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Selective Synthesis and Equilibration of Methylamines on Sodium Mordenite[1]

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Sodium mordenite catalyzes the sequential reactions of methanol and ammonia to give methylamine and dimethylamine, but little trimethylamine. The kinetics of this selective reaction are compared to the nonselective reaction catalyzed by Brønsted acids. Selective adsorption, not shape selectivity, is the critical factor in determining the catalyst's selectivity . © 1987 Academic Press, Inc.

INTRODUCTION

Methylamines are prepared industrially by the solid-acid catalyzed reaction of MeOH and NH_3 (*1*). The reaction proceeds to equilibrium among the four nitrogen-containing species. At 447°K, the equilibrium is (mole%) 55% NH_3, 12% MMA, 12% DMA, and 21% TMA. The equilibrium composition favors trimethylamine (TMA) (*2*), while the market demand is highest for the lower alkylated products mono- (MMA) and dimethylamine (DMA) (*3*). Generally unwanted TMA is recycled *in situ* with additional NH_3 over the same catalyst to produce additional MMA and DMA, an inefficient and energy intensive process. Catalysts selective to MMA and DMA are the goal of this work.

Hamilton (*4*) patented the concept of obtaining a selective mixture of mono- and dialkylamines from alcohols and ammonia using zeolites. Examples using the zeolites hydrogen mordenite, 5A, and three faujasites and two alcohols, ethanol and butanol, were presented. No examples with methanol were given, but the patent claims that methanol works with the zeolites described. We have not been able to reproduce this claim. In subsequent patents, other Mobil workers (*5, 6*) used pentasil zeolites to form amines from alcohols and ammonia. Several examples used methanol or dimethyl ether, but no particular selectivity toward MMA and DMA was apparent.

Kinetics of the methylamines reactions on several amorphous, solid-acid catalysts have been determined (*7*). The importance of adsorption effects and nonuniform catalyst sites was clearly described for these catalysts.

Thermodynamically the disproportionation of MMA and DMA to NH_3 and TMA is a favorable reaction. The opposite is true for the analogous reactions of the longer chain alkyl amines (*2*). MMA and DMA are uniquely difficult to produce because of this favorable disproportionation.

The selective synthesis of MMA from MeOH and NH_3 using sodium mordenite as a typical catalyst was first described in 1981 (*8*). This zeolite and others also catalyze the selective disproportionation of MMA to DMA and NH_3 (*9*). After these patents appeared, others expanded on the initial findings. Cochran and Deeba (*10*) patented the concept of using mordenite as the catalyst to selectively make MMA and then an equilibration catalyst to produce any other desired distribution of methylamines. Mochida and co-workers (*11*) studied a series of metal loaded mordenites, but found little advantage to these materials over the sodium form. The field is becoming popular (*12*).

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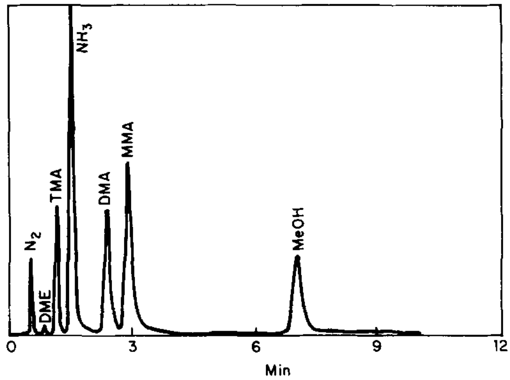

FIG. 1. A typical gas chromatogram of the methylamine system.

This paper presents a study of methylamine reactions with several different catalysts. The relative rate constants (times adsorption coefficients) of the reaction network can be used to discuss the surface interactions which are involved in the catalysis. Selective adsorption, and not shape selectivity, is the explanation of the difference between sodium mordenite and the more traditional acid catalysts. All the methylamines are small enough to diffuse through the pore structure of mordenite catalysts.

EXPERIMENTAL

One-atmosphere reactions were run in 3/8-in. Vycor tubes with ~3 g of catalyst. The bed temperature was measured by a coaxial thermocouple and a Doric digital thermometer and controlled by an Athena proportional controller. MeOH was fed by a Sage syringe pump. Gaseous NH_3 and methylamines were fed from commercial cylinders, measured by rotameters, and controlled by needle valves. Pressure experiments up to 100 psi were run in stainless-steel reactors heated in a fluidized sandbath. Pressure was regulated by a GO valve at the exit of the reactor. In the latter stages of this work, gas flows were controlled by Tylan mass flow controllers.

