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The role of Bronstead Acidity in poisoning the SCR-Urea reaction over FeZSM-5 catalysts.

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Abstract:

Two series of FeZSM-5 catalysts prepared from Na^+ and NH_4^+ ZSM-5 precursors are studied in the selective reduction of NO_x using NH_3 and urea as reducing agents. All Fe-containing catalysts are active for NO_x reduction in the SCR-NH_3 reaction with ex-NH_4^+ catalysts being more active than ex-Na^+ materials and the activity depending (to a minor extent within each series of catalysts) upon [Fe]. Catalysts with Bronstead acid sites also show a small transient deNOx activity at low temperatures. All catalysts are less active for the SCR-Urea reaction but the ex-Na^+ catalysts retain far more deNOx activity than the ex-NH_4^+ materials. NH_3 TPD shows that strongly binding Bronstead acid sites are present on the ex-NH_4^+ materials and H^+-treated parent zeolites while urea TPD shows that the mode of decomposition of urea differs as a function of initial zeolite counter-ion. Urea TPSR shows that the reaction between adsorbed urea and gaseous NO/O_2 is related to [Fe]. It is proposed that the decreased activity of the ex-NH_4^+ catalysts in the SCR-Urea reaction is due to a less favourable mode of decomposition over these catalysts. Furthermore it is suggested that the Bronstead acidity plays some part in this less favoured decomposition.

Keywords: FeZSM-5, deNOx, Urea, NH_3, TPD.

Introduction:

Fe-ZSM5 materials have been used in several selective oxidation reactions, e.g. where N_2O is used to oxidise benzene to phenol[1] and in the oxidative dehydrogenation of propane to propene[2]. This material has also been studied in the Selective Catalytic Reduction of NO_x using both hydrocarbons[3-5] and NH_3 as reducing agents[6-8].

Selective Catalytic Reduction involves the reduction of NO_x in the presence of a large excess of O_2. This reaction is important because of the detrimental effects of NO_x on the atmosphere (photochemical smog) the aqueous environment (acid rain) and human health (lung ailments). There are a large number of situations where NO_x exists in the presence of a large excess of O_2. These include the exhausts of stationary power sources, diesel and lean-burn gasoline exhausts where NO_x is formed at high temperatures from the NO + O_2 reaction via the Zeldovich mechanism, and the exhausts of FCC regeneration reactors where catalyst bonded coke is oxidised at high temperatures from the surface in order to regenerate active cracking catalysts. Any N-containing organic species in the coke will, under these conditions, be oxidised to NO_x[9].

The use of NH_3 as a selective reducing agent is feasible for large-scale power generation plants or FCC recycling units since these are, by definition, stationary and, once operational, they produce a constant amount of NO_x. Thus, NH_3 containment and dosage issues are much lessened. On board a vehicle it would not be possible to transport cylinders of NH_3 for use in exhaust after-treatment and for this reason many researchers are beginning to look at solutions of $(NH_2)_2CO$ (urea) as selective reduction agents[10-12]. In the presence of H_2O, urea should decompose according to equation 1 to form 2 NH_3 and one CO_2 molecule[13].

$$(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2 \qquad (1)$$

This reaction is reported to take place in two steps

$$(NH_2)_2CO \rightarrow NH_3 + HNCO \qquad (2)$$

$$HNCO + H_2O \rightarrow NH_3 + CO_2. \qquad (3)$$

Solutions of urea are non-toxic, non corrosive and odour-free and can be relatively concentrated and therefore may well provide a usable on-board reductant for the removal of NO_x from diesel engines and lean-burn-gasoline vehicles.

Recently Larsen et al. have studied the reactions of urea and NO over several zeolitic-type materials, including HZSM and FeZSM[14] using MAS NMR. In their studies these workers noted the production of NH_3 and CO_2 following the interaction between urea and FeZSM and H-ZSM and the formation of NH_3, CO_2 and N_2 over the same materials when the surface was dosed with both NO and urea. Production of N_2 was not seen over silicalite and these authors suggest that Bronstead acidity is important in promoting the desired reaction. Resonances due to the formation of melamine were observed after heat treatment of the silicalite in urea and NO/O_2[14].

In this work we have compared the efficiency of FeZSM-5 catalysts for the reduction of NO_x using both NH_3 and equivalent amounts of $(NH_2)_2CO$. The catalysts, and their interactions with NH_3 and urea, are characterised using NH_3 Temperature Programmed Desorption and Urea Temperature Programmed Decomposition and Temperature Programmed Surface Reaction. Our results suggest that materials with strong Bronstead acidity are less active in the SCR-Urea reaction.

Experimental:

Catalyst Preparation: Aliquots of two samples of commercially available ZSM-5 zeolites (AlsiPenta) were used as parent zeolites. These differ according to their initial parern counter ion, e.g. in one the parent counter-ion is NH_4^+ and in the second the parent counter-ion is Na^+. In each case the SiO_2/Al_2O_3 ratio is the same, i.e. 27 and thus the ion-exchange capacity of both zeolites is the same. Fe was introduced to the parent zeolites using standard ion-exchange techniques, *i.e.* the samples were shaken for 2 h in solutions of $FeSO_4$ of varied volume and concentration, then filtered, washed in deionised water to remove any residual counter ion (SO_4^{2-}), dried at 120 °C for 2 h to remove H_2O, and calcined at 500 °C for 2 h. The powder was then crushed and sieved and the fraction of catalyst between 212 and 600 μm were used in the subsequent analyses. Two "blank" catalysts were prepared by ion-exchanging the parent zeolites in H_2SO_4 (at equivalent SO_4^{2-} concentrations to those used in the FeZSM-5 preparations), washing, drying and calcining as before. The [Fe] within the zeolites following preparation was determined by Atomic Absorption spectroscopy following acid digestion.

One unusual feature, relating to a difference between the ex-Na^+ and ex-NH_4^+ catalysts, was noted during these preparations. In situations when the exact same protocol was used to prepare Fe-loaded catalysts the same mass of parent zeolite was shaken in an Fe solution of the same volume and concentration for the same period of time. Then the samples were washed in the same volume of hot distilled water, dried and calcined. Invariably catalysts prepared from parent zeolite with the NH_4^+ counter ion contained less Fe than those prepared from the parent zeolite with the Na^+ counter ion. As mentioned the SiO_2/Al_2O_3 ratio (and thus the ion-exchange capacity) of both parent zeolites is the same and thus some other feature must account for the differing concentrations in the final catalysts. One possible explanation of this difference lies in the fact that the pH of the exchanging solution changes as NH_3 is exchanged out of the samples while it remains essentially invariant during the Na^+ exchange. This changing pH might in some way influence the nature of the incoming Fe ions (perhaps causing precipitation of FeOx crystallites) and preventing further exchange. Similar effects have been noted when CuZSM-5 catalysts are prepared from these different parent materials[15].

