

Silver- alumina Catalysts for Lean NO_x Reduction:

Influence of Hydrothermal Ageing

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Abstract

For many years, catalysis has been a solution for the automobile industry to deal with the harmful byproducts from gasoline combustion. The main pollutants from car exhausts include CO, NO_x , hydrocarbons and particulate matter (PM). While the pollutants themselves are harmful, their potential further reactions in the atmosphere may produce even more toxic substances. Hence the efficient removal of such by-products is crucial for the protection of the environment and human health.

This thesis will examine the reduction of NO_x by hydrocarbons, utilizing a silver-alumina catalyst. The reducing agents used are n-octane, Swedish standard MK1 diesel and NexBTL, which is a commercial biodiesel produced by Neste Oil Corporation.

Silver-alumina catalysts have been examined extensively in the literature and are considered a promising candidate for selective catalytic reduction.

In this study, the NO_x conversion properties of silver alumina samples, with different loadings, were investigated in a synthetic gas bench reactor. In addition, one sample doped with 100 ppm of platinum was examined. The gas composition was chosen to mimic real lean-burn engine exhausts. Both fresh and aged samples were studied. FTIR-measurements were utilized to assess the NO_x conversion of the catalysts.

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1. Introduction

To increase fuel-economy, the vehicle industry has shifted to the use of lean-burn engines. However, while the lean-burn engine emits less CO_2 it also emits more NO_x .

The three way catalyst TWC, which has been used extensively in automobiles during the last 30 years, has proven to be effective in emission control, simultaneously removing CO, NO_x and un-burnt hydrocarbons. Under normal working conditions for a stoichiometric gasoline engine, temperatures in the range 400-800^oC are required. However, diesel engines and lean-burn gasoline engines produce an exhaust containing a large amount of excess oxygen. Under such conditions, the TWC is ineffective in NO_x reduction [1].

For many years the automobile industry has been investigating ways of reducing the NO_x emissions in lean exhausts from cars [2]. One promising technique is selective catalytic reduction with urea or hydrocarbons. This study is a continuation of Clément Cid's study at the *Competence Centre for Catalysis* (KCK) at Chalmers University of Technology and will focus on NO_x reduction at lean- burn conditions using selective catalytic reduction with hydrocarbons as reducing agent.

The HC-SCR method has been studied since the 1990's. One of the main advantages with HC-SCR is that hydrocarbons from the fuel tank can be used for NO_x reduction. The additional HC required is fed from the fuel tank. Hence no extra component needs to be added to the system. Compared to ammonia- SCR, reduction of NO_x using hydrocarbons is thus considered a better alternative, due to concerns with the safety of ammonia distribution [3] and the cost of building a urea distribution infrastructure.

In Cid's internship report titled *Silver-alumina Catalysts for Lean NO_x Reduction and Influence of Hydrothermal Ageing* [2] from 2010, it was mentioned that many catalysts have been tested for this reaction, among them Cu-ZSM-5 which contributes to a very active system, however it has a low water and sulphur tolerance. Non-zeolitic oxide supports like Al_2O_3 , TiO₂ and ZrO₂ loaded with different metals have also been studied. Platinum and palladium metal systems were found to be efficient for the SCR of NO_x due to a high conversion allowing for the formation of N₂ [1] but low selectivity. However, the system had drawbacks such as sulphur dioxide sensitivity and the fact that the performance is highly dependent on the support material [4].

Cid also referred to studies of combinations of noble and non-noble metals for catalysis with different oxide supports. Some examples are Co, Ni, Cu, Fe, Sn, Ga, Au, In and Ag [1]. NO_x reduction over base oxide/metal catalysts, like alumina or zeolites, is still not fully understood but it has been

proposed that both Lewis acid sites (provided by metallic cations like Ag) and basic sites, provided by hydroxide anions of base metal oxides are present in the system. It has previously been shown that the amount and dispersion of metallic sites on silver-alumina catalysts results in different reaction routes[2].

Some studies show that an increased amount of silver oxide increases NO_x reduction activity. Calcination in air should thus result in the production of silver oxide [2]. Hence, ageing in an oxidising atmosphere should facilitate silver oxidation, increasing the amount of silver oxides even further. The actual effect of ageing is disputed and how it affects NO_x reduction has not explicitly been proven. Breen et al. [5] proposed that the ageing process is linked to the temperature at which it takes place. At 600°C the presence of O_2 , NO, CO₂, H₂O and octane causes the impregnated silver-alumina catalyst to form small silver clusters consisting of an average of 3 atoms. At higher temperatures (800°C) the silver clusters disperse and form silver aluminate phases. According to Breen et al. [5] the silver clusters are the active sites for lean NO_x reduction.

According to Lee and Gulari, the problems with NO_x reduction that arise with the use of lean-burn engines can be regulated through a range of different approaches. In the diesel engine, hydrogen is usually present as a trace gas. Due to its ideal reducing properties, it can solve the problems that arise from using NH₃-SCR or HC-SCR in lean-burn conditions [6]. Several different catalytic materials have been studied for the purpose. Lee and Gulari noted that Pt is a good catalyst for NO_x removal at low temperatures in NO-H₂ systems. It may also work in a system containing NO, H₂ and O₂ but was shown to be a considerably poorer catalyst in an NO-H₂-CO-O₂ environment[6].

A different catalyst that has been reported to effectively reduce NO_x under lean conditions is Cu-ZSM-5[7]. Kung et al. referred to a previous observation that ion-exchanged ZSM-5 catalysts are more effective than catalysts on other supports. It was even suggested that ZSM-5 was a better support than other zeolites like zeolite Y and mordenite. It is also considered superior to other typical support materials such as alumina, zirconia and silica [7]. A drawback with ZSM-5 is that it lacks long term stability. Alumina on the other hand has a better hydrothermal stability compared to zeolites. Thus Kung et al. concluded that Ag/Al_2O_3 appeared to be the most promising of the different possible combinations.

The objective of finding a stable, active, economical catalyst that can operate at low temperatures in the presence of CO and H_2 has led to several studies. Lee and Gulari also commented on the significance of the preparation method, stating that the method used to prepare metal precursors and support also influences catalyst performance [6]. Kannisto et al. investigated the influence of preparation method on lean NO_x reduction over silver alumina catalysts [8]. The preparation methods investigated were the impregnation method, the thermally dried sol gel method and the freeze-dried

sol-gel method. Overall, the investigation suggested that the samples prepared using the sol-gel method contained more non-metallic silver as clusters and/or oxidized silver species. These were more finely dispersed throughout the alumina matrix compared to the impregnated sample. Furthermore, the freeze-dried sol-gel sample was shown to have more dispersed silver than the thermally dried sol-gel sample [8].

