Improved selectivity to lower substituted methylamines using hydrothermally treated zeolite Rho

Linda H. Callanan[*], Eric van Steen, Cyril T. O'Connor

Catalysis Research Unit, Department of Chemical Engineering, University of Cape Town, Rondebosch 7701, South Africa

Abstract

Zeolite Rho is of particular interest for the methanol ammination reaction. Reaction/regeneration cycles on Rho lead to improved activity and selectivity. This is shown to be caused by the combustion on the surface of residual methyl groups, which leads to in situ steaming of the catalyst. Mild hydrothermal treatment gives similar results. The results of both cases are attributed to physico-chemical changes within the catalyst. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Selectivity; Methylamines; Zeolite rho

1. Introduction

Methylamines are important chemicals in many industrial processes. They have been used as intermediates for the production of many compounds containing amino groups as well as being used on their own. The acid catalysed ammination of methanol generally yields a thermodynamically controlled product distribution. The equilibrium distribution for mono-, di-, and trimethylamine (MMA, DMA, and TMA), at 325°C and a molar methanol to ammonia ratio of 1, is 17, 21, and 62 mol%, respectively. The market demand, on the other hand, is for about 33, 53, and 14 mol% MMA, DMA and TMA [1].

Industrially, methylamines are formed by the reaction of methanol or dimethyl ether and ammonia over amorphous silica–alumina. This process involves large separation and recycle units which is both costly and energy intensive as the separation requires azeotropic distillation at 15 bar. Methylamines can be formed over other solid acid catalysts with definite crystal structures, namely zeolites. While being more active than amorphous silica–alumina, most zeolites do not show improved selectivity. Catalysts which have, however, been reported to show improved selectivity to DMA include zeolites Rho, ZK-5 and chabazite [1–3]. Certain forms of hydrothermally or surface treated catalysts can also produce non-equilibrium product distributions. An example of this is mordenite, which after hydrothermal treatment can give a selective product distribution [4,5].

It has been shown that hydrothermal treatment of Rho can improve its performance [2]. The effect of this type of treatment is to partially dealuminate the framework of the zeolite. Dealumination is a process by which some or most of the Al is removed from the catalyst framework. This can be done either by leaching out the Al with an acidic solution or by treating the

*Corresponding author. Fax: +27-21-6897579; e-mail: lindac@chemeng.uct.ac.za

catalyst with steam at high temperatures (hydrothermal treatment). Under steaming conditions, the water gives mobility to the Al and Si atoms. Shannon et al. [2] found that when the Al migrated out of the framework it annealed. They also noticed that there was an improvement in the structural stability of zeolite Rho after steaming. Dingerdissen et al. [15] assume that the extra-framework aluminium (EFAl) remains within the interior of the catalyst and thus improves selectivity by increasing diffusional constraints.

Surface coatings and other treatments can also improve the performance of zeolites. The catalyst selectivity can be increased by either poisoning or blocking any unselective sites or by increasing shape selectivity by narrowing the pore mouth and thus increasing the diffusion constraints [5–10]. It can therefore be said that a catalyst can be effectively designed for the methanol ammination reaction by narrowing the pores and/or inertising the external surface of an otherwise unselective catalyst.

Not all researchers, however, agree that EFAl enhances the catalytic performance of zeolites in the methanol ammination reaction. Segawa and Tachibana [5] state that EFAl is a hindrance to the catalyst performance. Ilao et al. [11] have also shown that γ-alumina alone produces exclusively dimethyl ether (DME). This is supported by Shannon et al. [2] who found that steaming of zeolite Rho above 600°C leads to a sharp increase in the amount of DME formed. This means that while dealumination can be used as a tool for the improvement of the selectivity it should be born in mind that too much extra-framework alumina could lead to the formation of excess DME. It still remains, however, that mild dealumination does not destroy the catalyst structure and in some cases improves the framework stability as well as reaction selectivity.

This paper presents results showing how hydrothermal treatment of zeolite Rho increases both activity and selectivity for the methanol ammination reaction. The results also show that for a given temperature there is fairly sharp maximum in the activity obtained vs. steaming time. It is thereby shown that catalysts should be compared against maximum activity attained rather than activity after a set steaming time. Finally, it is shown that the dealumination caused by steaming causes a change in the distribution of acid sites.