Activity measurements: The catalyst (25 mg) was held in a tubular quartz reactor using plugs of quartz wool. The reactants were blended using electronic mass flow controllers from cylinders of 1% NO and 1% NH_3 in He (BOC Special Gases), O_2 and He (BOC) to give a reaction mixture of [NO] = 1000 ppm, $[NH_3]$ = 1000 ppm and $[O_2]$ = 13% in a total flow of 100 ml/min. When solutions of urea were used as a reductant the liquid was introduced into a heated zone before the reactor from a calibrated syringe driver. Aqueous solutions of 5% urea were used at liquid flow rates which gave 1000 ppm urea in the final reaction mixture. The reactions (SCR-NH_3 and SCR-Urea) were studied under temperature-programmed conditions with a ramp rate of 10 °C/min (30 –500 °C for the SCR-NH_3 reaction and 120 – 500 °C for the SCR-Urea reaction. The NOx concentration in the exit gas was continuously monitored, following suitable dilution, using a Monitor Labs Inc. Nitrogen Oxides Analyser (Model 8840) connected to a PC.

NH_3-TPD: In these experiments the catalyst (50 mg) was dosed with NH_3 (2860 ppm) at 110 °C for 30 minutes. The NH_3 was then removed from the stream and the catalyst cooled to 50 °C in a flow of He (70 ml / min). The dosed catalyst was held at this temperature for 20 minutes in the He flow (until the NH_3 signal returned to the baseline) and then the temperature ramped from 50 to 550 °C at a ramp rate of 10 °C / min. Desorbed NH_3 is continually monitored as a function of temperature

using a Prolab mass spectrometer running in the multiple ion monitoring mode. The data is treated to remove interference from a signal for H_2O[16] and then converted into ppm-NH_3 for presentation.

Temperature Programmed Urea Decomposition: The interaction of the catalysts with urea was probed using Temperature Programmed Urea Decomposition[12]. In the case of a urea TPD the catalyst was repeatedly wet with an aqueous solution of (5%) urea a sufficient number of times to dose the 50 mg catalyst sample with 50 μmol of urea. The sample was then dried at 50 °C and placed in the reactor in a flow of 70 ml/min of He at a temperature of 50 °C. The temperature was ramped from 50 to 750 °C at a rate of 20 °C / min. The effluent gas was passed through a condenser at 0 °C in order to remove gas phase urea (to prevent its condensation within the capillary or the mass spectrometer chamber). Thus, only the products of the interaction between urea and the catalyst were monitored during decomposition.

The effluent gas was monitored continuously by mass spectrometry. Masses at 15, 16, 17, 18 (H_2O, NH_3 and various fragments of each), 28 (N_2, CO), 30 (NO), 32 (O_2) and 44 (CO_2, N_2O) were monitored as a function of temperature. The data were then corrected for overlapping masses (*e.g.* the contribution of the H_2O fragment at 17 to the NH_3 signal was removed)[16]. Following such corrections the data were converted into ppm readings using conversion factors determined by calibration. No calibrations were carried out for the HNCO intermediate so any data presented showing ppm or μmol HNCO are an approximation. In any case HNCO is never a major product of either the TPD or the TPSR experiments.

In order to discriminate between N_2 and CO profiles (and N_2O and CO_2 profiles) these experiments were repeated using a dose of ^{15}N labelled urea (99 atom% ^{15}N Aldrich). The plots presented here are combinations of those observed using the labelled and unlabelled urea dosages.

Urea TPSR: As a final characterisation the temperature programmed surface reaction of $(NO+O_2)_{(g)}$ with adsorbed urea was studied. In these experiments 10 mg of the catalyst was dosed with 50 μmol urea and then ramped from 50 °C to 750 °C in a flow of NO + O_2 (1000 ppm NO + 10% O_2) at 20 °C min^{-1}.

Results and Discussion:

Figure 1 shows the activity of all the catalysts in the temperature programmed SCR-NH_3 reaction. Both parent zeolites show a transient low temperature activity and generally comparable high temperature activity (with the ex-Na^+ catalyst being slightly more active than the ex-NH_4^+ at 500 °C). In the absence of Fe ions the treatment of both in dilute H_2SO_4 solutions generates catalysts with similar behaviours. This observation is again made later in the characterisation experiments and suggests that the acid treatment generated similar sites within both parents (through removing NH_4^+ and Na^+ and replacing these ions with H^+). Specifically the transient lower temperature activity is associated with Bronstead acid sites.

Within each zeolite family those catalysts containing Fe are more active than the proton exchanged materials. Also in both cases the % Fe exchanged within the zeolite does not dramatically affect the catalyst activity, i.e. in the case of the ex-NH_4^+ catalysts the 0.6% Fe catalyst is slightly more active than the 0.3% analogue while in the case of the ex-Na^+ materials the 1% Fe catalysts is slightly more active than the 0.7% analogue. The ex-NH_4^+ materials (even though these have lower Fe concentrations) were more active than the ex-Na^+ catalysts, reaching 10% conversion at 240 °C (compared to 280 °C for the ex Na^+) and 50 % conversion at 365 °C (compared to 395 °C for the ex-Na^+). They also show a higher maximum NOx conversion ~100% at 450 °C compared with ~ 90% at 495 °C.

These ex-NH_4^+ Fe-containing materials also show a lower temperature for turnover of activity (where the selectivity of the reaction changes and NH_3 begins to be combusted (470 compared to 500). They also show a transient low temperature activity between 250 and 280 which is absent in the ex-Na^+ materials. Strong Bronstead acid sites (as measured by NH_3 TPD) are present in all the samples which show this transient activity.

Similar transient low temperature activity peaks have been seen previously over high SiO_2–containing CuZSM-5 catalysts[15] and (albeit at lower temperatures) in the SCR-NH_3 reaction over FeZSM-5[17].

The temperature programmed SCR-Urea profiles are shown in Figure 2. There is a dramatic difference between the activities of both families of catalysts in the SCR-Urea reaction. Fe-containing materials prepared from Na-ZSM-5 are far more active than those prepared from NH_4^+-ZSM-5.

