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Article

Surface Species and Metal Oxidation State during H₂-Assisted NH₃-SCR of NO_x over Alumina-Supported Silver and Indium

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Abstract: Alumina-supported silver and indium catalysts are investigated for the hydrogen-assisted selective catalytic reduction (SCR) of NO_x with ammonia. Particularly, we focus on the active phase of the catalyst and the formation of surface species, as a function of the gas environment. Diffuse reflectance ultraviolet-visible (UV-vis) spectroscopy was used to follow the oxidation state of the silver and indium phases, and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to elucidate the formation of surface species during SCR conditions. In addition, the NO_x reduction efficiency of the materials was evaluated using H₂-assisted NH₃-SCR. The DRIFTS results show that the Ag/Al₂O₃ sample forms NO-containing surface species during SCR conditions to a higher extent compared to the In/Al₂O₃ sample. The silver sample also appears to be more reduced by H₂ than the indium sample, as revealed by UV-vis spectroscopic experiments. Addition of H₂, however, may promote the formation of highly dispersed In₂O₃ clusters, which previously have been suggested to be important for the SCR reaction. The affinity to adsorb NH₃ is confirmed by both temperature programmed desorption (NH₃-TPD) and in situ DRIFTS to be higher for the In/Al₂O₃ sample compared to Ag/Al₂O₃. The strong adsorption of NH₃ may inhibit (self-poison) the NH₃ activation, thereby hindering further reaction over this catalyst, which is also shown by the lower SCR activity compared to Ag/Al₂O₃.

Keywords: lean NO_x reduction; silver-alumina; indium-alumina; ammonia-SCR; hydrogen effect

1. Introduction

The development of fuel-efficient engines, operating under lean conditions, is motivated by fluctuating oil prices, more stringent emission legislations, and climate changes. Among the most attractive exhaust aftertreatment techniques for lean NO_x reduction is the selective catalytic reduction with either ammonia (NH₃-SCR) or hydrocarbons (HC-SCR). For example, Cu-based zeolites have recently been shown to exhibit high NO_x removal activity in a wide temperature range [1–3]. In contrast to NH₃-SCR, the HC-SCR catalysts need to be further improved as to be competitive. This puts pressure on building new understanding of the materials and mechanisms for HC-SCR. It seems, though, that NH₃ is a key intermediate for both techniques [4,5]. Due to its excellent thermal and mechanical stability, alumina is the most widely used catalyst support material [6]. The silver-alumina system has been studied for HC-SCR applications and with the pioneering work by Satokawa [7] in 2000, it was shown that the catalytic activity for NO_x reduction can be further improved by the addition of small amounts of hydrogen. This widely studied phenomenon [8–11] is denoted the ‘hydrogen effect’ and has previously been regarded as limited to silver-based catalysts only [12]. However, recently In/Al₂O₃, which also has been studied for SCR applications [13–19], was found to exhibit a hydrogen

effect, albeit to a lower extent compared to Ag/Al₂O₃ [20]. The hydrogen effect over Ag/Al₂O₃ has been suggested to originate from the reduction of adsorbed nitrogen species [10,21,22], changes in the type of Ag species [23–25], and/or enhanced activation of the reductant [9,11]. However, in contrast to other precious metal catalysts, alumina-supported silver is not active for H₂-SCR [26]. From a practical point of view, H₂ can be provided to the vehicle's exhaust after treatment by on-board reforming of for example solid amine salts or fuel [19,27].

Several studies have focused on the role of silver phases in the Ag/Al₂O₃ catalyst [28–33], suggesting the active phase for the selective reduction of NO_x to be Ag_n^{δ+}-clusters [32,33] and Ag⁺ ions [28,29], or a combination of these. Except for these species, metallic silver (Ag⁰) is recognized as responsible for complete combustion of the reductant [34]. In the In/Al₂O₃ catalyst, highly dispersed indium cluster sites (In³⁺) have been identified as the active component for hydrocarbon activation during HC-SCR [17].

A deeper understanding of the underlying mechanisms of the hydrogen effect is useful, not only to improve the SCR catalysts, but also for facilitating development of systems that reduce NO_x efficiently without the addition of hydrogen. In this study, we compare Ag/Al₂O₃ and In/Al₂O₃ catalysts, for the SCR of NO_x with ammonia as model reductant. In particular, we are focusing on how the catalytically active silver and indium phases are affected by the SCR environment, and how the formed surface species interact with these phases, using diffuse reflectance ultraviolet-visible (UV-vis) spectroscopy, in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and ammonia-temperature programmed desorption (NH₃-TPD).

2. Results

In this study, we compared H₂-assisted NH₃-SCR of NO_x over Ag/Al₂O₃ and In/Al₂O₃. In Section 2.1, we show the NO_x conversion and formed species during the SCR experiments. In addition, we compare the density of acidic sites by NH₃-TPD (Section 2.2). We have also focused on the possible changes in the active phase and surface species as a function of gas phase components. These results are presented in Sections 2.3 and 2.4

2.1. Catalytic Activity

The Ag/Al₂O₃ and In/Al₂O₃ samples were evaluated as NH₃-SCR catalysts using a flow reactor with a feed composition of 500 ppm NO, 500 ppm NH₃, 10% O₂, 5% H₂O, and Ar as carrier gas. The experiments were subsequently repeated with the addition of 1000 ppm H₂.

