¹³C and ¹⁵N solid-state MAS NMR study of the conversion of methanol and ammonia over H-RHO and H-SAPO-34 microporous catalysts

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¹³C and ¹⁵N MAS NMR have been used to study the conversion of methanol and ammonia over H-SAPO-34 and H-RHO using sealed glass ampoules as microreactors under static batch conditions. The product peaks were well resolved in the ¹³C NMR spectra whereas the ¹⁵N NMR spectra gave only a single broad peak making it impossible to follow the reaction by observing this nucleus. Both catalysts give the tetramethyammonium cation whereas only zeolite H-RHO produces the monomethylammonium cation.

Introduction

The production of methylamines from ammonia (NH₃) and methanol (MeOH) is an industrially important and well studied reaction, as evidenced by the great wealth of literature including a number of patents that give details of synthesis procedures.¹⁻⁴ A range of zeolites have been investigated for their suitability for this reaction including: ZSM-5, T, Y, A and erionite.⁵⁻¹⁰ Particular attention has been paid to mordenite,¹¹⁻¹³ RHO¹⁴⁻¹⁸ and ZK-5.^{15,19,20} Some of these papers include studies on modification of the catalyst, such as varying the alkali metal content⁶ and the deposition treatment with silicon tetrachloride,^{12,13} Al_2O_3 and/or SiO_2^{15} and trimethylphosphite¹⁶ to reduce further the egress of TMA into the product stream, and, in addition, to 'cap' any external active sites to reduce non-selective reactions. A communication by Subrahmanyam et al.²¹ reported the production of the three amines using CO (instead of methanol) and ammonia over ZSM-5, mordenite, zeolite Y and SAPO-5 catalysts.

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§ Present address: CRL, Springfields Works, BNFL plc, Salwich, Preston, Lancashire, UK PR4 0XJ. In this work we follow the reaction over zeolite RHO and H-SAPO-34 using ¹³C and ¹⁵N MAS (magic angle spinning) NMR on samples contained in sealed glass ampoules. This method has successfully been used by Ernst and Pfeifer²² who studied this reaction over ZSM-5 and mordenite using ¹³C MAS NMR techniques.

Experimental

Catalysts

Zeolite H-RHO and H-SAPO-34 were supplied by the Leverhulme centre for Innovative Catalysis at the University of Liverpool. Both microporous materials used in this investigation were characterised before use by solid-state MAS NMR (²⁷Al, ²⁹Si, ³¹P, ²³Na and ¹H nuclei), X-ray diffraction, microanalysis and scanning electron microscopy (SEM) in order to verify the sample quality (these results are reported in Table 1). The acidic form of zeolite RHO was prepared by two ammonium sulfate exchanges with subsequent washing with distilled water, followed by heating to 500 °C in dry air under shallow-bed conditions using two temperature ramps. First at 1 °C min⁻¹ to 105 °C, held for 2 h then at 2 °C min⁻¹ to 500 °C and held for 12 h. ²³Na MAS NMR indicated the complete removal of sodium cations, which was corroborated by microanalysis (<0.05 wt.%). The template in the SAPO-34

Table 1 Sample characterisation data of the H-SAPO-34 and H-RHO microporous catalysts in their final acidic forms

			MAS NMR resonance/ δ					
sample	unit cell composition	Si/Al	²⁷ Al ^a	²⁹ Si ^b	³¹ P ^c	${}^{1}\mathrm{H}^{b}$	EFA1 ^d	morphology ^e
H-SAPO-34 H-RHO	$\begin{array}{l} H_{1.5}[Si_{1.5}Al_{5.6}P_{4.8}O_{24}] \\ H_{8.1}Cs_{0.9}[Si_{38.9}Al_{9.0}O_{96}] \end{array}$	0.26 4.2	33.4 55.3, 0.7	-95.3 -92.2, -97.6 -102.0, -108.7	-29.8	$4.0^{f}, 1.6^{g}$ $4.2^{f}, 2.5^{h}$	0% 16%	cubic cubic

