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Published in:
Applied Catalysis B: Environmental

Link to article, DOI:
10.1016/j.apcatb.2011.11.042

Publication date:
2012

Citation (APA):
Study of the “Fast SCR”-like mechanism of H₂-assisted SCR of NOₓ with ammonia over Ag/Al₂O₃

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Abstract. It is shown that Ag/Al₂O₃ is a unique catalytic system for H₂-assisted selective catalytic reduction of NOₓ by NH₃ (NH₃-SCR) with both Ag and alumina being necessary components of the catalyst. The ability of Ag/Al₂O₃ and pure Al₂O₃ to catalyse SCR of mixtures of NO and NO₂ by ammonia is demonstrated, the surface species occurring discussed, and a ”Fast SCR”-like mechanism of the process is proposed. The possibility of catalyst surface blocking by adsorbed NOₓ and the
influence of hydrogen on desorption of NO$_x$ were evaluated by FTIR and DFT calculations.

Keywords: Ag/Al$_2$O$_3$; alumina; NO$_x$ SCR; Fast SCR; FTIR

1. Introduction

Nitrogen oxides (NO$_x$) are the most challenging pollutant to address for light-duty diesel vehicles and sophisticated techniques like advanced fuel injection, exhaust gas recirculation (EGR), turbocharging etc., are used by engine manufactures to reduce emissions. But, NO$_x$ removal by exhaust aftertreatment is still required due to stricter emission regulations and the trade off between fuel consumption and NO$_x$ emission, i.e., the price for reducing fuel consumption and CO$_2$ emission by ~15% equals to ~50% increase in NO$_x$ emissions [1].

Selective catalytic reduction (SCR) is the leading NO$_x$ control technique with ammonia as a reductant. Commonly used catalysts are vanadia-based catalysts, Cu and Fe-containing zeolites. However, none of the systems demonstrates high thermal durability together with a good activity throughout a broad temperature region from 150 to 550 °C [1]. This fact explains the reason for the on-going research of novel catalytic systems for NH$_3$-SCR, which are supposed to be non-toxic, inexpensive and durable.

Alumina supported metals, such as Ag, In, Sn etc. [2,3,4,5] are known to catalyse NO$_x$ SCR by hydrocarbons under the conditions of lean-burn engine exhaust. The major drawback of these catalytic systems is their very poor activity at low temperatures. It has been found that addition of hydrogen to the gas feed can substantially improve the low-temperature activity of Ag/Al$_2$O$_3$ [6,7,8]. Interestingly, several groups have also demonstrated the possibility of Ag/Al$_2$O$_3$ to facilitate SCR of NO$_x$ by ammonia or urea
with co-feeding hydrogen, resulting in nearly 90% \( \text{NO}_x \) conversion at temperatures as low as 200 °C [9,10].

Hydrogen for this reaction can be provided on board of the vehicle by two means depending on the used reductant. The required amount of hydrogen can be produced in an on-board fuel reformer without the necessity to change the existing fuel infrastructure. This is convenient for hydrocarbon SCR systems utilizing Ag/Al\(_2\)O\(_3\) catalysts and currently leads to fuel penalties from 5 to 10% [11, 12] which might be improved by the optimization of the system. For the NH\(_3\) SCR applications hydrogen can be produced by cracking of part of the ammonia. Pure NH\(_3\) required for this purpose can be stored on board in form of solid metal ammine salts [13]. The suggested system allows accurate and independent dosing of ammonia to the SCR catalyst and to the cracker where it can be decomposed to form the required hydrogen. Using ammonia for hydrogen storage has earlier been suggested for fuel cell applications but can also be applied for \( \text{NO}_x \) SCR applications [14, 15].

There is no general agreement about the necessary concentration of hydrogen for the effective reduction of \( \text{NO}_x \) by ammonia over Ag/Al\(_2\)O\(_3\). One can find H\(_2\)::\( \text{NO}_x \) ratios varying from 5 to 10 in the literature [9, 10, 16-18] which is a rather high value. However Shimizu and Satsuma have demonstrated ever increasing \( \text{NO}_x \) reduction rate in the interval of H\(_2\)::\( \text{NO}_x \) ratios from 0 to 50 [17] which makes the choice of H\(_2\) concentration a matter of finding the optimum between the amount of ammonia spent on hydrogen production and the SCR efficiency. We are considering a H\(_2\)::\( \text{NO}_x \) ratio 2.4 as an optimum in this work.

Hydrogen has also been considered as the only reductant in H\(_2\)-SCR of \( \text{NO}_x \), however currently available catalysts allow effective removal of \( \text{NO}_x \) only when using
H$_2$:NO$_x$ > 10 and such amount of hydrogen cannot be produced on board at an affordable price [19-21].

In this work we studied several catalysts: Ag supported on different carriers ($\gamma$-Al$_2$O$_3$, TiO$_2$ and ZrO$_2$), Sn and In supported on $\gamma$-Al$_2$O$_3$ and pure alumina under the conditions of H$_2$-assisted SCR of NO$_x$ with NH$_3$. The aim of this study is to investigate the possibility of replacing traditional NO$_x$ SCR catalysts by Ag/Al$_2$O$_3$ thus obtaining high catalyst activity even at low temperatures. Another goal of the study is to give insight to the mechanistic aspects of H$_2$-assisted NO$_x$ SCR by ammonia.

2. Experimental

2.1. Catalyst preparation

Parent $\gamma$-alumina (Puralox SCFa-140, 59 ppm Fe$_2$O$_3$ content) was kindly provided by SASOL. Prior to its study as a catalyst it was calcined at 550 °C for 4 hours in static air.

1%Ag/Al$_2$O$_3$, 3%Sn/Al$_2$O$_3$ and 3%In/Al$_2$O$_3$ were obtained by incipient wetness impregnation of parent $\gamma$-alumina by corresponding amounts of AgNO$_3$, SnCl$_4$·5H$_2$O and InCl$_3$·4H$_2$O (all from Sigma-Aldrich) solutions in deionized water. 1%Ag/TiO$_2$ and 1%Ag/ZrO$_2$ were obtained by incipient wetness impregnation of TiO$_2$ (anatase containing 10%SiO$_2$) and ZrO$_2$ (E10, Magnesium Elektron Ltd.) by the aqueous solution of AgNO$_3$. After impregnation all catalysts were dried at room temperature overnight and calcined at 550 °C for 4 hours in static air.

