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

Enno Eßer¹ · Daniel Schröder¹ · Anna V. Nartova² · Aleksey M. Dmitrachkov² · Sven Kureti¹

Received: 12 April 2021 / Accepted: 14 July 2021 / Published online: 26 July 2021
 © The Author(s) 2021

Abstract

This work addresses the reduction of NO_x by H₂ under O₂-rich conditions using Al₂O₃/SiO₂-supported Pt catalysts with different loads of WO_x 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 WO_x showed pronounced NO_x conversion below 200 °C, whereas highest efficiency was related to small Pt particles. The introduction of WO_x provided increasing deNO_x activity as well as N₂ selectivity. This promoting effect was referred to an additional reaction path at the Pt-WO_x/Al₂O₃/SiO₂ interface, whereas an electronic activation of Pt by strong metal support interaction was excluded.

Graphic Abstract

Keywords NO_x reduction · H₂ reductant · Pt catalyst · Al₂O₃/SiO₂ support · WO_x 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 NO_x, 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 NO_x reduction by H₂ ($2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$) 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 NO_x (SCR), which is well-established for diesel passenger cars and

✉ Sven Kureti
 kureti@iec.tu-freiberg.de

¹ Chair of Reaction Engineering, Institute of Energy Process Engineering and Chemical Engineering, Technical University of Freiberg, Fuchsmühlenweg 9, 09599 Freiberg, Germany

² Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russian Federation 630090

trucks. 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 NO_x storage reduction catalysts (NSR) are also applied consisting of Pt, Pd and Rh as well as NO_x adsorbents like Al₂O₃, CeO₂ and BaCO₃. The operation of NSR includes periodic storage and reduction of NO_x [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 NO_x 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-deNO_x 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/La_{0.7}Sr_{0.2}Ce_{0.1}FeO₃ [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-deNO_x, 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 NO_x reduction by hydrocarbons [23] as well as SCR [24].

The present paper aims to study Al₂O₃/SiO₂-based Pt catalysts with and without WO_x promotor for the NO_x reduction by H₂ under O₂-rich conditions. WO_x was shown to reveal high efficiency for lean H₂-deNO_x 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 deNO_x. Additionally, the H₂-deNO_x 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 WO_x 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 20

HPV, 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 WO_x 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)₆H₂W₁₂O₄₀•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

check possible SMSI effect. A sample mass of 2.00 g, which was prepared like for NH_3 -TPD, was introduced into the quartz glass tube reactor (i.d. 8 mm) and pre-treated in a mixture of 5 vol% O_2 and 95 vol% Ar at 500 °C for 15 min followed by flushing with pure Ar for another 20 min (500 ml/min, STP). At the same temperature, the sample was reduced by 3000 vppm CO in Ar (500 ml/min, STP) for 15 min and cooled down to 50 or 350 °C in Ar flow. After saturation at 50 or 350 °C with 3000 vppm CO in Ar (100 ml/min, STP), it was flushed with Ar and CO-TPD was started (150 ml/min, STP) by heating to 700 °C at the rate of 20 K/min. Temperature was recorded by a K-type thermocouple fitted directly in front of the sample. Desorbing CO and CO_2 was monitored by NDIR (X-Stream Enhanced XEGK, Emerson). For quantification of the active Pt sites, the CO and CO_2 TPD profiles were integrated. The evolution of CO_2 is ascribed to the oxidation of desorbed CO by the catalyst surface. A blank CO-TPD of the bare supports provided only minor amounts of CO and CO_2 , which were subtracted from the respective TPD traces of the catalysts. The amount of active Pt sites ($n_a(\text{Pt})$) was calculated based upon a CO/Pt adsorption stoichiometry of 1 [27]. Furthermore, from this number of active centres and the total abundance of Pt present in the catalyst (n_{Pt}) the dispersion of Pt ($D_{\text{Pt}} = n_a(\text{Pt}) / n_{\text{Pt}}$) was derived, while the mean size of Pt particles ($d_{\text{Pt}} = 6 V_{\text{Pt}} / (a_{\text{Pt}} D_{\text{Pt}})$) was calculated by assuming spheres; V_{Pt} amounts to $15.10 \text{ \AA}^3$ and is the volume of a Pt atom present in the bulk metal, a_{Pt} is equal to $8.07 \text{ \AA}^2$ 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 $\text{Co-K}\alpha$ radiation and VANTEC-1 detector. Diffractograms were taken from 5° to 100° 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 $\text{K}\alpha$ line was used as the primary excitation. For calibration, the $\text{Au}4f_{7/2}$ (binding energy BE = 84.0 eV), $\text{Ag}3d_{5/2}$ (BE = 368.3 eV) and $\text{Cu}2p_{3/2}$ lines (BE = 932.7 eV) from metallic gold, silver and copper foils were used [30]. Residual gas pressure was better than $2 \cdot 10^{-9}$ 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 spectrum 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 -deNO_x 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 ($p(\text{NO}): p(\text{H}_2): p(\text{O}_2) = 1: 5: 20$, 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-DeNO_x Studies

