Harmful by-products in selective catalytic reduction of nitrogen oxides by olefins over alumina

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The selective reduction of nitrogen dioxide and nitrogen monoxide by olefins (ethene, propene) has been studied over two different γ-aluminium oxides in the temperature range 473–873 K. Nitrogen dioxide was reduced more effectively than nitrogen monoxide with both, ethene and propene, as a reductant. At temperatures exceeding 700 K, ammonia was formed as a by-product over one type of alumina. Concentrations in the range 30–40 ppm were determined for propene in combination with both, NO and NO_2, while no ammonia was produced with ethene as a reductant. In addition, significant formation of hydrogen cyanide up to 70 ppm was observed with propene over both aluminium oxides starting from either NO or NO_2. In contrast, hydrogen cyanide formation remained below 10 ppm with ethene as a reductant. Nitrous oxide formation did not exceed 10 ppm for all investigations. The results show that for alumina catalysts ethene is a more suitable reductant than propene due to its lower tendency to form undesired by-products.

Keywords: ammonia; alumina; ethene; hydrogen cyanide; nitrous oxide; NO/NO_2; propene; selective reduction

1. Introduction

The removal of nitrogen oxides from the exhaust of diesel-fueled engines and lean-burn gasoline-fueled engines requires catalysts which selectively reduce NO_x in the presence of excess oxygen. Conventional three way catalysts show little ability to promote NO_x-reduction under net oxidizing conditions. Consequently, there is considerable interest in active and selective catalyst systems for the reduction of nitrogen oxides under lean conditions. A range of zeolites exchanged with various elements [1–19] as well as oxides, with [6,17–23] and without [6,13,17–23] transition metal, were reported to be effective for this reaction. Among the oxides investigated, alumina based catalysts have been well represented [6,13,17–23].

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Several aspects of lean NO_x reduction, such as the effects of hydrocarbon type [7,10,17,19,20,23,26] and concentration [4,20,26], effect of space velocity [4,8,14, 19,21,26], influence of H_2O and SO_2 [18,19,22,23,26], effect of oxygen concentration [4,6,10,13] as well as effect of nitrogen dioxide [6,11,13,16,17] have been investigated. Regarding the formation of nitrogen containing by-products, nitrous oxide [12,17] and hydrogen cyanide [12] were recently reported to be formed.

In this study we report the formation of harmful by-products such as hydrogen cyanide, ammonia and nitrous oxide in the selective catalytic reduction of nitrogen dioxide and nitrogen monoxide by either ethene or propene in the presence of excess oxygen over two different commercial γ-aluminium oxides. The effects of the type of alumina, of the chemical nature of the nitrogen oxide (NO or NO_2) and of the olefin employed as a reducing agent (C_2H_4 or C_3H_6) on the formation of the by-products and on the overall catalytic performance were examined.

2. Experimental

The investigations were performed using two commercially available aluminium oxides. Alumina A, (Alumina-C, Degussa Corp.) was agglomerated with water, dried at 393 K, calcined in air at 873 K and crushed to a sieve fraction of 120–150 μm. Alumina B, (Alumina-GX, Martinswerk) with an initial sieve fraction of 150–200 μm was treated similarly. BET surface areas determined by nitrogen adsorption measurements amounted to 109 $m^2\ g^{-1}$ for alumina A and 100 $m^2\ g^{-1}$ for alumina B, with corresponding average pore diameters of 29 and 9 nm, respectively. XRD analysis showed for alumina A only reflections due to γ-Al_2O_3, whereas alumina B was made up of approximately 90% γ-alumina and 10% α-Al_2O_3.