Again both parent zeolites show similar activity (including a transient increase in activity at 350-400 °C). In the case of the Fe-containing Na^+-derived zeolites the deNOx activity profile is shifted upwards in temperature by ~50 °C relative to activity in the SCR-NH_3 reaction but in the case of the Fe-containing ex-NH_4^+ materials the activity is almost totally quenched (notwithstanding the transient activity over the 0.6% Fe-ZSM catalyst at ~ 400 °C).

The reasons for these differences between activity in the SCR-NH_3 reaction and activity in the SCR-Urea reaction must originate in the manner in which urea interacts with the different catalysts since the presence of H_2O in the SCR-NH_3 reaction mixture (the only other difference between the reactants impinging on the catalysts in both cases) has very little effect on activity, i.e. a slight promotion of activity over ex-Na^+ catalysts and a slight poisoning effect over ex-NH_4^+ materials (results not shown)[15]. Similar results have been noted when comparing the SCR-NH_3 and SCR-Urea reactions over supported copper oxide catalysts[18].

In an attempt to gain an insight into the NH_3 and Urea handling characteristics of both series of catalysts a set of NH_3 and Urea Temperature Programmed Decomposition studies were carried out. The results of the NH_3 desorption experiments are presented in Figure 3. The shapes of the profiles are in good agreement with those recorded previously[6,7]. Both families of catalysts show desorption of NH_3 at several temperatures suggesting that there are different types of NH_3 coordination sites on the materials. No NH_3 oxidation products are detected during the temperature ramp.

The two parent zeolites both show three types of desorption with features at 140 °C, 220 °C and 445 °C. The latter feature is far stronger in the case of the ex-NH_4^+ material than from the ex-Na^+ catalyst suggesting that it relates to Bronstead bound NH_3 and that the concentration of sites available to form this type of $NH_{3\ ads}$ is far higher over this catalyst than over the non-acidic starting material. Thus we can say that even though the treatment in H_2SO_4 did confer some Bronstead acidity on the Na^+-ZSM-5 system (generation of a high temperature desorption peak), not all the sites able to form Bronstead sites in this material do so.

The high temperature peaks (which derive from desorption of a Bronstead acid bound NH_3 species[19]) are not present in the FeZSM-5 samples prepared from NaZSM-5 while they are present in the decomposition profiles seen from the ex-NH_4^+ catalysts. The ex-NH_4^+ Fe-containing samples also show two less well defined peaks at lower temperatures (140 °C and 200 °C) that are also present in the parent zeolite.

It is not possible to deconvolute the contributions here from any Fe-NH_3 surface complexes.

For the ex-NH_4^+ catalysts the overall acidity (as measured by the total amount of NH_3 desorption) decreases as Fe loading is increased but this is not the case for the ex-Na^+ materials (see Table 1). There is also an obvious and expected decrease in the concentration of sites which form the NH_{3ads} which is stable at high temperature - as protons are exchanged by Fe ions Bronstead acidity decreases. There are also two lower temperature peaks present in the TPD profiles seen from the ex Na-ZSM-5 catalysts. The temperature distribution of these peaks is wider than that seen over the NH_4^+-derived catalysts with peaks at 160 °C and 280 °C.

These differing desorption profiles show that there are differences in the interactions between NH_3 and the two types of Fe-containing materials. The most striking difference is the presence of a high temperature peak relating to the decomposition of a Bronstead-acid bound species in the ex-NH_4^+ catalysts which is absent in the ex-Na^+ materials. The presence (or absence) of this type of site obviously has very little detrimental impact on the activity of the catalyst in the SCR-NH_3 reaction; indeed it promotes this reaction and contributes to the transient lower temperature activity (Figure1). However it seems that the presence of this type of site, possibly through unfavourable interactions with the basic urea molecules, causes the decreased deNOx activity of the catalysts when urea is used as a reductant.

In order to clarify the interactions between the two families of catalysts and urea a series of urea Temperature Programmed Decompositions were carried out. For clarity only representative plots are shown, i.e. those relating to the 0.6% ex-NH_4^+ catalyst (figure 4) and 0.7% ex-Na^+ catalyst (figure 5). However, the other ex-NH_4^+ and ex-Na^+ Fe-containing catalysts behave similarly to these two examples. The two parent zeolites also behave in a similar manner to one another and the profiles shown in figure 6 shows how urea interacts with the H-exchanged zeolite. A large water evolution was found to peak at ~ 150 °C presumably due to physisorbed H_2O within the pores of the zeolite. There was also a smaller production of H_2O peaking at ~450 °C which can be ascribed to zeolitic dehydroxylation. These peaks have been found over all catalysts and are not shown for clarity. Decomposition products such as N_2O and CO are not found during these experiments (as probed using the labelled urea in order to discriminate between N_2/CO and N_2O/CO_2) and there was also negligible production of NO. Thus the main peaks of interest were CO_2, N_2, NH_3 and HNCO.

Figure 4 shows the main decomposition products seen during the temperature ramp over the 0.6% ex-NH_4^+ Fe ZSM-5 catalyst. The production of CO_2 seems to be a complex process with four bands visible during the temperature ramp. The first band peaks at 200 °C and the last at 450 °C. N_2 production commenced at ~ 400 °C and rose to a steady state which seemed to continue for the remainder of the experiment. The production of NH_3 begins at ~ 300 °C and rises to a peak at ~ 490 °C. This temperature of desorption (suggested to be from Bronstead sites) differs from that seen during the NH_3-TPD experiments (450 °C) but this may be an artefact of the different ramp rates used during these experiments (20 °C min^{-1}) and that used during NH_3 TPD (10 °C min^{-1}). This discrepancy might also suggest the decomposition of some NH_3 precursor at this temperature. However, no other gas phase species are detected in parallel with this NH_3 peak, suggesting that $NH_{3ads} \rightarrow NH_{3(g)}$ is the process being observed. The production of a relatively small amount of HNCO is noted between 200 °C and 250 °C (note the designation of this peak as representing ppm is an approximation).

If the adsorbed urea decomposed as suggested above (equations 1-3) it seems that any NH_3 formed during the initial decomposition is trapped on the zeolite and not released until a higher temperature. If the CO_2 is released immediately following initial urea decomposition (as seems likely since there are no surface basic sites available to trap it) then the profiles suggest that there is more than one type of catalytic site involved in the urea decomposition (leading to a four band profile for CO_2 evolution).

The peaks seen from the urea decomposition from the parent ex-NH_4^+ zeolite (Figure 6) show very similar trends regarding NH_3 evolution (including commencement of NH_3 production and T_{max}), N_2 production, CO_2 production (the same four bands observed) and HNCO production. This suggests that it is the zeolite itself is also able to catalyse the decomposition under these conditions.

