Reduction of NOx by H2 on WOx-Promoted Pt/Al2O3/SiO2 Catalysts Under O2-Rich Conditions

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Abstract
This work addresses the reduction of NOx by H2 under O2-rich conditions using Al2O3/SiO2-supported Pt catalysts with different loads of WOx promotor. The samples were thoroughly characterised by N2 physisorption, temperature-programmed desorption of CO, scanning electron microscopy, X-ray diffraction, laser raman spectroscopy, X-ray photoelectron spectroscopy and diffuse reflectance infrared fourier transform spectroscopy with probe molecule CO. The catalytic studies of the samples without WOx showed pronounced NOx conversion below 200 °C, whereas highest efficiency was related to small Pt particles. The introduction of WOx provided increasing deNOx activity as well as N2 selectivity. This promoting effect was referred to an additional reaction path at the Pt-WOx/Al2O3/SiO2 interface, whereas an electronic activation of Pt by strong metal support interaction was excluded.

Graphic Abstract

Keywords NOx reduction · H2 reductant · Pt catalyst · Al2O3/SiO2 support · WOx promotor

1 Introduction
The major sources of global energy production are combustibles like coal, natural gas, oil and fuel. However, a critical issue of these fossil fuels is the output of CO2 causing global warming. Therefore, sustainable strategies of energy supply are of marked relevance, especially for the important transport sector. Promising concepts of transportation imply biogenic fuels, synthetic fuels originated from biomass, fuel cells, batteries and hybrid engines. Furthermore, H2 combustion engines are also developed with particular focus on fleets of trucks and busses fuelled by regional filling stations. Sustainable production of H2 is associated with the electrolysis of water powered by photovoltaic and wind generators. However, a serious issue of H2 combustion engines is the output of NOx, which is associated with the formation of thermal NO, thus demanding the after-treatment of the exhaust to meet emission standards. For this purpose, the catalytic NOx reduction by H2 (2 NO + 2 H2 → N2 + 2 H2O) is a favourable tool using the engine slip of H2, whereas injection of H2 to the exhaust is also possible. As a consequence, the supply of an additional reductant such as urea is not necessary. Aqueous solution of urea (“AdBlue”) is employed for the on-board production of NH3 required for the selective catalytic reduction of NOx (SCR), which is well-established for diesel passenger cars and
In SCR, NO is reduced by NH₃ to yield N₂ and H₂O (4 NO + 4 NH₃ + O₂ → 4 N₂ + 6 H₂O). Traditional SCR catalysts are comprised of V₂O₅/WO₃/TiO₂, while for diesel vehicles Fe and Cu based zeolites are presently taken [1].

Furthermore, in the lean exhaust of passenger cars NOₓ storage reduction catalysts (NSR) are also applied consisting of Pt, Pd and Rh as well as NOₓ adsorbents like Al₂O₃, CeO₂ and BaCO₃. The operation of NSR includes periodic storage and reduction of NOₓ [2]. The reduction is performed under rich conditions temporarily induced by engine management and is substantially enhanced by the presence of H₂ [3].

Moreover, the reduction of NOₓ by H₂ also occurs effectively in the excess of O₂ when using Pt catalysts. Their operation range lies between 65 and 200 °C and is therefore relevant for low exhaust temperatures of lean-burn engines. However, a serious drawback is the marked selectivity of N₂O of up to 50%, whereas Mo and Co promoters are shown to decrease N₂O [4, 5]. Additionally, Ru, Ir, Rh, Pd and Ag [6–9] as well as mixed oxides like perovskites [10–13] and spinels [8] reveal lean H₂-deNOₓ activity, but also include substantial production of N₂O. A recent review also features several TiO₂-based precious metal catalysts with significant activity under lean conditions [14, 15]. Nevertheless, clearly diminished N₂O formation combined with high performance below 200 °C is only reported for a few catalysts, particularly Pt/La₀.₇Sr₀.₂Ce₀.₁FeO₃ [10, 16], Pt/MgO-CeO₂ [17–19] and Pt/WO₃/ZrO₂ [20]. Furthermore, Pd/WO₃/ZrO₂ catalysts exhibit selective formation of N₂ upon lean H₂-deNOₓ, but their activity is limited to a rather narrow operation range [21]. High activity and selectivity of N₂ is also evidenced for LaCoO₃-supported Pd [22]. Moreover, Ag/Al₂O₃ catalysts show an enhancing effect of H₂ for both NOₓ reduction by hydrocarbons [23] as well as SCR [24].