The experimental set-up used for the catalytic studies has been described in more detail elsewhere [12]. The apparatus consisted essentially of a dosing system for the reactant gases, a tubular fixed-bed micro reactor made of quartz glass and a FT-IR spectrometer (Bruker IFS 66), equipped with a heatable gas cell (100 ml volume; Infrared Analysis Inc.) and a MCT-detector, for gas analysis. The concentrations of the feed and effluent gases were calculated using an appropriate software package (Opus, Bruker). The accuracy in the concentration measurements by FT-IR (resolution 0.5 cm^{-1}, 50 scans per spectrum) was ±5% for all components.

Standard experiments were carried out using 0.25 g of catalyst with a total gas flow rate of 150 ml(STP)/min. The samples were pretreated with 5% oxygen in nitrogen (150 ml/min) at 873 K for 2 h and then cooled to 473 K. Subsequently the reactant gas mixture was passed through the catalyst bed. Steady-state measurements were performed by increasing the temperature in steps of 50 K with a duration of the isothermal steps of typically 1.5 h. Note that the catalytic data reported in this work have been collected during a successive repetitive cycle of the above procedure.

The reactant gas feeds, as specified in table 1, were mixed from pure components by means of mass flow controllers, as described in ref. [12]. The selection of either NO_2 or NO as the NO_x component was accomplished by mixing at room temperature 4.9% NO/N_2 with pure O_2 before and after dilution with nitrogen, respectively. In the former case, the high partial pressure of oxygen and nitrogen monoxide together with a residence time of >5 min facilitated the formation of NO_2. No NO was detected for feeds I and II (table 1), indicating that the conversion of NO to NO_2 was 100%.

3. Results

3.1. REDUCTION OF NITROGEN DIOXIDE

Fig. 1 depicts the temperature dependence of the activities of the two commercial aluminium oxides A and B for the reduction of nitrogen dioxide to NO and N_2 and for the oxidation of propene to CO and CO_2 (feed I). Oxidation of propene starts at slightly lower temperature for alumina A (565 K) compared to alumina B (625 K), with carbon monoxide being the major product besides slightly lower amounts of carbon dioxide. While propene conversion levelled off with alumina A for temperatures above 670 K, it steadily increased with alumina B. However, propene oxidation remained low over the temperature range investigated with ca. 35% CO and 25% CO_2 being formed at 820 K with both aluminas. The oxidation of propene is accompanied by the concurrent conversion of NO_2 to N_2. With alumina A, the N_2 yield reaches a maximum of 90% at 660 K, which is markedly higher than with alumina B where a maximum of 53% N_2 is found at 765 K. A significant decline in nitrogen yield from 90 to 65% is observed with alumina A for a temperature increase from 660 to 820 K. Increased NO-formation is found in parallel. In contrast, NO and N_2 are formed simultaneously with similar yields with alumina B over the temperature range investigated.

Fig. 2 illustrates the temperature dependence of the formation of ammonia, hydrogen cyanide and nitrous oxide over both aluminas for feed I. The formation of ammonia is observed only for alumina B, starting above 700 K. Ammonia concentration then increases steadily to reach a value of 32 ppm at 815 K. A low-tem-

Table 1
Feed gas composition employed for catalytic studies, balance nitrogen

	Feed I	Feed II	Feed III	Feed IV
NO (ppm)	0	0	970	970
NO_2 (ppm)	1000	990	0	0
C_2H_4 (ppm)	0	1450	0	1390
C_3H_6 (ppm)	880	0	950	0
O_2 (%)	1.9	1.9	2.0	2.0