The calcined catalysts were pressed, crushed and sieved to obtain the fraction 0.18 – 0.35 mm (mesh 80 – mesh 45).
2.2. TEM measurements

TEM measurements were carried out in a TECNAI T20 transmission electron microscope equipped with an Oxford Instruments EDX detector. For the measurements the catalyst powder (in a dry form) was dispersed on a copper TEM grid covered with a lacey carbon film. Images were acquired using DigitalMicrograph from Gatan Inc.

2.3. Catalytic studies

The catalytic measurements were carried out in a fixed-bed quartz flow reactor (inner diameter = 4 mm) in a temperature programmed mode while the temperature was decreased from 400 °C to 150 °C with a rate 2 °C/min. The temperature was controlled using an Eurotherm 2416 temperature controller with a K-type thermocouple. 45 mg of catalyst was diluted with 100 mg of SiC (mesh 60) and placed on a quartz wool bed. The bed height was ~11 mm and the GHSV, calculated using the volume of the pure catalyst was ~ 110,000 h⁻¹. The gas composition normally contained 500 ppm NO, 520 ppm NH₃, 8.3% O₂, and 7% water balanced with Ar. During some tests 1200 ppm of H₂ was added to the gas feed. The gas feed was mixed from 2000 ppm NO in Ar, 2000 ppm NH₃ in Ar, 4000 ppm H₂ in Ar (Air Liquide), oxygen and argon (AGA), dosed by individual mass flow controllers (UNIT Celerity). Water was dosed by an ISCO 100DM syringe pump through a heated capillary. Mixtures of NO and NO₂ were obtained by feeding NO and oxygen through a long capillary, giving NO₃ with 26 – 47% NO₂. Reaction products were analyzed by a Thermo Fisher Nicolet 6700 FTIR analyzer, equipped with a gas cell (2 m optical pathlength). Gas capillaries were heated to ~130 °C and the FTIR gas cell to 165 °C to avoid condensation of water and formation of ammonium nitrate. To simplify experimental procedure we are not using CO₂ in the
study as we have not observed CO$_2$ effect on the NO$_x$ SCR by NH$_3$ during the preliminary experiments with Ag/Al$_2$O$_3$ catalysts.

Conversions were calculated using the following equations:

$$X_{NOx} = 1 - \frac{C_{NOx}^{outlet}}{C_{NOx}^{inlet}}$$

(1)

where $X_{NOx}$ denotes total conversion of NO$_x$ and $C_{NOx}^{inlet}$ and $C_{NOx}^{outlet}$ is the NO$_x$ concentrations on the inlet and outlet of the reactor, where:

$$C_{NOx} = C_{NO} + C_{NO2}^*.$$  

(2)

NH$_3$ conversion (total), NH$_3$ conversion to NO$_x$ (when no NO$_x$ is fed) and NO conversion to NO$_2$ (when no NH$_3$ was fed) were calculated correspondingly:

$$X_{NH_3} = 1 - \frac{C_{NH_3}}{C_{NH_3}^{inlet}},$$

(3)

$$X_{NH_3\rightarrow NOx} = \frac{C_{NOx}^{outlet}}{C_{NH_3}^{inlet}},$$

(4)

$$X_{NO\rightarrow NO_2} = \frac{C_{NO_2}^{outlet}}{C_{NO}^{outlet}},$$

(5)

and the ratio of converted NO to converted NO$_2$ in the experiments with NO and NO$_2$ mixtures:

$$\frac{C_{NO}^{conv}}{C_{NO_2}^{conv}} = \frac{C_{NO}^{inlet} - C_{NO}^{outlet}}{C_{NO_2}^{inlet} - C_{NO_2}^{outlet}}.$$  

(6)

NH$_3$:NO$_x$ conversion ratio below 400 °C was always 1:0.95-1.05 for all tested catalysts, therefore we are presenting only NO$_x$ conversion values in the discussion.

2.4 DRIFTS studies
In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were performed using a BioRad FTS 6000 FTIR spectrometer equipped with a high-temperature reaction cell (Harrick Scientific, Praying Mantis) with KBr windows. The temperature of the reaction cell was controlled with a K-type thermocouple connected to a Eurotherm 2416 temperature controller. Gases were introduced into the reaction cell via individual mass flow controllers (Bronkhorst Hi-Tech). The gas composition at the outlet of the DRIFTS cell was analyzed by a mass spectrometer (Balzers QuadStar 420).

Each experiment was performed using approximately 100 mg of $\gamma$-Al$_2$O$_3$ powder, using new powder for each experiment. The powder was initially pretreated in a flow of 8% O$_2$ in Ar at 500 °C for 30 min, subsequently a background spectrum (60 scans, resolution 2 cm$^{-1}$ at 4000 cm$^{-1}$) was recorded in a flow of Ar. At 500 °C, 185 ppm NO$_2$, 315 ppm NO, 520 ppm NH$_3$ and 8.3% O$_2$ were added to the feed. Then the catalyst was cooled with a ramp rate of 10 °C/min in the reaction mixture to reaction temperature, where the temperature is held for 10 min for stabilization. Subsequently, NH$_3$ is removed from the feed gas mixture for 30 min and added again to it for 10 min. This procedure was repeated once. Thereafter, 1250 ppm H$_2$ were added for 10 min to the feed gas and, subsequently, NH$_3$ was removed again. The evolution of absorption bands in the spectra was followed using the kinetic mode (9 scans/spectrum, 6 spectra/min,) at a resolution of 2 cm$^{-1}$ at 4000 cm$^{-1}$. The data are presented as absorbance, which is defined as the logarithm of the inverse reflectance (log 1/R). All DRIFTS experiments were carried out using a total flow rate of 100 ml/min which corresponds to a space velocity of about 62 000 h$^{-1}$. 
2.5. DFT Calculations

Plane wave DFT code DACAPO is used to calculate the adsorption energies and the gas phase energies of the adsorbates. Plane wave cutoff of 340.15 eV and density cutoff of 680 eV are used for the calculations. The core electrons are described by the Vanderbilt ultrasoft pseudopotential [22]. RBPE is used as the exchange correlation energy function [23]. Fermi population of the Kohn-Sham states is \( k_B T = 0.1 \) eV. The convergence limit is set as maximum change in force constant \( f_{\text{max}} = 0.03 \) eV.

