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Continuous reduction of NO with octane over a silver/alumina catalyst in oxygen-rich exhaust gases: combined heterogeneous and surface-mediated homogeneous reactions

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Abstract

An Ag/alumina catalyst was prepared and tested for its HC(octane)-SCR activity using a gas mixture simulating exhaust gas from diesel and lean-burn vehicles. The catalyst showed excellent NO to N_2 activity, having a maximum conversion of approximately 90% at 450 °C and an average conversion of 66% in the temperature window 300–600 °C. During the high conversion of NO, formation of CO was recorded. A commercial oxidation (“cleanup”) catalyst was placed after the Ag/alumina in order to remove the formed CO as well as unburnt hydrocarbons. This resulted, however, in a drastic drop of NO conversion, which was more pronounced when the distance was short between the two catalysts. When the distance between the two catalysts was increased to 33 mm (maximum value) the conversion was almost unaffected. This raised the question how nitrogen, once formed from nitrogen oxides, can seemingly disappear over the oxidizing catalyst at temperatures far too low to make this phenomenon thermodynamically feasible. In this study we propose that the HC-SCR reaction mechanism over Ag/alumina involves a gas-phase reaction between species created over the catalyst surface, and that this reaction is dependent on the residence time behind the catalyst.

Keywords: Octane-SCR; Ag/alumina catalyst; Reaction mechanism; Gas-phase reaction; GC-MS; DRIFTS

1. Introduction

Combustion of fossil fuels in vehicle engines produces environmentally harmful and unwanted exhaust gases, such as nitrogen and carbon oxides. As agreed upon at the Kyoto conference [1] carbon dioxide is one of the greenhouse gases, which must be reduced in the outlet from, e.g., gasoline and diesel engines. Since the amount of carbon dioxide in the exhaust gases from these sources is directly proportional to the fuel consumed, an obvious solution is to design more fuel-efficient engines. This goal can only be reached by operating the vehicle engines under lean conditions, i.e., with a large excess of oxygen. The drawback is, however, enhanced formation of nitrogen oxides (NO_x), mainly nitrogen monoxide (NO) and nitrogen dioxide (NO_2).

As the permissible emission limits for nitrogen oxides in exhaust gases are continuously lowered by law, proper precautions must be considered. One possibility is to use catalytic after treatment analogous to the method used for traditional gasoline engines. The three-way catalyst (TWC) used in these vehicles, however, is designed to operate under stoichiometric conditions and cannot be applied to lean-burn engines. The challenge then is to create a catalyst over which the nitrogen oxides can be reduced to nitrogen in the oxygen-rich gas mixture, simultaneously permitting carbon monoxide and unburned hydrocarbons to be oxidized to their final products carbon dioxide and water. One way of reaching this goal is to use the NO_x storage technique, which is in fact the prevailing method today. Selective catalytic reduction (SCR) would, on the other hand, offer a more elegant, direct, and continuous method to reduce the NO_x concentration in exhaust gases. As the SCR method can be considered to be the ultimate solution to the catalytic after treatment of exhaust gases from lean-burn engines, it is the subject of the present investigation.

Traditionally, selective catalytic reduction of NO_x has been carried out using ammonia as the reducing agent. Although this method is applicable in large stationary plants,

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it is, for obvious reasons (ammonia slip from many small sources, etc), not suitable for use in small vehicles. A more attractive solution for this type of nitrogen oxide pollutant is to use hydrocarbons (HC-SCR), being more "natural" substances in the transport system, as reducing agents. Several investigations since the pioneering work of Held et al. [2] and Iwamoto et al. [3] have brought a lot of promising zeolitic and nonzeolitic materials to be considered for HC-SCR. It is commonly accepted that Ag/alumina is one of the most active material in these processes. Burch et al. [4] have in a recent review extensively presented the potential of Ag/alumina catalysts together with a discussion on the complicated mechanism, taking place over such a catalyst. In several investigations the hydrocarbons have been shown to act differently under similar conditions [5–7], which strongly indicate that a usable hydrocarbon must be chosen carefully and adapted to the catalyst. In earlier laboratory and engine tests [7] we have found good de-NO_x results over a silver/alumina catalyst with octane as the reducing agent in oxygen-rich exhaust gas mixtures. We noticed that a considerable amount of carbon monoxide was produced during the process, and that our efforts to eliminate this harmful substance over a subsequent oxidizing catalyst resulted in a decreased conversion of NO to N_2 as well. In the present report we try to identify and explain the puzzling question how nitrogen, once formed from nitrogen oxides, can seemingly disappear over the oxidizing catalyst at temperatures far too low to make this phenomenon thermodynamically feasible. In earlier work Lukyanov et al. and Vassallo et al. [8,9] have dealt with the role of gas-phase reactions in the mechanism of HC-SCR. In the study of Lukyanov et al. [8] NO or rather NO_2 was considered to act 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 combination of the formed organic nitro compounds and NO or NO_2. In this investigation we propose that an important step of HC-SCR, i.e., the formation of a significant amounts of N_2, may take place in the gas phase in immediate connection to the catalyst bed.

2. Experimental

2.1. The catalyst

The silver/alumina (Ag/Al_2O_3) catalyst was prepared according to the procedure further outlined in Ref. [7]. Analysis of the catalyst by DCP (Spectrascan IIIA) showed a silver average content of approximately 2 wt%. This value is essential since it has been reported in several studies [10–13] that silver loading of this order is optimal for the de-NO_x process of oxygen-rich exhaust gases. The N_2-physisorption measurements (Carlo Erba Sorptomatic 1900) over the received commercial alumina (A-201, LaRoche) support resulted in a BET surface area and pore volume of 289 m^2/g and 0.409 cm^3/g, respectively. Silver impregnation and calcination for 3 h at 550 °C lowered the surface area to 185 m^2/g. The pore volume did not change after addition of metal. The A-201 alumina is a mixture of rather unstable phases such as χ, ρ, η, and pseudo-γ. This could be one reason for the relatively high surface area loss during the calcination.

The silver distribution in the catalyst beads was investigated in more detail at four different places on the center cross section of a single bead by careful analysis of the amounts of Ag (Al and O as well) by SEM-EDXA (Cambridge Leica 360). The squares investigated (Fig. 1) were situated in the middle of the bead (bead diameter ~ 2.2 mm), 0.55 mm from the bead surface, as close as possible to the surface, and on the outer surface of the bead. The silver content in these areas was 2.1, 2.0, 2.4, and 3.7 wt%, respectively. An X-ray line analysis, with several hundreds of points along the cross section (~ 2.2 mm), was also performed. The scan did not reveal large deviations in the silver distribution pattern. The silver was comparatively evenly distributed within the bead, with somewhat higher values in the areas close to and on the outer surface. These higher values on the outer surface of the Ag/alumina can most probably be attributed to residual silver remaining from the impregnation procedure (no washing of the beads was carried out after impregnation). According to our results, however,

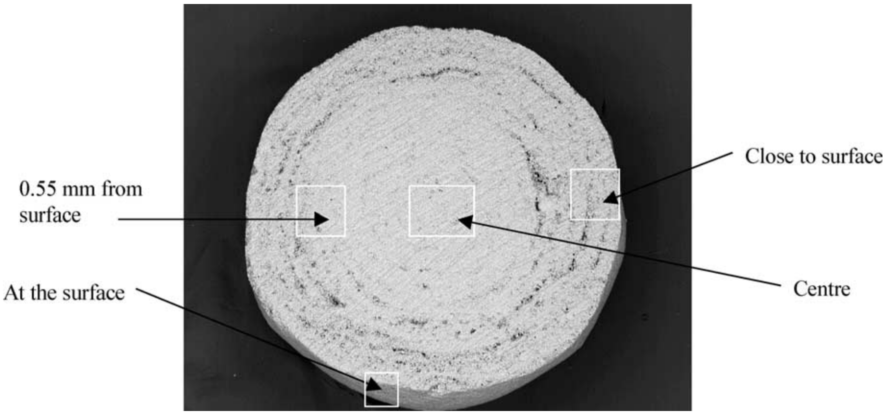

Fig. 1. Scanning electron micrograph of a cross section ($D \sim 2.2$ mm) of the Ag/alumina bead.

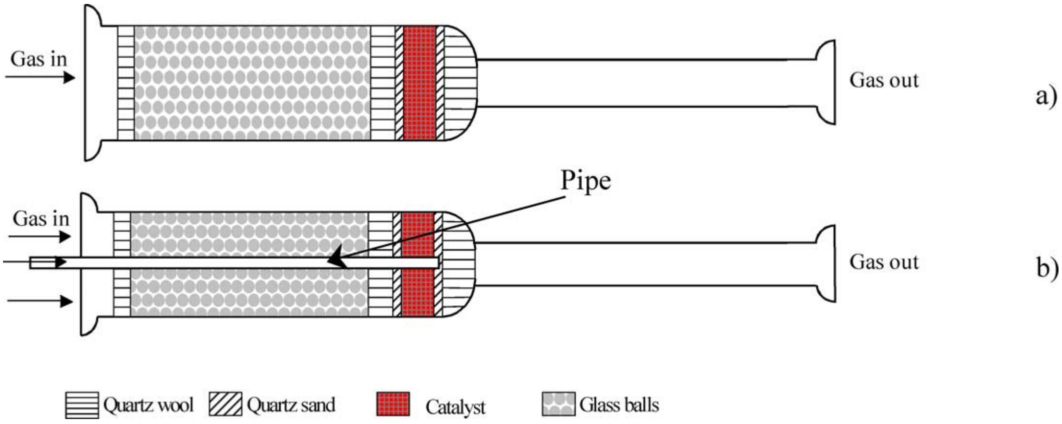

Fig. 2. The quartz microreactor (a) modified (b) with an inserted pipe.

there is only a very thin layer on the bead, which has a notably higher content of silver. It is, on the other hand, worth noting that the silver content in the three squares inside the Ag/alumina bead is in agreement with our earlier DCP measurements. On the basis of these results we conclude that crushing and sieving of the material prior to testing can be carried out while retaining the silver concentration.

2.2. Experimental setup

The crushed and sieved Ag/alumina granules (0.4 g, diameter distribution 250–500 µm) were tested in a quartz micro reactor (Fig. 2a) inserted in an oven equipped with a temperature controller. A temperature window of 150–600 °C with sampling under steady-state conditions (GHSV = 60,000 h^{-1} and 550 ml/min) was used for the catalytic activity runs. The temperature in the catalyst bed was monitored by a K-type thermocouple connected to a temperature controller (Eurotherm 900 EPC). In separate experiments it was verified that experimental data were free from mass-transfer limitations.