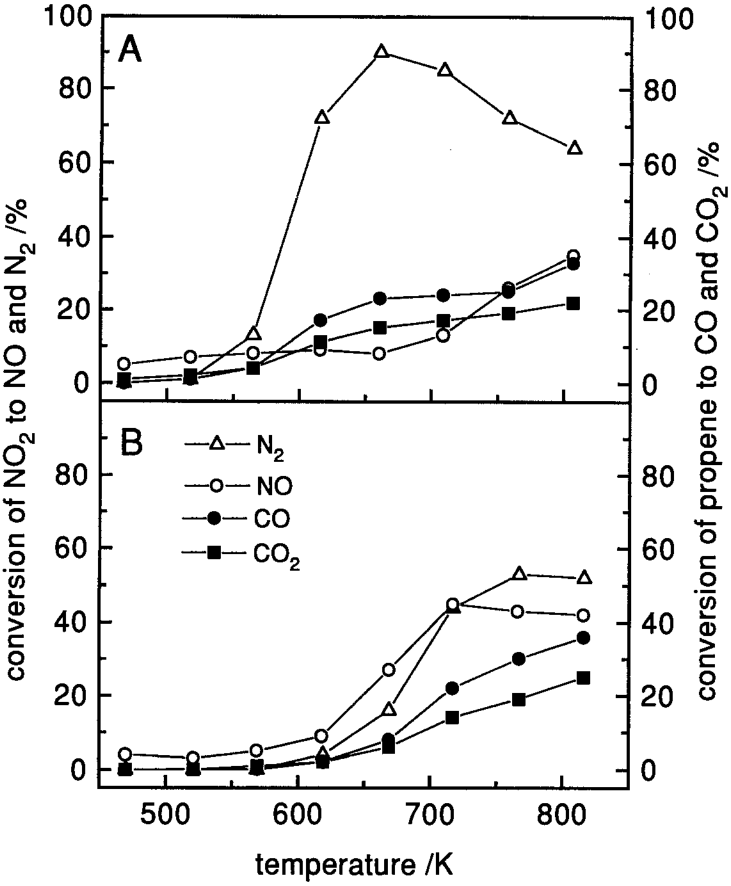

Fig. 1. Temperature dependence of the reduction of NO_2 to NO and N_2 and of propene oxidation to CO and CO_2 over (A) alumina A and (B) alumina B. Conditions (feed I): 1.9% O_2, 1000 ppm NO_2 and 880 ppm C_3H_6, balance N_2, $W/F = 0.1$ g s cm^{-3}.

perature peak of hydrogen cyanide formation with a maximum of 68 ppm at 565 K is observed for alumina A, while no such peak of hydrogen cyanide could be detected with alumina B at similar temperatures. Slightly increasing amounts of hydrogen cyanide are formed above 650 K with alumina B and to a lower extent with alumina A. Nitrous oxide formation peaks at 615 K with alumina A reaching a concentration of 10 ppm, while minor amounts of nitrous oxide are produced with alumina B at temperatures exceeding 600 K.

Similar behaviour as with propene is observed with ethene as a reductant (feed II), as emerges from fig. 3. With alumina A the ratio of ethene converted to carbon monoxide is slightly higher. Ethene oxidation and, more pronounced, nitrogen formation again takes place at significantly lower temperatures with alumina A as compared to alumina B. The conversion of NO_2 to N_2 reaches a value of 83% at 660 K with alumina A. No decrease in nitrogen formation was observed by further