The adsorption energies of O, NO, NO\(_2\) and NO\(_3\) are studied over six different transition metals (Ag, Cu, Pd, Pt, Rh, Ru) on both the (111) terrace and the (211) step surfaces. We use a \( 2 \times 2 \) surface cell for O and NO for (111) terrace, \( 2 \times 1 \) surface cell for O and NO for (211) step surface, \( 3 \times 3 \) surface cell for NO\(_2\) and NO\(_3\) adsorption study on (111) terrace and the \( 3 \times 1 \) surface cell for NO\(_2\) and NO\(_3\) adsorption study (211) step surfaces, with \( 8 \times 8 \times 1 \) Monkhorst-Pack \( \mathbf{k} \)-point sampling in the irreducible Brillouin zone for all the \( 2 \times 2 \) surface cells, \( 8 \times 6 \times 1 \) Monkhorst-Pack \( \mathbf{k} \)-point sampling in the irreducible Brillouin zone for all the \( 2 \times 1 \) surface cells and \( 4 \times 4 \times 1 \) Monkhorst-Pack \( \mathbf{k} \)-point sampling for both \( 3 \times 3 \) and \( 3 \times 1 \) surface cells. For all the (111) surfaces we use a four-layer slab where the two topmost layers are allowed to relax whereas for the (211) surfaces with \( 2 \times 1 \) surface cell we use a slab model with twelve layers where the topmost six layers are allowed to relax and for (211) surfaces with \( 3 \times 1 \) surface cell we use a slab model with nine layers where the topmost three layers are allowed to relax.

For the calculation of \( \gamma \)-Al\(_2\)O\(_3\) and the adsorption of different species on \( \gamma \)-Al\(_2\)O\(_3\) we also used the DACAPO code with a plane wave cutoff of 340.15 eV and a density cutoff of 680 eV. A \( 4 \times 4 \times 1 \) Monkhorst-Pack \( \mathbf{k} \)-point sampling in the irreducible Brillouin zone was used for \( \gamma \)-Al\(_2\)O\(_3\). The \( \gamma \)-Al\(_2\)O\(_3\) surface was modeled by a step on a
nonspinel $\gamma$-Al$_2$O$_3$ structure which was derived bulk $\gamma$-Al$_2$O$_3$ model [24]. The cell parameters for the $\gamma$-Al$_2$O$_3$ step closed packed surface are $a = 8.0680$ Å and $b = 10.0092$ Å and $\alpha = \beta = \gamma = 90^\circ$. For the $\gamma$-Al$_2$O$_3$ surface the bottom two layers were fixed whereas the top three layers were allowed to relax.

In all the model surfaces, the neighboring slabs are separated by more than 10 Å of vacuum.

NO$_x$ and HNO$_x$ adsorption energies were calculated relative to gas phase zero energy points of these species.

The energy minimum adsorption geometries used in the calculations are presented in the supplementary material.

### 3. Results and discussion

#### 3.1. Unique activity of Ag/Al$_2$O$_3$ in H$_2$-assisted NH$_3$-deNO$_x$

NO$_x$ conversions obtained over the prepared catalysts at 380 °C tested under the conditions of SCR of NO$_x$ with NH$_3$, without and with H$_2$ in the exhaust, are given in Table 1. In the absence of H$_2$ all the catalysts are inert with respect to NO$_x$ reduction or ammonia oxidation at temperatures below 400 °C. The hydrogen effect was observed only for Ag/Al$_2$O$_3$, Ag/TiO$_2$ and In/Al$_2$O$_3$ (Fig. 1). The former catalyst demonstrates extremely high performance with NO$_x$ conversion exceeding 80% at 200 °C at GHSV = 110 000 h$^{-1}$. No more than 5 ppm N$_2$O was observed in the products. Ag/TiO$_2$ is much less active with maximum NO$_x$ conversion of 25% at 380°C. The activity of In/Al$_2$O$_3$ below 400 °C is only marginal. Therefore only Ag/Al$_2$O$_3$ may be considered for practical applications among the tested catalysts. Furthermore, it is evident that both silver and alumina are necessary components of the catalyst to obtain a high
performance in deNOₓ. Removal or change of each of these components lead to almost inactive catalysts. Therefore, it is likely that both silver and alumina take part in the catalytic cycle or the active site is positioned on the interface between Ag and Al₂O₃.

3.1.1. TEM data on Ag/Al₂O₃ and Ag/TiO₂

In order to clarify if it is the catalyst morphology that determines the drastic difference in the SCR performance of Ag/Al₂O₃ and Ag/TiO₂, TEM images of the samples were obtained. These micrographs are compared in Fig. 2. The choice of the catalysts in question is dictated by their common properties (Ag loading, BET surface area of the support, preparation technique), which is in contrast to their very different catalytic activity.

EDX shows the presence of ~1% Ag in the both depicted catalyst grains. However, we were unable to locate any metal particles with diameters larger than 2-3nm in both catalyst samples. This confirms a high dispersion of Ag in both Ag/Al₂O₃ and Ag/TiO₂ catalysts, which might be in the form of clusters of 4-8 Ag atoms as suggested by Kondratenko et al. [16]. Therefore the large difference in SCR activity of Ag/Al₂O₃ and Ag/TiO₂ is not due to a large difference in Ag dispersion.

3.2. Study of the mechanism of H₂-assisted NH₃-deNOₓ

3.2.1. Experiments with Ag/Al₂O₃ where components of the feed are omitted

Studies of the mechanism of hydrogen-assisted NOₓ SCR by NH₃ on Ag/Al₂O₃ were already performed before [16, 17], where the attention was drawn to the state of silver. Our catalytic experiments show a uniqueness of the Ag/Al₂O₃ catalytic system, in which both components play a vital role.
To have a notion of the individual reactions occurring during NO\textsubscript{x} SCR by NH\textsubscript{3} we consecutively run catalytic tests with one of the components absent in the feed.

According to the results obtained so far it is already clear that the removal of hydrogen leads to a completely inactive catalyst with regards to NH\textsubscript{3}-deNO\textsubscript{x} (Table 1) or ammonia oxidation. The concentration of all monitored gases remained constant during temperature ramping from 400 to 100 °C when no H\textsubscript{2} was in the feed. The same is true for the removal of oxygen from the feed – no NO reduction or NH\textsubscript{3} oxidation was observed without O\textsubscript{2}.

When NH\textsubscript{3} was removed from the gas feed, a pronounced oxidation of NO to NO\textsubscript{2} starting from 100 °C was observed (fig. 3, solid line). Together with that a very low NO\textsubscript{x} to N\textsubscript{2} conversion (dotted line, max. 4%) was observed indicating that hydrogen normally acts not as the main reductant but as a co-reductant. When both ammonia and hydrogen were removed from the feed, no oxidation of NO to NO\textsubscript{2} was observed.