2. Experimental

The zeolite Rho used in this study was obtained from E.I. Dupont de Nemours in the Na/Cs form and was ion exchanged to the ammonium form by performing four cycles of ion exchange, each for 1 h in 10 wt% aqueous ammonium nitrate at 100°C under reflux.

Methanol ammination was carried out by feeding an equimolar mixture of methanol and ammonia, diluted in nitrogen (p_{MeOH}=p_{NH_3}=8 kPa, p_{tot}=atmospheric), to the reactor at 325°C. Samples were taken using the ampoule technique and analysed using a 5890 HP GC equipped with an FID. The separation of the compounds was achieved using a 4 m×3 mm ID glass column packed with 60/80 mesh Carbopack B/4% Carbowax 20 M/0.8% KOH.

Cycles of reaction and regeneration were performed as follows: The fresh catalyst was calcined in 60 ml/min (NTP) air at 500°C, after which it was flushed with nitrogen. After the calcination, reaction was carried out at the conditions mentioned above for 1.5 h. The catalyst was then flushed with nitrogen and reheated to 500°C. The catalyst was then recalcined in air. This cycle of reaction/regeneration was then repeated a number of times. Other series of cycles were performed in which either the reaction or the calcination time was varied.

In a separate set of experiments, hydrothermal treatment was performed on the catalyst by passing steam at 450°C and a partial pressure of 30 kPa over the catalyst. This feed was prepared by passing a nitrogen carrier gas (60 ml (NTP)/min) through a water saturator. These conditions represent mild hydrothermal treatment of the catalyst. The time of the steaming was varied from 0 to 22 h. Calcination was performed, prior to the hydrothermal treatment, for 2 h at 450°C in 60 ml/min (NTP) flowing air.

Temperature programmed desorption (TPD) of ammonia from the catalyst surface was performed to determine the number, strength and concentration of acid sites on the catalyst surface. For these experiments, 0.25 g of catalyst was loaded into a quartz reactor which was housed in a furnace. The catalyst was then dried in 70 ml (NTP)/min synthetic air at 200°C, after which it was flushed with He. Two per cent ammonia in helium was passed over the catalyst at 150°C and the uptake of ammonia was monitored

using a TCD cell. The amount of ammonia taken up represents the sum of both physisorbed and chemisorbed ammonia. The ammonia was switched off and the catalyst was left under flowing helium for 16 h to remove all physisorbed ammonia. The temperature was then ramped from 150°C to 700°C at 10°C/min and held at 700°C for 1 h. During this time, the volatile compounds desorbing from the catalyst were monitored using the TCD. The resulting spectra were deconvoluted to obtain the individual desorption peaks.

^{27}Al MAS NMR was performed on the catalysts to determine the co-ordination state of the Al atoms in the catalyst structure. This was done using a Varian Unity 4000 NMR spectrometer. For the [27]Al spectra, a resonance frequency of 104.252 MHz and a spinning rate of approximately 10 kHz were used. The repetition time was 10 s and the pulse length was adjusted to 8 μs.