Different profiles are seen in the case of the ex-Na^+ Fe-containing catalysts as represented by the 0.7% Fe ZSM catalyst profiles in Figure 5. There is no production of HNCO seen during the ramp. The production of CO_2 takes place in only two (rather than four) stages (peaking at 220 °C and 350 °C). NH_3 formation and desorption is at a far lower temperature (peaking at 300 °C). The latter result can be predicted from the TPD analysis where it was seen that the thermal stability of adsorbed NH_3 was lower on ex-Na^+ Fe-containing zeolites (since they lack the Bronstead acidity inherent in the ex-NH_4^+ materials). However, the lack of a peak due to HNCO is a significant difference between the profiles seen from the ex-NH_4^+ and the ex-Na^+ catalysts.

Thus these urea TPD experiments show that the decomposition of urea takes place in different manners over the two families of zeolite. These decompositions are significantly different to those seen over oxide supported CuO catalysts where most of the NH_3 and CO_2 decomposition products are removed from the catalyst surface at a temperature of ~250 °C[18]. The high temperature peaks seen during these reactions suggest that the interaction between urea and the zeolitic catalysts is far greater than the interactions between urea and the oxide supported CuO catalysts. This interaction presumably takes place between the acidic sites of the zeolites that are not present on the oxide catalysts. However, not all the urea that is dosed onto the catalyst remains anchored to the surface and available for decomposition. Previously we have noted that urea that is not co-ordinated to the catalyst surface simply sublimes from the reactor under the conditions of the experiment[12].

Table 2 shows the amounts of CO_2, NH_3, N_2 and HNCO produced during the temperature ramp. Note the figures given for HNCO are an approximation since the mass spectrometer was not calibrated for HNCO and the calibration factor for NO, is used to generate these figures. The error that this introduces is not large since the actual production of HNCO is relatively minor. The calibration factor for $^{15}N_2$ is assumed to be the same as that for $^{14}N_2$.

The catalysts were dosed with 50 μmol of urea sufficient, when reacted with water, to produce 50 μmol CO_2 and 100 μmol NH_3. It can be seen from the table that in no case are such amounts produced. The difference between the values expected and those observed can be accounted for by the Urea that sublimed from the reactor without decomposing as well as any fragments that remain on the surface following the temperature ramp (possibly through melamine formation).

It would be expected following a "clean" decomposition that the amounts of NH_3 produced should be roughly twice those of CO_2. While in most cases there is more NH_3 than CO_2 produced the ratios are not as would be expected (even when allowing for the production of N_2 and small amounts of HNCO). The 1% ex-Na^+

FeZSM-5 catalyst decomposes the most urea but there does not seem to be any correlation between the amounts of urea which decompose from the catalysts and the [Fe] or the nature of the initial zeolite.

One possible explanation for this discrepancy is the formation of melamine passivating layers on the surface as the temperature is raised. This has previously been regarded as one of the modes of deactivation of SCR-urea catalysts[20] and the layer is proposed to form through reaction between isocyanic acid (HNCO) and NH_3 (possibly through the formation of cyanuric acid – the cyclic trimer of HNCO)[21].

To further analyse how these different decomposition pathways affect the SCR-NH_3 and SCR-urea activities of the catalysts Temperature Programmed Surface Reaction (TPSR) experiments were carried out. In these experiments the catalyst surface was dosed with urea and then ramped in a flow of NO and O_2 (1000 ppm NO, 10% O_2). It is not possible to directly compare the TPD results above with the TPSR results here since the urea is dosed onto different masses of catalyst. This means that a larger proportion of the urea in this experiment is not chemisorbed and as stated urea that is not chemisorbed simply sublimes from the reactor under these conditions. Qualitative comparisons are possible. The profiles recorded for the ex-NH_4^+ Fe ZSM (0.6% Fe) are shown in figure 7(a) and 7(b).

Figure 7(a) shows the profiles relating to N_2, CO_2 and NO. The CO_2 formation peaks are less well defined than in the case of the Urea TPD seen in Figure 4 but there are still more than one such peak suggesting more than one type of urea decomposition site. Again it seems that any NH_3 formed during the decomposition is held on the catalyst rather than being immediately released. The N_2 and NO profiles mirror one another with main peaks and lower temperature shoulders at (375 °C and ~260 °C in the case of the sample shown). The absolute amounts of NO removed form the stream and N_2 and CO_2 formed also mirror one another with roughly 7µmol of NO being removed and between 6 and 7 µmol of CO_2 and N_2 being formed. The low temperature shoulder is present in the case of all ex-NH_4^+ Fe-containing materials and both “parent” zeolites but is absent in the case of the ex-Na^+ Fe-containing materials suggesting it is related to the Bronsead acidity of the sample (specifically from the interaction between NO and the species which led to HNCO formation in the Urea decomposition experiments above).

The formation of NH_3 and HNCO in the TPSR experiments is much decreased (roughly two orders of magnitude) relative to those seen in the Urea decompositions (compare figure 7(b) with figure 4).

It seems that instead of forming $NH_{3(g)}$ and $HNCO_{(g)}$ as was the case in the Urea TPD experiments these decomposition products go on to react with $NO_{(g)}$ to form N_2 leading to a peak in N_2 production from the $NH_3 + NO_{(g)}$ reaction at relatively high temperature (with the low temperature peak present over the materials that form HNCO being due to the $HNCO + NO_{(g)}$ reaction).

Thus, even though the ex-NH_4^+ Fe-containing materials are unable to catalyse the steady state SCR-urea reaction that they are able to react gaseous NO with an amount of adsorbed urea in a relatively efficient manner. This suggests that a steady state amount of urea (or urea decomposition products) are required to form the proposed deactivating melamine layer.

The formation of N_2 and CO_2 and removal of NO is also seen over the ex-Na^+ materials (figure 8). However the low temperature “bump” in NO removal and N_2 formation and is not seen (since HNCO is not formed over these materials) and the temperature of maximum reaction is slightly lower in this case (350 °C as against 380 °C). The amount of NH_3 being produced is also significantly higher than that seen in the same experiment over the ex-NH_4^+ catalyst (while being significantly less than what was produced during urea TPD over the same material (figure 5)). It is possible that the desorption of NH_3 (rather than its reaction to N_2) takes place because over these materials the NH_3 is not held on the strongly interacting Bronstead sites (these not being present) and thus can desorb before sufficient energy is available to cause the $NO_{(g)} + NH_{3ads}$ reaction to take place. In all other cases (results not shown) the temperature of maximum reaction decreases as the concentration of Fe increases.