The present paper aims to study Al₂O₃/SiO₂-based Pt catalysts with and without WO₃ promotor for the NOₓ reduction by H₂ under O₂-rich conditions. WO₃ was shown to reveal high efficiency for lean H₂-deNOₓ on Pt and Pd catalysts [15, 20, 21, 25]. The catalysts were prepared, thoroughly characterised and tested in synthetic model exhaust of H₂ combustion engines towards low-temperature deNOₓ. Additionally, the H₂-deNOₓ performance was correlated with the physical–chemical properties to unravel features, which drive the activity as well as N₂ selectivity of the catalysts. Also, possible strong metal support interaction (SMSI) was evaluated to enlighten the effect of the WO₃ promotor.

## 2 Experimental Section

### 2.1 Catalyst Preparation

A series of commercially available Al₂O₃/SiO₂ carriers with SiO₂ proportions of 20, 30 and 40 wt% was used (Siralox 20HPV, Siralox 30 HPV and Siralox 40 HPV, Sasol); respective codes are AlSi-20, AlSi-30 and AlSi-40. The carriers were modified with the active component Pt, whereas AlSi-20 was additionally coated with tungsten oxide promotor before introducing Pt. The codes of the tungsten-modified catalysts reflect the mass fraction of tungsten present in the sample, e.g. 11W/AlSi-20. The introduction of WO₃ and Pt was carried out by incipient wetness impregnation implying complete absorption of a defined volume of an aqueous solution of Pt(NO₃)₂ (Chempur) and (NH₄)₆H₂ W₁₂ O₄₀·H₂O (Honeywell), respectively. In accordance with previous work [20] the load of Pt was adjusted to be 0.25 wt% referring to bare substrate, and for AlSi-20 the content of W was varied between 0 and 85 wt% also referring to bare substrate. The highest loading of tungsten is related to a theoretical monolayer of planar WO₃ [26]. For special investigations, samples with a Pt load of 2.0 wt% were also prepared. After each impregnation, samples were dried in air for 1 h at 80 °C. Subsequently, the catalysts were activated by dosing a mixture of 10 vol% H₂ and 90 vol% N₂; temperature was ramped from 20 to 300 °C with 1.7 K/min and end temperature was held for 30 min. Finally, the samples were conditioned in static air at 500 °C for 5 h.

### 2.2 Catalyst Characterization

N₂ physisorption was made on a TriStar II (Micromeritics). From the equilibrated N₂ adsorption isotherms taken at -196 °C, BET surface area (S_BET) and total specific pore volume (V_p) were determined. Prior to N₂ exposure, sample was outgassed in vacuum (10⁻¹ mbar) at 350 °C for 16 h to remove adsorbed components, particularly H₂O. The BET surface area was derived from the adsorption data recorded at p/p₀ ratios from 0.05 to 0.20.

Acidity of the samples was characterized by temperature-programmed desorption of ammonia (NH₃-TPD). Before the analysis, respective sample was pelletised, granulated and sieved to a size of 125—250 µm to avoid discharge upon TPD. A sample mass of 500 mg was introduced into the quartz glass tube reactor (i.d. 8 mm) and pre-treated in N₂ flow (500 ml/min, STP) at 450 °C for 1 h. After cooling to 50 °C in N₂, the sample was exposed to a gas mixture (500 ml/min, STP) consisting of 1000 vppm NH₃ and N₂ (balance) until saturation was reached (min. 30 min). Weakly adsorbed NH₃ was then removed by flushing with N₂ until the NH₃ outlet fraction was below 5 vppm. Finally, TPD was started by heating at a rate of 10 K/min in flowing N₂ (500 ml/min, STP). Temperature was recorded by two K-type thermocouples fitted directly in front and behind the sample. NH₃ was continuously monitored by non-dispersive infrared spectroscopy (NDIR, X-Stream X2GP, Emerson).

Temperature-programmed desorption of CO (CO-TPD) was made to quantify the number of active Pt site and to
The amount of active Pt sites ($n_a(Pt)$) was calculated based on the number of active centres and the total abundance of Pt present in the catalyst ($n_p$) by assuming an approximation of CO/Pt adsorption stoichiometry of 1 [27]. Furthermore, the size of Pt particles ($D_{Pt} = \frac{n_a(Pt)}{n_p} \times \frac{aPt}{DPt}$) was derived, while the mean size of Pt particles ($D_{Pt}$) was calculated by assuming spheres; $V_{Pt}$ amounts to 15.10 Å$^3$ and is the volume of a Pt atom present in the bulk metal, $a_{Pt}$ is equal to 8.07 Å$^2$ and represents the surface area of a Pt atom located on a polycrystalline surface [27].

The size of Pt particles was also evaluated by a FEI Quanta FEG 250 scanning electron microscope (SEM) in BSE mode using an acceleration voltage of 2 kV. SEM was coupled with energy-dispersive X-ray spectroscopy (EDX).

X-ray diffraction (XRD) of the powder samples was performed at room temperature on a D8 Discover (Bruker-AXS) with Bragg–Brentano configuration. Fe-filtered Co-Kα radiation and VANTEC-1 detector. Diffractograms were taken from 5° to 90° in 2θ mode at a step width of 0.5° and an integration time of 250 s. The patterns were evaluated by using the database Powder Diffraction Files (PDF).