The latter observation agrees with the data obtained in [6, 16]. As suggested in [6], hydrogen addition promotes oxidation of NO. However, we observed no oxidation of NO to NO\textsubscript{2} during the experiments with Ag/TiO\textsubscript{2} and Ag/ZrO\textsubscript{2} catalysts. This shows once again that not only Ag, but also the support plays an important role in the catalytic activity of Ag/Al\textsubscript{2}O\textsubscript{3} which also agrees with the data on C\textsubscript{3}H\textsubscript{8}-SCR reported in [6].

The mechanism of O\textsubscript{2} activation by hydrogen has been suggested earlier [25, 26] as follows. On the first step hydrogen dissociates on active Ag\textsubscript{n+} sites on alumina to form an acidic proton and hydride Ag\textsubscript{n−}H. This hydride later reacts with oxygen to form a reactive oxidant, such as hydroperoxy radicals (HO\textsubscript{2}), peroxide (O\textsubscript{2}\textsuperscript{2−}), or superoxide ions (O\textsubscript{2}−) all of which later oxidize NO to NO\textsubscript{2}. 


When removing NO from the NO, NH₃, H₂, O₂ and H₂O containing feed, NH₃ oxidation to N₂ (fig. 4, solid line) and to NOₓ (fig. 4, dotted line) occurs at temperatures higher than 200 °C. Comparison of the data in fig. 3 and fig. 4 suggests that NO oxidative acivation starts at significantly lower temperature (corresponding to the NH₃-deNOₓ light-off temperature) than NH₃ oxidative activation. Therefore it is more likely that oxidative activation of NO is an important step in the overall catalytic mechanism of NOₓ SCR over Ag/Al₂O₃.

The data does not support a hypothesis of oxidative dehydrogenation of NH₃ (or NH₃-assisted NO decomposition) being the main catalysed step of H₂-assisted NH₃-deNOₓ over Ag/Al₂O₃ [18]. Ag/Al₂O₃ rather participates in NO activation and possibly in the reaction of NH₃ with NOₓ intermediates [16].

The hydrogen promoted oxidative activation of NO has been already reported by Satokawa et al. for NOₓ SCR by C₃H₈ [6]. However in that study oxidative activation of NO was not enough to initiate SCR and activation of C₃H₈ by H₂ has been reported to be necessary which makes it different from SCR by NH₃.

3.2.2. Experiments with feeding NO and NO₂ mixtures over Ag/Al₂O₃ and Ag/ZrO₂

After realizing that the hydrogen promoted oxidation of NO to NO₂ may be the first step in the H₂-assisted NH₃-deNOₓ we decided to do catalytic tests with a feed containing a mixture of NO and NO₂ as NOₓ. Since H₂ facilitates reversible NO-NO₂ tranformation, undesirable for these experiments, no H₂ was co-fed.

Fig. 5 shows NOₓ conversions to N₂ obtained over Ag/Al₂O₃ when a NO and NO₂ mixture is fed as NOₓ (containing 26, 34 and 47% NO₂) and over Ag/ZrO₂ with 34% NO₂ in NO as NOₓ. Surprisingly for all three cases we observe nearly equal, maximum
30%, NO\textsubscript{x} conversion which changes only slightly with temperature. NH\textsubscript{3} conversion profiles follow the NO\textsubscript{x} conversion profiles and they are therefore not shown. This observation allows us to conclude that oxidation of NO to NO\textsubscript{2} over Ag/Al\textsubscript{2}O\textsubscript{3}, at least, partially accounts for the activity of this catalyst in the NO\textsubscript{x} SCR. This agrees with previous works, evidencing oxidation of NO to NO\textsubscript{2} involving H\textsubscript{2} [25] and supposing it to be crucial for low-temperature NO\textsubscript{x} SCR by hydrocarbons [27].

Moreover, SCR of the NO and NO\textsubscript{2} mixture by NH\textsubscript{3} is not a unique feature of Ag/Al\textsubscript{2}O\textsubscript{3} but was also observed for other supports though to a less extent, e.g. with 15% maximum NO\textsubscript{x} conversion in the case of Ag/ZrO\textsubscript{2} (see Fig. 5, gray dotted line). Thus metal oxides other than alumina can catalyse NO+NO\textsubscript{2} SCR by NH\textsubscript{3} but Ag/Al\textsubscript{2}O\textsubscript{3} with H\textsubscript{2} co-feeding is required to oxidize NO at low temperatures. Therefore, we are focusing our study on Ag/Al\textsubscript{2}O\textsubscript{3} catalysts and the corresponding alumina support.

The effect of increasing the NO\textsubscript{x} SCR rate by feeding NO and NO\textsubscript{2} mixture has already been noticed for other catalytic systems including vanadia-based catalysts [28] and zeolites [29]. The effect is called “Fast-SCR” and characterized by a well-defined stoichiometry of NO:NO\textsubscript{2} being 1:1.

To check if the NO:NO\textsubscript{2} conversion without H\textsubscript{2} in the feed can be ascribed to “Fast SCR” [29], we calculated the ratio of consumed NO to consumed NO\textsubscript{2} (Fig. 6). In our case the ratio of consumed NO to consumed NO\textsubscript{2} changed with temperature from negative values (only NO\textsubscript{2} is consumed and a small amount of NO is produced from it) to positive values up to 1 in case of feeding 26% NO\textsubscript{2} (Fig. 6). Interestingly, the temperature at which NO starts to be consumed (~ 150 °C) coincides with the onset temperature of H\textsubscript{2}-assisted SCR (Fig. 1). Therefore we can suppose that parts of the mechanisms of both H\textsubscript{2}-assisted NO SCR by NH\textsubscript{3} and NO+NO\textsubscript{2} SCR by NH\textsubscript{3} are
similar. But in case of NO+NO₂ SCR we observed a conversion limit at ~30%, when almost 100% conversion is obtained in H₂-assisted NOx-SCR. This could be explained by blocking of the catalyst surface by adsorbed nitrate species [25]. The poisoning effect of surface nitrates for propane-SCR was observed in [26], where the authors also demonstrated the ability of hydrogen to effectively remove adsorbed nitrate species. Thus, introduction of hydrogen may facilitate not only NO to NO₂ conversion, but also regeneration of the catalyst surface, which removes the 30% conversion limit.

