Selective Reduction of NO by HNCO over Pt Promoted Al₂O₃

Filip Acke, *.†.§.¹ Björn Westerberg, *.‡ and Magnus Skoglundh*

* Competence Centre for Catalysis, †Department of Inorganic Chemistry, ‡Department of Chemical Reaction Engineering, Chalmers University of Technology, S-412 96 Göteborg, Sweden; and §Department of Inorganic Chemistry, Göteborg University

Received April 21, 1998; revised July 13, 1998; accepted July 14, 1998

The activity of Pt supported on γ -Al₂O₃ towards HNCO oxidation and reduction of NO by HNCO under oxygen excess is examined under transient conditions (temperature ramps between 100 and 500°C). Formation of N₂, N₂O, NO, and NO₂ is observed. Isotope labelled ¹⁵NO is used to show the scrambling of nitrogens in N₂ (¹⁴N¹⁵N) and N₂O (¹⁴N¹⁵NO). Adsorbed species on the surface are characterised by *in-situ* FTIR spectroscopy in order to obtain information on reaction intermediates. Adsorbed NH_x species are discussed as important intermediates in the N₂ and N₂O formation. The absence of Pt results in a delay in HNCO ignition and only a small N₂O formation is observed. © 1998 Academic Press

1. INTRODUCTION

Numerous combinations of catalytic materials and reducing species have been tested to reduce emissions of nitrogen oxides (NO_x) under net-oxidising (lean) conditions. At present, the most common technique for NO_x abatement from stationary sources is the selective catalytic reduction by ammonia. In search for alternative techniques, a process based on HNCO as reducing agent has been suggested: the RAPRENO_x process (1). HNCO was shown to reduce NO in diesel exhausts at temperatures above 400°C. The HNCO was produced from the decomposition of cyanuric acid. A reaction mechanism based on the formation of NH and NH₂ radicals was proposed; i.e., NH reacts with NO to form N₂O, whereas NH₂ is addressed as the precursor of N₂. However, an experimental and theoretical study of the homogeneous HNCO oxidation showed that a temperature of at least 1127°C was needed for a conversion of about 50% (2). The oxidation reaction proceeds mainly through an NCO intermediate, which subsequently oxidises to NO or reacts with this NO to form N₂ and N₂O.

The role of adsorbed -NCO species has also been discussed related to the reduction of NO by CO or hydrocarbons. Surface adsorbed -NCO has been observed by means of infra red spectroscopy in the reduction of NO by CO over oxide-supported noble metal catalysts. Numerous examples are reviewed by Matyshak and Krylov (3). O_2 , at high enough concentrations, has been shown to react with these adsorbed isocyanate species (4). Isocyanate formation has also been observed for the selective reduction of NO over supported noble metal catalysts by hydrocarbons under lean conditions. Infra red absorption bands assigned to adsorbed isocyanates were observed for the Rh/Al₂O₃ system after exposure to a C₃H₆/NO gas mixture (5) and for the Pt/ γ -Al₂O₃ system after exposure to a C₃H₆/NO/O₂ gas mixture (6). The observed absorption bands were assigned to -NCO adsorbed on the support, since the stability of these species adsorbed on the noble metal is low (7–10). It was also shown that the presence of Pt is not necessary for -NCO formation (11).

The role of the adsorbed isocyanate in the reduction of NO by CO or hydrocarbons is still the subject of considerable debate. Two opposing opinions, spectators or active intermediates, are still discussed. A role as spectator finds support in the very short lifetime of these species on Pt (10), in the observation that these species reside mainly on the support (12) and in the absence of a correlation between the intensity of an -NCO absorption band and conversion of NO (3). Others have proposed reaction mechanisms involving isocyanate as an active intermediate. Adsorbed -NCO species have been suggested to participate in the formation of N_2 , N_2O , NO_2 and adsorbed NH_2 and NH_3 (5, 13–15).

In this article the activity and selectivity of HNCO towards reduction of NO under oxygen excess are examined over γ -Al₂O₃-supported Pt at temperatures between 100 and 500°C by flow reactor studies and *in-situ* Fourier transform infrared (FTIR) spectroscopy. Isotope labelled ¹⁵NO is used to determine the origin of the nitrogen in the formed reaction products. Adsorbed NH_x species are discussed as important intermediates in the N₂ and N₂O formation in accordance with the reaction mechanisms available in the literature. The role of the noble metal is examined by comparing the activity and selectivity of the γ -Al₂O₃ support and Pt/ γ -Al₂O₃ sample. Finally, the role of substrate adsorbed -NCO species in the reduction of NO is discussed.

¹ Corresponding author. E-mail: filip@inoc.chalmers.se.

