

# Highly selective catalysts for conversion of ammonia to nitrogen in gasified biomass

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Almost zero emissions of  $\text{NO}_x$  can be achieved in the catalytic combustion of simulated biomass mixtures containing substantial amounts of ammonia by use of a heteropolyacid catalyst.

Renewable energy sources, such as biomass, will be of increasing importance in the future as part of a strategy to lower the total emissions of  $\text{CO}_2$ . Recently, the combustion of biomass-derived gas (biogas) for combined heat and power generation has been studied.<sup>1–3</sup> However, conventional flame combustion processes create problems because biogas contains significant quantities of  $\text{NH}_3$  (600–4000 ppm) in addition to fuel components ( $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ) and on combustion the  $\text{NH}_3$  is largely converted into  $\text{NO}_x$ . Catalytic combustion may overcome this problem but until now the selectivity for the conversion of  $\text{NH}_3$  to  $\text{N}_2$  is unsatisfactory, typically  $< 70\%$ .<sup>2,4</sup> Here, we describe a newly discovered process for removing  $\text{NH}_3$  from biogas with almost zero production of  $\text{NO}_x$ .

The novel solution to the selective oxidation of  $\text{NH}_3$  in a biogas fuel which we have discovered is to differentiate the feed components on the basis of their chemical properties. The crucial discovery is that ammonia, being a basic molecule, can be differentiated from carbon monoxide and hydrogen by using a catalyst which contains acidic sites, to preferentially adsorb the ammonia. Combination with redox sites allows the selective oxidation of ammonia to nitrogen.

The catalyst selected was 12-tungstophosphoric acid,  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (ex Acros, hereafter denoted HPW). It is a heteropoly acid material based upon the Keggin unit structure.<sup>5</sup> Such materials are well known for their strong and uniform acid sites arising from the charge balancing protons associated with the Keggin unit anion. In addition they also possess strong redox properties arising from surface and bulk electron transfer processes.<sup>5</sup>

Catalyst testing was performed in a standard quartz flow microreactor described previously<sup>6</sup> at a gas hourly space velocity (volume of reactants per volume of catalyst per hour) of  $250\,000\text{ h}^{-1}$ . The reaction mixture comprised 6.0%  $\text{CO}$ , 4.0%  $\text{H}_2$ , 0.5%  $\text{O}_2$ , 1050 ppm  $\text{NH}_3$ , and balance He. Product analysis was by mass spectrometry (Hiden DSMS) with  $\text{NO}_x$  emissions and residual  $\text{NH}_3$  levels being confirmed using an external  $\text{NH}_3$  oxidation reactor (with independent oxygen supply) coupled with a  $\text{NO}_x$  chemiluminescence detector (Signal series 4000). The partial salts of HPW were prepared by reflux of the parent acid with varying stoichiometries of  $\text{KNO}_3$  (Analar ex Aldrich) to produce  $\text{K}_{2.06}\text{H}_{0.94}\text{PW}_{12}\text{O}_{40}$  (hereafter KHPW) and  $\text{K}_{2.66}\text{H}_{0.34}\text{PW}_{12}\text{O}_{40}$  (hereafter KPW) using a standard exchange process.<sup>5</sup> Temperature-programmed desorption of  $\text{NH}_3$  was performed by saturation of the sample at  $150\text{ }^\circ\text{C}$  in 1%  $\text{NH}_3$ -He followed by purging in He. The sample was then ramped at  $12\text{ }^\circ\text{C min}^{-1}$  and the evolved species monitored by mass spectrometry.

Fig. 1 illustrates the  $\text{NH}_3$  TPD profile of HPW. The strong and uniform acidity of the material is demonstrated by the single, sharp combination of desorption peaks at ca.  $600\text{ }^\circ\text{C}$ . These comprise  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{N}_2$  and  $\text{NO}$ , the latter at two orders of magnitude lower concentration. This was a significant result since it demonstrated that  $\text{NH}_3$  may be fixed on the Brønsted

