Mechanistic study of silver nitrate during the selective catalytic reduction of NO_X with ammonia over Ag/Al_2O_3

Master of Science Thesis in the Master Degree Program, Innovative and Sustainable Chemical Engineering

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Department of Chemical and Biological Engineering

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Competence Centre for Catalysis

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Abstract

Recently, removal of NO_X from exhaust gas of diesel engines and lean-burn engines have been become an important issue because NO_X emissions contribute to the generation of photochemical smog and formation of ground-level ozone and acid rain. Selective Catalytic Reduction of NO_X with ammonia (NH_3-SCR) is one of the promising technologies for NO_X reduction from diesel and lean-burn engines. In this study the reduction of $AgNO_3$ as a component in the selective catalytic reduction of NO by NH_3 as a reducing agent promoted by hydrogen over alumina supported silver catalyst has been examined. In situ Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy is applied to investigate the species adsorbed on the surface of a model catalyst consisting of a physical mixture of silver nitrate and alumina catalyst during NH_3-SCR conditions. The effect of different gases H_2, NO, NH_3, O_2 on the decomposition of silver nitrate and the migration of nitrates to the alumina is studied. In addition, decomposition of $AgNO_3$ is evaluated by examination of various gas mixtures.

The results reveal that nitrates can migrate from the silver to the alumina in only argon however the migration rate will increase when H_2 and O_2 are added. Moreover, NH_3 is the essential element to decompose $AgNO_3$. The addition of hydrogen, which is essential for NO_X reduction over Ag/Al_2O_3 with NH_3, neither promotes nor hinders the decomposition.

Keywords: DRIFTS, NH_3-SCR, Ammonia, Ag/Al_2O_3, Silver nitrate, Silver oxide, NO_X reduction, Selective catalytic reduction, hydrogen, diffuse reflectance, mechanism

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Contents

1. Introduction

1.1 Background

Nowadays, global warming is one of the main issues, which refers to an increase in the average temperature of earth. An increase in the mean temperature of the earth's atmosphere of approximately 0.4-0.8 C has already been measured [1, 2]. Global warming has huge impacts in physical, ecological, social and economical aspects. Rising sea levels, melting glacier and changing the distribution of plants and animal species are some of the negative effects of global warming [2, 3]. One of the major and primary causes of global warming is the increase of greenhouse gases due to human related activities such as mobile and stationary combustion of fossil fuels, land cleaning, agriculture, and etc [1, 2]. The greenhouse gases in the atmosphere, which are mostly emitted due to the burning of fossil fuels, are mainly carbon dioxide, methane and nitrous oxide [1, 2]. Moreover, some of these gases cause severe environmental damages and various health problems. For instance, nitrogen oxides contribute to acidic rain, formation of photochemical smog and harmful impacts on respiratory system in humans [4, 5]. Therefore, several legislations have been enacted to control the emission of greenhouse gases such as "Kyoto Protocol" in 1997 and "Panel on Climate Change" in 2007 [6, 7]. The target of Kyoto Protocol legislation was to decrease the greenhouse gas emissions worldwide by 5.2% of 1990 levels. Sweden has agreed to decrease its greenhouse gas emissions and is one of the countries that follow this legislation. It has declined the greenhouse gas emission by 1.7 percent between 2005 and 2006. In addition, the emissions have decreased about 9% from 1990 which means that Sweden has reduced its greenhouse emission by 12.7% more than its target under the Kyoto Protocol [8]. Road transportation was one of the main sectors considered by Kyoto protocol since it is the greatest contributor to global warming and release major amounts of greenhouse gases in form of CO_2 and NO_X to the environment.

1.1.1 Role of transportation in global warming

It can be seen in Figure 1, that 97% of the fuel used in the transportation is oil and 81% of the fuel consumed for transportation is with road transport. Thus, road transportation is highly dependent on fossil fuels and attention should be paid to decrease the emission of greenhouse gases and thereby reduce the harmful effects of these gases.

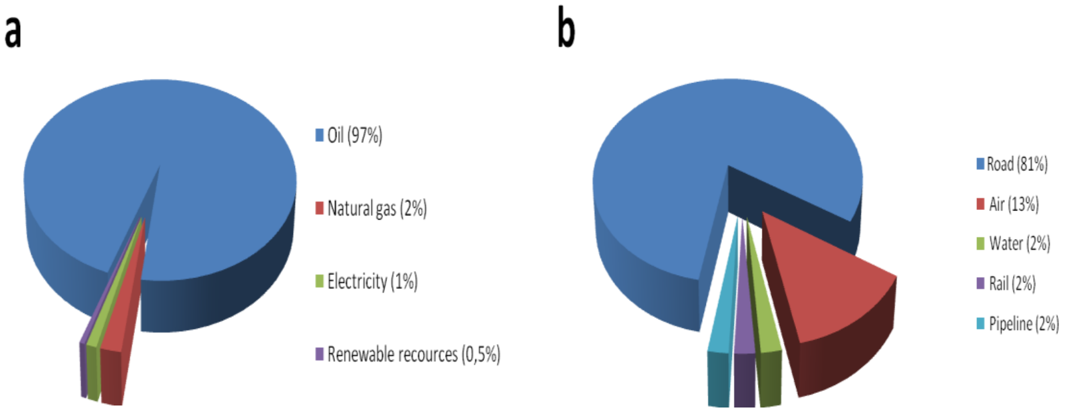


Figure 1. (a) Fuel use in the transportation sector in OECD (Organisation for Economic Cooperation and Development) countries and (b) shares of transport modes in OECD countries [1, 9].

Lean burn engines are mostly used in vehicles in order to reduce the fuel consumption and to enhance the performance of the engines. The concept of lean-burn engines means higher air to fuel ratio which decrease the fuel consumption drastically. In these types of engines the value of air to fuel ratio could be as high as 23:1 or even more. In today's designs for lean-burn engines , higher compression ratios are employed which provide better perfomance of the engine and less exhaust hydrocarbon emissions.

The major drawback of lean-burn engines is that traditional 3-way catalysts could not be used since those catalysts need air to fuel ratio close to stoichiometric values to have a favorable performance. Consequently, more complex catalytic convertors should be developed to be used in lean-burn engines.

1.2 Emissions from a combustion engine

Nitrogen oxide is one of the major polutants, which influences climate by altering levels of direct species. It produces tropospheric greenhouse gas (ozone) through photochemical reactions in the atmosphere. Nitrogen oxide is released to the atmosphere by both natural and human-related sources such as agricultural soil management, animal manure management, sewage treatment, combustion of fossil fuel in the vehicle engines, etc. The level of emission from a source can be varying depending on different factors such as industrial and agricultural production characteristics, combustion technologies, waste management practices, and climate, etc. For instance, in vehicle engines the presence and absence of control devices such as catalytic converters have a significant effect on the level of NO_X emission.

The three types of nitrogen oxides present in the atmosphere are nitric oxide (NO), nitrogen dioxide (NO_2) and smaller amount of nitrous oxide (N_2O). Nitrogen oxide is produced in the vehicle engines as a reaction of nitrogen and oxygen during fossil fuel combustion at high temperatures. The amount of nitrogen oxide emitted varies with the fuel type, technology, or pollution control device used, as well as maintenance and operating practices.

The significant global source of NO_X emission is that of fossil fuel burning. Consequently, there has been a move towards developing more fuel effective lean burn engines (i.e. operation with excess oxygen).

Another harmful component in the vehicle exhaust is carbon monoxide (CO) formed due to photochemical reactions in the troposphere, combustion engine, etc. One of the major causes of CO formation is incomplete combustion. When the air to fuel ratio is low and there is low amount of oxygen during the combustion, the fuel will not burned completely. CO is highly toxic and is one of the major atmospheric pollutants in urban areas.

Unburned hydrocarbons are also by-products in the combustion of fuel engines, which are categorized as Greenhouse Gases. They can be formed due to weak flame or when air-fuel mixture avoids flame zone in some parts of the combustion chamber.

1.3 Catalytic converter

The introduction of catalytic converter for reduction of NO_X from combustion engine refers to 25 years ago. It is one of the successful devices for cars emissions control and still being developed. The major harmful exhaust gas components are CO, partly burned HC and NO_X, which are emitted due to incomplete combustion in the vehicle's engine. These harmful gases are converted to harmless gases such as nitrogen, carbon dioxide and water before they leave the vehicle's exhaust system. As exhaust gases pass over the catalyst, it stimulates a chemical reaction, which converts the pollutant to harmless gases before they leave the car and remove a lot of the pollutant to the environment. Two main types of structure are available for catalytic converter, which are ceramic honeycomb and ceramic beads. However, most of the vehicles today use a honeycomb structure catalytic converter.

In order to decrease the fossil fuel emissions, modern vehicles are designed to reduce the fuel consumption and increase the conversion efficiency. The engine operation affects the feed gas composition of the catalytic converter and exhaust components. The aim in conventional gasoline engines is to keep the air to fuel ratio close to the stoichiometric point. If the ratio of air/fuel is not stoichiometric, conversion of NO_X or CO will deteriorate. Therefore, a closed-loop control system is used to maintain the mixture composition at stoichiometric ratio, which is 14.5:1. In the stoichiometric ratio, all of the fuel will be burned using all of the oxygen in the air.

1.4 Objective

Reduction of harmful NO_X emissions from diesel engines and lean-burn engines has been considered in several researches. It is not possible to use three way catalytic converters (TWCs) in diesel and lean-burn engines due to the presence of excess oxygen. One of the most common techniques used for automotive engines under lean condition, is selective catalytic reduction with ammonia (NH_3-SCR). In this study, $AgNO_3$, AgO and a mixture of $AgNO_3$ and Al_2O_3 are used as model catalysts for Ag/Al_2O_3. The objective of this study is to investigate the effect of NO, NH_3, O_2 and H_2 and mixtures of these gases on silver nitrate as an important part of the understanding of the mechanism of H_2 assisted NH_3-SCR over Ag/Al_2O_3.

2. Theoretical background

2.1 Three way catalyst

The three-way catalyst is used for conventional gasoline engines where the engine is operated within a narrow band around stoichiometry. If the air/fuel ratio is higher or lower than stoichiometric ratio, the engine is operating under lean or rich condition, respectively.

In stoichiometric conditions, the exhaust gas fluctuates between rich (excess fuel) and lean (excess oxygen) conditions. As illustrated in Figure 2 the conversion efficiency of all three harmful emissions is in highest level therefore described as “three way”.

Three-way catalyst (TWC) is a successful technology used to reduce emissions in engine’s exhaust. This method is employed in rich-burn, natural gas and stoichiometric engines. TWC can destroy up to 99% of the harmful pollutants such as partly burned hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxide (NO_X) by converting them simultaneously into less harmful gases such as water (H_2O), carbon dioxide (CO_2) and nitrogen (N_2). The major reactions on automotive catalysts are oxidation of CO and HC, reduction of NO_X and water gas shift reaction.