Laser raman spectroscopic (LRS) analyses were conducted by inVia Raman microscope (Renishaw) equipped with Nd:YAG laser (532 nm, 100 mW), grating with 1800 lines per mm and CCD array detector. The spectra were collected under ambient conditions from 10 to 1800 cm$^{-1}$ at a resolution of 1.6 cm$^{-1}$, an exposure time of 5–20 s and a laser power of 1–10 mW, while accumulating 3–12 scans to a spectrum.

Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) using CO as probe molecule was made to check interaction of support and Pt. Investigations were made on a Tensor 27 FTIR spectrometer (Bruker) equipped with Praying Mantis reflectance optics (Harrick Scientific) and MCT detector. The sample compartment was purged with $N_2$ to avoid diffusion of air. The heatable stainless steel IR cell (Harrick Scientific) contained ZnSe windows and was connected to a gas-handling system. For the DRIFTS investigation, respective catalyst was introduced into the sample cup of the cell and was heated in $N_2$ flow at 500 °C for 15 min. Then, it was cooled to 200 °C under flowing $N_2$ and a mixture of 4 vol% $H_2$ and 96 vol% $N_2$ was adjusted for 10 min to reduce the Pt component. After this, it was cooled to 50 °C in $N_2$ flow and a background spectrum was collected; whereas in some tests other temperatures (65–150 °C) were also established. Subsequently, the sample was exposed to a flowing mixture of 1 vol% CO and 99 vol% $N_2$. After saturation, a spectrum was taken under CO/$N_2$. Then, it was flushed with $N_2$ for 15 min to remove CO from the gas phase and another spectrum was recorded. The total gas flow was always kept at 200 ml/min (STP). Spectra were collected from 600 to 4000 cm$^{-1}$ with a resolution of 0.9 cm$^{-1}$, while 200 scans were accumulated to a spectrum resulting in an acquisition time of approx. 5 min.

X-ray photoelectron spectroscopy was performed with a High Pressure VG ESCALAB photoelectron spectrometer equipped with a special gas cell, which allows acquiring XPS spectra at elevated pressures, i.e. up to 0.02 mbar [28, 29]. The non-monochromatic Mg Kα line was used as the primary excitation. For calibration, the Au4f$_{7/2}$ (binding energy $BE = 84.0$ eV), Ag3d$_{5/2}$ (BE = 368.3 eV) and Cu2p$_{3/2}$ lines (BE = 932.7 eV) from metallic gold, silver and copper foils were used [30]. Residual gas pressure was better than 2·10$^{-9}$ mbar. Spectral analysis and data processing were made with XPSPeak 4.1 software. The BE values were determined after subtraction of Shirley background and analysis of line shapes. Curves were fitted by Gaussian–Lorentzian functions for each XPS region. The Si2p line (BE = 102.5 eV [31]) of substrate was chosen as internal standard for pressure calibrating. For in-situ XPS, samples were placed into a special basket made of tantalum foil with steel grid blown round with gases and heated by resistivity. K-type thermocouple spot-welded to the bottom of basket was used for measurements at temperatures up to 180 °C to evaluated changes on the catalyst surface in the relevant $H_2$-deNOx activity window. In addition to analyses in vacuum the following gas mixtures were used: 1) 0.0005 mbar of NO; 2) blend of 0.0005 mbar NO, 0.0020 mbar $H_2$ and 0.0100 mbar $O_2$ (p(NO): p($H_2$): p($O_2$) = 1: 5: 20, total pressure: 0.0125 mbar). Gas phase was controlled by a mass spectrometer with secondary electron multiplier detector (Pfeiffer Vacuum QME 220).
2.3 H2-DeNOx Studies

The catalytic H2-deNOx investigations were performed on a laboratory bench using a synthetic model exhaust typical for lean H2 combustion engines. The powder samples (200 mg) were charged into the quartz glass tube reactor (i.d. 8 mm), fixed with quartz wool and heated to 350 °C. Subsequently, the model exhaust was added and temperature was decreased to 80 °C with a rate (β) of 2.0 K/min. The feed consisted of 500 vppm NO, 2000 vppm H2, 6.0 vol% O2, 10 vol% H2O and N2 as balance; total flow was kept at 400 ml/min (STP) corresponding to a space velocity (S.V.) of 160,000 h−1. Two dosing lines were employed, whereas in the first line H2, NO and a part of N2 (200 ml/min, STP) was added. In the second one, H2, O2 and remaining N2 was supplied. For production of H2O, the later gas mixture was passed over a reactor unit with Pt/Al2O3 balls heated to 220 °C. Both lines were united in front of the reactor section. All gases were controlled by independent mass flow controllers (Bronkhorst).