The NO_x reduction and NH₃ conversion, as well as the formation of NO₂ and N₂O over Ag/Al₂O₃, are shown in Figure 1. Without the addition of H₂, the catalyst is inactive for NO_x reduction. However, H₂-assisted NH₃-SCR reduces NO_x in a broad temperature window and with a maximum reduction just above 80%. The selectivity towards N₂ is high, in accordance with previous reports [35,36], 80% when H₂ is present in the feed. It can also be seen that the low N₂O formation decreases even further when H₂ is present, confirming the results of Kondratenko et al., that H₂ suppresses the total N₂O production [25]. This is assigned to H₂-induced Ag⁰ formation, which likely is responsible for the N₂O decomposition [37]. The negative values of NO_x reduction above 350 °C observed when H₂ is absent (black line in Figure 1a) is likely due to the oxidation of NH₃ to NO, which also explains the significant amount of NH₃ converted in Figure 1b [35]. Shimizu and Satsuma [32] suggest that the addition of H₂ to NH₃ + O₂ enhances the oxidative activation of NH₃ by decreasing the activation energy of the rate-determining step, (i.e., formation of NH_x).

The In/Al₂O₃ catalyst is, like Ag/Al₂O₃, inactive for NO_x reduction with solely NH₃, as seen in Figure 2. With the addition of H₂, the NO_x reduction clearly increases, however, to a considerably lower level compared to Ag/Al₂O₃. In order to separate between the effect of the active phase and the Al₂O₃ support, the equivalent experiments were executed for γ-Al₂O₃, which is totally inactive for both the NO_x reduction and NH₃ conversion, even with addition of H₂ (results not shown), in accordance with the findings of Doronkin et al. [19].

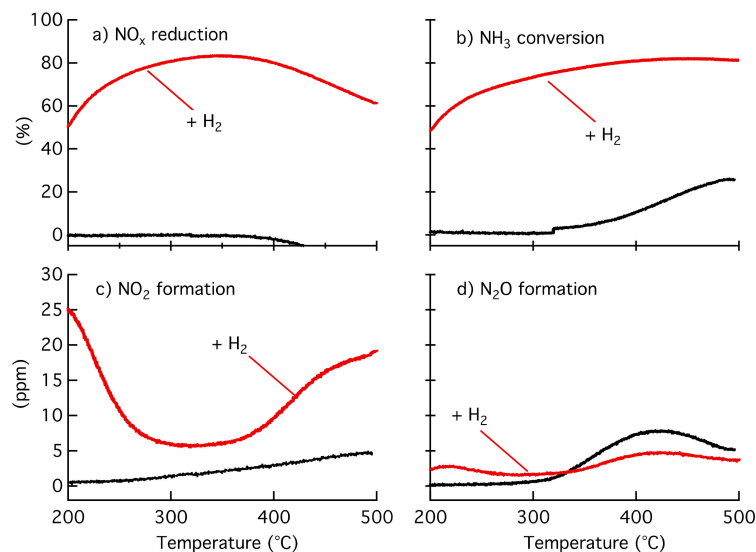


Figure 1. NH₃-SCR over Ag/Al₂O₃. (a) NO_x reduction; (b) NH₃ conversion; (c) NO₂ formation and (d) N₂O formation over the Ag/Al₂O₃ catalyst as a function of temperature. Inlet gas composition: 500 ppm NO, 500 ppm NH₃, 10% O₂ and 5% H₂O, Ar-bal. (red lines represents the addition of 1000 ppm H₂).

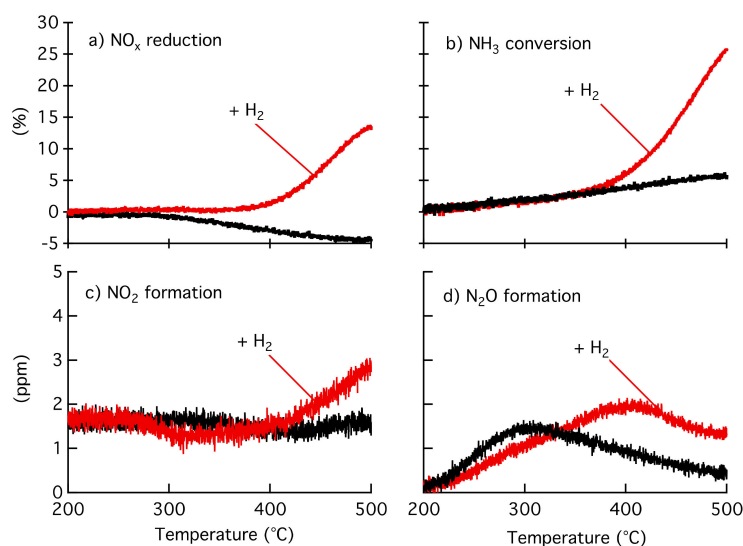


Figure 2. NH₃-SCR over In/Al₂O₃. (a) NO_x reduction; (b) NH₃ conversion; (c) NO₂ formation and (d) N₂O formation over the In/Al₂O₃ sample as a function of temperature. Inlet gas composition: 500 ppm NO, 500 ppm NH₃, 10% O₂ and 5% H₂O, Ar-bal. (red lines represents the addition of 1000 ppm H₂).