The gas mixture used in the activity tests consisted of 500 ppm NO, 375 ppm octane, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O, and He as balance. All gases were of high purity (AGA) and introduced into the reactor by means of mass-flow controllers (Brooks 5850). The water was added to the gas mixture by a liquid-flow controller (Bronkhorst HI-TEC), which was combined with a controlled evaporator mixer (Bronkhorst HI-TEC). The addition of octane took place via a syringe pump (CMA 102/Microdialysis), which was also used to introduce possible intermediates in the HC-SCR reactions, such as heptylisocyanate, acetonitrile, and heptanone oxime (Acros, LabScan, and Aldrich, respectively). Ammonia was also used as a reducing agent instead of octane and introduced to the system using a mass-flow controller. All the components were preheated before entering the reactor and the temperature in the pipes was kept constant with heating tapes. Oxygen was led separately into the reactor in order to avoid any reaction between NO and O_2 in the line before the catalyst bed.

In order to eliminate carbon monoxide and unburnt octane, a commercial Pt-supported oxidation catalyst (Johnson Matthey) was placed after the Ag/alumina catalyst. The two catalysts were arranged at various distances from each other, the extremes being complete physical mixing of the two catalysts and infinite spacing (no oxidation catalyst).

The concentrations of N_2, CO_2, CO, and O_2 were determined with the aid of a gas chromatograph (HP 6890) equipped with a GS Q column, a GS Molesieve column (J&W Scientific), and FI as well as TC detectors. Two condensers, kept at -5 and at -25 °C, were used to trap out the water from the gas prior to analysis. The concentration changes of NO_x ($NO + NO_2$), in the gas mixture, were recorded by a chemiluminescence NO_x analyzer (API 200 AH), whereas the specific conversion of NO to N_2 was calculated on the basis of the amount of nitrogen formed. This system facilitated a comparison of the NO conversions obtained with the two significantly different methods. High-purity calibration gases (AGA) were used for calibration of the NO_x analyzer and the gas chromatograph.

2.3. Experimental setup for gas-phase reaction investigations

For the purpose of investigating possible gas-phase reactions in the empty volume between the silver/alumina and the oxidation catalyst, the reactor was modified by inserting a pipe, which passed through the Ag/Al_2O_3 catalyst bed ending at its outlet surface (Fig. 2b). This modification enabled bypassing of any reactant to the immediate reaction space behind the first (reduction) catalyst. The experiments were carried out at two constant temperatures: 450 and 550 °C.

Two types of quartz reactors, having same free space but different surface to volume ratio behind the Ag/alumina catalyst, were used to investigate the importance of reactor design in the gas phase before the subsequent coolers and analyzing equipment. In these experiments the catalyst beds were identical and a volumetric flow rate of 550 ml/min at a GHSV = 60,000 h^{-1} was used.

The condensate (H_2O) trapped out during the activity tests (using the basic gas mixture) was subjected to GC-MS studies, in order to detect possible components taking part in the gas-phase or surface reactions. 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), was used in this study.

In a complementary experiment, the Ag/alumina powder catalyst was placed in a small-sized stainless-steel reactor, operating at 400 °C, which was directly connected to a cooled (0 °C) acetone trap. A gas mixture consisting of 500 ppm NO, 375 ppm octane, and 6 vol% O_2 was lead through the catalyst and the species formed on the catalyst surface or in the gas phase bubbled through the acetone trap. The acetone mixture was analyzed using the GC-MS technique, as described above.

The existing microreactor system was modified to fit a study of the formed organic species leaving the catalyst surface. In the new setup the Ag/alumina catalyst was placed in the GC injection liner, to which the column was directly connected, and different combinations of the gas mixture (NO, octane, and O_2) were pulsed into the catalyst using the gas-sampling valve.

In order to identify formed surface species on the Ag/alumina catalyst, in situ DRIFTS experiments were performed using an FTIR spectrometer (ATI Mattson Infinity) equipped with a high-temperature/vacuum chamber (Spectratech Inc.). Gases were introduced to the chamber using mass-flow controllers (Brooks 5890). The catalyst samples had a particle size of 90–125 µm and were pretreated in situ at 500 °C using a gas mixture containing 6 vol% O_2 in He. Both background and experimental scans were carried out at 350 °C with the spectral resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Activity testing

As already indicated we choose here to present results obtained by using octane as the reducing agent for nitrogen oxides over the Ag/alumina catalyst described in Section 2.1, although several other hydrocarbons [7] behave in a similar way (Fig. 3). Fig. 4 reveals that the conversion of NO to N_2 by octane, over Ag/alumina, reaches comparatively high values, with a maximum of 90% at 450 °C and a mean value of 66% in the temperature interval 300–600 °C. It is worth noting in Fig. 4, that two NO conversion curves are given: one is obtained with the chemiluminescence instrument and the other by GC measurements. The conversion calculated on the basis of the GC measurements represents exclusively the environmentally desired NO to N_2 reaction, whereas the chemiluminescence instrument shows variations in NO_x (NO + NO_2) only, and does not give any information about the reaction products. Absorption of NO_2 in the water of the condensers preceding the analyzers could not be excluded, a process which inevitably resulted in an apparently higher NO_x conversion. This might be the reason why the chemiluminescence technique usually gives higher conversion values.

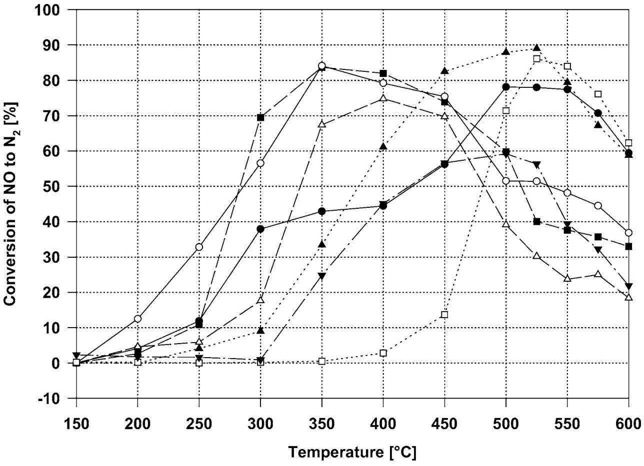

Fig. 3. NO to N_2 conversions over fresh Ag/Al_2O_3 as a function of temperature using different hydrocarbons as reductants. $HC_1/NO = 6$ and GHSV = 60,000 h^{-1}. (□) Propane + propene, (▲) octane, (●) isooctane, (▼) 1-octene, (○) octanal, (■) octanol, and (△) octanoic acid [7].

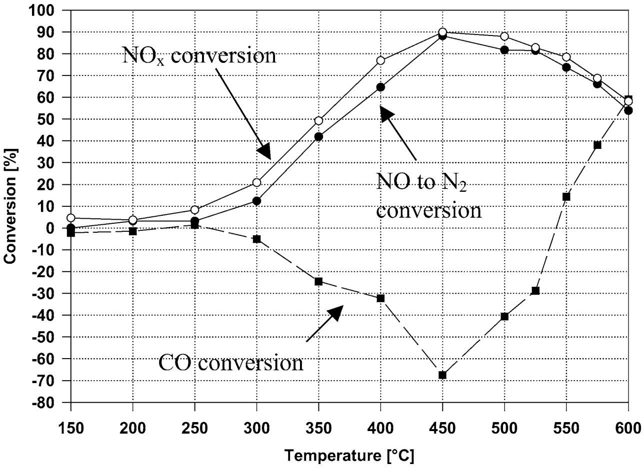

Fig. 4. Activity test over fresh 2 wt% Ag/alumina using following gas mixture: 500 ppm NO, 375 ppm octane, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O, and He as balance. GHSV = 60,000 h^{-1} and volume flow = 550 ml/min.

As shown in Fig. 4 the two conversion curves in this case follow each other quite closely when the only catalyst involved is the silver/alumina. The figure also reveals that there is no conversion of the added carbon monoxide in the temperature interval 150–540 °C. On the contrary, there is considerable production of CO with a maximum value at 450 °C. When the amount of carbon monoxide added serves as the reference, the amount of CO is almost doubled (CO conversion = −70%). Our conclusion is that selective reduction of NO with octane over the silver/alumina catalyst exhibited good NO reduction properties with the drawback of simultaneously generating carbon monoxide.

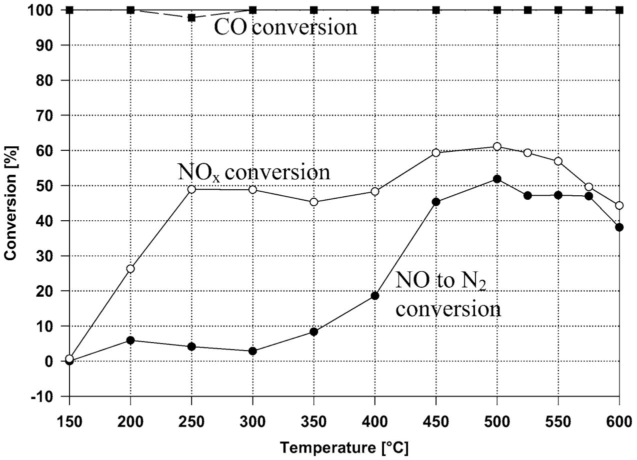

Fig. 5. Activity test over Ag/alumina + commercial oxidation catalyst (Pt supported, JM) with 0-mm distance between catalyst beds. 500 ppm NO, 375 ppm octane, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O, and He as balance. GHSV = 60,000 h^{-1} and volume flow = 550 ml/min.

In order to eliminate the harmful CO we added a commercial oxidation catalyst, delivered by Johnson Matthey, directly after the Ag/alumina bed, and, as shown in Fig. 5, the carbon monoxide conversion reached 100% at 150 °C. This result was expected, but surprisingly the addition of the "cleanup" catalyst changed the NO conversion dramatically. As can be seen in Fig. 5, the maximum conversion of NO to N_2 was decreased to 45% at 450 °C, as compared to 90% in Fig. 4, and the average conversion dropped to approximately 32% in the temperature interval 300–600 °C. Fig. 5 also shows that the NO_x conversion based on chemiluminescence measurements at 250 °C increases from about 5% without the oxidation catalyst to 50% with the catalyst.

This peculiar behavior was systematically explored by arranging the two catalysts in series at different distances as principally depicted in Fig. 6. The results of this investigation are given in Figs. 7–9 for distances of 2, 10, and 33 mm between the catalysts, respectively. In Fig. 10, a comparison of the different distances and their effect on NO to N_2 activity are presented, in addition to the physical mixing of the two catalysts and Ag/alumina alone.