3. Results

In initial reaction work on the ammination of methanol over zeolite Rho, it was observed that upon recalcination of the catalyst in air at 500°C, after reaction, the performance of the catalyst changed. Further investigation showed that the catalyst performance improved significantly, both in terms of activity and selectivity, with increasing reaction/regeneration cycles. The activity of the catalyst, as measured by methanol conversion (Fig. 1), increased with increas-
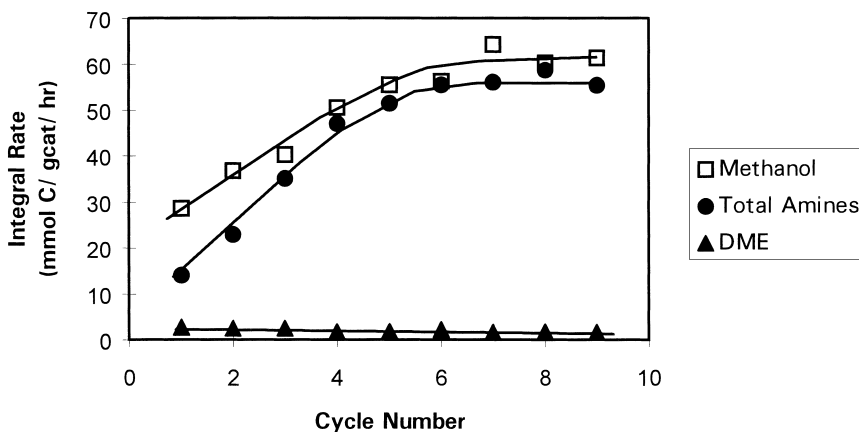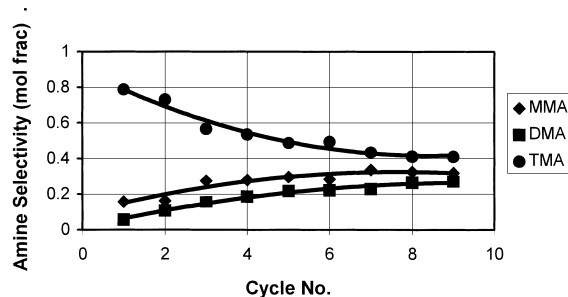

Fig. 2. Amine selectivity vs. number of reaction/regeneration cycles over zeolite Rho. $T_{reaction}$=325°C, $t_{reaction}$=1.5 h, p_{MeOH}=p_{NH_3}=8 kPa, p_{tot}=atmospheric, $T_{calcination}$=500°C, and $t_{calcination}$=5 h.

ing cycle number and reached a plateau after ca. seven cycles. The amine selectivity (Fig. 2) likewise changed with increasing cycle number. The trimethylamine selectivity decreased while the selectivities of both the mono- and dimethylamine increased.

To determine whether this trend observed was a function of the reaction time, a new series of reaction/regeneration cycles were carried out with different reaction times. The range of reaction times examined was between 1.5 and 22 h per cycle. It was found in this range that the reaction time did not affect the trends which were observed. The calcination time was similarly varied between 5 and 15 h per cycle and it was likewise found to have no effect on the observed trend.

Fig. 1. Integral rates of methanol consumption and product formation vs. number of reaction/regeneration cycles over zeolite Rho. $T_{reaction}$=325°C, $t_{reaction}$=1.5 h, p_{MeOH}=p_{NH_3}=8 kPa, p_{tot}=atmospheric, $T_{calcination}$=500°C, and $t_{calcination}$=5 h.

To test whether all the reaction products had desorbed with flushing in inert gas at 450°C, a catalyst sample which had been exposed to methanol and ammonia at 325°C for 1.5 h was tested by increasing the temperature from 30°C to 450°C in flowing helium and monitoring the exhaust gas with a GC–MS. At 450°C it was observed that the desorption had come to completion. Air was then pulsed over the catalyst at 450°C. Both CO_2 and water were detected in the exhaust directly after the air pulses. This showed that water could form during the calcination procedure due to the combustion of carbonaceous ($-CH_x-$) species on the catalyst surface.

To test the effect of steaming, the catalyst was subjected to mild hydrothermal treatment. A similar increase in activity and lower substituted amine selectivity was obtained with the hydrothermal treatment as was obtained with the reaction/regeneration cycles. At the given temperature and steam partial pressure, the activity of the catalyst increased with steaming time (Fig. 3) from 25% MeOH conversion to a maximum of ca. 86% MeOH conversion after 3 h. With further treatment, the activity of the catalyst dropped off. The selectivity of the catalyst to the lower substituted amines improved with steaming time, ultimately reaching a constant value (Fig. 4).

