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On the mechanism of the selective catalytic reduction of NO with higher hydrocarbons over a silver/alumina catalyst

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Abstract

The possibility of forming nitrogen in the gas phase by reaction of activated forms of NO_x with amines and ammonia as well as with other organic intermediates, which can be converted to amines and/or ammonia, was investigated. The activation of NO was carried out by passing NO together with oxygen and small amounts of hydrogen over an Ag/alumina catalyst. A special T-shaped reactor was used to produce activated forms of NO_x and to feed model compounds of proposed intermediates to the gas phase after the catalyst. Nitrohexane, hexylisocyanate, heptanenitrile, hexylamine, and ammonia were used as model compounds. The T-reactor tests showed that both ammonia and hexylamine react in the gas phase with activated NO_x species producing N_2. Hydrogen was shown to have at least two main functions. First, hydrogen contributed to improved oxidation of all involved species, resulting in faster production of key intermediates. Secondly, hydrogen assisted in the formation of activated NO_x species for the gas-phase reactions. Nitrohexane was transformed to NH_3 in the presence of O_2 over the Ag/alumina already at 250 °C and the amounts of NH_3 produced increased in the presence of H_2O. Hexylisocyante was hydrolyzed to amine and ammonia at 250 °C over the catalyst in the presence of O_2 but only to ammonia at 400 °C. At 250 °C the conversion to amine and ammonia was almost doubled by the addition of H_2O. Heptanenitrile was quite stable and only small amounts of NH_3 were observed at 400 °C; however, nitriles may react directly with activated forms of NO_x forming N_2. The importance of gas-phase reactions as a part of the HC-SCR mechanism is emphasized. R-NO_2, R-NCO, and R-CN are intermediates for the formation of amines and ammonia, which are consumed both on the surface of the catalyst and in the gas phase behind the catalyst bed by reactions with activated NO_x species.

Keywords: HC-SCR; Ag/alumina catalyst; Reaction mechanism; Gas-phase reaction; Hydrogen effect; GC-MS

1. Introduction

Selective catalytic reduction of NO with hydrocarbons (HC-SCR) has received much attention as one of the most promising and straightforward methods for reducing NO_x emissions under conditions of excess oxygen. Since the early work of Held et al. [1] and Iwamoto et al. [2] a large number of different materials have been proposed and tested for HC-SCR. Among these, Ag/alumina has shown high activity both in laboratory and in full-scale tests [3].

Several proposals to describe the reaction mechanism have been made. Because of the complicated reactions involved, the complete reaction mechanism is not yet fully understood. In the review by Burch et al. [4], the main observations obtained so far have been discussed. It is generally considered that the first step of HC-SCR over oxide catalysts involves the formation of strongly bound nitrites and nitrates. In addition, activation of the hydrocarbon takes place by partial oxidation to oxygenated compounds, such as acetates. Both the nitrite and nitrate species as well as acetates have been detected in FTIR studies by several research groups. The ad-NO_x species are supposed to react with the adsorbed and partly oxidized hydrocarbon species on the catalyst surface to yield organo-nitrogen species. Depending on the reaction conditions, the organo-nitrogen species can be transformed to highly reactive intermediates such as isocyanates, nitriles, amines, and oximes. These intermedi-

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ates are in the last step proposed to be directly involved in reactions with NO or NO_2 and/or R-ONO leading to formation of nitrogen [4]. However, it is possible that this kind of complex organic-inorganic reaction chain could involve a more complex mixture of intermediates, by-products, end products, and spectator species than noted above.

Recently, Satokawa [5] and Shibata et al. [6] showed that hydrogen enhances the HC-SCR reaction significantly. They found that hydrogen increased the concentration of acetate but decreased the concentration of nitrates on the catalyst surface during reaction conditions. Moreover, the formation rates of nitrates and acetates also increased.

Typically, most of the studies dealing with the reaction mechanism have been restricted to surface phenomena. In our previous study [7], it was shown that HC-SCR over Ag/alumina does not only take place on the surface of the catalyst but continues in the gas phase leading to the final products, i.e., nitrogen, carbon dioxide, and water. The evidence for the gas-phase reaction was based on activity tests, where the Ag/alumina was combined with an oxidation catalyst to remove CO, which is produced over the silver catalyst during the de-NO_x process. When the Pt-oxidation catalyst was placed immediately after the Ag/alumina, a significant drop in the NO to N_2 conversion was observed in comparison with the single Ag/alumina bed. As the distance between the two catalysts was extended, the conversion of NO to N_2 improved to levels close to those recorded over the single Ag/alumina bed.

In the work of Lukyanov et al. [8] and Vassallo et al. [9] the role of gas-phase reactions in the mechanism of HC-SCR was studied. Lukyanov et al. proposed that the SCR reaction over Co-ZSM-5 and H-ZSM-5 involves free radical chemistry and may partly be homogeneous. NO or rather NO_2 was acting as an effective oxygen carrier agent for the initiation of radical formation. The catalyst was discussed to be needed for the coupling of the N–N bond by a combination of the formed organic nitro compounds and NO or NO_2. Vasallo et al. suggested that NO acted as a homogeneous catalyst in the oxidation of hydrocarbons over Cu-, Co-, and H-mordenite and that methanol selectively reduced NO in the gas phase.

Nitrogen formation within organic reactions usually involves either hydrazine or deamination reactions [10,11]. In the latter case, nitrogen is known as one of the leaving groups in the reaction of primary amines and the nitrosonium ion NO^+, originating from nitrous acid. The intermediate, $R{-}N_2{}^+$ (diazonium ion), is very unstable and undergoes rapid fragmentation to nitrogen and an alkyl cation [11].

In this study, the possibility of forming nitrogen in the gas phase by reaction of activated forms of NO_x with amines and ammonia as well as with other organic intermediates, which can be converted to amines and/or ammonia, was investigated. The activation of NO was carried out by passing NO together with oxygen and small amounts of hydrogen over an Ag/alumina catalyst.

2. Experimental

2.1. Catalyst preparation

The Ag/alumina catalyst was prepared by impregnation of commercial alumina beads (A 201, LaRoche Chemicals Inc.) with a silver nitrate solution according to the procedure described in Ref. [3]. The catalyst was dried at room temperature and at 100 °C before calcination at 550 °C for 3 h. The silver content of the catalyst was approximately 2 wt%. Before testing, the catalyst was crushed and sieved to fractions between 250 and 500 µm.

2.2. Activity tests

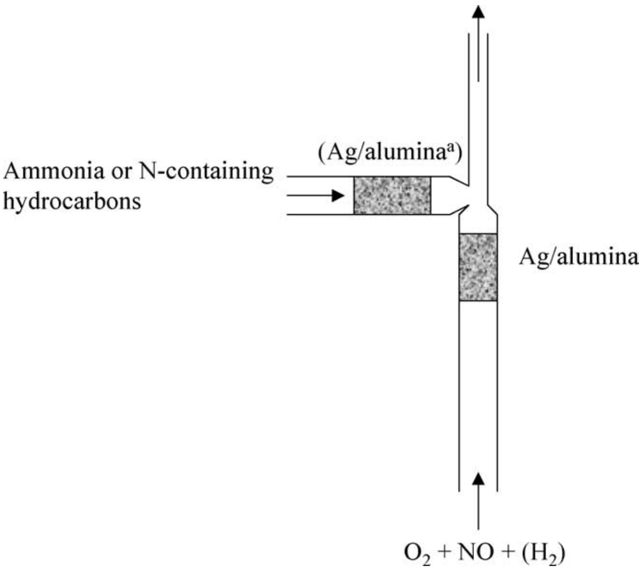
A quartz flow tube reactor, according to [3], was used in the activity tests. The Ag/alumina catalyst was tested under steady-state conditions in the temperature range 150–600 °C. The temperature of the catalyst bed was monitored by a K-type thermocouple connected to a temperature controller (Eurotherm 900 EPC). A basic gas mixture consisting of 500 ppm NO, 375 ppm octane, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, and 12 vol% H_2O in He (GHSV $= 60{,}000\ h^{-1}$ and volumetric flow rate $= 550$ ml/min) was used in the activity tests. The effect of hydrogen was studied by adding 1 vol% H_2 to the basic gas mixture. All gases (AGA) were of high purity and introduced into the reactor by means of mass-flow controllers (Brooks 5850E). Water was added to the gas mixture using a syringe pump in combination with a controlled evaporator mixer (Bronkhorst HI-TEC). Octane was also introduced using a syringe pump (CMA 102/Microdialysis).

A commercial Pt oxidation catalyst (Johnson Matthey) was placed directly after the Ag/alumina catalyst in some experiments to prove the gas-phase reactions.

The concentrations of N_2, CO_2, CO, and O_2 were determined with the aid of a gas chromatograph (HP 6890) and the concentration changes of NO_x ($NO + NO_2$) in the gas mixture were recorded by a chemiluminescence NO_x analyzer (API 200AH). Two condensers, kept at −5 °C and at −25 °C, were used to trap out the water from the gas prior to analysis.

2.3. GC/MS studies

In order to trap unreacted species in the gas phase after the catalyst, the Ag/alumina catalyst was placed at the entrance of a U-shaped stainless-steel tube, which was immersed in liquid nitrogen. A block heater was placed around the tube at the position of the catalyst. The isolated species were dissolved in acetone and injected into a GC-MS (HP 6890-5973) equipped with a 15 m, 0.25 mm (diameter), and 0.50 µm (film thickness) INNOWAX column (J&W Scientific). Prior to the experiments the catalyst was treated in a gas mixture containing 6 vol% O_2 at 400 °C for 30 min.



[a]Some tests were carried out in the absence of Ag/alumina in the side port.

Fig. 1. Schematic illustration of the T-shaped quartz reactor used for investigation of gas-phase reactions.

The following combinations of reactants were led through the catalyst bed, which was kept at 350 °C: (1) 375 ppm octane + 6 vol% O_2 in He; (2) 375 ppm octane + 6 vol% O_2 + 500 ppm NO in He; and (3) 375 ppm octane + 6 vol% O_2 + 500 ppm NO + 1 vol% H_2 in He.