The catalytic H₂-deNO_x 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 NO_x ($X(\text{NO}_x) = 1 - y(\text{NO}_x)_{\text{out}}/y(\text{NO}_x)_{\text{in}}$) and selectivity of N₂O ($S(\text{N}_2\text{O}) = 2 y(\text{N}_2\text{O}) / (y(\text{NO}_x)_{\text{in}} - y(\text{NO}_x)_{\text{out}})$) were used. The latter is exclusively presented for $X(\text{NO}_x) > 20\%$ to minimize error propagation. As a consequence, $S(\text{N}_2\text{O})$ data refer to a reduced temperature range as compared to the $X(\text{NO}_x)$ features.

Fig. 1 Correlation of BET surface area and number of available Pt sites of the Pt/AlSi-20 catalysts with and without load of tungsten (the line is a guide for the eyes)

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 WO_x-free samples (455–500 m²/g). Contrary, the BET surface area of the WO_x-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 WO_x-free catalysts reveal a similar number of available Pt sites (2.7–4.4 $\mu\text{mol/g}$), which is attributed to the resembling BET surface area of the supports. However, the available Pt sites of the WO_x-loaded Pt/AlSi-20 samples are strongly diminished from 3.3 to 0.2 $\mu\text{mol/g}$ 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 ($n_a(\text{Pt})$), Pt dispersion ($D(\text{Pt})$) and estimated Pt particle size ($d(\text{Pt})$) of the catalysts used

Support	W load [wt%]	Pt load [wt%]	S_{BET} [m^2/g]	$n_a(\text{Pt})^a$ [$\mu\text{mol/g}$]	$D(\text{Pt})^b$ [%]	$d(\text{Pt})^c$ [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

^aObtained from CO-TPD

^b $D_{\text{Pt}} = n_a(\text{Pt}) / n_{\text{Pt}}$

^c $d_{\text{Pt}} = 6 V_p / (a_{\text{Pt}} D_{\text{Pt}})$

Fig. 2 X-ray diffraction patterns of the Pt/AlSi-20 catalysts with different loads of tungsten (SiO₂ (x), WO₃ (+), γ-Al₂O₃ (°))

The XRD patterns of the bare supports (not shown) display one major SiO₂ reflex (PDF 00–050–0511), which increases with inclining proportion of Si, while the expected Al₂O₃ reflexes appear predominantly attributed to γ-Al₂O₃ (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 WO₃ (PDF 00–020–1324) are observed, whereas they are more pronounced for the higher W content. Contrary, only very weak reflexes of WO₃ 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} (ν_s(W=O)) and 888 cm^{−1} (ν_{as}(W=O)) related to polymeric WO₆ 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 WO₃ species, which is in line with XRD [34]. However, a signal at approx. 980 cm^{−1} (ν_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 WO₃ located at 270 (δ(WOW)), 715 and 805 cm^{−1} (ν(WOW)), which is in good agreement with XRD. Additionally, LRS implies a minor peak at 1000 cm^{−1} (ν_s(W=O)) showing some presence of amorphous WO_x species as well [33]. It should also be mentioned that the 11W/AlSi-20-supported

Fig. 3 Laser Raman spectra of the Pt/AlSi-20 catalysts with and without load of tungsten

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 d₅₀ of 17 nm (2Pt/AlSi-20) and 23 nm (2Pt/11W/AlSi-20), respectively.