The reaction products were passed through heated lines to a Valco 6-port sample valve in a Hewlett–Packard 5710 gas chromatograph (GC) with a thermal conductivity detector. Products were analyzed using a 10-ft × $\frac{1}{8}$-in. stainless-steel column packed with 25% Carbowax 400 and 2.5% KOH on acid-washed 80–100 mesh Chromosorb W with a carrier gas flow of 20 ml/min. The initial temperature was held at 65°C for 8 min and then programmed to 100°C (maximum) at 32°C/min and held there until water eluted. A typical chromatogram is shown in Fig. 1. The products exiting the GC were condensed and any remaining gases passed through 50% sulfuric acid to scrub the evil-smelling amines.

Silica/alumina (87 : 13) was obtained from Davison (D-970), alumina (AL-0104) from Harshaw, and REX (SK-500) and A's from Linde. The mordenites were obtained from Norton.

Thermal analyses were done on a Du Pont 900 thermal analyzer. Samples of each adsorbent were placed in the apparatus and heated to 400°C to remove water, then cooled to room temperature and weighed. An atmosphere of the adsorbate of interest was introduced and the weight gain noted.

All our experimental data was stored in a computer data base. Experiments done specifically for one purpose could later also be used to test other hypotheses. Theoretical kinetic analyses were performed using the Gear integration program HAVCHEM (*13*) modified for use within our PDP-10 time-sharing environment. Comparisons between theoretical kinetic models and experimental data were done by systematically varying the model's rate constants and visually determining the best fit with experimental data.

RESULTS

MeOH and NH_3 were passed over different catalysts at various temperatures, contact times, partial pressures, and ratios. Preliminary experiments verified that neither bulk mass transfer nor intrapellet mass transfer interfered with rate measurements (*14*). Essentially no hydrocarbon products are produced in this reaction except at the highest temperature. Hydrocarbon oligo-

TABLE 1

Activity of Selected Catalysts for Methylamine Synthesis[a]

Catalyst	% MeOH Conversion
D-970	6
HZSM-5	63
CaX[b]	76
REX[b]	84
HY(33-200)[b]	93

[a] 3 g catalyst, 3 ml/hr MeOH, MeOH/NH_3 = 1, 250°C.

[b] Union Carbide Products.

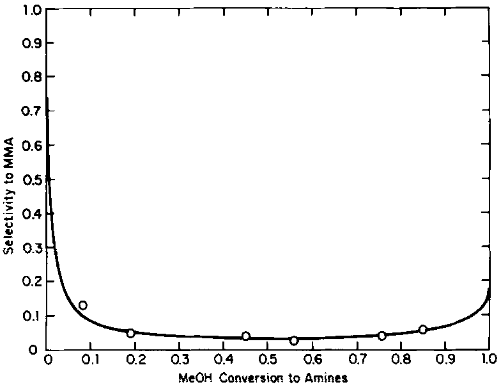

FIG. 2. Methylamine formation with an H-ZSM5 catalyst (C/N ~1).

mers trapped inside the pores may be coke precursors which reduce the useful catalyst life.

The activity of acid zeolites is much higher than the amorphous silica–alumina as shown in Table 1. The selectivity to the desired MMA and DMA is even lower than the equilibrium distribution at intermediate conversions as shown for MMA from H-ZSM5 in Fig. 2. Proceeding all the way to equilibrium gives the best selectivity to MMA and DMA with these catalysts. Sodium mordenite is essentially inactive at 250°C. The result agrees with that found by Kaeding (*6*).

Of the catalysts tested at higher temperatures sodium mordenite, but not hydrogen mordenite, showed interesting selectivity toward the lower methylamines at intermediate conversions. This catalyst was selected for more extensive characterization. H-Mordenite behaves like H-ZSM5 or H-Y.

Kinetic order. The kinetic order of MeOH and NH_3 in the initial alkylation was determined by varying the partial pressure of each species while holding constant the total pressure, temperature, and contact time. We define STY as the sum of all the amines produced per weight of catalyst per unit time. The results are given in Table 2. The reaction is essentially first-order in NH_3 and zero-order in MeOH for sodium mordenite.