The figures clearly show that the incorporation of an oxidation catalyst into the system resulted in decreased activity in terms of NO to N_2 conversion, together with improved CO oxidation reaching 100% below 200 °C. By increasing the distance between Ag/alumina and the cleanup catalyst, an improvement in the NO to N_2 conversion was obtained (Fig. 10). In the case, where the two catalysts were mixed, the conversion level of NO to N_2 did not exceed 10% (Fig. 10). The best NO to N_2 activity, regarding the combined system, was recorded over the catalysts having a distance of 33 mm between each other. The results obtained

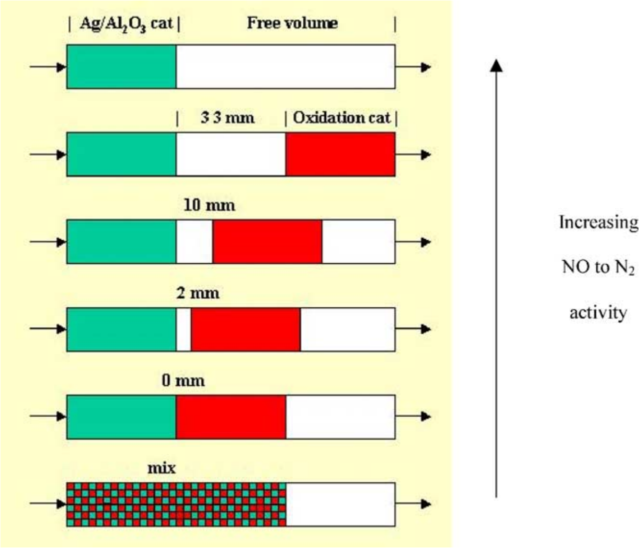

Fig. 6. Schematic illustration of the effect of different distance between Ag/alumina and Pt-oxidation catalyst.

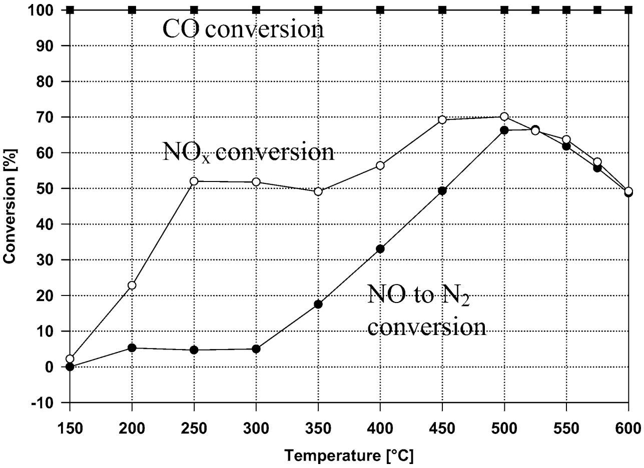

Fig. 7. Activity test over Ag/alumina + commercial oxidation catalyst (Pt supported, JM) with 2-mm distance between catalyst beds. 500 ppm NO, 375 ppm octane, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O, and He as balance. GHSV = 60,000 h^{-1} and volume flow = 550 ml/min.

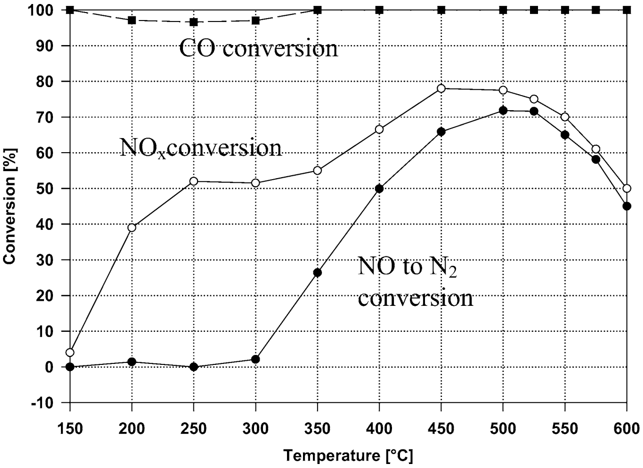

Fig. 8. Activity test over Ag/alumina + commercial oxidation catalyst (Pt supported, JM) with 10-mm distance between catalyst beds. 500 ppm NO, 375 ppm octane, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O, and He as balance. GHSV = 60,000 h^{-1} and volume flow = 550 ml/min.

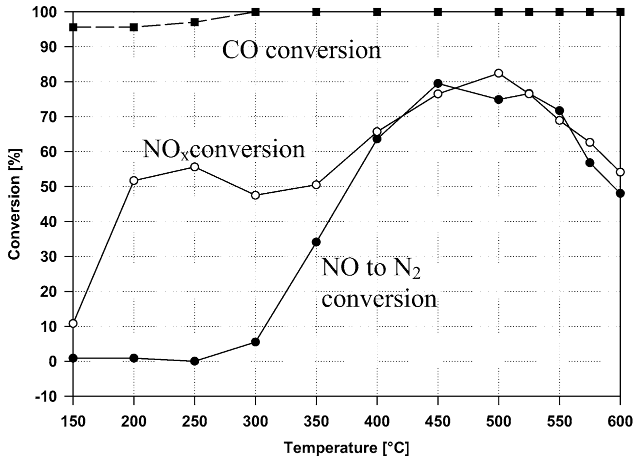

Fig. 9. Activity test over Ag/alumina + commercial oxidation catalyst (Pt supported, JM) with 33-mm distance between catalyst beds. 500 ppm NO, 375 ppm octane, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O, and He as balance. GHSV = 60,000 h^{-1} and volume flow = 550 ml/min.

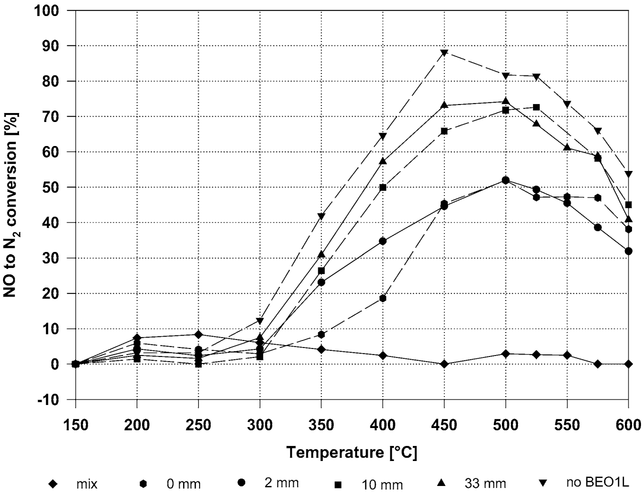

Fig. 10. Comparison of the effect on NO to N_2 activity by variation of the bed length between the Ag/alumina catalyst and the commercial (JM) Pt-supported oxidation catalyst. 500 ppm NO, 375 ppm octane, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O, and He as balance. GHSV = 60,000 h^{-1} and volume flow = 550 ml/min. no BEO1L, Ag/alumina alone; and mix, mechanical mixture of Ag/alumina and oxidation catalyst.

at a 10-mm distance did not, however, differ to a great extent from the 33-mm distance. Overall the dual-catalyst systems were significantly less active in terms of NO to N_2 conversion compared with the single Ag/alumina bed. The mean residence time between the two catalysts with 33-mm distance was calculated as 0.28 s, using the basic gas-flow rate equal to 550 ml/min. This value can be considered as a minimum for obtaining sufficiently high NO to N_2 conversion. It should be noted that a longer residence time is required to fulfill the conditions for the gas-phase reactions.

The high NO_x conversion obtained by chemiluminescence measurements at low temperatures, in the cases where an oxidation catalyst was used, could be explained by formation of N_2O and NO_2. N_2O cannot be detected using a NO_x chemiluminescence analyzer, but it has been shown [14,15] that platinum group catalysts have a tendency to form nitrous oxides during selective catalytic reduction of NO by, e.g., H_2. Cant et al. [15] in their work on the formation of nitrous oxide during the reaction of simulated exhaust gas streams over rhodium, platinum, and palladium catalysts, found that palladium-containing catalysts give rise to the formation of N_2O in two regimes. Below 200 °C the concentration of N_2O increased because of the reaction between NO and H_2, while above 300 °C the concentration increased by another process that persisted through to 500 °C. The $NO/H_2/O_2$ reaction forming N_2O on noble-metal catalysts, at low temperatures and under lean-burn conditions, has been found to be sensitive to the reaction conditions [14]. The formation of N_2O was strongly temperature dependent, being the major product at low temperatures. The selectivity to N_2O was significantly increased in the presence of water, but its formation, when the concentrations of NO or H_2 are varied, was complex. As the formation of NO_2 is thermodynamically favored at low temperatures, it will obviously be produced over an oxidation catalyst and part of it could be trapped (absorbed) in the coolers, resulting in the formation of HNO_3. This is supported by an earlier study carried out at our laboratory on the same subject [16], where decreased pH values of the condensed water (prior to the analyzing equipment) were reported.

3.2. *Bypassing of reactants through the catalyst bed*

In order to investigate possible gas-phase reactions, a pipe was used to bypass different reactants to the outlet surface of the catalyst bed. The results from the experiments (at 450 and 550 °C) are presented in Figs. 11–13. In the first experiment (Fig. 11) we passed the basic gas mixture through the catalyst, except NO and/or NO_2, which were bypassed to the outlet surface of the catalyst bed. Here the aim was to investigate if octane is partly oxidized to form a component that reacts with NO or NO_2 in the gas phase. The results were compared with the cases where NO and NO_2 were included in the base gas feed. As can be seen no conversion of NO_x to N_2 took place in the cases where NO, NO_2, or NO + NO_2 were bypassed. Bypassing NO and NO_2 also dramatically affected the CO formation pattern. With NO and NO_2 flowing through the catalyst, the formation of CO was almost doubled compared with the cases where these reactants were bypassed. This suggests that NO and/or NO_2 are strongly involved in the partial oxidation of octane and enhance the formation of species that should be active for gas-phase de-NO_x processes.