The catalytic H₂-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 N₂O (Fig. 4); no NH₃ was detected for any of the catalysts. Moreover, the Pt/AlSi samples indicate rather similar performances, which closely resemble Pt/Al₂O₃ reported in the literature [20, 35]. Pt/AlSi-20 tentatively

Fig. 4 NO_x conversion (left) and N₂O selectivity (right) in H₂-deNO_x on Pt/AlSi-20, Pt/AlSi-30 and Pt/AlSi-40. Conditions: *m* = 200 mg, *y*(NO) = 500 vppm, *y*(H₂) = 2000 vppm, *y*(O₂) = 6 vol%, *y*(H₂O) = 10 vol%, N₂ balance, *F* = 400 ml/min (STP), *S.V.* = 160,000 h⁻¹, *β* = 2 K/min

exhibits the highest maximum conversion of NO_x (57%) including a N₂O 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 N₂O (140 °C). This is associated with fast NO dissociation on the Pt sites enabling the recombination of adjacent N atoms to yield N₂. Contrary, at lower temperatures NO dissociation is not as fast thus leading to combination of NO and N adsorbates and pronounced formation of N₂O, 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 H₂-deNO_x as reflected by the maximum NO_x conversion, which increases from 58 to 72% (Fig. 5). Additionally, the minimum selectivity of N₂O 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 N₂O 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 N₂O selectivity mostly unaffected. When inclining the tungsten proportion even further to the theoretical monolayer of planar WO₃ (85 wt%), the maximum NO_x conversion is further

decreased to 50%. However, the selectivity of N₂O 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 N₂O selectivity (Supplement Fig. 3).

The combination of the H₂-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_x 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*_{Pt}) 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_x-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_x 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_x species partially reduced during H₂-deNO_x, appears unlikely. A possible SMSI effect was also checked by CO-TPD using Pt/AlSi-20 with and without W promotor (11 wt%). As a

Fig. 5 NO_x conversion (left) and N_2O selectivity (right) in H_2 -de NO_x on Pt/AlSi-20 with a W load of 11, 45 and 85 wt%. Conditions: $m=200$ mg, $y(\text{NO})=500$ vppm, $y(\text{H}_2)=2000$ vppm, $y(\text{O}_2)=6$

vol%, $y(\text{H}_2\text{O})=10$ vol%, N_2 balance, $F=400$ ml/min (STP), $\text{S.V.}=160,000$ h $^{-1}$, $\beta=2$ K/min

Fig. 6 Correlation of maximum NO_x conversion and number of available Pt atoms of all the catalysts (the lines are guides for the eyes); H_2 -de NO_x conditions are demonstrated in Figs. 4 and 5

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 $\text{W}4f_{7/2}$ XP spectra of 11W/AlSi-20 and reference catalyst 2Pt/11W/AlSi-20 demonstrate a BE of 36.0 eV clearly ascribed to WO_3 species (Fig. 8) [37].

Fig. 7 SEM image of Pt/AlSi-20 with a tungsten load of 85 wt%. Some Pt particles are exemplarily marked by white arrows

Position, shape and width of this $\text{W}4f$ peak of both samples do not indicate any existence of extra states of tungsten, which could support SMSI 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 $\text{Pt}4f_{7/2}$ 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), $\text{Pt}4f_{7/2}$ line shifts in the range from 71.3

Fig. 8 XPS W4f spectra of 2Pt/11W/AlSi-20 and 11W/AlSi-20 recorded in vacuum at room temperature

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).