External chemical shift references: a [Al(H₂O)₆]³⁺; b TMS; c H₃PO₄. d From ²⁷Al MAS NMR. e From SEM. f Brønsted acid sites. g Silanol groups. h This signal has previously been assigned to a second type of Brønsted acid site.²³

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sample was removed under similar conditions to give the acidic form. ¹H MAS NMR confirmed that there were no residual ammonium cations left after this calcination procedure (or AlOH/AlOOH groups caused by dealumination) and that only Brønsted acid sites and silanol groups were present. ²⁷Al MAS NMR of the final form of the RHO sample indicated the presence of 16% extra-framework aluminium (EFAI) ,with this information and knowing the bulk amount of aluminium as indicated by microanalysis we obtained a framework Si/Al ratio of 4.3. Information derived from the ²⁹Si MAS NMR spectrum of this sample gave a Si/Al ratio of 4.2, which is in close agreement to this value.

MAS NMR measurements

 $^{13}\mathrm{C}$ and $^{15}\mathrm{N}$ MAS NMR spectra were recorded on samples sealed under vacuum in glass ampoules, typically 50 \pm 1 mg of acid catalyst was used. Each sample was heated under vacuum to 400 °C for 24 h to remove water. Following complete dehydration of the sample, an aliquot of methanol vapour and gaseous ammonia was introduced over the sample and allowed to adsorb slowly. A stoichiometry of 1:1 methanol to ammonia was used. The total adsorbate used was sufficient to saturate the pores of H-RHO and H-SAPO-34. $^{13}\mathrm{CH_3OH}$ and $^{15}\mathrm{NH_3}$ were 99% enriched as supplied by Aldrich, methanol was purified by four freeze–pump–thaw cycles before use.

MAS NMR spectra were recorded using a Bruker MSL400 spectrometer in conjunction with a Chemagnetics double reso-



Fig. 1 13 C MAS NMR spectra of the reaction of co-adsorbed methanol and ammonia over H-SAPO-34 recorded with high-power decoupling after the following sample pretreatments: heated to (a) 240 °C for 30 min; (b) 265 °C for 30 min; (c) 265 °C for 90 min; and (d) 285 °C for 30 min

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Fig. 2 13 C MAS NMR spectra of the reaction of co-adsorbed methanol and ammonia over H-RHO recorded with high-power decoupling after the following sample pretreatments: heated to (a) 240 °C for 30 min; (b) 265 °C for 30 min; (c) 265 °C for 90 min; (d) 285 °C for 30 min; and (e) 400 °C for 60 min

nance 'Pencil' probe specially designed for stable spinning of sealed samples at high spinning rates, all spectra were recorded at a sample spinning speed of 3 kHz. ¹³C MAS NMR spectra were obtained with high-power proton decoupling using a ¹³C $\pi/2$ pulse width of 4 µs and a repetition time of 10 s. Tetramethylsilane (TMS) was used as an external standard. ¹⁵N MAS NMR spectra were also recorded with high-power proton decoupling using a $\pi/2$ pulse width of 10 μ s and a repetition time of 2 s, a saturated solution of NH₄¹⁵NO₃ was used as the external standard. In order to follow the progress of the methylamine synthesis the sealed sample (comprising the acid catalyst and adsorbed methanol and ammonia) was placed in a Carbolite furnace and heated to the required temperature for a given period of time. Following this, the sample was removed and allowed to cool to room temperature thereby effectively quenching the reaction. The ¹³C and ¹⁵N MAS NMR spectra were then recorded. All of the spectra presented within each stack plot are expanded as appropriate in order to facilitate observation of low intensity signals.

Results

Fig. 1 shows a stack plot of the ¹³C MAS NMR spectra obtained after heating the reactants over H-SAPO-34 from 240 to 285 °C. After heating to 240 °C for 30 min all of the products, including dimethylether (DME), and the tetramethylammonium cation (designated 4MA) can be observed together with unreacted methanol. Their respective chemical shift values (δ) vary within a small range (this was also found for H-RHO) and are: monomethylamine (MMA), or the MMAH⁺ cation, at $\delta = 24.8-25.3$, dimethylamine (DMA) at $\delta = 34.5-34.8$, trimethylamine (TMA) at $\delta = 44.7-45.2$, 4MA at $\delta = 56.6$, DME at $\delta = 59.8$ and unreacted methanol at $\delta = 49.3-49.6$. At higher temperatures methanol is completely consumed with a corresponding increase in the product concentration. The 4MA peak is noticeably sharper than the other lines in the stack plot.