Some of the most common chemical reactions occurring in TWC can be written as follows:

- $CO + 0.5O_2 \rightarrow CO_2$ (2.1)
- $C_3H_6 + 4.5O_2 \rightarrow 3CO_2 + 3H_2O$ (2.2)
- $NO + CO \rightarrow 0.5N_2 + CO_2$ (2.3)

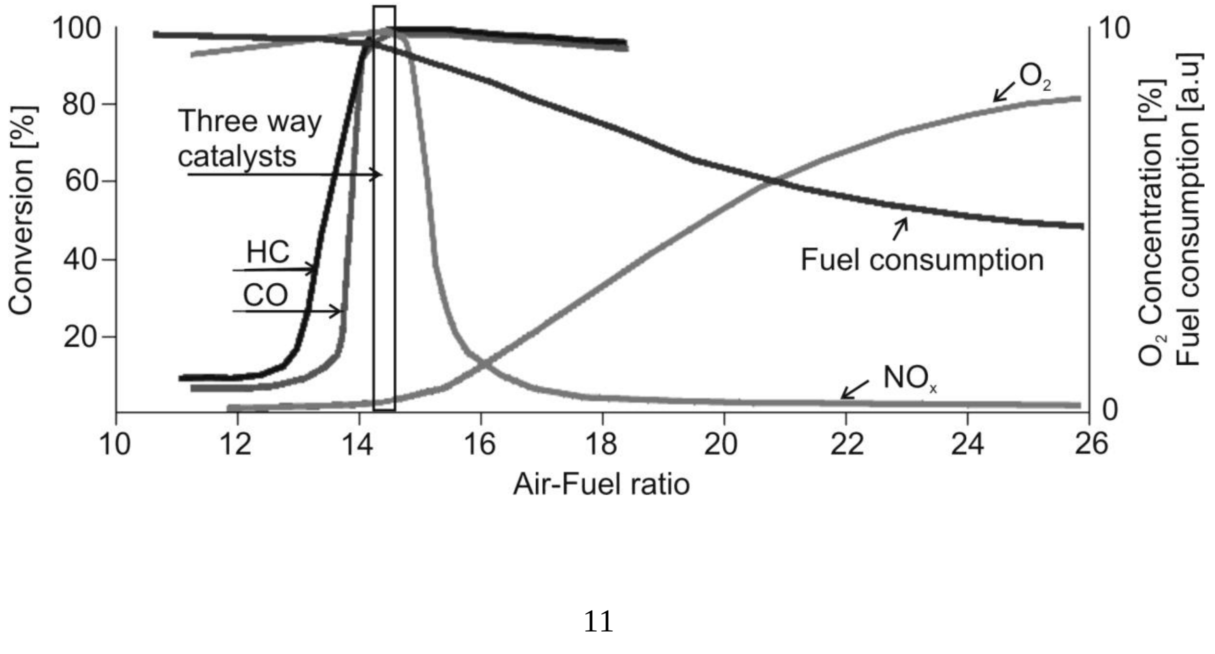


Figure 2. Oxygen concentration, fuel consumption and conversion efficiency of NO_X, HC and CO over a three-way catalyst, as a function of the air-fuel ratio [10].

The ratio of air to fuel has major influence on the quantity of harmful gases and determines the ability of a catalytic converter to clean them up. As can be seen in Figure 2, in rich condition, the ability of the three-way catalyst to reduce nitrogen oxide is high but has low efficiency for carbon monoxide and hydrocarbon reduction.

In the presence of excess oxygen, which air to fuel ratio is higher than stoichiometry (lean condition); NO_X reduction function of TWC is decreased drastically. Therefore, different methods have been developed for NO_X reduction under lean condition.

2.2 NO_X reduction methods in excess oxygen

Several technologies are available for reduction of NOx emissions from vehicle exhaust gases. Each NOx reduction technology is associated with advantages and disadvantages. The three main technologies are briefly described as below.

2.2.1 NOx storage and Reduction (NSR)

In the NO_X storage and reduction method, the engine is operated between lean and rich conditions. Under lean conditions, NO is oxidized to NO_2 over the precious metals and barium is used to store NO_X in the form of nitrates. Under rich conditions, the nitrates are reduced to N_2 by a reducing agent such as HC, CO or H_2 as illustrated in figure 3 [11]. NSR catalyst usually contains precious metals such as Pt, Pd or Rh and a storage component such as barium.

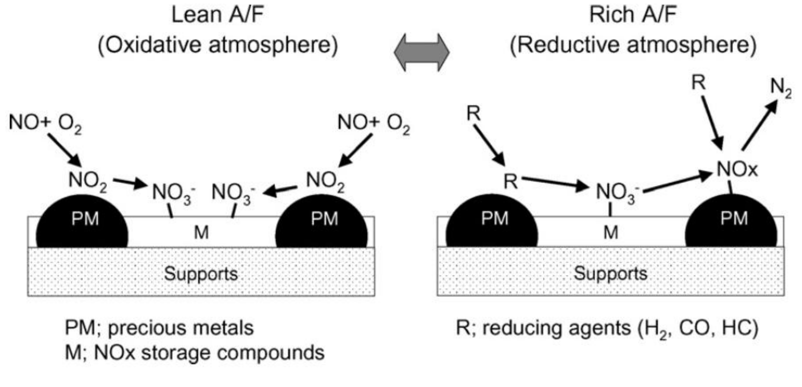


Figure 3. Schematic view of NO_X Storage and Reduction method [11].

2.2.2 Hydrocarbon SCR

Several technologies have been proposed to remove NO_X. The Selective Catalytic Reduction (SCR) is a common and effective technology with the ability of converting NO_X to N_2 by a reducing agent over an active catalyst in the presence of excess oxygen. Reducing gas could be hydrocarbons or ammonia.

Hydrocarbon SCR is one of the remarkable technologies for NO_X emissions control, which uses hydrocarbons as the reducing agent. The following are typical reactions for HC-SCR:

$$(6\mathrm{m}+2)\mathrm{NO}+2\mathrm{C_m}H_{2m+2} \leftrightarrow (3m+1)N_2+2mCO_2+(2m+2)H_2O \tag{2.4}$$

$$6\mathrm{mNO}+2\mathrm{C_m}H_{2m+1}OH \leftrightarrow 3mN_2+2mCO_2+(2m+2)H_2O \tag{2.5}$$

Iwamato et al. and Hamada et al. studied on reduction of NO_X by hydrocarbon SCR in oxidizing atmosphere by Cu/ZSM-5 catalyst [12]. Further studies on Cu/ZSM-5 show that this catalyst is not the proper catalyst for HC-SCR. One of the reasons is deactivation of Cu/ZSM-5, when exposed to sulfur. In addition, it has poor hydrothermal stability in diesel exhaust engines [13, 14]. Later works by Hamada et al. [15] and Obuchi et al. [16] show that platinum group metals are more effective for HC-SCR particularly at low temperature (i.e. 200-350°C). Furthermore, they have high resistance to water and SO_X poisoning and high hydrothermal stability [13, 17]. However, further studies demonstrate that at higher temperature, they have poor selectivity for N_2 formation and they are active in very narrow temperature window for NO reduction due to the oxidation of reducing agent (i.e. hydrocarbon) at high temperature [18].

2.2.3 Ammonia SCR

The selective catalytic reduction of NO_X is also based on a catalyst that can convert NO_X to N_2 with ammonia. Engelhard Corporation patented the method of nitrogen oxides reduction by ammonia selective catalytic reduction in the U.S. in 1957 [19]. The development of this technology aimed mainly at NO_X reduction in stationary application such as boilers, incinerators and power plants [20]. In mobile applications, the ammonia is often replaced by a urea-solution, which decomposes to ammonia at elevated temperatures. This method is very promising and can reduce up to 90% of the NO_X contents. Ammonia is employed due to the high selectivity toward NO_X reduction even under highly oxygen-rich conditions. In this method ammonia used as a reducing agent, can reduce NO_X of excess oxygen conditions in the temperature range 200-450 °C. Ammonia is added to the NO_X containing exhaust gas, which is then absorbed by a catalyst. Over the catalyst, chemical reactions take place to form nitrogen and water, which are released into the atmosphere. The amount that is removed depends on the SCR method that is used and the type of operation it is used with [21]. Using modern selective catalytic reduction methods it is now possible to remove 70 to 95% of the nitrogen oxides that are emitted from the engine.

2.3 NH_3-SCR reactions

A large fraction of the NO_X in exhaust gas is usually in the form of NO [22]. Hence, the main reaction which usually termed the standard SCR reaction, refer to the one between NO and NH_3. Two major desirable reactions for ammonia SCR are;

$$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O \tag{2.6}$$

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \tag{2.7}$$

The reaction (2.6) occurs in the presence of both NO and NO_2 and is called fast SCR reaction since the SCR activity is increased [23].

Apart from the desirable reactions, there are also some undesirable reactions, which can take place simultaneously and compete with the desirable reactions. The undesirable reactions can either produce secondary emissions or, at best, unproductively consume ammonia. Two such side reactions are:

$$4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O \tag{2.8}$$

$$6NH_3 + 8NO_2 \rightarrow 7N_2O + 9H_2O \tag{2.9}$$

$$xNH_3 + yO_2 \rightarrow N_2 + H_2O \tag{2.10}$$

It is possible that only one (or more than one) reaction mechanism occurs during the NO_X reduction. Indeed, the effective factors comprising the reaction mechanisms are the type of the catalyst, operation temperature and feed gas composition.

2.4 Catalysts for NH_3-SCR

There are various types of catalysts for ammonia SCR, which can be classified in three categories: nobel metals, metal oxides and zeolites [24] as illustrated in Figure 4. Although nobel metals such as platinum have high activity at low temperature, they have poor selectivity at high temperature and form N_2O instead of the desired N_2 [25]. On the other hand, metal oxides catalysts have shown good activity in a wide intermediate temperature range. One of the promising catalyst of this category is vanadia supported on titania used for NO_x reduction of stationary sources [26]. Zeolites are active at a broad temperature range to a maximum of 600°C [27].

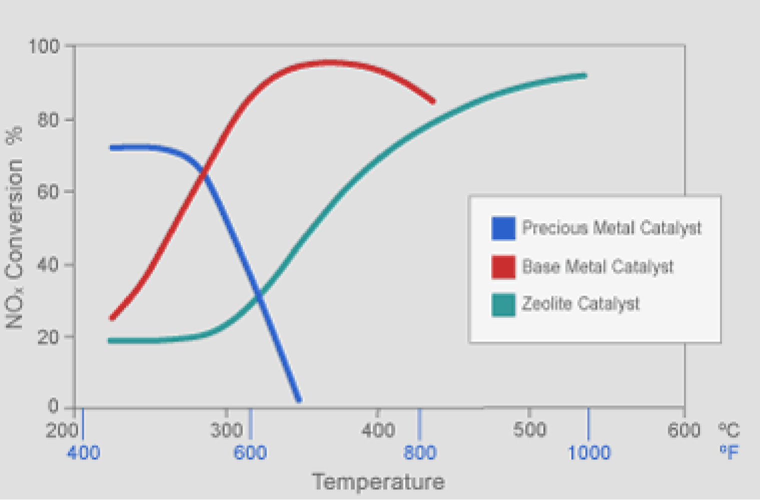


Figure 4. Ammonia SCR catalyst operating window [28].

2.4.1 Silver Alumina catalyst

Silver Alumina is one of the most active catalysts for selective catalytic reduction of NO_X with hydrocarbons (HC-SCR) in diesel engines and lean-burn engines [29]. However, silver-alumina catalyst has some low- temperature activity limitation and the activity decrease at low temperature regions between 150-300°C. It has been shown that the limitation of Ag/Al_2O_3 activity at low temperature is due to both deposition of C-containing species and nitrate (NO_3^+) species [30]. Many studies have been done to improve the limitation of Ag/Al_2O_3 catalyst. It has been shown that, addition of hydrogen into the exhaust gas upstream improve the Ag/Al_2O_3 low temperature HC-SCR activity and prevent catalyst poison accumulation significantly [31-33].