In a complex reaction network such as this, product weight is not an accurate indication of reaction rate, but trends certainly are valid. Zero-order kinetics implies a surface saturated with that species so that increasing its partial pressure has no further effect on the surface rate. Presumably, the reaction would be first-order in each species at some sufficiently low pressure.

The dependence on total pressure holding the reactant ratios constant is shown in Table 3. Over a fourfold increase in pressure the STY increases only by 20%, in spite of the increase in contact time. At greater than atmospheric pressure, the total reaction order approaches zero. This result suggests that the surface is becoming increasingly saturated and adsorption–desorption processes dominate the kinetics.

TABLE 2

Kinetics of Methylamine Formation on Sodium Mordenite[a]

NH_3 (ml/min)	MeOH (ml/min)	STY (mg/g/hr)
14	20	203
14	28	207
14	40	202
10	28	164
14	28	207
20	28	286

[a] 3 g sodium mordenite, 325–330°C, N_2 to give a total of 80 ml/min flow.

TABLE 3

Effect of Pressure on Reaction Rate[a]

Pressure (psia)	STY (mg/g/hr)
25	330
55	370
95	410

[a] 2.1 g catalyst, 28 ml/min NH_3 at STP, C/N = 1.0 ± 0.1, 335°C.

Catalyst deactivation is more severe at higher pressures. Extracting used catalyst with organic solvents gave a variety of products including long-chain alkylamines. These would be volatile at the reaction temperature and 1 atm but less so at 100 psi. High boiling by-products could remain in the pore structure, and eventually become coke.

If we focus on catalyst selectivity as the dependent variable, the only important independent variables are the $MeOH/NH_3$ feed ratio and MeOH conversion. Neither temperature, pressure, nor contact time have a significant effect on the catalyst selectivity, though they do affect activity.

Coordinate system. The coordinate system chosen for this study requires some discussion. The conventional abscissa is contact time or a parameter linearly related to it. The ordinate is usually concentration. In heterogeneous catalysis controlling the activity of a catalyst is difficult, even with materials purchased from reputable suppliers. Noncommercial catalysts show even more variability. Zeolites are notoriously difficult to synthesize reproducibly, as minor variations in preparation conditions can lead to major changes in crystal properties.

Traces of impurities in the feeds can have dramatic effects on reaction rates, either as poisons or promoters. Temperature control is difficult in small reactors. Not only can the heat of the reaction cause deviations from isothermal behavior, but gradients introduced by the heaters are also present. While these can be minimized at some inconvenience to the experimenter, we chose to deemphasize the absolute activity of a catalyst and concentrate only on the relative rates of the series of sequential reactions in the network. This is done by setting the rate of the reaction $MeOH + NH_3 \rightarrow MMA + H_2O = 1.00$ and relating all the other rates in Table 4 to this one.

Selectivity is chosen as the ordinate to spread out the data. If concentration is the Y axis, all products extrapolate to zero at zero conversion. Primary products have a finite slope, while secondary and tertiary products have zero slopes. With selectivity

TABLE 4

Comparison of Rate Constants for Methylamine Reactions at 1 atm over Selected Catalysts

Equation	NaMo	D-970	Al_2O_3	REX
(1) $NH_3 + MeOH \rightarrow MMA + H_2O$	$\equiv 1$[a]	$\equiv 1$[a]	$\equiv 1$[a]	$\equiv 1$[a]
(2) $MMA + MeOH \rightarrow DMA + H_2O$	0.7	20	15	>100
(3) $DMA + MeOH \rightarrow TMA + H_2O$	0.5	120	45	>10,000
(4) $MMA + MMA \rightarrow DMA + NH_3$	0.09	4	27[b]	"like" D-970
(5) $DMA + DMA \rightarrow TMA + MMA$	0.0022	7.2	0.65[b]	
(6) $MMA + DMA \rightarrow TMA + NH_3$	0.045	20.4	13.5[b]	
(7) $MeOH + MeOH \rightarrow DME + H_2O$	<0.01	~1	$\gg 1$	~1

[a] All rates relative to this value.

[b] Relative values from MMA disproportionation.