TPD of ammonia from the catalyst surface was performed to determine the number, strength and concentration of acid sites on the catalyst as a function of steaming time (Fig. 5). These TPD spectra were deconvoluted into three peaks (Table 1). In each case, peaks I and II (ca. 450°C and 600°C) represent the
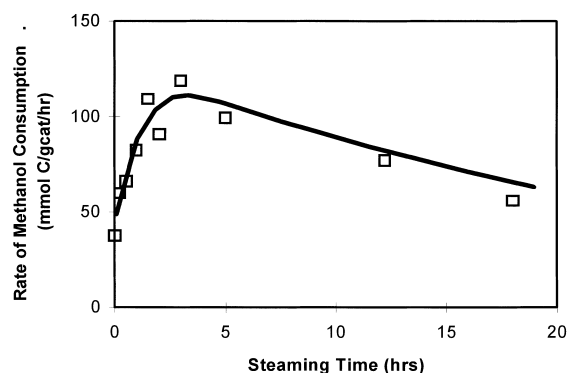

Fig. 3. Integral rate of methanol consumption vs. steaming time over zeolite Rho. T_{steam}=450°C, p_{steam}=30 kPa, $T_{reaction}$=325°C, $t_{reaction}$=1.5 h, p_{MeOH}=p_{NH_3}=8 kPa, and p_{tot}=atmospheric.
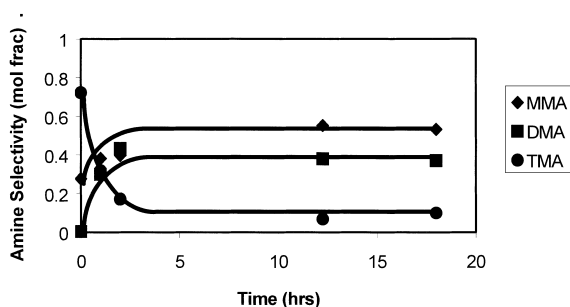
Fig. 4. Amine selectivity vs. steaming time over zeolite Rho. T_{steam}=450°C, p_{steam}=30 kPa, $T_{reaction}$=325°C, $t_{reaction}$=1.5 h, p_{MeOH}=p_{NH_3}=8 kPa, and p_{tot}=atmospheric.

desorption of ammonia from two types of acid sites. Peak III (680°C) occurs due to dehydroxylation of the
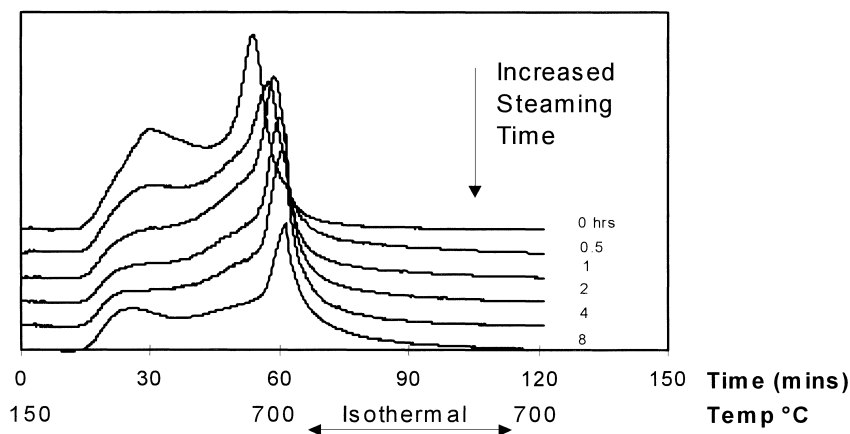

Fig. 5. Comparison of TPD spectra for increasing steaming time.

Table 1
Comparison of TPD peaks for different steaming times

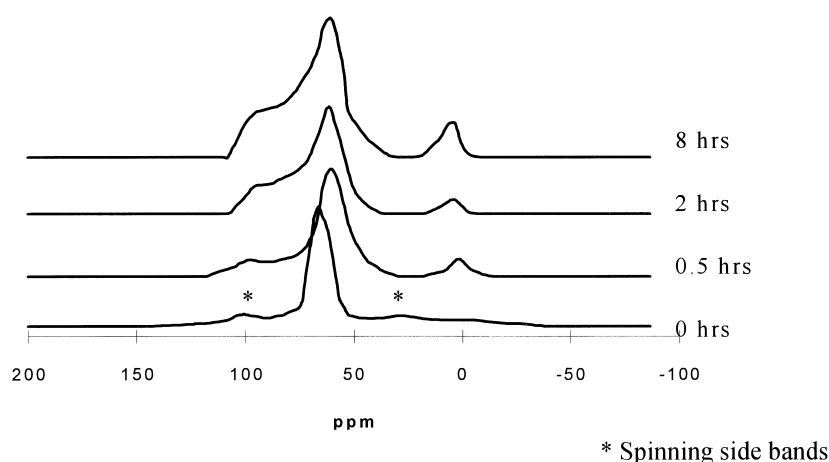| Steaming time (h)	Peak I (mmol/g_{cat})	Peak II (mmol/g_{cat})	Total desorption (mmol/g_{cat})	Peak II/peak I	Peak III relative
0	1.67	0	1.67	0	1
0.5	1.14	0.53	1.67	0.47	1
1	0.81	0.50	1.31	0.61	1.05
2	0.68	0.44	1.12	0.64	0.93
4	0.61	0.39	1.00	0.64	0.89
8	0.65	0.45	1.10	0.69	0.66