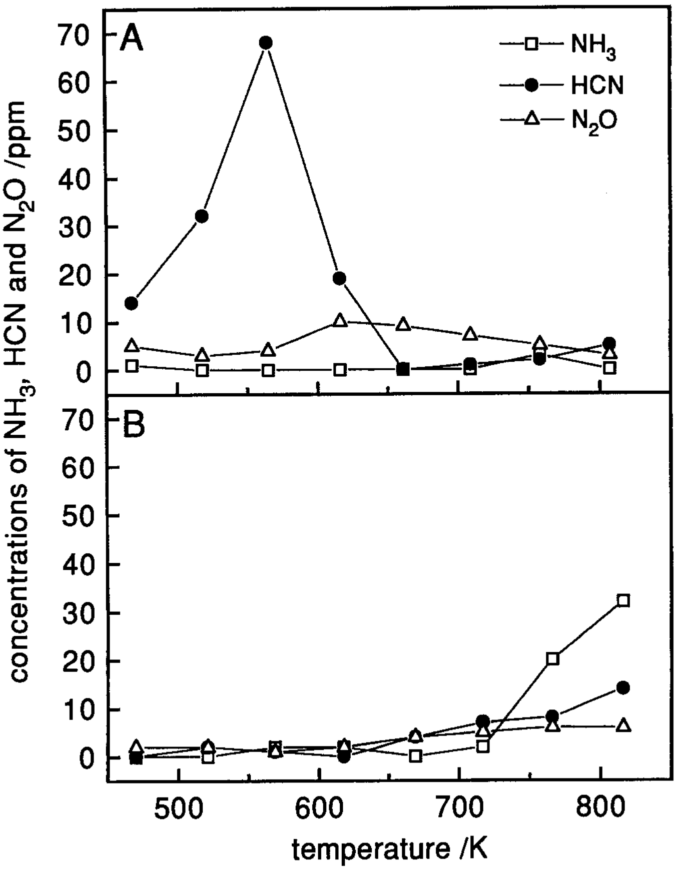

Fig. 2. Temperature dependence of formation of ammonia, hydrogen cyanide and nitrous oxide with propene as reductant over γ-Al_2O_3. Concentrations of NH_3, HCN and N_2O versus temperature over (A) alumina A and (B) alumina B. Conditions (feed I): 1.9% O_2, 1000 ppm NO_2 and 880 ppm C_3H_6, balance N_2, $W/F = 0.1$ g s cm^{-3}.

increasing the temperature, which contrasts the findings with propene. Simultaneously, no increase in nitrogen monoxide production with temperature was found with this sample. With B formation of nitrogen monoxide starts at 670 K, while nitrogen production begins above 675 K, which is 60 K higher than with propene as a reductant. Nitrogen and nitrogen monoxide formation then increase steadily and reach values of 51 and 46%, respectively, at 815 K.

With respect to the formation of ammonia and hydrogen cyanide, ethene as a reductant showed a markedly different behaviour than propene. With both aluminas no ammonia was detected over the temperature range investigated (fig. 4). The formation of hydrogen cyanide shows the same temperature dependence as found for propene but with significantly less hydrogen cyanide being produced, as emerges from fig. 4. Maximum concentrations of 9 and 6 ppm hydrogen cyanide were observed with alumina A and B, respectively. Note that with alumina A no