Silver alumina is even active at low temperature for NH_3-SCR but hydrogen is required. Hydrogen addition increases the performance of Ag/Al_2O_3 and dramatically enhances the NO_X conversion over a wide temperature range [34, 35].

2.5 Infrared Spectroscopy

In general, the information from IR absorption is presented in the form of absorption intensity or percent transmittance as function of wavelength or wavenumber.

Transmittance, T, is the fraction of incident light, which is passes through a sample at a specified wavenumber. In other word, it is the ratio of the intensity of light coming out of the sample, I, (transmitted light intensity) to the intensity of entered light, I_0.

$$T = \frac{I}{I_0} \tag{2.11}$$

Absorbance, A, is the logarithmic measurement of the absorbed light as light passes through the sample at a specified wavenumber. Two important factors influencing absorbance in a sample are the thickness of the sample and the concentration of the absorbing species in the sample [36].

$$A = \log_{10}(\frac{1}{T}) = -\log_{10} T = -\log_{10}(\frac{I}{I_0}) \qquad (2.12)$$

2.5.1 Theory of IR Absorbance

At a temperature above zero, atoms of a molecule vibrate continuously and the molecule can absorb the radiation if the frequency of a specific vibration is equal to the frequency of the IR radiation oriented to the molecule [36]. The absorbed frequencies are specific to the structure of the absorbing molecule and can therefore be used for identification.

2.6 In Situ DRIFTS Study

Transmission infrared spectroscopy is a suitable technique, which is used for quantitative measurements and gives information about the type and the amount of the species adsorbed on the surface of the catalyst. However, this technique is unable to analyze some samples due to the lack of mechanical strength and/or transmission [37, 38].

In situ diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy is another powerful tool to investigate the surface species involved in NO_X reduction. DRIFTS was used as early as 1913 by Coblentz for IR analysis [39].

DRIFT Spectroscopy has shown to be more sensitive to surface species than transmission measurements. It assists to circumvent the above obstacles and can analyze samples under reactive atmosphere without internal mass transport limitations. DRIFT spectroscopy has its own advantages and disadvantages like any other technique. One of the main advantages of DRIFTS is that it is able to obtain infrared spectra of solid materials without cumbersome sample preparation. In addition, it is a powerful tool to analyze the changes in the species on the sample surface and to record the spectrum of the powder at elevated temperature and/or under pressure.

On the other hand, it is difficult to evaluate the obtained spectra from DRIFTS due to its high sensitivity to different operation conditions such as temperature, preparation method, etc. For instance, each preparation methods influence the diffusion coefficient and can cause difficulties to compare two spectra of the same material recorded in two different experiments. Another drawback of this technique refers to the temperature gradient, which exists between the upper edge and bottom of the crucible containing the catalyst. It should be mentioned that in DRIFTS measurements, the infrared radiation can only detect the sample surface and it is unable to assess the whole thickness of the catalytic bed. Therefore, the reactivity observed by changes in the species band on the surface might be different from the one obtained by analyzing the presence gases in the cell. Consequently, results from DRIFT spectrometer are insufficient and the gases leaving the DRIFTS cell should be analyzed either by infrared analysis or by mass spectrometry to prove the results [40]. Figure 5, shows a schematic view of in situ DRIFT spectroscopy cell.

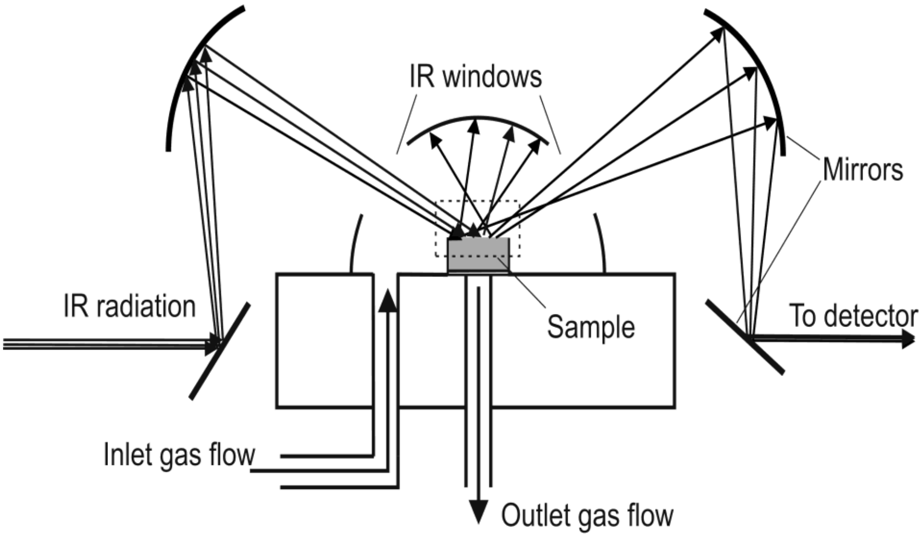


Figure 5. Set-up of the DRIFT instrument.

As can be seen in figure 5, the IR radiation beam enters the DRIFTS cell and is focused by a spherical mirror on the surface of the sample placed inside a sample holder. Another mirror collects the diffuse radiation generated by the sample and directs it to the detector. The gases get in from the top of the sample and pass downward through the sample bed, as shown in figure 6. Two windows (KBr) allow IR transmission and the third (Quartz) can be used for optical inspection (Figure 6).

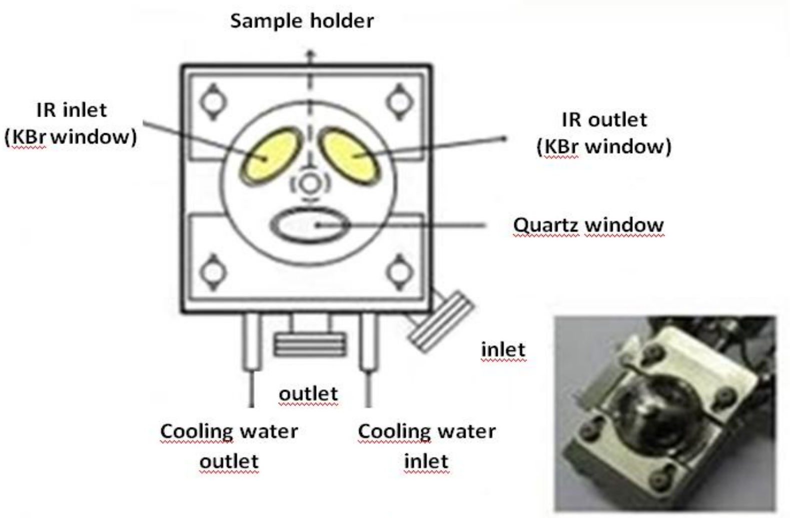


Figure 6. Photo and schematic set-up of the Praying Mantis™ DRIFT cell by Harrick used in the study.

3. Experimental

3.1 Catalyst Preparation

$AgNO_3$ (VWR, GPR RECTAPUR) and AgO (Riedel-de Haën AG) was used as received. A mixture of Al_2O_3 (SASOL Puralox SBa-200) and $AgNO_3$ with 20 wt% Ag loading was used as a model for Ag/Al_2O_3 catalyst. To prepare that, 28.25 wt% $AgNO_3$ powder and 71.75 wt% alumina powder (Appendix 1) were mixed by mortar and pestle to get an even and well-mixed powder.

In this project, different gases (NO, NH_3, H_2 and O_2) were used to assess the effect of gas composition on the reduction of silver nitrate.

3.2 DRIFTS experiments

In-situ DRIFT spectroscopy 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 mass spectrometry (Balzers QuadStar 420). In each experiment, the temperature is increased to 100°C with the ramp speed of 10°C/min in Ar and is kept unchanged for 20 minutes. Background spectrum is taken 4 minutes before adding the gases. For the background spectra 60 scans were added to reduce the noise. Afterward, the first gas mixtures are exposed to the sample. It should be noted that a contineous DRIFT measurment started 1 minute before gases were added. The spectra are scanned every 30 sec. Thus, a total of 120 scans were recorded, during a period of up to 60 min, over the spectral range 700–4000 cm^{-1} at a resolution of 2 cm^{-1}.

The background spectra were collected at the same temperature as the DRIFT sample spectra and they were automatically subtracted from the sample spectra.

The concentration of gases introduced to the DRIFT cell were 500ppm NO, 500ppm NH_3, 1250ppm H_2 and 10% O_2. The total flow rate in all of the DRIFTS experiments was 100 ml/min.

In-situ DRIFTS experiments are carried out in a BIO-RAD FTS 6000. Mass flow controllers (Bronkhorst Hi-Tech) are used to introduce the gases to the DRIFTS cell.

3.3 Experimenting different temperature on $AgNO_3$ in only Argon

The stability of $AgNO_3$ at 20°C, 40°C, 60°C and 100 °C was examined in the presence of only argon to figure out which temperature is suitable for silver nitrate to be stable. After finding the right temperature, the experiments were continued by evaluating the effect of gases on the activity of catalyst.

To avoid sticking of $AgNO_3$ to the cell's wall due to heating, the cell was covered by aluminum foil to remove the treated sample easily.

After putting the sample ($AgNO_3$ powder) in the DRIFT cell, Argon gas was flushed to the cell and temperature was increased to 20°C and was kept for 1 hour. As the next experiment, the temperature was increased to 40°C with the ramp speed of 4°C/min and was kept at that temperature for 1 hour (in only Argon). It should be noted that the background is taken before increasing the temperature. In the third experiment, Argon was flushed to the cell and the temperature was increased to 60°C with the ramp speed of 10°C/min and was kept there for 90 minutes. In forth experiment, after flushing Ar to the system, the temperature was increased to 100°C with the ramp speed of 10°C/min and was kept there for 90 minutes.

3.4 Experimenting different gas mixtures on $AgNO_3$ at 100°C

To study the effect of different gas mixtures on the decomposition of $AgNO_3$ eight experiments were performed as shown in table 1.

Exp.	Step 1	Time	Step 2	Time	Temp.
1	$NH_3 + O_2$	20 min	$NO + H_2$	20 min	100°C
2	NH_3	20 min	$NO + H_2 + O_2$	20 min	100°C
3	$NH_3 + O_2 + H_2$	20 min	NO	20 min	100°C
4	$NH_3 + O_2 + NO$	20 min	H_2	20 min	100°C
5	$NO + O_2$	20 min	$NH_3 + H_2$	20 min	100°C
6	$NO + O_2 + H_2$	20 min	NH_3	20 min	100°C
7	$H_2 + O_2$	20 min	$NH_3 + NO$	20 min	100°C
8	$NH_3 + NO + H_2 + O_2$	20 min	-	-	100°C

Table 1. Experiment with $AgNO_3$ at 100°C.

In each experiment, the sample was located in the DRIFT cell and Argon was flushed over the sample's surface. As it can be seen in Figure 7, temperature is increased to 100°C with the ramp speed of 10°C/min and is kept unchanged for 20 minutes. Afterward, the first gas mixtures were exposed to the sample. It should be highlighted that the background was taken 4 minutes before adding the gases. Next, the rest gas mixtures were added and after 20 minutes all gases -except argon- were removed from the DRIFTS.