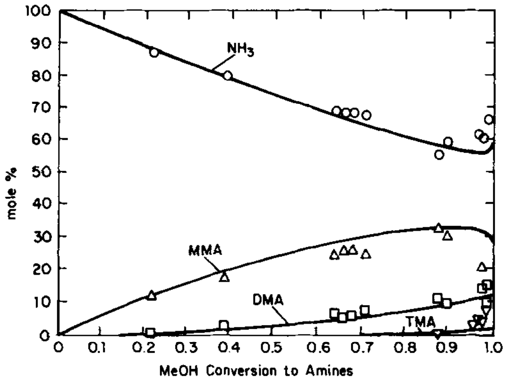

FIG. 3. Methylamine formation with a sodium mordenite catalyst (0.5 < C/N < 0.7).

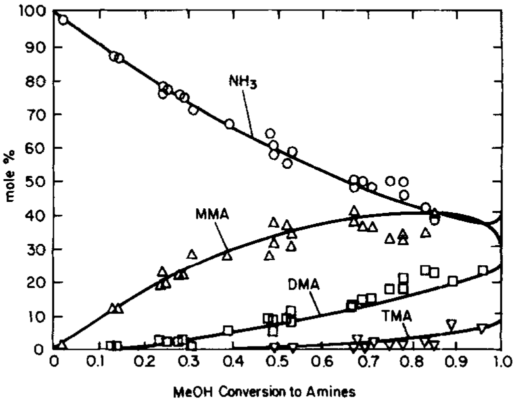

FIG. 4. Methylamine formation with a sodium mordenite catalyst (0.95 < C/N < 1.05).

as the ordinate, primary products have a non-zero intercept, while all others still have zero intercepts. Secondary products have a finite slope at the origin while tertiary and higher products still have both zero slopes and intercepts.

If the activation energies of all the reactions are the same, the relative rates are temperature independent. Data from all temperatures can be combined and gradients become irrelevant. This must be an approximation, as the temperature effects on the equilibrium constants of the amines equilibration are already known (*2*), but these effects are small and will be ignored for the purpose of this paper.

Kinetic model. The path which the system $MeOH/NH_3$ takes to reach equilibrium is shown for sodium mordenite with several different C/N ratios in Figs. 3 to 5. The points are experimental values for a variety of temperatures, flow rates, particle sizes, linear velocities, and pressures. The only selection was for C/N feed ratio within the windows specified. The other variables, if they have any effect at all, contribute only to the scatter in this representation. The lines are theoretical paths calculated from the reaction networks to be discussed later.

The selectivity to MMA is 100% at zero conversion and drops only slowly as conversion increases. The yield of MMA is the product of conversion and selectivity, and its maximum is a function of the C/N ratio of the feed. At equilibrium, the maximum yield of MMA is 11% at a C/N feed = 1.0; sodium mordenite can produce more MMA than this at all C/N ratios.

Similar paths for D-970 are shown in Figs. 6 and 7. Although the selectivity for MMA is also 100% at zero conversion, the selectivity is not maintained as conversion increases with this catalyst as well as with sodium mordenite. Only by operating at equilibrium and at low C/N ratios can a good yield of MMA be obtained. This is at the expense of a large NH_3 recycle. With these acidic catalysts, in order to obtain

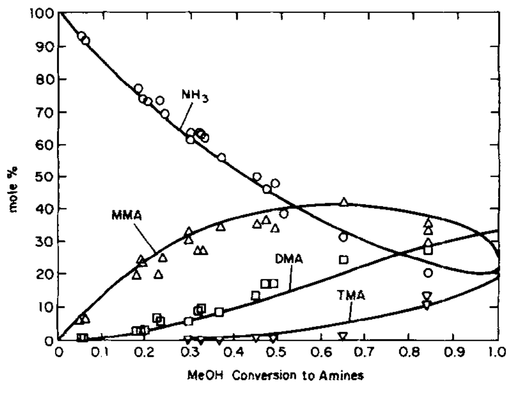

FIG. 5. Methylamine formation with a sodium mordenite catalyst (1.45 < C/N < 1.55).