The next step in these experiments was to find out whether nitrous oxide is an important component during the HC-SCR. In these experiments N_2O or N_2O + NO were led both through the catalyst and through the pipe to the outlet surface of the catalyst bed. As a main observation it can be concluded that no N_2O to N_2 activity was recorded in these experiments (Fig. 12), irrespective of whether the N_2O was

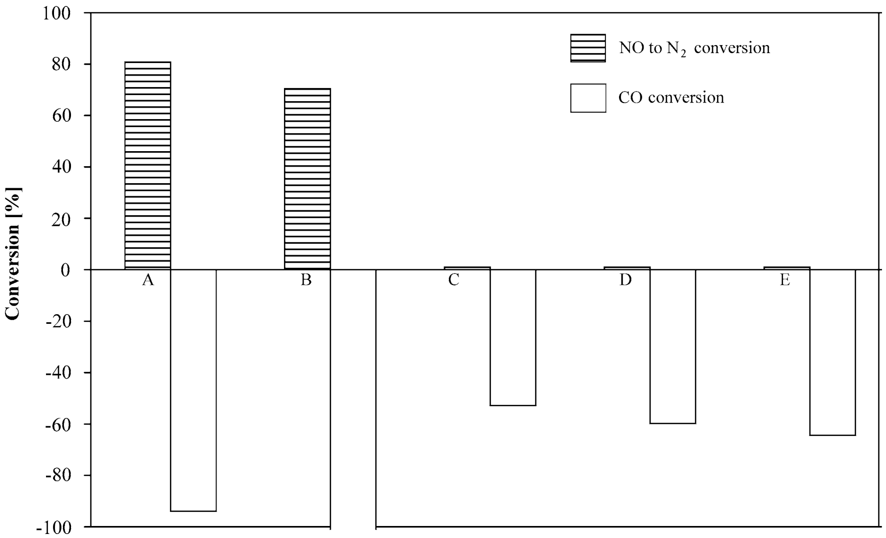

Fig. 11. Activity test over Ag/alumina at 450 °C where a pipe was used to bypass different reactants (Fig. 2b) to the outlet of the catalyst bed. Basic gas mixture: 375 ppm octane, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O, and He as balance. (A) 500 ppm NO in basic gas mixture through catalyst, (B) 250 ppm NO and 250 ppm NO_2 in basic gas mixture through catalyst, (C) 250 ppm NO and 250 ppm NO_2 through pipe and rest of the basic gas mixture through catalyst, (D) 500 ppm NO_2 through pipe and rest of the basic gas mixture through catalyst, (E) 500 ppm NO through pipe and rest of the basic gas mixture through catalyst.

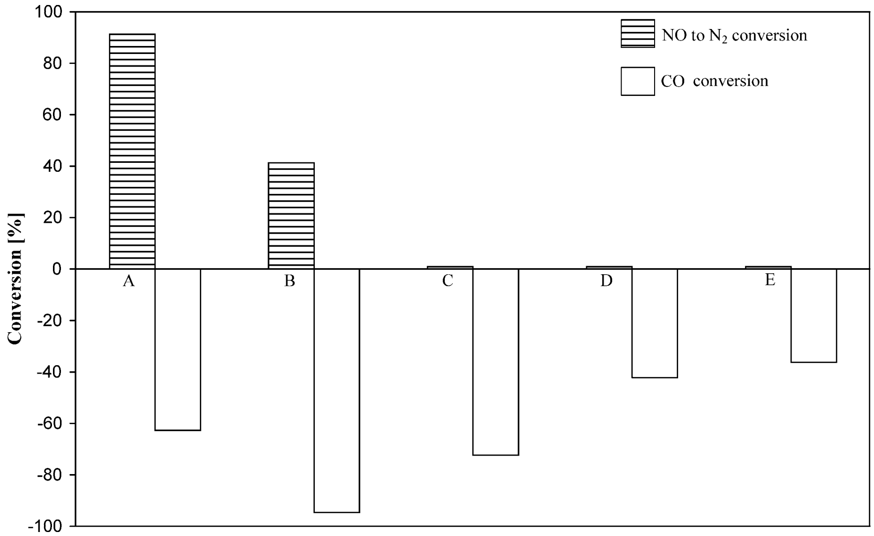

Fig. 12. Activity test over Ag/alumina at 450 °C where a pipe was used to bypass different reactants (Fig. 2b) to the outlet of the catalyst bed. Basic gas mixture: 375 ppm octane, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O, and He as balance. (A) 500 ppm NO in basic gas mixture through catalyst, (B) 250 ppm NO and 125 ppm N_2O in basic gas mixture through catalyst, (C) 250 ppm N_2O in basic gas mixture through catalyst, (D) 250 ppm NO and 125 ppm N_2O through pipe and rest of the basic gas mixture through catalyst, (E) 250 ppm N_2O through pipe and rest of the basic gas mixture through catalyst.

bypassed or not. All the produced nitrogen seemed to originate from the introduced NO. It can be concluded that the formation of N_2O as an intermediate component is unlikely and if formed during the HC-SCR it can be considered as a by-product. Surprisingly, the amount of CO produced was quite equal in the experiments, where NO was replaced by N_2O and no bypassing of the catalyst bed was carried out. When NO together with N_2O was flowed through the catalyst, the formation of CO was actually higher than when only NO was included in the feed gas. This means that nitrous oxide effectively takes part in the partial oxidation of octane, resulting in the formation of CO. However, in this case the created species do not participate in the formation of N_2.

In the experiments, where octane was bypassed to the outlet surface of the Ag/alumina and the rest of the feed gas mixture was flowed through the catalyst, no NO/NO_2 to N_2 conversion was detected (Fig. 13). Approximately 12% of octane was converted to CO_2 in the gas phase and the oxidation was improved at higher temperatures (550 °C). Based

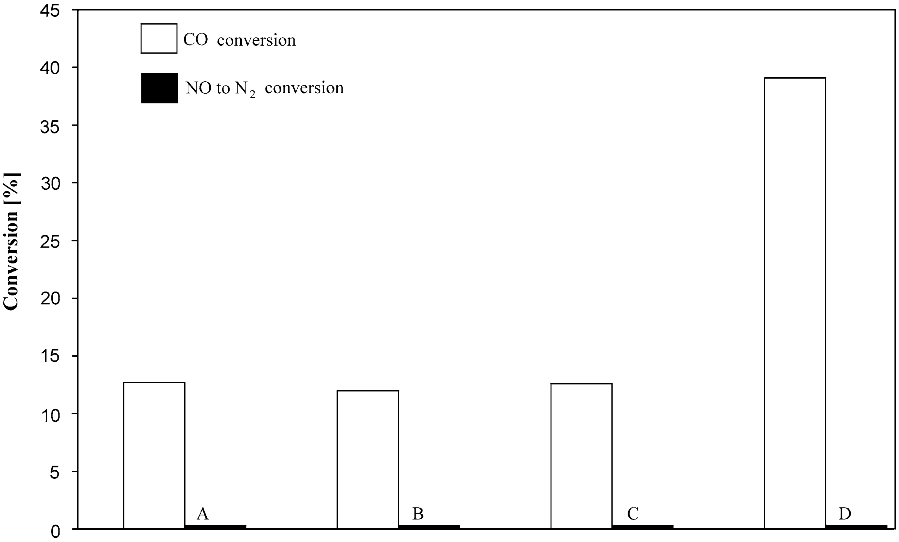

Fig. 13. Activity test over Ag/alumina at 450 °C where a pipe was used to bypass different reactants (Fig. 2b) to the outlet of the catalyst bed. Basic gas mixture: 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O, and He as balance. (A) 375 ppm octane through pipe and 500 ppm NO + basic gas mixture through catalyst, (B) 375 ppm octane through pipe and 250 ppm NO + 250 ppm NO_2 in basic gas mixture through catalyst, (C) 375 ppm octane through pipe and 500 ppm NO_2 in basic gas mixture through catalyst, (D) (at 550 °C) 375 ppm octane through pipe and 250 ppm NO + 250 ppm NO_2 in basic gas mixture through catalyst.

on this observation it can be stated that octane must be lead through the catalyst together with NO in order to form oxygenated species, which consequently react further on the surface and in the gas phase to form N_2.

The importance of the CO formed during the HC-SCR was investigated by replacing octane with 3500 ppm CO (i.e., $C_1/NO = 6$), and leading the full gas mixture through the catalyst. No formation of N_2 was detected during this test and the conversion of CO was below 20%. This means that CO as a by-product does not itself contribute to the reduction of NO, but the formation of CO, coinciding with high N_2 production, indicates the formation of an efficient reductive intermediate.

As a summary it can be concluded that both nitric oxide and octane must flow through the catalyst to obtain high NO reduction. The two reactants interact on the catalyst surface and form species that consequently react both on the surface and in the gas phase forming the final products, e.g., nitrogen.

3.3. *Influence of surface to volume ratio of the chamber behind the catalyst bed*

It is commonly known that many homogeneous oxidation reactions of hydrocarbons involve radical chain reactions. One important step in this chain reaction is termination. According to theory, termination of a radical chain reaction is dependent on the surface to volume ratio [17] or the radius of the reactor in the postcatalyst chamber. Termination requires collisions with a third body, which in our case could be the wall or the packing material such as quartz wool. To find out whether the termination of a possible homogeneous radical chain reaction or the residence time in the free space behind the catalyst is the dominating factor in obtaining high NO to N_2 conversion, the volume of the free space behind the catalyst was set identically in both reactors, but the diameter was varied to obtain different S/V ratios of 1.98 and 4.52 cm^{-1}, respectively. The residence time was identical in both cases. It is worth noting that there was no temperature gradient between the reactor wall and the catalyst bed and the temperature in the gas phase was identical for both reactors. We did not detect any significant difference in the activity of NO to N_2 in the two reactors (Fig. 14). This means that residence time in the free space is of great importance for the homogeneous part of the mechanism leading to N_2 formation. Possible termination of radical reactions on the walls of reactor seems not to steer the reaction. On the other hand, if termination does not occur on the walls, but with "non"-radicals present in the gas mixture, the radical chain reaction would depend on the residence time in the same way as a purely homogeneous reaction. Therefore the possibility of important radical chain reactions taking place during the HC-SCR over Ag/alumina cannot be excluded.

The results obtained in the present study show that gas-phase reactions are part of the total reaction mechanism. The formation of N_2 in the gas phase seems to be a result of a homogeneous reaction consisting either of a decomposition reaction of an N-containing hydrocarbon (preferably having two N atoms such as hydrazines, hydrazones, and azines) or a reaction between formed intermediates. The decomposition theory is backed up by the fact that N-containing hydrocarbons are certainly oxidized by the cleanup catalyst resulting in the formation of NO and NO_2. On the other hand, a generated N-containing hydrocarbon intermediate could also be oxidized before reaction to NO_x and CO_2.

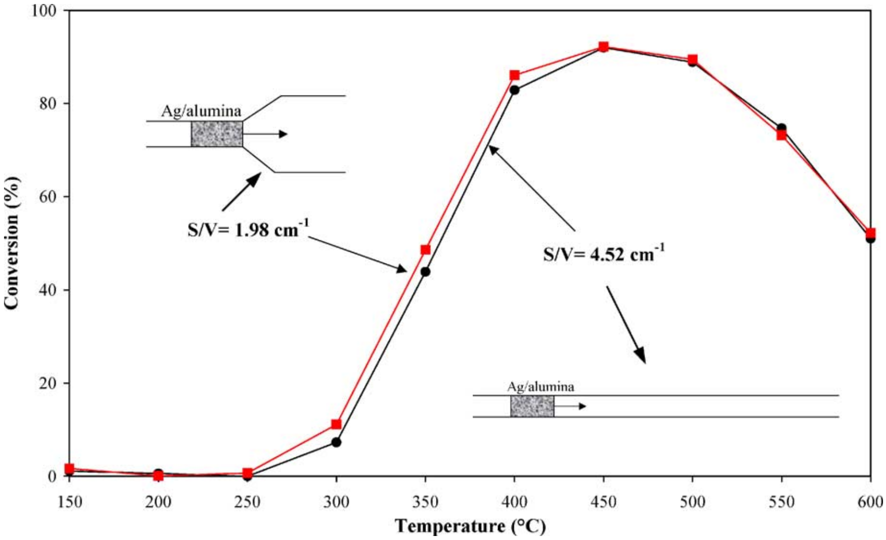

Fig. 14. Comparison of NO to N_2 conversion over Ag/alumina using reactors with different surface to volume ratios after the catalyst bed. Volume in the free space behind catalyst was 19.89 cm^3 in both reactors. Gas mixture: 500 ppm NO, 375 ppm octane, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O, and He as balance. GHSV = 60,000 h^{-1} and volume flow = 550 ml/min.