Kannisto has also noted that metallic silver on alumina activates the hydrocarbons by partially oxidising it and also oxidising NO to NO_2 . Oxidized silver in the form of for example silver ions, silver aluminate or oxides was observed to promote the formation of N_2 during HC-SCR conditions [8].

This study is based on and a continuation of a previous study, performed by Cid [2]. Cid found that the hydrothermal ageing effect had a positive impact on NO_x conversion and suggested that ageing caused a structural change within the catalyst. He suggested that the 24 hour ageing process that was performed contributed to an increase in the concentration of silver oxides in the catalyst, which lead to a higher NO_x reduction. This contradicts the theory that catalytic particles should sinter at high temperatures and therefore result in a lowered activity.

The aim of this project is to investigate the effect of hydrothermal ageing on the lean NO_x reduction for fresh and aged samples of freeze-dried sol gel silver-alumina catalysts. The HC-SCR activity for fresh and aged samples was evaluated using n-octane, MK1 diesel and NexBTL biodiesel as reducing agent.

2. Theory

2.1 Lean No_x Reduction

Lean-burn gasoline engines operate with a higher air-to-fuel ratio than the stoichiometric ratio required for the combustion of hydrocarbon fuel. This has been observed to save up to 15% of fuel in conventional engines [6]. Generally, higher air-to-fuel ratio in lean-burn engines produce fewer pollutants [7]. However, a drawback of using lean burn engines is that the NO_x reduction efficiency in the TWC is poorer. In 1996, Kung et al. [7] discussed the catalytic reduction of NO_x to N₂ using hydrocarbons (which are present as a result of incomplete combustion) in the exhaust stream [7]. It was also noted that a conversion of 80% in the presence of about 6% O₂ and 5-10% H₂O vapour in the temperature range 673-973K will be required for commercial applications. Furthermore, an ideal NO_x reduction catalyst especially defined for the above application will be required to maintain such an activity for 10 years or 100 000 miles of operation [7].

2.1.1 Selective Catalytic Reduction (SCR)

Selective catalytic reduction using urea has been shown to be a highly effective method for NO_x reduction, however the by-products of this reaction and the fact that the car will need a separate urea tank for the reaction makes hydrocarbons a more favourable alternative as reducing agent [9].

In Urea-SCR, the reducing agent is usually applied as an aqueous solution and if the solution is atomised into the hot exhaust gas stream, the water will evaporate, which gives rise to solid or molten urea according to the following expression [10]:

$$NH_2$$
-CO- NH_2 (aqueous) $\rightarrow NH_2$ -CO- NH_2 (solid)+ x H₂O(gas)

The solid or molten pure urea will then thermally decompose as shown below. This results in the formation of ammonia and isocyanic acid [10]:

$$NH_2$$
-CO- $NH_2(solid)$ \rightarrow $NH_3(gas)$ + $HNCO(gas)$

Isocyanic acid is very stable in the gas phase but can easily hydrolyse on many solid oxides when in contact with water [10]:

$$HNCO(gas)+H_2O(gas)\rightarrow NH_3(gas)+CO_2(gas)$$

Isocyanic acid is known for its negative impact on health, inducing hyper reactive respiratory diseases. Also, urea has a high freezing point (-11^oC), which causes problems in real life situations (e.g. during winters). There is also a risk of other undesirable bi-products like biuret, melamine and cyanuric acid being formed [10].

In HC-SCR, on the other hand, the use of hydrocarbons in the fuel itself as reducing agent, will eliminate the problem of having to supply a separate source of reducing agent.

The main reaction believed to take place in HC-SCR is the oxidation of hydrocarbons by nitrogen oxide shown below [2]:

$$C_n H_{2m} + (2n+m)NO \xrightarrow{catalyst} (n+m/2)N_2 + nCO_2 + mH_2O$$

Although HC-SCR is considered a more practical alternative when it comes to supplying it to the system, there are certain setbacks. Niemi et al. compared the NO_x removal efficiency of HC-SCR and urea-based-SCR over an Ag-alumina catalyst in a turbocharged, inter-cooled direct-injection off-road diesel engine. They found that the efficiency of a urea-based reducing agent was 90% while the HC-SCR system had a 70% [11]. They also noted the impact of several other factors that may affect the NO_x reduction performance, including HC_1/NO_x ratio as well as the operating temperature over the catalyst and the volumetric flow rate of the exhaust gas [11].

2.1.2. The Hydrogen Effect

Satokawa discovered in 2000 that adding hydrogen to the reaction atmosphere increased NO_x reduction [2]. The effect of hydrogen gas on the selective reduction of NO by light hydrocarbons over silver alumina under lean conditions was investigated [12]. The reducing hydrocarbon used was propane and it was concluded that the hydrogen should act as a promoter for other hydrocarbon reductants as well in similar lean NO_x reduction reactions. The reaction was carried out in a low temperature region (590-760K) [12].

An explanation to the hydrogen effect could be found in a study conducted by Eränen et al. [13] They proposed that hydrogen had at least two main functions in the reduction process. First of all, hydrogen contributes to improved oxidation of all species that are involved in the reaction. This results in faster formation of key intermediates. Secondly, hydrogen improves the formation of activated NO_x species for gas-phase reactions. Furthermore, the improved low-temperature activity could be explained by the theory that hydrogen boosts the formation rate of isocyanate [2].

Burch et al. have also concluded through their study that hydrogen removes nitrate species, which are strongly adsorbed to silver sites. This is achieved by reducing them to nitrites, which are easier to desorb, making it easier to free active sites on the catalyst for HC-SCR reaction [2].

2.2 Ageing

Ageing is the process that catalysts undergo when exposed to high temperatures and contaminants, which is inevitable for NO_x reduction catalysts during real life usage. Fernandes et al. [14] have shown

that catalysts exposed to high ageing temperatures undergoes a high surface area loss and experienced pore expansion [14]. They also proposed that such thermal effects plays a major role in catalyst deactivation.

A study done by Schmieg and Belton [15] showed that hydrothermal ageing at 1000^oC severely reduced the oxygen storage and release activity in a commercial automotive catalyst containing Pt, Rh, Ni and Ce [15]. This was believed to be due to sintering of catalyst particles, which reduces the active area, causing catalyst deactivation.