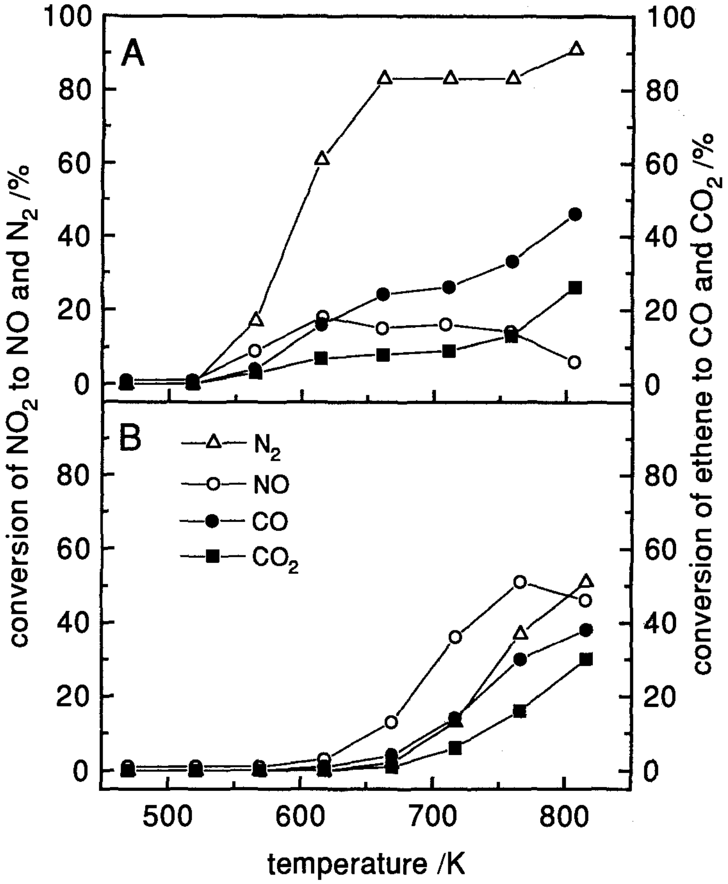

Fig. 3. Temperature dependence of the reduction of NO_2 to NO and N_2 and of ethene oxidation to CO and CO_2 over (A) alumina A and (B) alumina B. Conditions (feed II): 1.9% O_2, 990 ppm NO_2 and 1430 ppm C_2H_4, balance N_2, $W/F = 0.1$ g s cm^{-3}.

hydrogen cyanide was produced at high temperatures. On the contrary, no difference in the formation of nitrous oxide as a function of temperature could be observed by changing from propene to ethene as a reductant.

3.2. REDUCTION OF NITROGEN MONOXIDE

The use of nitrogen monoxide (feeds III and IV) instead of nitrogen dioxide resulted in comparable results for both reductants. The conversion of both, the olefin and the nitrogen monoxide, showed similar behaviour with the use of either ethene or propene. Figs. 5 and 6 depict the results obtained with propene as a reductant.

In fig. 5, the yields of nitrogen, carbon monoxide and carbon dioxide are plotted for experiments with feed III. Formation of nitrogen and oxidation of propene

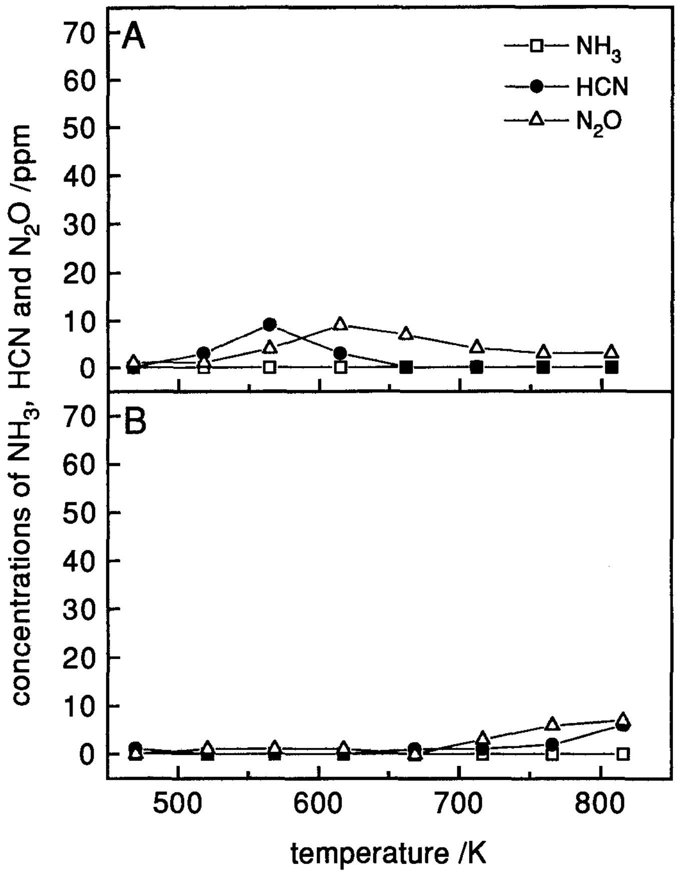

Fig. 4. Temperature dependence of formation of ammonia, hydrogen cyanide and nitrous oxide with ethene as reductant over γ-Al_2O_3. Concentrations of NH_3, HCN and N_2O versus temperature over (A) alumina A and (B) alumina B. Conditions (feed II): 1.9% O_2, 990 ppm NO_2 and 1430 ppm C_2H_4, balance N_2, $W/F = 0.1$ g s cm^{-3}.