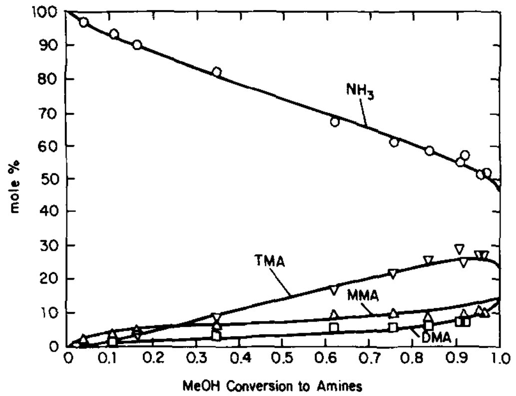

FIG. 6. Methylamine formation with a silica–alumina catalyst (0.9 < C/N a 1.1).

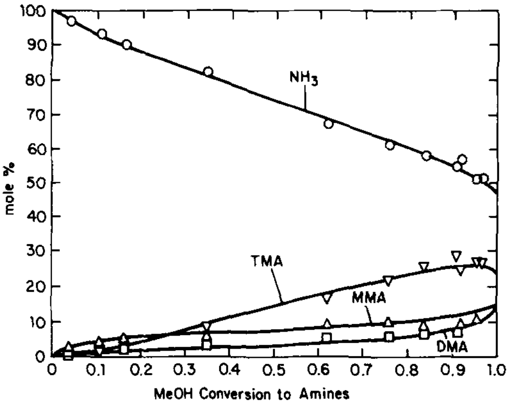

FIG. 8. Methylamine formation with an alumina catalyst (1.09 < C/N 1.21).

sufficient MMA and DMA to sell, a large recycle of either NH_3 or TMA must be tolerated, depending on the C/N ratio chosen. The path for alumina shown in Fig. 8 is similar to that of D-970.

An alternate coordinate system is based on the conservation of nitrogen. The concentrations of the four amines can be represented as a point in a tetrahedral space. Each vertex represents one pure component, each edge a binary mixture, each face a ternary mixture, and compositions having all four components are represented by a point in the interior of Fig. 9. This representation can dramatically illustrate the differences between classes of catalysts with a single trajectory. Two views of this tetrahedron show clearly that of the three catalysts sodium mordenite is the only one which makes more than an equilibrium amount of MMA at any conversion.

Dimethyl ether. Dimethyl ether (DME) as the carbon source behaves like MeOH on conventional solid-acid catalysts in the amines synthesis reaction. On these materials equilibration of MeOH with DME and water is fast compared to any amine formation (*6*), and significant amounts of DME are formed from MeOH at low conversions.

The behavior of DME is quite different on sodium mordenite. First, hardly any DME is formed when MeOH and NH_3 are passed over sodium mordenite. Second, when DME and NH_3 are fed to sodium mordenite the ratio of DMA to MMA as a function of conversion, as shown in Fig. 10, illustrates a parallel component to the reac-

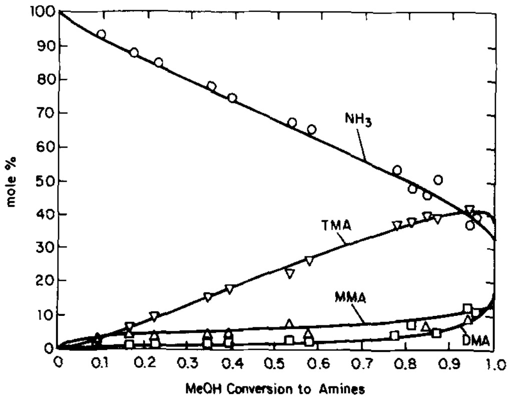

FIG. 7. Methylamine formation with a silica–alumina catalyst (1.5 < C/N 1.7).

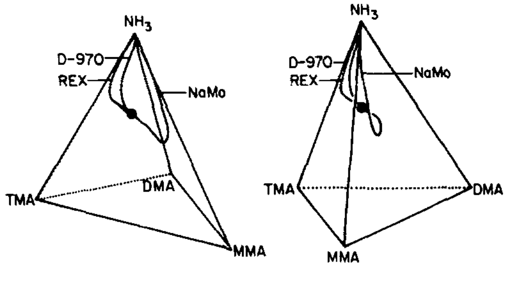

FIG. 9. Tetrahedral representation of methylamine reaction paths.

