

An investigation of the selective oxidation of NH₃ to N₂ in gasified biomass in the presence of excess CO and H₂ using zeolite catalysts

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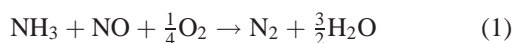
The selective oxidation of NH₃ to N₂ in simulated biogas containing a large excess of CO and H₂ has been examined using zeolite catalysts. Of the materials examined zeolite Beta gave the highest N₂ yield (85% at 475–575 °C), while ZSM5 produced 75% at 575 °C, but HY was both less active and selective. In all cases N₂ is formed via an internal selective catalytic reduction between NO_x (derived from the oxidation of NH₃) and NH₃ adsorbed on Brønsted sites of the zeolite.

Keywords: biomass, heterogeneous catalyst, selective NH₃ oxidation, zeolite

1. Introduction

The use of renewable energy sources is widely accepted as an essential element of a strategy to both extend fossil fuel reserves and lower CO₂ emissions. This has led to an examination of the use of biomass-derived gas (biogas) for combined heat and power generation [1–8]. However, attempts to utilise biogas in conventional burners have encountered problems due to high NO_x emissions. These arise from the total oxidation of the NH₃ (600–4000 ppm) formed during gasification of fuel-bound nitrogen in biomass. Catalytic combustion may overcome this problem but to date the selectivity for the conversion of NH₃ to N₂ is unsatisfactory, typically <70% [2,4].

Conversely, NH₃ is used to reduce NO_x emissions by the selective catalytic reduction process (SCR) [9] following equation (1):



We have demonstrated that the selective oxidation of NH₃ to N₂ over heteropoly acids and Al₂O₃-supported oxides occurs via a similar mechanism, namely the internal (or *in situ*) SCR (*i*SCR) [5,7,8]. In this process part of the NH₃ is oxidised to NO_x but then this is reduced by the remaining NH₃ to give N₂ yields >90%, significantly higher than in previous studies [2,4]. Moreover, in the case of heteropoly acids it was found that strong Brønsted acidity facilitated the adsorption and specific reaction of NH₃ [7]. A possible extension of this methodology is the use of zeolites, which

are well known for their strong acidity [10–14] and ability to facilitate SCR-type reactions [9,11].

Thus we have studied the efficacy of zeolite catalysts for biogas oxidation, with emphasis on the selective oxidation of NH₃ to N₂ even in the presence of a large excess of other, very reactive, reductants, namely CO and H₂. This paper presents our findings and briefly examines the possibility that the *i*SCR may be a generic mechanism for N₂ production with solid acid catalysts.

2. Experimental

All reactions were performed in a conventional atmospheric pressure microreactor unit described previously [7]. The reaction mixture was regulated by independent mass flow controllers and typically comprised 1.5% CO, 1.0% H₂, 7.5% O₂, 1000 ppm NH₃, balance He. Reactions were performed using 60 mg of sample in a flow of 300 ml min^{−1} (effective GHSV of ca. 240 000 h^{−1}). Product analysis was by mass spectrometry (Hiden DSMS with appropriate corrections for *m/z* overlaps) with NO_x emissions and residual NH₃ levels being confirmed using an external NH₃ oxidation reactor (with independent O₂ supply) coupled to a NO_x chemiluminescence detector (Signal series 4000). All zeolites (Y, Beta, ZSM5 with SiO₂:Al₂O₃ ratios of 4, 20 and 31, respectively) were supplied in their protonic form by Zeolyst International and used without further treatment.

3. Results and discussion

Figure 1 illustrates the temperature response of HZSM5 for biogas oxidation. The data reflect the low inherent com-

