, NH₃ adsorption was investigated at 50 °C (660 ppm NH₃, 5 % H₂O in N₂) similarly to the NO_x adsorption/desorption experiment but with a flushing time of 1.5 h. Calculation of the amounts of released gases during the TPD experiments and the method for calculating the average selectivity are detailed in the SI with equations (SI 1) and (SI 2).

3. Results and discussion

3.1. Catalysts characterization

The specific surface areas of the as-prepared samples determined by N₂ physisorption are listed in Table 1. In general, similar surface areas were measured for the two promoted catalyst series. However, in comparison to the unpromoted titania reference, a decrease between ~9–25 % was observed for the promoted samples. According to the ICP-

Table 1

Specific surface area and elemental composition of the different TiO₂- and CeO₂-supported catalysts.

Sample	Specific surface area [m ² g ⁻¹]	Platinum content [wt%]	Promoter concentration (Mg, Ba, W, Nb) [wt%]
Pt-Mg-Ti	77	0.46	7.6
Pt-Ba-Ti	65	0.45	9.7
Pt-Ti	86	0.48	-
Pt-W-Ti	75	0.47	8.3
Pt-Nb-Ti	67	0.48	7.8
Pt-Mg-Ce	88	0.47	10.0
Pt-Ba-Ce	63	0.46	9.1
Pt-Ce	109	0.44	-
Pt-W-Ce	85	0.46	9.9
Pt-Nb-Ce	86	0.47	9.1

OES analysis, the loadings achieved for most samples during the catalyst synthesis are more or less within the targeted ranges for both the promoters and the noble metal (Table 1). Only for the Pt-Mg-Ti and Pt-Nb-Ti samples the promoter concentration was slightly lower.

Due to the low platinum loading and relatively high surface area of the two supports, a high noble metal dispersion was expected for these catalyst series. This assumption was confirmed by the XRD measurements conducted for the as prepared samples, as no platinum reflexes corresponding to Pt or PtO₂ were detected (Fig. 1). Only for the Pt-Nb-Ti catalyst, minor reflexes of metallic platinum (ICSD: 243678) were visible, suggesting the presence of larger particles in this sample. The obtained diffractograms are shown in Fig. 1. The TiO₂ anatase (ICSD: 9852) and CeO₂ (ICSD: 24887) phases were detected in the respective catalysts. Additionally, MgO (ICSD: 9863) reflexes were visible for both groups of samples. Besides, the Ba-promoted samples presented reflexes of BaTiO₃ (ICSD: 19798) or BaCO₃ (ICSD: 15196) when titania or ceria were used as supports, respectively. This is most probably due to the higher molar concentrations of alkaline metals in comparison to the other elements used as dopants. Additionally, the presence of BaTiO₃ indicates that a solid-state reaction occurred during the catalyst synthesis, which is in line with previous studies [57]. This process could explain the lowest specific surface area of the Pt-Ba-Ti sample. Barium is also known to interact with CeO₂, leading to the formation of BaCeO₃. However, such a solid-state reaction was observed only above 500 °C in previous literature [58,59], which is outside the temperature window applied during Pt-Ba-Ce catalyst synthesis. Nevertheless, we cannot exclude the interaction between Ba species and CeO₂, which would also explain their good dispersion and the low intensity of the corresponding XRD patterns. Similarly, the formation of MgTiO_x, NbTiO_x and NbCeO_x mixed oxides is anticipated [60–62], but the appearance of well-defined

phases could not be unambiguously confirmed in the corresponding catalysts.

The HAADF-STEM images combined with EDXS elemental mapping of the ceria- and titania-supported catalysts are presented in Fig. 2 and Fig. 3, respectively. Generally, when ceria was used as a support, a high dispersion of platinum was observed in all as prepared catalysts, in line with the XRD data reported in Fig. 1. After the harsh reductive treatment (hR) at 500 °C, which is expected to lead to the reduction and sintering of noble metal particles [32], slightly larger Pt nanoparticles of approx. 1 – 1.2 nm were detected in all samples. The corresponding histogram of particle size distribution is presented in Figure SI 2a) for each reduced ceria-based catalyst. The calculated mean size diameters and the corresponding deviations are provided in Table 2. The calculated surface-averaged particle sizes according to the formula (6) indicate similar trends with maximum deviation of 0.2 nm. Only a slight tendency to form larger particles was noticed for the catalysts promoted with alkaline earth metals. Hence, the well-known strong noble metal-support interaction between ceria and platinum [63] is the predominant effect observed in all ceria-supported catalysts, while the basic and acidic properties of the promoters only slightly affect the noble metal dispersion.

On the other hand, by examining the electron microscopy data obtained for the titania-based catalysts (Fig. 3), it was noticed that the majority of the as prepared catalysts already contain larger Pt particles in comparison to the CeO₂-based samples. The corresponding size distribution histograms are shown in Figure SI 2b-c). Noble metal nanoparticles in a size range of 1 – 9 nm were found on the pure TiO₂-support, with a mean diameter d_m of ~1.4 nm. The addition of basic dopants resulted in a decrease in particle size (mean diameter of ~1.1 nm for Pt-Mg-Ti), and no particles could be distinguished in the Pt-Ba-Ti catalyst. In contrast, the number of large Pt particles increased in the presence of WO₃ (mean diameter 1.1 nm) and Nb₂O₅ (mean diameter 26.3 nm). For Pt-Nb-Ti, the formation of large Pt-containing particles is also indicated by the XRD data (Fig. 1) and by the surface-averaged particle sizes (Table 2). This tendency is in line with previous studies, which reported the presence of larger metallic Pt particles on acidic supports [64–66].

Irrespective of the catalyst dopant, the reductive treatment at 500 °C resulted in the formation of Pt nanoparticles with a mean size around 1 nm on ceria and 1.5 nm when titania was used as a support. In comparison to the CeO₂-supported catalysts, an inverse trend was noticed for the reduced titania-based samples: the earth alkaline metal-promoted samples exhibit smaller mean particle sizes compared to the unpromoted Pt-Ti sample. Moreover, the small Pt nanoparticles are accompanied by larger particles in the catalysts containing acidic promoters, similarly as in the freshly prepared catalysts.

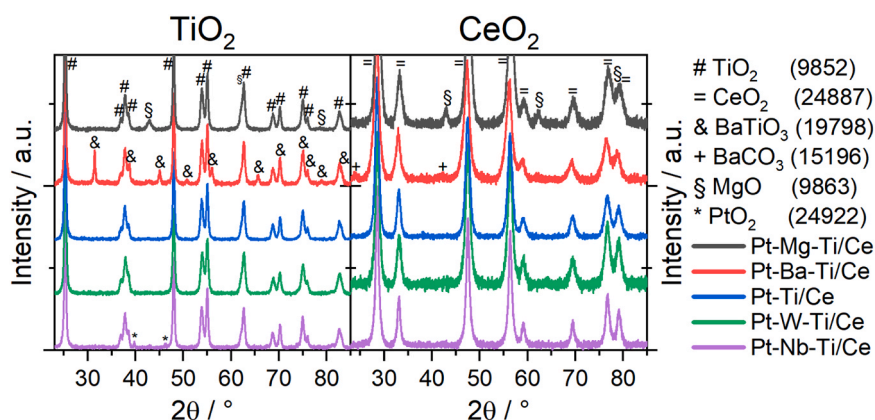


Fig. 1. X-ray diffractograms of the synthesized catalysts. Left side titania-supported (from the top to the bottom, 0.5 wt% Pt-10 wt% Mg-Ti, 0.5 wt% Pt-10 wt% Ba-Ti, 0.5 wt% Pt-Ti, 0.5 wt% Pt-10 wt% W-Ti, 0.5 wt% Pt-10 wt% Nb-Ti) and ceria-supported samples on the right side (from the top to the bottom, 0.5 wt% Pt-10 wt% Mg-Ce, 0.5 wt% Pt-10 wt% Ba-Ce, 0.5 wt% Pt-Ce, 0.5 wt% Pt-10 wt% W-Ce, 0.5 wt% Pt-10 wt% Nb-Ce).

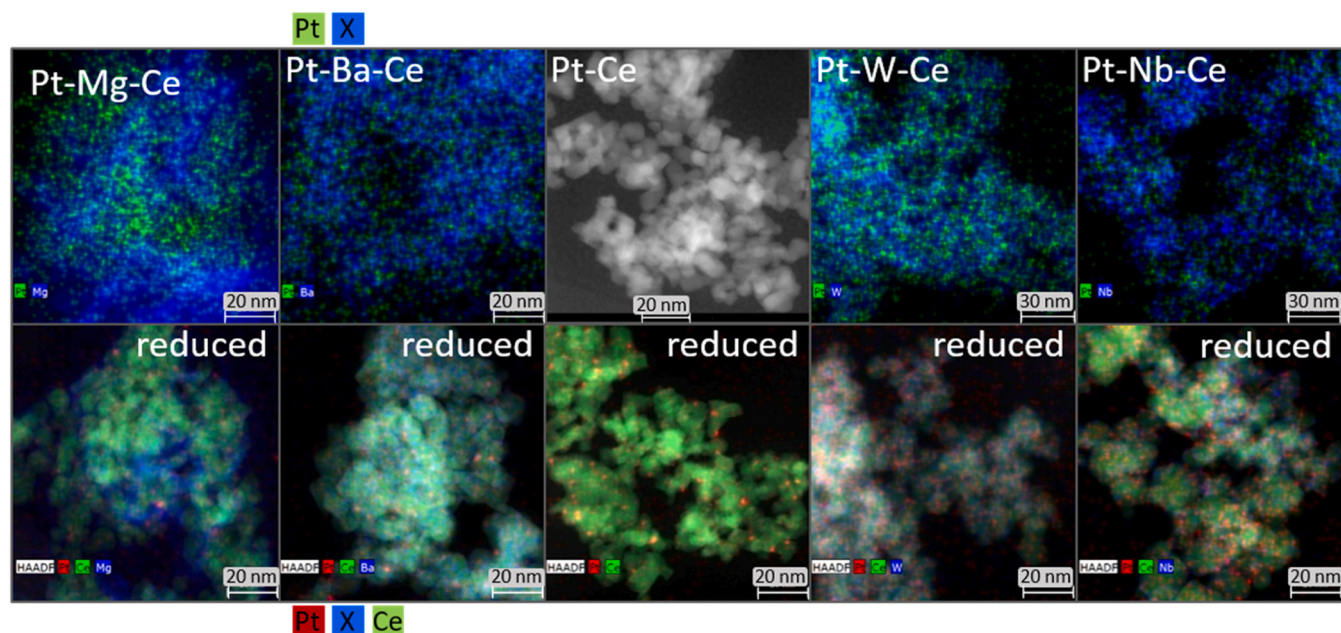


Fig. 2. HAADF-STEM images and corresponding EDXS maps of as-prepared (top row) and reduced samples (bottom row) at 500 °C for one hour (2 % H₂ in N₂ balance) ceria-supported catalysts. From left to right the chemical composition is shown for 0.5 wt% Pt-10 wt% Mg-Ce, 0.5 wt% Pt-10 wt% Ba-Ce, 0.5 wt% Pt-Ce, 0.5 wt% Pt-10 wt% W-Ce and 0.5 wt% Pt-10 wt% Nb-Ce, respectively.