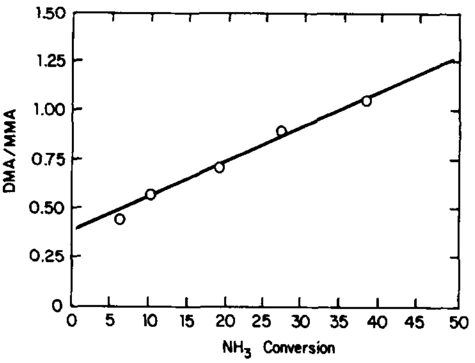

FIG. 10. Ratio of DMA to MMA from DME and ammonia on a sodium mordenite catalyst.

TABLE 5

Kinetics of Amine Formation from DME and NH_3[a]

NH_3 (ml/min)	DME (ml/min)	STY (mg/g/hr)
42	15	65
42	21	90
42	30	130
30	21	100
42	21	70
60	21	90

[a] 3 g sodium mordenite, 370°C.

tion network. DMA is apparently formed from DME, in part, without gas phase MMA as an intermediate.

Table 5 shows the kinetics of amines formation over sodium mordenite using DME as the carbon source. The reaction is essentially first-order in DME and zero-order in NH_3, the opposite of MeOH as the carbon source.

Amine disproportionation. DMA is the most desired of the three methylamines, and industrially even some MMA must be recycled. This is conventionally done in the same reactor as the synthesis reaction, and is very inefficient. Most of the MMA becomes unwanted NH_3 and TMA, and only about 10% is converted to DMA. The selective disproportionation of MMA to DMA and NH_3 is also a valid goal.

MMA was passed over some catalysts of interest and the paths to equilibrium determined. The results for sodium mordenite and D-970 are shown in Fig. 11. MMA disproportionation followed a different path on sodium mordenite versus typical acid catalysts. At any conversion sodium mordenite gave more DMA and less TMA. Other zeolites such as ferrierite and phillipsite were also selective toward DMA and NH_3; faujasites, the pentasils, and the A's were not. DMA disproportionation is too slow on sodium mordenite to provide useful kinetic path data.

Effect of water. Water is an obligatory product of the synthesis of methyl amines from methanol and NH_3. Amine disproportionation can be carried out in an anhydrous system. Adding water to the MeOH/NH_3 feed at constant contact time and temperature decreases the conversion on sodium mordenite significantly more than can be attributed to equilibrium effects, and must be due to competitive adsorption.

Alumina is a selective MMA disproportionation catalyst (*15*), but shows no unusual alkylation selectivity (*16*). A possible explanation of this dichotomy was found when MMA disproportionation was studied in the presence of water. Selective MMA disproportionation catalysts can be further

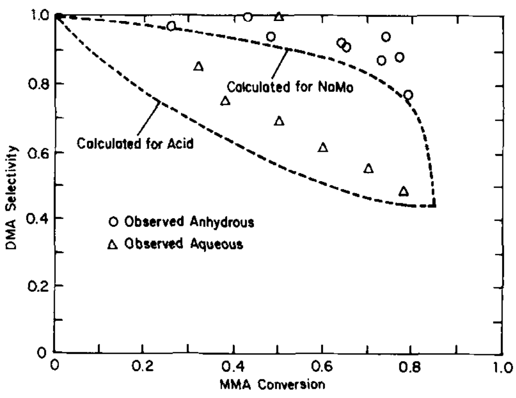

FIG. 11. MMA disproportionation on selected catalysts.

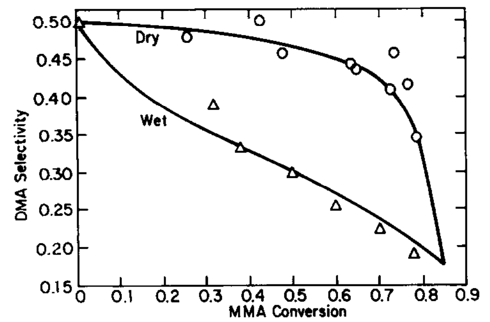

FIG. 12. Effect of water on MMA disproportionation on alumina.

TABLE 6

Adsorption Capacity of Solids for Amine Synthesis Reagents[a]

	3A	4A	5A	NaMo	HMo	NaY	D-970	P/P_0
H_2O	20[b]	22[b]	21.5[b]	15.0	22.3	28.5	—	1.0
NH_3	11.7	13.3	12.6	9.7	9.3	13.0	2.2	0.035
MMA	10.7	11.4	13.1	10.7	11.3	14.3	—	0.08
DMA	—	18.2	—	10.4	11.0	15.8	—	0.10
TMA	—	—	—	11.5	10.4	14.1	2.4	0.22
MeOH	17.1	17.3	17.9	13.0	14.3	18.7	7.8	1.0

[a] Weight percentage.