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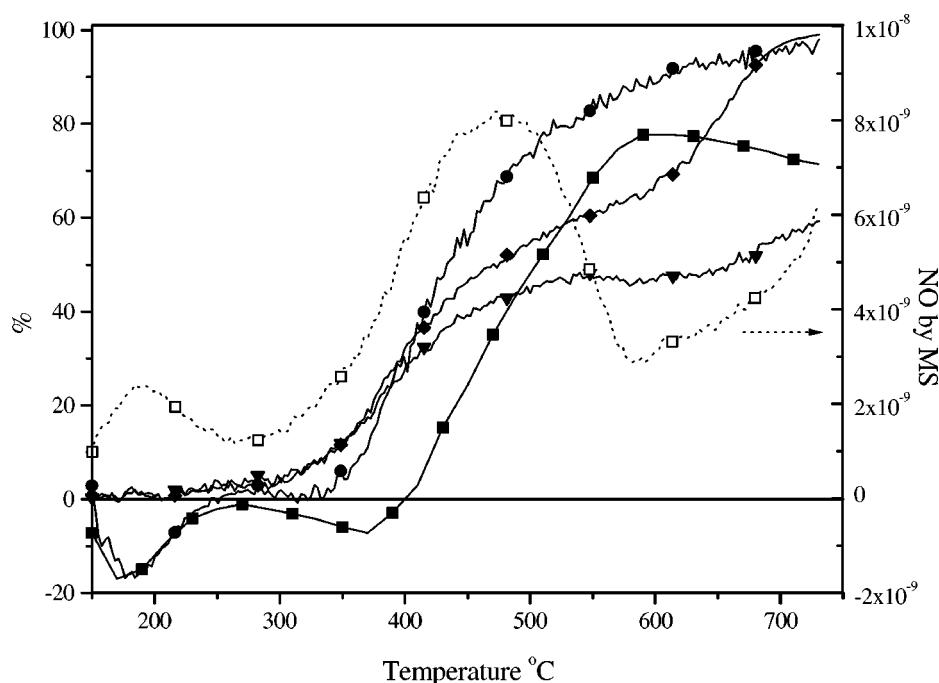


Figure 1. Conversion of simulated biogas over HZSM5. Reaction conditions: 1.5% CO, 1% H₂, 1000 ppm NH₃, 7.5% O₂, GHSV = 240 000 h⁻¹. (●) NH₃ conversion by MS, (■) NH₃ to N₂ by NO_x analysis, (▼) CO conversion by MS, (◆) H₂ conversion by MS and (□) NO concentration by MS (Y2 axis).

bustion activity of the non-exchanged zeolite with light-off (>20% conversion of fuel) only occurring at ca. 360 °C. Below this temperature there is an apparent negative peak in conversion of NH₃/N₂ production due to the desorption and oxidation of physisorbed species (150–250 °C). A second, smaller negative N₂ production peak is recorded upon light-off at 360 °C, coincident with the reported temperature of desorption of NH₃ from weaker Brønsted acid sites [12]. The low combustion activity below NH₄⁺ dissociation temperatures is similar to the behaviour observed on heteropoly acids [5] and suggests that free acid sites are necessary for combustion. Above 360 °C, N₂ production then increases rapidly, as does conversion of all of the feed components, albeit with the slight preference: NH₃ > H₂ > CO, in contrast to the specificity exhibited by heteropoly acids [5]. Peak N₂ production is 75% and occurs at ca. 575 °C, correlating with the reported NH₃ desorption maximum for strong Brønsted acid sites [12]. In contrast, there is a small sharp peak of NO_x production (ca. 300 ppm NO plus trace levels of NO₂) centred some 100 °C lower, coincident with the NH₃ desorption minimum reported by Le Van Mao et al. [12].

The link between N₂ production and NH₃ desorption is consistent with an *i*SCR mechanism. This is further supported by the behaviour of HZSM5 for the NH₃–NO–CO–H₂–O₂ reaction (figure 2). On exchanging 1% NH₃/He (1000 ppm NH₃) for pure He, there is a drop in the NO conversion, while re-introduction of NH₃ restores full activity, confirming that the N₂ production does not occur through the NO–CO or NO–H₂ reactions. These data and the possibility of the *i*SCR reaction are also in agreement with

the findings of Richter et al. [11] who have used NH₃ adsorbed upon Brønsted acid sites to facilitate the NH₃–NO_x reaction at low temperatures. In addition previous work concerning selective oxidation of NH₃ has shown that activation of NH₃ to produce an oxidised intermediate is the rate-determining step and introduction of NO facilitates N₂ production at significantly lower temperatures [7,8].

The effect of choice of zeolite upon N₂ production was examined by a comparison of HZSM5 (figure 1) with Beta and HY (figures 3 and 4, respectively). The latter two samples present very different activities, with Beta producing a small peak of NO_x upon light-off followed by increasing N₂ production to give a yield of N₂ of 80%, between 475 and 575 °C above which temperature NO_x again increases. Thus in general, Beta presents a similar reactivity profile to HZSM5. In contrast, the reaction profile over HY is markedly different. N₂ production is significant only at higher temperatures and peaks at 70% N₂ at ca. 675 °C. Concomitant with this, HY also produces significantly more NO_x over the whole of the temperature range.

These results again illustrate the strong connection between activity and acidity. In the case of Beta, Nivarthi et al. [13] have demonstrated that NH₃ desorption occurs, as with HZSM5, in a bimodal manner, with a low-temperature maximum at ca. 310 °C and a broad high-temperature feature centred around 510 °C, with NH₃ desorption decreasing at *T* > 550 °C. These figures compare extremely favourably to light-off (ca. 300 °C), peak N₂ production (approximately 510 °C), and increasing NO_x for *T* > 550 °C observed in this study, following the same trends observed for HZSM5.

