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Low-temperature, clean catalytic combustion of N-bearing gasified biomass using a novel NH_3 trapping catalyst

Robert Burch and Barry W. L. Southward*

School of Chemistry, The Queen's University of Belfast, Belfast, UK BT9 5AG. E-mail: b.w.l.southward@qub.ac.uk

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Substantially reduced NO_x emissions are obtained in the low temperature catalytic combustion of NH_3-bearing simulated biogas by use of a novel 1%Pt/20%CuO/Al_2O_3-trapping catalyst and cyclic operation between fuel lean and rich conditions.

The exploitation of renewable energy sources to both limit CO_2 emissions and extend fossil fuel reserves is a subject of considerable interest with the former aspiration being embodied in the landmark Kyoto agreement.[1] This interest is exemplified by the various attempts to harness biomass-derived fuels for combined heat and power generation.[2–7] However, during gasification, biogenic nitrogen, fixed during plant growth, is converted into significant quantities of NH_3 (600–4000 ppm) in addition to the main fuel components, CO (9.8–17.2%) and H_2 (9.8–13.2%) as well as CH_4, CO_2, H_2O and N_2.[2] The presence of this NH_3 is a particular obstacle to the exploitation of biogas as a fuel since its combustion in a conventional burner results in the formation of significant amounts of nitrogen oxides (NO_x) which are well-known atmospheric pollutants.[8]

Attempts to overcome this problem by catalytic combustion of the NH_3/fuel mix have met with limited success with N_2 yields of $< 70\%$ being typical.[3,4] In contrast, we have demonstrated substantially improved performance using either redox-acid catalysts, such as 12-tungstophosphoric acid which yield *ca.* 85% N_2,[5] or by use of a catalyst which can couple NH_3 oxidation and NO_x reduction using the fuel components of the biogas mixture[6] giving close to 100% N_2 selectivity. However, in order to achieve these high conversions of NH_3 to N_2, both catalysts must be operated at temperatures $\geqslant$ 600 °C. We have now discovered for the first time a procedure for the selective oxidation of NH_3 to N_2 in simulated biogas, which can operate at temperatures as low as 200 °C.

The catalyst used was 1%Pt/20%CuO/Al_2O_3 (hereafter referred to as PtCu) prepared by sequential incipient wetness impregnation of Al_2O_3 (Criterion CK300, surface area 200 m^2 g^{-1}). The dried Al_2O_3 (120 °C, 24 h) was first impregnated with $CuSO_4 \cdot 5H_2O$ (ex Aldrich 98%) dried (24 h at room temperature, 24 h at 120 °C), and calcined (500 °C, 24 h). The process was repeated for the addition of 1% Pt ($PtDNDA_{aq}$ ex Johnson Matthey, 2.28% Pt). The preparation of 1%Pt/Al_2O_3 was performed in an identical manner. Catalyst testing (60 mg) was performed in a standard quartz flow microreactor described previously[7] at a gas flow rate of 300 cm^3 min^{-1}, (GHSV of *ca.* 240 000 h^{-1}). NO_x emissions and residual NH_3 levels were determined using an external NH_3 oxidation reactor (with independent oxygen supply) coupled to a NO_x chemiluminescence detector (Signal series 4000 with data logging at 1 s intervals using Signal SIGLOG). Switching between lean and rich fuel conditions was achieved using a pressure-balanced three-way valve immediately prior to the O_2 mass flow controller. This enabled the oxidant to be 'switched' from 20% O_2/He (lean conditions) to 1%O_2/He (rich conditions).