Fig. 9 XPS Pt4f (solid line) and Al2p (dashed line) spectra of 2Pt/11W/AlSi-20 and 2Pt/AlSi-20 recorded in vacuum at room temperature

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 WO_x-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

Fig. 10 DRIFT spectra of bare and WO_x -loaded Pt/AlSi-20 after exposure to CO at 50 °C followed by N_2 flushing

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 $\nu(\text{CO})$ band occurs for the three tungsten-loaded catalysts and the band is very close to that of the WO_x -free sample (2070 cm^{-1}), specific electronic interaction of the crystalline and amorphous WO_x species with Pt is rather excluded. Additionally, the location of the $\nu(\text{CO})$ 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_2O_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 -de NO_x performance of the WO_x -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 $\nu(\text{CO})$ 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 $\nu(\text{CO})$ 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 -de NO_x efficiency as compared to the WO_x -promoted catalysts.

Moreover, additional insights into the role of the WO_x promoter were gained from H_2 -de NO_x investigations made at an extremely high space velocity ($480,000\text{ h}^{-1}$). 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 ($160,000\text{ h}^{-1}$, Fig. 12), whereas the W-promoted sample again shows higher H_2 -de NO_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_2O [41], which starts as low as approx. 90 °C (Figs. 12 and 13). Like at lower S.V. the N_2O 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 -de NO_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 -de NO_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 ($5\text{ NO} + 5\text{ NH}_3 + \text{O}_2 \rightarrow 5\text{ N}_2 + 6\text{ H}_2\text{O}$). 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 ($4\text{ NH}_3 + 3\text{ O}_2 \rightarrow 2\text{ N}_2 + 6\text{ H}_2\text{O}$), 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_2O ($2\text{ NH}_3 + 2\text{ O}_2 \rightarrow \text{N}_2\text{O} + 3\text{ H}_2\text{O}$) as evidenced for both catalysts investigated (Fig. 12) [42]. Additionally, some N_2O 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

Fig. 11 NO_x conversion (left) as well as N₂O and NH₃ formation (right) in H₂-deNO_x on Pt/AlSi-20 with and without a W load of 11 wt%. Conditions: m = 50 mg, y(NO) = 500 vppm, y(H₂) = 2000 vppm,

y(O₂) = 6 vol%, y(H₂O) = 10 vol%, N₂ balance, F = 400 ml/min (STP), S.V. = 480,000 h⁻¹, β = 2 K/min

Fig. 12 NH₃ and NO_x conversion (left) as well as N₂O formation (right) in NH₃-SCR on Pt/AlSi-20 with and without a W load of 11 wt% (the lines are guides for the eyes). Conditions: m = 50 mg,

y(NO) = 500 vppm, y(NH₃) = 100 vppm, y(O₂) = 6 vol%, y(H₂O) = 10 vol%, N₂ balance, F = 400 ml/min (STP), S.V. = 480,000 h⁻¹

100 and 140 °C with lower yield of N₂O. In the H₂-deNO_x 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 NO_x conversion on Pt/AlSi-20 is clearly higher as compared to the experiment

Fig. 13 NH₃ and NO_x conversion (left) as well as N₂O formation (right) upon NH₃-SCR in the presence of H₂ on Pt/AlSi-20 with and without a W load of 11 wt% (the lines are guides for the eyes).

without H₂ (Fig. 12, left). For instance at 140 °C, the NO_x conversion amounts to 36%, whereas in NH₃-SCR it is 8% only; also, slightly higher NO_x reduction is obtained compared to bare H₂-deNO_x (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-deNO_x 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-deNO_x 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 NO_x conversion is markedly above that observed in H₂-deNO_x, i.e. without additional NH₃ supply; at 140 °C deNO_x amounts to 56% with H₂/NH₃, whereas with H₂ only it is 44% and with NH₃ it is 6%. These results clearly demonstrate a synergetic effect of H₂ and NH₃ in the NO_x reduction on the W-promoted catalyst. Moreover, it is apparent that the lower N₂O formation in the H₂-deNO_x 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-deNO_x enhances the NO_x 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-deNO_x on W-promoted Pt catalysts can adsorb on

