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Clean catalytic combustion of nitrogen-bearing gasified biomass

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Zero NO_x emissions are obtained in the catalytic combustion of simulated biomass mixtures containing substantial amounts of ammonia by optimisation of NH_3 oxidation and NO_x reduction using a 2%Rh–Al_2O_3 catalyst.

Renewable energy sources will be of increasing importance for power generation in the future. Attempts have been made to harness biomass-derived fuels for combined heat and power generation.[1–3] However, gasified biomass contains significant quantities of NH_3 (600–4000 ppm) in addition to substantial amounts of CO (9.8–17.2%), H_2 (9.8–13.2%) as well as CH_4, CO_2, H_2O and N_2.[3] The NH_3 represents a particular challenge since its combustion in the gas phase results in the formation of an equivalent amount of NO_x.

The environmental benefits of cleaner power generation has prompted much interest in catalytically stabilised combustion to reduce harmful emissions of nitrogen oxides (NO_x) and unburnt fuels.[1,2,4] A key question is whether catalytic combustion of biomass-derived gases can be controlled so as to avoid the conversion of ammonia into NO_x. The novel solution to this problem which we have discovered,[5] and which is reported here, is to first oxidise all the ammonia to NO_x and then utilise the large excess of CO and H_2 in the gas stream to reduce the NO_x to N_2 through the NO/CO and NO/H_2 reactions.

The catalyst used was 2%Rh–Al_2O_3 prepared by incipient wetness impregnation of CK300 Al_2O_3 (ex Akzo, surface area 200 m^2 g^{-1}). The dried Al_2O_3 (120 °C, 24 h) was impregnated with Rh III nitrate (ex Johnson Matthey) and dried at room temperature for 24 h, then at 120 °C for a further 24 h prior to calcination at 700 °C in flowing O_2/He for 12 h. A second catalyst comprising 2%Rh–10%CeO_2–Al_2O_3 was prepared by sequential impregnation/calcination of $Ce(NO_3)_3{\cdot}6H_2O$ followed by $Rh(NO_3)_3$. Catalyst testing (60 mg, prereduced for 4 h at 700 °C in CO/H_2/He) was performed in a standard quartz flow microreactor at a GHSV of 240000 h^{-1}. Product analysis was by mass spectrometry (Hiden DSMS) with NO_x emissions and residual NH_3 levels being corroborated using an external NH_3 oxidation reactor (with independent oxygen supply) coupled with a NO_x chemiluminescence detector (Signal series 4000).

A conventional direct oxidation of NH_3 over 2%Rh–Al_2O_3 at typical gasifier output temperatures (Fig. 1) shows a low conversion initially but with a high selectivity to N_2. However, whilst both conversion and N_2 yields increase with temperature, N_2O and NO are also formed. N_2O and N_2 concentrations peak at *ca.* 375 °C (*ca.* 85–90% N_2) before decreasing, consistent with previous results,[2,6] whilst NO formation is seen to increase steadily with temperature to become the major product at $T >$ 500 °C. Fig. 1 therefore illustrates the difficulty of selectively oxidising NH_3 by conventional methods.

However, such problems may be overcome by making use of the other components of the biomass gas, namely CO and H_2 and by controlling the process conditions. Thus, catalytic reduction of NO by CO is very facile,[7] and the reduction of NO_x by H_2 has also been demonstrated.[8] Therefore, if NH_3 is first oxidised to NO_x, the other components of the biomass gas (CO and H_2) could be used for the catalytic reduction of NO_x to N_2. Hence by coupling NH_3 oxidation with NO_x reduction in an oxygen-limited environment it should be possible to convert NH_3 completely to N_2 in a pseudo-two-stage process. Thus, the strategy we propose is to first catalyse the complete oxidation of the NH_3 to NO_x in a limited amount of O_2, followed by catalytic reduction of NO_x by the CO or H_2 present in the biomass gas.