2.4. *Experimental setup for gas-phase reaction studies*

A special T-shaped quartz reactor, as shown in Fig. 1, was constructed to study the formation of nitrogen from different kinds of proposed intermediate species in the gas phase. The basic idea was to investigate if an amine or ammonia (introduced from the side of the reactor) reacts in the gas phase with species, resulting from reactions of NO + O_2 as well as NO + O_2 + H_2 over Ag/alumina, to form N_2. In addition, possible intermediates, which can be converted, hydrolyzed, or decomposed to amines/ammonia over Ag/alumina, were tested in the same manner. In separate tests, FTIR analysis using a heated long-path gas cell (Graseby Specac Ltd) in combination with GC measurements were used to determine the gas product distribution after the catalyst. Model components for the intermediates were hexylamine, $C_6H_{13}NH_2$ (Acros Organics), heptanenitrile, $C_6H_{13}CN$ (Acros Organics), hexylisocyanate, $C_6H_{13}NCO$ (Acros Organics), and 1-nitrohexane, $C_6H_{13}NO_2$ (Aldrich).

In additional experiments, the same model intermediates were tested for their activity to reduce NO over Ag/alumina. These experiments were carried out by feeding 250 ppm of the N-containing hydrocarbon together with 500 ppm NO and 6 vol% O_2 in He over the Ag/alumina bed at temperatures ranging from 150 to 600 °C. A reference run using 250 ppm *n*-hexane, 500 ppm NO, and 6 vol% O_2 in He was carried out to measure the effect of the C_6 hydrocarbon chain on the NO to N_2 conversion.

2.5. *FTIR analysis*

In situ IR spectra were recorded on an ATI Mattson Infinity FTIR spectrometer equipped with an IR cell made of stainless steel. A mixture containing 1000 ppm NO and 6 vol% O_2 in presence and absence of 1 vol% H_2 in He was introduced to the chamber using mass-flow controllers (Brooks 5850E). In some tests 750 ppm of octane was introduced by saturation of gas. The catalyst was pressed into a self-supporting wafer (weight 0.021 g) and mounted in the IR cell. In situ pretreatment of the catalyst at 400 °C, using a gas mixture containing 6 vol% O_2 in He, was performed before each experiment. All experiments were conducted at 250 °C. The spectra were measured by accumulating 64 scans at a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. *Activity tests*

In our previous study [7] it was shown that the 2 wt% Ag/alumina is a very active catalyst for the reduction of NO using octane as reducing agent. However, the activity is limited to temperatures above 300 °C. As reported by Satokawa [5], hydrogen significantly enhances the HC-SCR reaction, especially at low temperatures. In order to investigate the effect of hydrogen on the NO conversion, 1 vol% H_2 was added to the basic gas mixture and the result compared to conversions obtained without H_2 is shown in Fig. 2. As can be seen, conversion values close to 60% were recorded already at 250 °C in the presence of hydrogen. On the other hand, hydrogen alone exhibited practically no capacity to reduce NO to N_2.

A substantial amount of carbon monoxide is formed in parallel with the NO to N_2 conversion [7]. The CO can easily be removed by using an oxidation catalyst. However, adding an oxidation catalyst directly after the Ag/alumina bed reduces the NO_x conversion dramatically as shown in Fig. 3. Interestingly, addition of 1 vol% H_2 to the feed reduces almost completely the contribution of the gas-phase reaction to the conversion of NO to N_2, as visualized in Fig. 4. The rather high NO conversion at 150 °C (over 30%) with H_2 in the feed is due to the activity of the oxidation catalyst. According to a test with only the oxidation catalyst, the activity at temperatures higher than 150 °C can be related to the Ag/alumina catalyst. It seems that the hydrogen effect is either due to increased reaction rate of surface reactions or reactions in the gas phase (the reactions are completed already in the pores and in the void space between particles). The role of hydrogen will be dealt with more in detail later in this study.

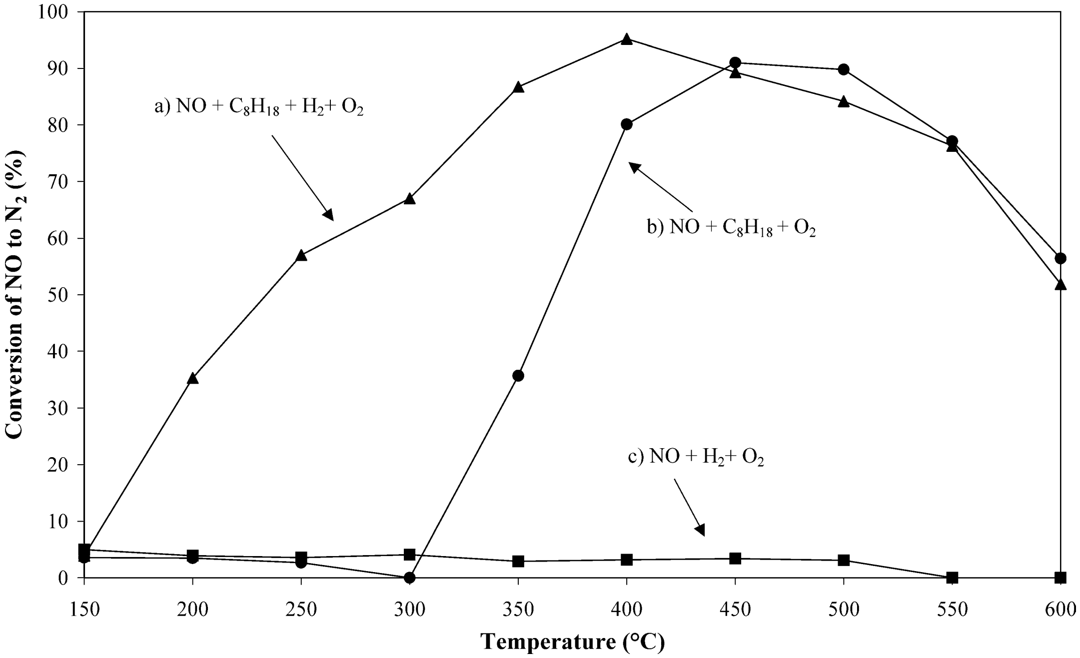


Fig. 2. Activity tests over Ag/alumina in the presence and absence of hydrogen. Gas mixtures: (a) 500 ppm NO, 375 ppm C_8H_{18}, 1 vol% H_2, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O in He. (b) 500 ppm NO, 375 ppm C_8H_{18}, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O in He. (c) 500 ppm NO, 1 vol% H_2, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O in He. GHSV = 60,000 h^{-1} and volumetric gas flow = 550 ml/min.

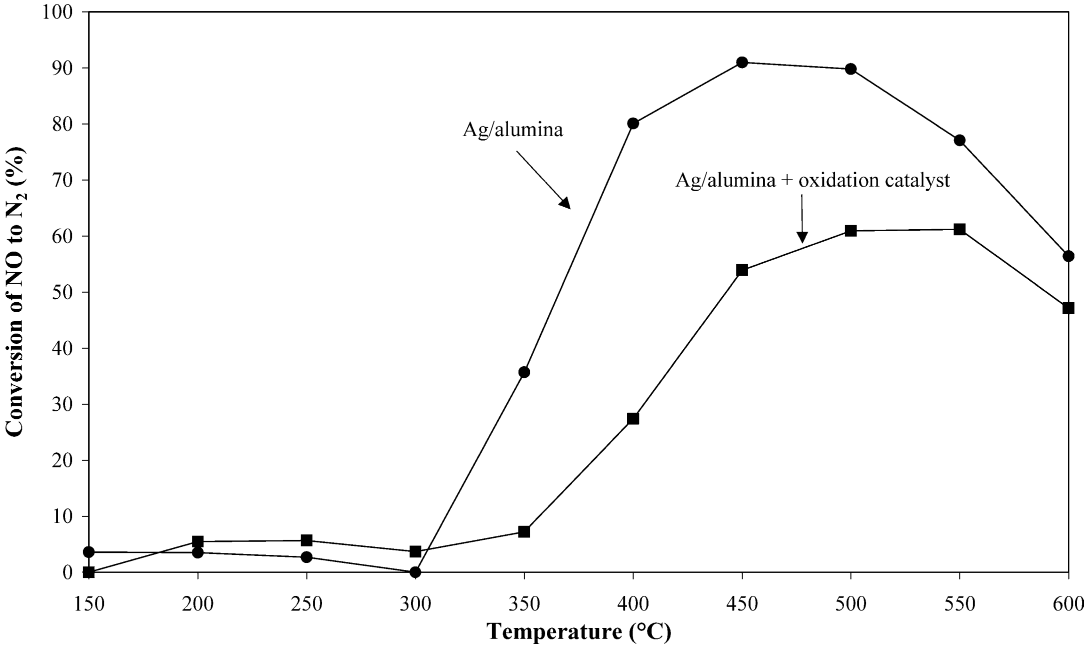


Fig. 3. Comparison of the conversion obtained over Ag/alumina (single bed) and over Ag/alumina in combination with a Pt oxidation catalyst (0 mm between beds). Gas mixture: 500 ppm NO, 375 ppm C_8H_{18}, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O in He. GHSV = 60,000 h^{-1} and volumetric gas flow = 550 ml/min.

3.2. GC-MS studies

In order to investigate how addition of hydrogen to the feed influences the formed gas-phase species, GC-MS studies on trapped compounds after the catalyst were carried out. During these experiments a U-shaped reactor was placed in a bath filled with liquid nitrogen in order to trap (isolate) species formed over the catalyst surface. The trapped species were dissolved in acetone and injected into a GC-MS. In the first experiment, using only octane and oxygen, some partially oxidized hydrocarbons such as 2-propenoic acid, crotonic acid, and acetophenone were detected. In addition, some cyclization seemed to take place as well as dimerization to decane. The very low amount of products in this test