In Cid's study, the ageing of catalysts showed the reverse effect than that expected from sintered and thus degraded samples. Cid referred to Naktasjui et al. [16] when explaining the contradicting views on the effect of ageing on catalyst activity. If an increase in the amount of silver oxide, brought about by ageing, leads to higher NO_x reduction, then ageing may even have a promoting effect on the catalyst.

2.3 Catalytic Deactivation

Catalytic deactivation is the loss of catalytic activity and/or selectivity over time [17]. All catalysts degrade, some faster than others. The process of deactivation is both of a chemical and physical nature and occurs simultaneously with the main reaction [18]. Catalytic degradation has been divided into six distinct types, as summarised below.

2.3.1 Poisoning

Poisoning is defined as the strong chemisorption of reactants, products or impurities on catalytic sites. Whether a species will act as a poison depends on how strongly adsorbed to the site it will be. A particular species may or may not act as a poison depending on the reaction. Oxygen can be a reactant in partial oxidation of ethylene to ethylene oxide on a silver catalyst. However, it may also act as a poison in hydrogenation of ethylene on nickel [17].

A poison may act by blocking an active site in a catalyst or alter the adsorption properties of other species. This is generally achieved through electronic effects. Because poisons can modify the properties of the active sites, they can give rise to the formation of new compounds on the catalyst surface, thus altering its performance [18].

Poisons can be "selective", "non-selective" or anti-selective [17]. In non-selective poisoning, the catalyst surface sites are uniform to the poison, which can be represented by a linear function of net activity plotted against amount of poison that is chemisorbed [18]. In selective poisoning, the strongest active sites will be poisoned first and the activity does not decrease linearly with concentration of poison. The contrary is true for anti-selective poisoning when sites with lower activity are blocked first. The three different types of selectivity-related poisoning are illustrated below:



Figure 1: An illustration of three types of poisoning. The normalised activity is shown as a function of the normalised poison concentration [17].

A different way of classifying poisons is by dividing them into "reversible" and "irreversible" poisons. If a poison is reversible, it usually means that it is not very strongly adsorbed to the catalyst surface, which may allow for regeneration of the catalyst by removing the poison [18]. Irreversible poisons, on the other hand, cannot be removed and the damage they cause is thus considered permanent.

2.3.2 Fouling

Fouling is the deposition of species, mechanically from the fluid phase onto the catalyst surface. This results in activity loss since it blocks sites and pores. When fouling has advanced too far, it may disintegrate catalyst particles and be a cause of plugging in reactor voids[17]. Examples of fouling include the deposition of carbon and coke in porous catalysts. The definition of carbon and coke is however not very clear and a typical conventional definition would be that carbon is typically a product of CO disproportionation, while coke is formed through the decomposition or condensation of hydrocarbons on catalyst surfaces and often consists of polymerized heavy hydrocarbons [17]. However coke may be present in varying forms of both high and low molecular weight.

Carbon may chemisorb strongly on metal catalyst surfaces. It adsorps on mono-or- multilayers and prevents reactants from accessing metal surface sites [17]. It may also completely encapsulate a metal particle or plug micro-and- mesopores which denies access to crystallites inside the pores. In extreme cases, strong carbon filaments may accumulate in pores, causing stress and fracture in the support material, which disintegrates the catalyst pellets and plug the reactor voids [17].

2.3.3 Thermal Degradation

The deactivation process considered to be the most relevant for this study is sintering, which falls under the category of thermal degradation.

Thermal degradation of catalysts may result from [17]:

- 1. The loss of catalytic surface area due to crystallite growth of the catalytic phase
- 2. Support area loss due to collapse of support and of catalytic surface area due to collapse of pores on crystallites of the active phase
- 3. Chemical transformations of catalytic to non-catalytic phases.

In the definition of sintering, the first two processes above are included. Sintering generally takes place at temperatures higher than 500° C and is in general accelerated if water vapour is present[17]. There are three main mechanisms of metal crystallite growth: (1) migration of crystallite, (2) atomic migration, (3) vapour transport at very high temperatures.

In crystallite migration, the entire crystallites migrate over the support surface, followed by collision and coalescence[17]. In atomic migration, metal atoms detach from crystallites and migrate over the support surface. These atoms will eventually be captured by larger crystallites[17].

Sintering is generally a kinetically slow process and difficult to reverse[17]. Sintering rates generally increase exponentially with temperature. In oxygen, metals have been observed to sinter rapidly compared to in hydrogen. However, metal re-dispersion can be achieved through exposure at high temperatures to oxygen and chlorine, followed by reduction. The sintering rate is also increased by water vapour[17].

Sintering is affected by promoters or impurities and re-dispersion by either increasing or decreasing the mobility of the metal atom on the support. Support surface defects or pores may also impede the migration of metal particles on the surface.

The following equation was constructed using raw data to illustrate the sintering rate in a simple power law expression (SPLE):

$$-\frac{d\left(\frac{D}{D_0}\right)}{dt} = k_s \left(\frac{D}{D_0}\right)^n$$

 k_s = rate constant

D₀= initial dispersion

n= sintering order (typically between 3 and 15)

SPLE is unfortunately a very inaccurate method of calculating sintering rates because it assumes that the surface area or dispersion ultimately reaches zero after a certain amount of time has passed[17]. What actually happens is that for a specific temperature and atmospheric condition, a non-zero or limiting dispersion is observed after a long time. SPLE is also questionable because variations in sintering order have been shown to be a function of time and temperature for given catalysts in specific atmospheric conditions. From this, it follows that data taken from different samples cannot be quantitatively compared[17]. However, a relationship between the effects of temperature, atmosphere, metal, promoter and support can be determined by fitting sintering kinetic data to the general power law expression (GPLE)[17]:

$$-\frac{d\left(\frac{D}{D_0}\right)}{dt} = k_s \left(\frac{D}{D_0} - \frac{D_{eq}}{D_0}\right)^m$$

The added term D_{eq}/D_0 accounts for the observed asymptotic approach of the typical dispersion versus time curve to a limiting dispersion D_{eq} at infinite time. Here the order of sintering, m, is found to be either 1 or 2.

Sintering may have positive or negative effects on the specific activity in catalysis. If the reaction is structure-sensitive the specific activity can either increase or decrease with increasing metal crystallite size during sintering. If the reaction is independent of changes in metal crystallite size, it is known to be structure-insensitive [17].

Deactivation caused by a reaction of vapour phase with the catalyst surface may be caused by the production of inactive bulk and surface phases or volatile compounds which may exit the catalyst and reactor in gas phase. Solid state deactivation includes catalytic solid-support or catalytic solid-promoter reactions, and solid-state transformation of the catalytic phases during chemical reactions [17].