3.4. GC-MS studies

In order to identify the gaseous intermediates formed on the surface of the catalyst, the condensate (H_2O) produced in the activity tests and trapped in the water collector was subjected to GC-MS studies. In these analyses, different types of ketones (2.5-octanedione, acetophenone, 2.5-diethyltetrahydrofuran, and 2-hexanone) and aldehydes (pentanal) were mainly recorded. In classical organic chemistry aldehydes and ketones are formed via the oxidation of primary and secondary alcohols, respectively. In this investigation the initial step may proceed via partial oxidation of octane to yield alkenes, and further on through oxidation reactions alcohols are gained. The single most important reaction of aldehydes and ketones is the nucleophilic addition reaction [18]. In our case the negatively charged cyanide ion and neutral nucleophiles such as ammonia and amines are of greatest interest since these are species which, in the literature, have often been reported [19–22] to be formed as intermediates on the surface and in the gas phase. The observed components, however, could be end or side products, which are trapped in the water or have been formed via hydrolysis of a ketoxime [23].

Nanba et al. [24] have made product analysis of SCR of NO_2 with C_2H_4 over H-ferrierite. Nitroethylene (NE), HNCO, and HCN were detected as nitrogen-containing by-products. It was proposed that there were two reaction pathways for N_2 formation. Direct reaction between NE and NO_2 and NE decomposition followed by the formation and hydrolysis of HNCO. The latter pathway led to the formation of NH_3, which further reacted with NO to form N_2. However, the long analyzing time of their FTIR equipment (about 80 s) might lead to a situation where some “short” living intermediates cannot be detected. This is very important, when considering our observations of the gas-phase reaction taking place behind the catalyst bed, as we suggested an approximate residence time of 0.28 s for the full reaction to be completed. Therefore a supplementary experiment at 400 °C was performed, where the Ag/alumina catalyst was placed in close connection to a cooled (0 °C) acetone trap to minimize the possibility for the reaction to proceed completely. In this experiment a large variety of nitriles (nitromethane), ketones, and cyclic products were found dissolved in acetone. The main single product detected in the GC-MS experiment was acetonitrile (Fig. 15). When NO was excluded from the gas mixture, only minor nitrile formation was observed. It seems as if the catalyst surface was not fully cleaned from adsorbed NO_x, which resulted in slight nitrile formation. Nitriles are usually formed through nucleophilic addition of the negatively charged CN^- ion to aldehydes and ketones. One could speculate that the nitriles take part in the gas-phase reactions behind the catalyst bed, but as shown later, this is not the case. Ketoximes have also been shown [25] to yield nitriles by the action of proton or Lewis acids. In addition to nitriles, for example, α-dialkylaminoketoximes also give amines and aldehydes or ketones. If the ketoximes are considered to be important species in the HC-SCR, as shown by [23,26,27], the conclusion would be that the nitriles and ketones (aldehydes), detected in the GC-MS experiments, are side products. The reason why acetonitrile is the main species in these GC-MS experiments may be found in the fact that in earlier studies [7], longer hydrocarbon chains were proven to be the most active reducing agents. Therefore “leftover” acetone oxime might have reacted over the Ag/alumina forming acetonitrile and the longer chains consumed during the HC-SCR.

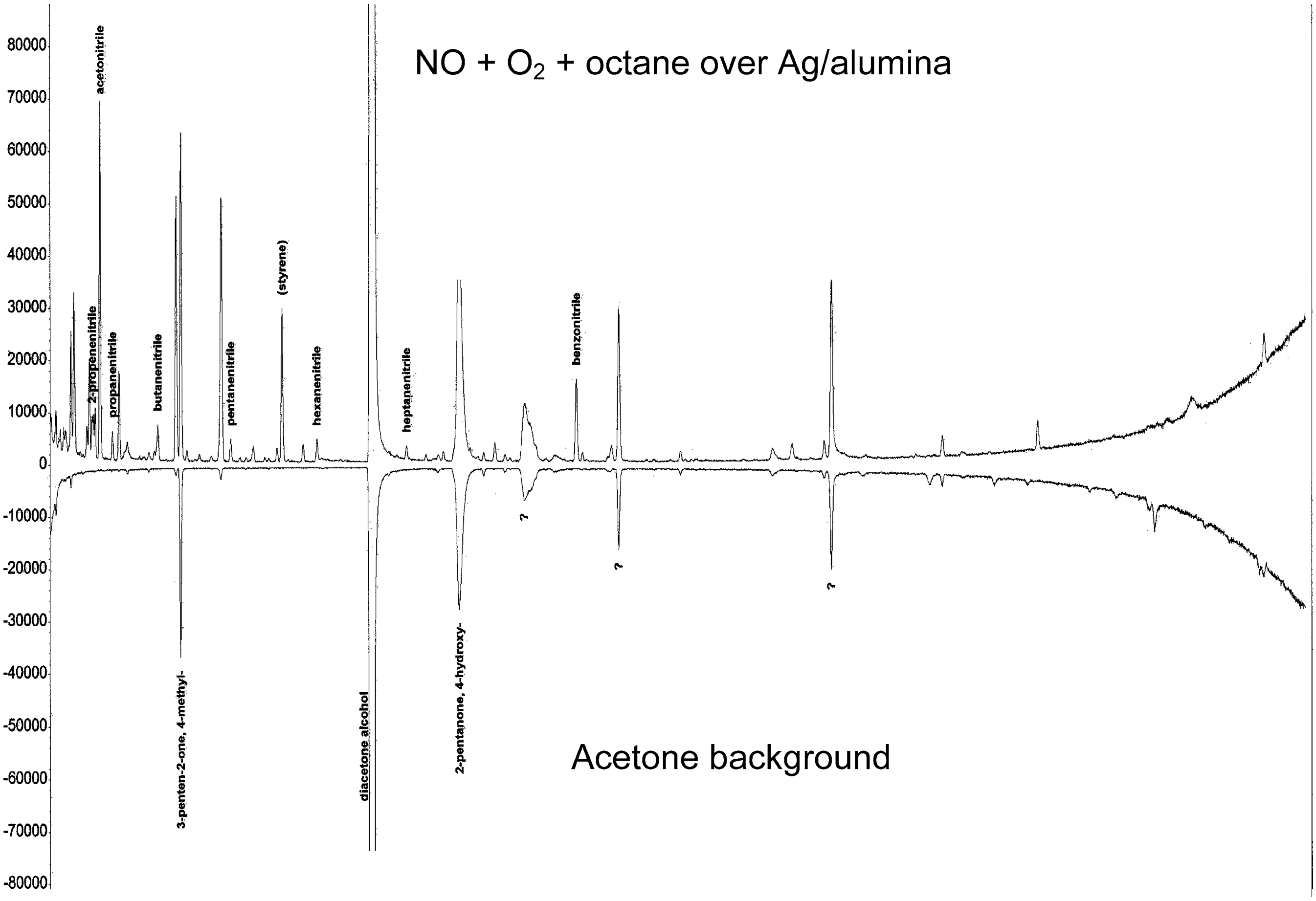

Fig. 15. GC-MS chromatogram of reaction products formed over Ag/alumina and dissolved in acetone. Gas mixture 500 ppm NO, 375 ppm octane, and 6 vol% O_2 at 400 °C.

3.5. Pulse studies

In an additional attempt to facilitate a study of the formed organic species leaving the catalyst surface, the Ag/alumina catalyst was placed in the inlet liner of the GC split/splitless injector. Because the column is directly connected to this liner, a fast separation of the formed species from each other could be expected. Different combinations of the gas mixture (NO, octane, and O_2) were pulsed into the catalyst using the gas-sampling valve. The main observation in these tests was that octane is fully transformed into different components in the presence of NO and O_2 at 400 °C (Fig. 16). NO strongly acts as a reactant together with oxygen in the conversion of octane to oxygenated species. This was further proved by tests, where only octane and oxygen were pulsed through the catalyst. In this experiment the octane was partly transformed/reacted into similar species as in the case where all three reactants are used, but the octane peak in the chromatogram was still significant (Fig. 16). Thermal cracking/decomposition of octane (in the absence of O_2) did not take place, even in the case where the catalyst surface was preoxidized. We did not detect any great differences between the experiments where prenitrated surfaces were compared with untreated ones.

3.6. FTIR

Several DRIFTS experiments were performed according to Table 1 at 350 °C. In experiments 1–3 (Table 1) the first step was to create adsorbed NO_x species by conducting NO and O_2 over the catalyst. During the first 20 min of the experiments (step 1) several bands around 1233 cm^{-1} and very weak bands at approximately 1550 cm^{-1} started to appear. With time on stream the bands at 1258, 1550, 1563, and 1584 cm^{-1} increased in strength (Fig. 17). These peaks can be attributed to different nitrate (NO_3^-) species adsorbed on the catalyst surface [28–31]. The bands appearing at about 1235 cm^{-1} have been suggested to be adsorbed nitrite (NO_2^-) species [28].