Conditions: $m = 50$ mg, $y(\text{NO}) = 500$ vppm, $y(\text{H}_2) = 2000$ vppm, $y(\text{NH}_3) = 100$ vppm, $y(\text{O}_2) = 6$ vol%, $y(\text{H}_2\text{O}) = 10$ vol%, N₂ balance, $F = 400$ ml/min (STP), $S.V. = 480,000$ h⁻¹

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-deNO_x 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 deNO_x 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 WO_x/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-deNO_x 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 WO_x promotor revealed a strong dependency of their lean H₂-deNO_x activity by the number of active Pt sites. The presence of the tungsten oxide promotor led to a clear increase in NO_x conversion as compared to the WO_x-free catalysts, whereby the presence of amorphous WO_x entities, very probably polymeric WO₆ units, seems to be most advantageous. Interestingly, tungsten oxide was also reported to

enhance the H₂-deNO_x 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-deNO_x reaction, which was assumed to contribute to the NO_x conversion. The superior activity of the W-promoted catalysts compared to the W-free samples was ascribed to ammonia species at the Pt-WO_x/Al₂O₃/SiO₂ interface participating in the NO_x reduction, in addition to the H₂-NO_x reaction on the Pt sites. Moreover, the more homogeneous nature of the Pt sites of the W-promoted catalysts might also assist the H₂-deNO_x efficiency. Contrary, a SMSI effect of the tungsten oxide promotor was clearly excluded.

The best catalyst (Pt/11W/AlS-20) provided maximum NO_x 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 NO_x reduction in H₂ combustion engines keeping NO_x emissions within current and future emission limits.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10562-021-03747-w>.

Acknowledgements The authors thank Sasol Germany for supplying the Al₂O₃/SiO₂ carriers. XPS experiments were conducted within the framework of the budget project for Boreskov Institute of Catalysis SB RAS (project AAAA-A21-121011390011-4). DS and SK thankfully acknowledge the financial support from the Development Bank of Saxony (Sächsische Aufbaubank) as a subsidiary of the European Regional Development Fund (EFRE) under the project RedNO_x (100367274).

Funding Open Access funding enabled and organized by Projekt DEAL.