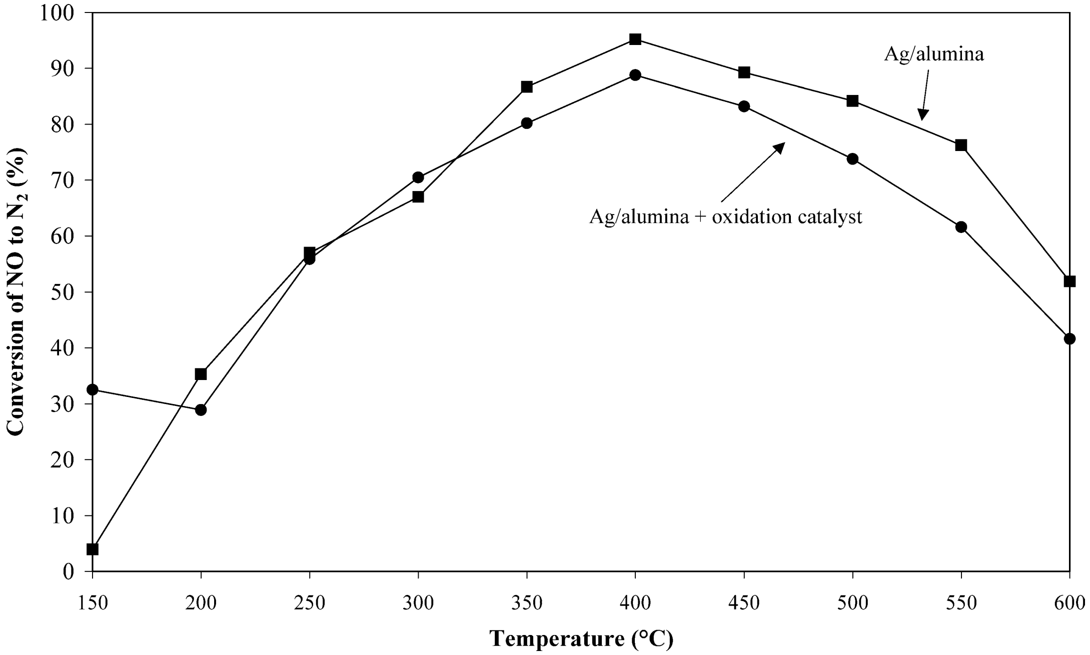


Fig. 4. Comparison of the conversion obtained over Ag/alumina (single bed) and over Ag/alumina in combination with a Pt oxidation catalyst (0 mm between beds) in the presence of hydrogen. 500 ppm NO, 375 ppm C_8H_{18}, 1 vol% H_2, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O in He. GHSV = 60,000 h^{-1} and volumetric gas flow = 550 ml/min.

could depend on the low catalyst temperature (350 °C) resulting in minimal activity for oxidation of octane or the lack of a highly reactive component such as NO and/or hydrogen. When NO was added to the gas mixture, the distribution of species changed significantly. The majority of compounds belonged to the nitrile group. Also some ketones, aldehydes, and carboxylic acids were formed. Again also some cyclization could be observed. The nitriles may be formed through nucleophilic addition of cyanide ions (on the surface) to aldehydes and ketones (formed through partial oxidation via alcohols over Ag/alumina). It is also possible that the nitriles are by-products, which are not important during effective HC-SCR. Another hypothesis would be that the nitriles are hydrolyzed to amides, which are then further hydrolyzed to carboxylic acids and ammonia or amines [12]. In this case the reason for the high number of nitriles in the GC-MS spectrogram would be that effective hydrolysis did not take place. On the other hand, it has been proposed that cyanide species on the catalyst surface are slowly converted into isocyanate species [4]. Isocyanate species are widely considered to be potential intermediates in the HC-SCR reaction. Due to the slow rearranging of the CN group into the NCO group a majority of the untransformed cyanide ions could form the detected nitriles together with left over aldehydes and ketones.

When hydrogen was added to the gas mixture at the same temperature (350 °C) the GC-MS spectra changed completely. Almost no compounds of interest, except some partially oxidized hydrocarbons (ketones), were seen, most probably due to the complete oxidation of the hydrocarbons and/or very high HC-SCR activity. It could be that hydrogen transforms the nitriles into a more reactive form or that hydrogen speeds up the transformation of cyanide species to isocyanate species on the surface. On the other hand, the effect of hydrogen might be in several parallel processes including the activation of NO. It is possible that without H_2, the activation process of NO at this temperature is limited.

3.3. Gas-phase reaction studies involving intermediates

In all tests the formation of the desired product N_2 was determined by means of gas chromatographic analyses and the amount of formed N_2 was used to calculate the conversion of NO. Conversion of NO in the reaction between NO and N-containing functional groups in the gas phase has been calculated assuming that one NO molecule reacts with one N-containing functional group to form one molecule of N_2:

$$\text{Conversion of NO (\%)} = \frac{c_{\mathrm{N_2(out)}}}{c_{\mathrm{NO(in)}}} \qquad (1)$$

When the reaction is taking place over the catalyst, also a possible contribution of the hydrocarbon chain to reduction of NO must be taken into account, especially at temperatures above 350 °C. By measuring the amount of N_2 produced it was not possible to distinguish between these two possible reactions and thus the conversions in these cases were calculated as conversion of N-containing compounds:

$$\text{Conversion of N-containing comp. (\%)} = \frac{2 \times c_{\mathrm{N_2(out)}}}{c_{\text{N-containing comp. (in)}}} \qquad (2)$$

In the cases where a hydrocarbon (no N-containing functional group) was used as reducing agent, the conversion was calculated as

$$\text{Conversion of NO (\%)} = \frac{2 \times c_{N_2(\text{out})}}{c_{NO(\text{in})}}. \tag{3}$$

In this case all the N_2 formed is originating from the introduced NO, which is consumed both in the formation of N-containing species and in the reaction with these species to form N_2.

3.3.1. Ammonia

The results of the gas-phase reaction at 250 and 400 °C between NO + O_2 as well as NO + O_2 + H_2 (flowing through the catalyst) and ammonia are shown in Fig. 5. Passing NO + O_2 over the catalyst and introducing NH_3 after the catalyst bed resulted in a NO conversion of about 9.5%. The conversion was almost exactly the same both at 250 °C and at 400 °C. By addition of H_2 to the NO + O_2 mixture, a significant improvement of the NO conversion was observed. At the first point, which was analyzed 6 min after the H_2 introduction, approximately 26% of NO was converted to N_2 in the gas phase at both temperatures. With time on stream the conversion slightly decreased. The NO conversion value of 26% means that approximately half of the available ammonia is used for the reduction of NO to N_2. According to the stoichiometry of the SCR of NO with ammonia, the NO/NH_3 ratio is usually adjusted to 1. In fact, when 500 ppm NH_3 was introduced after the catalyst bed and 500 ppm NO + 6 vol% O_2 + 1 vol% H_2 was flowing through the catalyst, the NO conversion increased to 43.7% (not shown). Empty reactor tests showed about 3% conversion and there was no effect of hydrogen addition. Moreover, in a separate test it was confirmed that introducing 1 vol% H_2 to a mixture of 500 ppm NO and 6 vol% O_2 flowing through the catalyst in the bottom part and with only He from the side did not result in any formation of N_2.

The importance of this new finding lies in the fact that it is possible to homogeneously convert NO to N_2 by reaction with NH_3 in excess of oxygen at temperatures far below those reported to be valid for selective noncatalytic reduction of NO. Depending on the gas components and their concentrations, NO reduction by ammonia in the gas phase should by no means take place below 600–700 °C [13]. The crucial point is to activate NO over the Ag/alumina catalyst for further reaction with ammonia. Some activation seems to take place without a reducing agent, but hydrogen is a good activator for NO. It can be assumed that also hydrocarbons during the HC-SCR process are involved in the activation process of NO probably as a source of hydrogen. It is generally known that nonthermal plasma treatment induces activation of both NO and hydrocarbon. In our case a similar kind of activation seems to take place over the Ag/alumina catalyst and is enhanced by addition of hydrogen.

The conversion of NO to N_2 using ammonia as a reducing agent over the Ag/alumina as a function of temperature is shown in Fig. 6. As can be seen, the conversion of NO at 250 and 400 °C was 0 and 8.0%, respectively. The conversion increased with the temperature and was about 20% at 600 °C. The lower conversion in this test both at 250 °C and at 400 °C compared to the T-reactor test may be due to adsorbed ammonia on the catalyst, which partly inhibits the activation of NO. A similar activity pattern as shown in Fig. 6 was also shown by Richter et al. for the SCR of NO_x by ammonia over Ag/alumina [14]. They reported that in the presence of hydrogen almost complete conversion of NO to

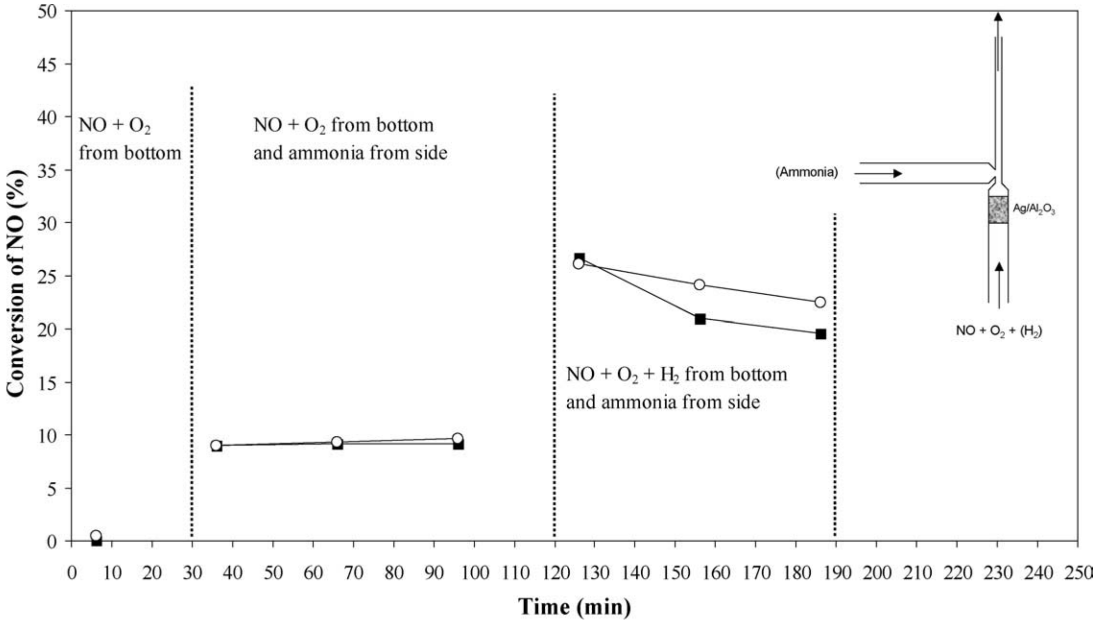


Fig. 5. T-reactor tests with ammonia at 250 °C (■) and at 400 °C (○). Gas mixture through bottom port: 500 ppm NO + 6 vol% O_2 in presence and absence of 1 vol% H_2 in He. Gas mixture through side port: 250 ppm NH_3 in He.