In general, the ratio of converted NO to converted NO₂ depends on the total amount of NO₂ in the feed and decreases with increase in NO₂ content. The higher the NO₂ content – the larger is the part of NO₂ in the NOx that is converted to N₂. Independent on this, the ratio of converted NOₓ to converted NH₃ was always 1:1 and maximum conversion remained constant at ~30%.

3.2.3. Experiments with feeding NO and NO₂ mixtures over pure γ-Al₂O₃

In some of the papers on H₂-assisted NO SCR by NH₃, published earlier [16, 17], alumina was considered only as a support for the active Ag nanoparticles. In this case, the properties of alumina could influence the catalyst activity indirectly by tuning the Ag particle size and distribution. In the following we test this assumption.

With or without hydrogen γ-alumina stays inactive under the experimental conditions of NOₓ SCR by ammonia when NO is the only component of NOₓ in the feed. This changes when NO₂ is introduced. Fig. 7 shows a comparison of NOₓ (26% NO₂ of total NOₓ at the reactor inlet) conversion by NH₃ obtained over pure Al₂O₃ (solid line) and Ag/Al₂O₃ (dotted line) with no H₂ in the feed. The profiles are almost identical indicating that presence of Ag in the catalyst is important only for the H₂-
assisted reaction. Taking into account the overall quantity of NO₂, which can be produced from NO in presence of H₂ over Ag/Al₂O₃ (Fig.3), it is evident that alumina can significantly contribute to the overall H₂-assisted NO SCR mechanism. Thus, it cannot be neglected that alumina is an active part of the catalyst. Moreover the stoichiometry of NO+NO₂ SCR conversion over alumina follows the same trend as for the Ag/Al₂O₃ (Fig. 8), which may demonstrate the same mechanism is working in both cases. Running NO+NO₂ SCR with H₂ in the feed over pure Al₂O₃ yield almost the same NOₓ conversion as as for the test without H₂ (Fig.7, solid line).

Thus the presence of Ag and H₂ is mostly important for oxidative activation of NO and possibly removal of adsorbed species blocking the catalyst surface. The reaction of NO and NH₃ with the obtained NO₂ can proceed further over pure Al₂O₃ yielding N₂. This result agrees with the results of J. Lee et al. [30], who demonstrated the ability of pure alumina to catalyse the reduction of NO, activated over Ag/Al₂O₃, by partially oxidized hydrocarbons. At the same time, Meunier and Ross [31] observed the ability of pure alumina to run the propene SCR of NO₂ (but not of NO).

From the analysis of the stoichiometry of the NO+NO₂ SCR reaction (Figs. 6 and 8) it can be concluded that at temperatures lower than 150°C only NO₂ reacts with NH₃. The production of NO from NO₂ can also be observed, which is thermodynamically not possible and is likely due to an uncomplete SCR reaction between NO₂ and NH₃. Above 350 °C NO₂ decomposition to NO is thermodynamically favorable, and this may be a reason of decreasing apparent amount of consumed NO [32]. Only between 150 and 350°C NO consumption is significant and almost equal to NO₂ consumption in the case of 26%NO₂ in NOₓ feed. Based on the knowledge of the “Fast SCR” [29] the following reactions can be proposed:
\[
2\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow 2\text{NH}_4^+ + \text{O}_2^-
\] (7)
\[
2\text{NO}_2 \leftrightarrow \text{N}_2\text{O}_4
\] (8)
\[
\text{N}_2\text{O}_4 + \text{O}_2^- \leftrightarrow \text{NO}_2^- + \text{NO}_3^-
\] (9)
\[
\text{NO}_2^- + \text{NH}_4^+ \leftrightarrow [\text{NH}_4\text{NO}_2] \rightarrow \text{N}_2 + 2\text{H}_2\text{O}
\] (10)
\[
\text{NO}_3^- + \text{NH}_4^+ \leftrightarrow \text{NH}_4\text{NO}_3
\] (11)
\[
\text{NH}_4\text{NO}_3 \leftrightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}
\] (12)
\[
\text{NO} + \text{NO}_3^- \leftrightarrow \text{NO}_2 + \text{NO}_2^-
\] (13)

According to the scheme, at temperatures higher than 150 °C reactions (7), (8), (9), (10), (11) take place yielding nitrogen and surface nitrate species. Disproportionation of adsorbed NO\(_2\) (8), (9) was also suggested by DFT calculations earlier [33]. A small part of the surface nitrates is decomposed to N\(_2\)O (12), trace amount of which (< 5ppm) is observed in the reaction products at high temperatures. NO production from NO\(_2\) (negative NO\(_{\text{converted}}\)/NO\(_2\)\(_{\text{converted}}\) ratio at T<150 °C on Fig.6) and the observation that the higher the NO\(_2\) content – the larger is the part of NO\(_2\) in the NO\(_x\) that is converted to N\(_2\) in the NO/NO\(_2\) experiments can be explained by reverse (13). NO reacts with surface nitrates according to (13) to form NO\(_2\) and nitrite, which is readily decomposed to nitrogen (10). With that nitrates are partly removed from the catalyst surface and higher NO\(_x\) conversion is obtained.

With decreasing reaction temperature from 400 to 200 °C an increase in the NO\(_x\) conversion is observed. The effect is particularly evident for the 47% NO\(_2\)+NO mixture (Fig.5, solid curve) and may be due to the formation of surface NH\(_4\)NO\(_3\). NH\(_4\)NO\(_3\) formation is also consistent with decreased NO\(_{\text{converted}}\)/NO\(_2\)\(_{\text{converted}}\) ratio below 180 °C (Fig. 8) due to reaction stoichiometry:

\[
2\text{NH}_3 + 2\text{NO}_2 \rightarrow \text{NH}_4\text{NO}_3 + \text{N}_2 + \text{H}_2\text{O},
\] (14)
which is, in fact, a combination of (7) + (8) + (9) + (10) + (11), but without (12) and (13), which are too slow at this temperature. It is also rather indicative of NH₄NO₃ formation that below 200 °C we do not observe N₂O evolution, while above this temperature its decomposition (12) yields N₂O. Therefore, below 200 °C nitrate formation and subsequent blocking the alumina surface limits NOₓ conversion.