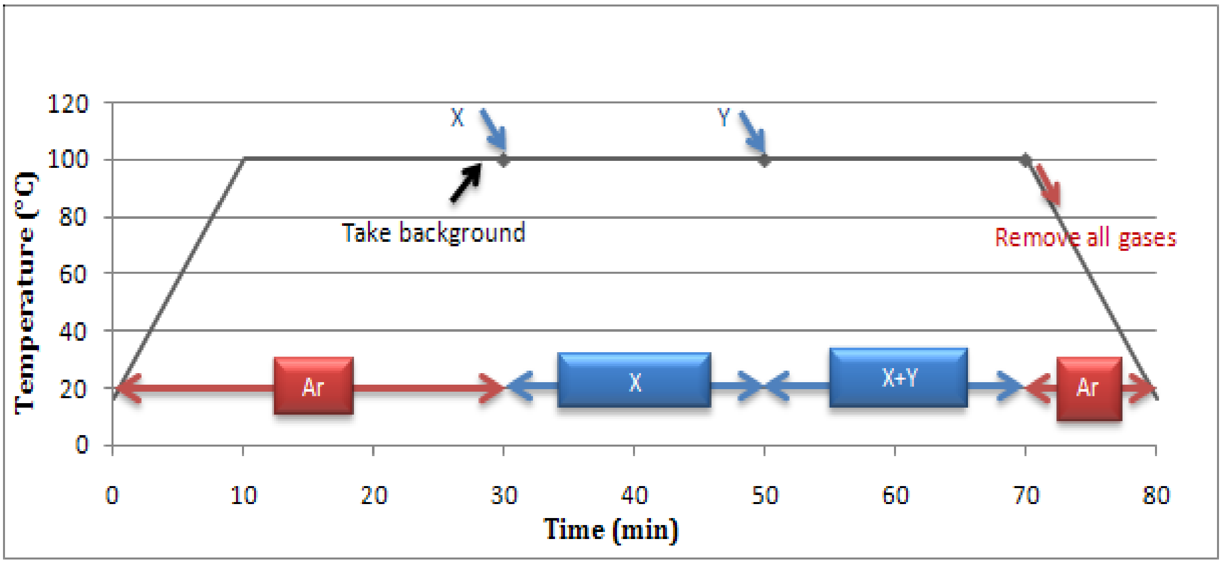


Figure 7. Different experiments in DRIFT Spectroscopy; X is the gas mixtures of step 1 and Y is the gas mixtures of step 2.

3.5 Experimenting different gas mixtures on $AgNO_3/Al_2O_3$ at 100°C

The same experiments were done on the silver nitrate alumina to see what will happen on the alumina at the same time. In this case eight experiments were performed with different gas compositions (Table 1). In each step the temperature was increased to 100°C in an argon flow with the ramp rate of 10 °C min^{-1} and remained for 20 minutes. Afterward gas component are exposed to the surface of the catalyst and after 20 minutes the further gases are introduced.

4. Results and discussions

4.1 Decomposition of $AgNO_3$

There is a big debate in the literature that hydrogen can reduce nitrates on Ag/Al_2O_3. In this study, the purpose is further investigation of this issue and considering what happen with the silver nitrate.

Generally, when Ag/Al_2O_3 is used as a catalyst, silver nitrate will be formed on silver particles during the reaction and will eventually block them and decrease the performance of the catalyst. To overcome the blocking problem, decomposition of $AgNO_3$ was examined to see how silver nitrate decompose and if this goes much faster in certain gas compositions than in others.

4.2 Test the stability of $AgNO_3$ at 20°C, 40°C, 60°C and 100°C

In order to study the $AgNO_3$ it is required to find the most appropriate temperature. As mentioned before, to investigate the optimum temperature for decomposition of $AgNO_3$ as a function of gas composition, four different temperatures were examined. The purpose was to find the highest temperature at which $AgNO_3$ is stable in order to compare the reaction conditions. The results from experiments on $AgNO_3$ at 20°C, 40°C and 60°C in only argon show that these temperatures are not suitable for decomposition of $AgNO_3$ since they are too low and there is no changes at mentioned temperatures. Therefore, 100°C is taken for $AgNO_3$ decomposition due to the stability of sample at this temperature and it is high enough for the reaction condition. In general, the maximum activity of Ag/Al_2O_3 for NO_X reduction occurs between 150 and 500°C. It should be noted, that the melting point of $AgNO_3$ is 212°C and it decomposes while heated above 100°C and it is quite stable in temperature below 100°C.

4.3 Conversion of silver nitrate to silver oxide

When all the gases are present on the sample, many peaks can be observed in the spectra. Although some of them might be due to the absorption of ammonia, most of them are due to the silver nitrate, which disappeared and probably converted to silver oxide. It is expected that silver nitrate is reduced and silver oxide is likely to be formed during the decomposition of $AgNO_3$. The background spectrum contains all the structural information of the material, which is used in the DRIFT spectroscopy. Therefore, to verify whether silver oxide is formed, a background of silver oxide is subtracted from the background of $AgNO_3$ and compared to a spectra formed during the reaction. The spectra are shown in figure 8:

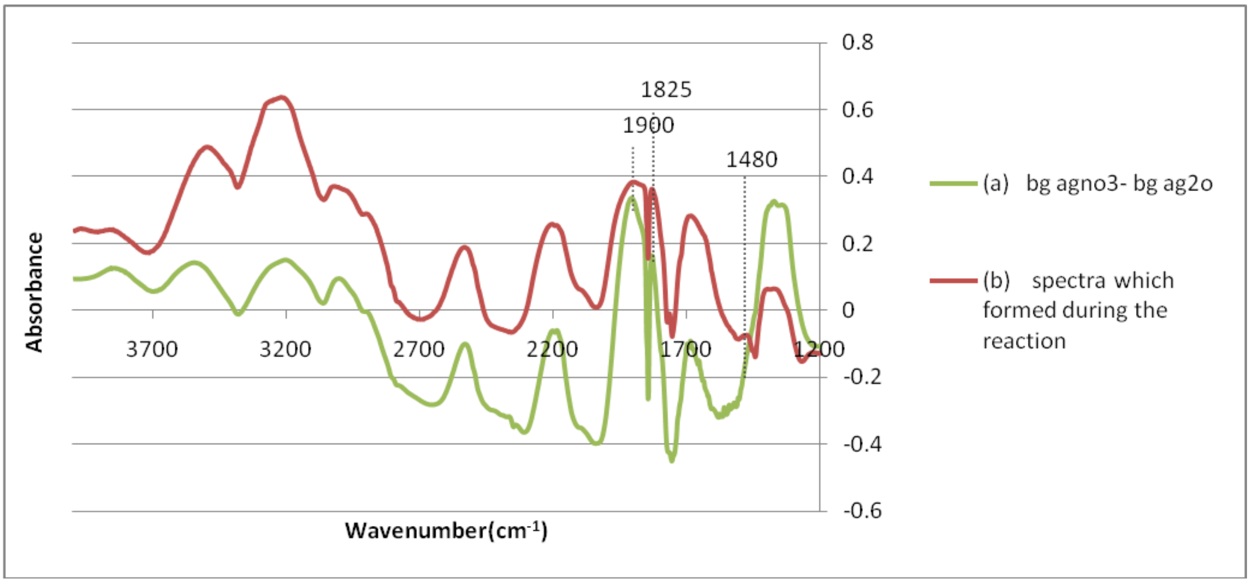


Figure 8. Comparison of a spectrum obtaind by subtraction of a background of $AgNO_3$ from a background of AgO (a) and a spectrum taken in the presence of 500 ppm NO, 500 ppm NH_3, 1250 ppm H_2 and 10% O_2 in Ar over the $AgNO_3$ sample (b) - 100°C

As can be seen in figure 8, the spectra are very similar but from totally different experiments. On the one hand the normal experiment and on the other hand a simulated spectra, obtained by subtraction of one background from another. It illustrates that silver nitrate is converted to silver oxide, since under a normal run over a $AgNO_3$ sample the background is taken on $AgNO_3$. This background later is subtracted from the spectra obtained by the reduced sample. Another evidence to the silver oxide formation is the color of sample after treatment. The color of $AgNO_3$ powder is white and the color of silver oxide is dark gray or black. Since the sample goes to gray color after decomposing, it can be concluded that silver oxide is formed.

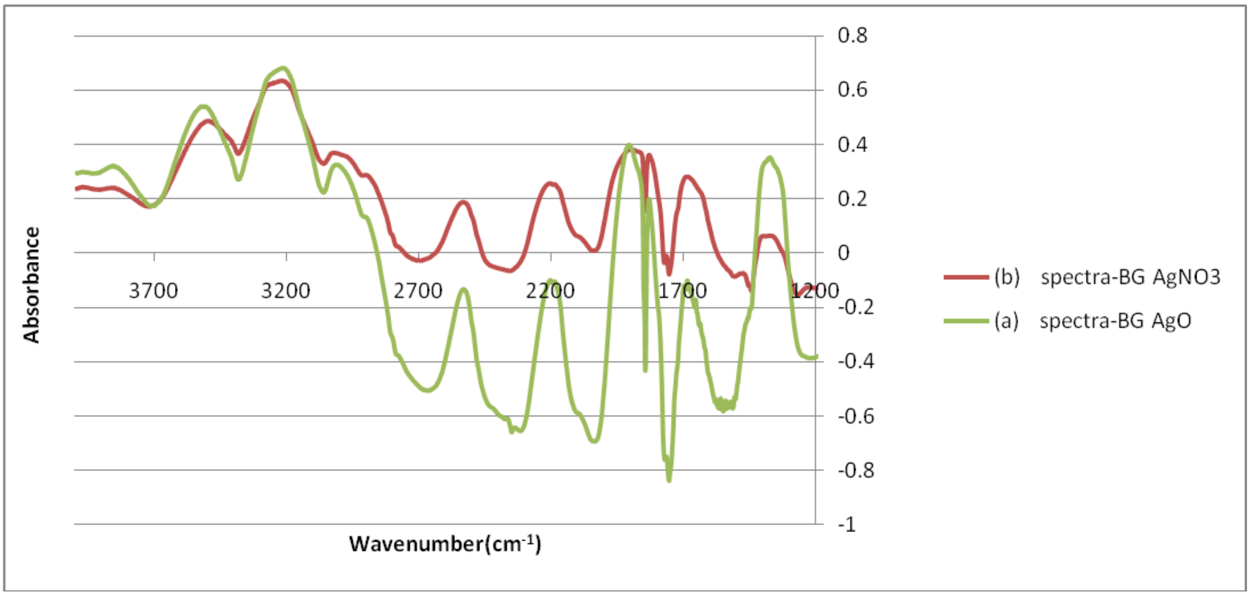
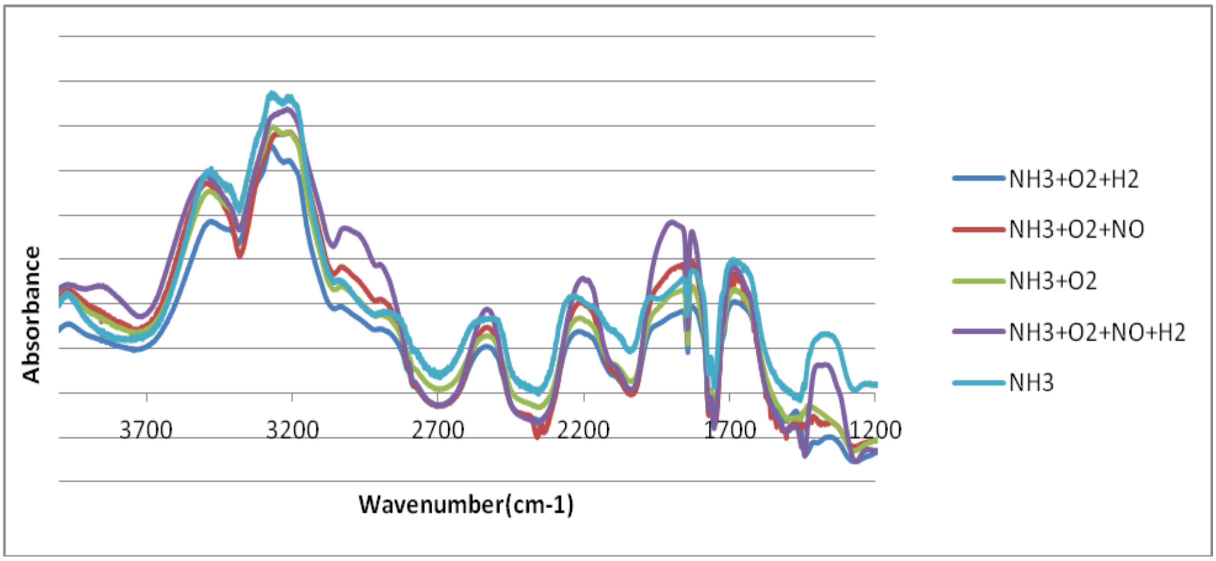


Figure 9. Subtraction of the background of $AgNO_3$ (a) and AgO (b) from sample spectra of all gases together -100°C (Replacing the background of silver oxide with the background of $AgNO_3$).