Conclusions:

Fe ZSM-5 catalysts prepared from both Na^+ and NH_4^+ ZSM-5 materials are active catalysts in the SCR-NH_3 reaction. The activity of the catalysts depends on the initial starting material (with the ex-NH_4^+ catalysts being slightly more active than the ex-Na^+ materials) and, to a relatively minor extent, upon the concentration of Fe (with activity being directly proportional to [Fe]. When urea was used as a reducing agent the ex-NH_4^+ catalysts lost most of their deNOx activity while the activity of the ex-Na^+ materials was only partially suppressed.

NH_3 TPD has shown the presence of Bronstead acid sites within the ex-NH_4^+ zeolite (and also shows that an acid treatment can generate Bronstead sites within Na-ZSM-5). Temperature programmed urea decomposition showed that those catalysts which contain Bronstead acid sites also generate HNCO during urea decomposition. HNCO and NH_3 are intermediates in formation of melamine[21] and it is proposed that layers of this may be formed over these catalysts resulting in decreased activity in the SCR-urea reaction.

Temperature programmed surface reaction shows that it is possible under transient conditions to react these HNCO (and NH_3) adsorbed species with gas phase

NO/O_2 to form N_2 over all the catalysts with the temperature of maximum reaction being inversely proportional to the [Fe]. This suggests that under these transient conditions experiments do not mimic the conditions seen under steady state reaction where the proposed melamine deactivating layers form.

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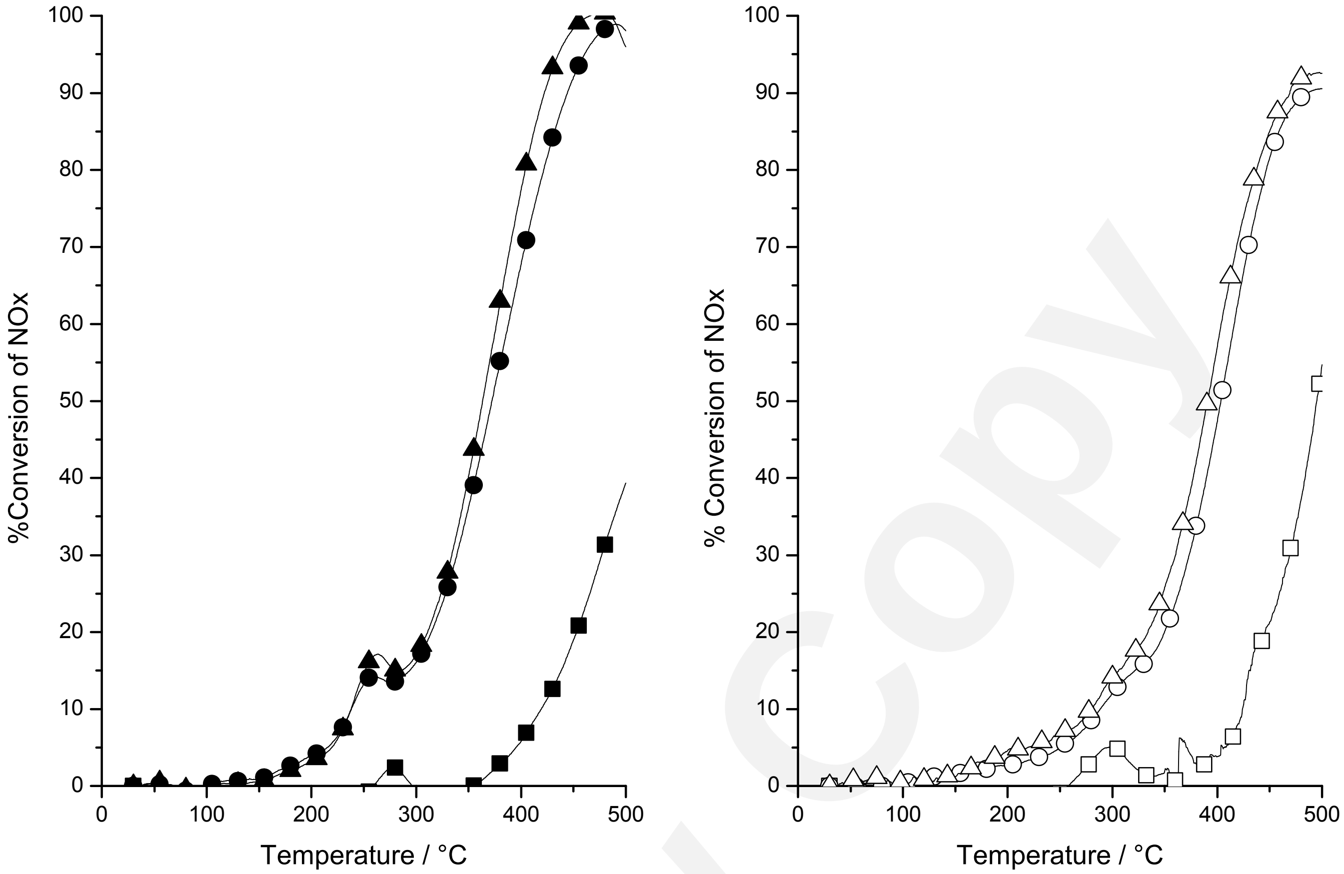

Figure 1: Temperature Programmed SCR NH_3 activity of the various catalysts (10 mg) (a) ex-NH_4^+ ZSM-5 catalysts, 0% Fe (■), 0.3% Fe (●), 0.6%Fe (▲), and (b) ex-Na^+ ZSM-5 catalysts 0% Fe (□), 0.7%Fe (❍), 1.0% Fe (△).