Fig. 6. NMR spectra for increasing steaming times.

framework and not desorption of ammonia. This was verified using thermogravimetric analysis.

Peak II did not occur on the parent sample but was rather seen to develop after steaming. It reached a maximum quickly and then slowly tapered off. This peak can be assigned to stronger acid sites. The area of peak II relative to peak I increased and then began to level off with steaming time. Peak I and the total surface coverage decreased with steaming time, indicating a decrease in the total number of acid sites, corresponding to framework dealumination. Peak III, the dehydroxylation peak, shifted to a higher temperature and decreased in intensity with increased steaming time.

The change in distribution of Al species with steaming time was monitored with ^{27}Al MAS NMR (Fig. 6). The peaks were assigned according to the chemical shifts given by Engelhardt and Michel [12], where the peak at 0 ppm corresponds to octahedral alumina and that at 65 ppm to tetrahedral alumina.

The amount of extra-framework aluminium increased with increasing steaming time and the amount of framework aluminium decreased. This showed framework dealumination with steaming time. The shoulder which developed at about 90–100 ppm was attributed to other forms of extra-framework Al or Al which is partly removed from the framework as opposed to Al^{VI} at 0 ppm.

4. Discussion

As the trends observed with the reaction/regeneration cycles were not a function of either reaction or calcination time and the catalyst was flushed with N_2 at 325°C, prior to calcination, it was concluded that the trends observed must be a function of in situ steaming caused by water formed by the combustion of residual carbonaceous species on the catalyst surface. The formation of water during the calcination procedure was proved by the GC–MS experiments.

The presence of carbonaceous species at the surface can be explained by the decomposition of the methyl ammonium ions. It is known that both di- and tri-methylamine decompose on the surface to form carbonaceous species [13]. The residual methyl groups may also be formed by the decomposition of tetra-methyl ammonium ions, since these are known to exist at the catalyst surface during reaction [14]. It is not unreasonable to suppose that the water formed during the calcination procedure causes mild steaming and therefore dealumination of the catalyst.

The catalytic performance of the Rho sample after mild hydrothermal treatment is unexpected, since it would be expected that with increasing conversion of methanol in this series type reaction, an increase, rather than a decrease, in the final product of the series would be observed, i.e. that the trimethylamine selectivity would increase. The resulting improved activity and selectivity must therefore be attributed to "different" physico-chemical changes within the catalyst and that there must therefore be more than one change taking place within the catalyst during steaming.

At a first glance it might appear that the increase in strong acid sites and the increase in conversion are related. However, it can be seen that while there is very little increase in the concentration of the strong acid sites between 0.5 and 4 h of steaming, there is a significant increase in the conversion over this time. Also, while the concentration of strong acid sites remains approximately constant after between 4 and 8 h of steaming the conversion drops off again. It is also possible that, for the parent (unsteamed) sample, the peak for the strong acid sites is there but over-shadowed by the earlier dehydroxylation peak. In that case it could be said that within the error of the deconvolution there was no change in the concentration of strong acid sites. The increase in activity also can not be related to the weaker acid sites as these show a definite decrease while the activity is increasing.