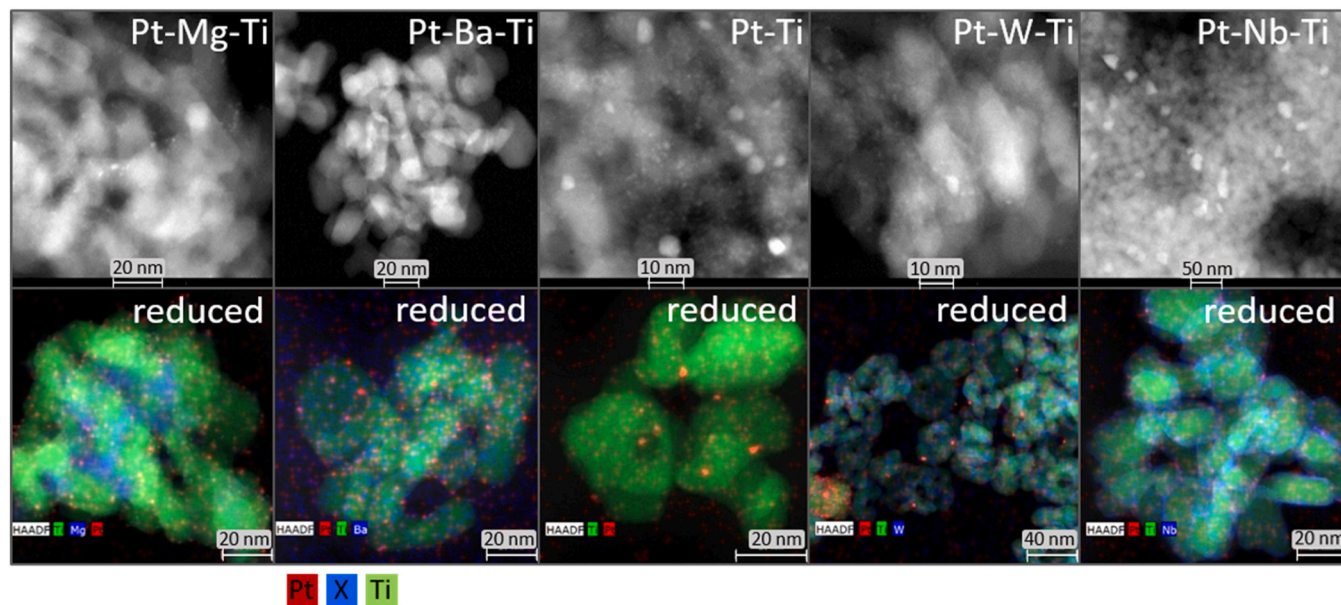


Fig. 3. HAADF-STEM images of the as-prepared titania-supported samples (top row), and HAADF-STEM images overlapped with their corresponding EDXS maps after catalyst reduction at 500 °C for one hour in 2 % H₂ in N₂ (bottom row). From left to right the chemical composition is shown for: 0.5 wt% Pt-10 wt% Mg-Ti, 0.5 wt% Pt-10 wt% Ba-Ti, 0.5 wt% Pt-Ti, 0.5 wt% Pt-10 wt% W/Ti, 0.5 wt% Pt-10 wt% Nb-Ti, respectively.

To confirm the observed differences in the noble metal particle sizes between the used supports, *ex situ* XAS spectra at Pt L₃ edge were collected for selected calcined samples. The obtained XANES spectra are shown in Figure SI 3 together with those of PtO₂ and Pt foil references. A visual comparison of the white line intensity and profile reveals that already in the as prepared catalysts the noble metal species are in a more reduced oxidation state when supported on titania. This can be associated with the presence of larger particles in these samples, as indicated

by the XRD and HAADF-STEM investigations (Table 2 and Fig. 1). Such particles are known to be less prone to oxidation when exposed to ambient air [67]. In contrast, a high oxidation state was identified for Pt on CeO₂, almost independent of the presence of other catalyst dopants. This trend confirms the stronger interaction between the noble metal and the ceria support, leading to the formation of highly dispersed species.

Table 2

Platinum particle size and distribution on ceria and titania-supported catalysts before and after harsh reductive treatment (hR, 2 % H₂ in N₂ at 500 °C for 1 h); d_m represents the calculated mean particle size by Gauss term fitting with the deviation given in brackets; d_{NP} represents the calculated surface-averaged particle size using formula (6).

Catalyst Fresh	d _m [nm]	d _{NP} [nm]	Catalyst Reduced (hR)	d _m [nm]	d _{NP} [nm]
Pt-Mg-Ce	-	-	Pt-Mg-Ce	1.3 (±0.02)	1.4
Pt-Ba-Ce	-	-	Pt-Ba-Ce	1.5 (±0.03)	1.7
Pt-Ce	-	-	Pt-Ce	1.2 (±0.02)	1.4
Pt-W-Ce	-	-	Pt-W-Ce	0.9 (±0.04)	1.0
Pt-Nb-Ce	-	-	Pt-Nb-Ce	0.9 (±0.01)	1.1
Pt-Mg-Ti	1.1 (±0.01)	1.6	Pt-Mg-Ti	1.1 (±0.01)	1.3
Pt-Ba-Ti	-	-	Pt-Ba-Ti	1.1 (±0.01)	4.8
Pt-Ti	1.4 (±0.02)	4.9	Pt-Ti	1.2 (±0.05)	1.7
Pt-W/Ti	1.1 (±0.02)	12.9	Pt-W/Ti	1.9 (±0.10)	3.6
Pt-Nb-Ti	26.3 (±1.0)	31.0	Pt-Nb-Ti	1.0 (±1.50)	34.6

3.2. Acidic and basic properties

NO_x and NH₃ storage and release capacities were systematically evaluated for selected TiO₂- and CeO₂-supported catalysts, namely unpromoted and barium- or tungsten-promoted catalysts. In this way, the overall impact of basic or acidic dopants on the catalyst properties could be assessed.

3.2.1. NO_x storage and release

The storage behavior of unpromoted catalysts and those promoted with barium or tungsten was investigated according to the protocol shown in Figure SI 1c. The adsorption of NO_x at 50 °C was conducted by dosing a gas mixture of 1000 ppm NO, 10 % O₂, 5 % H₂O in N₂ for one hour. At this temperature, the oxidation of NO is known to be rather low over Pt-based catalysts [68]. After flushing with dry nitrogen for one hour, the desorption of the adsorbed species was monitored while heating of the catalyst bed up to 500 °C. Due to the calcination of the catalysts in static air at 500 °C for five hours, only a minor impact of the TPD experiments on the catalyst performance was expected. Irrespective of the carrier material, the WO₃-doped samples did not present any notable storage of NO_x at 50 °C (Fig. 4). The corresponding molar

amounts, which were calculated based on the NO_x-TPD data, are presented in Table SI 2. A similar behavior was observed for the unpromoted Pt-Ti catalyst, which displayed only a minor release of NO around 150 °C. In contrast, significant release of NO and NO₂ was measured for the Pt-Ce sample between approximately 100 – 275 °C and 275 – 450 °C. This difference could be explained by the strong interaction between WO₃ and CeO₂ [69–71], which probably blocks the NO_x storage sites on the support surface. The capability of ceria-based materials to store NO_x on its surface as nitrosyl, nitrites and nitrates has been acknowledged by previous studies [72–77], with the nitrites desorbing at lower temperatures in comparison with the nitrates [78]. In line with previous literature [75], the addition of Ba as promoter resulted in a significant increase of the NO_x storage capacity for both carriers. Similar as measured for Pt-Ce, the release of NO and NO₂ was detected within two temperature ranges for the Pt-Ba-Ti catalyst: 50 – 350 °C and 350 – 500 °C. A total of 115.2 μmol·g⁻¹ NO_x was measured during the TPD experiment while unpromoted titania stored 6.52 μmol·g⁻¹ of NO_x, highlighting the major effect of barium on the overall NO_x storage capability. Comparable enhancement of the storage capability was observed for the Pt-Ba-Ce catalyst, which displayed the highest NO_x storage capacity of 115.2 μmol·g⁻¹ compared to 107.1 μmol·g⁻¹ for unpromoted ceria, with a considerable NO release of 66.4 μmol·g⁻¹ at low temperatures. Consistent with their basic surface properties, all CeO₂-based catalysts showed higher NO_x adsorption potentials in comparison to the TiO₂-based counterparts, which are further enhanced by the presence of basic promoters such as barium. On the contrary, acidic promoters suppressed the NO_x adsorption ability, as illustrated in this study for the Pt-W-Ce and Pt-W/Ti samples.