The introduction of octane in step 3 (experiments 1–3) did not change the FTIR spectra. No consumption of the adsorbed NO_x species was observed. The reintroduction of NO (experiment 2, step 4) did not influence the peak pattern either. However, adding oxygen to the gas feed (experiment 2, step 5) changed the spectra drastically (Fig. 18). The band at 1550 cm^{-1} strongly decreased in intensity during time on stream, while the band at 1584 cm^{-1} significantly grew and a new strong band at 1590 cm^{-1} appeared. On the same type of catalysts, peaks at 1585 and 1595 cm^{-1} have been

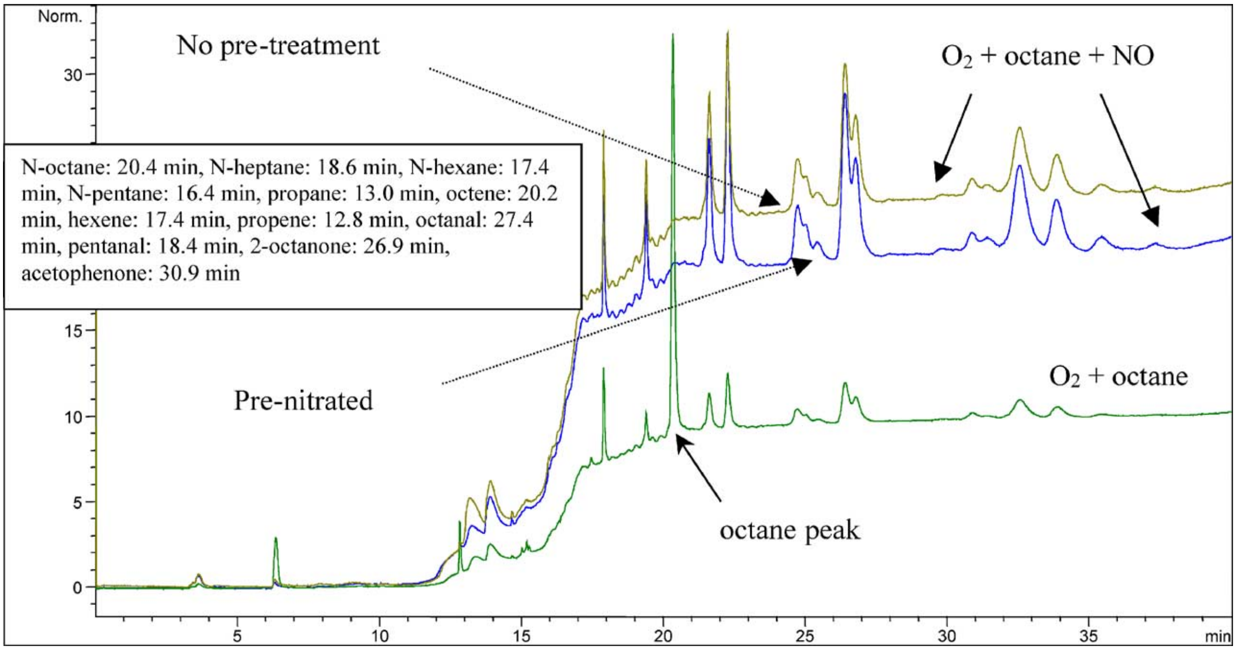

Fig. 16. Comparison of chromatograms received in the modified system, where the Ag/alumina catalyst is placed in the injection liner, which is directly connected to the column of the GC. Retention times for some hydrocarbons are given in the box (left).

Table 1
Experimental conditions used in DRIFTS studies

	Step 1	Step 2	Step 3	Step 4	Step 5
Exp. 1	$NO/O_2/He$	He flushing	C_8H_{18}/He		
Exp. 2	$NO/O_2/He$	He flushing	C_8H_{18}/He	$C_8H_{18}/NO/He$	$C_8H_{18}/NO/O_2/He$
Exp. 3	$NO/O_2/He$	He flushing	C_8H_{18}/He	$C_8H_{18}/O_2/He$	$C_8H_{18}/O_2/NO/He$
Exp. 4	$C_8H_{18}/O_2/He$	He flushing	NO/He	$NO/O_2/He$	$C_8H_{18}/NO/O_2/He$
Exp. 5	$C_8H_{16}O_2$	He flushing	NO/He	$NO/O_2/He$	

NO, 1000 ppm; $C_8H_{18} = 750$ ppm; O_2, 6 vol%; $C_1/NO = 6$, and $T = 350\,^\circ C$.

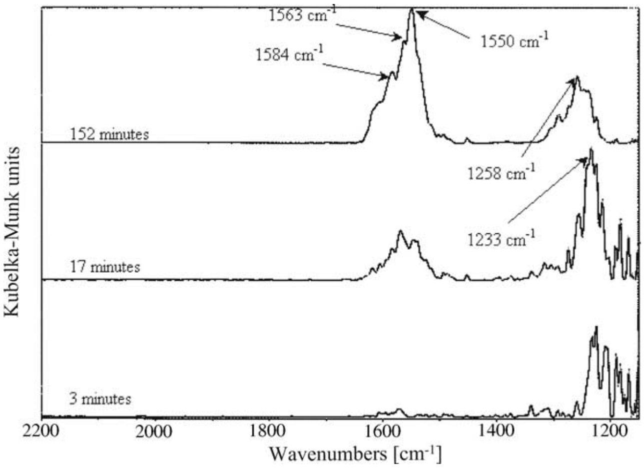

Fig. 17. Time on stream in situ DRIFTS over Ag/alumina at 350 °C using 1000 ppm NO and 6 vol% O_2 (Table 1, experiments 1–3, step 1).

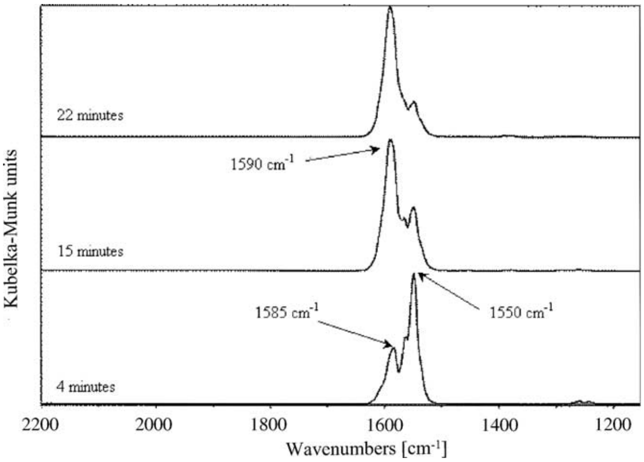

Fig. 18. Time on stream in situ DRIFTS over Ag/alumina at 350 °C using 1000 ppm NO, 375 ppm octane, and 6 vol% O_2 (Table 1, experiment 2, step 5).

assigned as carboxylate and formate surface species, respectively [20]. Careful investigation of the region at 1200–1500 cm^{-1} revealed peak appearances with time on stream at 1380 and 1390 cm^{-1}. These peaks have also been attributed to formate species [15]. Also small bands at 2134, 2157, and 2228 cm^{-1} started to appear. In Refs. [32,33], cyanide (–CN) and isocyanate (–NCO) were detected at 2135 and 2230 cm^{-1}, respectively.

In experiment 3 step 4, where O_2 was added to an octane/He mixture, the same type of change of the peaks at 1550, 1584, and 1590 cm^{-1} could be observed as in experiment 2 step 5. On the other hand no bands corresponding to cyanide and isocyanate species were seen. As expected these bands were again visible when NO was added to O_2/C_8H_{18}/He mixture (experiment 3, step 5).

In experiment 4 step 1, octane and oxygen were passed over the catalyst in order to first create adsorbed oxygenated hydrocarbon species and to check whether these react with NO or adsorbed NO species in the next steps. Major peaks were formed at 1454, 1571, and 1583 cm^{-1}. In addition small peaks at 1304 and 2942 cm^{-1} were observed. These bands are assigned to N-free species on the catalyst surface, because no catalyst pretreatment by NO was performed. In Ref. [11], the peaks at 1298 cm^{-1} (small), 1377, 1455, 1565, 1642, and 2945 cm^{-1} (small) were detected when a silver/alumina catalyst was exposed to a propene/oxygen mixture. The peaks were assigned as follows: $\nu_{C\text{–}C}$ vibration at 1298 cm^{-1}, $\delta_{C\text{–}H}$ vibration at 1377 cm^{-1}, ν_{aCOO} and ν_{asCOO} (carboxylate group) stretching modes at 1455 and 1565 cm^{-1}, respectively, and $\nu_{C=C}$ stretching mode at 1642 cm^{-1}. The band at 2945 cm^{-1} was stated as the C–H stretching vibrations of the corresponding $C_xH_yO_z$ species. Introducing NO to the O_2/C_8H_{18}/He-treated catalyst (experiment 4 step 3) resulted in small changes in the band pattern. The peak at 1571 cm^{-1} slightly decreased in intensity, whereas the peak at 1583 cm^{-1} became more dominant. In the case where oxygen was added to the feed (experiment 4 step 4), the peak at 1454 cm^{-1} decreased considerably and some new peaks appeared around 1274 cm^{-1}.

When all the reactants were put on-line (experiments 2–4, steps 5 and 4), peak formation was detected at around 3500 cm^{-1}. In [19], a strong band close to 3500 cm^{-1} was assigned to adsorbed water belonging to hydrocarbon combustion. This band appeared when several reactions were carried out, suggesting the possibility that the hydrolysis of –CN and –NCO species to ammonia and amines takes place. In the same reference [19], weak but distinctive IR bands at 3390 and 3410 cm^{-1} were recognized and attributed to the N–H stretching region. Also in the present study, additional weak peaks having a maximum at approximately 3400 cm^{-1} were recorded.

In experiment 5, step 1, hexylacetate was passed over the catalyst. This molecule was used as a model oxygenated hydrocarbon compound. Major bands were formed at 1573 and 1468 cm^{-1}. In addition we detected weaker peaks with a broad shape at approximately 2936, 2870, and 1332 cm^{-1}. Meunier et al. [20], in their DRIFTS studies over cobalt- and silver-promoted alumina catalysts, attributed wavelengths of 1575 and 1460 cm^{-1} as free carboxylate COO^-/acetate (ν^aOCO and ν^sOCO, respectively). The band at 2941 cm^{-1} has been assigned as acetate (ν(CH)) [32]. When NO was passed over the hexylacetate pretreated catalyst (experiment 5, step 3), the same base peak pattern, recorded in step 1, appeared. Interestingly, a rather strong extra band at 2234 cm^{-1} was detected, during the 25 min of NO addition, which earlier was proposed as isocyanate surface species [33,34]. This is in agreement with the higher NO to N_2 activity, which was recorded when oxygenated hydrocarbons were used as reducing agents in an earlier study [7]. The rate-determining step in the HC-SCR has been thought [27] to involve the H-abstraction of the alkane. Using hexylacetate this step is avoided and cyanate species are readily formed as intermediates or side products on the surface even in the absence of oxygen. During step 4 (experiment 5), when both NO and O_2 (25 min) were passed over the catalyst, the main peaks detected were at 1299, 1469, 1578, and 2235 cm^{-1} (Fig. 19). In [20], a band at 1300 cm^{-1}, was believed to be caused by bulk-like nitrite (NO_2^-). The broad peak at 2936 cm^{-1}, which was visible in step 1 and step 3 (experiment 5), decreased considerably in size, which could be an indication that the oxygenated compound has been consumed.

In a separate experiment, the preoxidized (500 °C) catalyst was subjected to another oxygenated model component, i.e., octanal, at 350 °C. This experiment was carried out due to the fact that octanal has so far resulted in the best HC-SCR activity (Fig. 3), over Ag/alumina, compared with other C_8 species. Peaks were detected at 1326, 1462, 1575, 2865, and 2933 cm^{-1}, which were close to the corresponding bands recorded using hexylacetate.