Fig. 1 illustrates both the lean steady state and switching activity of the PtCu for the oxidation of NH_3 under comparatively mild conditions (1000 ppm NH_3, 1.02% CO, 0.68% H_2). The steady-state N_2 yield was *ca.* 94%, already a significant improvement upon previous data[3,4] and is ascribed to the establishment of an *internal selective catalytic reduction* (*i*SCR) mechanism[5,7]

However, unlike previous metal and metal oxide systems for NH_3 oxidation, the PtCu catalyst is unique and may be considered to be a composite material with a strong synergy between two very specific but different active sites. Pt provides the first site whose function is the activation of NH_3, which has been shown to be the rate limiting step of the *i*SCR reaction.[7,9,10] The second site then resides on the Cu, which adsorbs NH_3 to produce an NH_x(ads) species (as shown by NH_3 TPD[11]) These NH_x(ads) species then react with the NO_x formed on the Pt to give N_2, consistent with the proposals of Janssen *et al.*[12]

The synergistic effect is particularly apparent when comparing the activity of the PtCu with both 10%Cu/Al_2O_3 and 1%Pt/Al_2O_3. 10%Cu/Al_2O_3 was found to require temperatures of *ca.* 400 °C to produce high yields of N_2 ($> 90\%$) while although 1%Pt/Al_2O_3 was active at lower temperatures it gave only a very low selectivity (*ca.* 29% N_2 at 200 °C).

The high N_2 yields of the PtCu were further improved by transient switching of the oxidant (15 s rich, 45 s lean). Indeed, by switching it was possible to obtain peak N_2 yields of 100% before N_2 production decreased over some 500 s to the values obtained under steady state conditions. This reflects the buffering of the system *via* the reservoir of NH_x(ads) species on the Cu. Under lean conditions these species are 'titrated' by *in situ* NO but in the absence of sufficient O_2 for full reaction the Cu accumulates an NH_x(ads) adsorbate layer, thus preventing NH_3 'slip'.

The importance of transient operation is seen even more clearly when we compare the activities of 1%Pt/Al_2O_3 with the PtCu catalyst in a more realistic feed stream containing high levels of the fuel components (5.1% CO and 3.4% H_2) (Fig. 2). In this case under lean conditions NH_3 conversion was again 100%, but in both cases NH_3 was predominantly converted into NO, reflecting an interception of any NO–NH_3 reaction. Moreover, as can be seen in Fig. 2 (filled diamonds) oxidant

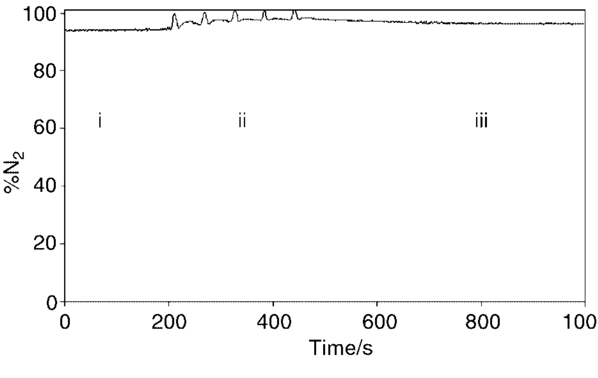

Fig. 1 N_2 production from the selective catalytic oxidation of NH_3/CO/H_2 over 1%Pt/20%CuO/Al_2O_3 at 200 °C (1000 ppm NH_3, 1.02% CO, 0.68% H_2, with either 2.1% O_2 (lean conditions) or 0.1% O_2 (rich conditions), balance He). Key: i, first 200 s of operation is under lean conditions; ii, cyclic operation 15 s rich/45 s lean for 300 s; iii, final 500 s operation is under lean conditions.

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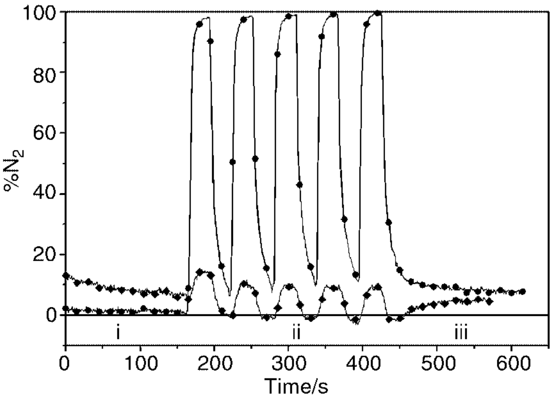