2.2. Surface Acidity

The surface of the alumina support consists of a combination of aluminum and oxygen ions, which may exhibit lower coordination numbers compared to ions of the bulk. The surface ions hold vacant sites, which, at ambient temperature, are always occupied by either dissociatively adsorbed water in the form of surface hydroxyl (OH) groups, or by coordinated water molecules [38]. Twelve different configurations of OH can be present at the surface, bearing slightly different net charges, consequently possessing different properties, such as variations in acidity [39,40].

Ammonia-TPD experiments were performed in order to investigate the surface acidity of the samples. The desorption profiles of NH₃ during the NH₃-TPD measurements over the γ -Al₂O₃, Ag/Al₂O₃ and In/Al₂O₃ samples, are shown in Figure 3. The total amount of desorbed ammonia,

summarized in Table 1, shows that the highest concentration of acidic sites is found for the γ -Al₂O₃ sample, followed by In/Al₂O₃ and Ag/Al₂O₃, which possessed the lowest concentration of acidic sites. Comparing the NH₃ desorption peaks for the samples; the weakest type of acidic site (i.e., the peak with lowest desorption temperature) is found at a higher temperature for the γ -Al₂O₃ sample, corresponding to 19% of the total desorbed amount of NH₃, compared to the Ag/Al₂O₃ (49%) and In/Al₂O₃ (16%) samples, respectively. The peak representing the strongest type of acidic site, i.e., the peak at the highest temperature, is also found at a higher temperature for the γ -Al₂O₃ sample. In addition, the highest desorption-temperature peak of the impregnated samples corresponds to the middle-temperature desorption peak of γ -Al₂O₃, indicating that the impregnation with silver and indium, respectively, results in less strong acidity for these samples. For the γ -Al₂O₃ sample, 33% of the total desorbed amount of NH₃ is adsorbed on this (strongest acidic) type of site, compared to 6% in the Ag/Al₂O₃ and 52% in the In/Al₂O₃ sample. However, the Gaussian peak representing the strongest acidic sites of the γ -Al₂O₃ sample is centered around almost 100 °C higher temperature compared to the peak holding the most acidic site of In/Al₂O₃. This implies that the impregnation procedure of γ -Al₂O₃ leads to an electronical modification and physical blockage of acidic sites at the catalyst support.

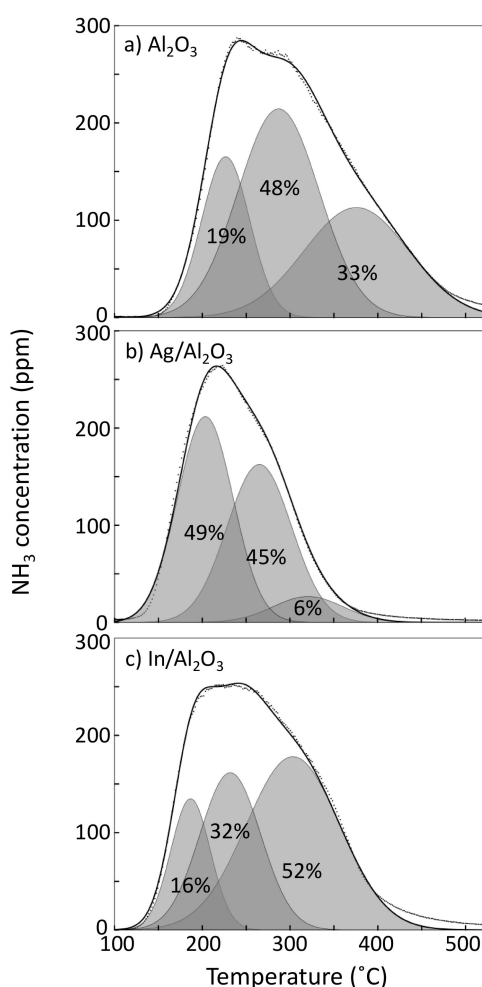


Figure 3. NH₃-temperature programmed desorption (TPD) profiles for (a) γ -Al₂O₃; (b) Ag/Al₂O₃ and (c) In/Al₂O₃, with the desorbed NH₃ concentration as a function of the temperature. The desorbed amount of NH₃ in the deconvoluted peaks are denoted in percentage of the measured total desorbed amount of NH₃.

Table 1. Total desorbed amount of NH₃ during the NH₃-TPD experiments.