The NMR data obtained show framework dealumination. There are two possible results of having this EFAl within the catalyst. Firstly, the EFAl may improve selectivity for the methanol ammination reaction by increasing the diffusional constraints as suggested by Herrmann and Fetting [6]. The EFAl could also be responsible for the decrease in activity

observed at longer steaming times, i.e. as more EFAl forms, it prohibits even the smaller molecules, methanol and ammonia, from entering or exiting the pores. This would be in agreement with the findings of Segawa and Tachibana [5]. There must therefore be some optimal amount of EFAl at which the selectivity is improved without detrimentally affecting the activity of the catalyst.

Having accounted for the change in selectivity and decrease in activity at long steaming times, it remains to explain the initial increase in activity with steaming. The dealumination may also cause a change in the adsorption properties of the catalyst which can cause the change in the distribution of the surface species. This would lead to a situation similar to that found by Gründling et al. [10] over modified mordenite where an increase in the concentration of the higher sub-stituted methylamine species on the catalyst surface was found to lead to greater activity due to the increased nucleophilic behaviour of these species.

5. Conclusions

It has been confirmed that the performance of zeolite Rho for the methanol ammination reaction can be dramatically improved by mild hydrothermal treatment. The selectivity to DMA in particular increases to industrially attractive levels.

Although work has previously been done on the steaming of Rho [2,5], it can be seen from the work presented here that at a given steaming temperature there is a sharp maximum in the activity obtained at different steaming times. At the same time, the selectivity improves and reaches a steady state. There is, therefore, an optimum time for the steaming of the catalyst as too long a time results in decreased activity with no further gain in selectivity.

It can be concluded therefore that care needs to be taken when comparing catalysts steamed at different temperatures. In the previous works, the steaming of Rho was compared for a number of steaming temperatures at a fixed time. However, as can be seen in this work, the catalyst activity should not be merely compared after a set time as the catalyst may either not have reached the optimum activity/selectivity point or it may have already exceeded this point. Rather, the activity progression with time should be examined to determine the optimum treatment.

It has also been shown that the dealumination occurs on zeolite Rho with steaming, which causes a change in the distribution of acid sites as seen by TPD. What this shows is that steaming has changed the state of the catalyst and that there is, therefore, some optimum state at which the best activity and selectivity are achieved for the ammination reaction.

Acknowledgements

References

[1] M. Keane, G.C. Sonnichsen, L. Abrams, D.R. Corbin, T.E. Gier, R.D. Shannon, Appl. Catal. 32 (1987) 361–366.

[2] R.D. Shannon, M. Keane, L. Abrams, R. Staley, T.E. Gier, D.R. Corbin, G.C. Sonnichsen, J. Catal. 113 (1988) 367–382.

[3] L. Abrams, D.R. Corbin, M. Keane, J. Catal. 126 (1990) 610–618.

[4] Y. Ashina, T. Fujita, M. Fukatsu, K. Niwa, J. Yagi, Stud. Surf. Sci. Catal. 28 (1996) 779–786.

[5] K. Segawa, H. Tachibana, Stud. Surf. Sci. Catal. 75 (1993) 1273.

[6] C. Herrmann, F. Fetting, Appl. Catal. 39 (1988) 213–226.

[7] H.E. Bergna, M. Keane, D. Ralston, G.C. Sonnichsen, L. Abrams, R.D. Shannon, J. Catal. 115 (1989) 148–158.

[8] D.R. Corbin, M. Keane, L. Abrams, R. Farlee, P. Bierstedt, T. Bien, J. Catal. 124 (1990) 268–280.

[9] K. Segawa, H. Tachibana, J. Catal. 131 (1991) 482–490.

[10] C. Gründling, G. Eder-Mirth, J.A. Lercher, J. Catal. 160 (1996) 299–308.

[11] M.C. Ilao, H. Yamamoto, K. Segawa, J. Catal. 161 (1996) 20–30.

[12] G. Engelhardt, D. Michel, High-Resolution Solid-State NMR of Silicates and Zeolites, 1987.

[13] C. Merz, F. Fetting, F., Chem. Eng. Technol. 119 (1996) 526–537.

[14] C. Gründling, V.A. Veefkind, G. Eder-Mirth, J.A. Lercher, Stud. Surf. Sci. Catal. 105 (1997) 591–598.

[15] E. Dingerdissen, E. Nagy, F. Fetting, Chem.-Ing.-Tech. 63 (1991) 625–628.