4.4 Introducing gas components to $AgNO_3$ at 100°C

To investigate the effect of different gases on the decomposition of $AgNO_3$, eight different experiments with different gas components were carried out at 100°C, which are shown in the figure 10.



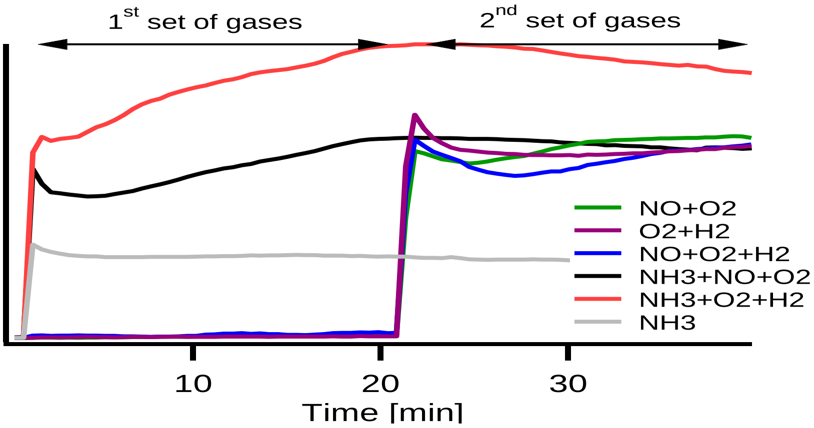


Figure 10. $AgNO_3$ exposed to a feed gas containing different mixture of NH_3,NO,O_2, H_2 after 30 min at 100°C.

In the presence of all gases together at the same time (NH_3+O_2+NO+H_2) the bigest changes in the spectra happened as shown clearly in figure 10. These big changes in the spectra can either indicate that more species were adsorbed on the surface of silver alumina or that $AgNO_3$ is decomposed faster.

It should be mentioned that no changes were observed in the spectra when the sample was exposed to the below gas mixtures:

1- H_2+O_2 (for 20 min-100°C)

2- NO+O_2 (for 20 min-100°C)

3- NO+H_2+O_2 (for 20 min-100°C)

The background of silver nitrate is taken in the beginning and all the nitrates that is available in the sample is subtracted away. Therefore it is not possible to see any nitrate and when NO and O_2 are introduced over the sample no additional nitrate is formed since it is already exist in the sample. By comparing the observations from different gas mixtures, it can be concluded that ammonia is the gas which is needed to convert the silver nitrate and the decomposition does not happen in the absence of NH_3; while other components (NO, O_2 and H_2) do not have significant effect on the decomposition of silver nitrate.

4.4.1 The effect of H_2, NO and O_2

As it can be seen in figure 11, both H_2 and NO slightly increased silver nitrate decomposition.

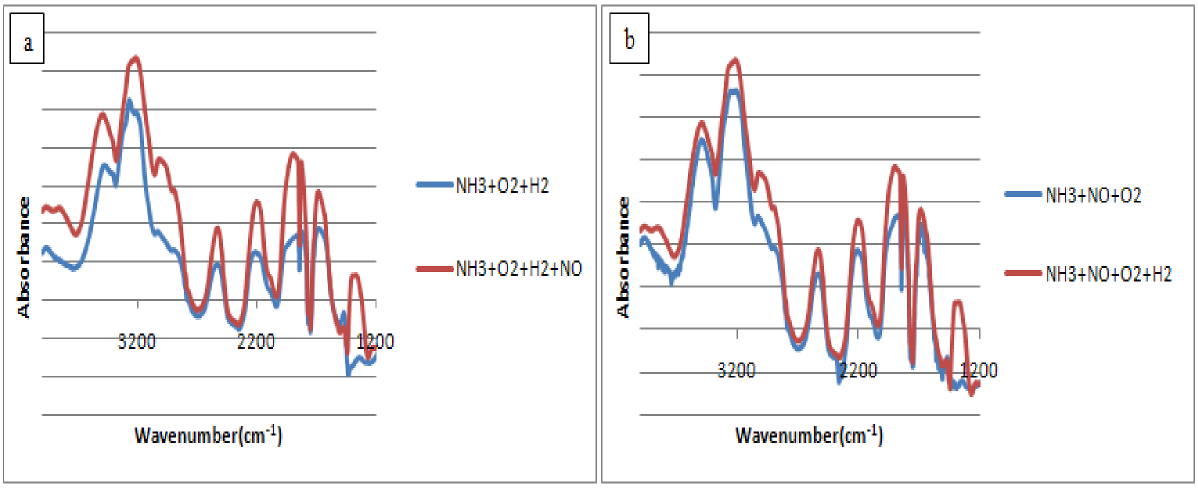


Figure 11. $AgNO_3$ exposed to NH_3+H_2+O_2 for 20 min (blue) and to NH_3+NO+O_2+H_2 for 20 min (red) at 100°C (a), $AgNO_3$ exposed to NH_3+NO+O_2 for 20 min (blue) and to NH_3+NO+O_2+H_2 for 20 min (red) at 100°C (b).

Figure 12 shows three different gas mixtures over $AgNO_3$ at 100°C. It can be seen that addition of O_2 does not clearly accelerate $AgNO_3$ decomposition.

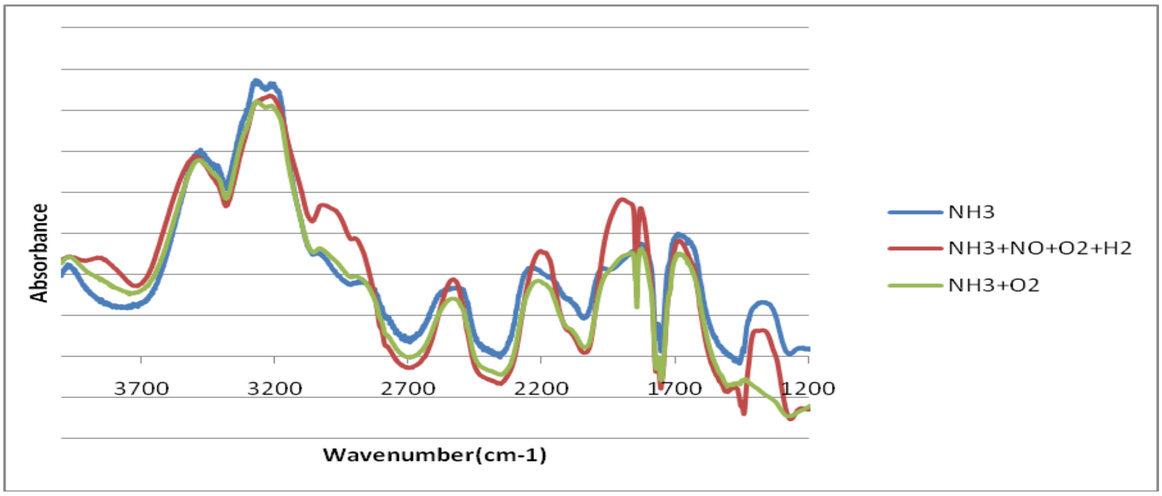


Figure 12. $AgNO_3$ exposed to NH_3 for 20 min (a), to NH_3+NO+O_2+H_2 for 20 min (b) and to NH_3+ O_2 for 20 min (c) at 100°C.

4.5 Results from mass spectrometry

As mentioned in section 2.6, analyzing the results from the mass spectrometer could be helpful and can be used as a complementary tool to investigate the effect of different gases on NO_X reduction.

Formation of N_2 is an evidence for NO_X reduction. However, detection of N_2 could be due to another reason, which is the leakage of air into the pipe of system. Figure 13 shows the formation of N_2 during the introducing of different gas components to the surface of $AgNO_3$.

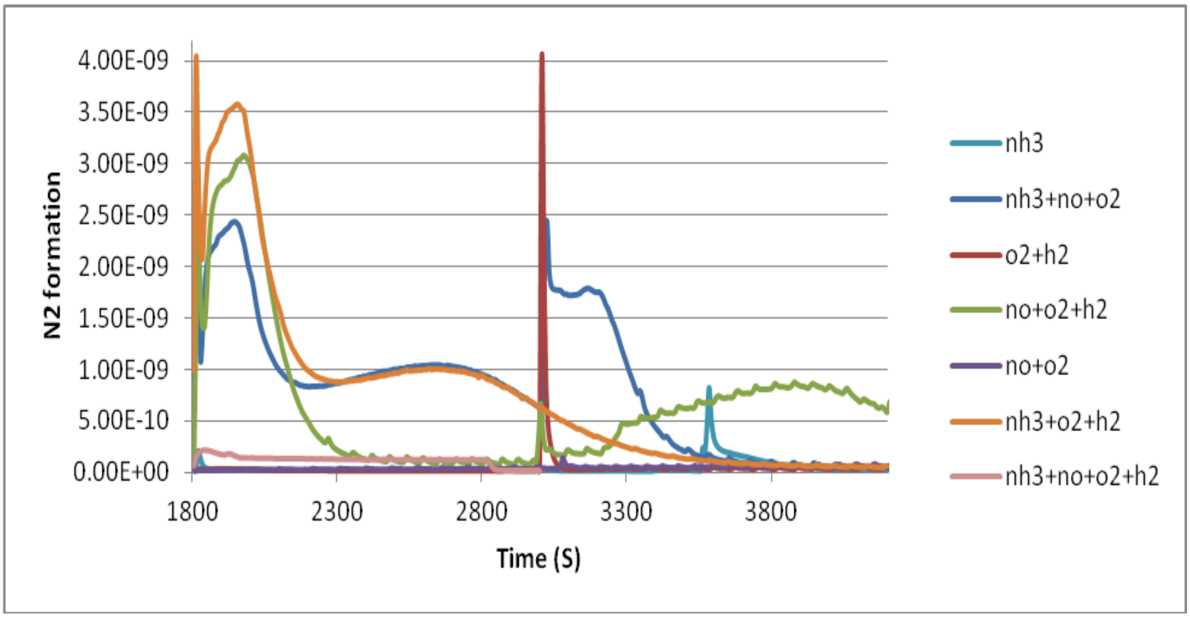


Figure 13. Effect of different gases on formation of N_2 by $AgNO_3$ at 100°C- Mass Spectrometry results.