starts at 650 K and increases steadily with temperature. Similar activity for propene oxidation was found with both aluminas but with carbon monoxide being the prevailing oxidation product over alumina A and carbon dioxide over alumina B. For corresponding temperatures, the activity for olefin oxidation was significantly lower with nitrogen monoxide as compared to nitrogen dioxide. Similarly, conversion of nitrogen monoxide to nitrogen was lower as compared to the reduction of nitrogen dioxide. Formation of nitrogen reached 34% at 855 K for alumina A, while only 17% nitrogen were observed with alumina B at 860 K. Note that production of nitrogen dioxide was negligible over the temperature range investigated.

The concentrations of ammonia, hydrogen cyanide and nitrous oxide as a function of temperature are presented in fig. 6 for feed III. As in the case of feed I, ammonia was only observable with alumina B, attaining a concentration of 30 ppm at 860 K. Hydrogen cyanide production started at 670 K for both alumi-

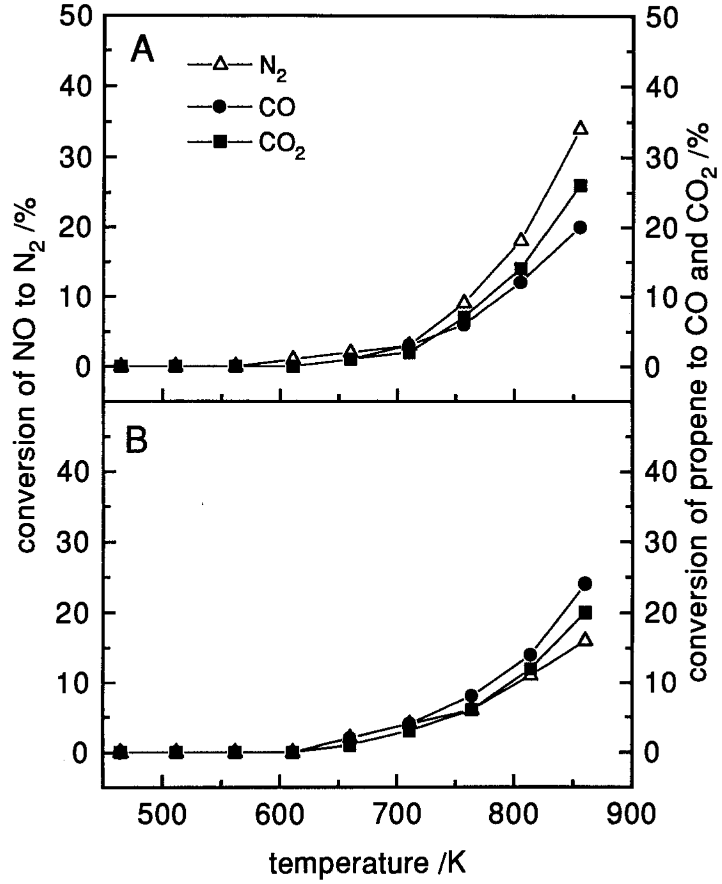

Fig. 5. Temperature dependence of the reduction of NO to N_2 and of propene oxidation to CO and CO_2 over (A) alumina A and (B) alumina B. Conditions (feed III): 2% O_2, 970 ppm NO and 950 ppm C_3H_6, balance N_2, $W/F = 0.1$ g s cm^{-3}.

nas and reached values of 17 and 50 ppm at 860 K for alumina A and B, respectively. In contrast to the findings with nitrogen dioxide, no hydrogen cyanide formation was observed at low temperatures for alumina A. Formation of nitrous oxide was negligible for the temperature range investigated.