2.3.4 Attrition and Crushing

Attrition and crushing are both types of mechanical failure. Crushing of pellet or monolithic catalyst forms may occur due to a mechanical load. Attrition is the size reduction and/or breakup of catalyst granules or pellets, producing fines, which are especially common in fluid or slurry beds. A third type of mechanical failure is erosion. Catalyst particles or the monolith coating may erode at high fluid velocities[17].

Attrition can be detected if a reduction in particle size is observed using an electron microscope or if the catalyst particle is rounded or smoothed [17]. An optical or electron microscope may also be used to observe if there is a loss in washcoat. Large increases in pressure drop in a catalytic process may indicate fouling, masking or the fracturing and accumulation of attrited catalyst in the reactor bed [17].

2.4 Catalyst Synthesis

2.4.1 Sol-gel synthesis

Sol- gel synthesis is commonly applied in catalysis. It is an efficient method for controlling morphology and reactivity of solids [19]. A sol gel is created through a process in which nanoparticles are dispersed in a liquid (sol). The particles agglomerate to form a continuous three-dimensional network extending throughout the liquid, known as a gel [20].

The process takes place in a series of steps. First of all different precursors are added, usually consisting of a metal or metalloid element that is surrounded by various reactive ligands. The material is processed to form a dispersible oxide and the formation of a sol is initiated through contact with water or dilute acid. When the liquid is removed from the sol, the gel forms and the sol/gel transition controls the particle size and shape. The metal oxide is formed through calcination [21]. An example of a sol-gel synthesis is the hydrolysis and condensation of alkoxide-based precursors such as Si(OEt)₄ (tetraethyl orthosilicate, or TEOS). The hydrolysis and condensation of metal alkoxides M(OR)_z (where M denotes the metal and R denotes the hydrocarbon chain) can be represented by the following equations [21]:

$$MOR + H_2O \rightarrow MOH + ROH (hydrolysis)$$

$$MOH + ROM \rightarrow M - O - M + ROH$$
 (condensation)

The sol-gel synthesis process can be divided into a series of steps.

- 1. Different stable solutions of the alkoxide or solvated metal precursor are formed (the sol).
- Oxide or alcohol-bridge networks (the gel) are formed as a result of gelation. A
 polycondensation or polyesterification reaction triggers this step, which also sees a dramatic
 increase in the viscosity of the solution.
- 3. The gel is aged (syneresis). During the ageing process, the polycondensation reactions continue until the gel transforms into a solid mass. The gel network will contract and solvent is expelled from the gel pores.
- 4. The gel is dried through the removal of liquid from the gel network.
- 5. The dehydration step, which involves the removal of M-OH groups from the surface, which stabilizes the gel and prevents rehydration. This is done through calcination.
- 6. Densification and decomposition of the gels at temperature typically above 750°C. The pores of the gel network collapse and the remaining organic species are volatilized [21].

2.4.2 Freeze-dried sol-gel synthesis

The difference between the freeze-dry method and that described above is that step 5 is achieved through sublimation instead of vaporization [9]. The freeze drying preserves the microporous structure to a higher degree than thermal drying. Thermal drying may cause the pores to implode due to a drop in pressure. A high porosity in turn will contribute to a larger specific surface area, which is favourable for catalysis. Furthermore, the particles are unable to migrate since the solvent is frozen.

2.5 Experimental Methods

2.5.1 BET

The BET method for surface area measurements is based on the adsorption and desorption of N_2 molecules on the catalyst surfaces. Assuming that N_2 molecules tend to form monolayers at low temperatures, which depend only on the size of the N_2 molecule, it can effectively be used to measure the surface area of the material on which it is adsorbed. To calculate the surface area, the BET equation, derived by Brunauer, Emmett and Teller is used [22]:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \times \frac{P}{P_0}$$

P is the equilibrium pressure for a particular surface coverage represented by V.

 V_m is the volumetric uptake of nitrogen. It is the volume required to cover the surface to one monolayer thickness.

C is a constant, defined by condensation coefficients on surface layers, molecular oscillation frequencies and heat of condensation [23].

During the experiment, the samples are kept at 77K using liquid nitrogen. The amount of nitrogen molecules adsorbed on a sample is measured as a function of N_2 pressure ratio over the sample. A high pressure ratio indicates a low amount of molecules adsorbed.

BET calculations:

The catalyst surface area can be derived from the monolith surface area in the following way:

The surface area for each monolith can be calculated by multiplying the weight of the monolith by the BET surface area denoted SA.

$$m_{monolith} \times SA = A_{tot}$$

$$A_{tot}/(m_{wash-coat} \times 0.8) = SA_{cat}$$

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The total catalyst surface area can be calculated by dividing the total monolith surface area by the weight of the amount of catalyst present. Since the coating consists of 20% binder and 80% catalyst, the washcoat mass is multiplied by a factor of 0.8.

2.5.2 FTIR

Fourier Transform Infrared Spectroscopy is used to analyse the the reaction products formed in the reactor experiments [24]. The method is chemically specific, which allows for the identification of chemical compounds and functional groups from the analysed data, by the absorption of infrared light by the molecules. The infrared radiation transfers energy to the gas molecules, which start vibrating with increasing amplitude [25]. The energy transfer results in a decrease in intensity of some wavelengths of the transmitted infrared radiation [26]. The source of the radiation sends a broad band of wavelengths through the sample and some wavelengths are partially absorbed by it. Each molecule has a unique combination of atoms, causing them to absorb radiation at different wavelengths.

The transmittance is the intensity of the infrared radiation passing through the sample gas divided by the intensity of the radiation that enters the gas sample. This is illustrated by equation (1)





T= transmittance

I= intensity of light passing through the sample gas

I₀= intensity of light entering sample

The absorption of the infrared radiation is given by the logarithm of the inverse of the transmittance

 $A = \log(1/T)$ where A denotes absorbance.

The transmitted radiation reaches the detector. The signal which is detected is digitalized and Fourier transformed by a computer to obtain the infrared spectrum of the sample. All gas molecules have a unique spectrum, making it possible to identify the different gases from the sample spectrum using a reference spectrum.