3.2.2. NH₃ adsorption and desorption

As a commonly applied method to investigate the acidity of NO_x removal catalysts [36,37,42], NH₃ adsorption tests followed by TPD under inert atmosphere were conducted for the same samples as used during the NO_x storage investigations. All NH₃ storage experiments were performed in the presence of water, since this is always present in the exhaust of H₂-combustion engines. The results obtained during the NH₃-TPD tests are reported in Fig. 5. The corresponding amounts of evolved gases are presented in Table SI 3. Additionally, the NH₃ adsorption capacity was calculated for each sample based on the storage step of the experimental procedure (Table SI 3). For both unpromoted

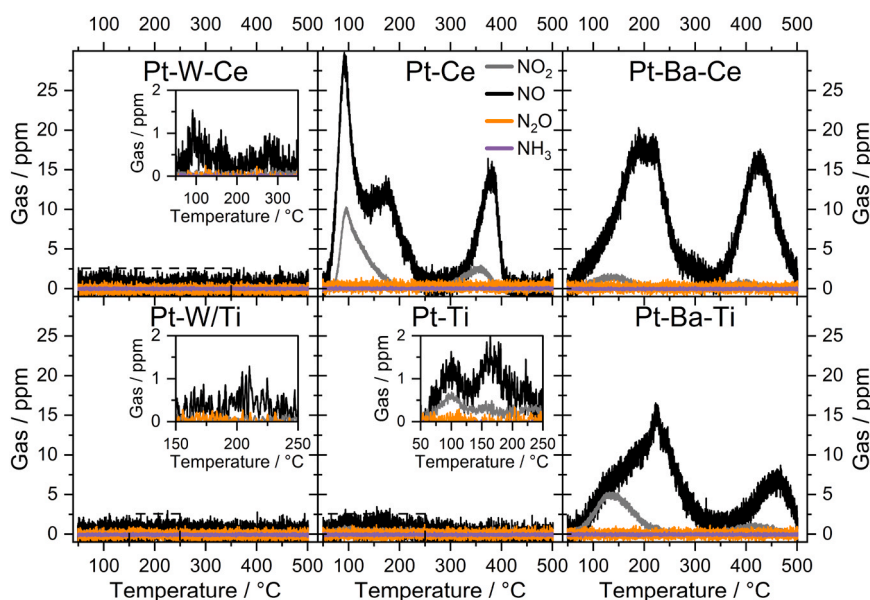


Fig. 4. Gas release during temperature-programmed desorption (50 – 500 °C, ramp of 5 K·min⁻¹) after NO_x adsorption (1000 ppm NO, 10 % O₂, 5 % H₂O in N₂) at 50 °C for one hour and dry flushing (N₂) for 0.5 wt% Pt-10 wt% W-Ce, 0.5 wt% Pt-Ce, 0.5 wt% Pt-10 wt% Ba-Ce, 0.5 wt% Pt-10 wt% W/Ti, 0.5 wt% Pt-Ti, and 0.5 wt% Pt-10 wt% Ba-Ti (60,000 L·(h·g_{Pt})⁻¹). Inset graphs present the corresponding smoothed data (Savitzky-Golay method, 30-point window, 2nd polynomial order).

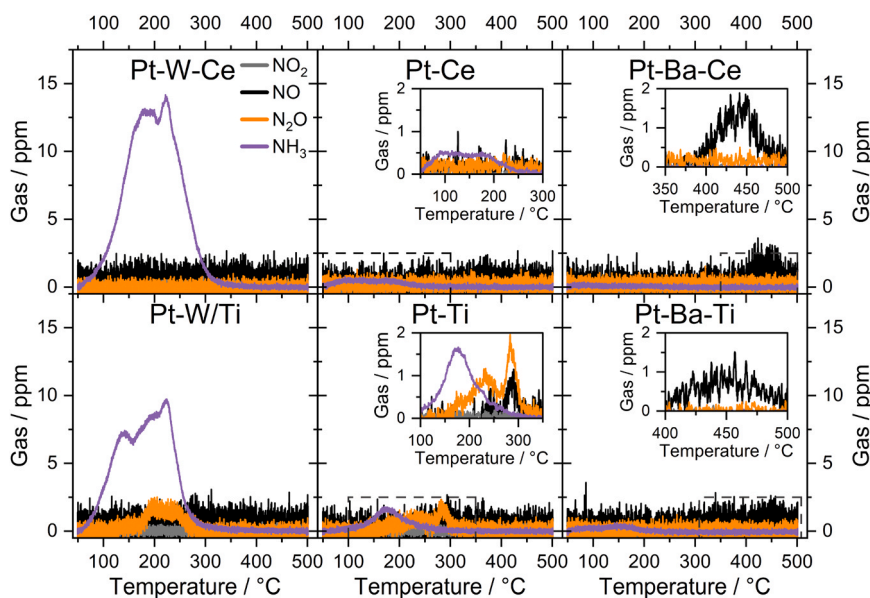


Fig. 5. Gas release during temperature-programmed desorption (50 – 500 °C, ramp of 5 K*min⁻¹) after NH₃ adsorption (660 ppm NH₃, 5 % H₂O in N₂) at 50 °C for one hour and dry flushing (N₂) for 90 min for 0.5 wt% Pt-10 wt% W-Ce, 0.5 wt% Pt-Ce, 0.5 wt% Pt-10 wt% Ba-Ce, 0.5 wt% Pt-10 wt% W/Ti, 0.5 wt% Pt-Ti, and 0.5 wt% Pt-10 wt% Ba-Ti (60,000 L*(h*g_{Pt})⁻¹). All graphs present smoothed data (Savitzky-Golay method, 30-point window, 2nd polynomial order).

Pt/CeO₂ and Pt/TiO₂ catalysts, only minor release of NH₃ was detected below 500 °C. Particularly for the TiO₂-supported catalyst, this low amount is partly caused by the inhibition by H₂O of NH₃ adsorption. However, the presence of strongly adsorbed NH₃, which potentially desorbs at higher temperatures cannot be completely excluded. In fact, based on the profile of the NH₃ adsorption curves, the calculated amounts of stored NH₃ indicate a significantly higher storage capacity for the Pt-TiO₂ catalyst in comparison to Pt-CeO₂ (Table SI 3). As shown by Kulkarni and Muggli [79], water competes with NH₃ for adsorption at both Lewis and Brønsted sites on the titania surface. Nevertheless, the same authors reported the release of a small NH₃ amount above 450 °C after adsorption in the presence of H₂O.

Adding a basic promoter further suppressed NH₃ adsorption on both catalyst series. The presence of small NH₃ amounts on Pt-Ba-Ce and Pt-Ba-Ti surface was indicated only by the low amounts of NO formed between 400 – 500 °C due to the release and oxidation of NH₃ (2.6 and 2.7 μmol*g⁻¹ of NO respectively). In contrast, the formation of acidic sites on the catalyst surface upon WO₃ addition was confirmed by the evolved NH₃ during the TPD experiments conducted for Pt-W-Ce and Pt-W/Ti samples. For the Pt-W-Ce catalyst, NH₃ release was recorded between 100 – 350 °C with two maxima around 180 °C and 222 °C. The overall quantity of N-containing species (NH₃ and NO_x) corresponds to 58.1 μmol*g⁻¹. The amount of stored NH₃ on the Pt-W/Ti catalyst was as well enhanced in comparison to that measured for the unpromoted Pt-Ti sample. Also in this case, the evolution of N-containing species was observed below 350 °C, reaching two maxima for NH₃ release at 138 °C and 222 °C. This profile could be correlated with the formation of both Lewis and Brønsted acidic sites on the catalyst surface, considering the relatively high WO₃ loading in these samples. According to Wachs et al. [80], surface polytungstate species are expected to be present on the catalyst surface alongside crystalline WO₃ nanoparticles. Additionally, from 165 °C up to 270 °C the formation of N₂O was detected for the Pt-W/Ti catalyst, possibly due to oxidation of ammonia by H₂O traces or lattice oxygen. Between 350 – 500 °C no additional gases were released, and a total of evolved nitrogen species of 43.4 μmol*g⁻¹ was calculated for this catalyst.

Overall, distinct variations in surface acidity and NH₃ adsorption capacity were observed across CeO₂- and TiO₂- supported catalysts. As anticipated, these trends are inversely correlated with those derived from the NO_x storage measurements — Pt-CeO₂ catalysts doped with

basic promoters exhibited the lowest density of acidic sites, whereas TiO₂-supported systems incorporating acidic dopants showed the highest surface acidity.

3.3. Catalytic activity tests

As it will be reported in the following, the influence of different dopants, gas hourly space velocity and noble metal loading on the catalyst performance was investigated for the as-prepared catalysts and after soft or harsh reduction steps at 300 °C (sR) or 500 °C (hR), respectively. While the pre-reductive treatment at 300 °C aligns with the typical H₂-SCR operating temperature of noble metal-based catalysts, reduction at 500 °C is anticipated to induce more pronounced modifications in catalyst structure, namely noble metal reduction and particle growth (Fig. 2).

3.3.1. Influence of promoters and pre-treatment procedure

Fig. 6 and Fig. 7 report the NO_x removal activity along with the N₂, NH₃ and N₂O selectivity for the different catalysts investigated in this study at a WHSV of 90,000 L*(h*g_{Pt})⁻¹. All activity trends were obtained after treating the catalyst in oxidizing atmosphere (pre-oxidation in 10 %O₂ in N₂) at 350 °C followed by conditioning during a first light-off/light-out cycle to 300 °C (Figure SI 1). Considering the low temperature range of the H₂-SCR reactions, the activity during the light-out part of the cycle was used during data evaluation to avoid interference from prior stored surface species. In the as-prepared state, the Pt-Ce, Pt-Ba-Ce and Pt-Nb-Ce catalysts displayed no NO_x removal activity (Fig. 6). Even the conversion of H₂ was limited, suggesting an almost inactive state of the noble metal species in these samples. This behavior could be explained by the strong interaction between Pt and CeO₂ resulting in the formation of highly dispersed Pt clusters/single atoms [32,63,81], which were shown to be poorly active for oxidation reactions [82]. According to our results, such a structure for the noble metal is not beneficial for deNO_x either. Furthermore, the presence of Ba and Nb species on the catalyst surface did not seem to affect the overall noble metal performance. In contrast, Mg and W promoters slightly increased the performance of the Pt-Ce catalyst: about 10 % NO_x conversion was measured over the Pt-Mg-Ce and Pt-W-Ce samples around 150 – 200 °C, with S(N₂, NO_x) of over 60 % for most of the investigated temperature window. Hydrogen conversion reached only 50 – 60 % at 300 °C.

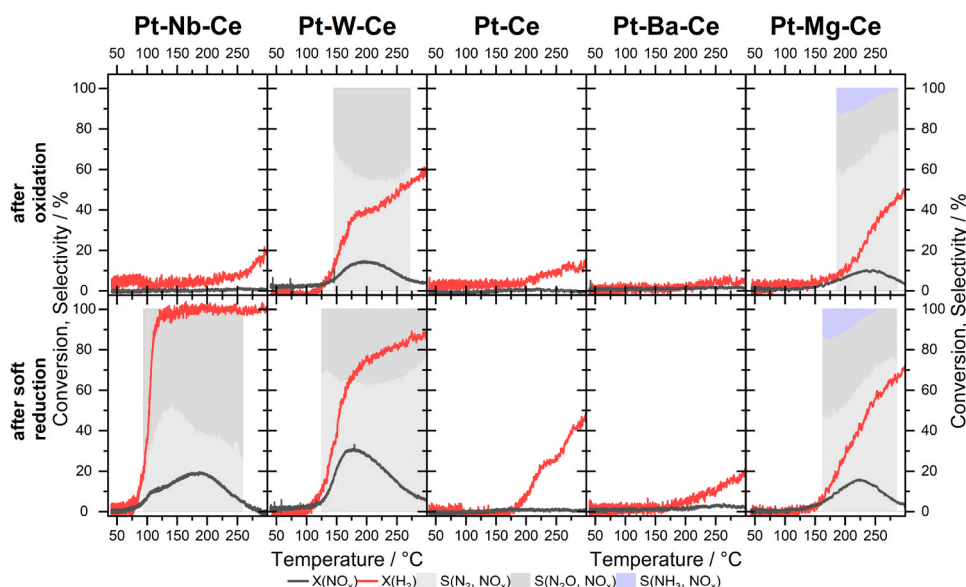


Fig. 6. The second light-out activity of ceria-supported, unpromoted and niobium-, tungsten-, barium-, or magnesium-promoted catalysts, after pre-oxidation [top row], and soft reduction (1 h at 300 °C in 2 % H₂ in N₂) [bottom row]: X(NO_x) [black], X(H₂) [red], and stacked areas of S(N₂, NO_x) [light grey, bottom], S(N₂O, NO_x) [grey, middle], and S(NH₃, NO_x) [purple, top] are shown for a gas composition of 1000 ppm NO, 5000 ppm H₂, 8 % O₂, 5 % H₂O in N₂ at a WHSV of 90,000 L*(h*g_{PT})⁻¹.