Sample	Desorbed NH ₃ (mmol/cm ²)
γ-Al ₂ O ₃	11.2
Ag/Al ₂ O ₃	7.4
In/Al ₂ O ₃	9.5

2.3. Characterization of the Oxidation State of the Active Phase

Silver and indium species present in the catalyst samples were characterized using diffuse reflectance UV-vis spectroscopy. In order to investigate the influence of the NH₃-SCR reaction components, the samples were pretreated with NO, NH₃ and H₂, respectively. The UV-vis spectrum of the fresh (i.e., non-pretreated) Ag/Al₂O₃ sample (alumina subtracted) is shown in Figure 4, with absorbance peaks assigned according to Table 2. The spectrum shows that the sample contains a mixture of isolated Ag⁺-ions, Ag_n^{δ+}-clusters and Ag⁰. Note that some isolated Ag⁺-ions, which exhibited peaks below 200 nm, may have been present in the samples without being detected, since the spectrum only contained signals above 200 nm due to instrument limitations [41].

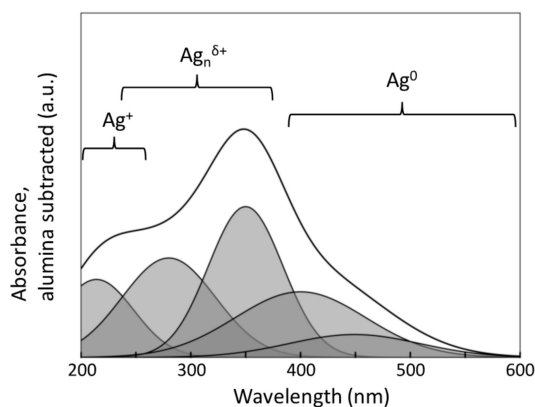


Figure 4. Ultra-violet (UV)-vis spectrum of the fresh (i.e., non-pretreated) Ag/Al₂O₃ sample, with the absorbance for the alumina sample subtracted, as a function of the wavelength. The peak ranges assigned to isolated Ag⁺-ions, Ag_n^{δ+}-clusters and Ag⁰ are denoted.

Table 2. Assignment of absorption peaks in the UV-vis spectra of Ag/Al₂O₃.

Species	Wavelength [nm]	Reference
Isolated Ag ⁺ -ions	192–250	[32]
	196, 212, 224	[42]
	220	[43]
	215–240	[44]
	212, 260	[44]
Ag _n ^{δ+} -clusters	260–370	[37]
	238–272	[45,46]
	322	[42]
	350, 285	[32]
Ag ⁰	>390	[28,29,32,42,46–48]

Figure 5 shows, in the same scale as Figure 4, the UV-vis spectra of the Ag/Al₂O₃ sample after pretreatments in H₂, NO and NH₃ at 300 °C. The H₂ pretreatment results in increased intensity of the bands at wavelengths corresponding to Ag_n^{δ+}-clusters and metallic silver, as shown in Figure 5a. In contrast, the absorption spectrum recorded after pretreatment in NO (Figure 5b) shows decreased

intensity, compared to the fresh sample, at wavelengths corresponding to $\text{Ag}_n^{\delta+}$ -clusters and metallic silver, indicating that NO slightly oxidizes the catalyst surface at 300 °C. In Figure 5c, the spectrum recorded after NH_3 -pretreatment shows that the surface is reduced by NH_3 . Compared to the fresh sample, this pretreatment shifts peaks from clusters to more completely reduced Ag phases.

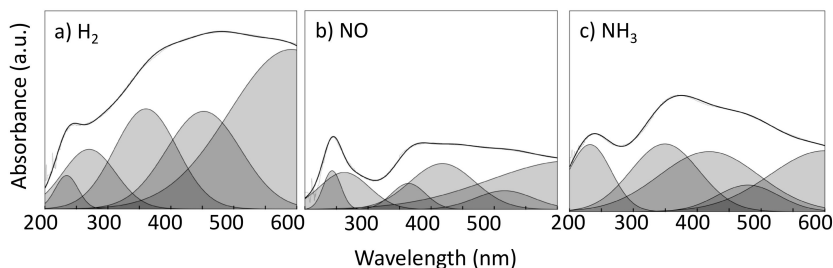


Figure 5. UV-vis spectra for the $\text{Ag}/\text{Al}_2\text{O}_3$ sample, with the absorbance for the alumina sample subtracted, plotted as a function of the wavelength. The graphs represent the spectra after pretreatment in (a) H_2 , (b) NO , and (c) NH_3 at 300 °C. The scale of these figures is the same as of Figure 4.

The UV-vis spectrum of the fresh (i.e., non-pretreated) $\text{In}/\text{Al}_2\text{O}_3$ sample is shown in Figure 6. Absorption peaks in the range 200–450 nm are assigned to In_2O_3 [49–54]. Lv et al. [49] experienced that increased concentration of In_2O_3 results in a broadening and a redshift of the absorbance edge. The spectrum recorded after the H_2 -pretreatment shows broadened absorption peaks with a slight redshift (see Figure 7a). However, peaks at wavelengths above 450 nm increases somewhat after the H_2 -pretreatment, indicating the presence of more reduced indium species. Increased and broadened absorption peaks in the range 200–450 nm are detected after pretreatments also with NO and NH_3 at 300 °C (see Figure 7b,c), which could indicate increased In_2O_3 concentration in the sample.