The main challenge is to selectively oxidise NH_3 in the presence of a large excess of CO and H_2. Our success in achieving this with a Rh catalyst is illustrated in Fig. 2. This shows that conversion of NH_3, rather than reaction selectivity, is the limiting factor for the selective oxidation. Thus, at low temperatures NH_3 does not react but H_2 and CO are very reactive. In contrast, at higher temperatures, the NH_3 begins to react and by around 600 °C the conversion of ammonia is effectively 100% whereas the combustion of H_2 has dropped to close to zero. Of course, the overall levels of oxidation are limited, deliberately, by controlling the O_2 concentration. Clearly, with this catalyst the selective oxidation of NH_3 to NO_x in the presence of a large excess of CO and H_2 has been achieved. The second stage, namely, the reduction of the NO_x

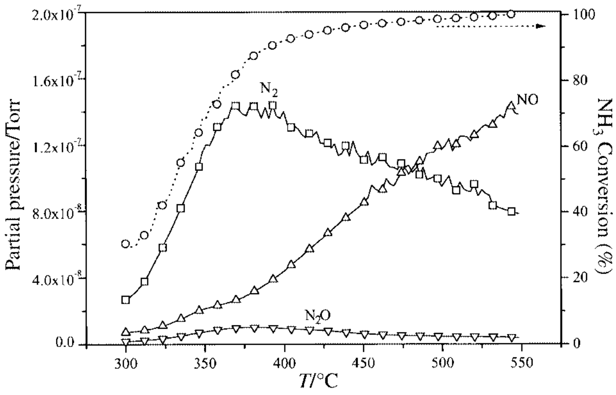

Fig. 1 Nitrogen-bearing products and NH_3 conversion for the selective catalytic oxidation of NH_3 over 2%Rh–Al_2O_3 (1000 ppm NH_3, 18% O_2, balance He). Key: □, N_2; ▽, N_2O; Δ, NO; ○, NH_3 conversion.

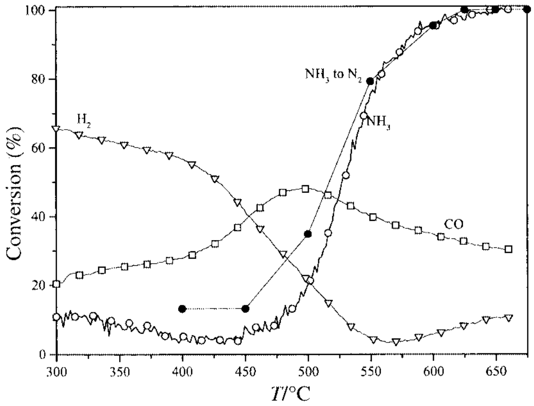

Fig. 2 Conversion profiles for the O_2 lean combustion of simulated biomass over 2%Rh–Al_2O_3 (1000 ppm NH_3, 0.275% O_2, 1.02% CO, 0.68% H_2, balance He). Key: ○, NH_3; □, CO; ▽, H_2, ●, NH_3 as determined by external oxidation reactor/chemiluminescence.

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Table 1 Lifetime performance of (1) 2%Rh–Al_2O_3 and (2) 2%Rh–10%CeO_2–Al_2O_3

Entry	%O_2 : CO/H_2 : H_2O	%N_2 at 1 h	%N_2 at 2 h	%N_2 at 3 h	%N_2 at 4 h	%N_2 at 5 h
1	0.275 : 1.7 : 0	98.3	97.5	96.7	96.6	96.6
2	0.275 : 8.9 : 2.5	100	100	100	99.9	99.8

by residual CO and/or H_2 occurs sequentially within the same bed of catalyst because the only nitrogen-containing product detected is N_2. This methodology has also been examined for its efficacy under more severe conditions for extended periods with minimal loss of activity (Table 1) underlining its potential for commercial application. Moreover it should be stressed that in case of the 2%Rh–10%CeO_2–Al_2O_3 catalyst, a significantly higher CO/H_2 concentration was employed, which in theory should mitigate *against* the activation of the NH_3 due to significantly enhanced competition for active sites, when in fact this sample exhibited almost no deactivation over the duration of the experiment.

In conclusion, we have developed a strategy for the complete removal of NH_3 from biomass-derived gases by coupling the total oxidation of NH_3 with the reduction of NO_x by CO and/or H_2. Experiments have demonstrated that the concept is viable and provides a novel way to overcome the environmenal problems associated with the direct combustion of biomass-derived gas. The strategy is equally applicable to any comparable gasification gas (from coal, or from other renewable sources). Future work will examine the potential poisoning effects of sulfur, alkali metals and chloride ions on activity, although given the net reducing conditions employed in this new process the impact of the former is expected to be limited given previous experience of the negligible effect of sulfur on 3-way catalysts.[9]

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