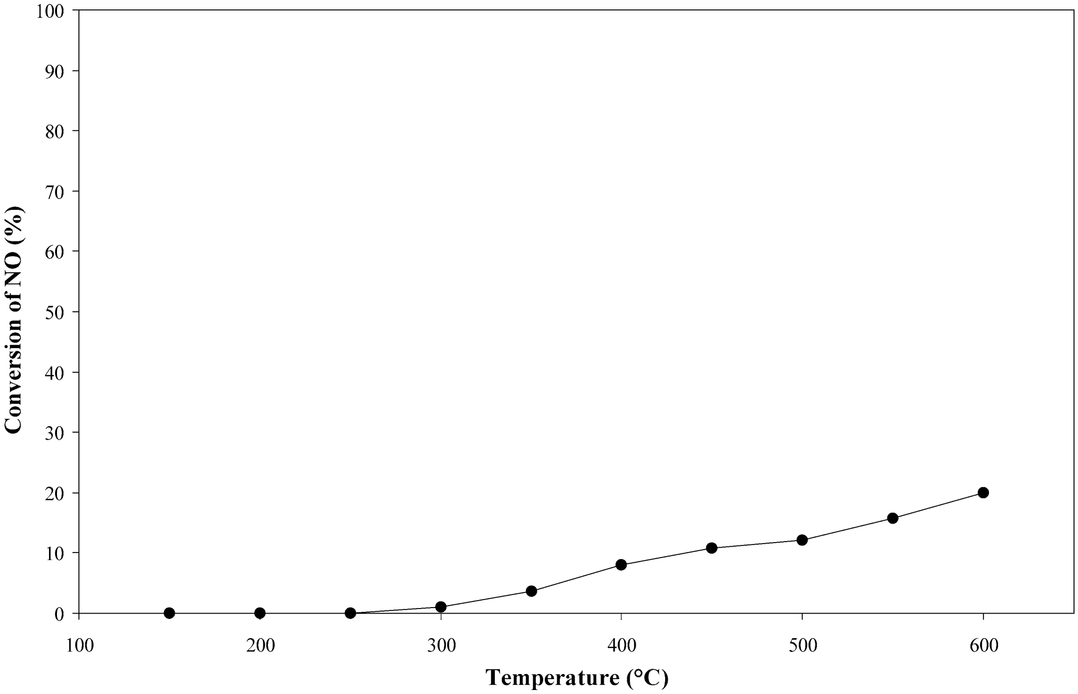


Fig. 6. The conversion of NO over Ag/alumina as a function of temperature using NH_3 as reducing agent. Gas mixture: 500 ppm NO, 250 ppm NH_3, and 6 vol% O_2 in He. GHSV = 60,000 h^{-1} and volumetric gas flow = 550 ml/min.

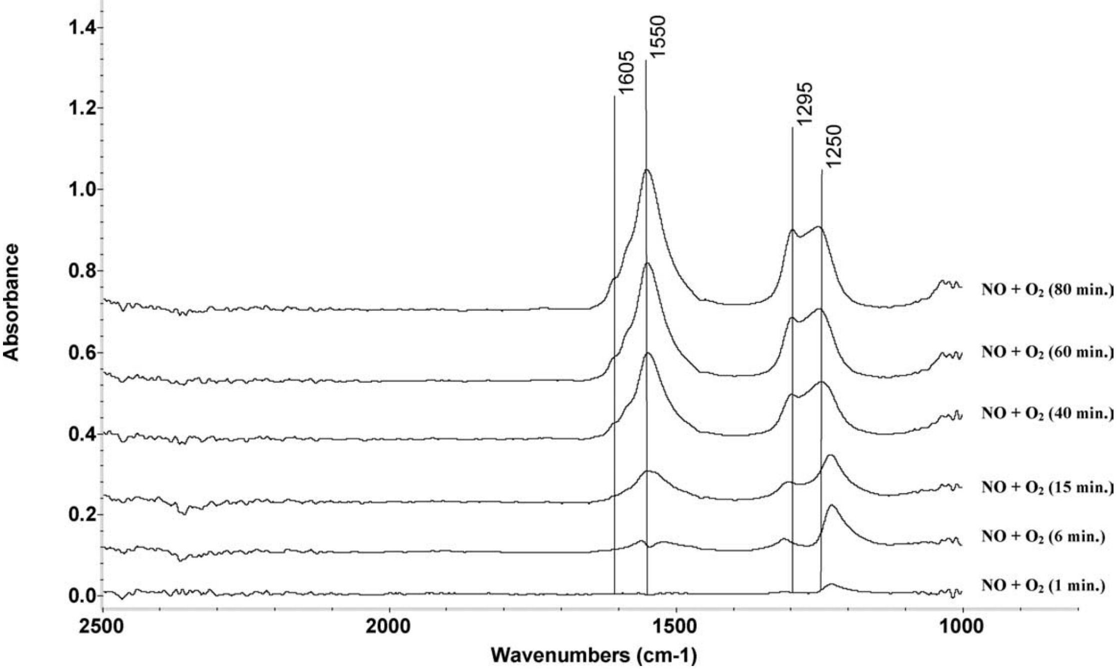


Fig. 7. Time on stream in situ FTIR on Ag/alumina at 250 °C in a flow of 1000 ppm NO and 6 vol% O_2 in He.

N_2 was observed at temperatures starting from 200 °C. The boosting effect of hydrogen on the NO conversion in our T-reactor test is in good agreement with their results taking into account that we used 500 ppm NO and 250 ppm NH_3 compared to 1000 ppm NO and 1000 ppm NH_3 in [14].

The effect of hydrogen on the formation of ad-NO_x species was studied by in situ FTIR at 250 °C. The results of flowing NO + O_2 as well as NO + O_2 + H_2 over the Ag/alumina as a function of time are shown in Figs. 7 and 8. In the case of NO + O_2 flowing over the catalyst, slow formation of peaks mainly at 1250, 1295, and 1550 cm^{-1} was recorded. Additionally a shoulder at about 1605 cm^{-1} was detected. These peaks have been attributed to monodentate nitrate (peaks at 1250 and 1550 cm^{-1}) and bidentate nitrate

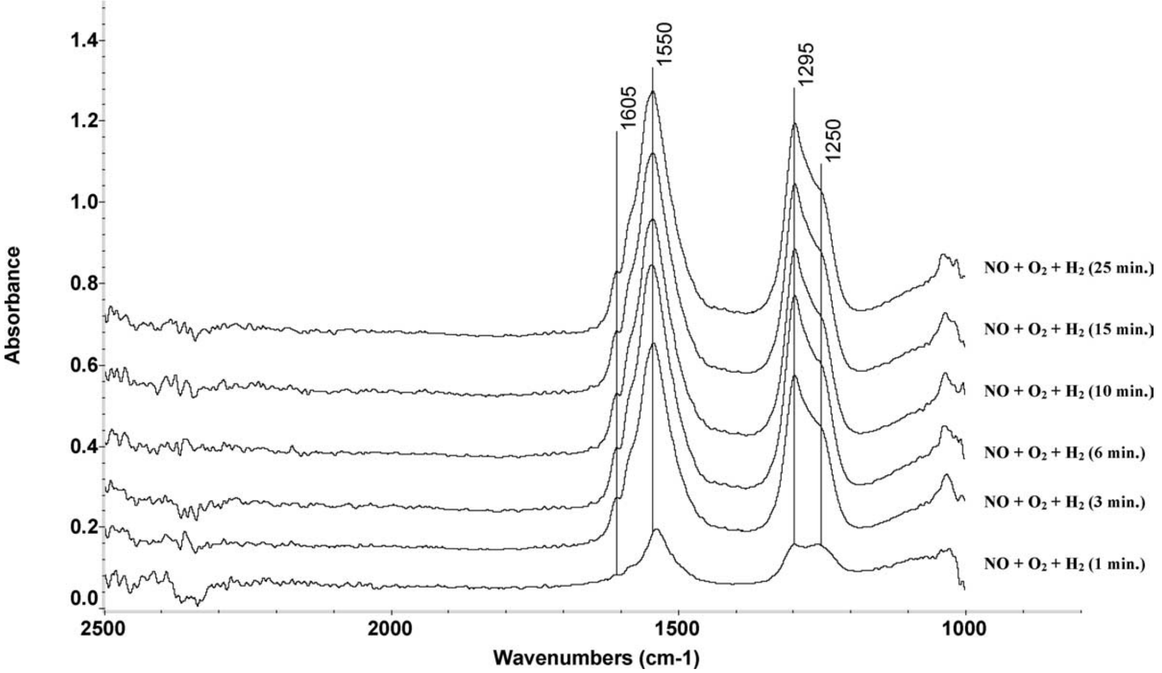


Fig. 8. Time on stream in situ FTIR on Ag/alumina at 250 °C in a flow of 1000 ppm NO, 6 vol% O_2, and 1 vol% H_2 in He.

(peaks at 1295 and 1605 cm^{-1}) [15]. When H_2 was added to the feed together with NO + O_2, the formation of the nitrate species was significantly accelerated. As a matter of fact, the same amount of surface nitrates was achieved already in less than 3 min in the presence of H_2 compared with the amount formed during 80 min in the absence of H_2. This is in good agreement with the work of Shibata et al. [6]. In a separate test at 250 °C, simulating introduction of H_2 in the T-reactor test, the effect of introduction of H_2 on adsorbed nitrates was investigated. The adsorbed nitrates were produced in a flow of 1000 ppm NO and 6 vol% O_2 in He for 80 min. Addition of H_2 to the mixture of NO and O_2 resulted in rapid growth of the bands corresponding to nitrates, especially at 1295 and 1550 cm^{-1}, as can be seen in Fig. 9. No decrease in peak intensity of other detected peaks or growth of new peaks could be observed. In addition, the adsorbed nitrate species seemed to be quite stable. In a flow of 6 vol% O_2 and 1 vol% H_2 (in absence of NO) no decrease in intensity of the peaks corresponding to the nitrates could be detected, but in a flow containing 1 vol% H_2 alone, the peaks disappeared in about 3 min.

Addition of 1 vol% hydrogen to a flow of 750 ppm octane and 6 vol% oxygen at 250 °C resulted in a similar enhancing effect on the formation of oxygenated hydrocarbon species on the catalyst surface. In a flow of octane and O_2 slow formation of very weak peaks at about 1378, 1392, 1456, and 1574 cm^{-1} were detected. These peaks have been assigned to formate (1378 and 1392 cm^{-1}) and acetate (1456 and 1574 cm^{-1}) species on Ag/alumina [6]. Addition of H_2 resulted in a rapid growth of especially the acetate bands and comparing the amount of formed acetate for 80 min with and without H_2 in the feed revealed that the amount was about 8.5 times higher in the presence of H_2.