2. EXPERIMENTAL

2.1. HNCO Production

The isocyanic acid (HNCO) is produced by depolymerising the cyclic trimer of cyanuric acid (16 and references therein). Cyanuric acid starts to sublimate around 330° C. A gaseous trimer (HNCO)₃ is formed. This trimer depolymerises into HNCO by increasing the temperature to 700°C. The process is not complete and monomer, trimer, as well as HCN, CO, CO₂, NH₃, and H₂O are found in the gas flow. The HCN is oxidised to HNCO using a silver catalyst (Ag₂O) at room temperature. Both monomer and trimer are then condensed at -80° C and a distillation at -32° C results in liquid HNCO without any trimer.

2.2. Catalyst Preparation

The catalyst support material, γ -Al₂O₃, was prepared by calcining boehmite (Disperal, Condea) in air at 600°C for 8 h. The calcined alumina was sieved and the 125 to 210 μ m fraction was used for further preparation. This fraction was dispersed in distilled water. The pH was adjusted by ammonia (NH₄OH solution, 25%, Riedel-de Haën) to about 11. A platinum hydroxide solution (Tetraammineplatinum(II)hydroxide, Johnson Matthey) was added dropwise under continuous stirring to yield a Pt loading of 2 wt%. The slurry was kept under continuous stirring for 1 h. The slurry was then freeze dried and finally calcined in air at 550°C for 1 h.

2.3. Flow Reactor Studies

The flow reactor experiments were made in a vertical fixed bed reactor. The quartz reactor (ID 22 mm, length 500 mm) had an asymmetric construction to avoid heating of the upper metal fitting and the vacuum tight Viton O-ring. The gases were analysed using a Fourier transform infra red gas analyser (Bruel & Kjär) or a quadropole mass spectrometer (QMG 421 from Balzers). The latter was only used for experiments using the isotope labelled ¹⁵NO. The temperature was measured with a K-type thermocouple, 4 mm below the sample supporting sintered quartz filter. Linear temperature ramps were obtained by controlling the temperature with a second K-type thermocouple in contact with the heating coil and connected to a Eurotherm temperature controller. Temperature ramps, using cooling and heating rates of 6 K/min, were started at 500 and 100°C, respectively.

The bed consisted of a mixture of 200 mg of active material, γ -Al₂O₃ catalyst or γ -Al₂O₃ support, with 1500 mg of quartz sand. The quartz sand was added to reduce the pressure drop over the bed. The space velocity, defined as the ratio between the flow rate and the void volume of the bed, was between 71,000 and 125,000 h⁻¹, corresponding to flows of 500 and 873 ml/min, respectively. The bed materials

Composition of the Respective Gas Mixtures for the Flow Reactor and the FTIR Studies

TABLE 1

		Gas composition ^a				
Experiment		HNCO ^b	O ₂	NO	¹⁵ NO	Gas flow
		(ppm)	(vol%)	(ppm)	(ppm)	(ml/min)
Flow reactor study	Stabilisation HNCO oxidation NO reduction ¹⁵ NO reduction	200-350 200-350 200-350 200-350	9.7 9.7 9.2	475 - 475 -	- - 475	748 748 748 873
FTIR	HNCO oxidation	350–550	8	-	-	500
study	NO reduction	350–550	8	1000	-	500

 a All gas compositions for the flow reactor studies are balanced with Ar; the others are balanced with N₂.

^bApproximate values are given for the HNCO concentration since several parameters (temperature, flow) influence the concentration and it was experienced to be difficult to obtain reproducible HNCO amounts.

were initially stabilised for 30 min in a gas mixture containing HNCO and NO in Ar at 500°C. Concentrations and flow rates are given in Table 1. Temperature ramps were done in gas flows of HNCO, NO, and O_2 , as well as HNCO and O_2 . The HNCO was added to the reaction mixture by flowing small amounts of Ar over liquid HNCO in a wash bottle which was kept in an isothermic bath at -30° C. The gases used in the experiments were 99.99(9)% Ar, 99.99(9)% O₂, 5000 ppm NO, and 3000 ppm¹⁵NO, the latter both in Ar. The gas flows were controlled by mass flow controllers (Brooks, type 5850E). The amount of HNCO in the gas mixture was initially determined by absorption of the feed gas in an acidic aqueous solution (100 ml 0.1 MH₂SO₄). HNCO is hydrolysed by H₂O and forms NH₄⁺ ions. The amount of ammonium ions, which is thus a measure for the HNCO concentration, was determined by titration (17). Once the HNCO concentration was known from the wet chemical method, the FTIR gas analyser could be calibrated; the absorption peak at 2280 cm^{-1} was used.