For H-RHO (Fig. 2) we observe that products are produced at 240 °C with the appearance of MMA, DMA and DME. With increasingly severe reaction conditions methanol is consumed and eventually all of the amines are produced. DME (which is initially produced in significant quantities) is also consumed similarly to methanol until at 400 °C, where no DME can be observed, there are also insignificant amounts of 4MA produced compared with the H-SAPO-34 sample. In the MMA region of the ¹³C NMR spectrum there are two peaks assigned to MMA and the protonated cation, these assignments are discussed later. The chemical shift values for this sample are: MMAH⁺ cation at $\delta = 24.3-24.8$ and MMA at $\delta = 26.9-27.5$, DMA at $\delta = 34.8-35.2$, TMA at $\delta = 45.7$ and 46.1, 4MA at δ = 56.6, DME at δ = 59.5–60.5 and unreacted methanol at $\delta = 49.3-49.8$. Heating this sample to 500 °C (spectrum not shown) resulted in the production of alkanes in the region of $\delta = -11-25$ and also CO and CO₂. The aromatic region was broad and poorly defined. At 600 °C only methane, ethane CO and CO₂ were observed (spectra not shown), these assignments were confirmed by the J-coupled spectra in which a quintet and quartet were observed for the first two signals, respectively, and two singlets for the later two.

Fig. 3 shows two ¹⁵N MAS NMR spectra typical of those recorded in this work, one of unreacted ammonia at room temperature and the other showing a single peak correspond-

Fig. 3 Representative ¹⁵N MAS NMR spectra of the reaction of coadsorbed methanol and ammonia over H-SAPO-34 recorded with high-power decoupling after the following sample pretreatments: (a) room temperature showing unreacted protonated ammonia; and (b) heated to 265 °C for 30 min showing a significant amount of unreacted protonated ammonia and a downfield resonance assigned to the three amine products and the 4MA cation

ing to all of the methylamines and an upfield peak corresponding to unreacted ammonia over H-SAPO-34. These ¹⁵N MAS NMR spectra are representative for both samples. Ammonia gave a resonance at $\delta = -357.3$ on the H-SAPO-34 sample and for H-RHO a band at $\delta = -358.5$ was observed (this band shifted to $\delta = -359.4$ in the presence of the reaction products for both catalysts). The four methylamines gave unresolved resonances within the band centred at $\delta = -351.3$ over both catalysts. In spectra in which methylamines were consumed to give hydrocarbons, CO and CO₂ a single ¹⁵N NMR resonance is observed at the original prereaction chemical shift value (spectrum not shown) indicating rejuvenation of ammonia.

Discussion

The ¹³C NMR chemical shift values of the amines in both catalysts are adequately separated so that complete resolution of signals arising from the products is observed. These signals are very close to the values obtained by Ernst and Pfeifer²² who used mordenite, ZSM-5 and alumina. Also in agreement with their findings is the significantly narrower linewidth of the tetramethylammonium cation peak compared to the linewidths of the bands assigned to mono-, di-, and trimethylamine.

A particularly interesting feature of the results in this work is the two signals in the MMA region of the ¹³C MAS NMR spectrum for zeolite RHO. A previous study by Vega and Luz²⁴ concerning the adsorption of the three methylamines over H-RHO gave values almost identical to those reported in this work (MMA/MMAH⁺ at $\delta = 24.4$, DMA at $\delta = 34.1$ and TMA $\delta = 46.4^{24}$). The band at $\delta = 24.4$ was assigned to MMAH⁺ therefore we assign the upfield band in Fig. 2 at $\delta = 24.3 - 24.8$ to the cation and the downfield band to physisorbed MMA. These values vary from zeolite to zeolite, for example Meinhold et al.25 found that physisorbed MMA and the MMAH⁺ cations give resonances at $\delta = 31$ and 26.4, respectively, over H-ZSM-5. No evidence of the protonated forms of DMA or TMA was found. The close proximity of the ¹³C NMR chemical shift values of methylamines and their respective protonated forms coupled with the broad ¹⁵N MAS NMR peak add a degree of uncertainty to this assignment.