Temperature was measured by two K-type thermocouples each located directly in front of and behind the catalyst bed. Maximum difference of inlet and outlet temperature was 8 K. The simultaneous analyses of NO, NO2, N2O, NH3, and H2O was carried out by a hot measuring FTIR spectrometer (MULTI-GAS Analyzer 2030, MKS Instruments). O2 was monitored by a lambda probe (LSU 4.9, Bosch).

For assessment of the catalysts, the conversion of NOx (X(NOx) = 1—y(NOx)out/y(NOx)in) and selectivity of N2O (S(N2O) = 2 y(N2O) / (y(NOx)in—y(NOx)out)) were used. The latter is exclusively presented for X(NOx) > 20% to minimize error propagation. As a consequence, S(N2O) data refer to a reduced temperature range as compared to the X(NOx) features.

3 Results and Discussion

The most important physical–chemical properties of the catalysts are summarized in Table 1 demonstrating rather similar BET surface area for the WOx-free samples (455–500 m2/g). Contrary, the BET surface area of the WOx-loaded catalysts is decreased with inclining content of tungsten, i.e. from 386 m2/g to 169 m2/g. This effect is in line with the negligible surface area of bare tungsten oxide (approx. 5 m2/g [32]). Furthermore, the WOx-free catalysts reveal a similar number of available Pt sites (2.7–4.4 µmol/g), which is attributed to the resembling BET surface area of the supports. However, the available Pt sites of the WOx-loaded Pt/AlSi-20 samples are strongly diminished from 3.3 to 0.2 µmol/g in accordance with the drastic decline in BET surface area (Fig. 1). As a consequence, the Pt dispersion of these catalysts is decreased from 26 to 1%.

Table 1 BET surface area (S_BET), specific pore volume (V_p), number of available Pt sites (n_a(Pt)), Pt dispersion (D(Pt)) and estimated Pt particle size (d(Pt)) of the catalysts used

| Support | W load [wt%] | Pt load [wt%] | S_BET [m^2/g] | n_a(Pt) [µmol/g] | D(Pt) [%] | d(Pt) [nm] |
|---------|--------------|--------------|--------------|-----------------|-----------|------------|
| AlSi-40 | 0            | 0.25         | 455          | 3.3             | 26        | 4          |
| AlSi-30 | 0            | 0.25         | 500          | 2.7             | 21        | 5          |
| AlSi-20 | 0            | 0.25         | 475          | 4.4             | 35        | 3          |
| AlSi-20 | 11           | 0.25         | 386          | 3.3             | 26        | 4          |
| AlSi-20 | 45           | 0.25         | 333          | 1.3             | 10        | 11         |
| AlSi-20 | 85           | 0.25         | 169          | 0.2             | 1         | 96         |

*a Obtained from CO-TPD

b D_Pt = n_a(Pt) / n_Pt

c d_Pt = 6 V_p / (a_Pt D_Pt)
The XRD patterns of the bare supports (not shown) display one major SiO$_2$ reflex (PDF 00–050-0511), which increases with inclining proportion of Si, while the expected Al$_2$O$_3$ reflexes appear predominantly attributed to γ-Al$_2$O$_3$ (PDF 01–075-0921). Very similar reflexes are observed for the tungsten-loaded Pt catalysts (Fig. 2). For the WO$_x$-promoted samples with a W load of 45 and 85 wt% clear reflexes ascribed to orthorhombic WO$_3$ (PDF 00-020-1324) are observed, whereas they are more pronounced for the higher W content. Contrary, only very weak reflexes of WO$_3$ exist in the sample with the lowest W content (11 wt%) indicating clear presence of amorphous tungsten oxide entities (Fig. 2). This interpretation is substantiated by the LRS trace of this sample evidencing signals of amorphous WO$_x$ species at approx. 980 cm$^{-1}$ ($\nu_s$(W=O)) and 888 cm$^{-1}$ ($\nu_{as}$(W=O)) related to polymeric WO$_6$ units (Fig. 3) [33]. Furthermore, the catalyst with a W fraction of 45 wt% reveals relatively broad features at about 700 and 800 cm$^{-1}$, which are referred to slightly distorted (W=O) stretching vibrations of bridging (W–O–W) groups. Additionally, a peak is observed at approx. 270 cm$^{-1}$ ascribed to the bending vibration of bridging (W–O–W) moieties [34]. These LRS features are associated with crystalline WO$_3$ species, which is in line with XRD [34]. However, a signal at approx. 980 cm$^{-1}$ ($\nu_s$(W=O)) also appears indicating additional existence of amorphous WO$_x$ entities as found for the catalyst with a W content of 11 wt%. Moreover, the sample with 85 wt% W exhibits well defined peaks of crystalline WO$_3$ located at 270 (δ(WOW)), 715 and 805 cm$^{-1}$ ($\nu$(WOW)), which is in good agreement with XRD. Additionally, LRS implies a minor peak at 1000 cm$^{-1}$ ($\nu_{as}$(W=O)) showing some presence of amorphous WO$_x$ species as well [33]. It should also be mentioned that the 11W/AlSi-20-supported reference sample with a Pt load of 2.0 wt% provides a very similar LR spectrum.