2.4. FTIR Studies

The FTIR-experiments were performed using thin discs (approximately 15 mg/cm²) of catalyst in a reaction chamber with CaF₂-windows, similar to that described by Basu *et al.* (18). The disc was fixed in between a folded tungsten grid placed in the centre of the reaction chamber. The temperature was measured with a thermocouple, in contact with the grid and controlled via the voltage applied over the grid. The reaction chamber was placed in a FTIR spectrophotometer. All spectra were measured with a resolution of 4 cm⁻¹. The fresh samples were reduced in 30% H₂ in N₂ (total flow rate of 100 ml/min) at 450°C for 30 min, stabilised in a gas mixture with 5% O₂, 1000 ppm NO, and 3000 ppm C₃H₆ in N₂ (total flow rate 500 ml/min) for 30 min

and finally degassed in N_2 (500 ml/min) at 550°C for 30 min. The *in-situ* FTIR-measurements were performed with gas mixtures and flows according to Table 1. The experiments commenced at 450°C and the temperature was then decreased in steps of 50°C with a 5-min interval. Spectra from an average of 50 scans were taken the last minute of each interval. Reference spectra were taken with pure N_2 in an otherwise identical sequence.

3. RESULTS

3.1. Flow Reactor Studies

HNCO oxidation. The activities of the Pt/γ -Al₂O₃ catalyst and the γ -Al₂O₃ support were tested towards HNCO oxidation. Concentrations and flow rates are given in Table 1. The reacted HNCO (HNCO_{reacted}), the nitrogen balance (N_{bal}) , the NO_x $(NO + NO_2)$ and NO concentrations are displayed versus ramp temperature for the Pt containing catalyst (Fig. 1). The temperature axis starts at the high temperature (500°C) to stress the experimental conditions, i.e. a cooling ramp. The reacted HCNO is defined as the HNCO bypass value minus the amount of unreacted HNCO after passing the reactor. The nitrogen balance is calculated as the sum of the concentrations of all infra red detectable nitrogen-containing species ([NO] + [NO₂] + $2 [N_2O]$). The quantification of the different reaction products, NO₂, N₂O, and N₂, can be found in Fig. 1 as the difference between the concentration curves of NO_x and NO, and half the difference between N_{bal} and NO_x and HNCO_{reacted} and N_{bal}, respectively. Complete HNCO conversion is observed for temperatures from the starting temperature at 500°C down to 204°C. Initially, the major part of the HNCO nitrogen is oxidised to form NO, while a minor part is further oxidised to NO₂. Some N₂O formation is also observed. Decreasing the temperature results in increased formation



FIG. 1. Product distribution of nitrogen containing species during HNCO oxidation over a 2% Pt/ γ -Al₂O₃ catalyst in a cooling ramp, including the concentrations for NO. (\Box), NO_{*x*} (\triangle), N_{bal} (\diamond), and HNCO_{reacted} (∇).



FIG. 2. The fate of the carbon during HNCO oxidation over a 2% Pt/γ -Al₂O₃ catalyst in a cooling ramp, including the concentrations for CO₂ (Δ), HNCO (\Diamond), and HNCO_{reacted} (∇).

of NO₂ and N₂O, together with a continuous decrease in NO formation. The maxima in the NO2 and N2O formations are observed around 380 and 260°C, respectively. No formation of NO, N₂O, or NO₂ is observed for temperatures below 180°C. However, at this temperature there is still a considerable HNCO conversion. Gas analysers equipped with an infra red cell are limited since no homonuclear molecules, such as N₂, can be detected. The difference between the HNCO_{reacted} and the N_{bal} is then likely to be assigned to formation of N₂. The validity of this assignment will be shown later. It can be observed that for temperatures between 225 and 140°C, the N₂ formation is predominant, whereas above 225°C, the N₂O formation becomes substantial. Overlap between N₂O, NO₂, and NO is observed. The ratio between the latter two is thermodynamically (at high temperatures) or kinetically (at low temperatures) controlled. The HNCO and CO₂ concentration as well as the HNCO_{reacted} are displayed versus ramp temperature in Fig. 2. A discrepancy is observed between the HNCO_{reacted} and the CO₂ production for temperatures between 232 and 134°C. This discrepancy indicates incomplete oxidation of the HNCO carbon.

The experiment was then repeated in the absence of Pt. The activity of γ -Al₂O₃ towards HNCO oxidation is shown in Fig. 3. The HNCO oxidation, displayed as HNCO_{reacted} in Fig. 3, is slower in the absence of Pt as is shown by T_{50} , the temperature of 50% HNCO conversion. An increase from about 160°C for the Pt/ γ -Al₂O₃ system to approximately 320°C in the absence of Pt is observed. The shift in the T_{50} temperature illustrates the importance of the noble metal in the oxidation of HNCO. Almost all HNCO nitrogen is oxidised to NO over γ -Al₂O₃. A small amount is further oxidised to NO₂ at higher temperatures. The ratio between NO and NO₂ is kinetically controlled. A maximum in NO₂ formation of 15 ppm is observed at 460°C. No N₂ is formed during the HNCO conversion, while only a minor part of the HNCO nitrogen is oxidised to form N₂O. The maximum in



FIG. 3. Product distribution of nitrogen-containing species during HNCO oxidation over a γ -Al₂O₃ substrate in a cooling ramp, including the concentrations for NO (\Box), NO₂ (\triangle), N₂O (\bigcirc), and HNCO_{reacted} (∇).