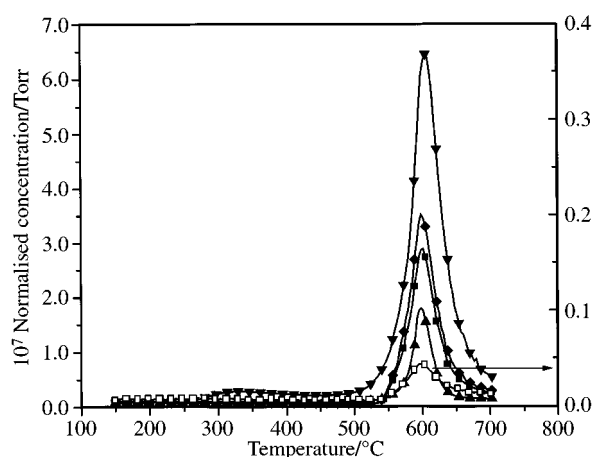


Fig. 1  $\text{NH}_3$  TPD results for HPW. Key: ( $\square$ )  $\text{NO}$  ( $m/z$  30), ( $\blacktriangle$ )  $\text{N}_2$  ( $m/z$  28), ( $\blacktriangledown$ )  $\text{H}_2\text{O}$  ( $m/z$  18), ( $\blacklozenge$ )  $\text{NH}_3$  ( $m/z$  17, corrected for  $\text{H}_2\text{O}$  contribution), ( $\blacksquare$ )  $\text{NH}_3$  ( $m/z$  16).

acid sites of HPW and then converted into  $\text{N}_2$  and  $\text{H}_2\text{O}$  by an internal reaction with labile oxygen from the Keggin anion. This reaction is presumed to proceed *via* the condensation of  $\text{NO}$  with  $\text{NH}_3$ , a proposal which is supported by temperature programmed reaction of a  $\text{NO-CO-H}_2$  mix (1050 ppm 6.0% : 4.0%) over  $\text{NH}_3$  pretreated HPW. This yielded  $\text{N}_2$  as the only product with peak  $\text{N}_2$  production occurring at ca.  $600\text{ }^\circ\text{C}$ , the dissociation temperature of the  $\text{NH}_4$ -Keggin unit complex.<sup>7</sup> The amount of  $\text{N}_2$  produced was consistent with a catalytic reaction between the  $\text{NO}$  and  $\text{NH}_3$ .

Fig. 2 shows the reaction of HPW pre-treated with  $\text{NH}_3$  and then heated in the full reaction mixture. The results show that this material displays little or no catalytic function at temperatures below the  $\text{NH}_4^+$  dissociation temperature. However, simultaneous with the onset of  $\text{NH}_4^+$  dissociation there is a

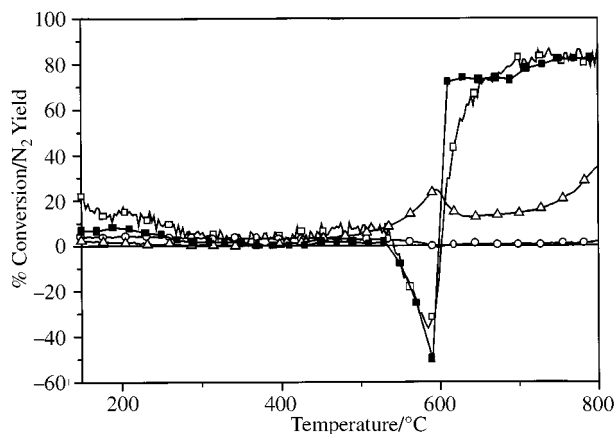


Fig. 2 Conversion profiles for simulated biomass stream over HPW. (6.0%  $\text{CO}$ , 4.0%  $\text{H}_2$ , 0.5%  $\text{O}_2$ , 1050 ppm  $\text{NH}_3$  balance He). Key: ( $\square$ )  $\text{NH}_3$  conversion by MS ( $\triangle$ )  $\text{H}_2$  conversion by MS, ( $\circ$ )  $\text{CO}$  conversion by MS, ( $\blacksquare$ ) %  $\text{N}_2$  yield by  $\text{NO}_x$  chemiluminescence.