Experiments with feed IV resulted in similar catalytic activities as observed with feed III. However, the formation of by-products remained low (< 10 ppm) for all temperatures as already observed with feed II. It is interesting to note that by using alumina A for several pretreatment/reaction cycles, conversion of NO to N_2 reached 93% at 860 K with ethene, as compared to 33% with a fresh catalyst. This is a strong indication that the surface chemical properties of the alumina change upon its exposure to reaction conditions, a phenomenon which merits further investigation. The formation of by-products was not significantly altered.

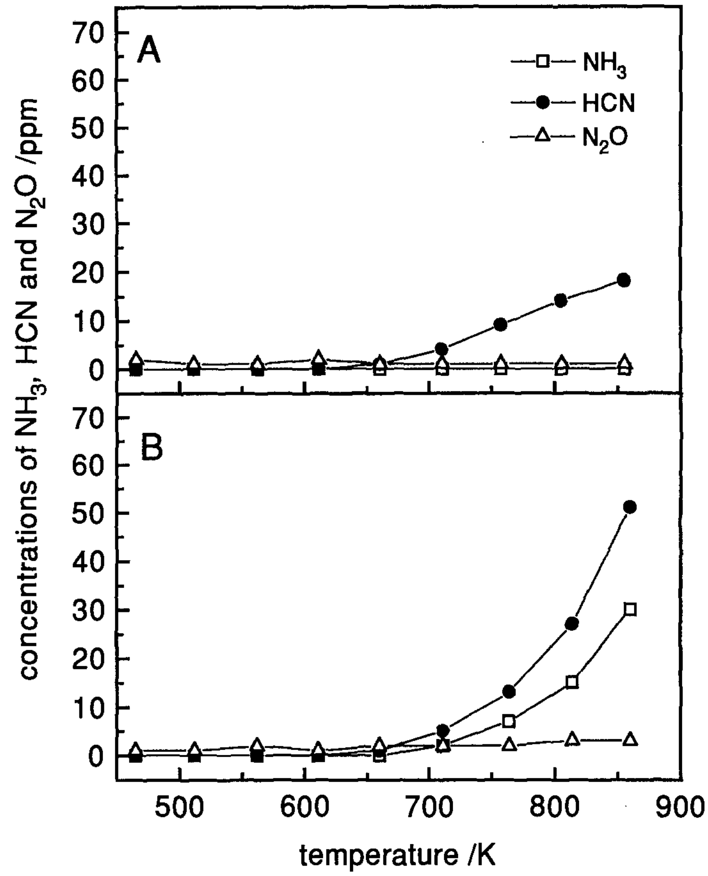

Fig. 6. Temperature dependence of formation of ammonia, hydrogen cyanide and nitrous oxide with propene as reductant over γ-Al_2O_3. Concentrations of NH_3, HCN and N_2O versus temperature over (A) alumina A and (B) alumina B. Conditions (feed III): 2% O_2, 970 ppm NO and 950 ppm C_3H_6, balance N_2, $W/F = 0.1$ g s cm^{-3}.

4. Discussion

4.1. FORMATION OF HARMFUL BY-PRODUCTS

Hydrogen cyanide. The formation of hydrogen cyanide in the reduction of both, NO and NO_2 over alumina A and B is more critical if propene is used as a reductant. HCN concentration did not exceed 10 ppm with ethene. This differs from findings with Cu/ZSM-5 [12], where significant hydrogen cyanide production was observed with both reductants. Low temperature formation of hydrogen cyanide, as observed with alumina A in combination with feed I, peaked at a temperature coincident with the onset of nitrogen formation. Hydrogen cyanide production then declines in parallel with the NO_2 concentration. Interestingly, no such low temperature HCN production was observed with alumina B. A second temperature regime for HCN formation, which is more pronounced for alumina B, is noticed with feeds I and III for temperatures exceeding 650 K. The occurrence of two temperature regimes for hydrogen cyanide formation suggests two different mechanisms to take place in either regime. High temperature HCN formation seems to be related to the NO concentration in the gas phase, as significantly more HCN was produced with feed III compared to feed I.