 N_2O formation, approximately 40 ppm, is reached around 335°C. The N_2O formation is significantly lower than in the presence of Pt, while the temperature of the maximum N_2O formation is shifted towards higher temperatures.

NO reduction. In a second set of experiments, the activity and selectivity of HNCO as reducing agent for the reduction of NO in oxygen excess was investigated during cooling ramps. Concentrations and flow rates are given in Table 1. In Fig. 4a, the NO, NO₂, and N₂O concentrations, as well as the HNCO_{reacted} are shown for Pt- γ Al₂O₃ versus ramp temperature. Initially (high temperatures), the HNCO nitrogen is oxidised to NO and NO₂. In addition, parts of the feed NO is also oxidised by the O₂. The ratio between NO and NO₂ is thermodynamically controlled at these high temperatures. Formation of small amounts of N₂O (about 20 ppm) are observed around 500°C. Decreasing the temperature results in an increased NO₂ formation, obtaining a maximum around 370°C, followed by a maximum in N₂O formation,

around 240°C. A further decrease in temperature results in an increase in NO concentration and at 140°C, the bypass value of NO is obtained. However, there is still a significant HNCO conversion left at this temperature. The fate of the HNCO nitrogen around this temperature becomes clear in Fig. 4b, where the HNCO_{reacted}, using an offset of 475 ppm, N_{bal}, NO_x, and NO are displayed versus ramp temperature. The offset for the HNCO_{reacted} was chosen so that a zero HNCO conversion coincides with the NO bypass value. This was done to visualise the N₂ formation. In contrast with the HNCO oxidation (see Fig. 1), N₂ formation is observed for the complete investigated temperature interval. At a temperature of 224°C, a maximum in the NO_x reduction is found, corresponding to a conversion of about 87% of the feed NO. Comparison of the NO_x signal with the N_{bal} signal, shows that almost all NO_x reduction can be accounted for by the amount of N₂O that has been formed. This does not mean that all the N-atoms from the NO molecule react to form a N₂O molecule as will be shown later under ¹⁵NO reduction. Addition of NO to the reaction mixture also affects the HNCO oxidation. This is observed as a decrease, compared to the HNCO oxidation, of the T_{50} temperature with approximately 15°. In Fig. 5 the HNCO_{reacted} and the HNCO and CO₂ concentrations are displayed versus ramp temperature. An incomplete HNCO carbon oxidation is initially observed.

The activity of the γ -Al₂O₃ support for reduction of NO by HNCO under net oxidising conditions was also tested. The results, displayed in Fig. 6, are very similar as for the HNCO oxidation in the absence of noble metal: a shift in HNCO conversion to higher temperatures in the absence of Pt, only a minor maximum in N₂O formation, no N₂ production at all and almost no NO₂ formation. The only major effect observed is the oxidation of the HNCO nitrogen to NO.



FIG. 4. Product distribution of nitrogen-containing species during reduction of NO by HNCO under net oxidising conditions over a 2% Pt/ γ -Al₂O₃ catalyst in a cooling ramp, including in Fig. 4a the concentrations for NO (\Box), NO₂ (\triangle), N₂O (\bigcirc), and HNCO_{reacted} (∇) and in Fig. 4b for NO (\Box), NO_x (\triangle), N_{bal} (\diamond), and HNCO_{reacted} (∇).

TABLE 2



FIG. 5. The fate of the carbon during reduction of NO by HNCO under net oxidising conditions over a 2% Pt/ γ -Al₂O₃ catalyst in a cooling ramp, including the concentrations for CO₂ (\triangle), HNCO (\diamond), and HNCO_{reacted} (∇).

¹⁵NO Reduction. So far, the N₂ formation has been calculated from the nitrogen balance, assuming the missing part to be N₂. Homonuclear molecules, such as N₂, can be measured using a mass spectrometer (N_2 : m/e signal 28). Interpretation of the m/e signal 28 is complicated since CO and cracking products of CO2, N2O, and HNCO interfere on this mass. Isotope labelled ¹⁵NO (m/e signal 31) can be used to avoid this. The reduction of ¹⁵NO by HNCO under net oxidising conditions is shown in Figs. 7a (cooling ramps, 400-100°C) and b (heating ramps, 100-500°C). Concentrations and flows are given in Table 1. In Figs. 7a and b the m/e signals 28, 29, 30, and 31, respective, 44, 45, and 46 are plotted versus ramp temperature. The molecules corresponding to the respective m/e signals and interference of cracking products from other molecules are listed in Table 2.