Fig. 2 N_2 production from the selective catalytic oxidation of $NH_3/CO/H_2$ over 1%Pt/Al_2O_3 and 1%Pt/20%CuO/Al_2O_3 at 200 °C (1000 ppm NH_3, 5.1% CO, 3.4% H_2, 9.3% O_2 (lean conditions) or 0.5% O_2 (rich conditions), balance He). Key: i, first 180 s operation is lean; ii, cyclic operation 30 s rich/30 s lean for 300 s; iii, final operation under lean conditions. (◆) 1% Pt/Al_2O_3, (●) 1%Pt/20%CuO/Al_2O_3.

cycling had a minimal effect on N_2 yields for the 1%Pt/Al_2O_3 catalyst. In contrast, with the PtCu catalyst (filled circles), under transient conditions there was a sudden and dramatic improvement in catalyst selectivity, with >98% N_2 production being recorded.

These observations are entirely consistent with the proposed *i*SCR reaction, and may be rationalised as follows: in the case of the PtCu sample only, on switching to rich operation, the CuO was partially reduced by NH_3 to produce a reservoir of NH_x(ads). Then, on switching to lean conditions, all the gas phase NH_3 was again fully oxidised to NO on the Pt, but the NO formed is reduced to N_2 by NH_x(ads) on the Cu. However, this reduction process is limited by the concentration of NH_x(ads) and once these species are consumed excess NO is observed, in agreement with our experimental observations.

Further evidence of the trapping mechanism is found by examination of the effect of switching time on activity. Fig. 3 illustrates the activity of PtCu, under dilute fuel conditions at 200 °C when the rich phase is extended to 120 s. Again the initial increase in N_2 is observed (*cf.* Fig. 1). However, extending the period under rich conditions leads to a saturation of the trap and the breakthrough of NH_3/loss of N_2, clearly demonstrating the link between cyclic operation and high N_2 yields.

In conclusion, we have developed a potential strategy for the low-temperature removal of NH_3 from biomass-derived gases by the cyclic operation of a regenerable NH_3 trap catalyst which facilitates an *i*SCR-type reaction. Experiments have demonstrated that the concept is viable and provides a further novel method to overcome the environmental problems associated with the direct combustion of biogas. The strategy may be equally applicable to any comparable gasification gas derived from coal, or other renewable source. The concept is a further example of the advantages which may be gained by forcing catalysts to work harder by periodic perturbation of the reaction conditions.[13–15]

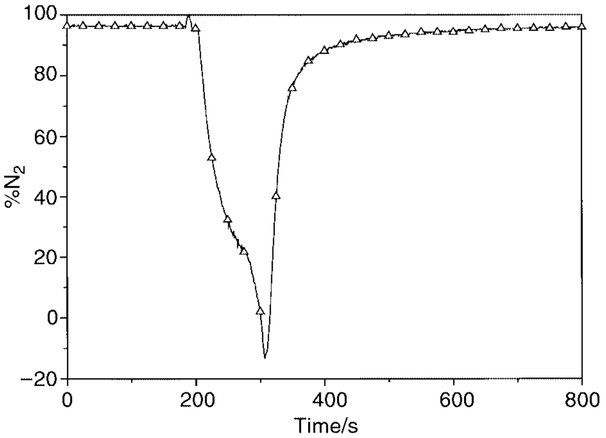

Fig. 3 N_2 production from the selective catalytic oxidation of $NH_3/CO/H_2$ over 1%Pt/20%CuO/Al_2O_3 at 200 °C (1000 ppm NH_3, 1.02% CO, 0.68% H_2, with either 2.1% O_2 (lean conditions) or 0.1% O_2 (rich conditions), balance He). Key: i, first 180 s of operation is under lean conditions; ii, rich operation for 120 s; iii, final 500 s operation is under lean conditions.

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