As mentioned before, presence of NH_3 is essential to decompose $AgNO_3$. It is obvious from the mass spectrometer figure that NH_3 is a main factor to reduce nitrate and N_2 is formed by the gas mixtures consisted of ammonia. However, formation of N_2 is less when there is only ammonia in the system. In the presence of only ammonia, there is a fast change in the beginning and then it becomes stable. It means that when ammonia is introduced, some N_2 is formed immediately and then the surface of the sample is poisoned and it becomes stable.

It should be noted that the large peaks in the beginning of three gas mixtures ($NH_3+O_2+H_2$, $NO+O_2+H_2$ and NH_3+NO+O_2) are due to the leakage of air into the pipe of system. Since, these are the first experiments of the day and air comes into the pipe during the night. In addition, 3000s is the time when the rest gases are added to the system. In the gas mixture with H_2+O_2 the large peak around 3000s is not due to the formation of N_2 but it is due to the N_2 leakage since it is the first experiment of the day

The gas mixtures are separated in two categories as following. One category is belonging to the gas mixtures, which are inert in the beginning, and another one are gas mixtures that cause changes both in the gas phase (Figure 13) and on the sample surface (Figure 10) in the beginning.

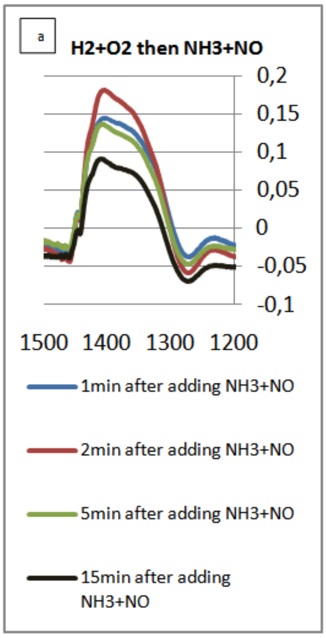
Inert in the beginning	Cause changes in the beginning
H_2+O_2	NH_3
$NO+O_2$	NH_3+O_2
$NO+O_2+H_2$	$NH_3+O_2+H_2$
	NH_3+O_2+NO
	$NH_3+NO+O_2+H_2$

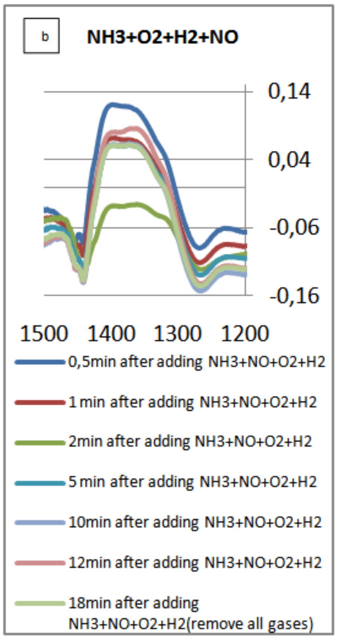
Table 2. Two different categories of gas mixtures according to their behavior in the beginning of introducing to the system.

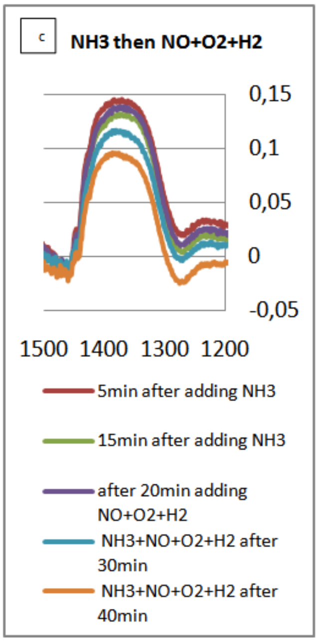
As mentioned before, three gas mixtures (H_2+O_2, $NO+O_2$ and $NO+O_2+H_2$) have no effect on decomposition of $AgNO_3$ and they are inert in the beginning. On the other hand, five gas mixtures (NH_3, NH_3+O_2, $NH_3+O_2+H_2$, NH_3+O_2+NO, $NH_3+NO+O_2+H_2$) shown in table 2 cause changes immediately in the beginning and decompose $AgNO_3$. This issue can be seen from the mass spectrometer as well. N_2 is formed from the gas mixtures that can decompose $AgNO_3$ (included of NH_3) and cause changes on the sample surface in the beginning.

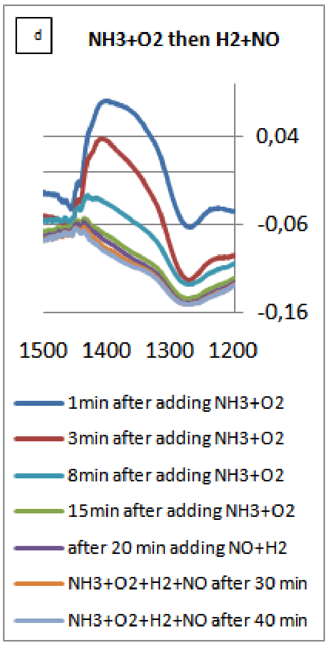
4.6 Different trend of spectra around 1400cm^{-1}

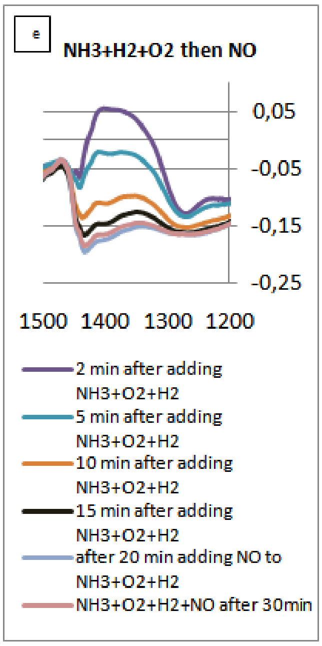
In figure 10, it can be observed that the gas mixtures, which contain NH_3, can decompose $AgNO_3$. The biggest difference between the spectra of different gas mixtures is observed in the region around 1400 cm^{-1} and the rest is almost stable. For further investigation, this region is focused for each gas mixtues in different times.

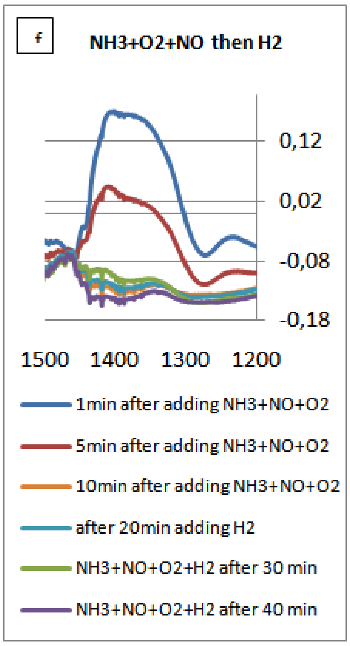

a
H2+O2 then NH3+NO
0,2
0,15
0,1
0,05
0
-0,05
-0,1
1500 1400 1300 1200
1min after adding NH3+NO
2min after adding NH3+NO
5min after adding NH3+NO
15min after adding NH3+NO


b
NH3+O2+H2+NO
0,14
0,04
-0,06
-0,16
1500 1400 1300 1200
0,5min after adding NH3+NO+O2+H2
1 min after adding NH3+NO+O2+H2
2min after adding NH3+NO+O2+H2
5 min after adding NH3+NO+O2+H2
10min after adding NH3+NO+O2+H2
12min after adding NH3+NO+O2+H2
18min after adding NH3+NO+O2+H2(remove all gases)


c
NH3 then NO+O2+H2
0,15
0,1
0,05
0
-0,05
1500 1400 1300 1200
5min after adding NH3
15min after adding NH3
after 20min adding NO+O2+H2
NH3+NO+O2+H2 after 30min
NH3+NO+O2+H2 after 40min


d
NH3+O2 then H2+NO
0,04
-0,06
-0,16
1500 1400 1300 1200
1min after adding NH3+O2
3min after adding NH3+O2
8min after adding NH3+O2
15min after adding NH3+O2
after 20 min adding NO+H2
NH3+O2+H2+NO after 30 min
NH3+O2+H2+NO after 40 min


e
NH3+H2+O2 then NO
0,05
-0,05
-0,15
-0,25
1500 1400 1300 1200
2 min after adding NH3+O2+H2
5 min after adding NH3+O2+H2
10 min after adding NH3+O2+H2
15 min after adding NH3+O2+H2
after 20 min adding NO to NH3+O2+H2
NH3+O2+H2+NO after 30min


f
NH3+O2+NO then H2
0,12
0,02
-0,08
-0,18
1500 1400 1300 1200
1min after adding NH3+NO+O2
5min after adding NH3+NO+O2
10min after adding NH3+NO+O2
after 20min adding H2
NH3+NO+O2+H2 after 30 min
NH3+NO+O2+H2 after 40 min

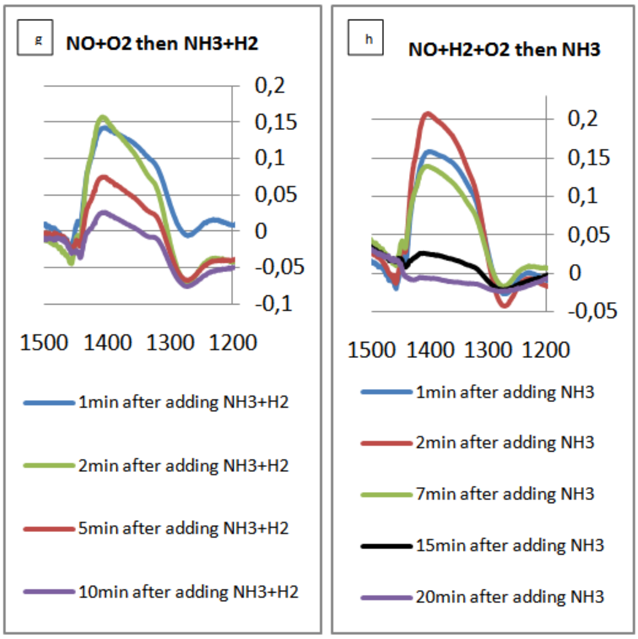


Figure 14. $AgNO_3$ exposed to a feed gas containing different mixture of NH_3,NO,O_2, H_2 after 40 min at 100°C ,Wavenumber between 1200-1500 cm^{-1}

It can be seen from figure 14 that in some of the gas mixtures, the spectra are quite stable and in some of them, they change a lot. Plots a, b and c which are correspond to the gas components as below:

a : H_2+O_2 then NH_3+NO

b : NH_3+NO+O_2+H_2

c : NH_3 then NO+O_2+H_2

shown that these gas mixtures do not cause any changes on the sample surface during the time and it can be seen from mass spectrometer as well (Figure 15).