A variable temperature study of MMA adsorbed on H-Y discovered that at room temperature a ¹H NMR resonance intermediate between a value for MMA and MMAH⁺ was produced from species undergoing rapid proton transfer.²⁶ At -140 °C this exchange process was frozen out and two resonances were observed for MMA and the MMAH⁺ cation. It is possible that such an exchange process is occurring in H-RHO but is slow enough to give rise to the two signals on the NMR timescale at room temperature. Although less likely we cannot rule out completely the possibility that the two signals arise from MMA adsorbed on two adsorption sites such as EFAl and Brønsted acid sites, however Meinhold et al.25 found no evidence of amines interacting with EFA1 in H-ZSM-5. A more interesting scenario, which takes into consideration the structure of zeolite RHO, is that one of the signals arises from MMA, which has entered the double 8-ring prisms during heating of the sample. Upon cooling a proportion of the MMA becomes trapped within the double 8-ring prisms.

No 13 C MAS NMR data are currently available in the literature for the three methylamines adsorbed on H-SAPO-34 and so it is possible that the signal assigned to MMA in this work might correspond to MMAH⁺, as the chemical shift values observed are close to the MMAH⁺ cation chemical shift values found for H-RHO.

Pre-reaction NH₃ adsorbed on H-SAPO-34 gave rise to a signal at $\delta = -357.3$ in the ¹⁵N NMR spectrum corresponding to the formation of ammonium cations produced by



protonation of NH₃ by the Brønsted acid sites. NH₃ adsorbed on H-RHO gave a band at $\delta = -358.5$, which is assigned to ammonium cations involved in hydrogen bonding to adjacent ammonium cations.²⁷ This explanation fits in with the proximity of Brønsted acid sites relative to each other, in H-SAPO-34 the ammonium cations are isolated whereas in H-RHO there are eight Brønsted acid sites per unit cell that can facilitate the interaction between neighbouring ammonium species.

Previous ²H NMR studies of the three methylamines adsorbed on zeolite Y and ZK-5 (which has a similar structure to RHO) by Kustanovich et al.28 postulated that tri-, bi- and mono-pod structures were formed by MMA, DMA and TMA, respectively, when interacting with Brønsted acid sites. The structures are formed by hydrogen bonds between the Brønsted acid site and the electron lone pair on the N atom of the amine and by the protons directly bonded to the N atom interacting with bridging oxygens in the catalyst framework. The broad nature of the ¹⁵N resonance provides further evidence for these surface structures; MMA contributes the most to the broad signal being the most abundant product and is also the most rigidly bound of the three methylamines according to the above model. For the tetramethylammonium cation it was observed that the ¹³C resonance was significantly sharper compared with the product species, this can be explained in terms of the mobility of the methyl groups and of the molecule as a whole. MMA and DMA have N-H bonds, the protons of which can form hydrogen bonds with the framework oxygen atoms which then restricts their motion. TMA and the tetramethylammonium cation on the other hand do not have any N-H bonds so these two species can rotate freely about the N atom-Brønsted acid site hydrogen bond.

Conclusions

At around 240 °C zeolite H-RHO and H-SAPO-34 convert methanol and ammonia to methylamines under static batch conditions using a 1:1 ratio of the two reactants, in addition both catalysts form the tetramethylammonium cation but only H-RHO forms the monomethylammonium cation. At higher temperatures amines produced by H-RHO are cracked and the reactive species give hydrocarbons and ammonia.

While ¹³C MAS NMR proved to be a good method for following the reaction, ¹⁵N MAS NMR of the products gave rise to a single broad band containing all resonances of the amine products and therefore provided no futher insight into the reaction.

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