The absorbance is directly proportional to the path length and concentration of the sample gas. Lambert Beer's law is used to calculate the concentration of an absorbing species in a sample. It is the linear relationship between the absorbance and the concentration of absorbing species. The general Lamber-Beer's law is shown below:

A = a(1)bc a(1) = absorption coefficient

b= path length

c= analyte concentration

The theoretical background behind FTIR is based on the use of an interferometer. Most interferometers are designed as two-beam interferometers, using a design very similar to the one built by Michelson in 1891. The Michelson interferometer, can divide a beam of radiation into two paths and then recombine the beams after a path difference has been introduced[25]. This causes interference between the beams. The variation of intensity of the beam emerging from the interferometer can thus be measured as a function of path difference.

The simplest form of the Michelson interferometer is described below:

It has 2 perpendicular plane mirrors, one which is moveable along an axis, perpendicular to its plane. A beamsplitter bisects the moveable and fixed mirror. In the beamsplitter, a collimated beam of radiation from an external source can be partially reflected to the fixed mirror and partially transmitted to the movable mirror. When the beams return to the beamsplitter, they interfere and are partially reflected and transmitted. Due to interference, the intensity of each beam passing to the detector and returning to the source depends on the difference in path of the beams in the two arms of the interferometer. The variation in intensity of the beams passing to the detector and returning to the source as a function of the path difference yields the spectral information in a Fourier transform spectrometer.

A disadvantage with using FTIR is that water can give spectral interferences. These are of great importance in qualitative analysis due to the resulting overlap of signals that make identification difficult. Absorption bands for CO_2 and N_2O are relatively close to each other and may result in interference at high concentrations [26].

3. Experimental Procedure

Five 2 wt% Ag-alumina samples [2] were evaluated in a flow reactor, using n-octane as reductant. Furthermore, studies on MK1 diesel and NexBTL biodiesel as reductant were also carried out over pure 2 wt% and 6 wt% Ag-alumina samples and over a 4 wt% Ag-alumina sample doped with 100 ppm Pt.

3.1 Preparation of Catalysts

The catalyst samples were prepared by Cid according to the method described in [2] and briefly described below.

Initially, aluminium isopropoxide (AIP) was gelled together with silver nitrate (AgNO₃) to form a mix of Ag-Al-O(H) and Al-O(H)-Al network via a hydrolysis condensation through the addition of HNO₃. The process could be described by the following reaction:

$$Al(OiPr)_3 + 3H_2O \rightarrow Al(OH)_3 + 3iPrOH$$
$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

After the initial step, the gel was freeze dried to produce a homogeneous and porous solid powder. The freeze drying causes solidification of water in the gel pores and subsequent elimination of water by sublimation at low pressure (i.e. less than 1hPa). This prevents collapsing of the pores due to mechanical constraints, which is common during evaporation of liquid solvents in gel pores.

The 2 wt% Ag-Alumina samples were prepared in the following way [2]:

Silver nitrate (>99.5%; VWR) in the ratio 8.04 mg/g aluminium isopropoxide (3.718 mmol) were dissolved in 1200 ml of milli-Q water. 78.525 g (0.3845 mol) of aluminium isopropoxide (98+%; Aldich) was slowly added to the Ag NO₃ solution during vigorous stirring. The resulting slurry was covered with aluminium foil to prevent photo-reduction of silver by light and heated to 82° C. 33 ml of nitric acid (10%; Fluka) was added drop-wise until the slurry had a clear appearance (light yellowish colour observed). The sol was covered and stirring was continued over night for gelation to be achieved. After gelation, the gel was separated into three flasks and excess solvent was removed using a vacuum pump at 38° C, until complete gelation. The gel was stored in a freezer for a few days at 18° C before it was freeze- dried at about 0.5 hPa for four days. The resulting crystal-shaped cryogel was heated at 600° C at the rate of 2° C per minute from room temperature (RT) and calcined at 600° C for six hours. The resulting aerogel was crushed into a fine white powder.

In addition, two powder samples with 4 wt% Ag and 100 ppm Pt and 6 wt% Ag were prepared accordingly.

3.2 Monolith Dip-coating

Corderite monoliths with a diameter of 20 mm and length of 20 mm (400 channels per square inch, 188 channels) were dip coated with a boehmite and Ag/Al₂O₃ slurry. The boehmite (Disperal Sol P2, Condea), an aluminium oxide hydroxide γ -AlO(OH) mineral acts as a binder between the cordierite and the Ag-Al₂O₃ powder. The process was repeated for each monolith until the desired amount of wash-coat was added. The monolith was first calcined at 600 ^oC for 5 minutes and subsequently dipped in water (milli-Q) and in the boehmite- Ag/Al₂O₃ slurry (weight-ratio 1:4) in minimum amount of water. Afterwards, the monolith was dried at 90^oC and calcined for 1 minute at 600^oC to form oxides from hydroxides through the elimination of water. The process was repeated until the weight of dried mass added to the monolith was about 800 mg. The dip-coated monoliths were then calcined at 600^oC for 3 hours (heating ramp of 2^oC per minute from RT). The 2 wt% Ag samples were aged in 10% O₂, 10% H₂O and N₂ at different temperatures for 24 hours.

For the samples used in the NexBTL tests, the catalyst powders containing 2% Ag, 4% Ag with 100ppm Pt and 6% Ag, the monolith dip-coating process were repeated. For these three samples, reactor tests were conducted, first using the fresh monoliths. Then the samples were aged at the same gas composition at 500^oC for 12 hours. The samples are shown in table 1B.

Name of monolith	Ageing Temperature	Ageing conditions	Ageing time (hours)
	(⁰ C)		
Ag2_700A	700	10% O ₂ 10% H ₂ O	24
Ag2_700B	700	10% O ₂ 10% H ₂ O	24
Ag2_750A	750	10% O ₂ 10% H ₂ O	24
Ag2_750B	750	10% O ₂ 10% H ₂ O	24
Ag2_750C	750	10% O ₂ 10% H ₂ O	24
Ag 2%	500	10% O ₂ 10% H ₂ O	12
Ag4Pt100	500	10% O ₂ 10% H ₂ O	12
Ag 6%	500	10% O ₂ 10% H ₂ O	12

Table 1: Catalysts used in flow reactor experiments and ageing temperatures.

3.3 BET Measurements

For the BET measurements, the monoliths were first weighed, then dried in an oven at 225° C for about 2 hours to remove moisture due to the importance of obtaining the monolith's dry weight. Afterwards each sample was put in a glass holder especially designed for the BET measuring device. The glass holder and sample was weighed together before it was attached to the BET-machine (Image 1). The weight of the monolith was entered into a computer program before it was run which allowed it to calculate the BET-surface area of the sample. Directly below the sample, a container was filled with liquid nitrogen. During initiation, the sample temperature is lowered through the exposure to liquid nitrogen. When the right conditions have been achieved, adsorption takes place through the addition of gaseous nitrogen. The nitrogen gas will adsorb onto the sample surface and the surface area can be calculated by measuring the number of molecules adsorbed on the surface as a function of N₂ pressure over the sample.