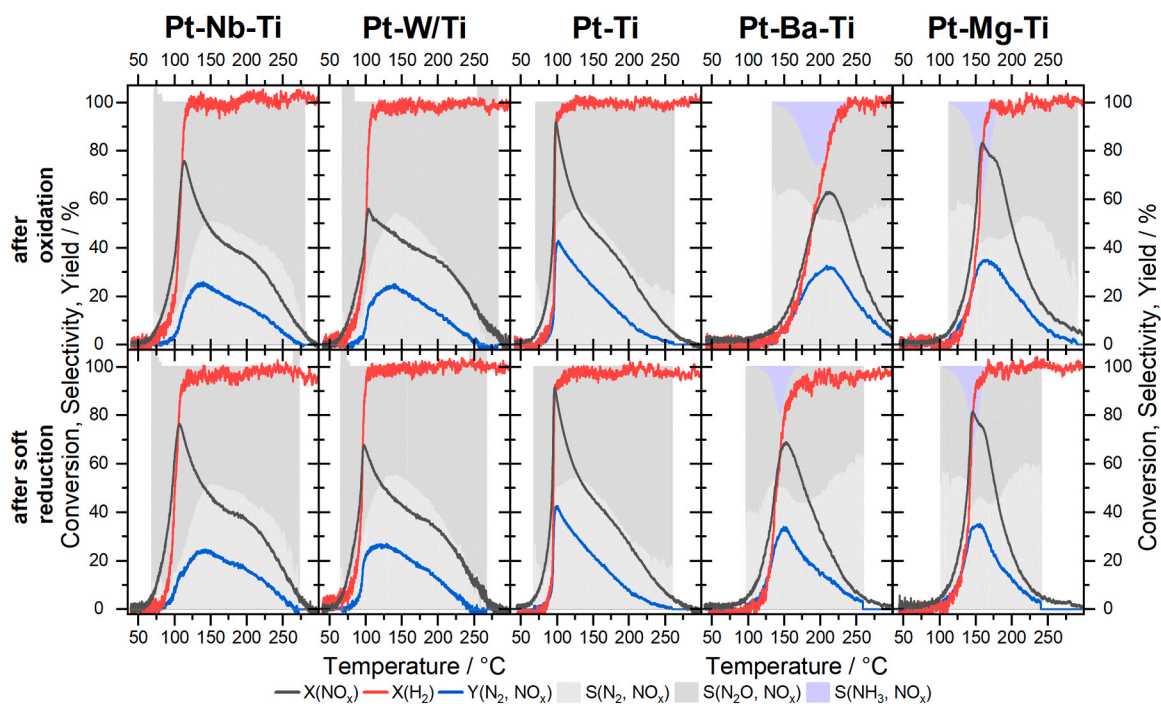


Fig. 7. The second light-out activity of titania-supported, unpromoted and niobium-, tungsten-, barium-, or magnesium-promoted catalysts, after pre-oxidation [top row], and after soft reduction (1 h at 300 °C in 2 % H₂ in N₂) [bottom row]: X(NO_x) [black], X(H₂) [red], Y(N₂, NO_x) [blue], and stacked areas of S(N₂, NO_x) [light grey, bottom], S(N₂O, NO_x) [grey, middle], and S(NH₃, NO_x) [purple, top] are shown for a gas composition of 1000 ppm NO, 5000 ppm H₂, 8 % O₂, 5 % H₂O in N₂ at a WHSV of 90,000 L*(h*g_{PT})⁻¹.

As a reaction byproduct, N₂O was detected over both samples while NH₃ formation was observed only for the Pt-Mg-Ce catalyst. Our performance trends are in agreement with the observations of Machida et al. [28] for similar systems. However, the outcome is apparently in contrast to the results reported by Costa and Efstathiou [27] for analogous Pt/CeO₂ and Pt/Mg-Ce-O catalysts, which is probably caused by the higher O₂ and lower H₂ concentrations used during our investigations (8 % O₂ and 0.5 % H₂ vs. 5 % O₂ and 1 % H₂). In addition to

the reaction conditions, the high surface area of the CeO₂ support used in this study might sustain a highly dispersed and inactive state for Pt [83].

Notably higher catalytic performance was measured for the TiO₂-supported samples, as presented in Fig. 7. Within a very narrow temperature window, the highest NO_x conversion was attained by the undoped Pt-Ti catalyst (90 % around 125 °C and a nitrogen yield of 42 %), which towards 200 °C quickly dropped to about 40 %

conversion. This catalyst also displayed a selectivity $S(\text{N}_2, \text{NO}_x)$ between 40 – 50 %. Both Pt-Mg-Ti and Pt-Nb-Ti catalysts showed comparable high NO_x removal activity. However, the Mg-doped catalyst, which was active over a broader temperature range, achieved a maximum nitrogen yield of 34 % versus 25 % as measured for the Nb-doped sample. Analogous, the NO_x conversion was shifted by almost 100 °C to higher temperatures when Ba was used as a promoter (maximum yield of 33 %). This catalyst also showed higher N_2 selectivity (50 – 60 %) at all investigated temperatures accompanied by NH_3 formation between 125 – 250 °C. Both samples promoted by acidic dopants, i.e. Pt-Nb-Ti and Pt-W/Ti, displayed activity in a broader temperature range, and higher NO_x conversion at low temperatures in comparison to the unpromoted Pt-Ti catalyst. However, these trends were accompanied by a lower selectivity toward N_2 formation below 100 °C. For all titania supported samples, complete H_2 conversion was measured with similar onset temperatures as observed for the NO_x reduction. Catalyst pre-treatment in reductive atmosphere at 300 °C only led to a slight increase of H_2 conversion for the Pt-Ce (50 % at 300 °C) and Pt-Ba-Ce (20 % at 300 °C) catalysts, due to partial redispersion of Pt particles under reaction conditions [83].

In contrast, for the Pt-Nb-Ce catalyst 20 % NO_x removal was attained around 190 °C with a $S(\text{N}_2, \text{NO}_x)$ between 30 – 40 %, which was accompanied by complete H_2 conversion. An increase of NO_x reduction at lower temperatures was also measured for the Pt-W-Ce and Pt-Mg-Ce catalysts. The Mg-promoted catalyst achieved 71 % H_2 conversion at 300 °C with relatively low NO_x removal activity (15 % between 215 – 230 °C) and a N_2 selectivity between 40 – 60 %. For this sample, the formation of NH_3 (up to 15 % selectivity around 160 °C) was encountered alongside N_2O emissions. For the WO_3 -containing sample, $X(\text{NO}_x)_{\text{max}}$ increased to 30 % around 175 °C simultaneously with the enhancement of the nitrogen selectivity (>60 %). In line with most CeO_2 -supported samples, this catalyst showed only partial hydrogen conversion (about 90 % at 300 °C).

A significantly lower impact of the mild pre-reductive treatment was noticed for the TiO_2 -supported catalysts, suggesting minor variations in catalyst structure at 300 °C. For the undoped Pt- TiO_2 sample, a slight decrease in the overall N_2 yield was noticed. In the presence of acidic promoters, a small increase in NO_x conversion was observed at lower temperatures for Pt-W/Ti while hardly any change was visible in the performance of Pt-Nb-Ti. Only the Ba- and Mg-promoted catalysts displayed a shift and narrowing of the NO_x conversion window towards lower temperatures after H_2 -reduction. This behavior indicates a slightly detrimental effect of pre-reductive treatments on this class of catalysts.

In agreement with this observation, excepting the Pt-W/Ti sample, all undoped and doped TiO_2 -based samples displayed an overall lower NO_x conversion and N_2 yield after the pre-reduction step at 500 °C (Figure SI 4). In a similar manner, while H_2 conversion was enhanced the NO_x removal performance decreased for nearly all CeO_2 -based samples, after increasing the catalyst pre-reduction temperature to 500 °C (Figure SI 5). A decrease in NO_x conversion and shift of the activity window towards lower temperatures was measured for the Pt-Ba-Ce catalyst (Figure SI 5), which also displayed an improved N_2 selectivity. Both Pt-Mg-Ce and Pt-W-Ce samples showed a narrowing of the NO_x conversion region. At the same time, no significant variation in the reactivity of Pt-Ce and Pt-Ba-Ce samples was observed, except for a minor increase in H_2 oxidation. This tendency is due to the increase of the NM particles, as confirmed by HAADF-STEM measurements and EDXS analysis (Fig. 2). Only for the Nb-doped catalyst, a small increase of the NO_x conversion and N_2 selectivity was noticed.

3.3.2. Effect of space velocity

Considering the broad variation in the reaction conditions used for testing H_2 -SCR catalysts [16,18,36,49] as well as different possible applications of H_2 combustion engines, selected catalysts of the TiO_2 - and CeO_2 -series were also tested at a lower weight hourly space velocity of $60,000 \text{ L}^*(\text{h}^*\text{g}_{\text{Pt}})^{-1}$. The H_2 -SCR activity was evaluated for the as-prepared and harshly pre-reduced states (500 °C, 1 h) of the undoped

and Ba/W-doped catalysts. The results obtained for the samples supported on ceria and titania are presented in Figure SI 6 and Figure SI 7, respectively. As already observed under higher WHSV conditions, both Pt-Ce and Pt-Ba-Ce catalysts do not present any catalytic activity besides minor hydrogen conversion. Treating these samples under reductive conditions at 500 °C resulted in an increase of H_2 consumption (70 % at 300 °C for Pt-Ce). For the Pt-W-Ce catalyst, the pre-reduced state exhibited a NO_x conversion of 38 % at 195 °C with 69 % selectivity towards nitrogen formation. Analogous, an almost identical trend was measured for the fresh and reductively treated Pt-Ti, Pt-Ba-Ti and Pt-W/Ti samples when varying the WHSV. Decreasing the space velocity led to only minor changes in activity and onset temperatures. This behavior suggests that the reaction kinetics are not significantly affected when this parameter was varied. A similar moderate change in activity was previously reported by Koch et al. [84] during tests with a catalyst coated honeycomb at higher space velocities. According to the calculated amounts of overall NH_3 emissions in our study (Figure SI 8), the path towards NH_3 formation over Pt-Ba-Ti catalyst decreased at this lower WHSV of $60,000 \text{ L}^*(\text{h}^*\text{g}_{\text{Pt}})^{-1}$. Eßer et al. [85] reported similar observations of enhanced ammonia formation at higher space velocities. The increased ammonia production window may result from a reduced residence time of the gas mixture in the catalyst bed, leading to higher unconverted ammonia concentrations at the reactor outlet. In this regard, its slower conversion rate in the low temperature range via the standard NH_3 -SCR reaction is further limited at higher WHSV [31].