Furthermore, all the X-ray diffraction patterns of the samples with a Pt loading of 0.25 wt% exhibit no Pt-related reflexes, as expected from the little Pt proportion. Contrary, the reference catalysts with 2 wt% Pt (Supplement Fig. 1) indicate clear reflexes ascribed to elemental Pt (PDF 00-004-0802). Calculation of the Pt crystallite size for 2Pt/AlSi-20 and 2Pt/11W/AlSi-20 using the Scherrer equation results in 16 nm for the former and 17 nm for the later catalyst. These particle sizes (Supplement Fig. 2) are confirmed by analysis of TEM images providing a $d_{50}$ of 17 nm (2Pt/AlSi-20) and 23 nm (2Pt/11W/AlSi-20), respectively.

The catalytic H$_2$-deNO$_x$ studies show that the three Pt/AlSi catalysts reveal prominent conversion of NO$_x$ in a narrow temperature window from 120 to 160 °C with significant selectivity of N$_2$O (Fig. 4); no NH$_3$ was detected for any of the catalysts. Moreover, the Pt/AlSi samples indicate rather similar performances, which closely resemble Pt/Al$_2$O$_3$ reported in the literature [20, 35]. Pt/AlSi-20 tentatively
exhibits the highest maximum conversion of NO$_x$ (57%) including a N$_2$O selectivity of about 50%. It is also worth to notice that the temperature of maximum conversion of NO$_x$ coincides with the temperature of minimum selectivity of N$_2$O (140 °C). This is associated with fast NO dissociation on the Pt sites enabling the recombination of adjacent N atoms to yield N$_2$. Contrary, at lower temperatures NO dissociation is not as fast thus leading to combination of NO and N adsorbates and pronounced formation of N$_2$O, respectively [36]. Furthermore, preliminary investigations demonstrated that the temperature ramp adjusted provokes steady state. Additionally, blank experiments made with the empty reactor provide no reduction of NO$_x$ clearly evidencing the catalytic effect of the samples.

The introduction of 11 wt% W to Pt/AlSi-20 clearly enhances H$_2$-deNO$_x$ as reflected by the maximum NO$_x$ conversion, which increases from 58 to 72% (Fig. 5). Additionally, the minimum selectivity of N$_2$O is declined from ca. 50 to 20%. Moreover, the operation window of Pt/11W/AlSi-20 is significantly broadened ranging from 100 to 300 °C. It is also noteworthy that the temperature of maximum conversion of NO$_x$ (110 °C) is shifted to lower temperatures, whereas the temperature of minimum selectivity of N$_2$O has changed to higher temperatures (160 °C) as compared to the unpromoted catalyst. Additionally, the increase in the W content from 11 to 45 wt% results in decreasing NO$_x$ reduction (maximum deNO$_x$: 57%) while leaving the N$_2$O selectivity mostly unaffected. When inclining the tungsten proportion even further to the theoretical monolayer of planar WO$_3$ (85 wt%), the maximum NO$_x$ conversion is further decreased to 50%. However, the selectivity of N$_2$O is not significantly influenced below 160 °C, but above it is diminished to 20%. Furthermore, the 11W/AlSi-20-supported reference catalyst with 2 wt% Pt shows slightly higher NO$_x$ conversion (up to 90%) with very similar N$_2$O selectivity (Supplement Fig. 3).

The combination of the H$_2$-deNO$_x$ results with the physical–chemical features of the samples shows that in each series of promoted and unpromoted catalysts the number of available Pt sites correlates well with the maximum NO$_x$ conversion (X(NO$_x$)$_{max}$) taken as a measure for the activity (Fig. 6). However, as higher NO$_x$ conversions are achieved for the WO$_3$ containing catalysts at a lower number of active Pt sites, the promoting effect of tungsten oxide is evident.

Furthermore, from the abundance of active Pt present in Pt/AlSi-20 (W load: 85 wt%) a mean particle size (d$_{50}$) of 96 nm is derived (Table 1). Indeed, SEM coupled with EDX clearly confirms the substantial existence of Pt particles with sizes of approx. 100 nm (Fig. 7). Contrary, no Pt particles were found for the remaining WO$_3$-loaded samples due to the limited resolution of the SEM in accordance with the small particle sizes deduced (4 and 11 nm, Table 1). The SEM studies clearly confirm that the increase in WO$_3$ load, associated with decreasing BET surface area, results in growing Pt particles affecting the catalytic performance. Thus, a strong metal support interaction (SMSI), which potentially implies decoration of Pt particles by WO$_3$ species partially reduced during H$_2$-deNO$_x$, appears unlikely.