FIG. 6. Product distribution of nitrogen-containing species during reduction of NO by HNCO under net oxidising conditions over a γ -Al₂O₃ substrate in a cooling ramp, including the concentrations for NO (\Box), NO₂ (\triangle), N₂O (\bigcirc), and HNCO_{reacted} (\bigtriangledown).

Correspondence	between	m/e å	Signals	and	Molecules	as	well
as Interference on	These Ma	asses	by Crac	king	Products	of C)ther
Molecules							

m/e signal	Molecules	Cracking fragments of
28 29 30 31 44 45 46	¹⁴ N ¹⁴ N, CO ¹⁵ N ¹⁴ N ¹⁵ N ¹⁵ N, ¹⁴ NO ¹⁵ NO ¹⁴ N ¹⁴ NO, CO ₂ ¹⁵ N ¹⁴ NO ¹⁵ N ¹⁵ NO, ¹⁴ NO ₂	¹⁴ N ¹⁴ NO, CO ₂ , HNCO ¹⁵ N ¹⁴ NO ¹⁵ N ¹⁵ NO, ¹⁴ NO ₂ ¹⁵ NO ₂

The formation of ¹⁵N¹⁴N (m/e signal 29) at temperatures between 400 and 150°C for cooling ramps, shows a scrambling of nitrogen during the reaction between ¹⁵NO and H¹⁴NCO. Oxidation of the H¹⁴NCO nitrogen results in ¹⁴NO formation (m/e signal 30) at 400°C, which steadily decreases under the cooling ramp and finally disappears at 220°C. The absence of a peak in this signal suggests that there is no formation of ¹⁵N¹⁵N. The small peak in the m/e signal 28 at temperatures between 178 and 130°C is assigned, by comparison with Fig. 5, to incomplete oxidation of HNCO to CO. Interference with cracking products of CO₂ is observed as the decreasing background on this m/e signal between 400 and 120°C. The scrambling of nitrogens is also observed in the N₂O formation, i.e. ¹⁵N¹⁴NO (m/e signal 45). No formation of ${}^{15}N^{15}NO$ (m/e signal 46) is observed, and the change in m/e signal 44 can be ascribed to the oxidation of HNCO carbon to form CO2. At 400°C the formation of ¹⁵N¹⁴NO is lower than the production of ¹⁵N¹⁴N; however, it increases faster than the ¹⁵N¹⁴N formation resulting in a higher maximum value. Qualitatively, these results correspond well to the results shown in Fig. 4b, where the N₂ concentration was calculated from a mass balance. After finishing the cooling ramp, the isotope experiment was continued with a heating ramp to 500°C (same ramp speed, 6 K/min). The result is shown in Fig. 7b. It can be observed that the overall ¹⁵NO reduction is enhanced under heating ramps. This is due to a surface adsorption of reactants at low temperatures. The maxima in ¹⁵N¹⁴N and ¹⁵N¹⁴NO are higher than for cooling ramps. The adsorption effect also becomes clear when the m/e signals 28, 30, and 44 are compared for cooling respective heating ramps. Desorption peaks at 250°C, ascribed to CO₂ are observed on mass 44 and 28 (cracking to CO). The small peak at this temperature on mass 30 is assigned to NO formation from the adsorbed HNCO nitrogen.

3.2. Determination of Surface-Adsorbed Species by Infra Red Spectroscopy

Infra red spectra obtained by exposing γ -Al₂O₃ to a gas mixture containing HNCO and O₂ at temperatures between



FIG. 7. Product distribution of nitrogen- and carbon-containing species as measured by mass spectrometry during reduction of ¹⁵NO by H¹⁴NCO under net oxidising conditions over a 2% Pt/ γ -Al₂O₃ catalyst in a cooling ramp (a) and heating ramp (b). Included are the masses 28 (\bigcirc), 29 (\square), 30 (\triangle), 31 (\bigtriangledown), 44 (\blacksquare), 45 (\blacksquare), and 46 (\blacktriangle).

450 and 100°C are shown in Fig. 8. Gas concentrations and flow rates are given in Table 1. Absorption bands associated with the degenerate stretching of surface isocyanate $(2263 \text{ and } 2240 \text{ cm}^{-1})$ and with the stretching of surface hydroxyl groups (at 3550 cm⁻¹) are observed at 450°C. When the temperature is decreased, bands associated with surface coordinated ammonia and ammonium ions becomes apparent. These are the bands at 1587 and 1270 cm^{-1} assigned to the asymmetric and symmetric bending of surface coordinated ammonia, the band at 1656 cm⁻¹ assigned to the symmetric bending of hydrogen bonded ammonium ions and the degenerate bands at 1500 and 1477 cm⁻¹ assigned to the asymmetric bending of ammonium ions. The absorbance for all bands increases when the temperature is decreased (Fig. 8). At 200°C the asymmetric and symmetric stretching bands of surface coordinated ammonia at 3388 and 3292 cm^{-1} becomes apparent. No major difference is observed when the experiment is repeated, adding NO to the gas mixture (Fig. 9).