Regarding the selectivity towards NH_3 formation of the samples promoted with basic dopants, decreased NH_3 emissions were observed for Pt-Ba-Ti and Pt-Mg-Ti catalysts after pre-reduction at both WHSV applied in this study (Figure SI 8). In contrast, the trend in the generated NH_3 amounts was reversed for Pt-Mg-Ce and Pt-Ba-Ce during H_2 -SCR tests at lower WHSV after catalyst pre-reduction due to an increased NO_x conversion. Therefore, partial (N_2O) or complete (NH_3) reduction of NO_x seems to be highly sensitive not only to the catalyst composition but also to small variations in the noble metal state, i.e. Pt particle size. Generally, due to the inactive nature of the highly dispersed Pt species in ceria catalysts, the as prepared TiO_2 -supported catalysts are superior in ammonia formation (> 40 fold) compared to ceria samples with a release of 1695 and $1320 \mu\text{mol}^*\text{g}^{-1}$ against 38.5 and $27.8 \mu\text{mol}^*\text{g}^{-1}$ at $90,000$ WHSV for magnesia- and barium-promoted titania- and ceria-supported samples, respectively. Considering the differences in the NO_x conversion measured for the two catalyst series, an overview on the average NH_3 and N_2O selectivity is reported in Figure SI 9 for selected TiO_2 - and CeO_2 -supported samples together with the corresponding mean Pt particle size. Despite the increase in Pt particle size upon the harsh pre-reduction treatment was not clearly indicated for all samples by the HAADF-STEM measurements, a general tendency can be derived from our study: the selectivity for NH_3 formation decreases with the increase of Pt particle size while the selectivity for N_2O formation is enhanced.

Overall, the effect of a mild pre-reduction treatment, which corresponds to reduction of Pt and slight increase of the noble metal particle size [32], was found to enhance the performance of CeO_2 -supported catalysts. However, after a harsh reductive treatment, the NO_x removal activity decreased for most samples, almost irrespective of the dopant type. For the TiO_2 -catalyst series, any increase in the noble metal nanoparticle size resulted in diminished activity. Furthermore, this was accompanied by an enhanced N_2O formation and decreased N_2 yield (Fig. 7, Figure SI 5, Figure SI 7). This difference between the CeO_2 - and TiO_2 -supported catalysts could be explained by the stronger interaction between Pt and CeO_2 , which ensures a certain reversibility of Pt particle formation even at these low temperatures [86]. In contrast, the formation of larger and more stable Pt particles on TiO_2 leads to a more permanent change in deNO_x activity upon induced Pt sintering by reduction.

3.3.3. Impact of noble metal loading

Considering the general effect of a pre-reductive treatment and noble metal particle size on the H_2 -SCR performance, additional investigations were conducted for samples containing a higher noble metal loading of 1 wt%. Previous studies have shown that an increased Pt concentration might be advantageous for preserving the metallic state, which was found to be essential for promoting the low-temperature H_2 -SCR activity [29,38]. However, according to Costa and Efstathiou [18], the rate of N_2 production decreases for CeO_2 supported catalysts if higher Pt loadings are used. Generally, a higher noble metal surface concentration is also known to enhance the probability of noble metal clusters/particle formation [86]. Nonetheless, on strongly interacting supports like CeO_2 , this process is additionally controlled by the specific surface area of the carrier material. Accordingly, only slight variations in the H_2 -SCR activity of the as prepared CeO_2 -supported catalysts were measured in this study upon increasing Pt loading from 0.5 wt% to 1 wt% (Fig. 8). Hydrogen conversion increased for the unpromoted and barium promoted samples to 45 and 14 %. Pt-W-Ce showed again activity over a broader temperature range with a maximum NO_x conversion of 17 % for the 1 wt% Pt loading compared to 14.6 % as obtained for the 0.5 wt% Pt-W-Ce sample. At the same time, a comparable high nitrogen selectivity of 73.7 % at maximum conversion was measured versus 54.6 % for the lower noble metal loading.

For TiO_2 -catalyst series, a broadening of the activity window was noticed. Overall, the conversion maxima decreased from about 61, 90 and 73 % to approximately 51, 81 and 72 % for Pt-W/Ti, Pt-Ti, and Pt-Ba-Ti samples, respectively. These were accompanied by a comparable or slightly enhanced nitrogen selectivity when barium was added. Additionally, Pt-Ba-Ti displayed an earlier onset of NO_x conversion (> 38 °C lower temperature). Herein, ammonia formation decreased while

nitrogen formation increased, resulting in a slightly higher maximum yield for this sample at lower temperatures than the sample with 0.5 wt % Pt at the same space velocity.

3.4. Insights into the H_2 -SCR reaction mechanism

In order to understand the observed trends in the H_2 -SCR activity and selectivity of differently doped Pt-based catalysts, several aspects were studied in detail, including the effect of H_2O and O_2 concentration as well as the reactivity of the stored surface species.

3.4.1. Influence of water on the activity and selectivity

As reported by several working groups, water can act either as a promoter or as an inhibitor for the H_2 -SCR reactions [13,17,18,87]. Deactivation is proposed to occur due to the competitive adsorption of NO and water at the active sites [87]. In contrast, the dissociation of water was suggested to increase the presence of adsorbed hydrogen, leading to higher activity [18,88,89]. Despite its presence cannot be completely eliminated as water is a reaction product, additional tests were conducted in this study with a dry gas atmosphere for selected as-prepared and harshly reduced catalysts at 500 °C for 1 h. The results obtained for the undoped and Ba/W-doped catalysts supported on CeO_2 and TiO_2 are presented in Fig. 9 and Fig. 10, respectively.

In the absence of additional water, unpromoted Pt-Ce showed the ability to catalyze NO_x reduction irrespective of the catalyst state, which directly confirms the H_2O inhibitory effect. Maximum NO_x conversion of about 20 % with 42 % nitrogen selectivity were measured post-oxidation and post-reduction. Moreover, complete H_2 conversion was achieved at 300 °C. The steeper H_2 conversion curve obtained for the reduced sample was in line with the formation of larger Pt particles on

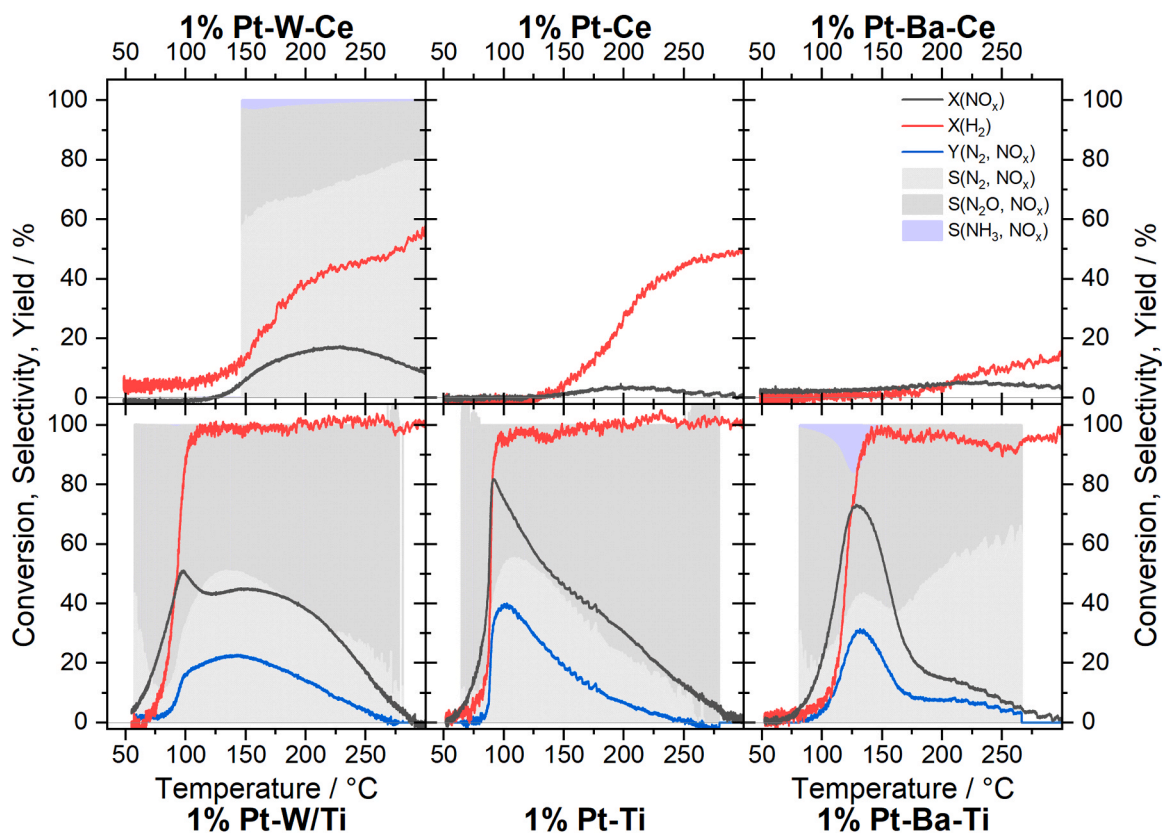


Fig. 8. The second light-out activity of ceria- [top row] and titania-supported [bottom row], unpromoted and tungsten- or barium-promoted catalysts with a platinum loading of 1 wt%, after sample pre-oxidation: $X(NO_x)$ [black], $X(H_2)$ [red], $Y(N_2, NO_x)$ [blue], and stacked areas of $S(N_2, NO_x)$ [light grey, bottom], $S(N_2O, NO_x)$ [grey, middle], and $S(NH_3, NO_x)$ [purple, top] are shown for a gas composition of 1000 ppm NO , 5000 ppm H_2 , 8 % O_2 , 5 % H_2O in N_2 at a WHSV of $60,000 L^*(h^*g_{Pt})^{-1}$.