Based on the FTIR experiments one can conclude that if an alkane (octane) is used as the reducing agent both NO and O_2 are needed for the effective formation of oxygenated species. Isocyanate and cyanide species could not be detected in the experiments where only octane and oxygen flowed over a prenitrated catalyst surface. This means that NO needs to be included in the gas phase as it strongly participates as a reactant/oxidant in forming the initial and important oxygenates and breaking the C–H bond of the alkane (which could be the rate-determining step) [27]. This was

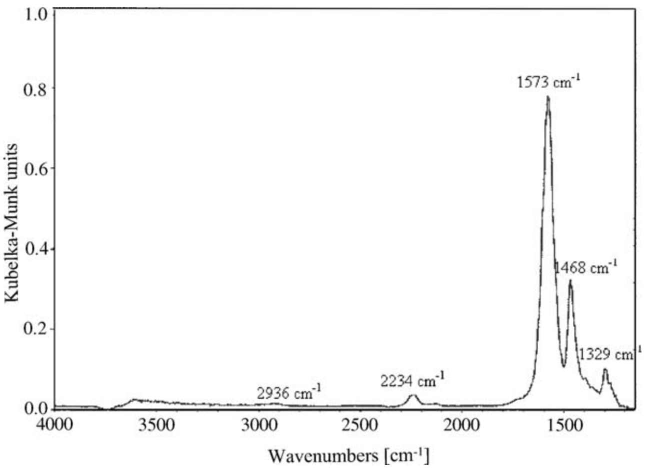

Fig. 19. Time on stream in situ DRIFTS experiment at 350 °C where 1000 ppm NO is flowing over a Ag/alumina catalyst, which has been pretreated with hexylacetate + oxygen in helium (Table 1, experiment 5, step 3).

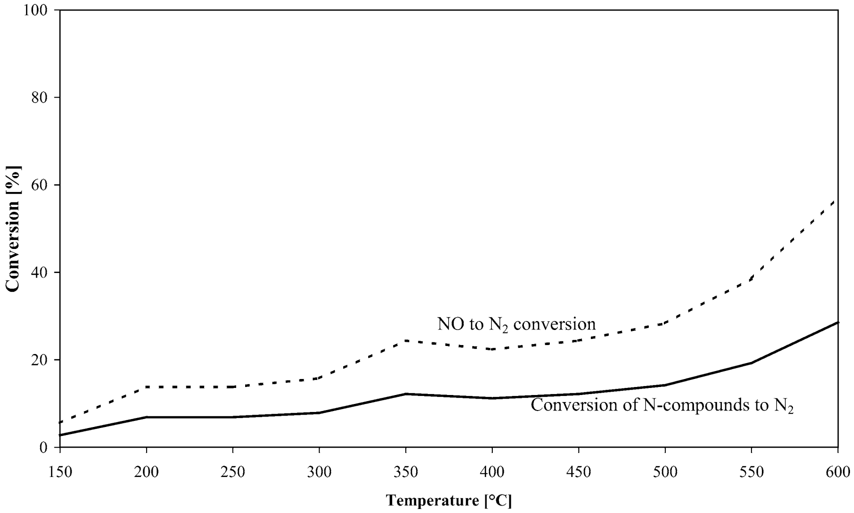

Fig. 20. Activity test over Ag/alumina using ammonia as the reducing agent. Gas mixture: 500 ppm NO, 500 ppm NH_3, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O, and He as balance. GHSV = 60,000 h^{-1} and volume flow = 550 ml/min.

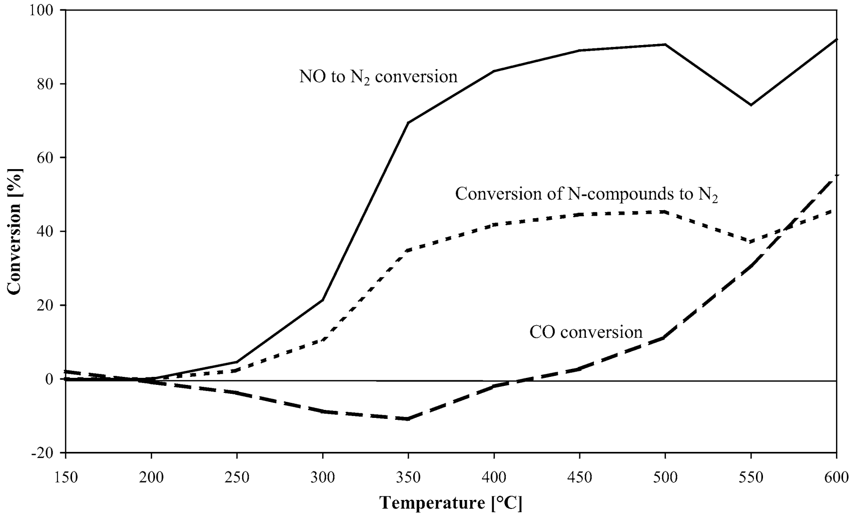

Fig. 21. Activity test over Ag/alumina using acetonitrile as the reducing agent. Gas mixture: 500 ppm NO, 500 ppm acetonitrile, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O, and He as balance. GHSV = 60,000 h^{-1} and volume flow = 550 ml/min.

demonstrated in the experiment where isocyanate species were created on the catalyst in the absence of oxygen and in the presence of NO, when the surface had been pretreated by an oxygenate such as hexylacetate. These findings are supported by the pulse studies and the activity tests.

3.7. Activity tests using possible intermediates as reducing agents

The activity of NO to N_2 was investigated in the presence and absence of the Ag/alumina catalyst using heptylisocyanate, acetonitrile, ammonia, or heptanone oxime as reducing agents. These kinds of species have been proposed in the literature to act as possible HC-SCR intermediate species [19,22,23,26,27]. These species substituted octane as the reducing agent for NO. Some of the components were led together with NO, as well as separately through the catalyst bed in excess oxygen. The results of these experiments are illustrated in Figs. 20–23. As indicated in the figures the conversion of NO to N_2 was calculated in two ways: (1) as normally based on the introduced 500 ppm NO (NO to N_2), and (2) based on the assumption that 1000 ppm of NO was introduced to the catalyst, half of which formed the intermediate via reactions with the hydrocarbon (conversion of N compounds to N_2).

In the experiment where ammonia was fed together with NO over the catalyst, using a ratio of 1/1 (500/500 ppm), moderate conversion of NO to N_2 was detected at temperatures below 500 °C (Fig. 20). This experiment shows quite clearly that even if ammonia were to be formed during the HC-SCR, it would not contribute to the NO reduction activity over Ag/alumina to a great extent.

When octane (375 ppm) was substituted by acetonitrile (500 ppm), the conversion of N compounds to N_2 showed

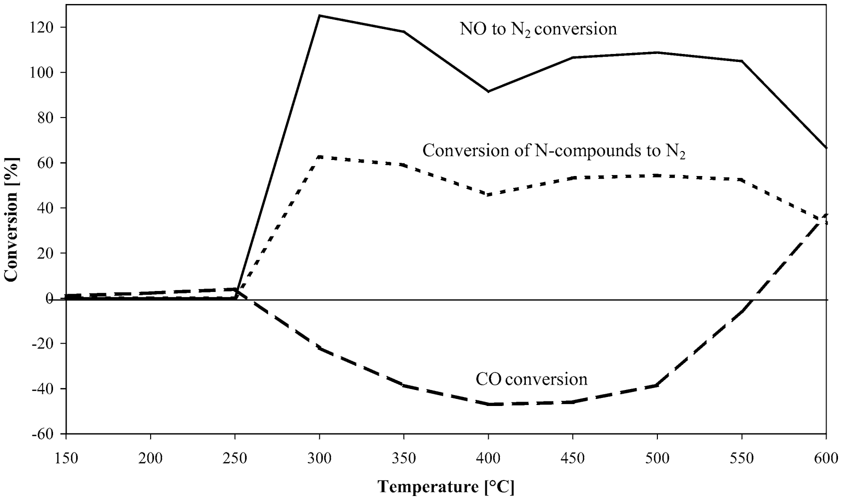

Fig. 22. Activity test over Ag/alumina using heptylisocyanate as the reducing agent. Gas mixture: 250 ppm NO, 250 ppm heptylisocyanate, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O, and He as balance. GHSV = 60,000 h^{-1} and volume flow = 550 ml/min.

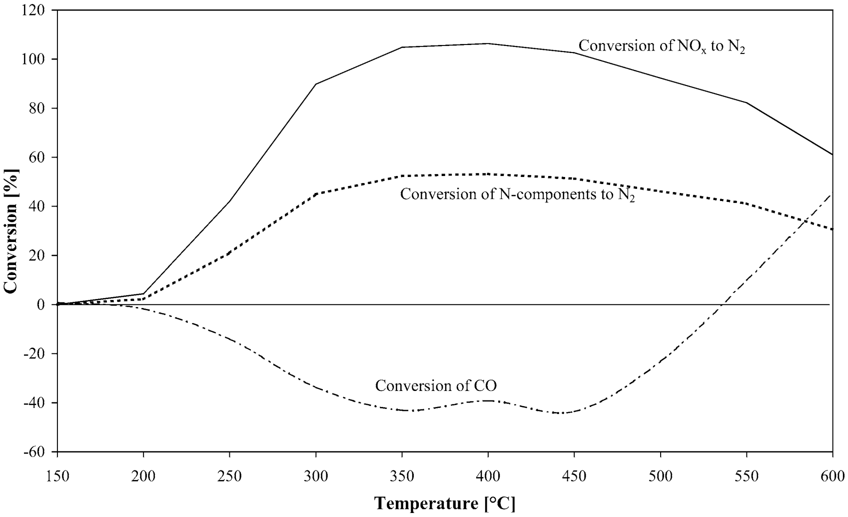

Fig. 23. Activity test over Ag/alumina using heptanone-oxime as the reducing agent. Gas mixture: 250 ppm NO, 250 ppm heptanone-oxime, 6 vol% O_2, 10 vol% CO_2, 350 ppm CO, 12 vol% H_2O, and He as balance. GHSV = 60,000 h^{-1} and volume flow = 550 ml/min.

an average of approximately 40% in the temperature window 350–600 °C (Fig. 21). If only the introduced (500 ppm) NO is used for calculations, excellent conversion of NO is obtained. When acetonitrile was led through the catalyst in the absence of NO, we did not record any significant formation of N_2 over the Ag/alumina, except at 500 °C, the temperature at which 20% acetonitrile to nitrogen conversion took place. These results suggest that nitriles and/or the oxygenated hydrocarbon part of the nitriles are able to reduce NO over Ag/alumina. In the absence of a catalyst we did not detect any NO conversion when acetonitrile was used as the reducing agent for NO.

High conversion levels of N compounds exceeding 50% were detected between 300 and 550 °C, when 250 ppm heptylisocyanate was used as the model intermediate and passed together with 250 ppm NO in excess oxygen over the Ag/alumina catalyst (Fig. 22). In the experiment where heptylisocyanate was introduced through the catalyst alone, no nitrogen formation was seen. Also in the absence of a catalyst when NO and heptylisocyanate were both present in the gas feed, we did not detect any NO conversion.