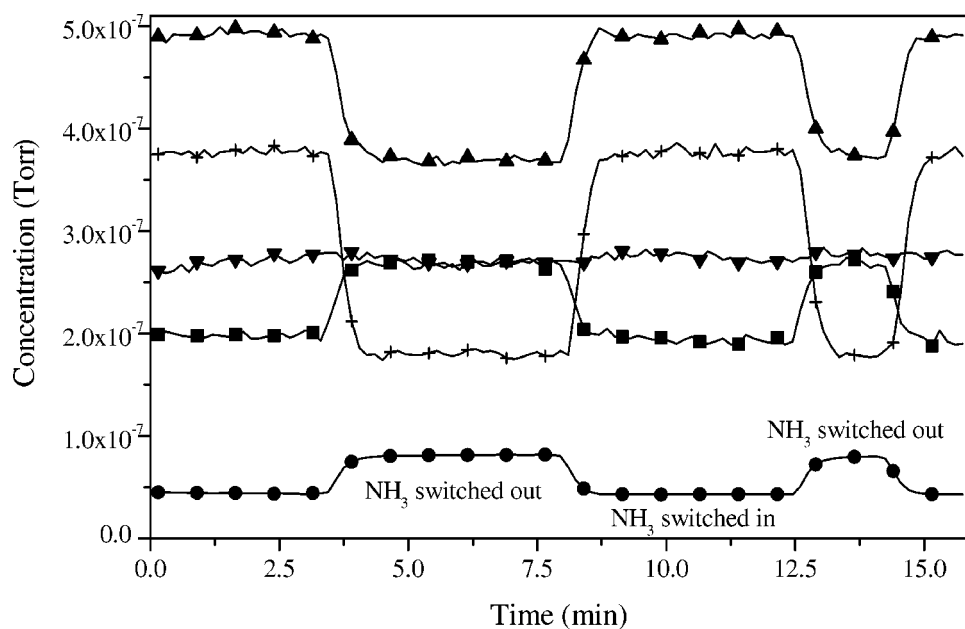


Figure 2. Effect of NH_3 switches on the $\text{NO-CO-H}_2\text{-O}_2\text{-(NH}_3\text{)}$ reaction over HZSM5. Reaction conditions: 1000 ppm NO, 1.5% CO, 1% H_2 , 7.5% O_2 , 1000 ppm NH_3 switched in/out, GHSV 240 000 h^{-1} . (■) $m/z = 44$ (N_2O or CO_2), (●) $m/z = 30$ (NO), (▲) $m/z = 28$ (CO or N_2), (▼) $m/z = 18$ (H_2O) and (+) $m/z = 2$ (H_2).