In a separate experiment the catalyst was first exposed to a flow of 1000 ppm NO and 6 vol% O_2 for 80 min at 250 °C to generate nitrates on the catalyst surface. As expected, addition of 750 ppm octane to the feed for 60 min did not change the spectra due to the low temperature (no reaction took place). However, addition of 1 vol% H_2 resulted in a drastic change of the peak pattern. After 3 min the intensity of the band belonging to bidentate nitrate at 1295 cm^{-1} was doubled. In addition, the band at 1250 cm^{-1} belonging to monodentate nitrate had disappeared. Weak bands of acetate and formate species as well as a strong band at 1586 cm^{-1}, which has been assigned to carboxylate species [16], were also immediately formed and the intensities of these bands increased with time on stream. Moreover, in the spectra recorded at 30 min after introduction of H_2, a weak band at 2228 cm^{-1} could be detected. This band has been assigned to NCO species [6,16]. The intensity of the band belonging to bidentate nitrate at 1295 cm^{-1} did not change with time on stream; i.e., the intensity was the same both at 3 min and 30 min. In addition, no increase of the other bands of nitrates as observed in the experiment using a flow of NO, O_2, and H_2 (Fig. 8) was found. Thus it seems that in presence of octane the continuously formed nitrates are consumed by taking part in the reaction or by desorption into the gas phase.

In addition to the surface studies, the effect of hydrogen addition on the gas composition after the catalyst was investigated by FTIR studies using a gas cell. At 250 °C no NO_2 was detected when a gas mixture containing 500 ppm NO and 6 vol% O_2 was led over the catalyst. At 400 °C small

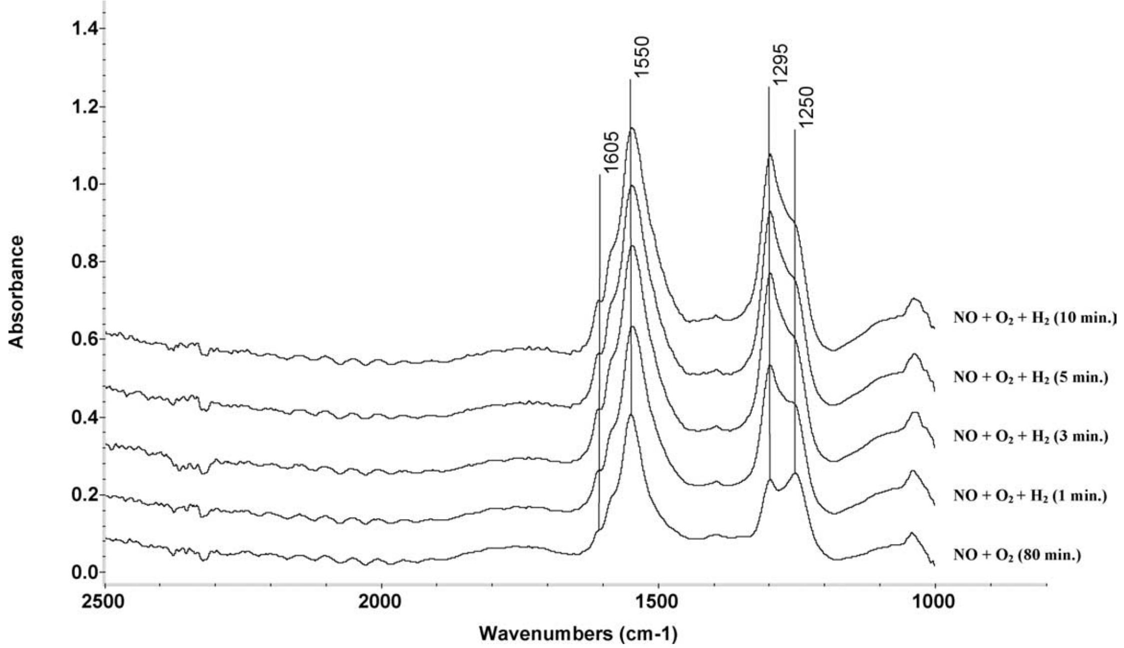


Fig. 9. The effect of addition of 1 vol% H_2 to the flow of 1000 ppm NO and 6 vol% O_2 in He on nitrates adsorbed on Ag/alumina. Catalyst temperature: 250 °C.

amounts (below 10 ppm) of NO_2 were observed. Addition of 1 vol% H_2 led to a significant conversion of NO to NO_2, being 68% at 250 °C and 57% at 400 °C under steady-state conditions. Also strong peaks related to water were present. In addition, a small peak at 1260 cm^{-1} was observed. This peak could possibly be attributed to *trans*-HONO [17]. No peaks corresponding to formation of N_2O were observed.

It is clear that the rate of formation of nitrates on the catalyst is drastically changed in the presence of small amounts of hydrogen. In the T-reactor test with NH_3 (and also in the corresponding tests with other intermediates described in the following sections) addition of H_2 to the flow of $NO + O_2$ resulted in such a strong formation of ad-NO_x species that a decrease in the NO_x concentration at the reactor outlet could be detected for at least 10 min as observed from NO_x analyzer values. Moreover, in a recent study it was shown that hydrogen dissociated and exchanged with deuterium (D_2) on oxidized Ag/alumina to form HD [18]. This could mean that the catalyst has an ability to form HONO and $HONO_2$ from the nitrates on the catalyst surface in the presence of dissociated hydrogen. It is possible that electron-deficient oxides of nitrogen such as NO^+ and $NO_2{}^+$ are formed from the decomposition of HNO_2 and HNO_3. In the case of zeolites, NO_x activation by interaction with acidic hydroxyls was considered to take place and generate nitrosonium ions NO^+ in a process involving H^+ [19,20]. Iglesias-Juez et al. [21] have detected these kinds of species on Ag/alumina during reaction conditions and showed that acidic hydroxyls are recovered by interaction with the hydrocarbon or derived products, thus closing the catalytic cycle and regenerating the active surface species. It can be speculated that H_2 in our case is acting in the same manner. Furthermore, Hadjiivanov et al. [20] discussed that NO^+ and nitrate precursor molecules can be simultaneously formed by disproportionation of N_2O_3 and N_2O_4.

Another possible explanation of the effect of hydrogen is that it boosts the formation of highly reactive radicals, such as NO•, NO_2•, O•, H•, and OH•. Richter et al. [14] have proposed that hydrogen generates on short-term scale zero-valent silver. Reactive O (and/or OH) species are formed via dissociative interactions of O_2 (and H_2) with these metallic silver species. These reactive oxygen atomic species should then accelerate the necessary oxidative transformation of gaseous NO to adsorbed nitrite/nitrate species. The increased concentrations of NO_2 in the gas phase in the presence of H_2 in our case might be due to the reaction between O radicals and NO. It is possible that also some of the formed NO_2 species are of radical character. Whether these kinds of radicals directly react with NH_3 or N-containing hydrocarbons forming N_2 is unclear. It is worth noting that in an ongoing parallel work dealing with EPR combined with matrix isolation technique, there were indications of low molecular weight radicals trapped in the matrix behind the Ag/alumina catalyst.

It is commonly known that NO^+ reacts with alkylamines to form an alkyl diazonium ion [11]. In case of a primary amine this diazonium ion is very unstable and decomposes to nitrogen and to a highly reactive alkyl cation. This alkyl cation reacts with nucleophiles, for example, $NO_2{}^-$ to give nitroalkanes. The nitrosation of a primary amine with NO^+ proceeds according to the following reaction [11]:

$$R\text{–}NH_2 + NO^+ \rightarrow R\text{–}\overset{+}{N}{\equiv}N\colon \rightarrow N_2\uparrow + R^+. \qquad (4)$$

As shown in the following section, a similar type of deamination reaction is indeed taking place after the Ag/alumina catalyst bed and is thus suggested to be part of the HC-SCR reaction. As shown above, it seems that some kind of activated NO_x species also reacts with ammonia. Whether these are the same kind of species that react with the amine is not clear.

Anyway, one important role of the Ag/alumina catalyst during the HC-SCR is to feed the gas phase with activated oxides of nitrogen as well as ammonia and/or amines (formed by surface reactions between hydrocarbons and NO_x). Reaction between these activated nitrogen oxides and ammonia is proposed to be the final step in the HC-SCR mechanism over Ag/alumina.

3.3.2. Hexylamine

The results of the gas-phase reaction of species formed by passing $NO + O_2$ as well as $NO + O_2 + H_2$ through the catalyst with hexylamine at 400 °C are shown in Fig. 10. Passing $NO + O_2$ over the catalyst and introducing hexylamine after the catalyst bed resulted in a NO conversion of about 4.3%. When H_2 was added to the feed together with $NO + O_2$ a significant increase of the NO conversion was obtained. The conversion increased by time and the maximum conversion obtained was approximately 18% in the gas phase. The corresponding empty reactor test showed a conversion of about 3.5% with no effect of H_2 addition. It is obvious that the role of hydrogen is to activate NO over the Ag/alumina catalyst as explained in the previous section and hereby generate enough reactive NO^+ species, which react with the amine to form diazonium ions according to reaction (4). These diazonium ions are then subsequently decomposed forming N_2.

In a separate test the temperature dependence of the gas-phase reaction between hexylamine and activated forms of NO_x was examined and the result is shown in Fig. 11. In this experiment 250 ppm hexylamine was continuously introduced after the catalyst bed and a mixture of 500 ppm NO, 6 vol% O_2 and 1 vol% H_2 was flowing through the catalyst. As can be seen, the temperature strongly influences on the conversion and the highest conversion (about 26%) of NO was obtained between 200 and 250 °C. This means that half of the available amine was consumed at these temperatures in the gas-phase reaction.