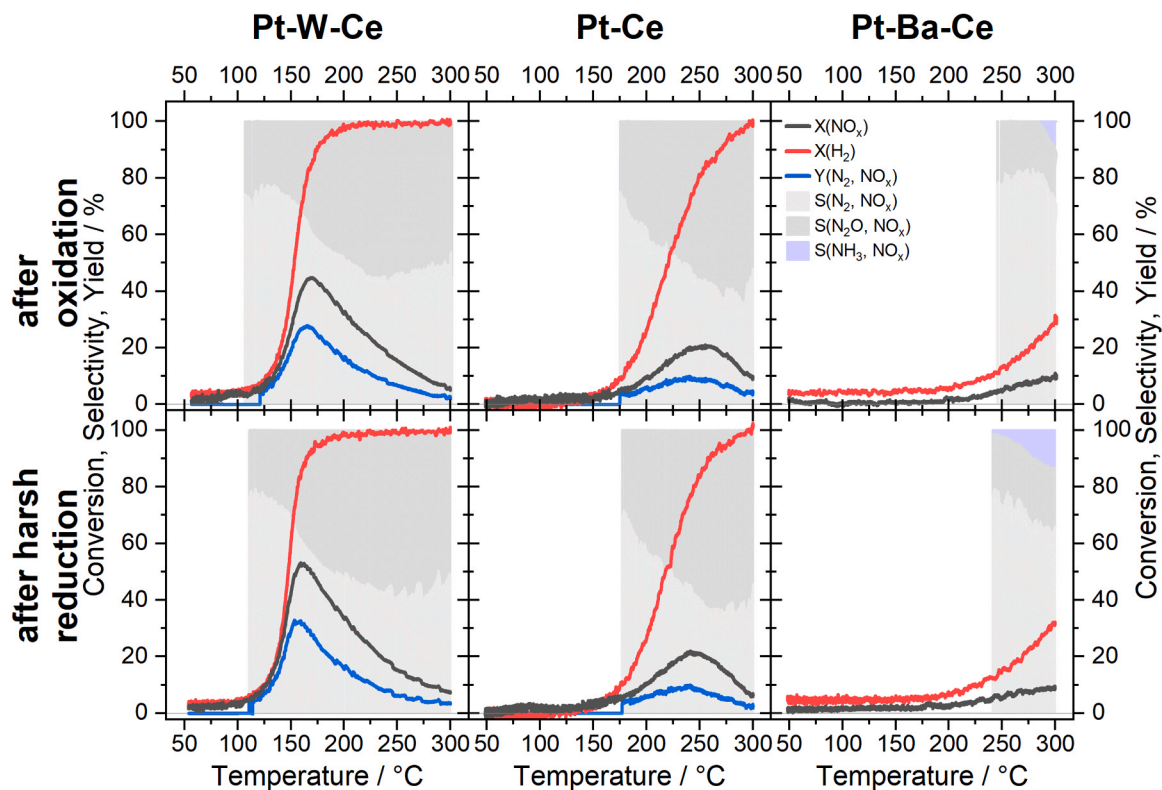


Fig. 9. The second light-out activity of ceria-supported catalysts under dry reaction conditions after sample pre-oxidation and harsh reduction (500 °C): X(NO_x) [black], X(H₂) [red], Y(N₂, NO_x) [blue], and stacked areas of S(N₂, NO_x) [light grey, bottom], S(N₂O, NO_x) [grey, middle], and S(NH₃, NO_x) [purple, top] are shown for a gas composition of 1000 ppm NO, 5000 ppm H₂, 8 % O₂ in N₂ at a WHSV of 60,000 L*(h*g_{PT})⁻¹.

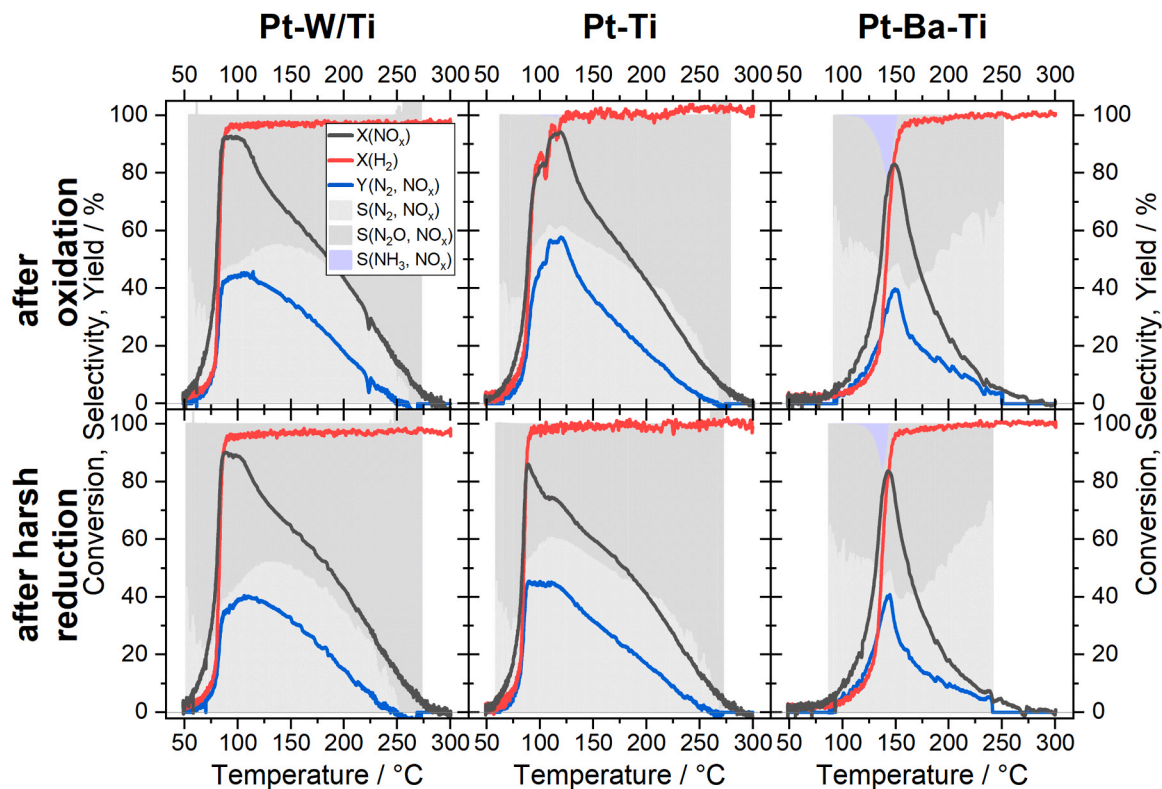


Fig. 10. The second light-out activity of titania-supported catalysts under dry reaction conditions after pre-oxidation and harsh reduction: X(NO_x) [black], X(H₂) [red], Y(N₂, NO_x) [blue], and stacked areas of S(N₂, NO_x) [light grey, bottom], S(N₂O, NO_x) [grey, middle], and S(NH₃, NO_x) [purple, top] are shown for a gas composition of 1000 ppm NO, 5000 ppm H₂, 8 % O₂ in N₂ at a WHSV of 60,000 L*(h*g_{PT})⁻¹.

the catalyst surface. Less pronounced enhancement of the catalytic performance in the dry gas mixture was also measured for the Pt-Ba-Ce catalyst.

About 10 % NO_x are converted under these conditions with a N_2 selectivity around 80 %. Even NH_3 emissions were detected at elevated temperatures, with higher levels observed for the pre-reduced catalyst. In comparison to the catalytic performance recorded in wet gas mixture, also the NO_x removal activity of Pt-W-Ce increased by almost 20 % at low temperatures. Catalyst pre-reduction produced no notable changes except a minor shift of the NO_x conversion towards lower temperatures with a slight activity increase. NO_x conversion reached 45 % at 170 °C and a $\text{S}(\text{N}_2, \text{NO}_x)$ of ~ 60 % after the pre-oxidation step and 53 % with 60 % nitrogen selectivity at 161 °C after reduction. Additionally, complete hydrogen conversion was achieved during both tests.

A similar behavior was noted for the TiO_2 -supported catalysts in the absence of water. For the Pt-Ti catalyst, a maximum NO_x conversion of over 95 % was measured along a broader activity window. Besides, N_2 selectivity was enhanced, especially at low temperatures, for both catalyst states. This trend is consistent with the H_2O inhibition effect, which is expected to adsorb on the catalyst surface particularly at low temperatures [21,90]. Accordingly, the NO_x removal activity still dropped with increasing temperature. For the W-promoted sample, a temperature window of nearly 150 °C with NO_x conversion between 60 % and 95 % and a N_2 selectivity of > 40 % were recorded independent of the catalyst pre-treatment. The improvement in NO_x conversion was not as significant for Pt-Ba-Ti, which displayed an activity shift of 40 °C towards lower temperatures, while the activity increased by ~ 15 % (85 % vs. 70 % under wet conditions). Additionally, the NH_3 selectivity was reduced and narrowed to a shorter temperature window in the absence of additional water — 22 % maximum selectivity at 142 °C compared to 49 % at 172 °C. After catalyst reduction, NH_3 emissions are further decreased, as already observed in wet conditions, along an overall diminishment in the NO_x removal activity, following the established trends under wet conditions.

All in all, water was found to inhibit the NO_x conversion for both CeO_2 - and TiO_2 -supported catalysts. Particularly at low temperatures, water is probably adsorbing on the catalyst surface preventing an early

reaction onset. While an improvement in performance was observed over the entire temperature range for the CeO_2 -supported catalysts, undoped Pt-Ti and Pt-W/Ti sample, the increase in the NO_x conversion was accompanied by a narrowing of the activity window for the Pt-Ba-Ti catalyst. In all cases, an enhancement of the N_2 selectivity was additionally observed. For the samples doped with basic dopants, the lower NH_3 formation selectivity could be correlated with the observed shift of the H_2 and NO_x conversion curves towards lower temperatures, where NH_3 release was encountered in a wet gas mixture. This difference could be as well caused by a higher conversion of the *in situ* generated ammonia under dry conditions.