Image 1: The BET measuring device. ASAP 2010.

In order to measure the surface area of the monoliths, the BET method (ISO 9277) was applied using a Micrometrics ASAP 2010 instrument. The equipment automatically calculated the BET-surface area and the C-constants on the linear BET equations for every sample.

3.4 Reactor Experiments

3.4.1 Reducing agents

The catalytic conversion was tested for three different types of reducing agents; n-octane, MK1 diesel and NexBTL (biodiesel).

N-octane is a straight chain hydrocarbon, which makes it very easily handled in the reactor. Previous studies on NO_x reduction have involved shorter chain hydrocarbons like propane, but Kannisto et al. [8] claim that lower activation temperature is required for the reaction if longer chained hydrocarbons are used.

MK1 (miljöklass 1) Diesel, is graded according to a Swedish system to fulfil environmental restrictions. There are three grades for Swedish diesel. Grade 1, which was used in the study, and grade 2 are considered the cleaner ones and are also more expensive to produce, but they are designed to reduce the emission of particulates, hydrocarbons, sulfur containing compounds and NO_x [27]. MK3 diesel is cheaper but contains more polycyclic aromatic hydrocarbons (PAH) [28]. MK1 diesel is characterized by its low sulfur and aromatics content as well as its faourable anti-coking properties, easy ignition and high cetane number. [29]

NexBTL is a type of biodiesel that is produced through hydrotreating vegetable oils. It has the chemical composition of traditional diesel and it can also be produced using waste animal fat from the food industry. NexBTL is free from sulfur, oxygen, nitrogen and aromatics and is thus considered a very clean, renewable fuel. According to Neste Oil, the company that produces NexBTL, tests have shown that the use of NexBTL reduces greenhouse gas emissions by 50% [30].

3.4.2 Flow Reactor

The gas flow reactor consisted of a horizontal quartz tube. The monolith to be tested was attached to a thermo element inside the tube. The sample was placed in between two cordierite monoliths in order to reduce heat losses from radiation. The sample monolith was also insulated with a thin layer of quartz wool to prevent gas slip.

The quartz tube had a heating coil wound around the outside of the tube to enable heating at set temperatures for the experiments. After the tube had been sealed, glass wool was wrapped around it for insulation.

The reducing agent and water were supplied by an externally controlled evaporator mixer (CEM) system where the liquid and the carrier gas were mixed at constant temperature $(100^{\circ}C)$. The argon carrier gas was controlled by two separate mass flow controller, (MFC). The outlet gases were

analysed by FTIR machine (MKS 2030). After analysis, data for the concentrations of CO, CO_2 , H_2O , NO, NO₂ and N₂O was obtained from the FTIR measurements.



Image 2: Synthetic Gas Bench Reactor

The fresh and aged monolith samples were evaluated in flow-reactor experiments with respect to lean NO_x reduction using n-octan, MK1 diesel and NexBTL as reducing agents.

Previous studies have shown that the C_1/NO_x ratio for the reactor experiment has an optimum value of 6. This ratio was used for the n-octane experiments and the same ratio was also adjusted for the diesel fuels, which are assumed to have an average molecular chain length of 16 carbons, which is twice the chain length for n-octane.

The gas fed into the reactor consisted of 150 ppm n-octane (corresponding to 1200 ppm C_1), 200 ppm NO, 1000 ppm H_2 , 5% H_2O and 10% O_2 in Ar as the carrier gas. The monoliths were pre-treated in 10% O_2 with Ar at 550°C before the tests for the purpose of removing the adsorbed organic molecules from previous experiments or contaminants that may have been deposited by touching the samples.

All n-octane samples were run at the same steady state conditions, while 2 samples had and additional ramp experiment after the steady state experiment had been completed.



Figure A: The graph illustrates a typical steady state experiment with time in seconds plotted against temperature in ^oC.



Figure B: The graph illustrates a typical steady state experiment with ramps at the end with time in seconds plotted against temperature in ^oC.

5 samples were tested using octane. Two additional samples were tested using MK1 diesel and three fresh samples, of which one was doped with 100 ppm platinum (2% Ag, 4% AgPt100 and 6% Ag), were first evaluated using NexBTL as reducing agent, then aged for 12 hours at 500° C before the same evaluation was conducted on the aged samples. The NO_x conversion of the fresh and aged samples was then compared to each other.

4. Results and Discussion

The aim of this work is to evaluate the influence of hydrothermal ageing on the lean NO_x reduction by hydrocarbons over Ag-alumina catalysts with varying Ag content. The 2 wt% Ag samples were evaluated with respect to BET-surface are before and after the reactor experiments.

4.1 BET-measurements

Table. 2: BET surface area measurements of aged monoliths before flow reactor experiments.

Sample	Ageing temperature	Calculated BET	Calculated total monolith
name	(⁰ C)	Surface area	surface area (m^2)
		(m^2/g)	
Ag2_700A	700	25.9	111
Ag2_700B	700	28.4	107
Ag2_750A	750	24,9	108
Ag2_750B	750	21.7	91.6
Ag2_750C	750	24.5	104

Table.3: BET surface area measurements of aged monoliths after flow reactor experiments.

Sample	Ageing temperature	Calculated BET	Calculated total monolith
name	(⁰ C)	Surface area	surface area (m ²)
		(m^2/g)	
Ag2_700A	700	22.8	111
Ag2_700B	700	25.8	97.8
Ag2_750A	750	23.1	100

The change in surface area before and after the reactor experiment is shown to have an average value of less than 9%. The influence on the catalytic performance is thus considered to be negligible.

4.2 Flow Reactor Experiments

The results from the flow reactor experiments are shown in the three graphs below. Figure 2 shows the lean NO_x reduction over aged 2 wt% Ag-alumina samples with n-octane as reducing agent. In Figure 3 the results for lean NO_x reduction over aged 2wt% Ag-alumina catalysts are shown for diesel (MK1) and biodiesel (NexBTL) as reducing agents. In Figure 4, the lean NO_x reduction over high-loaded Ag-alumina samples (4wt% Ag with 100 ppm Pt and 6wt% Ag) using biodiesel (NexBTL) as reducing agent, is compared to the NO_x reduction performance over fresh and aged 2wt% Ag-alumina samples.