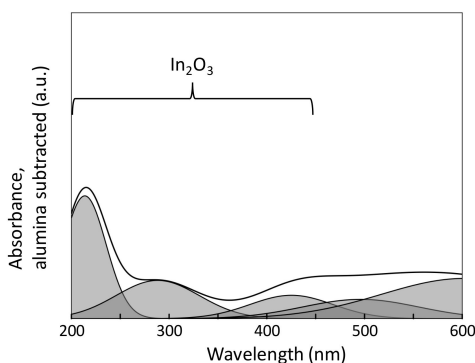


Figure 6. UV-vis spectrum of the fresh (i.e., non-pretreated) $\text{In}/\text{Al}_2\text{O}_3$ sample, with the absorbance for the alumina sample subtracted, as a function of the wavelength. The peak range assigned to In_2O_3 is denoted.

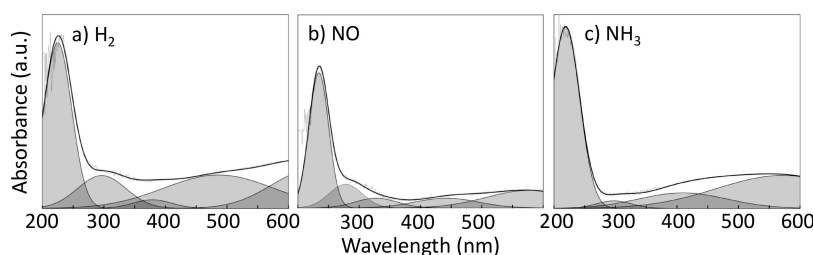


Figure 7. UV-vis spectra for the $\text{In}/\text{Al}_2\text{O}_3$ sample, with the absorbance for the alumina sample subtracted, plotted as a function of the wavelength. The graphs represent the spectra after pretreatment in (a) H_2 , (b) NO , and (c) NH_3 at 300 °C. The scale of these figures is the same as of Figure 6.

2.4. Evaluation of Surface Species

The gas environment influences the surface of the catalyst, and in order to study the active phase and connect that to the reaction itself, DRIFTS was used to follow the formation of surface species at reaction conditions. Figure 8 shows the formation of surface species for the Ag/Al₂O₃, In/Al₂O₃ and γ -Al₂O₃ samples during exposure to NO, NH₃, H₂ and O₂ at 300 °C. The measurements were performed after 10 min exposure to the gas mixture in the last measurement sequence (see Table 3). All observed peaks remained after the specific gas component that gave rise to the corresponding absorption band, was switched off. This indicates that the surface species are chemisorbed to the samples. Below, absorption bands assigned to the adsorption of NO and NH₃ are presented separately. Also, absorption bands assigned to hydroxyl groups (i.e., bands at 3500–3800 cm⁻¹ [55]) were observed (Figure 8). Comparing the relative peak intensities within the OH-band area of the infra-red (IR) patterns, it can be shown that the spectrum of the γ -Al₂O₃ sample resembled the one of In/Al₂O₃ more closely, compared to Ag/Al₂O₃.

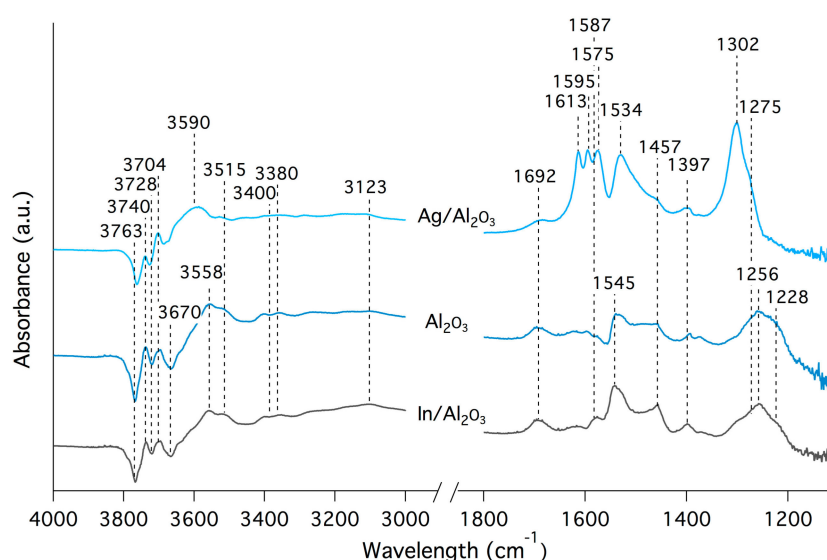


Figure 8. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra showing formation of surface species for the Ag/Al₂O₃, In/Al₂O₃ and γ -Al₂O₃ samples during the exposure to selective catalytic reduction (SCR) reaction conditions (NO, NH₃, H₂, O₂, Ar-bal.) at 300 °C.

Table 3. The seven DRIFTS sequences. Gas condition: 500 ppm NO, 1000 ppm H₂ and 500 ppm NH₃. All sequences included 10% O₂ and Ar as the carrier gas.