To check the reaction scheme during an Al₂O₃ activity test, temperature ramping was stopped at 500, 210 and 100 °C. After the concentrations of the outlet gas components were stabilised, NH₃ was switched off from the feed. Following the removal of NH₃ from the inlet gas at 500 and 100 °C the concentrations of NO and NO₂ equalled these concentrations at the reactor inlet (no reaction with adsorbed nitrates (13) was observed). However, the removal of NH₃ from the feed at 210 °C (Fig. 9) resulted in consumption of NO and release of NO₂. This is in agreement with NO consumption in the NOₓ SCR over alumina, which takes place between 150 and 350 °C (Fig. 8). The ratio of evolved NO₂ to consumed NO was approximately 1.7. This ratio can be achieved by combination of the competing reactions (10), which gives no NO₂, reverse (9) and (8), which give 2 NO₂ molecules, and, of course (13), which initiates the NO consumption and yields 1 NO₂ molecule. Thus the mechanism of NOₓ SCR by NH₃ over Al₂O₃ and Ag/Al₂O₃ could share most of the reaction steps with “Fast SCR”.

3.2.4 Surface species during NH₃-SCR over Al₂O₃

Diffuse reflectance infrared spectroscopy is a powerful tool to complement observations from catalytic experiments with observations of surface species. Fig. 10 shows the evolution of species on the Al₂O₃ surface, when switching off NH₃ from a feed containing NO, NO₂, NH₃ and O₂ at 150 °C and at 500 °C. Similar spectra were
observed at 300 and 400 °C but not shown. The first spectra are taken in a feed containing NH₃ and the following spectra 5, 10, 15 and 25 min after the NH₃ was switched off. When all gases are present in the first spectra, bands at 1690, 1623, 1533, 1474, 1398, 1314 and 1236 cm⁻¹ can be distinguished at 150 °C. According to literature, the bands at 1623, 1533 and 1236 cm⁻¹ which are accompanied by bands at 3355, 3271 and 3173 cm⁻¹ (not shown) can be assigned to deformation vibrations and stretching vibrations of ammonia, respectively [34-37]. Bands at 1690 and 1474 cm⁻¹ have previously been assigned to deformation vibrations of NH₄⁺ or NH₃ [34, 35, 37]. At 500 °C all the bands are much smaller. But even there, mainly bands due to NH₃ or NH₄⁺ can be observed. Thus under NH₃-SCR conditions, mainly ammonia is adsorbed on Al₂O₃ and very little nitrates and nitrites are adsorbed. When turning off ammonia in the feed first the bands of adsorbed NH₃ at 1236, 1623, 3355, 3271 and 3173 cm⁻¹ decrease at 150 °C. Somewhat later, the NH₄⁺ bands at 1690 and 1474 cm⁻¹ start to decrease and two new bands at 1612 and 1585 cm⁻¹ grow. At the same time, the bands around 1551 and 1308 cm⁻¹ shift in wavenumber and increase. The shifts in wavenumber as well as the new bands are all caused by the stretching of the N=O bond of differently bound nitrate species [35-45] which start accumulating in the absence of NH₃. That the bands of adsorbed NH₃ diminish before the bands of adsorbed NH₄⁺ species start to decrease is in accordance with reaction (14). Switching back to SCR reaction conditions, the NH₃ and NH₄⁺ species start growing again at 150°C while the nitrate species decrease but do not completely disappear, even in the presence of H₂ as shown by the first spectra in Fig. 11.

At 500 °C, the bands of adsorbed NH₄⁺ at 1690 and 1464 cm⁻¹ disappear previous to the bands of adsorbed NH₃ between 3355 and 3173 cm⁻¹ (not shown), while the nitrate
band at about 1551 cm\(^{-1}\) increases. The remaining nitrates may be regarded as inactive. However, whether the accumulation of these species reduce the activity for NO\(_x\) reduction and, thus, poison the surface or only act as spectator species, cannot be answered by the available data.

Fig. 11 shows, moreover, the evolution of bands when switching off NH\(_3\) from a H\(_2\) containing feed at different temperatures. At all temperatures, the spectra are dominated by nitrates with bands at 1551, around 1585, 1612 and around 1304 cm\(^{-1}\). The amount of adsorbed species decreases with increasing temperature as indicated by fewer and smaller peaks at higher temperatures. When the ammonia is switched off from the feed containing H\(_2\) at 150°C the bands assigned to NH\(_3\) and NH\(_4^+\) species on the surface decrease while the nitrate bands around 1615, 1585, 1551 and 1301 cm\(^{-1}\) increase. This evolution of the bands is similar to the case without H\(_2\) in the feed. At 300 °C, only the nitrate band at 1585 cm\(^{-1}\) increase, while the other nitrate bands are stable or decrease. At even higher temperatures, all NH\(_x\) bands are very tiny or hardly visible while all nitrate bands clearly decrease showing that the addition of H\(_2\) to the feed has an influence on γ-Al\(_2\)O\(_3\) without silver. For this observed effect of hydrogen at high temperatures (400 and 500 °C) there are two reasonable explanations: hydrogen may either itself reduce the nitrates as observed by [26, 31, 46] on Ag/Al\(_2\)O\(_3\) or it partially reduces some of the NO\(_2\) to NO which in turn can reduce nitrates to nitrites (reaction 13). Moreover, less new nitrates will be formed on the catalyst surface when the NO\(_2\) concentration is decreased by partial reduction to NO.

### 3.3. DFT calculations

#### 3.3.1. Oxidation of NO to NO\(_2\) and NO\(_3\) on the surface of transition metals
Figure 12 shows the potential energy surface diagram for the absorption of NO and O₂ leading to NOₓ, i.e. NO₂ and NO₃ calculated for 6 different transition metal catalysts Ag, Cu, Pd, Pt, Rh and Ru. For all six different transition metal catalysts both the (111) terrace surface model and (211) step surface model were investigated and the results are similar for both surfaces. The diagram shows that among the transition metals studied the formation of NO₂ on (111) terraces is favorable for both Ag and Cu, whereas the formation of NO₃ is favorable only on Ag. On (211) step surface the formation of NO₂ and NO₃ via oxidation of NO is significantly favorable only on Ag. For other metals NO adsorption without oxidation to NOₓ is preferred. That supports the idea of Ag being necessary catalyst component for the oxidation of NO to NOₓ species as potentially first step of NO SCR.

3.3.2. Adsorption of NOₓ and HNOₓ on the step γ-Al₂O₃ surface

The model of the step on the γ-Al₂O₃ (representing uncoordinated Al sites) was used for calculations of NOₓ adsorption energy as the most abundant surface of γ-Al₂O₃ crystals is the step surface [24]. It has been demonstrated by Donghai Mei et al. [33] that NO₃ adsorbs rather strongly on the γ-Al₂O₃ (100) and γ-Al₂O₃ (110) surfaces than compared to NO and NO₂.