Figure 2: Lean NO_x reduction over fresh and aged 2 wt% Ag- alumina catalysts with n-octane as reductant: All black indicator dots denote catalysts aged at 750° C (• **A =**) while the open triangles \bigtriangledown denote a sample aged at 700° C. The tests were run at steady state conditions with 150 ppm n-octane, 200 ppm NO, 1000 ppm H₂ and 10% O₂ in Ar gas.

It can be seen that the catalyst aged at a lower temperature has the generally higher NO_x conversion, which implies less impact by sintering. Furthermore, these results are compared to previous results from similar experiments (performed by Cid) [2], where the overall trend is that conversion was as high as 70-80% for all ageing temperatures (500,550,600 and 650°C) at the two higher reactor temperatures $350^{\circ}C$ and $400^{\circ}C$, while it was never over 65% for the two lower reactor temperatures (250 and $300^{\circ}C$) for any of the aged samples.

A summary of the n-octane experimental results can be seen in Table 4 below.

Table 4: Average NO_x conversion of Ag-alumina samples at different ageing temperatures. The results are obtained from average values from steady state experiments.

Sample	Ageing	NO _x Conversion (%)	
	temperature		
	(^o C)		
1	500	Temperature	
		250	37
		300	62
		350	89
		400	84
2	550	Temperature	
		250	31
		300	56
		350	82
		400	77
3	600	Temperature	
		250	30
		300	55
		350	86
		400	84
4	650	Temperature	
		250	37
		300	63

		350	87
		400	79
5	700	Temperature	
		250	5
		300	33
		350	65
		400	69
6	750	Temperature	
		250	5
		300	15
		350	35
		400	70
7	Fresh sample	Temperature	
		250	23
		300	42
		350	74
		400	72



Figure 3: Lean NO_x reduction over aged 2 wt% Ag- alumina catalysts with MK1 Diesel (\blacksquare) and NexBTL(\bullet) as reductant. The catalysts used were aged at 650^oC (\blacksquare) and 750^oC (\bullet). The tests were run at steady state conditions with 300 ppm of each reducing agent, 200 ppm NO, 1000 ppm H₂ and 10% O₂ in Ar gas.

A couple of samples were tested using MK1 diesel, however due to a too low vapourisation temperature, the diesel clogged the system, making most of the results ,apart from the one shown above, un-reliable. The difference between the NexBTL's ability to reduce NO_x compared to MK1 is clearly visible in Figure 3. This resulted in further tests using NexBTL as reducing agent.

In Figure 3, the difference in NO_x conversion between using the two reducing agents is demonstrated and the composition of the reducing agent is thus shown to have an effect on the conversion.



Figure 4: Lean NO_x reduction over fresh and aged Ag- alumina catalysts with NexBTL as reductant. Aged (white markers) and fresh (black markers) catalysts with different silver loadings, ascending from left to right; 2% ($\bullet \circ$) Ag, 4% Ag-Pt100(\blacktriangle) and 6% Ag($\blacksquare \Box$).The tests were run at steady state conditions with 300 ppm of each reducing agent, 200 ppm NO, 1000 ppm H₂ and 10% O₂ in Ar gas. It should be noted that the fresh 2% Ag sample was not aged. Instead, another aged 2 wt% Ag sample was inserted into the diagram to give a representative data curve.

The results presented in Figure 3 illustrate the influence of different types of reducing agents on the lean NO_x reduction and stress the importance of metal loading for hydrocarbon activation. A clear trend in increasing NO_x reduction with increased silver loading on the catalyst is seen. Furthermore, the fresh silver catalysts have a significantly higher NO_x reduction potential compared to after ageing in Figure 3. However the sample doped with Pt had nearly the same NO_x conversion both when fresh and after ageing. This is an interesting outcome. Kannisto [31] observed two samples containing 2% Ag, one of which was doped with 100 ppm Pt. The Pt-doped sample showed significantly higher NO_x conversion at high C/N rations compared to the undoped one [31]. This is in accordance with the results in Figure 4 that suggest Pt doping is favourable and needs to be investigated further. Furthermore, the occurrence of a point of maximum conversion, which is clearly visible in the third graph of Figure 4 is also very interesting. It suggests that 350° C is an optimum temperature for the sample containing 6% Ag.

2% Ag has for a long time been known to be an optimum silver loading on alumina support for the purpose of NO_x reduction [31]. However this is in conflict with the obtained results. It is also widely acknowledged that other factors may influence the performance of catalysts with different silver loadings. Furthermore, the 2% optimum should also be a reducing agent specific property.

5. Conclusions

The results in Figure 2 suggest that ageing temperature of 700° C is more favourable for the reduction of NO_x compared to an ageing temperature of 750° C. Previous results for catalysts aged at 500° C, 550° C, 600° C and 650° C show that aged catalysts have a higher NO_x conversion activity than fresh samples [2].

Overall, the results for NO_x reduction with biodiesel as reducing agent suggest the higher the loading, the better the conversion, while ageing in general is unfavourable for NO_x reduction. It is interesting to see that the difference between the fresh and aged sample in the middle graph depicting the performance of the catalyst with 4% silver loading (doped with 100ppm platinum) which showed a smaller difference between the fresh and aged catalyst. This suggests Pt doping has a stabilising effect on the catalyst.

6. Future Work

Due to time limitations, a limited number of samples were tested. An expanded version of the experiment should also include the reaction of other gases and also investigate the conversion of NO_x using a wider range of silver loadings and ageing temperatures.

Park and Boyer [32] have showed that the introduction of SO_2 in the reaction gas stream can enhance lean-NO_x reduction performance on a silver alumina catalyst, claiming the improved NO_x reduction properties was due to the formation of Ag₂SO₄ phase from silver oxide or silver metal phases that are present in the catalyst. Furthermore, silver sulfate phases are known to be more active and selective than silver oxide in lean-NO_x catalysis since it produces more- NCO species. However the risk of SO₂ poisoning will pose a major drawback and reduce activity [32]. Future studies where the impact of SO₂ is further investigated may therefore be favourable for a better understanding of how the catalyst behaves under different conditions.