The infra red spectra obtained by exposing the Pt/ γ -Al₂O₃ catalyst to a gas mixture containing HNCO and O₂ at temperatures between 450 and 100°C are shown in

Fig. 10. When Figs. 8 and 10 are compared, it is observed that Pt addition results in stronger surface isocyanate bands at lower temperatures. The absorbance of the surface hydroxyl band (at 3550 cm^{-1}) is about the same at 450° C, but



FIG. 8. Infra red absorption spectra of surface species on γ -Al₂O₃ exposed to HNCO and O₂. The spectra are successively recorded after 5 min at 450, 400, 350, 300, 250, 200, 150, and 100°C. The wavenumber scale is split at 2000 cm⁻¹ and the baselines are separated by 0.1.



FIG. 9. Infra red absorption spectra of surface species on γ -Al₂O₃ exposed to HNCO, NO, and O₂. The spectra are successively recorded after 5 min at 450, 400, 350, 300, 250, 200, 150, and 100°C. The wavenumber scale is split at 2000 cm⁻¹ and the baselines are separated by 0.1.

increases more with decreasing temperature in the presence of Pt. At 450°C the bands associated with surface coordinated ammonia and ammonium ions are absent. Instead bands at 1560, 1298, and 1247 cm⁻¹ assigned to the asymmetric and symmetric stretch of mono and bidentate nitrate can be observed. The absorbance of the nitrate bands increases in each successive spectra until the temperature reaches 250°C. At 250°C bands associated with surface coordinated ammonia and ammonium ions become apparent. The absorbance of these bands increases when the temperature is decreased. The absorbance of the overlapping bands of mono and bidentate nitrate remains at approximately the same level. When the same experiment is repeated with NO added to the gas mixture (Fig. 11), no major difference is observed in the absorbance of the surface isocyanate bands or the bands associated with surface coordinated ammonia and ammonium ions. The surface hydroxyl bands are somewhat more intense at the lower temperatures and the nitrate bands are stronger at all temperatures, when compared to the same experiment without NO.



FIG. 10. Infra red absorption spectra of surface species on 2% Pt/ γ -Al₂O₃ exposed to HNCO and O₂. The spectra are successively recorded after 5 min at 450, 400, 350, 300, 250, 200, 150, and 100°C. The wavenumber scale is split at 2000 cm⁻¹ and the baselines are separated by 0.05.



FIG. 11. Infra red absorption spectra of surface species on 2% Pt/ γ -Al₂O₃ exposed to HNCO, NO, and O₂. The spectra are successively recorded after 5 min at 450, 400, 350, 300, 250, 200, 150, and 100°C. The wavenumber scale is split at 2000 cm⁻¹ and the baselines are separated by 0.05.

4. DISCUSSION

The main results of the oxidation of HNCO and the reduction of NO by HNCO under net oxidising conditions from both flow reactor and FTIR studies are summarised and possible intermediates for the reaction of HNCO with NO and/or O_2 over Pt/γ -Al₂O₃ are discussed. HNCO oxidation over γ -Al₂O₃ supported Pt leads to the formation of substantial amounts of N_2 and N_2O (Fig. 1). In the absence of Pt only a minor formation of N₂O is observed, all of the remaining HNCO nitrogen is oxidised to NO (Fig. 3). Bands in infra red spectra assigned to adsorbed isocyanate, surface hydroxyl groups, and surface coordinated ammonia and ammonium ions are observed during exposure of the γ -Al₂O₃ substrate to a gas mixture containing HNCO and O₂. More bands, assigned to mono and bidentate nitrate, appear in the infra red spectra when the alumina is promoted by Pt. That these species do not appear in the absence of Pt is not surprising since γ -Al₂O₃ has a low activity towards the oxidation of NO to NO₂ (see Fig. 3). High conversions of NO are observed for the reduction of NO by HNCO over Pt/ γ -Al₂O₃. Isotope studies, using ¹⁵NO, show a mixing of nitrogen isotopes in N₂ ($^{15}N^{14}N$) and N₂O ($^{15}N^{14}NO$): the HNCO nitrogen is coupled with the nitrogen of a NO molecule. An increased activity for reduction of NO is observed under heating ramps, compared to cooling ramps (Fig. 7b versus 7a). The corresponding infra red spectra clearly show adsorbed -NCO species at temperatures below about 350 to 300°C. Surface coordinated ammonia and ammonium ions are also present from 300 down to 100°C (Fig. 11). The increased activity during heating ramps is ascribed to desorption or spillover of reducing species that have been adsorbed on the alumina surface at low temperatures. A similar effect has been discussed previously for the reduction of NO by propene under lean conditions over Pt/γ -Al₂O₃, where heating ramp results were compared with steady state results. It was observed that the temperature interval of NO reduction coincided with that of surfacebound isocyanate species (6). In the absence of noble metal, HNCO showed no activity towards the reduction of NO.