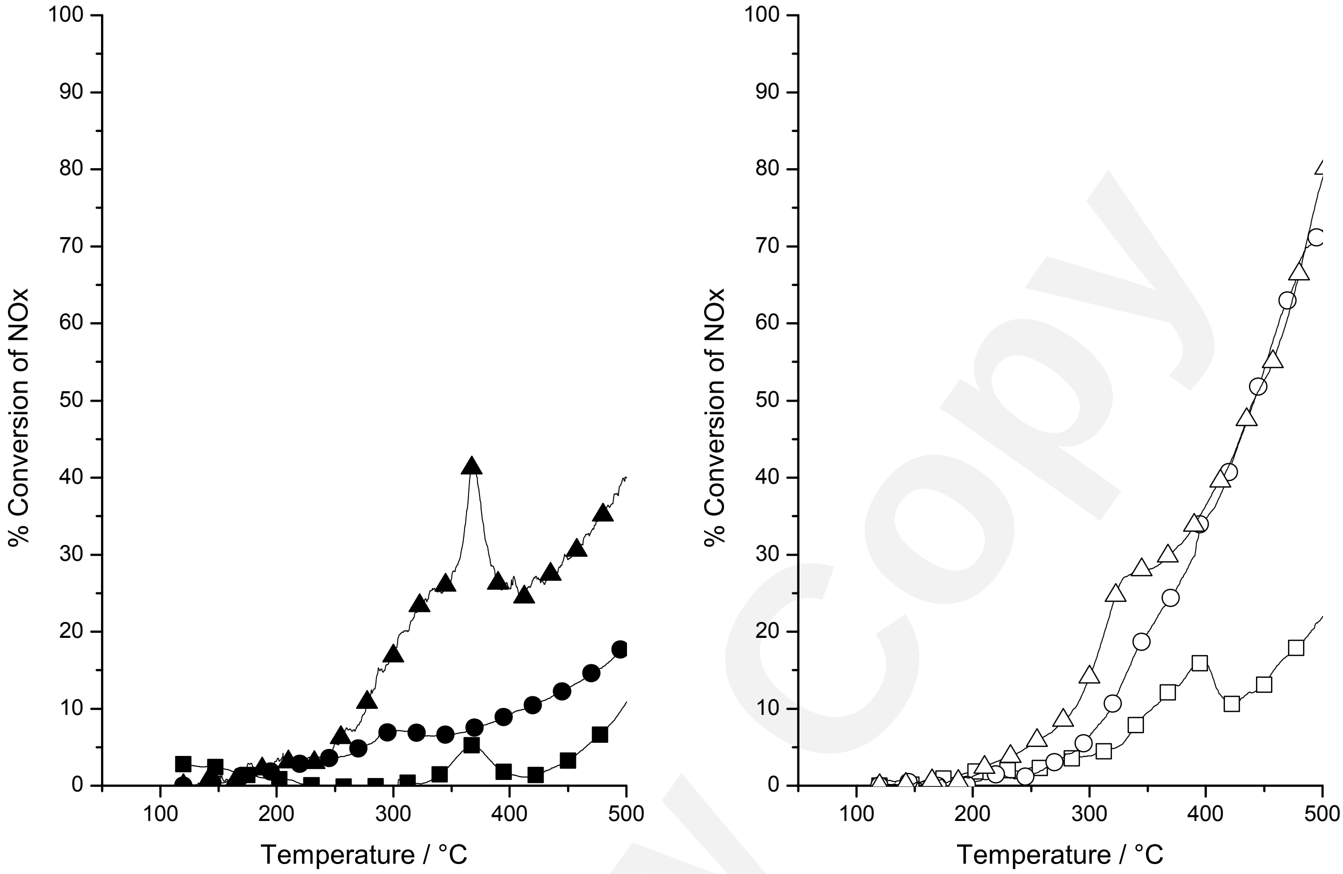

Figure 2: Temperature Programmed SCR-Urea activity of the various catalysts (10mg) (a) ex-NH_4^+ ZSM-5 catalysts, 0%Fe (■), 0.3% Fe (●) and 0.6% Fe(▲) and (b) ex-Na^+ ZSM-5 catalysts, 0% Fe(□), 0.7% Fe (○) and 1.0% Fe (△).

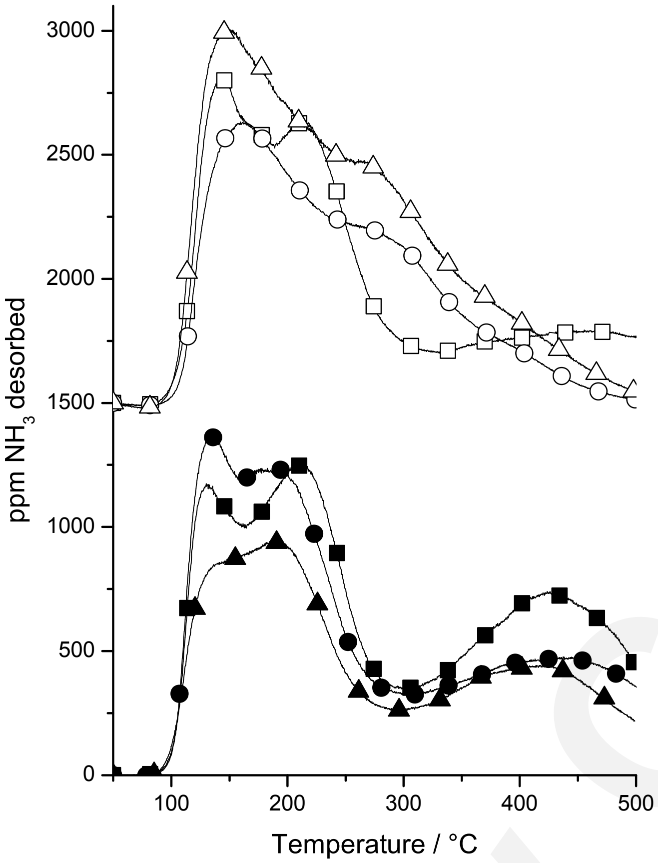

Figure 3: Temperature Programmed NH_3 desorption from the various catalysts ex-NH_4^+ ZSM-5 catalysts, 0%Fe (■), 0.3% Fe (●) and 0.6% Fe(▲) and (displaced upwards) ex-Na^+ ZSM-5 catalysts, 0% Fe(□), 0.7% Fe (❍) and 1.0% Fe (△).

	% Fe	total NH_3 desorbed / μmol g^{-1}	NH_3 desorbed at ~ 400 °C / μmol g^{-1}
ex-NH_4^+	0	1923	890
	0.3	1790	829
	0.6	1557	696
ex-Na^+	0	1544	584
	0.7	1258	0
	1	1745	0

Table 1 showing the overall amounts of NH_3 desorbed (μmol g^{-1}) for each catalyst. Also showing amounts desorbed in the high temperature peak associated with Bronstead acidity