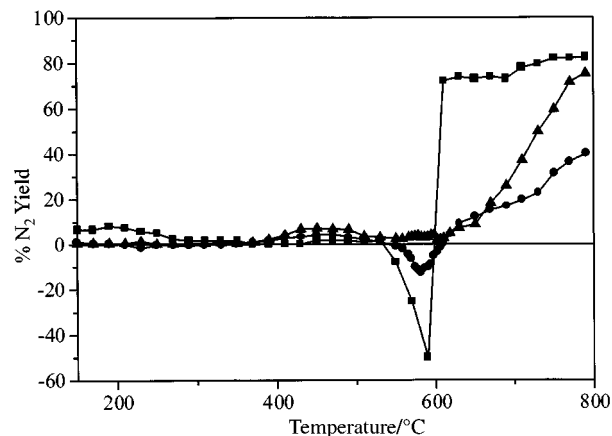
sharp evolution of  $\text{NO}_x$ , as reflected in the negative  $\text{N}_2$  production.

After this initial burst of  $\text{NO}_x$ , the catalyst then becomes active and highly selective for  $\text{N}_2$  production, giving *ca.* 85% conversion of  $\text{NH}_3$  and 100% selectivity to  $\text{N}_2$ . There is no measurable production of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$  or  $\text{HCN}$ , and the nitrogen mass balance from both the mass spectrometry and  $\text{NO}_x$  analysis is 100% within experimental error. At the same time as we observe this very high conversion of ammonia, we see that the conversion of  $\text{CO}$  is <1% and there is <20% conversion of  $\text{H}_2$  in the temperature range 600–750 °C.

These data for ammonia oxidation are consistent with an 'internal selective catalytic reduction' mechanism which can be summarised as follows. The Keggin unit oxidises the adsorbed  $\text{NH}_3$  (trapped as  $\text{NH}_4^+$ ) to  $\text{NO}_x$  using labile oxygen from the anion. The  $\text{NO}_x$  formed is retained briefly as part of the anion, and reacts with an  $\text{NH}_3$  molecule to give  $\text{N}_2$  and  $\text{H}_2\text{O}$ . The Keggin unit then re-oxidises by reaction with gas phase oxygen. This last step further accounts for the high chemical specificity of the process as it limits the concentration of active oxygen to react with  $\text{CO}$  and/or  $\text{H}_2$ . The rapid turnover between the proton and  $\text{NH}_4^+$  states also prevents over reduction and collapse of the Keggin unit through dehydration,<sup>8</sup> with the result that the HPW is stable over the course of 6 h.

The requirement for protonic sites for the reaction was confirmed by the synthesis and testing of full and partial salts. The results in Fig. 3 show that, in comparison with the parent acid, KHPW displays a smaller  $\text{NO}_x$  formation (negative) peak and a lower activity, which increases gradually with temperature. KPW shows no negative  $\text{NO}_x$  peak and then an increasing level of  $\text{N}_2$  production with temperature. For both the full and partial salts (KPW and KHPW) the activity for ammonia conversion to  $\text{N}_2$  is much lower than for the HPA over most of the temperature range from 600–800 °C. The lower activity at *ca.* 600 °C is consistent with the requirement for acid sites to adsorb  $\text{NH}_3$ .

In conclusion, we have developed a strategy for the selective conversion of  $\text{NH}_3$  from biomass-derived gases into  $\text{N}_2$  by selective oxidation in competition with a large excess of  $\text{CO}$  and  $\text{H}_2$ . The key feature is the use of a catalyst which contains acid sites, to differentiate ammonia from  $\text{CO}$  and  $\text{H}_2$ , and redox properties, to oxidise the adsorbed species. Heteropoly acid catalysts have been used to demonstrate that the concept is viable and provides a novel way to overcome the  $\text{NO}_x$  formation associated with the direct combustion of biogas.



**Fig. 3**  $\text{N}_2$  production profiles for HPW and its salts. (6.0%  $\text{CO}$ , 4.0%  $\text{H}_2$ , 0.5%  $\text{O}_2$ , 1050 ppm  $\text{NH}_3$  balance He). Key: (■) HPW ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ), (●) KHPW ( $\text{K}_{2.06}\text{H}_{0.94}\text{PW}_{12}\text{O}_{40}$ ), (▲) KPW ( $\text{K}_{2.66}\text{H}_{0.34}\text{PW}_{12}\text{O}_{40}$ ).

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