3.4.2. Influence of oxygen on the course of H_2 -SCR reaction

To better understand the course of the NO_x reduction reactions, supplementary tests were conducted for selected catalyst samples after removing oxygen from the H_2 -SCR gas mixture (noO). Fig. 11 and Figure SI 10 present the obtained light-out and light-off activity measurements for the undoped and W/Ba-doped catalysts after pre-reduction at 500 °C and several light-off cycles. This experimental procedure implies that at the start of the noO test (light-off) the catalyst surface is covered with adsorbed species formed during the light-out of the H_2 -SCR reaction in the presence of oxygen. Accordingly, upon interacting with NH_3 and NO under lean conditions, nitrosyl/nitrites/nitrates could form on the support surface or at the basic promoters (i.e. Ba and Mg) [8,91]. NH_3 could as well adsorb at the Brønsted and Lewis acidic sites of TiO_2 or catalyst dopants (W, Nb) [70]. On the contrary, during the light-out of the H_2 -SCR in the absence of O_2 , the formation of nitrates is most probably limited in the low-temperature range. However, at moderate temperatures the contribution of CeO_2 lattice oxygen was found to promote their formation [92]. Nevertheless, partial reduction of the support surface and noble metal species is most likely occurring considering the reduction potential of the applied gas mixture. At the same time, the adsorption of NO as nitrosyl/nitrites and of NH_3 at the acidic sites is still expected to occur in this temperature range [92], as it will be demonstrated in the following. Hence, all these differences will influence the course of the NO reduction by H_2 in the O_2 -free gas mixture.

During the noO light-off, a clear tendency from partial to complete

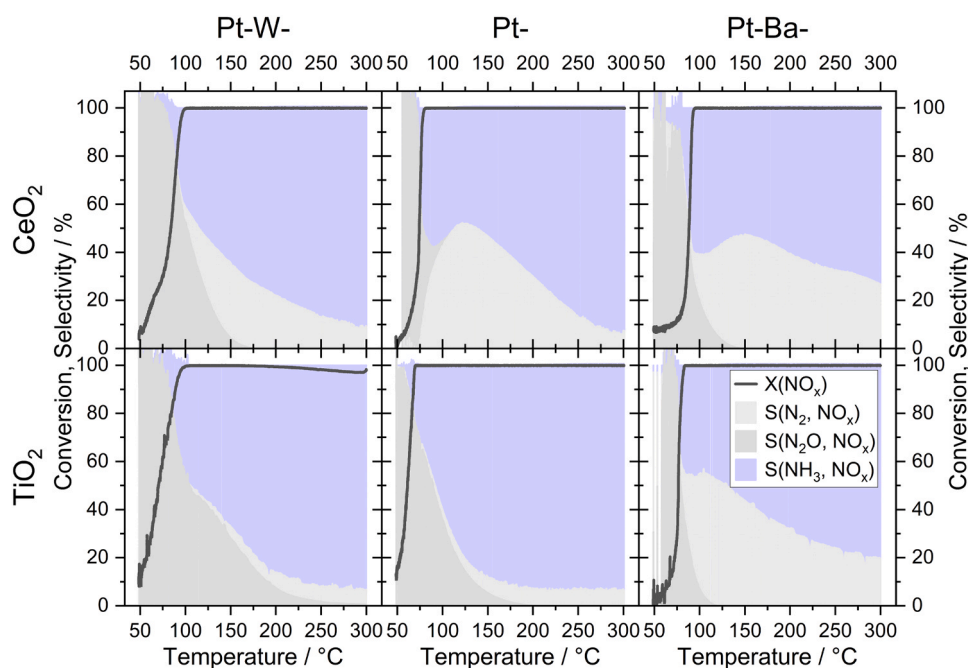


Fig. 11. The light-out activity of ceria (top) and titania (bottom) supported catalysts after pre-reduction at 500 °C and several light-off cycles: $X(\text{NO}_x)$ [black], and stacked areas of $\text{S}(\text{N}_2, \text{NO}_x)$ [light grey, middle], $\text{S}(\text{N}_2\text{O}, \text{NO}_x)$ [grey, bottom], and $\text{S}(\text{NH}_3, \text{NO}_x)$ [purple, top] are shown for a gas composition of 1000 ppm NO, 5000 ppm H_2 , 5 % H_2O in N_2 at a WHSV of $60,000 \text{ L}^*(\text{h}^*\text{g}_{\text{Pt}})^{-1}$.

NO_x reduction was observed for all catalysts with the increase of temperature. During initial stages of conversion, N_2O formation is predominant, rapidly declining thereafter in the favor of NH_3 formation. In most cases, N_2 selectivity remained at low values across the entire temperature range. According to Kubiak et al. [93], N_2O formation at low temperatures does not involve stored nitrates but gas-phase NO and N-adsorbed species formed by NO dissociation on partially reduced Pt surface, a path also proposed by Burch et al. [94] during the H_2 -SCR reaction. The only role of H_2 is to remove O-adsorbed atoms upon NO dissociation. The formation of N_2O stops with the increase of temperature, while the complete dissociation of NO over completely reduced Pt sites prevails [95]. In agreement with these observations, our experimental results showed the formation of N_2O emission at low temperatures for all samples, irrespective of their basic or acidic surface properties (Fig. 11 and Figure SI 10). In fact, higher N_2O concentrations were detected for the catalysts with a higher NO_x storage capacity (Fig. 4). The only noticeable difference was the onset temperature for N_2O formation, which was lower for the TiO_2 -supported catalysts. This trend could be explained by the higher oxygen reservoir of the CeO_2 -supported catalysts [63] in comparison with TiO_2 -samples, which prevents the reduction of Pt at lower temperatures. Moreover, the strong interaction between the noble metal and ceria was predicted to maintain a higher dispersion and a decreased reducibility for Pt species [32], as also indicated by the HAADF-STEM data (Fig. 2 and Fig. 3). Hence, the higher dynamicity of the CeO_2 -catalyst series shifts both the NO reduction and N_2O formation towards higher temperatures during the reaction light-off by limiting platinum reduction.

The unpromoted Pt-Ce sample during the light-out cycle exhibited the onset of NO_x conversion around 150 °C, which completed at ~210 °C with a maximum N_2 selectivity of 10 %. In a similar manner, the NO_x reduction activity ignited above 125 °C for the Pt-Ba-Ce catalyst, reaching full conversion at 175 °C. This catalyst was found to contain larger Pt particles after the pre-reduction step (Table 2), which could contribute to the lower light-off temperature in comparison to the unpromoted sample. However, the interaction with both barium species and ceria is projected to lead to partial noble metal redispersion at higher temperatures in an O_2 -rich atmosphere (previous catalytic cycles, Figure SI 4), in line with the relatively modest activity of this sample below 100 °C [6,7,63]. An even earlier onset temperature was measured for the Pt-W-Ce sample (below 100 °C), however, the reaction was completed at 220 °C. Due to the lower reaction onset temperature, a broader temperature window for N_2O emissions was observed for this catalyst.

As illustrated in Figure SI 10, NO reduction was completed over Pt-Ti already at 100 °C with up to 90 % selectivity towards N_2O formation between 130 – 150 °C. In the same temperature range, N_2 selectivity reached a maximum of 17 %. The addition of tungsten further enhanced NO conversion, which was already complete at 80 °C. In the temperature range between the onset temperature and full conversion, N_2O was detected as the sole product. Among the TiO_2 -supported samples, only Pt-Ba-Ti presented a distinct behavior, which was most probably caused by the strong interaction between platinum and barium species, leading to the formation of mixed oxides at elevated temperatures [96]. Analogous to CeO_2 -based catalysts, the reduction of Pt is probably also in this case the rate determining step for the onset of NO reduction. Further studies to understand the oxidation state of platinum during this mixture need to be conducted to proof this hypothesis.

While N_2O formation was predominant during the reaction light-off (Figure SI 10), complete reduction to NH_3 was measured at temperatures above 70 °C. Due to the pronounced reducing conditions at these higher temperatures, the N_2 selectivity was rather modest for the undoped and W-doped catalysts. Only for the Pt-Ba-Ce and Pt-Ba-Ti samples the N_2 selectivity exceeds 20 % above 150 °C, during complete NO conversion. In fact, excepting the Pt-W-Ce catalyst, all investigated samples catalyzed N_2 and NH_3 formation mainly after 100 % NO conversion was attained.

These general trends are maintained during the light-out step of the H_2 -SCR process in the absence of O_2 . However, while an increase in the N_2 selectivity was observed over the CeO_2 -supported catalysts, the opposite effect was measured for Pt-Ti and Pt-W/Ti samples (Fig. 11). For the later cases, a broadening of the N_2O formation window was noticed. Only for the Pt-Ba-Ti catalyst the gain in NO activity at low temperatures was complemented by a significant share of N_2 formation (up to 55 % selectivity around 100 – 125 °C).

Since all samples were exposed to the same conditions during the light-off, these differences could be linked to the initial state of Pt that affects its evolution under reaction conditions. All samples originally containing highly dispersed Pt species, exhibit a higher N_2 selectivity during the light-out. Hence, more pronounced sintering of Pt particles could be speculated to occur during light-off in the Pt-Ti and Pt-W/Ti samples. This corroborates with a related effect of tungsten species on ceria, since Pt-W-Ce samples exhibits the lowest N_2 selectivity and the highest N_2O emissions amongst CeO_2 -supported catalysts. Furthermore, the presence of WO_3 on TiO_2 and CeO_2 expands the window for N_2O formation significantly above the temperature of 100 % NO conversion, which was not observed for the other catalysts.

Overall, titania-supported catalysts demonstrated superior activity and greater resistance to inhibition by oxygen. Acidic promoters were found to enhance the catalytic activity but resulted in reduced nitrogen selectivity, whereas basic promoters support nitrogen formation at the expense of the low-temperature catalytic performance during the light-off cycle. An interesting observation across all tested samples is that the onset of N_2 formation corresponds to full NO_x conversion. This pattern is consistent during both light-off and light-out processes for titania-based samples and during the light-off for ceria-based samples. Conversely, for ceria supported samples during light-out process, it is the nitrous oxide selectivity that diminishes at the NO_x conversion transition points.

At the end of the light-off/light-out cycle conducted in the absence of oxygen, a temperature programmed desorption (TPD) step was performed in dry N_2 to identify the nature of the surface species stored on a partially reduced catalyst surface. The results obtained are shown in Figure SI 11, and the calculated amounts of released gases are reported in Table SI 4 for both ceria and titania-based catalysts. While NH_3 desorption was only observed for the Pt-W/Ti sample, NO release was detected for all samples and especially for the catalysts with higher surface basicity. The rather similar evolution of NO during the TPD of Pt-Ba-Ce and Pt-Ba-Ti indicated that its storage on the catalyst surface was mostly related to Ba species differently interacting with the two supports [75]. For Pt-Ce, the adsorption of NO_x as nitrites or nitrates can be traced back to different Ce-O surface sites [73]. The formation of nitrates on ceria was also indicated by the simultaneous NO_2 release. Very small N_2O emissions were as well measured but only for the samples doped with acidic promoters. The formation of N_2O at low temperatures was probably due to the unselective reaction between adsorbed NO and NH_3 , since its evolution stopped at higher temperatures where NH_3 release was detected.