The reaction path for the formation of N₂ and N₂O during reduction of NO includes coupling of unpaired nitrogens. It has been suggested that this coupling is enhanced if the reducing agent already contains an unpaired nitrogen atom, as is the case for ammonia, urea, and cyanuric acid (19,20). Otto et al. (19) studied the surface reaction between NO and ammonia over Pt/Al₂O₃ using nitrogen-15 isotope labelling at temperatures between 200 and 250°C. N₂ was shown to be mainly formed from the interaction of a ¹⁵NH₃ molecule with a ¹⁴NO molecule resulting in a mixing of isotopes, i.e. $^{15}N^{14}N$, whereas N₂O was suggested to be predominantly formed from the interaction of two ¹⁴NO molecules in the presence of chemisorbed hydrogen (14N14NO). Adsorbed NH₂ species were pointed out as the intermediate leading to N₂ formation, whereas adsorbed HNO species were suggested to give N₂O. Similar results were obtained for Cu(II)Y Zeolites at temperatures below 110°C (21). The experiments with isotope labelled ¹⁵NO and HNCO presented in this investigation show a similar effect for the formation of N₂, i.e. a coupling of a nitrogen from a HNCO molecule with one from NO. A similar mechanism as for the reduction of NO by NH₃ could be suggested, since surface coordinated ammonia and ammonium ions are observed in the in-situ infra red spectra (Figs. 8 and 9). These species also form in the absence of Pt. but the noble metal is necessary in a further reaction to N2 and N2O. The N2O formation appears to be controlled by a similar mechanism as the one for the formation of N₂. No ¹⁵N¹⁵NO is observed, as could be expected from the NH₃ results as presented by Otto et al. (19). On the contrary, a mixing of isotopes is formed with one nitrogen from the HNCO molecule and one from the NO. This is in agreement with the reaction scheme as proposed by Perry and Siebers (1) for the reduction of NO by HNCO under lean conditions. NH species were suggested to be the active intermediates forming N₂O. For ^{15}NO and H¹⁴NCO, such a reaction scheme will lead to the formation of an N₂O with a mixing of isotopes. The intermediate that was suggested by Perry and Siebers to form N₂ is the same as when NH3 is used as reducing agent and, indeed, similar results are found for isotope studies with HNCO (1) and ammonia (19).

Resemblance is also observed between the oxidation of HNCO and ammonia, since in both cases nitrogen from the reducing species has to be coupled. The oxidation of ammonia has been studied in detail and the involvement of an adsorbed NO molecule, formed by the oxidation of NH₃, was suggested (22–24). This adsorbed NO reacts then further with the available ammonia, as described previously. A similar mechanism can be assumed for the oxidation of



FIG. 12. Relative size (by deconvolution) of the bands at 1247 (\diamond), 1270 (\Box), and 1298 (\triangle) cm⁻¹ for Pt/ γ -Al₂O₃ exposed to HNCO and O₂.

HNCO and support for this is found in the FTIR results. Deconvolution of the bands in the 1200–1300 cm⁻¹ region for the experiment with γ -Al₂O₃ exposed to HNCO and O₂ shows an increase of surface bound nitrates down to 150°C (Fig. 12), indicating the formation of NO. The major difference between the HNCO oxidation and the reduction of NO by HNCO in oxygen excess is the overlap in N₂ and N₂O formation for the latter (Figs. 1 and 4b). This overlap is also observed in the experiments with isotope labelled ¹⁵NO (Fig. 7) and must be related to the presence of NO in the feed gas.

The debate on the role of support-adsorbed -NCO on the reduction of NO has been mentioned in the Introduction. Comparison of the reduction of NO by HNCO under cooling and heating ramp conditions (Figs. 7a and b) shows an increased reduction of NO with a corresponding increased formation of N₂ and N₂O during heating ramps. This increased reduction of NO is ascribed to the presence of adsorbed -NCO, adsorbed at the end of the cooling, as well as at the beginning of the heating ramp. Support for the presence of adsorbed -NCO species is found in the overshoot in mass 44 in Fig. 7b when compared to Fig. 7a. Comparison with data from the FTIR gas analyser allowed us to ascribe this overshoot on mass 44 to the formation of CO_2 . No reduction of NO by HNCO was observed in the absence of noble metal. This was also seen for the reduction of NO by ammonia over Al_2O_3 (19). The presence of infra red absorption bands assigned to adsorbed -NCO in the absence of noble metal (11) shows that the noble metal is not needed for the formation of adsorbed -NCO, but for the further reaction to N₂ and N₂O.