3.3.3. Formation of amines and/or ammonia from hexylisocyanate, heptanenitrile, and nitrohexane over Ag/alumina

Isocyanate species and nitro compounds are widely proposed to be important intermediates in the HC-SCR reaction. In addition, the GC-MS analysis of the compounds trapped behind the Ag/alumina catalyst revealed a large formation of nitriles during the HC-SCR reaction. Also in the in situ FTIR experiments bands corresponding to the isocyanate group were detected. Isocyanates are easily hydrolyzed to amines in the presence of water. Also nitriles are known to undergo hydrolysis in the presence of H_2O and as noted earlier, the first hydrolysis product is the corresponding amide, which is then further hydrolyzed to carboxylic acid and ammonia [12]. Nitrocompounds such as $R\text{-}NO_2$ have been proposed as intermediates originating from the reaction of adsorbed NO_x species (mainly nitrates) and partly oxidized hydrocarbons (mainly acetates) [4]. As noted earlier, the nitrosation of primary amines results in the formation of a highly reactive alkyl cation. This alkyl cation reacts with

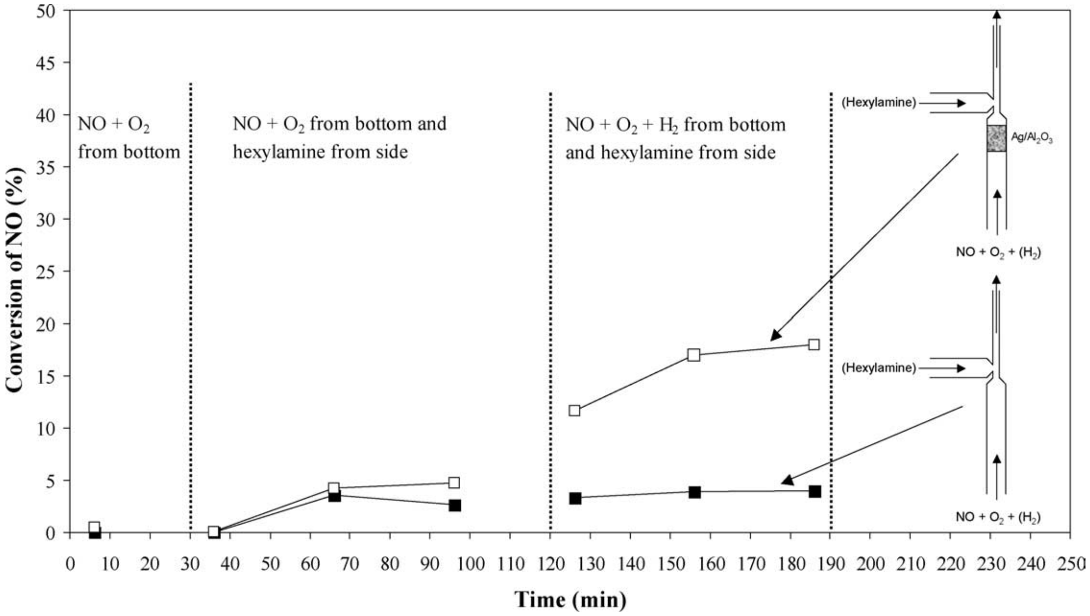


Fig. 10. T-reactor tests with hexylamine at 400 °C with catalyst (□) and without catalyst (■) in the bottom part. Gas mixture through bottom port: 500 ppm NO and 6 vol% O_2 in the presence and absence of 1 vol% H_2 in He. Gas mixture through side port: 250 ppm hexylamine in He.

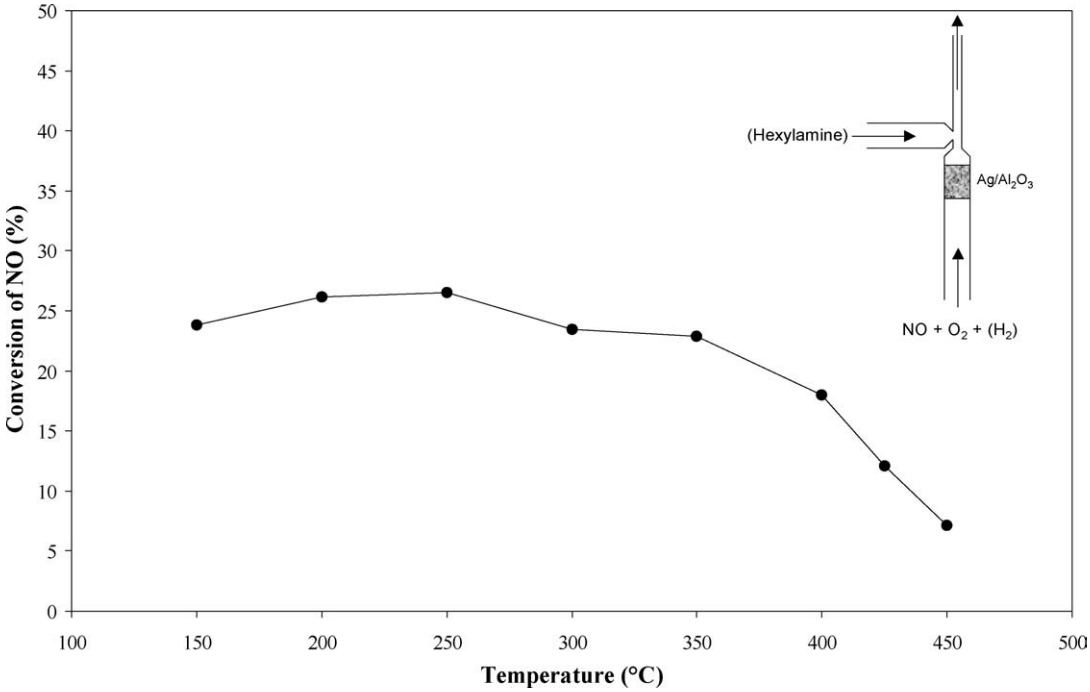


Fig. 11. The temperature dependence on the conversion of NO in the gas-phase reaction using hexylamine as reducing agent. Gas mixture through bottom port: 500 ppm NO, 6 vol% O_2, and 1 vol% H_2 in He. Gas mixture through side port: 250 ppm hexylamine in He.

Table 1
The formation of R-NH_2 and/or NH_3 from hexylisocyante, heptanenitrile, and 1-nitrohexane, under dry and wet conditions at 250 and 400 °C

Intermediate	Condition	250 °C		400 °C	
		Conversion to R-NH_2 (%)	Conversion to NH_3 (%)	Conversion to R-NH_2 (%)	Conversion to NH_3 (%)
Hexylisocyanate	Dry[a]	23.0	8.0	0.0	36.0
	Wet[b]	43.0	13.1	0.0	46.0
Heptanenitrile	Dry	0.0	0.0	0.0	17.2
	Wet	0.0	5.6	0.0	23.6
1-Nitrohexane	Dry	0.0	8.0	0.0	36.2
	Wet	0.0	13.3	0.0	55.5

Gas mixture: 250 ppm of N-containing hydrocarbon and 6 vol% O_2, (1 vol% H_2O) in He.
[a] No H_2O in the feed.
[b] With 1 vol% H_2O in the feed.

$NO_2{}^-$ to give nitroalkanes and this offers an alternative route for producing these species.

In order to test if amines and/or ammonia are formed from isocyanates, nitriles, or nitroalkanes over the Ag/alumina, experiments were carried out where mixtures of 250 ppm hexylisocyanate, heptanenitrile, or nitrohexane and 6 vol% O_2 in presence and absence of 1 vol% H_2O were fed over the Ag/alumina catalyst. The components at the reactor outlet were analyzed by FTIR using a gas cell and the results are shown in Table 1.

Under dry conditions at 250 °C, about 23 and 8% of the introduced hexylisocyanate was converted into amine and ammonia, respectively. When 1 vol% of water was added to the feed, the conversion of hexylisocyanate to amine and ammonia increased to approximately 43 and 13.1%, respectively. Interestingly, at 400 °C about 36% of hexylisocyanate was converted into ammonia under dry conditions and the corresponding value in the presence of water was 46%. At this temperature no amine was detected. It is evident that if isocyanate species are formed over the catalyst, they are easily transformed into amines and ammonia, which, as shown above, can react with activated nitrogen oxides in the gas phase to form N_2.

In the case of heptanenitrile, no conversion to amine or ammonia was observed at 250 °C and under dry conditions. Adding water to the feed resulted in a conversion of 5.6% of the nitrile to ammonia, the rest being unreacted. At 400 °C, the corresponding conversions to ammonia were 17.2% (dry) and 23.6% (wet). No amine or amide formation was detected in any of these tests. It is quite clear that heptanenitrile is much more stable in terms of hydrolysis and decomposition than the corresponding hexylisocyanate.

At 250 °C and under dry conditions, 8% of nitrohexane was converted to NH_3 and at 400 °C the corresponding value

Table 2
T-reactor tests with hexylisocyanate, heptanenitrile, and 1-nitrohexane at 250 and 400 °C

Time (min.)	Feed from bottom port	Feed from side port	Hexylisocyanate				Heptanenitrile				1-Nitrohexane			
			250 °C		400 °C		250 °C		400 °C		250 °C		400 °C	
			X_{NO} (%)	Max. X_{NO}[a] (%)	X_{NO} (%)	Max. X_{NO}[a] (%)	X_{NO} (%)	Max. X_{NO}[a] (%)	X_{NO} (%)	Max. X_{NO}[a] (%)	X_{NO} (%)	Max. X_{NO}[a] (%)	X_{NO} (%)	Max. X_{NO}[a] (%)
6	$NO + O_2$	O_2	0.0	0.0	0.5	0.0	0.0	0.0	0.5	0.0	0.0	4.0	0.5	18.1
30	$NO + O_2$	O_2 + R–X												
36	$NO + O_2$	O_2 + R–X	0.9	15.5	6.7	18.0	1.1	0.0	6.3	8.6	0.8	4.0	6.7	18.1
66	$NO + O_2$	O_2 + R–X	5.2	15.5	8.9	18.0	1.5	0.0	7.0	8.6	3.2	4.0	9.8	18.1
90	$NO + O_2$	O_2 + R–X + H_2O												
96	$NO + O_2$	O_2 + R–X + H_2O	6.0	28.1	9.7	23.0	0.9	2.8	7.9	11.8	4.5	6.7	14.5	27.8
126	$NO + O_2$	O_2 + R–X + H_2O	4.5	28.1	10.5	23.0	0.9	2.8	6.7	11.8	4.5	6.7	13.0	27.8
150	$NO + O_2 + H_2$	O_2 + R–X + H_2O												
156	$NO + O_2 + H_2$	O_2 + R–X + H_2O	30.4	28.1	23.7	23.0	8.5	2.8	23.3	11.8	14.3	6.7	27.0	27.8
186	$NO + O_2 + H_2$	O_2 + R–X + H_2O	16.5	28.1	12.8	23.0	0.5	2.8	8.1	11.8	3.6	6.7	21.3	27.8
216	$NO + O_2 + H_2$	O_2 + R–X + H_2O	14.4	28.1	11.0	23.0	0.5	2.8	6.0	11.8				

[a] Maximum conversion of NO obtained if all the R-NH_2 and/or NH_3 formed react(s) with NO to form N_2. R–X = hexylisocyanate, heptanenitrile or 1-nitrohexane. Gas concentrations: 500 ppm NO, 6 vol% O_2, 1 vol% H_2, 250 ppm hexylisocyanate, heptanenitrile, or 1-nitrohexane, 1 vol% H_2O, balance: He.

was 36.2%. In the presence of 1 vol% H_2O, the conversion to NH_3 increased to 13.3% at 250 °C and to 55.5% at 400 °C. Thus, it seems that ammonia is easily formed from nitrohexane especially at higher temperatures. No conversion of nitrohexane to amines was detected in any of these tests.