The total release of N-containing species increases for both catalyst series from acidic-promoted, over unpromoted to basic-promoted samples. Furthermore, using ceria as a support increased the overall NO_x storage capacity (147 $\mu\text{mol}\cdot\text{g}^{-1}$ for Pt-Ba-Ce vs 54 $\mu\text{mol}\cdot\text{g}^{-1}$ for Pt-Ba-Ti). Finally, the result of these tests indicate that oxygen is inherently not necessary for NO storage in this temperature range.

3.4.3. Reactivity of adsorbed species

To better understand the interaction of H_2 with the adsorbed surface species, temperature programmed reaction tests were conducted after exposing the as-prepared catalyst to the reaction mixture at 50 °C (after sample conditioning during several H_2 -SCR light-off/light-out). The results obtained for selected ceria- or titania-supported catalysts are shown in Fig. 12. The overall measured amounts for NO_x , NH_3 and N_2O are reported in Table SI 5.

The obtained results align very well with the trends observed during

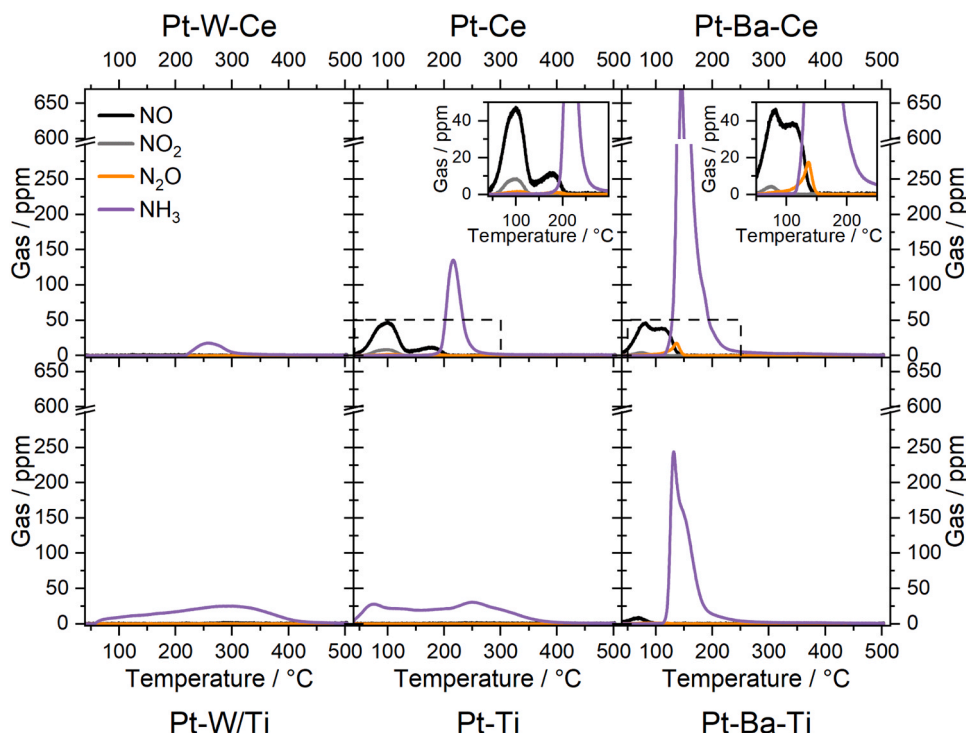


Fig. 12. Evolution of gases during temperature-programmed reduction (50 – 500 °C, ramp of 5 K*min⁻¹, 5 % H₂ in N₂) after the first light-off/light-out cycles for 0.5 % Pt-10 wt% W-Ce, 0.5 wt% Pt-Ce, 0.5 wt% Pt-10 wt% Ba-Ce, 0.5 wt% Pt-10 wt% W/Ti, 0.5 wt% Pt-Ti, and 0.5 wt% Pt-10 wt% Ba-Ti (90,000 L*(h*g_{Pt})⁻¹).

the H₂-SCR tests in the absence of O₂. NO_x release was detected only in the low-temperature range for the samples able to store NO_x but not yet active to catalyze its reduction, i.e. Pt-Ce, Pt-Ba-Ce and Pt-Ba-Ti. Due to a higher surface acidity (Fig. 4), no NO_x emissions were measured for the Pt-W-Ce sample. On the other hand, NH₃ release was observed already at low temperatures for Pt-Ti and Pt-W/Ti (122 and 128 μmol*g⁻¹, respectively), which stored NH₃ on the surface at the support and dopant Brønsted/Lewis acidic sites (Fig. 5). Moreover, these samples are highly active in converting NO in the absence of O₂ (Fig. 11 and Figure SI 10). The highest NH₃ amounts were observed to form *via* reduction of stored nitrites/nitrates in Pt-Ce, Pt-Ba-Ce and Pt-Ba-Ti (89, 420, and 189 μmol*g⁻¹, respectively). Hence, this process could be an additional path for NH₃ generation besides the direct reduction of NO on reduced noble metal sites [97]. In fact, considering that in the presence of oxygen the complete reduction of Pt across the catalyst bed was challenging while the adsorption of NO_x at basic sites could occur (Fig. 4), the formation of NH₃ *via* nitrosyl/nitrites/nitrates reduction could be an important step during the H₂-SCR mechanism. In contrast, N₂O formation does not seem to occur by means of nitrites/nitrates reduction, and only minor traces were detected during the H₂-TPR experiments. This outcome is as well in line with previous literature [93,98]. However, to elucidate the trends reported in this study and to gain further insights into the reaction mechanism and promoter influence, additional *operando* and *in situ* studies are necessary in the future.

4. Conclusions

This study reports a systematic analysis of the effects of the carrier material and promoters on the activity of Pt-based catalysts in the selective catalytic reduction of NO_x with H₂. Factors affecting the NO_x conversion and reaction selectivity were evaluated for CeO₂ and TiO₂ supported catalysts containing acidic (WO₃, Nb₂O₅) or basic (BaO, MgO) promoters. By combining extensive catalytic testing with various sample pre-treatment procedures and substantiating the obtained results with complementary characterization of the catalyst properties, the following main conclusions were drawn:

- Depositing Pt on CeO₂ resulted in the formation of highly dispersed species due to the strong noble metal-support interaction, which were found to be poorly active for both NO_x and H₂ conversion. In contrast, the moderate interaction with TiO₂ led to the formation of larger Pt nanoparticles, which exhibited good NO_x conversion below 200 °C but also produced relatively high N₂O emissions.
- Among the basic promoters, only MgO was found to slightly improve the performance of Pt-CeO₂, while their presence shifted the activity window towards higher temperatures for the TiO₂ supported catalysts. Additionally, NH₃ was detected alongside N₂O as a reaction byproduct.
- Acidic dopants and especially WO₃ increased the NH₃ storage capacity and the H₂-SCR activity for both catalyst series and broadened the selectivity window for Pt-TiO₂ samples, likely due to usage of *in situ* generated ammonia.
- Mild catalyst pre-reduction at 300 °C enhanced the H₂-SCR activity of all Pt-CeO₂ catalysts, irrespective of the dopant nature. However, after a harsh reductive treatment at 500 °C, which promoted stronger sintering of Pt particles, the NO_x removal activity slightly decreased for most samples. This tendency was identified after both catalyst reductive treatments for the TiO₂-catalyst series, accompanied by enhanced N₂O formation.
- Only a slight variation in the H₂-SCR activity was observed upon increasing the Pt loading from 0.5 to 1 wt% for CeO₂-supported catalysts, while a broadening of the activity window was noticed for the corresponding TiO₂-based samples.
- Water was found to inhibit the NO_x conversion over both CeO₂- and TiO₂-supported catalysts, especially at low temperature, where its adsorption seems to prevent an early reaction onset and high N₂ selectivity.
- Most probably due to its promoting effect on Pt redispersion on CeO₂, a clear enhancement of the NO_x conversion was measured in the absence of oxygen for the Pt-CeO₂ catalysts. At the same time, TiO₂-supported samples demonstrated a higher resistance towards oxygen inhibition. In both cases notable NH₃ emissions were detected,

highlighting the possible contribution of the NH_3 -SCR reaction to the H_2 -SCR mechanism, independent of the catalyst formulation.

- Based on the observed reactivity of stored species and their desorption trends, an additional path for ammonia generation was identified, namely *via* the reduction of nitrate/nitrites/nitrosyl species formed at the basic catalyst sites. Despite being detected for all catalysts at low temperatures, samples with a high NO_x storage capacity were also linked to increased N_2O emissions at low temperatures. In our study, this trend also aligned with the smaller size of Pt entities and the lower reducibility of CeO_2 -based samples.

Overall, the results obtained allow a better understanding of the effects of catalyst composition on the H_2 -SCR activity and selectivity of Pt-based catalysts. This knowledge is expected to serve as an important basis for the rational design of improved H_2 -SCR catalysts, which are relevant to the future energy transition toward carbon-neutral fuels. Further studies could address the stability of the catalyst in the presence of SO_2 (these emissions could, e.g., occur due to Lubricant Oil Consumption, cf. ref. [99]) as well as additional characterization methods to gain deeper insights into the structural dynamics of the catalyst and the influence of the promoters.

CRedit authorship contribution statement

Jan-Dierk Grunwaldt: Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. **Radian Popescu:** Formal analysis, Data curation. **Marc Maurer:** Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Maria Casapu:** Writing – review & editing, Supervision, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Heike Störmer:** Formal analysis, Data curation.

Funding

This work was supported by the Materials and Technologies for the Energy Transition (MTET) program of Helmholtz association.

Finally, the authors thank DAPHNE4NFDI (DFG project under project number 460248799) as well as further NFDI-consortia for fruitful discussion and valuable input for implementing FAIR data principles in this work.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Armin Lautenbach (IKFT, KIT) for ICP-OES analysis, Lukas Braun (ITCP, KIT) and Andrea de Giacinto (ITCP, KIT) for XRD measurements, Thomas Jackson Eldridge (IKFT/ITCP, KIT), Sarina-Lena Heck (ITCP, KIT) and Simon Bastian (ITCP, KIT) for N_2 -physisorption measurements. Heike Störmer and Radian Popescu (LEM, KIT) for TEM imaging and analysis.

We acknowledge the European Synchrotron Radiation Facility (ESRF) for provision of synchrotron radiation facilities under proposal number CH-6595 and we would like to thank Davide Salusso for assistance and support in using beamline BM23 (for the data please refer to doi: 10.1515/ESRF-ES-1214160061).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2025.126347.

Data availability

Research data is available on the KITopen platform at: <https://dx.doi.org/10.35097/OneOfakaqd3ay9nh>

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