Some important characteristics for a NO_x reduction mechanism over Pt/γ -Al₂O₃ under oxygen excess can be proposed by combination of results presented here and those available in the literature. The main feature for every reaction mechanism concerning lean NO_x reduction is the removal of adsorbed oxygen, poisoning the catalytic sites. The heating ramps with HNCO show initially no oxidation of the reducing agent. Increasing the temperature results in a partial oxidation of the HNCO, first to -NH₂ and then to -NH, where the -NH₂/-NH ratio is determined by the temperature and the presence of oxygen on the surface. The former has been pointed out as the precursor for N₂, while the latter was suggested to be the precursor for N₂O. Finally, at high temperatures, the reducing agent is fully oxidised to H₂O, CO₂, and NO/NO₂ and the Pt surface is covered by oxygen.

5. CONCLUSIONS

Reduction of NO by HNCO under oxygen excess over Pt/γ -Al₂O₃ was shown to result in the formation of N₂ and N₂O. The use of isotope labelled ¹⁵NO showed a scrambling of nitrogens between NO and HNCO, i.e. formation of ¹⁴N¹⁵N and ¹⁴N¹⁵NO. A reaction mechanism based on NH_x species is proposed. Support for such a reaction mechanism is found in the presence of adsorbed ammonia and ammonium ions as observed by *in-situ* FTIR spectroscopy.

The absence of Pt results in a delay in HNCO ignition. Only a small formation of N_2O is observed due to the thermodynamical instability of the reactive intermediates, i.e. NH and NH₂, at increased temperatures.

ACKNOWLEDGMENTS

We thank Dr. M. Abul-Mihl at the department of Inorganic Chemistry (Göteborg University) for synthesising the HNCO. This work has been performed within the Competence Centre for Catalysis, which is financed by NUTEK—The Swedish Board for Industrial and Technical Development, Chalmers University of Technology, AB Volvo, Saab Automobile AB, Johnson Matthey-CSD, ABB Fläkt Industri AB, Perstorp AB, and AB Svensk Bilprovning.

REFERENCES

- 1. Perry, R. A., and Siebers, D. L., Nature 324, 657 (1986).
- Glaborg, P., Kristensen, P. G., Jensen, S. H., and Dam-Johansen, K., Combust. Flame 98, 241 (1994).
- 3. Matyshak, V. A., and Krylov, O. V., Catal. Today 25, 1 (1995).
- 4. Chang, C. C., and Hegedus, L. L., J. Catal. 57, 361 (1979).
- Bamwenda, G. R., Obuchi, A., Ogata, A., and Mizuno, K., *Chem. Lett.*, 2109 (1994).
- Acke, F., Westerberg, B., Eriksson, L., Johansson, S., Skoglundh, M., Fridell, E., and Smedler, G., *in* "Studies in Surface Science and Catalysis; Catalysis and Automotive Pollution Control IV" (N. Kruse, A. Frennet, and J.-M. Bastin, Eds.), Vol. 116, p. 285. Elsevier, Amsterdam, 1998.
- 7. Unland, M., J. Catal. 31, 459 (1973).
- 8. Solymosi, F., Völgyesi, L., and Raskó, J., Z. Phys. Chem. 120, 79 (1980).
- 9. Gorte, R. J., Schmidt, L. D., and Sexton, B. A., J. Catal. 67, 387 (1981).
- 10. Raskó, J., and Solymosi, F., J. Catal. 71, 219 (1981).
- 11. Westerberg, B., unpublished results.
- 12. Dalla Betta, R. A., and Shelef, M., J. Mol. Catal. 1, 431 (1975/1976).
- Voorhoeve, R. J. H., Patel, C. K. N., Trimble, L. E., Kerl, R. J., and Gallagher, P. K., *J. Catal.* 45, 297 (1976).
- Voorhoeve, R. J. H., Patel, C. K. N., Trimble, L. E., and Kerl, R. J., J. Catal. 54, 102 (1978).
- 15. Voorhoeve, R. J. H., and Trimble, L. E., J. Catal. 54, 269 (1978).
- 16. Belson, D. J., and Strachan, A. N., Chem. Soc. Rev. 11, 41 (1982).
- 17. Rüütelmann, M., Report OOK 93:03 (1993).
- Basu, P., Ballinger, T. H., and Yates, J. T., *Rev. Sci. Instrum.* 59, 1321 (1988).
- 19. Otto, K., Shelef, M., and Kummer, J. T., J. Phys. Chem. 74, 2690 (1970).
- 20. Shelef, M., Chem. Rev. 95, 209 (1995).
- 21. Williamson, W. B., and Lunsford, J. H., J. Phys. Chem. 80, 2664 (1976).
- Fogel, Y. M., Nadykto, B. T., Rybalko, V. F., Shvachko, V. I., and Korobchanskaya, I. E., *Kinet. Katal.* 5, 431 (1964).
- Ostermaier, J., Katzer, J. R., and Manogue, W. H., J. Catal. 33, 457 (1974).
- Pusateri, R. J., Katzer, J. R., and Manogue, W. H., AIChE. J. 20, 219 (1974).