3.3.4. *T-reactor tests with hexylisocyanate, heptanenitrile, and nitrohexane*

Similar kinds of T-reactor tests were performed with hexylisocyanate, heptanenitrile, and nitrohexane as with ammonia and hexylamine. However, in order to form ammonia and amines from these reactants, the T-reactor was equipped with two similar Ag/alumina beds, one was placed in the side tube and the second one was placed in the bottom part. Mixtures of NO and O_2 as well as NO, O_2, and H_2 were fed from the bottom of the reactor and hexylisocyanate, heptanenitrile, or nitrohexane and O_2 with and without the addition of water was fed from the side. The results of these tests are shown in Table 2.

Passing NO + O_2 from the bottom and hexylisocyanate together with O_2 from the side resulted in a NO conversion of about 5.2 and 8.9% at 250 and 400 °C, respectively. Theoretically, according to the amounts of amine and ammonia formed at 250 °C, the conversion of NO could in the best case be 15.5% (dry conditions) and 28.1% (wet conditions). At 400 °C the corresponding values are 18 and 23%, respectively. Adding water together with hexylisocyanate did not affect the conversion probably due to the limited amount of activated NO_x species present. As expected, the conversion of NO was significantly improved in the gas phase immediately when hydrogen was added to the bottom feed containing NO and O_2. At the first measurement point (wet conditions) at 250 °C the conversion was about 30%, which means that all the available amine and ammonia is consumed. However, a drastic drop in the activity took place as a function of time. It might be that during the first experimental point after addition of H_2, an excess of activated forms of NO_x is released, resulting in high N_2 formation. The excess of these species depends on whether the catalyst has become saturated by nitrates due to the flow of NO + O_2 through the bed in the first part of the test. At the moment of hydrogen addition, a lot of activated NO_x species desorbs into the empty space after the bed and reacts further with the available amines and ammonia. Under steady-state conditions, the amount of the reactive species desorbed into the gas phase is probably much lower. It is worth noting that in this case there is also a possibility for the activated NO_x species to react not only with formed amine and ammonia (from isocyanate), but also with unreacted hydrocarbon species and water. This might explain the more pronounced drop in conversion of NO compared to the test with ammonia, where a similar trend, but weaker, was visible. Also at 400 °C, the same type of increase in activity was observed when H_2 was added to the bottom feed. In this case as well, the conversion observed at the first measurement point (about 23%) is exactly what one could expect if the activated forms of NO_x react with all the ammonia available. No nitrogen was formed directly by reaction of hexylisocyanate and oxygen over the Ag/alumina catalyst as evidenced by a separate test.

Maximum NO conversions of about 1.5 and 7% in the gas phase at 250 and 400 °C, respectively, were achieved by passing NO + O_2 from the bottom and heptanenitrile together with O_2 from the side. Adding water to the feed from side did not change the activity pattern. The low conversion at 250 °C was expected, as there was simply no NH_3 in the gas phase. When hydrogen was introduced to the bottom part of the feed, an increase in the conversion of NO was again observed. The conversion at the first experimental point reached values over 8.5% at 250 °C and 23.3% at 400 °C. The amount of N_2 formed at this first point exceeds the conversion values corresponding to the amount of ammonia available and apparently the activated NO_x species react directly with a part of the –CN group. On, the other hand, the effect of hydrogen was only short termed and the activity decreased by time to values obtained without hydrogen in the feed.

Passing NO + O_2 from the bottom and nitrohexane together with O_2 from the side resulted in a maximum NO conversion in the gas phase of about 3 and 9.8% at 250 and 400 °C, respectively. Adding water to the feed of nitrohexane and O_2 increased the conversion slightly. When hydrogen was added to the bottom part of the feed, the expected increase in the conversion of NO was observed. The conversion of NO measured 6 min after H_2 introduction was 14.3% at 250 °C and 27.0% at 400 °C. The conversion of NO at 250 °C exceeds the expected value of 6.7% but at 400 °C the conversion corresponds exactly to the amount of ammonia available, i.e., about 27%.

3.3.5. *T-reactor test with octane*

To test if the reaction of octane with NO and O_2 over the Ag/alumina catalyst generates ammonia and/or amines after the catalyst bed, similar types of T-reactor tests as above were performed at 250 and 350 °C. In this case, mixtures of O_2, NO + O_2 or NO + O_2 + H_2 in He were fed through the catalyst in the bottom part and NO + O_2 + octane was flowing through the catalyst placed in the side port. The results of these tests are shown in Fig. 12. When O_2 (6 vol% in He) was fed from the bottom and NO + O_2 + octane from the side, the conversion at 250 and at 350 °C was about 5 and 26%, respectively. Adding NO to the bottom feed did not change the conversion. However, when H_2 was added to the feed together with NO and O_2, a similar kind of increase in conversion at 350 °C was observed as in the cases above. No increase in conversion was obtained at 250 °C. When octane was used as the reducing agent in the standard activity test, there was almost no conversion of NO at 250 °C (see Fig. 2, test without H_2). This explains why no increase in conversion is observed in the T-reactor test at 250 °C. The reaction to generate intermediates, which form amines, ammonia, or nitriles, is simply not taking place at such low temperatures due to poor hydrocarbon oxidation activity.

Due to the same type of conversion increase as in the T-reactor tests above, it is reasonable to assume that ammonia and/or amines are also formed in the reaction of NO + O_2 + octane over Ag/alumina. On the other hand, in the T-reactor test with heptanenitrile, higher conversion of NO than expected (from the amount of NH_3 available) was observed. Because of this, it seemed that the nitrile group reacted directly with activated NO_x and it is possible that also the nitriles are responsible for the increase in conversion in the test with octane. The detected nitriles in the GC-MS studies support this theory.

3.3.6. *Activity of hexylamine, hexylisocyanate, heptanenitrile, and 1-nitrohexane as reducing agents*

Hexylamine, hexylisocyanate, heptanenitrile, and 1-nitrohexane were also tested as reducing agents for NO over the Ag/alumina catalyst and their activities were compared to the activity of hexane. The results of these tests are shown in Fig. 13. Using hexylamine as reducing agent, two maxima of the conversion curve at 250 and 550 °C were recorded. A comparison of this activity pattern with the corresponding curve obtained using hexane reveals that the first maximum is probably due to the reaction involving the amine group. With hexane as reducing agent this maximum is missing be-

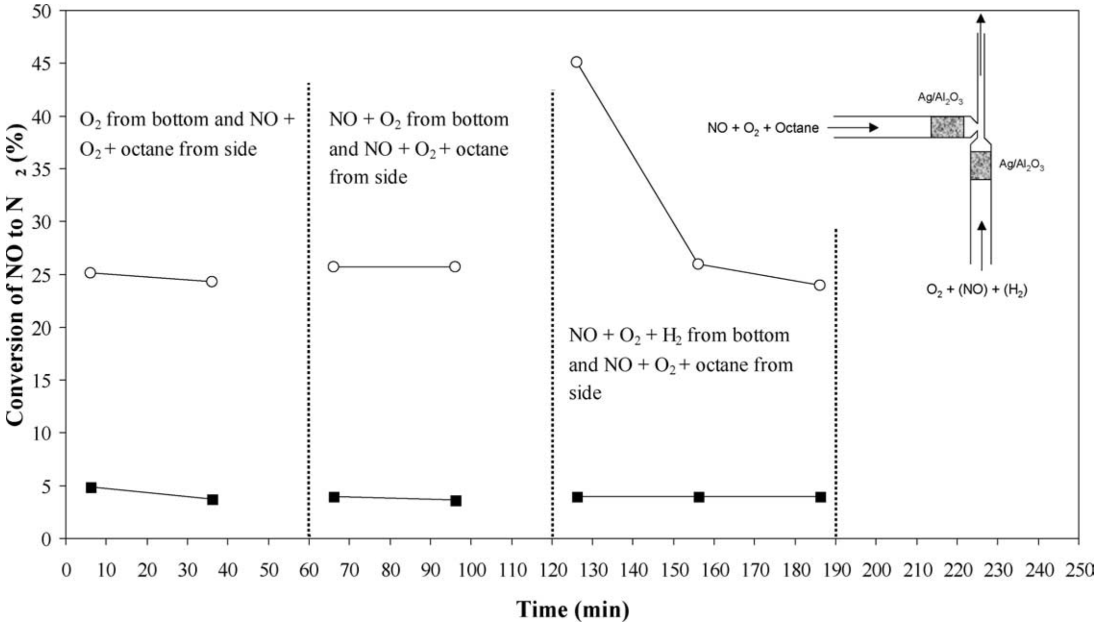


Fig. 12. T-reactor tests with octane at 250 °C (■) and at 400 °C (○). Gas mixture through bottom port: 500 ppm NO and 6 vol% O_2 in the presence and absence of 1 vol% H_2 in He. Gas mixture through side port: 500 ppm NO, 250 ppm octane, and 6 vol% O_2 in He.