On the other hand, in figure 14, the plots d, e, f, g and h which are changing during the time, have the same behavior in mass spectrometry in figure 13. Only the changes of spectra correspond to NO+O_2 is not clear in figure 13 and if that spectra is focused the changes become obvious:

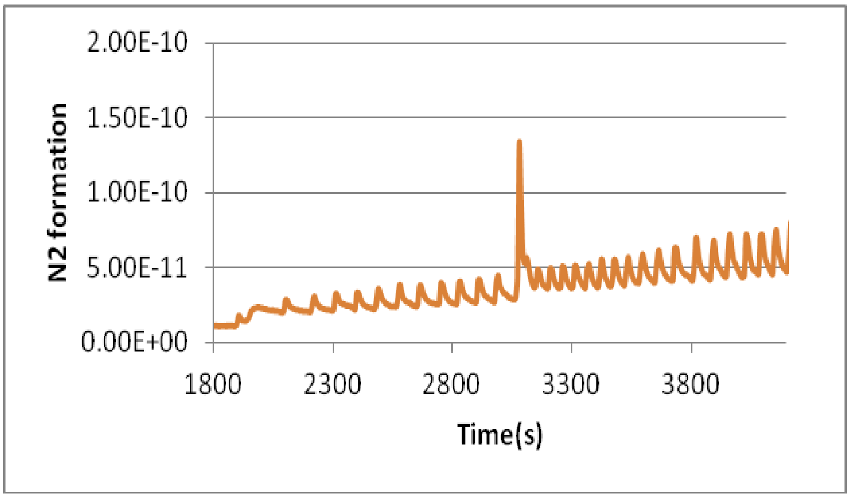


Figure 15. Effect of NO+O_2 on formation of N_2 by $AgNO_3$ at 100°C- Mass Spectrometry results.

It can be concluded that at the beginning we have silver nitrate powder and when it is exposed to ammonia, silver oxide is formed which is a powder as well. However, as can be seen in the Figure 14, different gases shows different behavior around region 1400 cm^{-1}. In other words, in this region, some of the gasses maintain a constant trend but in some of them there is a drop in the bands. A possible explaination to the change in the region between 1500 and 1300 cm^{-1} is that nitrates are adsorbed on the surface of silver oxide. This phenomena can be explained using the fact that nitrates have high absorption rates in this wavenumber. These adsorbed nitrates could give similar adsorbtion bands in the obsered region as silver nitrate.

To further investigation of our hypothesis, another experiment is carried out. In this experiment, a sample of silver oxide is used which is exposed to three different gas mixtures (NH_3+O_2, NO+O_2 and NO+O_2+H_2). The goal of this experiment is to provide similar condition as the previous experiment to see how the spectrum changes when nitrates are formed on silver oxide.

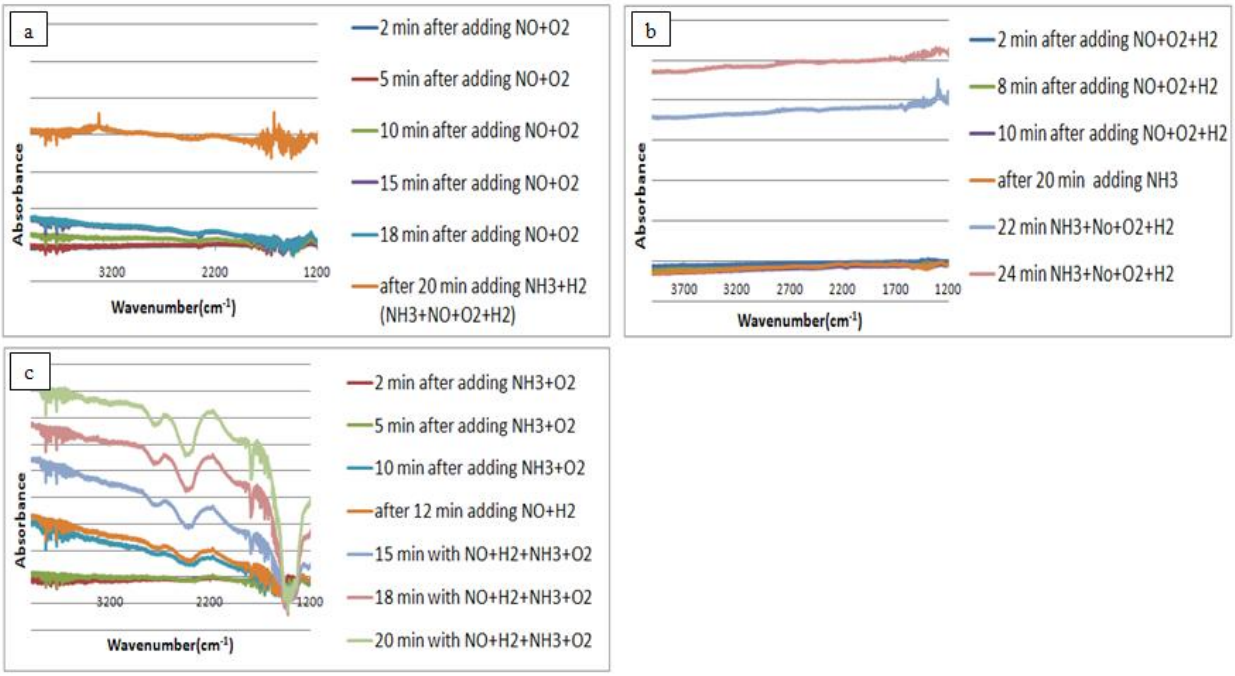


Figure 16. Silvernitrate exposed to NO+O_2 (a), NO+O_2+H_2 (b) and NH_3+O_2 (c) at 100°C.

As it mentioned earlier and is clear from figure 16, (a) and (b) when NO+O_2 and NO+O_2+H_2 are added to silver oxide, the spectra maintain a constant trend, that is no changes occur which means no nitrate formation is observed. However, when NH_3 is added to the gas mixtures, some jumps are observed in the spectra. In figure 16 (c) Changes is spectra are the same as in figure 14. However, for further investigation XPS can be used.

4.7 DRIFT experiments with $AgNO_3/Al_2O_3$ at 100°C

4.7.1 DRIFT study of ammonia and nitrate adsorption

In figure 17, H_2+O_2 were introduced to the DRIFT cell and after 20 min NH_3 and NO were added. In figure 18 and 19. NO+O_2 and NO+O_2+H_2 were introduced to the system, respectively, and after 20 min the rest of gases were added. As shown in figure 17, 18 and 19, there are only small changes before adding ammonia to the gas mixture. Thus the presence of ammonia is necessary for observing gas species on the catalyst surface.

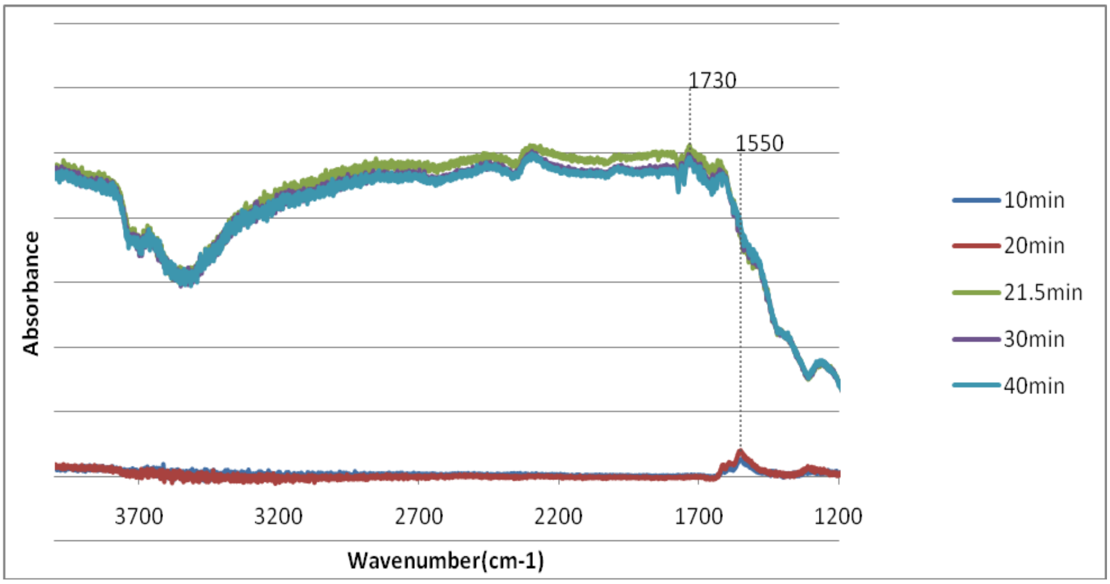


Figure 17. $AgNO_3/Al_2O_3$ exposed to H_2+O_2 for 20 min and followed by introduction of NH_3+NO for 20 min at 100°C.

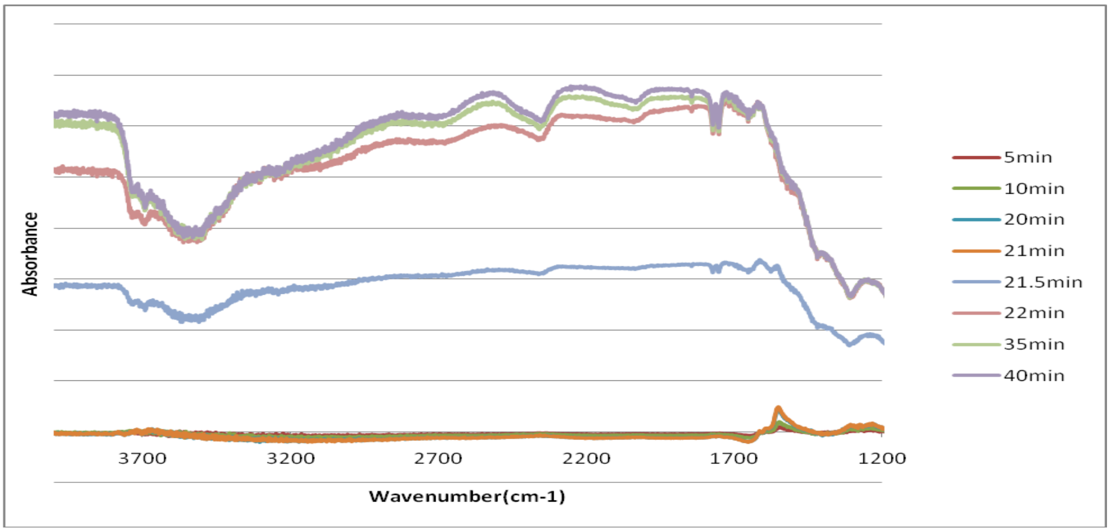


Figure 18. $AgNO_3/Al_2O_3$ exposed to $NO+O_2$ for 20 min and followed by introduction of NH_3+H_2 for 20 min at 100°C.