Ammonia. Formation of NH_3 was observed with both reactants, NO and NO_2, but only with alumina B in combination with propene as a reductant. This finding suggests that the production of ammonia is related to the structural characteristics of the alumina employed as a catalyst. Note that ammonia formation remained negligible with alumina A, transformed to α-alumina by heat treatment. Alumina B treated in the same way still produced up to 36 ppm ammonia. This indicates that it is not the α-alumina in sample B which is responsible for ammonia formation. Ammonia formation was not detected in similar experiments with a Cu/ZSM-5 catalyst [12] or remained negligible with an alumina catalyst [26].

Nitrous oxide. Production of N_2O showed a distinct dependence on the chemical nature of the nitrogen oxide used (NO or NO_2). Starting from feeds III and IV (containing NO), only insignificant amounts of N_2O were detected, while up to 10 ppm N_2O were produced with NO_2-containing feeds (I, II). Nitrous oxide formation was repeatedly reported to be negligible in the reduction of NO_x by hydrocarbons starting from NO [13,17,25].

4.2. COMPARISON OF REACTION SYSTEMS

Compared to nitrogen monoxide, nitrogen dioxide was frequently reported to be more reactive in the selective reduction of NO_x over alumina [6,13,17] and zeolite type catalysts [6,17]. This finding is confirmed in the present investigation, where activity for nitrogen formation was consistently higher in the NO_2-containing system. Oxidation of NO to NO_2, although favoured by thermodynamic equilibrium at temperatures below 600 K [11], was negligible under reaction conditions, presumably due to kinetic reasons. The findings are consistent with results reported by Hamada and co-workers [6,13] for the reaction of NO and O_2 in the absence of hydrocarbons over alumina. Little activity was reported for a feed containing 1% O_2, while up to 29% NO_2 were produced with 10% O_2 [13]. The formation of NO_2 from NO and O_2 seems to be strongly governed by the partial pressure of the reactants, by their residence time and by the temperature profile in front of the catalyst bed.

Starting from feeds I and II, NO_2 completely reacted to NO and N_2 above 660 K over alumina A, with N_2 being the prevailing reaction product (figs. 1A and 3A). In contrast, with alumina B reaction of NO_2 started at significantly higher temperature leading to NO as a primary product besides lower amounts of N_2 (figs. 1B and 3B). The results indicate NO_2 either to be reduced to N_2 or to decompose to form NO, with the former reaction taking place at lower temperature.

Note that NO-reduction took place at markedly higher temperatures and to a lower extent as compared to NO_2-reduction (fig. 5). The aluminium oxides used exhibit significantly different activities for the two NO_2 consumption mechanisms, the low temperature NO_2 reduction seems to be favoured on alumina A. The decline in N_2 formation observed at high temperatures with alumina A may be associated with an increased activity for NO_2-decomposition in the presence of propene as no such effect was noticed with ethene as a reductant.

With respect to the use of either ethene or propene as a reductant no significant change in catalytic activity was observed with both aluminas, starting from NO or NO_2, respectively.

5. Conclusions

The selective catalytic reduction of nitrogen oxides by hydrocarbons in excess oxygen over γ-alumina can produce substantial amounts of hydrogen cyanide and ammonia, while the formation of nitrous oxide remains low. The type of alumina, the hydrocarbon used as a reductant and, to a lesser extent, the use of either NO or NO_2 in the reactant gas strongly influence the formation of the undesired by-products.

Catalytic tests showed that the reduction of nitrogen dioxide to nitrogen proceeds more efficiently than the corresponding reaction with nitrogen monoxide. Similar results were obtained for either ethene or propene as a reductant. The properties of the alumina seem to play a crucial role in governing the overall catalytic behaviour. Investigations towards elucidation of the relationship between the structural and chemical properties of alumina and its behaviour in the selective catalytic reduction of NO_x by hydrocarbons are presently undertaken in our laboratory.

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