A clear decrease of concentration of surface nitrates has been observed by FTIR after addition of hydrogen at high temperatures (experiments at 400 and 500 °C in the section 3.2.4). Such removal of strongly bound nitrates which block the alumina surface can partly explain the positive effect of H₂ on the activity of Ag/Al₂O₃ catalysts in NOₓ SCR.
Though authors of [33] have done extensive calculation for the adsorption of NO$_x$ on γ-Al$_2$O$_3$ (100) and γ-Al$_2$O$_3$ (110) surfaces, however no effect of H$_2$ on the stability of surface nitrates on γ-Al$_2$O$_3$ has been considered.

We have calculated the adsorption energy of NO$_3$ and HNO$_3$ on our model γ-Al$_2$O$_3$ step surface representing uncoordinated Al surface sites. Five different uncoordinated Al sites are present in our model alumina surface as derived from the bulk γ-Al$_2$O$_3$ geometry in [24]. These have all been used for the calculations, however only the most energetically favorable (energy minimum among studied) adsorption geometries with two oxygen atoms of NO$_3$ and HNO$_3$ bridging with two Al sites of γ-Al$_2$O$_3$ are reported here. See supplementary information for more details on the used geometries.

The calculated adsorption energy of HNO$_3$ (Fig. 13) on the model surface of γ-alumina is considerably smaller than that of NO$_3$ (which agrees with [33]), which increases the probability of HNO$_3$ removal from the alumina surface compared to NO$_3$ in the absence of hydrogen. This supports the suggestion of H$_2$ facilitating removal of strongly bound NO$_3$ from the alumina.

The mechanism of reduction of adsorbed NO$_x$ species by hydrogen with the formation of N$_2$ has been previously suggested for Pt/MgO-CeO$_2$ catalysts for H$_2$-SCR of NO$_x$ [20, 21]. This mechanism includes dissociative adsorption of hydrogen on the metal nanoparticle, spillover of the formed atomic hydrogen on the support to the two neighboring NO$_x$ species and their reduction with subsequent release of surface sites. However, this is not a major pathway of the SCR in our case because SCR in the absence of NH$_3$ is insignificant (Fig. 3, dotted line). Here we suggest that atomic hydrogen reacts rather with a single nitrate or nitrite group with subsequent release of
HNO₃ and adsorption sites on alumina. The evolved HNO₃ can recombine with the formation of water and nitrogen oxides.

4. Conclusions

Ag supported on γ-Al₂O₃ is a very promising catalytic system which can be used for the removal of nitrogen oxides from the exhaust of diesel engines in the presence of H₂. It is vital that both Ag and alumina are present in the catalyst formulation. The primary role of Ag is the H₂-assisted oxidative activation of NO and the reaction of oxidized NO and NH₃ can proceed further on alumina. Hydrogen also facilitates removal of nitrates from the alumina surface, as supported by DRIFTS experiments and DFT calculation.

The studied catalysts facilitate NO+NO₂ mixture reduction without H₂ in the feed with the Al₂O₃ support defining the catalytic activity. Therefore, tuning the alumina support, not only the metal, is vital for obtaining active Ag/Al₂O₃ catalyst.

5. Acknowledgments

This work was supported by grant 09-067233 from The Danish Council for Strategic Research. TEM images were acquired with the support of Center for Electron Nanoscopy (DTU CEN) and personally by Thomas W. Hansen. We acknowledge the supply of the commercial alumina for the study by the SASOL Germany.

The authors also wish to thank Dr. Alexander Yu. Stakheev and Dr. Jakob Weiland Høj for fruitful discussions.
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Figure legends

**Figure 1.** NO\textsubscript{x} conversion profiles obtained over Ag/Al\textsubscript{2}O\textsubscript{3}, Ag/TiO\textsubscript{2}, and In/Al\textsubscript{2}O\textsubscript{3}. Reaction conditions: 500 ppm NO, 520 ppm NH\textsubscript{3}, 1200 ppm H\textsubscript{2}, 8.3\% O\textsubscript{2}, 7\% H\textsubscript{2}O in Ar, GHSV = 110 000 h\textsuperscript{-1}.

**Figure 2.** TEM images of Ag/Al\textsubscript{2}O\textsubscript{3} (left) and Ag/TiO\textsubscript{2} (right) calcined at 550\textdegree}C in air.

**Figure 3.** NO conversion to NO\textsubscript{2} (solid line) and NO\textsubscript{x} conversion to N\textsubscript{2} (dotted line) over Ag/Al\textsubscript{2}O\textsubscript{3} without ammonia in the feed. Reaction conditions: 500 ppm NO, 1200 ppm H\textsubscript{2}, 8.3\% O\textsubscript{2}, 7\% H\textsubscript{2}O in Ar, GHSV = 110 000 h\textsuperscript{-1}.

**Figure 4.** Total NH\textsubscript{3} conversion (solid line) and NH\textsubscript{3} conversion to NO\textsubscript{x} (dotted line) over Ag/Al\textsubscript{2}O\textsubscript{3} with no NO in the feed. Reaction conditions: 520 ppm NH\textsubscript{3}, 1200 ppm H\textsubscript{2}, 8.3\% O\textsubscript{2}, 7\% H\textsubscript{2}O in Ar, GHSV = 110 000 h\textsuperscript{-1}.

**Figure 5.** NO\textsubscript{x} conversion over Ag/Al\textsubscript{2}O\textsubscript{3} and Ag/ZrO\textsubscript{2} without H\textsubscript{2} in the feed, when NO and NO\textsubscript{2} mixture is fed as NO\textsubscript{x} (NO\textsubscript{2} content is specified, NO is the rest of 500 ppm NO\textsubscript{x}). Conditions: 500 ppm NO\textsubscript{x}, 520 ppm NH\textsubscript{3}, 8.3\% O\textsubscript{2}, 7\% H\textsubscript{2}O in Ar, GHSV = 110 000 h\textsuperscript{-1}.