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Bibliography

- 1. Burch, R., J.P. Breen, and F.C. Meunier, *A review of the selective reduction of NOx with hydrocarbons under lean-burn conditions with non-zeolitic oxide and platinum group metal catalysts.* Applied Catalysis B: Environmental, 2002. **39**(4): p. 283-303.
- 2. Cid, C., Silver-alumina catalysts for lean NO_x reduction: Influence of hydrothermal ageing in Department of Chemical and Biological Engineering, Competence Centre for Catalysis (KCK). 2010, Chalmers University of Technology: Gothenburg. p. 35.
- 3. Seijger, G.B.F., et al., *Screening of silver and cerium exchanged zeolite catalysts for the lean burn reduction of NOx with propene.* Applied Catalysis B: Environmental, 2003. **40**(1): p. 31-42.
- 4. Martinez-Arias, J.C.C., M. Frenández-García, and J.A. Anderson, *Supported Metals in Catalysis*. 2005, London: Imperial College Press.
- 5. Breen, J.P., et al., *An investigation of the thermal stability and sulphur tolerance of Ag/[gamma]-Al2O3 catalysts for the SCR of NOx with hydrocarbons and hydrogen.* Applied Catalysis B: Environmental, 2007. **70**(1-4): p. 36-44.
- 6. Lee, Y.-W. and E. Gulari, *Improved performance of NOx reduction by H2 and CO over a Pd/Al2O3 catalyst at low temperatures under lean-burn conditions.* Catalysis Communications, 2004. **5**(9): p. 499-503.
- 7. Kung, M.C., et al., *Catalysts for lean NOx reduction: structure-property relationship.* Applied Surface Science, 1997. **121-122**: p. 261-266.
- 8. Kannisto, H., H.H. Ingelsten, and M. Skoglundh, *Ag-Al2O3 catalysts for lean NOx reduction--Influence of preparation method and reductant.* Journal of Molecular Catalysis A: Chemical, 2009. **302**(1-2): p. 86-96.
- 9. Gunnarsson, F., *Lean NO_x reduction over silver alumina*, in *Department of Chemical and Biological Engineering*. 2009, Chalmers University of Technology: Gothenburg. p. 36.
- Koebel, M., M. Elsener, and M. Kleemann, Urea-SCR: a promising technique to reduce NOx emissions from automotive diesel engines. Catalysis Today, 2000. 59(3-4): p. 335-345.
- 11. Niemi, S., Kaj Lundin, Janne Perus, Mika Laurén, Jani Hoikkala, Krister Ekman, Pekka nousiainen, Kalle Arve, Kari Eränen, Dmitry Yu. Murzin. *HC-SCR Catalyst for NO_x Reduction in an Off-Road Diesel Engine*. Available from: http://www.ffrc.fi/FlameDays_2009/4A/NiemiPaper.pdf.
- 12. Satokawa, S., et al., *Promotion effect of H2 on the low temperature activity of the selective reduction of NO by light hydrocarbons over Ag/Al2O3.* Applied Catalysis B: Environmental, 2003. **42**(2): p. 179-186.
- Eränen, K., et al., On the mechanism of the selective catalytic reduction of NO with higher hydrocarbons over a silver/alumina catalyst. Journal of Catalysis, 2004.
 227(2): p. 328-343.
- 14. Fernandes, D.M., et al., *Commercial automotive catalysts: Chemical, structural and catalytic evaluation, before and after aging.* Catalysis Today. **133-135**: p. 574-581.
- 15. Schmieg, S.J. and D.N. Belton, *Effect of hydrothermal aging on oxygen storage/release and activity in a commercial automotive catalyst.* Applied Catalysis B: Environmental, 1995. **6**(2): p. 127-144.

- Nakatsuji, T., et al., *Catalytic reduction system of NOx in exhaust gases from diesel engines with secondary fuel injection*. Applied Catalysis B: Environmental, 1998.
 17(4): p. 333-345.
- 17. Bartholomew, C.H., *Mechanisms of catalyst deactivation*. Applied Catalysis A: General, 2001. **212**(1-2): p. 17-60.
- 18. Forzatti, P. and L. Lietti, *Catalyst deactivation*. Catalysis Today, 1999. **52**(2-3): p. 165-181.
- 19. Lecloux, A.J. and J.P. Pirard, *High-temperature catalysts through sol-gel synthesis.* Journal of Non-Crystalline Solids, 1998. **225**: p. 146-152.
- 20. *The Sol-Gel Process*. 2011-07-31]; Available from: http://www.aerogel.org/?p=992.
- 21. University, G. *Wet Chemical Synthesis of nanomaterials (Sol-gel process):*. Available from:

http://gitam.edu/eresource/nano/NANOTECHNOLOGY/bottamup%20app.htm.

- 22. Bowker, M., *The Basis and Applications of Heterogeneous Catalysis*. 6th ed. 1998, Oxford: Oxford University Press. 90.
- 23. Pomonis, P.J., et al., *A novel method for estimating the C-values of the BET equation in the whole range 0<P/Po<1 using a Scatchard-type treatment of it.* Microporous and Mesoporous Materials, 2004. **69**(1-2): p. 97-107.
- 24. Eaton, P., *FTIR Tutorial*, University of Porto.
- 25. Peter R. Griffiths, J.A.d.H., *Fourier Transform Infrared Spectrometry*. 2nd ed. 2007, New Jersey: John Wiley & Sons. 527.
- 26. Sjövall, H., FTIR Study on Diesel Exhaust: Measurements Up- and Downstream Oxidation and DeNO_x Catalysts, in Dept. of Chemical Engineering and Environmental Studies. 2003, Chalmers University: Göteborg. p. 50.
- 27. Transportstyrelsen. Available from: http://www.transportstyrelsen.se/sv/Vag/Fordon/fordonsregler/Miljokrav/Av gaser/Miljoklassade-branslen/.
- 28. Statoil. *Statoil Faktablad No 1 2008*. 2008; Available from: http://www.statoil.se/file_archive/sed/Faktablad_1_2008.pdf.
- 29. CTN. *CTN: Norbers oljor och tillbehör*. Available from: http://www.ctn.nu/diesel.
- 30. Oil, N. *NexBTL Diesel*. [cited 2011 2011-07-20]; Available from:
- http://www.nesteoil.com/default.asp?path=1,41,11991,12243,12335.
 31. Kannisto, H., et al., *Efficient low temperature lean NOx reduction over Ag/Al2O3*—
- *A system approach.* Applied Catalysis B: Environmental, 2011. **104**(1-2): p. 74-83.
 Park, P.W. and C.L. Boyer, *Effect of SO2 on the activity of Ag/[gamma]-Al2O3*
- *32.* Park, P.W. and C.L. Boyer, *Effect of SO2 on the activity of Ag/[gamma]-Al2O3 catalysts for NOx reduction in lean conditions.* Applied Catalysis B: Environmental, 2005. **59**(1-2): p. 27-34.