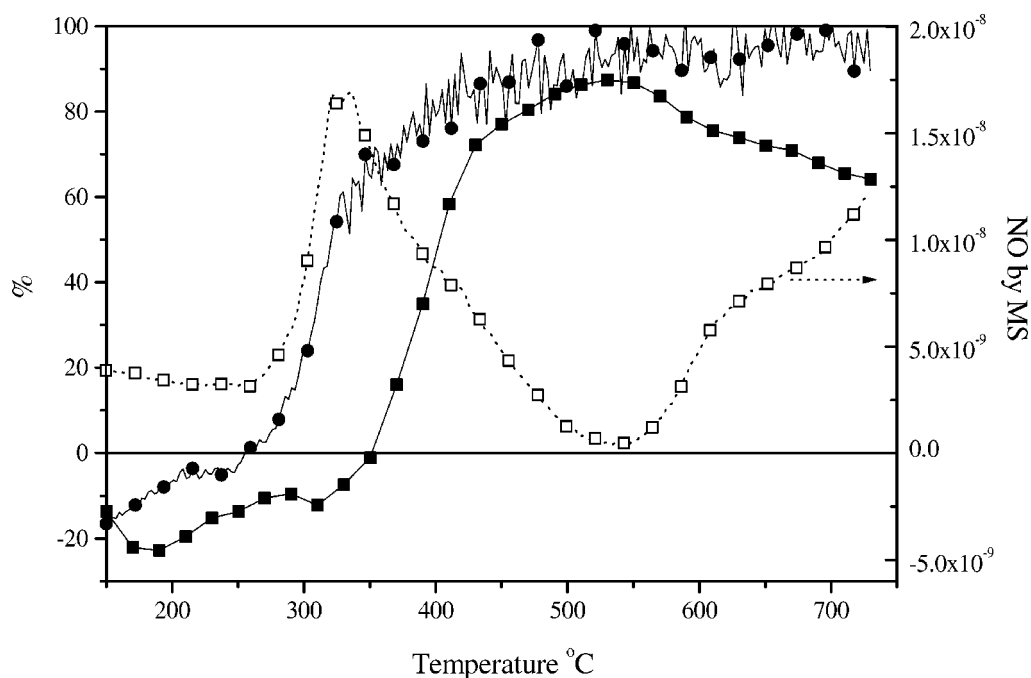


Figure 3. Nitrogen-containing products from the conversion of simulated biogas over zeolite Beta. Reaction conditions: 1.5% CO, 1% H_2 , 1000 ppm NH_3 , 7.5% O_2 , GHSV = 240 000 h^{-1} . (●) NH_3 conversion by MS, (■) NH_3 to N_2 by NO_x analysis and (□) NO concentration by MS (Y2 axis).

In the case of HY, recent results [14] have indicated that NH_3 desorption does not follow the bimodal distribution of HZSM5 or Beta. Moreover, the Brønsted acid sites are weaker with an NH_3 desorption maximum at ca. 310 °C [14], again coincident with the light-off point of the catalyst. However, the same study reports pyridine TPD data showing the presence of both weak and strong acid sites

(maxima at 264 and 555 °C), which may account for the high-temperature activity. Thus the high N_2 yields on Beta and HZSM5 seem to occur because the weaker acid function provides NO_x , from the oxidation of meta-stable adsorbed NH_3 , which then reacts with NH_3 adsorbed on stronger Brønsted sites to give N_2 , in similar fashion to that reported by Richter et al. [11]. Conversely, for HY,

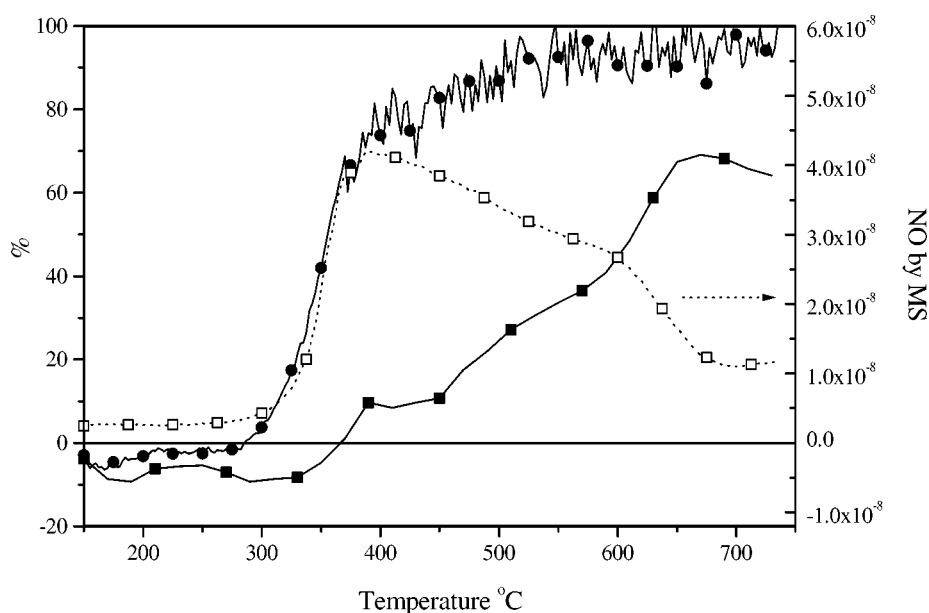


Figure 4. Nitrogen-containing products from the conversion of simulated biogas over HY. Reaction conditions: 1.5% CO, 1% H₂, 1000 ppm NH₃, 7.5% O₂, GHSV = 240 000 h⁻¹. (●) NH₃ conversion by MS, (■) NH₃ to N₂ by NO_x analysis and (□) NO concentration by MS (Y2 axis).

the lower concentration of available NH₄⁺ to participate in reaction results in higher NO_x emissions and lower N₂ formation.

4. Conclusions

The selective oxidation of NH₃ to N₂ in simulated biogas is possible using zeolite catalysts. In all cases N₂ is formed from the reaction of NO_x, produced from non-selective oxidation of NH₃, and NH₃ adsorbed on Brønsted sites. Hence N₂ production is dependent upon acid site strength and distribution with a bimodal distribution of weak and strong sites giving the highest N₂ yields.

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