**Figure 6.** Ratio of consumed NO to consumed NO\textsubscript{2} for simultaneous NO + NO\textsubscript{2} reduction by NH\textsubscript{3} over Ag/Al\textsubscript{2}O\textsubscript{3}. Reaction conditions: 500 ppm NO\textsubscript{x} (NO\textsubscript{2} fraction is stated near the corresponding curves), 520 ppm NH\textsubscript{3}, 8.3\% O\textsubscript{2}, 7\% H\textsubscript{2}O in Ar, GHSV = 110 000 h\textsuperscript{-1}.
**Figure 7.** NO\textsubscript{x} conversion over Al\textsubscript{2}O\textsubscript{3} (solid line) and Ag/Al\textsubscript{2}O\textsubscript{3} (dotted line, for a comparison) without H\textsubscript{2} in the feed, when NO and NO\textsubscript{2} mixture is fed as NO\textsubscript{x}. Reaction conditions: 500 ppm NO\textsubscript{x} (37\% NO\textsubscript{2}), 520 ppm NH\textsubscript{3}, 8.3\% O\textsubscript{2}, 7\% H\textsubscript{2}O in Ar, GHSV = 110 000 h\textsuperscript{-1}.

**Figure 8.** Ratio of consumed NO to consumed NO\textsubscript{2} for NO + NO\textsubscript{2} simultaneous reduction by NH\textsubscript{3} over Al\textsubscript{2}O\textsubscript{3} (solid line) and Ag/Al\textsubscript{2}O\textsubscript{3} (dotted line, for a comparison). Reaction conditions: 500 ppm NO\textsubscript{x} (26\% NO\textsubscript{2}), 520 ppm NH\textsubscript{3}, 8.3\% O\textsubscript{2}, 7\% H\textsubscript{2}O in Ar, GHSV = 110 000 h\textsuperscript{-1}.

**Figure 9.** Change of NO, NO\textsubscript{2} and NO\textsubscript{x} concentrations after removing NH\textsubscript{3} from the feed. Catalyst: Al\textsubscript{2}O\textsubscript{3}. Reaction conditions: 500 ppm NO\textsubscript{x} (37\% NO\textsubscript{2}), 520 ppm NH\textsubscript{3}, 8.3\% O\textsubscript{2}, 7\% H\textsubscript{2}O in Ar, GHSV = 110 000 h\textsuperscript{-1}, temperature 210°C.

**Figure 10.** Change in surface species after removing NH\textsubscript{3} for the first time from the feed over a fresh Al\textsubscript{2}O\textsubscript{3} catalyst. Reaction conditions: 500 ppm NO\textsubscript{x} (37\% NO\textsubscript{2}), 520 ppm NH\textsubscript{3}, 8.3\% O\textsubscript{2} in Ar. Spectra were taken from gray to black: with NH\textsubscript{3} in the feed, and 5, 10, 15 and 25 min after switching off NH\textsubscript{3}.

**Figure 11.** Change in surface species after removing NH\textsubscript{3} from the hydrogen-containing feed over Al\textsubscript{2}O\textsubscript{3}. Reaction conditions: 500 ppm NO\textsubscript{x} (37\% NO\textsubscript{2}), 520 ppm NH\textsubscript{3}, 1250 ppm H\textsubscript{2}, 8.3\% O\textsubscript{2} in Ar. Spectra were taken from gray to black: with NH\textsubscript{3} in the feed, and 5, 10, 15 and 25 min after switching off NH\textsubscript{3}.
**Figure 12.** Potential energy surface diagram for the formation of NO$_x$ via the oxidation of NO over (111) and (211) surfaces of the selected transition metals.

**Figure 13.** NO$_3$ and HNO$_3$ adsorption geometries and adsorption energies on the model step closed packed gamma alumina surface. All the adsorption energies are given with the reference to the gas phase zero energy points of the respective species.
<table>
<thead>
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<th>Catalyst</th>
<th>Metal loading, wt%</th>
<th>Support BET surface area, m²/g</th>
<th>NOₓ conversion</th>
<th>0 ppm H₂</th>
<th>1200 ppm H₂</th>
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<td>Al₂O₃</td>
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<td>140</td>
<td></td>
<td>0</td>
<td>10.5</td>
</tr>
</tbody>
</table>

Table 1. Studied catalysts and NOₓ conversions obtained at 380°C without and with H₂ in the feed gas. Reaction conditions: 500 ppm NO, 520 ppm NH₃, 8.3% O₂, 7% H₂O in Ar, GHSV = 110 000 h⁻¹.
Figure 3 revised
Figure 4 revised

\[ \text{NH}_3 \rightarrow \text{N}_2 + \text{NO}_x \]
Figure 5 revised

![Graph showing NOx conversion vs. temperature for different samples of Ag/Al2O3 and Ag/ZrO2.]

- Ag/Al2O3 (47% NO2)
- Ag/Al2O3 (34% NO2)
- Ag/Al2O3 (26% NO2)
- Ag/ZrO2 (34% NO2)
Figure 6 revised

Temperature, °C

NO converted / NO₂ converted

26% NO₂
34% NO₂
47% NO₂
Figure 8 revised

The graph shows the conversion of NO to NO2 as a function of temperature. Two curves are depicted:

- **Ag/Al2O3**
- **Al2O3**

The x-axis represents the temperature in °C, ranging from 100 to 400. The y-axis represents the ratio of NO converted to NO2 converted, ranging from -0.2 to 1.0.
Figure 9 revised
Figure 10 revised
Figure 11 revised

[Graph showing absorbance over wavenumber with specific wavenumbers at 150°C, 300°C, 400°C, and 500°C for 0 min and 25 min with absorbance peak at 1551 cm⁻¹ for 150°C, and 1615 cm⁻¹ for 400°C at 25 min.]
Figure 12: Graphs showing the adsorption energy (eV) for different metal surfaces and species.

For the (111) metal surface:
- Cu
- Ag
- Pt
- Pd
- Rh
- Ru

For the (211) metal surface:
- Cu
- Ag
- Pd
- Pt
- Rh
- Ru

Species include: NO(g), NO(g), NO₂(g), NO₃(g), NO⁺(g), NO⁺₂(g), NO⁺⁺(g), NO⁻(g), NO⁻⁺(g), NO⁻⁻(g).
\[ \text{NO}_3@\gamma-\text{Al}_2\text{O}_3: -0.90 \text{ eV} \]

\[ \text{HNO}_3@\gamma-\text{Al}_2\text{O}_3: 0.02 \text{ eV} \]
\[ \text{NO}_3@\gamma-\text{Al}_2\text{O}_3: -0.90 \text{ eV} \]

\[ \text{HNO}_3@\gamma-\text{Al}_2\text{O}_3: 0.02 \text{ eV} \]