Sequence	NO	H ₂	NH ₃
1	NO		
2	NO	H ₂	
3	NO	H ₂	NH ₃
4		H ₂	NH ₃
5			NH ₃
6	NO		NH ₃
7	NO	H ₂	NH ₃

2.4.1. Assignment of NO Absorption Bands

Exposing Al₂O₃-based catalysts to NO and O₂ (or to NO₂) leads to the formation of surface nitrate and nitrite species. Nitrites have been recognized as an intermediate state in the formation of nitrates over Ag/Al₂O₃ [21], which may be a reason for the nitrite band to appear at 1228 cm⁻¹ in the γ -Al₂O₃ and In/Al₂O₃ spectra, but not in the spectrum of Ag/Al₂O₃. Absorption bands related to the

symmetric N=O stretching vibrations are located in the region between 1650 and 1500 cm^{-1} , while the asymmetrical stretching of the O–N–O group can be detected between 1200 and 1350 cm^{-1} [21,34,56]. The spectra of In/ Al_2O_3 and $\gamma\text{-Al}_2\text{O}_3$ exhibit broad peaks centered around 1256 cm^{-1} , as shown in Figure 8. This band is assigned to (bidentate) nitrate [57]. In the same region, at 1302 cm^{-1} , Ag/ Al_2O_3 exhibits a sharp peak, which is assigned to monodentate nitrate [21,57]. The three peaks located at 1575, 1595 and 1613 cm^{-1} for the Ag/ Al_2O_3 sample are assigned to bridged-, bidentate- and mono-dentate nitrate, respectively [21,41]. A summary of all absorption band assignments upon NO exposure is found in Table 4.

Table 4. Assignments of infra-red (IR) peaks associated with nitrite and nitrate species.

Wavenumber (cm^{-1})	Appears in Sample	Surface Species	References
1228	Al_2O_3 , In/ Al_2O_3	Nitrite	[21]
1256	Al_2O_3 , In/ Al_2O_3	Bidentate nitrate	[21,58]
1302	Ag/ Al_2O_3	Monodentate nitrate	[21]
1534	Ag/ Al_2O_3	Monodentate nitrate	[21]
1545	Al_2O_3 , In/ Al_2O_3	Monodentate nitrate	[21]
1575	Ag/ Al_2O_3	Monodentate nitrate	[21]
1595	Ag/ Al_2O_3	Bidentate nitrate	[21]
1613	Ag/ Al_2O_3	Bridged nitrate	[21,59,60]

2.4.2. Assignment of NH_3 Absorption Bands

The symmetric and asymmetric vibration of surface coordinated NH_3 results in absorption bands at 1275 and 1587 cm^{-1} , respectively [61]. Moreover, the bands at 1397 and 1692 cm^{-1} are likely due to the adsorption of NH_4^+ ions at Brønstedt acidic sites [61,62]. The less pronounced absorption bands at 3380 and 3400 cm^{-1} are assigned to the symmetric and asymmetric N–H stretching vibrations of NH_3 hydrogen bonded to surface OH [62,63]. A summary of the absorption bands associated with ammonia is found in Table 5.

Table 5. Assignments of IR peaks associated with ammonia surface species.

Wavenumber (cm^{-1})	Vibration	Reference
1275	Symmetric bending of surface coordinated NH_3	[61]
1397	NH_4^+ ions at Brønstedt acidic site	[62,63]
1587	Asymmetric bending of surface coordinated NH_3	[61]
1692	NH_4^+ ions at Brønstedt acidic site	[62,63]
3380	Symmetric NH stretching vibrations of NH_3 hydrogen bonded to surface OH	[62,63]
3400	Asymmetric NH stretching vibrations of NH_3 hydrogen bonded to surface OH	[63]

3. Discussion

The NH_3 -SCR results (Figures 1 and 2) show that the H_2 -assisted reduction of NO at 300 °C is high over the Ag/ Al_2O_3 sample and low over the In/ Al_2O_3 sample. In situ DRIFTS results (Figure 8) show that the formation of NO-containing species is higher over the Ag/ Al_2O_3 sample compared to the In/ Al_2O_3 and $\gamma\text{-Al}_2\text{O}_3$ samples at this temperature. An efficient adsorption of the gas phase species is crucial for achieving an effective catalytic conversion. However, all absorption bands assigned to NH_3 adsorption are more pronounced for the $\gamma\text{-Al}_2\text{O}_3$ and In/ Al_2O_3 samples, compared to the Ag/ Al_2O_3 sample. This indicates that the adsorption of NH_3 -surface species is more efficient over the former two samples compared to the latter, which is supported by the NH_3 -TPD (Figure 3), showing that the $\gamma\text{-Al}_2\text{O}_3$ and In/ Al_2O_3 samples provide higher density of acidic sites, compared to the Ag/ Al_2O_3 sample. Furthermore, the DRIFTS spectra show differences at the wavelengths corresponding to OH-groups. The In/ Al_2O_3 pattern resembles the one of $\gamma\text{-Al}_2\text{O}_3$ to a higher degree compared to Ag/ Al_2O_3 . Since alumina is impregnated with Ag and In in equivalent molar amounts, this implies

that Ag affects the acidic properties of the OH-rich alumina surface to a higher degree compared to In, resulting in a lower concentration of acidic sites for Ag/Al₂O₃.