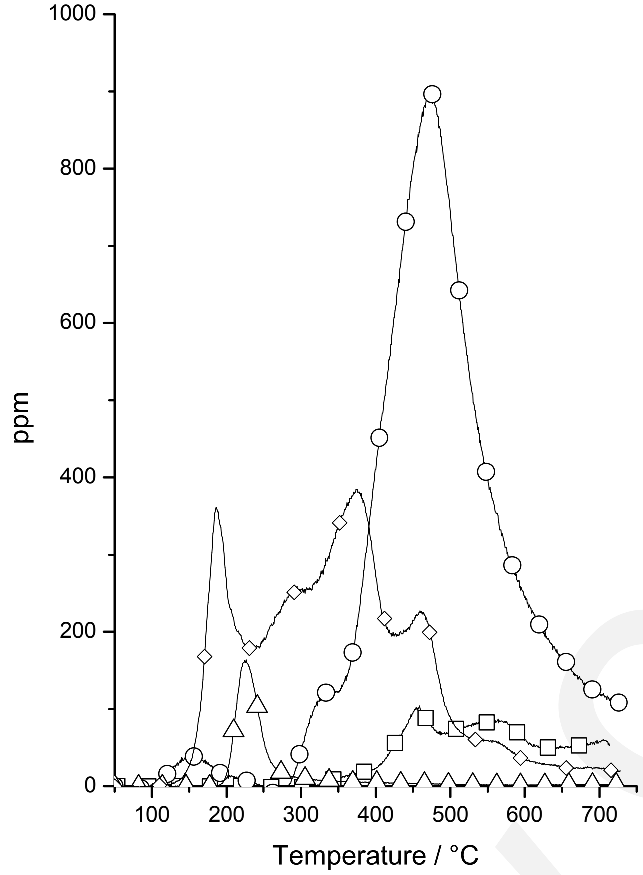

Figure 4: Main peaks of interest following temperature programmed decomposition of urea over ex-NH_4^+ FeZSM-5 (0.6% Fe). NH_3 (❍), N_2 (from an experiment using labelled urea) (☐), CO_2 (✧) and HNCO (△) (estimate) (similar profiles were seen from the 0.3% ex-NH_4^+ Fe material).

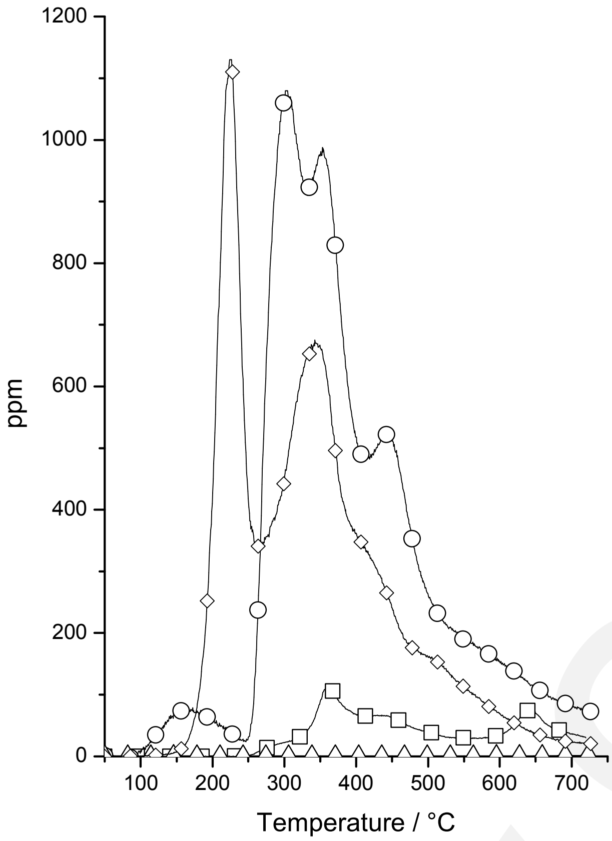

Figure 5: Main peaks of interest following temperature programmed decomposition of urea over ex-Na^+ FeZSM-5 (0.7% Fe). NH_3 (❍), N_2 (from an experiment using labelled urea) (☐), CO_2 (✧) and HNCO (△) (estimate). Similar profiles were seen from the 1.0% ex-Na^+ Fe-containing material).

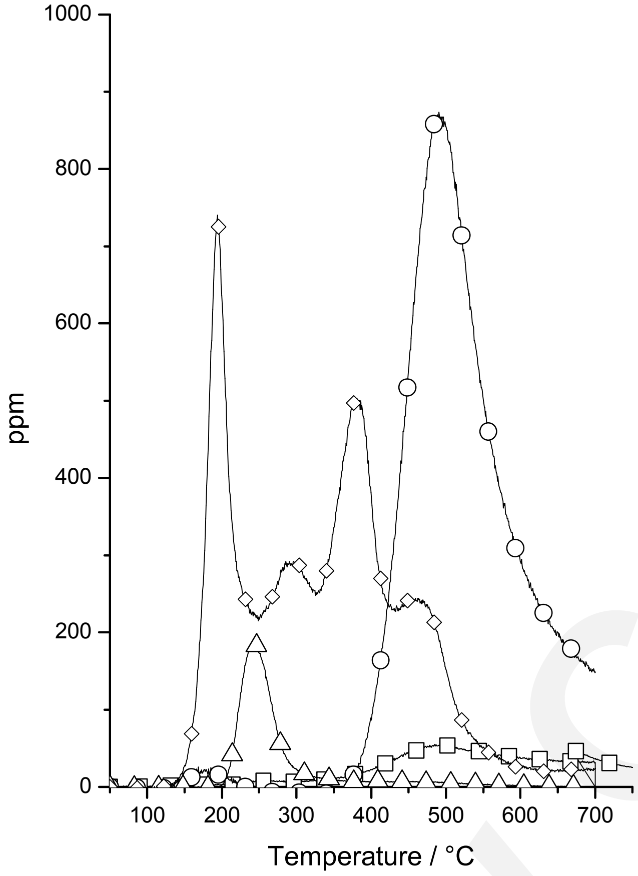

Figure 6: Main peaks of interest following temperature programmed decomposition of urea over ex-NH_4^+ H ZSM-5. NH_3 (❍), N_2 (from an experiment using labelled urea) (☐), CO_2 (✧) and HNCO (△) – (estimate) (similar profiles were seen from the ex-Na^+ H ZSM-5 material).

	CO_2	NH_3	N_2 *	HNCO **
Ex-NH_4^+, 0.3%Fe	23.9	33.0	2.3	1.2
Ex-NH_4^+, 0.6%Fe	13.1	22.1	3.0	1.1
Ex-NH_4^+, Parent	16.2	24.1	2.0	1.6
Ex-Na^+ 0.7%Fe	22.9	29.1	3.4	0.0
Ex-Na^+ 1%Fe	33.6	33.9	3.2	0.0
Ex-Na^+ Parent	19.8	28.1	1.1	0.5

Table 2: Amounts of NH_3, CO_2, N_2 and HNCO seen in the gas phase during Temperature Programmed Decomposition of 50 μmol Urea. * $^{15}N_2$ from an experiment using labelled urea, ** approximation since accurate calibration factors for HNCO are not known.