Declarations

Conflict of interest The authors declare no conflict of interest.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Twigg MV (2007) Appl Catal B 70:2–15
- Liu G, Gao P-X (2011) Catal Sci Technol 1:552–568
- Nova I, Lietti L, Castoldi L, Tronconi E, Forzatti P (2006) J Catal 239:244–254
- Frank B, Lübke R, Emig G, Renken A (1998) Chem Eng Technol 21:498–502
- Frank B, Emig G, Renken A (1998) Appl Catal B 19:45–57
- Roy K, Jain R, Gopinath CS (2014) ACS Catal 4:1801–1811
- Breen JP, Burch R, Hardacre C, Hill CJ, Krutzsch B, Bandl-Konrad B, Jobson E, Cider L, Blakeman PG, Peace LJ (2007) Appl Catal B 70:36–44
- Cai X, Sun W, Xu C, Cao L, Yang J (2016) Environ Sci Pollut Res 23:18609–18620
- Roy K, Gopinath CS (2014) ChemCatChem 6:531–537
- Costa CN, Stathopoulos VN, Belessi VC, Efstathiou AM (2001) J Catal 197:350–364
- Lindstedt A, Strömberg D, Milh MA (1994) Appl Catal A 116:109–126
- Ferri D, Forni L, Dekkers MAP, Nieuwenhuys BE (1998) Appl Catal B 16:339–345
- Voorhoeve RJH, Remeika JP, Trimble LE, Cooper AS, Disalvo FJ, Gallagher PK (1975) J Solid State Chem 14:395–406
- Liu Z, Wu J, Hardacre C (2018) Catal Surv Asia 22:146–155
- Liu Z, Lu Y, Yuan L, Ma L, Zheng L, Zhang J, Hu T (2016) Appl Catal B 188:189–197
- Costa CN, Savva PG, Andronikou C, Lambrou PS, Polychronopoulou K, Belessi VC, Stathopoulos VN, Pomonis PJ, Efstathiou AM (2002) J Catal 209:456–471
- Olympiou GG, Efstathiou AM (2011) Chem Eng J 170:424–432
- Costa CN, Savva PG, Fierro JLG, Efstathiou AM (2007) Appl Catal B 75:147–156
- Costa CN, Efstathiou AM (2007) J Phys Chem C 111:3010–3020
- Schott FJP, Balle P, Adler J, Kureti S (2009) Appl Catal B 87:18–29
- Leicht M, Schott FJP, Bruns M, Kureti S (2012) Appl Catal B 117:275–282
- Chiarello GL, Ferri D, Grunwaldt J-D, Forni L, Baiker A (2007) J Catal 252:137–147
- Breen JP, Burch R, Hardacre C, Hill CJ, Rioche C (2007) J Catal 246:1–9
- Fogel S, Doronkin DE, Høj JW, Gabrielsson P, Dahl S (2013) Top Catal 56:14–18
- Zhang X, Wang X, Zhao X, Xu Y, Liu Y, Yu Q (2015) Chem Eng J 260:419–426
- Liu YJ, Zhao M, Guo QL, Gui LL, Xie Y-C, Tang Y-Q (1985) Acta Chim Sin Engl Edit 3:313–320
- Bergeret G, Gallezot P (2008) Handbook of heterogeneous catalysis. Wiley, Weinheim
- Knop-Gericke A, Kleimenov E, Hävecker M, Blume R, Teschner D, Zafeirotas S, Schlögl R, Bukhtiyarov VI, Kaichev VV, Prosvirin IP (2009) Adv Catal 52:213–272
- Nartova AV, Gharachorlou A, Bukhtiyarov AV, Kvon RI, Bukhtiyarov VI (2017) Appl Surf Sci 401:341–347
- Chastain J, King RC Jr (1992) Perkin-Elmer Corp 40:221
- Ayame A, Kitagawa T (1991) Bunseki Kagaku 40:673–678
- Lu Z, Kanan SM, Tripp CP (2002) J Mater Chem 12:983–989
- Ross-Medgaarden EI, Wachs IE (2007) J Phys Chem C 111:15089–15099
- Daniel MF, Desbat B, Lassegues JC, Gerand B, Figlarz M (1987) J Solid State Chem 67:235–247
- Shelef M, Jones JH, Kummer JT, Otto K, Weaver EE (1971) Environ Sci Technol 5:790–798
- Hahn C, Endisch M, Schott FJP, Kureti S (2015) Appl Catal B 168:429–440
- Nefedov V, Salyn YV, Leonhardt G, Scheibe R (1977) J Electron Spectrosc Relat Phenom 10:121–124
- Davydov AA, Sheppard NT (2003) Molecular spectroscopy of oxide catalyst surfaces. Wiley, Chichester

39. Lévy PJ, Pitchon V, Perrichon V, Primet M, Chevrier M, Gauthier C (1998) *J Catal* 178:363–371
40. Komatsubara M, Koga A, Tanaka M, Hagiwara R, Iwamoto M (2016) *Catal Sci Technol* 6:7398–7407
41. Pignet T, Schmidt LD (1975) *J Catal* 40.2:212–225
42. Sun M, Wang S, Li Y, Xu H, Chen Y (2017) *Appl Surf Sci* 402:323–329
43. Kondratenko VA, Baerns M (2007) *Appl Catal B* 70:111–118
44. Barton DG, Soled SL, Iglesia E (1998) *Top Catal* 6:87–99
45. Stephens KJ, Allgeier AM, Bell AL, Carlson TR, Cheng Y, Douglas JT, Howe LA, Menning CA, Neuenswander SA, Sengupta SK, Thapa PS, Ritter JC (2020) *ACS Catal* 10:12996–13007

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.