Silver clusters (Ag_{*n*}^{δ+}) have previously been identified as the prime species for the activity in H₂-assisted NH₃-SCR [64], and it has been shown that the activity is linearly proportional to the relative amount of these clusters [32]. Shimizu and Satsuma [32] suggest the following reaction mechanism for H₂-NH₃-SCR over Ag/Al₂O₃: (i) dissociation of H₂ on the Ag site, (ii) spillover of H⁺ to form a proton on Al₂O₃, (iii) aggregation of isolated Ag⁺ ions to Ag_{*n*}^{δ+}-clusters (*n* ≤ 8), (iv) reduction of O₂ promoted by Ag_{*n*}^{δ+}-clusters and H⁺ to O₂[−], H₂O and Ag_{*n*}^{(δ+x)+} or Ag⁺, (v) N–H activation by O₂[−] to yield NH_{*x*} (*x* ≤ 2) (vi) oxidation of NO by O₂[−] forming NO₂, (vii) reaction between NH_{*x*} and NO to yield N₂ and H₂O. The study by Tamm et al. [65] confirms that silver is needed for the dissociation of H₂, which directly participates in the reaction mechanism and also that the NO to NO₂ oxidation is part of this mechanism.

The UV-vis spectra of the In/Al₂O₃ sample show increased peak intensity for bands assigned to In₂O₃ but also increased absorbance at higher wavelengths (>450 nm) after pretreatment in H₂. The reaction mechanism of H₂-assisted NH₃ over In/Al₂O₃ could therefore resemble what Shimizu et al. suggested for Ag/Al₂O₃. However, the NH₃-TPD profiles of the catalysts elucidate the difference in acidity between the catalysts, where the In/Al₂O₃ sample contains significantly stronger acidic sites compared to the Ag/Al₂O₃ sample. An important difference in the mechanisms between the two catalysts could therefore be the stronger affinity between NH₃ and In/Al₂O₃, possibly hindering the NH₃ activation and thereby hindering further reaction over this catalyst to a higher extent compared to Ag/Al₂O₃. Another possible issue that may restrain the NO_x conversion over In/Al₂O₃ is the lower adsorption of NO species at the catalyst surface.

4. Materials and Methods

4.1. Catalyst Preparation and Basic Characterization

Two catalyst samples, 2.0 wt % Ag/Al₂O₃ and 2.1 wt % In/Al₂O₃ (which corresponds to equivalent molar amount of Ag and In, respectively), were prepared by incipient wetness impregnation of γ-Al₂O₃ (PURALOX[®]SBa 200, Sasol, Hamburg, Germany) using freeze-drying, according to the procedure described in detail previously [20], and briefly below. Silver nitrate (≥99.0% Sigma-Aldrich/Merck, Darmstadt, Germany) and indium nitrate hydrate (99.99% Sigma-Aldrich) were used as the active phase precursor for Ag and In, respectively. After impregnation, the samples were frozen in liquid nitrogen, subsequently freeze-dried, and finally calcined in air at 600 °C for four hours. The as prepared powder samples were characterized with respect to surface area by N₂ sorption (BET) and crystal structure by X-ray diffraction (XRD), as described in details elsewhere [20].

For the evaluation of the catalytic activity for NH₃-SCR, monolith samples with 188 channels (400 CPSI, Ø = 20 mm, L = 20 mm) were cut from a commercial cordierite honeycomb structure (Corning, Corning, NY, USA) and calcined in air at 600 °C for one hour. Binder agent (DISPERAL[®] P2, Sasol) and one of the powder catalysts (ratio 1:4) in 1:1-ratio ethanol-water solutions were mixed to form washcoat slurries. The monoliths were dipped into the slurries, gently shaken for removal of excess slurry, dried (90 °C in air), and subsequently calcined (500 °C, 3 min). The coating procedure was repeated until the washcoat mass corresponded to 20% of the coated monolith mass. Finally, the monolith samples were calcined in air (600 °C, 1 h).

The catalyst samples have previously been characterized with respect to surface area and crystal structure [20]. The specific surface areas are 197, 185, and 188 m²/g, for γ-Al₂O₃, Ag/Al₂O₃ and In/Al₂O₃, respectively. X-ray diffractograms indicate that the main crystalline phase in all samples is γ-Al₂O₃, and other crystalline phases (if any) are only present as particles smaller than 3–5 nm [66], in line with previous studies [17,18].