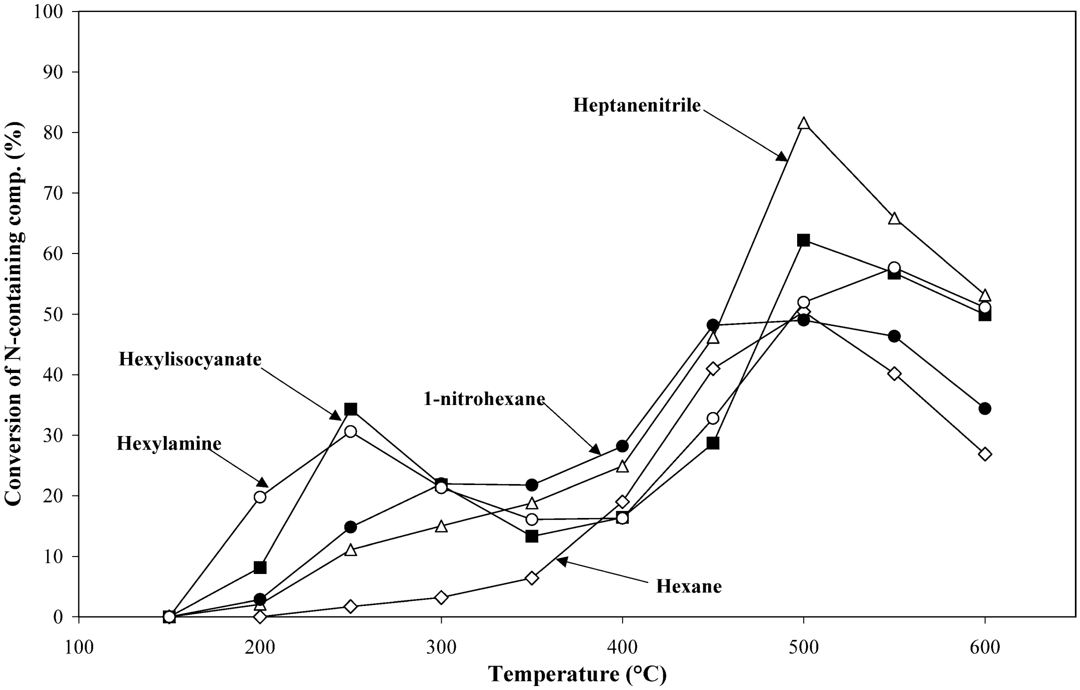


Fig. 13. Conversion of N-containing compounds to N_2 as a function of temperature using hexane, hexylamine, hexylisocyante, heptanenitrile, and 1-nitrohexane as reducing agents. Gas mixture: 500 ppm NO, 6 vol% O_2, and 250 ppm of reducing agent in He. GHSV = 60,000 h^{-1} and volumetric gas flow = 550 ml/min.

cause the formation of amines or other reactive intermediates is restricted to higher temperatures. The second maximum is probably obtained as a combined effect of the hydrocarbon chain together with the remaining amine or its decomposition product ammonia.

A similar trend was observed using hexylisocyanate and nitrohexane as reducing agents. In the case of hexylisocyante the first maximum is probably due to the reaction involving the amine group and ammonia formed by the hydrolysis and decomposition of the isocyanate. The second maximum seems to originate from both the hydrocarbon chain and the ammonia formed from the isocyanate group. With nitrohexane the first maximum was not as pronounced as for hexylisocyanate.

Opposite to the cases of hexylamine, hexylisocyanate, and nitrohexane there was only one clear maximum at 500 °C in the activity pattern when using heptanenitrile as reducing agent. The activity related to this intermediate is restricted to higher temperatures because of its stability. If the temperature is high enough (over 400 °C) the heptanenitrile is a very active reducing agent for NO. The activity seems to be a result of formed ammonia in combination with the hydrocarbon chain or possibly of the –CN group itself.

3.4. *Mechanistic aspects*

It is clear that gas-phase reactions are involved in the HC-SCR process over Ag/alumina. It is also evident that the components participating in these gas-phase reactions include a nitrogen-containing functional group that reacts with activated forms of NO_x to form N_2. Upon oxidation of these N-containing compounds over an oxidation catalyst, NO is reproduced. It is well known that ammonia and amines, for instance, are oxidized to NO. The presence of ammonia and amines in the gas phase could explain the observed behavior when adding the oxidation catalyst after the Ag/alumina bed. The T-reactor tests show that activated forms of NO_x react with these species in the gas phase producing N_2. In addition, it seems that also nitriles react in the same way.

The role of hydrogen on the HC-SCR process is interesting, as it has at least two main functions. First of all, improved oxidation of all components involved is obtained. In the presence of hydrogen the oxidation of octane is improved as evidenced by a test in which 1 vol% H_2 was added to a mixture of 375 ppm octane and 6 vol% O_2 at 350 °C. Without H_2 in the feed the conversion of octane was 41.2%. By introduction of 1 vol% H_2, the conversion increased to 73%. In addition, as shown earlier, the rate of formation of adsorbed NO_x species is much higher in the presence of hydrogen than in the absence of H_2. The improved oxidation of the hydrocarbon also results in faster formation of different oxygenates which react with these ad-NO_x species to form N-containing compounds. From these N-containing compounds amines and ammonia are easily formed as shown by our FTIR gas cell experiments. Secondly, in this study hydrogen has been shown to activate NO over the Ag/alumina catalyst to react with the produced amines and ammonia or with other N-containing species in gas phase, but the same reactions certainly also take place on the surface of the Ag/alumina catalyst. Hydrocarbons could be a source of

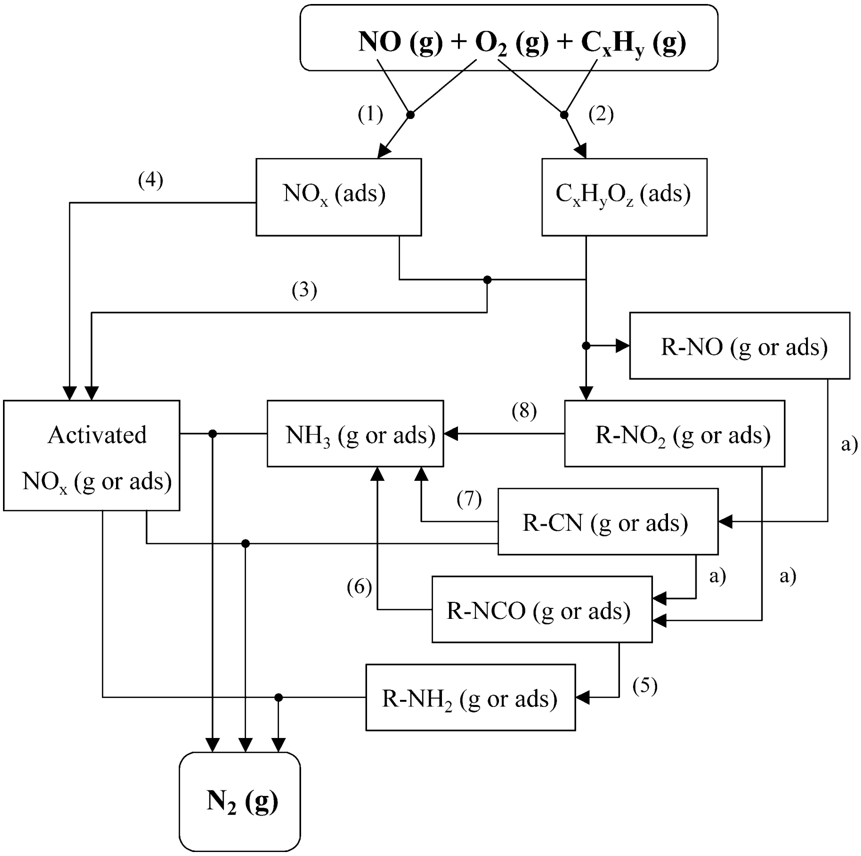


Fig. 14. Schematic illustration of the proposed reaction mechanism during HC-SCR over Ag/alumina. Reactions 1–4 are accelerated by addition of hydrogen. Higher concentrations of ammonia and amines are formed in presence of water in steps 5–8. Steps 5 and 6 proceed at 250 °C, but at 400 °C step 5 is not taking place. The transformation of nitrile to NH_3 in step 7 is restricted to high temperatures. Step 8 is pronounced at high temperatures. (a) From the literature [4].

hydrogen and may at temperatures where partial oxidation takes place play an important role in the activation procedure of NO_x.

The observations made within the present study fit well into the mechanism proposed by Meunier et al. [16], where a similar kind of Ag/alumina catalyst was used. We would like to stress the importance of gas-phase reactions as a part of their proposed mechanism. A schematic illustration, of the proposed mechanism of HC-SCR over Ag/alumina including the new observations made within this study is shown in Fig. 14. In this mechanism, R-NO_2, R-NCO, and R-CN are intermediates for the formation of amines and ammonia, which are consumed both on the surface of the catalyst as well as in the gas phase behind the catalyst bed by reaction with activated NO_x species. The nitriles are quite stable and transform to ammonia only at high temperatures. Therefore, it is unlikely that these species are the key intermediates at temperatures below 400 °C. Isocyanate species, on the other hand, can be responsible for the activity also at low temperatures, as they easily hydrolyze to form amines and ammonia at temperatures below 250 °C. It was shown that hydrogen boost the formation rate of isocyanate and thereby enhances the low-temperature activity during the HC-SCR process.

4. Conclusions

The possibility of forming nitrogen in the gas phase by reaction of activated forms of NO_x with amines and ammonia or with other organic intermediates, which can be converted to amines and/or ammonia, was investigated. Both ammonia and hexylamine were shown to react in the gas phase with activated NO_x species to produce N_2. This new finding reveals that it is possible to homogeneously convert NO to N_2 by reaction with NH_3 in excess oxygen at temperatures far below those reported for selective noncatalytic reduction of NO. Components such as R-NO_2, R-NCO, and R-CN were proved to be intermediate species from which amines and ammonia are formed for the last step of the HC-SCR reaction mechanism. Nitrohexane was transformed to NH_3 in the presence of O_2 over the Ag/alumina already at 250 °C and the amount of NH_3 produced increased by the addition of H_2O. Hexylisocyante was hydrolyzed to amine and ammonia at 250 °C over the catalyst under conditions of excess oxygen but only to ammonia at 400 °C. At 250 °C the conversion to amine and ammonia was almost doubled by the addition of H_2O. Heptanenitrile was very stable and only small amounts of NH_3 were observed at 400 °C; however, nitriles can react directly with activated NO_x species forming N_2.

The role of hydrogen on the HC-SCR process involves several functions. Improved oxidation of all components was obtained in the presence of H_2. In the oxidation of octane, addition of hydrogen increased the conversion from 41 to 73% at 350 °C. As a consequence, the improved oxidation rate of the hydrocarbon also results in faster formation of different oxygenates, which react and form N-containing species. The rate of formation of adsorbed NO_x species was also found to be much higher in the presence of hydrogen. In addition, hydrogen was shown to activate NO over the Ag/alumina catalyst for further reactions with the produced amines and ammonia or with other N-containing species in the gas phase. The activated NO_x species may be of radical or ionic character.

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