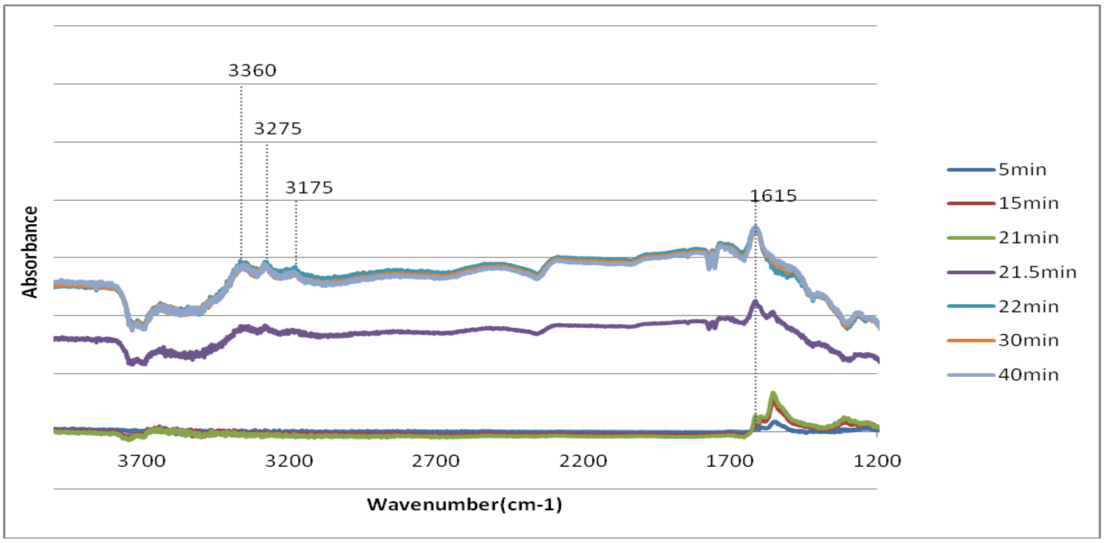


Figure 19. $AgNO_3/Al_2O_3$ exposed to $NO+O_2+H_2$ for 20 min and followed by introduction of NH_3 for 20 min at 100°C.

In figure 19, the band observed at 1615 cm^{-1} is assigned to asymmetric deformation modes of NH_3 coordinated on lewis acid sites [41]. Moreover, the adsorption bands at 3175, 3275 and 3360 cm^{-1} is due to adsorbed NH_X species [42] and nitrates at 1615 cm^{-1}.

As it is mentioned before NO, O_2 and H_2 could not decompose silver nitrate in the absence of ammonia. In the presence of NH_3, decomposition of $AgNO_3$ starts as indicated by the bands at 1730 cm^{-1}.

The small bands observed around 1550 cm^{-1} are due to nitrates and/or nitrites on Al_2O_3 [42]. This means that the nitrates migrate from the $AgNO_3$ to the Al_2O_3 in the presence of $H_2+ O_2$. To ensure that the migration of nitrate from the $AgNO_3$ to the Al_2O_3 is due to the presence of $H_2+ O_2$, similar experiment is carried out in the absence of mentioned gases and in presence of only argon. As can be seen in figure 20 and 21, the experiment result shows that the migration takes place even in the absence of $H_2+ O_2$ but the migration rate will increase dramatically in the presence of mentioned gases.

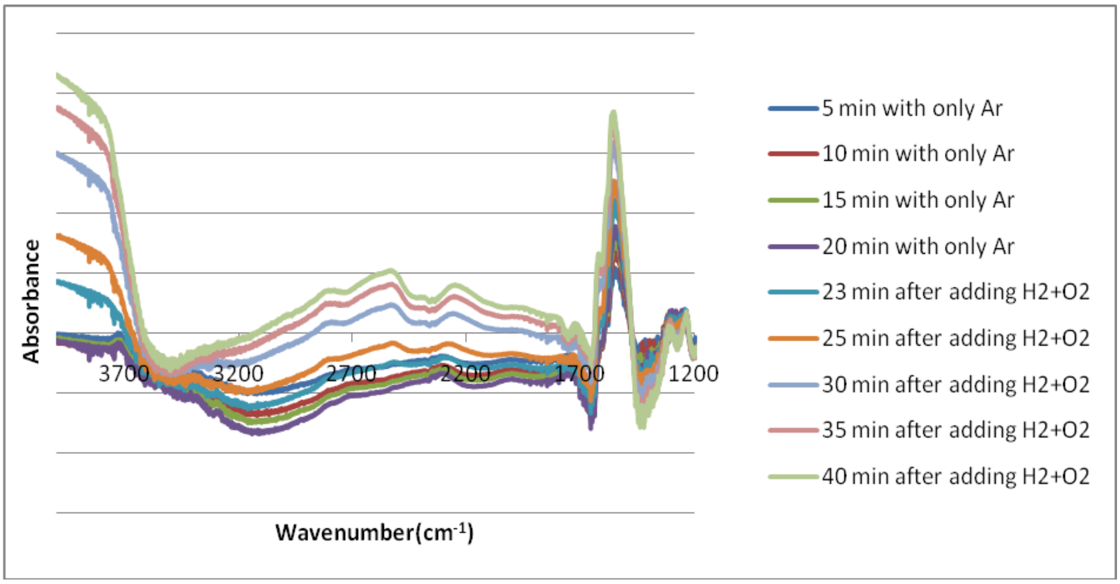


Figure 20. $AgNO_3/Al_2O_3$ exposed to NH_3,NO,O_2 and H_2 for 20 min at 100°C.

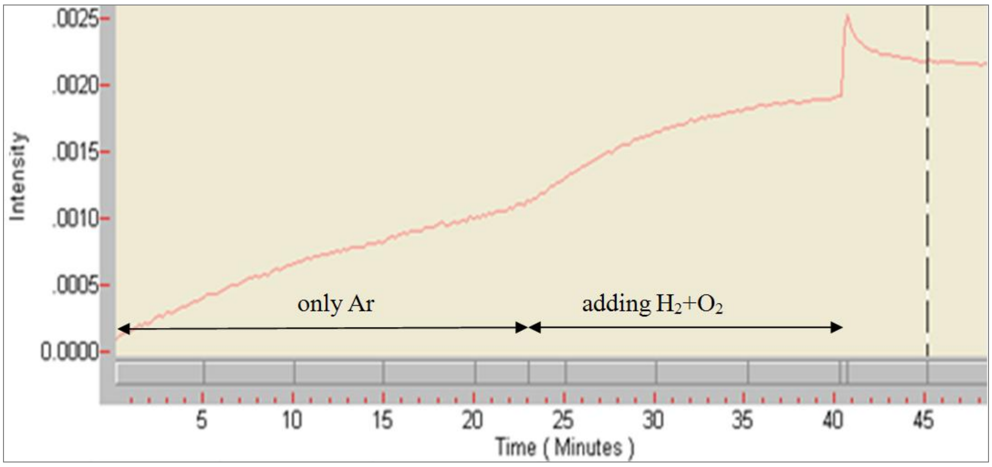


Figure 21. $AgNO_3/Al_2O_3$ exposed to NH_3,NO,O_2 and H_2 for 20 min at 100°C.

In figure 22 the bands observed at 1265 and 1615 cm^{-1} are assigned to symmetric and asymmetric deformation modes of NH_3 coordinated on lewis acid sites respectively [41]. The negative bands at 1750 and 1775 cm^{-1} are attributed to the reduction of silver nitrate to silver oxide and the band at 2300 cm^{-1} is due to adsorbed N_2O species [43]. The bands at 3180, 3280 and 3360 cm^{-1} are assigned to N-H stretching on Al_2O_3 [42]which disapear when the other gases are introduced to the ammonia. The broad negative band centred at 3550 cm^{-1} and 3720 cm^{-1} is assigned to O-H stretching [42].

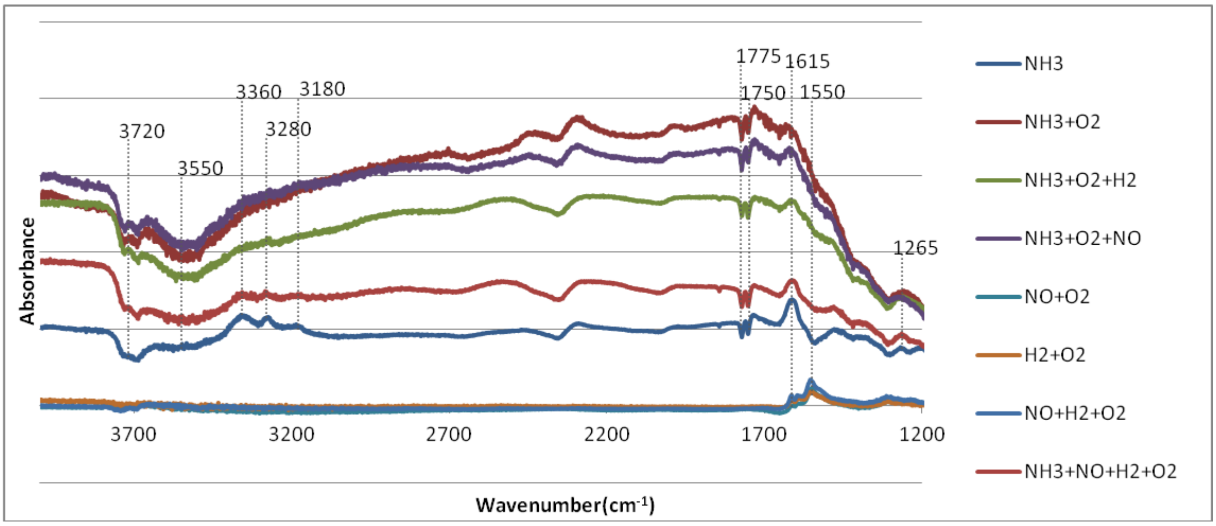


Figure 22. $AgNO_3/Al_2O_3$ exposed to NH_3,NO,O_2 and H_2 for 20 min at 100°C.

5. Conclusions

This report has discussed the reduction of $AgNO_3$ as a component in the selective catalytic reduction of NO by NH_3 as a reducing agent promoted by hydrogen over alumina supported silver catalyst. We performed a series of experiments in order to investigate the effect of the different gases NH_3, NO, H_2 and O_2 on the decomposition of silver nitrate using DRIFT spectroscopy. In addition, some experiments on a model catalyst consisting of a physical mixture of silver nitrate and alumina catalyst were carried out to investigate the species adsorbed on the surface of model catalyst during NH_3-SCR conditions.

The conclusions of the experiments are that $AgNO_3$ is decomposed in the presence of NH_3. Moreover, silver nitrate is converted to silver oxide during the decomposition of silver nitrate. Nitrate can immigrate from silver nitrate to alumina in only argon and the migration rate will increase when H_2 and O_2 are added. The addition of hydrogen, which is essential for NO_X reduction over Ag/Al_2O_3 with NH_3, neither promote nor hinder the decomposition.

6. Future work

As a future work, further investigate about the oxidation state of silver using XPS is recommended. In addition, more DRIFTS experiments can be carried out to understand the reason for different trend around region 1400 cm^{-1}.

Appendix

Calculation regarding catalyst preparation

	Ag	$AgNO_3$	Al	Al_2O_3
Molecular Weight (g/mol)	107.86	169.87	26.98	101.96

Ag/Al_2O_3 is prepared from mixture of $AgNO_3$ and Al_2O_3. To prepare 2g, Ag/Al_2O_3 sample with 20 wt% Ag loading, the amount of Ag and Al_2O_3 in the sample should be as following:

$$2g(Ag/Al_2O_3)\times\frac{20(Ag)}{100(Ag/Al_2O_3)}=0.4g(Ag)$$

$$2g(Ag/Al_2O_3)\times\frac{80(Al_2O_3)}{100(Ag/Al_2O_3)}=1.6g(Al_2O_3)$$

This amount of Ag is obtained from 0.63g $AgNO_3$ as below:

$$0.4g(Ag)\times\frac{169.87(AgNO_3)}{107.86(Ag)}=0.63g(AgNO_3)$$

As a result, 0.63g (≈28.25 wt%) $AgNO_3$ and 1.6g (≈71.75 wt%) Al_2O_3 are mixed to prepare $AgNO_3/Al_2O_3$ with 20% Ag.

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