A possible SMSI effect was also checked by CO-TPD using Pt/AlSi-20 with and without W promoter (11 wt%). As a
result of the TPD studies each performed after CO exposure at 500 °C and subsequent saturation at 50 °C or 350 °C, the atomic ratio of available Pt sites of both samples remained almost the same (0.75 at 50 °C and 0.72 at 350 °C) thus excluding a substantial SMSI effect.

Additionally, the W4f7/2 XP spectra of 11W/AlSi-20 and reference catalyst 2Pt/11W/AlSi-20 demonstrate a BE of 36.0 eV clearly ascribed to WO3 species (Fig. 8) [37]. Position, shape and width of this W4f peak of both samples do not indicate any existence of extra states of tungsten, which could support SMIS effect. Moreover, tungsten spectra do not change under in-situ XPS conditions using the gas mixtures (Sect. 2.2) up to 180 °C.

According to XPS data Pt4f7/2 BE is 71.3 eV for 2Pt/AlSi-20 sample and 71.2 eV for 2Pt/11W/AlSi-20 sample corresponding to metallic Pt (Fig. 9) [30]. During in-situ XPS experiments, performed with the different gas phase compositions between room temperature and 180 °C (Supplement Fig. 5), Pt4f7/2 line shifts in the range from 71.3
to 71.8 eV for 2Pt/AlSi-20 and 71.2–71.4 eV for 2Pt/11W/AlSi-20, which is still metallic platinum BE. No changes of chemical state of platinum under the established reaction conditions were found thus also excluding significant SMSI effects. Note that the Pt particle sizes of both samples demonstrated above (d_{50}(2Pt/AlSi-20) = 17 nm and d_{50}(2Pt/11W/AlSi-20) = 23 nm) are out of range of XPS size effects [29]. Hence, size effects are not relevant for the spectrum interpretation. Small shifts of Pt4f line (well seen with respect to Al2p line), found under in situ XPS experiments, correlating with gas phase composition and sample temperature (Supplement Fig. 5) in the range from room temperature to 180 °C, can be explained by the fine electronic effects, particularly due to formation of surface and subsurface oxygen at platinum particles. It should be mentioned, that ex situ XPS study does not show the difference in platinum spectra for W-modified and non-modified samples (Fig. 9). Divergence between samples 2Pt/11W/AlSi-20 and 2Pt/AlSi-20 becomes apparent during in situ XPS experiments (Supplement Fig. 5). This observation can be explained by the heterogeneity of the Pt/AlSi-20 catalyst discussed below in the CO-DRIFTS section, particularly, surface structure and surface defects resulting in the difference in accumulation of the oxygen associated with Pt.

The interaction of the WOₓ-modified AlSi-20 supports with the Pt component was also investigated by DRIFTS using CO as probe molecule (Fig. 10). The DRIFT spectrum of Pt/AlSi-20 with 11 wt% W collected after exposure to CO at 50 °C shows a band at 2065 cm⁻¹, which is referred to stretching vibrations of CO linearly coordinated to Pt sites (ν(CO)) [38]. Bridging CO species expected at ca. 1850 cm⁻¹ do not appear. The intensity of the ν(CO) band clearly declines with increasing load of tungsten in
line with the number of active Pt sites. Consequently, the sample with 85 wt% W indicates only negligible intensity [39]. Since no significant shift of the ν(CO) band occurs for the three tungsten-loaded catalysts and the band is very close to that of the WOx-free sample (2070 cm\(^{-1}\)), specific electronic interaction of the crystalline and amorphous WOx species with Pt is rather excluded. Additionally, the location of the ν(CO) band is obviously not affected by the mean Pt particle size of the tungsten-loaded samples, which ranges from 4 to 96 nm (Table 1). Indeed, the effect of Pt particle size on the CO stretching vibration is known from the literature for Pt/SiO\(_2\) and Pt/Al\(_2\)O\(_3\), but it only appears for much smaller particles below approx. 2 nm [38], as similarly discussed for XPS. From the DRIFTS studies it is deduced that the H\(_2\)-deNO\(_x\) performance of the WOx-loaded Pt/AlSi-20 catalysts is primarily driven by the number of active Pt sites as demonstrated in Fig. 6.