As already noted, the isocyanate species have commonly been mentioned as important intermediates on the surface or in the gas phase. The high activity achieved using heptylisocyanate, is in close agreement with these proposals. However, Beutel et al. [23] have proposed that the NCO intermediate is not crucial for HC-SCR since NO reacts with the oxime to form N_2 below decomposition temperature. In their work NCO is considered to be a decomposition product of acetone oxime. If this approach is correct it indicates that the oxygenated hydrocarbon part of the heptylisocyanate reacts together with NO forming N_2. Here again, the rate-determining step of H-abstraction of the alkane can be avoided and therefore the higher activity in terms of

NO to N_2 is obtained at low temperatures. On the other hand, a significantly higher amount of hydrocarbon (reducing agent), based on carbon atoms, was used in this experiment compared with the experiment where acetonitrile was used. It was shown in [7] that a C_1H_x/NO ratio equal to 6 is quite optimal for the NO conversion when dealing with an Ag/alumina catalyst. This could explain why the highest activity was recorded in the experiment using heptylisocyanate. This kind of approach requires that the oxygenated hydrocarbon is considered to be the active reducing agent, not the NCO or CN^- group. On the other hand, Haneda et al. [19] in their study on reaction intermediates in the selective NO reduction with propene over Ga_2O_3–Al_2O_3 and In_3O_3–Al_2O_3 showed that the concentration of oxygenated and nitrile compounds decreased continuously as the reaction temperature increased. They proposed that this indicates that oxygenated and nitrile compounds act as the intermediates leading to the formation of N_2.

Heptanone oxime was shown to be an active reducing agent for NO_x. In a test where 250 ppm hexanone oxime was led together with 250 ppm NO, the same kind of activity pattern was seen as in the test where the isocyanate was used as a reducing agent (Fig. 23). The conversion of N compounds to N_2 reached values higher than 50% between 350 and 450 °C. In addition the activity was slightly improved using the oxime compared with the isocyanate at the starting temperatures. In the absence of NO in the gas feed the conversion of N compounds did not reach values higher than 10% below 500 °C. At the final temperature (600 °C) the conversion of NO rose to approximately 20%. In the absence of the Ag/alumina catalyst, when the oxime and NO were both present in the gas mixture, the conversion of N compounds to N_2 was less than 3% below 500 °C and at the final temperature the conversion was equal to 4.5%. This means that the reaction for N_2 formation cannot be carried out without the catalyst using the oxime as the reducing agent, but the full mechanism certainly involves a surface-generated gas-phase reaction and the oxime could be involved here as an intermediate.

3.8. Kinetic considerations

Kinetic investigations were reported in the literature for NO reduction with propene [35] and octane [36]. In the former case the reaction orders for all components (NO, oxygen, and hydrocarbon) were fractional. It is interesting to note that for one of the catalysts a rather surprising result was observed: namely that the reaction order in NO was equal to zero, indicating that the rate of NO reduction, over the Ga_2O_3–Al_2O_3 catalyst investigated, was independent of NO partial pressure. Reaction orders in oxygen were around 0.5, while typically the order in propane was approximately 0.3. Conversion of NO over Pt catalysts [36] was proportional to almost the fourth order in n-octane at low C_8H_{18} concentrations, attaining a plateau with octane concentration increase. It is important to note that the rate of NO reduction followed the rate of octane oxidation. The same trend was visible for the dependence of these reactions in oxygen and NO concentration, the reaction orders being higher than one in the former and negative in the latter. Our preliminary kinetic studies demonstrated [37] that the rates of NO reduction and total octane oxidation over Ag/alumina catalyst could be described by a simple power-law model with the reaction orders in octane and oxygen similar for both reactions and close to unity. Moreover the reaction order in NO for the NO conversion was close to zero. Based on the observations and measurements from this study and [37], it is apparently clear that octane reactivity dominates the rate of NO reduction. This is clearly seen directly from the experiments bypassing octane to the outlet surface of the catalyst (Fig. 13) as well as from experiments with concentration variation of components. A rather surprising observation is that NO reduction over a silver catalyst depends only slightly on the concentration of NO, which also supports the concept that reactions involving octane determine the overall reactor performance. NO reacts with O_2 over the catalyst, forming nitrite and nitrate species. The latter species seem to be formed slowly with time on stream, as evidenced by FTIR measurements. Octane reacts with the aid of predominantly oxygen over the Ag/alumina catalyst, to form an oxygenated hydrocarbon (via H-abstraction). As noted earlier, such abstractions could be the rate-determining step. This statement is supported by kinetic studies showing the zero-order dependence of NO reduction on NO concentration. At the same time as demonstrated in the pulse studies, octane does not transform totally in the absence of NO in the gas feed. This means that although (at least in the range of parameters studied) the influence of NO is not manifested kinetically, meaning that the coverage of adsorbed NO or nitrates (nitrites) is small, the presence of NO is vital to create active intermediates for the reactions to proceed. An alternative explanation, which could account for zero order in NO is that the surface is almost completely covered by NO_x-containing species [4]. Detailed kinetic studies are in progress with the purpose of discriminating between these mechanisms.

4. Conclusions

A 2 wt% Ag/alumina catalyst was shown to be highly active for continuous NO reduction by octane in excess oxygen. A maximum NO to N_2 conversion of approximately 90% at 450 °C and an average conversion of 66% in the temperature range 300–600 °C was recorded. This study shows that the octane-SCR over the Ag/alumina catalyst involves an important gas-phase reaction, which is initiated on the catalyst surface, during which the preferable product N_2 is formed. The gas-phase reaction was proved by placing an oxidation catalyst after the Ag/alumina catalyst in order to remove CO and unburnt hydrocarbons. When the oxidation catalyst was placed in immediate connection with the Ag/alumina or mixed with it, almost all activity in terms of NO to N_2 activity was lost. By extending the distance between the two catalyst beds, the NO conversion was significantly improved which means that the residence time of the postcatalytic chamber is of high importance. Additional tests show that termination on the walls of possible radical reactions does not influence the NO to N_2 conversion.

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References

[1] Kyoto Protocol to the United Nations Framework Convention on Climate Change, 1997.
[2] W. Held, A. König, T. Richter, L. Puppe, SAE Tech. Pap. Ser. No. 900496 (1990).
[3] M. Iwamoto, H. Yahiro, S. Shundo, Y. Yu-u, N. Mizuno, Appl. Catal. 70 (1991) L15.
[4] R. Burch, J.P. Breen, F.C. Meunier, Appl. Catal. B 39 (2002) 283.
[5] K. Shimizu, A. Satsuma, T. Hattori, Appl. Catal. B 25 (2000) 239.
[6] A. Fritz, V. Pitchon, Appl. Catal. B 13 (1997) 1.
[7] K. Eränen, L.-E. Lindfors, A. Niemi, P. Elfving, L. Cider, SAE paper 2000-01-2813, 2000.
[8] D.B. Lukyanov, G. Sill, J.L. d’Itri, W.K. Hall, J. Catal. 153 (1995) 265.
[9] J. Vassallo, E. Miró, J. Petunchi, Appl. Catal. B 7 (1995) 65.
[10] T.E. Hoost, R.J. Kudla, K.M. Collins, M.S. Chattha, Appl. Catal. B 13 (1997) 59.
[11] A. Martínez-Arias, M. Fernández-García, A. Iglesias-Juez, J.A. Anderson, J.C. Conesca, J. Soria, Appl. Catal. B 28 (2000) 29.
[12] A. Niemi, Masters thesis, Åbo Akademi 38, 1999.
[13] T. Nakatsuji, R. Yasukawa, K. Tabata, K. Ueda, M. Niwa, Appl. Catal. B 17 (1998) 333.
[14] R. Burch, M.D. Coleman, Appl. Catal. B 23 (1999) 115.
[15] N.W. Cant, D.E. Angove, D.C. Chambers, Appl. Catal. B 17 (1998) 63.
[16] M. Vikman, Masters thesis, Åbo Akademi 39, 1997.
[17] N.M. Emanuel, D.G. Knorre, in: Chemical Kinetics, Vyshaya Sckola, Moscow, 1984, p. 463.
[18] J. McMurry, Organic Chemistry, Brooks/Cole, CA, 1988.
[19] M. Haneda, N. Bion, M. Daturi, J. Saussey, J.-C. Lavalley, D. Duprez, H. Hamada, J. Catal. 206 (2002) 114.
[20] F.C. Meunier, V. Zuzaniuk, J.P. Breen, M. Olsson, J.R.H. Ross, Catal. Today 59 (2000) 287.
[21] A. Obuchi, C. Wögerbauer, R. Köppel, A. Baiker, Appl. Catal. B 19 (1998) 9.
[22] M. Haneda, E. Joubert, J.-C. Ménézo, D. Duprez, J. Barbier, N. Bion, M. Daturi, J. Saussey, J.-C. Lavalley, H. Hamada, J. Mol. Catal. A 175 (2001) 179.
[23] T. Beutel, B. Adelman, W.M.H. Sachtler, Catal. Lett. 37 (1996) 125.
[24] T. Nanba, A. Obuchi, Y. Sugiura, C. Kouno, J. Uchisawa, S. Kushiyama, J. Catal. 211 (2002) 53.
[25] J. March, in: Advanced Organic Chemistry, Wiley–Interscience, New York, 1985, p. 931.
[26] R.H.H. Smits, Y. Iwasawa, Appl. Catal. B 6 (1995) L201.
[27] B.J. Adelman, T. Beutel, G.-D. Lei, W.M.H. Sachtler, Appl. Catal. B 11 (1996) L1.
[28] M. Schraml-Marth, A. Wokaun, A. Baiker, J. Catal. 138 (1992) 306.
[29] W.S. Kijlstra, D.S. Brands, E.K. Poels, Bliek, J. Catal. 171 (1997) 208.
[30] A.D. Cross, Introduction to Practical IR Spectroscopy, Buttersworth, London, 1964.
[31] N.B. Colthup, L.H. Daly, S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, Boston, 1990.
[32] K. Shimizu, H. Kawabata, A. Satsuma, T. Hattori, J. Phys. Chem. B 103 (1999) 5240.
[33] Y. Ukisu, T. Miyadera, A. Abe, K. Yoshida, Catal. Lett. 39 (1996) 265.
[34] G.R. Bamweda, A. Obuchi, A. Ogata, K. Mizuno, Chem. Lett. 2109 (1994).
[35] M. Haneda, Y. Kintaichi, H. Shimada, H. Hamada, J. Catal. 192 (2000) 137.
[36] R. Burch, P. Fornasiero, T.C. Watling, J. Catal. 176 (1998) 204.
[37] GROWTH Project GRD1-1999-10957 KnowNOx.