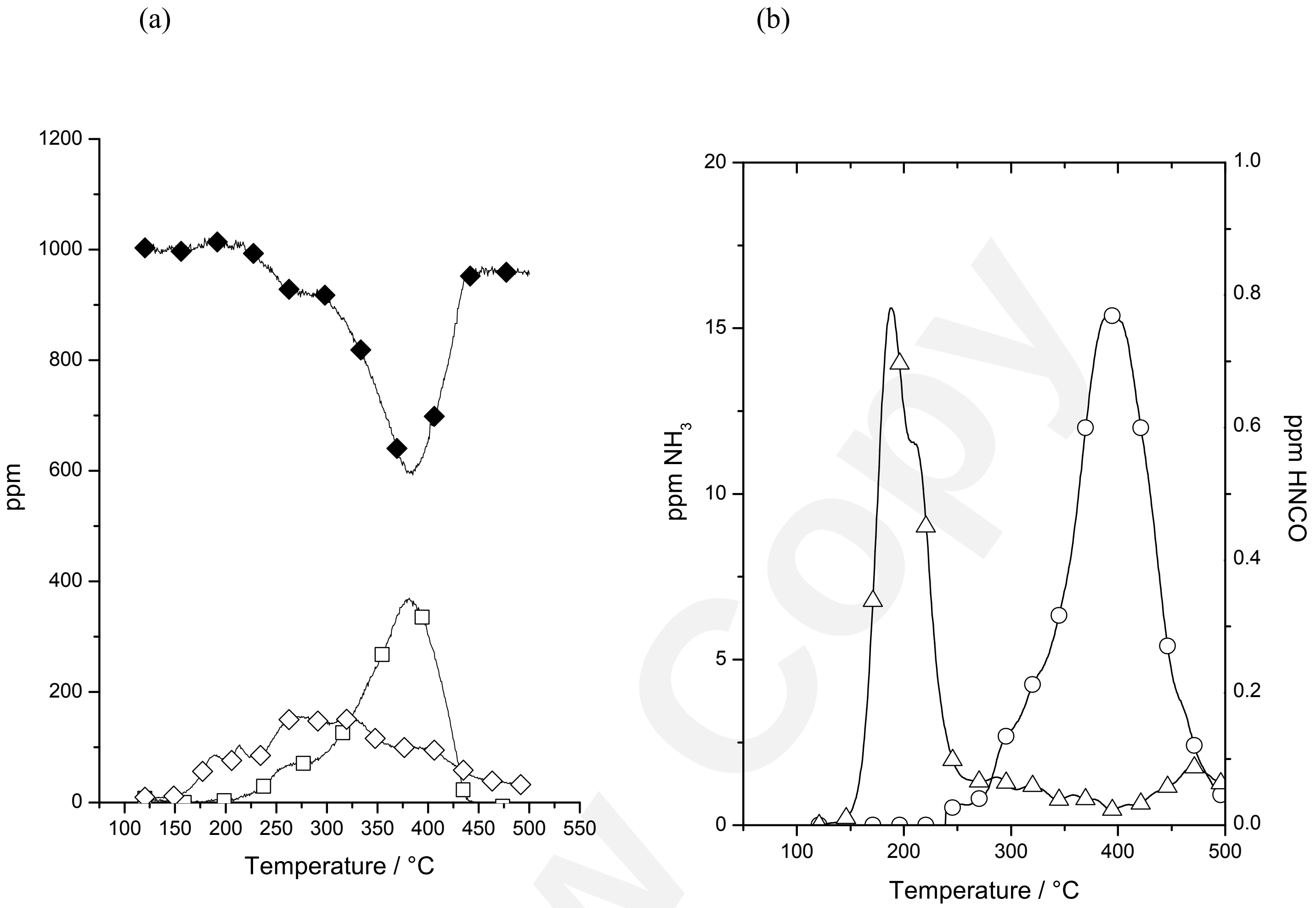

Figure 7: Main peaks of interest following Temperature Programmed Surface Reaction of Urea$_{ads}$ + NO/O$_{2\ (g)}$ over ex-NH$_4^+$ Fe ZSM-5 (0.6% Fe). (a) N$_2$ (☐), CO$_2$ (✧) and NO (◆) (b) NH$_3$ (❍) and HNCO (△) (estimate).

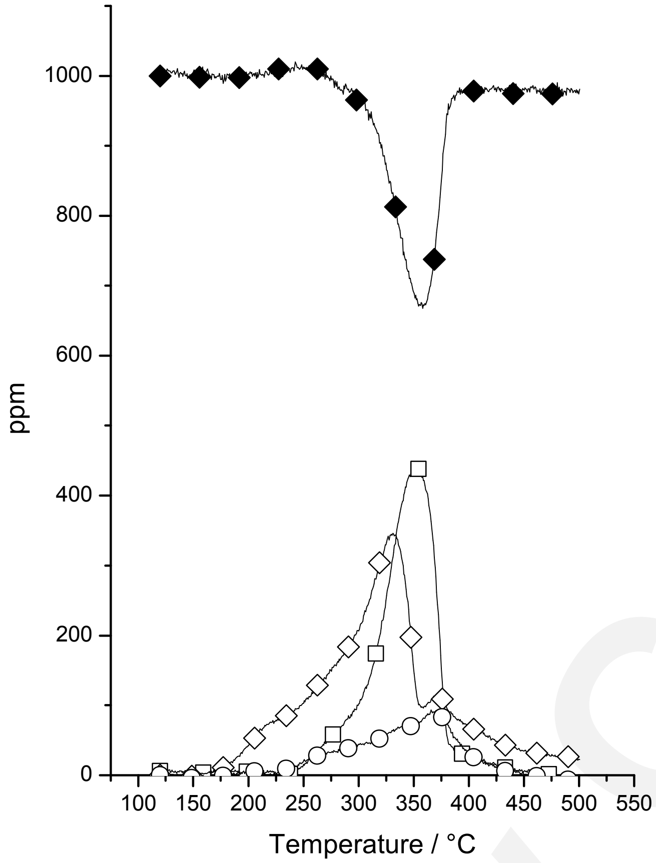

Figure 8: Main peaks of interest following Temperature Programmed Surface Reaction of Urea$_{ads}$ + NO/O$_{2\ (g)}$ over ex-Na^{+} Fe ZSM-5 (0.7% Fe). (a) N_2 (☐), CO_2 (✧) and NO (◆) and NH_3 (❍).