Furthermore, it should be stated that the DRIFT spectrum of the W-free Pt/AlSi-20 sample shows a band at 2070 cm\(^{-1}\) with a marked shoulder at 2095 cm\(^{-1}\) both ascribed to ν(CO) vibration mode of linearly coordinated CO species [38]. The splitting of the DRIFTS feature evidences considerable heterogeneity of the Pt sites, which implies CO adsorbates with weaker binding strength to the active component. As a result, some blue shift of the ν(CO) vibration occurs relative to the 2070 cm\(^{-1}\) band. Note that the feature at 2095 cm\(^{-1}\) completely vanishes when exposing Pt/AlSi-20 to CO at 65 °C, while the band at 2070 cm\(^{-1}\) clearly remains (not shown). This disappearance of the 2095 cm\(^{-1}\) band already at slightly increased temperature substantiates the low stability of the corresponding adsorbates. It may be supposed that this heterogeneity of the Pt/AlSi-20 catalyst, which includes less stable adsorbates and likely less active Pt sites, results in lower H\(_2\)-deNO\(_x\) efficiency as compared to the WOx-promoted catalysts.

Moreover, additional insights into the role of the WOx promotor were gained from H\(_2\)-deNO\(_x\) investigations made at an extremely high space velocity (480,000 h\(^{-1}\)). These studies were carried out with lesser catalyst mass using Pt/AlSi-20 with and without 11 wt% W, which both reveal very similar numbers of available Pt sites (Table 1). As expected from the increased S.V., the NO\(_x\) conversion of both catalysts is diminished as referred to the lower space velocity (160,000 h\(^{-1}\), Fig. 12), whereas the W-promoted sample again shows higher H\(_2\)-deNO\(_x\) performance (Fig. 11, left). In contrast to the studies at the lower S.V., the catalysts exhibit significant NH\(_3\) formation below 160 °C with a broader and stronger appearance for the unpromoted catalyst. The NH\(_3\) yield is attributed to the reaction of N adsorbates, originated from NO dissociation, with hydrogen species on the Pt sites [40]. Obviously, at the high space velocity NH\(_3\) is not completely converted. In line with literature [41], the NH\(_3\) conversion mainly occurs by reaction with O\(_2\) to form N\(_2\) and N\(_2\)O [41], which starts as low as approx. 90 °C (Figs. 12 and 13). Like at lower S.V. the N\(_2\)O formation is higher for the unpromoted catalyst (Fig. 11, right). As the decreased NH\(_3\) formation on the 0.25Pt/11W/AlSi-20 catalyst correlates with higher NO\(_x\) conversions, it may be deduced that ammonia species are also involved in the NO\(_x\) reduction, in addition to the H\(_2\)-deNO\(_x\) reaction on the Pt sites [36]. For this reason, NH\(_3\) (100 vppm) was added to the gas flow in presence and absence of H\(_2\) to check a possible contribution of the NH\(_3\)-SCR reaction. These studies performed with both catalysts were conducted at selected temperatures providing stationary conditions to exclude ammonia storage effects.

Figure 12 demonstrates that the NH\(_3\)-SCR reaction in the absence of H\(_2\) results in only little NO\(_x\) conversion on both catalysts (maximum 16% at approx. 160 °C). Therefore, it is unlikely that SCR plays a major role in H\(_2\)-deNO\(_x\). Note that due to the NH\(_3\) proportion of 100 vppm maximum NO\(_x\) conversion of only 20% is possible according to the stoichiometry of SCR reaction (5 NO + 5 NH\(_3\) + O\(_2\) → 5 N\(_2\) + 6 H\(_2\)O). Additionally, the NH\(_3\)-SCR tests substantiate high NH\(_3\) conversion on both catalysts (approx. 90% at 160 °C) due to the oxidation of ammonia (4 NH\(_3\) + 3 O\(_2\) → 2 N\(_2\) + 6 H\(_2\)O), which clearly exceeds the NO\(_x\) reduction. Contrary, the NH\(_3\) oxidation to NO can be excluded at temperatures below 200 °C [41]. Marked NH\(_3\) oxidation even at low temperatures is typical for Pt catalysts and implies strong formation of N\(_2\)O (2 NH\(_3\) + 2 O\(_2\) → N\(_2\)O + 3 H\(_2\)O) as evidenced for both catalysts investigated (Fig. 12) [42]. Additionally, some N\(_2\)O formation is also ascribed to the SCR reaction on Pt in line with literature [43]. It should also be stated that the W-loaded catalyst provides slightly higher NH\(_3\) conversion between

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**Fig. 10** DRIFT spectra of bare and WOx-loaded Pt/AlSi-20 after exposure to CO at 50 °C followed by N\(_2\) flushing
100 and 140 °C with lower yield of N₂O. In the H₂-deNOₓ reaction (Fig. 11), this superior N₂ selectivity may contribute to the lower N₂O production of Pt/11W/AlSi-20, associated with the oxidation of NH₃ formed as side-product. Indeed, tungsten promotion was previously reported as beneficial for the oxidation of NH₃ to N₂ on Pt/W/ZrO₂ catalysts [42].