4.2. Lean NO_x Reduction Experiments

The catalytic activity for NH₃-SCR was evaluated in extinction experiments (500–100 °C, 10 °C/min) at a flow rate of 3500 mL/min (GHSV of 33,400 h⁻¹) in a flow reactor setup previously described by Kannisto et al. [67]. Briefly, the reactor consisted of a horizontal quartz tube ($L = 80$ cm, $\varnothing_i = 22$ mm) heated by a metal coil. The catalyst sample was positioned close to the tube outlet, surrounded by bare monoliths for shielding of heat radiation to the thermocouples [68], which were placed inside and just before the coated monolith. Prior to each measurement, the sample was pretreated in 10% O₂ (Ar-balance) at 500 °C for 30 min. During the experiments, the gas composition was 500 ppm NO, 500 ppm NH₃, 10% O₂, and 5% H₂O, in the presence or absence of 1000 ppm H₂ (Ar-balance). The outlet gas composition was analyzed by a gas phase Fourier transform infrared (FTIR) spectrometer (MKS 2030, MKS Instruments, Telford, UK). The reduction of NO_x and conversion of NH₃ were obtained from the ratios of the differences between the inlet and outlet concentrations to the corresponding inlet concentration.

4.3. UV-Vis Spectroscopy

The samples, pretreated in varying SCR gas components, were characterized by diffuse reflectance UV-vis spectroscopy. Reflectance spectra in the wavelength range 200–1200 nm were recorded using a Varian Cary 5000 UV-vis near-IR (NIR) spectrophotometer, equipped with an external DRA-2500 unit (Agilent, Santa Clara, CA, USA). The same flow reactor equipment as in the NO_x reduction experiments was used for the pretreatments, where the samples were exposed to NO (1500 ppm, Ar balance), NH₃ (1500 ppm, Ar balance), and H₂ (3000 ppm, Ar balance), respectively. The pretreatments were carried out in a gas flow of 100 mL/min for 20 min at 300 °C. During data processing, the spectrum of the alumina support (which was pretreated in the same way as the Ag/Al₂O₃ and In/Al₂O₃ samples) was subtracted, and each spectrum was deconvoluted using Gaussian peaks for evaluation purposes.

4.4. In Situ DRIFTS

The surface species on the samples were characterized during SCR reaction conditions by in situ DRIFTS. The instrument used was a Bruker Vertex70 spectrometer equipped with a high-temperature reaction cell (Harrick Scientific, Pleasantville, NY, USA) with KBr windows. Prior to the measurements, the samples were pressed into tablets and then crushed by a mortar, in order to enlarge the powder particles to avoid channeling during the measurement. Subsequently, the powder fraction of the crushed tablets was sieved to a size range of 38 to 75 μm.

After placing the sample in the reaction cell, the Ag/Al₂O₃ and In/Al₂O₃ samples were pretreated at 500 °C in NO (2000 ppm, Ar-bal.) for 30 min, followed by O₂ (10%, Ar bal.) for 45 min, and finally H₂ (1000 ppm, Ar bal.) for 15 min. The γ-Al₂O₃ sample was pretreated in O₂ (10%, Ar bal.) for 45 min and then H₂ (1000 ppm, Ar bal.) for 15 min. The gas conditions during the measurement sequence is listed in Table 3, and corresponded to 500 ppm NO, 500 ppm NH₃, 1000 ppm H₂, and 10% O₂ (Ar balance). Each sequence lasted for 10 min and data were collected a few seconds after starting the experiment, after 5 min, and finally after 10 min. A resolution of 1 cm⁻¹ was adapted, and 128 scans were recorded for the background spectra (recorded in Ar at 300 °C), and 64 scans for the measurements. All experiments were carried out at 300 °C in a flow rate of 100 mL/min and the data are presented as absorbance ($\log I/R$).

4.5. NH₃-TPD

The concentration and strength of acidic sites of the coated monolith samples were measured by NH₃-TPD. The flow reactor presented in Section 2.2 was used for this purpose, where the sample first was pretreated in 10% O₂ (20 min) in order to remove carbonaceous matter, flushed with argon (5 min), and then exposed to 1000 ppm H₂ (20 min) at 550 °C. During the following NH₃-TPD experiment, the catalyst surface was exposed to NH₃ (1000 ppm) at 100 °C until saturation, followed by Ar

flushing until the NH₃ signal vanished. The temperature was subsequently increased linearly to 550 °C (20 °C/min) while the desorbed NH₃ was measured continuously. For peak identification purposes, the NH₃-TPD profiles obtained are deconvoluted into Gaussian peaks.

5. Conclusions

This work shows that NO-species are formed to a higher extent over Ag/Al₂O₃ during SCR conditions, compared to In/Al₂O₃. The latter provide higher density of acidic sites, quantified by NH₃-TPD, and also exhibit higher NH₃ adsorption, as shown by DRIFTS. Moreover, the Ag/Al₂O₃ sample is more clearly reduced by H₂, compared to In/Al₂O₃. However, H₂ seems to promote the formation of highly dispersed In₂O₃ clusters, which previously have been suggested to be crucial for HC-SCR and could be important for the activation of the reducing agent also during H₂-assisted NH₃-SCR. Since adsorption of reactants in suitable proportions is crucial for high catalytic activity, an important difference between the two catalysts could be the stronger affinity for NH₃ over In/Al₂O₃, compared to Ag/Al₂O₃. This can possibly inhibit the NH₃ activation over the former, and thereby hindering further reaction over this catalyst, which is also shown by the lower SCR activity, compared to Ag/Al₂O₃.

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