Furthermore, when simultaneously dosing 2000 vppm H₂ and 100 vppm NH₃ (Fig. 13, left), the NOₓ conversion on Pt/AlSi-20 is clearly higher as compared to the experiment.
without H₂ (Fig. 12, left). For instance at 140 °C, the NOₓ conversion amounts to 36%, whereas in NH₃-SCR it is 8% only; also, slightly higher NOₓ reduction is obtained compared to bare H₂-deNOₓ (31%, Fig. 11). Interestingly, at around 140 °C the NH₃ conversion seems to be smaller in the presence of H₂. This effect is explained by the formation of NH₃ by the H₂-deNOₓ reaction, as indicated in Fig. 11, formally decreasing the conversion of NH₃. Additionally, the significant production of N₂O (Fig. 12, right) is referred to H₂-deNOₓ as well as the follow-up reactions of NH₃, namely NH₃ oxidation and SCR.

In the investigation of Pt/11W/AlSi-20 performed in simultaneous presence of H₂ and NH₃ (Fig. 13), the NH₃ conversion is increased above 110 °C referred to the study without H₂ (Fig. 12). Also, the NOₓ conversion is markedly above that observed in H₂-deNOₓ, i.e. without additional NH₃ supply; at 140 °C deNOₓ amounts to 56% with H₂/ NH₃, whereas with H₂ only it is 44% and with NH₃ it is 6%. These results clearly demonstrate a synergistic effect of H₂ and NH₃ in the NOₓ reduction on the W-promoted catalyst. Moreover, it is apparent that the lower N₂O formation in the H₂-deNOₓ reaction on Pt/11W/AlSi-20 (Fig. 11) coincides with the diminished N₂O production during the NH₃ oxidation (Fig. 12). Therefore, it is inferred that ammonia formed in H₂-deNOₓ enhances the NOₓ reduction on the one hand side, while on the other hand side its oxidation results in lesser proportion of N₂O.

It is known from literature that NH₃ originated from H₂-deNOₓ on W-promoted Pt catalysts can adsorb on Bronsted acid W-OH sites [15, 25] leading to the formation of NH₄⁺ species. The NH₃-TPD analysis of W-promoted and bare AlSi-20 (Supplement Fig. 4) shows that the promotor slightly increases the NH₃ uptake capacity from 1.4 µmol/m² to 1.7 µmol/m². Additionally, it is assumed that in H₂-deNOₓ some hydrogen spillover from Pt to adjacent W = O species, evidenced by LSR (Fig. 3), can occur increasing the number of W-OH Bronsted acid sites in proximity of the Pt particles [44, 45]. From the discussion of above deNOₓ and TPD studies as well as the cited literature it is drawn the conclusion that ammonium species, formed at the interface of Pt and the WOₓ/Al₂O₃/SiO₂ support, may react with NO likely adsorbed on Pt to yield N₂ and H₂O. This participation of ammonia surface species reasonably explains the increased H₂-deNOₓ performance and lower N₂O selectivity of the W-promoted Pt/AlSi-20 catalyst compared to the unpromoted sample.

4 Conclusion

The Al₂O₃/SiO₂-based Pt catalysts with and without WOₓ promoter revealed a strong dependency of their lean H₂-deNOₓ activity by the number of active Pt sites. The presence of the tungsten oxide promoter led to a clear increase in NOₓ conversion as compared to the WOₓ-free catalysts, whereby the presence of amorphous WOₓ entities, very probably polymeric WOₓ units, seems to be most advantageous. Interestingly, tungsten oxide was also reported to
enhance the H₂-deNOₓ conversion on related ZrO₂-based Pt and Pd catalysts [20, 21]. For the W-promoted catalysts, a high BET surface area was beneficial to increase the number of available Pt sites.

Additionally, NH₃ appeared as side-product of the H₂-deNOₓ reaction, which was assumed to contribute to the NOₓ emissions within current and future emission limits. The superior activity of the W-promoted catalysts compared to the W-free samples was ascribed to the ammonia species at the Pt-WOₓ/Al₂O₃/SiO₂ interface participating in the NOₓ reduction, in addition to the H₂-deNOₓ reaction on the Pt sites. Moreover, the more homogeneous nature of the Pt sites of the W-promoted catalysts might also assist the H₂-deNOₓ efficiency. Contrary, a SMSI effect of the tungsten oxide promoter was clearly excluded.

The best catalyst (Pt/11W/AIS-20) provided maximum NOₓ conversion of approx. 70% implying a significantly broadened temperature window from 100 to 300 °C, even in presence of H₂O. Simultaneously, the selectivity towards N₂O was lowered to approx. 20%. The wide temperature window and the pronounced activity in the low temperature region (< 200 °C) makes this catalyst a promising basis for the efficient NOₓ reduction in H₂ combustion engines keeping NOₓ emissions within current and future emission limits.

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Declarations

Conflict of interest The authors declare no conflict of interest.

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