[b] Ref. (*17*).

subdivided with regard to the effect of water on their selectivity. The effect was first discovered with alumina as shown in Fig. 12.

The MMA disproportionation path on Al_2O_3 was different with anhydrous and aqueous MMA. Alumina is selective to DMA and NH_3 in the absence of water, resembling sodium mordenite, and nonselective in the presence of water, resembling the acidic catalysts. The zeolites ferrierite, phillipsite, and clinoptilolite resemble mordenite in that they retain their selectivity in the presence of water (*9*). Zeolite erionite, like alumina, is selective when dry, but loses its selectivity in the presence of water (*9*). Zeolites such as the faujasites, the pentasils, and the A's are not selective toward DMA either wet or dry.

Adsorption. The adsorption capacities of several zeolites for the compounds of interest were determined by TGA measurements. The results are given in Table 6. The amines have essentially the same size as their isostructural hydrocarbon counterparts. The zeolite 3A adsorbs NH_3 and MMA, but is too small to admit DMA or TMA. Zeolite 4A in addition adsorbs DMA but still rejects TMA. Both sodium and hydrogen mordenite, faujasites, and amorphous silica–alumina adsorb all three methylamines. Adsorption capacity of the zeolites is greater than for D-970 for all species tested.

DISCUSSION

Kinetic model. The amine reaction network can be modeled by the six bimolecular, equilibrium equations given in Table 4. Three involve amine synthesis from MeOH, and three involve amine equilibration. DME and MeOH are treated as equivalent species in this model. For acidic catalysts MeOH and DME do rapidly equilibrate; over sodium mordenite hardly any DME is formed. This model does not explicitly include adsorption. Even so, the model requires 12 rate constants, a formidable problem. Setting $k_1 = 1.00$ and determining the relative rates, reduces the problem only slightly.

The equilibrium constants for all six pairs of reactions are known (*2*). Only five independent rate constants are therefore necessary to fit conversion vs selectivity data. The remaining rate constants can be determined from the known equilibrium constants. This problem is still too difficult to solve in one step, so we work sequentially. For further simplicity we assume that the three MeOH alkylations go to completion and neglect the back-hydrolyses of the methylamines. This introduces only minor errors at MeOH conversions above 95%.

The determination of the relative rate constants proceeds in three steps. At low conversions, where the concentration of MeOH is high compared to the methylamines, methylation dominates equilibration and the system can be simply modeled by the three, sequential, second-order, methylation reactions. Setting the rate constant for the methylation of NH_3 to unity, the two relative rate constants for MMA and DMA methylation can be determined.

$$NH_3 \xrightarrow[=1.0]{MeOH} MMA \xrightarrow[k_2]{MeOH} DMA \xrightarrow[k_3]{MeOH} TMA$$

Next the amine equilibration system is solved by fitting the data for MMA disproportionation. This involves six equations, but again only two unknowns because all three equilibrium constants are known and the rates of equations 5 and 6 are determined relative to equation 4 which is arbitrarily assigned a rate constant = 1.00.

At some intermediate conversion of MeOH and NH_3 the relative contributions of methylation and equilibration are comparable. Adjusting the relative rates of the two sets of reactions (one unknown) gives a complete description of the methylamine system over all conversions.

Since no statistical tests could be made, the uniqueness and reliability of the rate constants could not be determined. The patterns are of greater interest than the exact values. The validity of the approach is demonstrated by the ability of a small number of rate constants to fit a large amount of data (see Figs. 2–8).

The method breaks down when adsorption differences must be explicitly considered. Apparently for both sodium mordenite and the nonselective, solid acids, one species dominates the surface sites over essentially the entire reaction profile. From the kinetic parameters presented in Tables 1 and 2, this species is MeOH on mordenite and NH_3 on strong acid catalysts. On mordenite, MeOH is preferentially adsorbed over NH_3, while NH_3 is preferentially adsorbed over DME.

The relative rates for the five independent reactions for several different catalysts are given in Table 4. For the acid catalysts the methylation rate constants parallel the pK_b of the base involved. This is not the case for sodium mordenite. Each successive methylation is slower than the previous one. There is no sharp break between DMA and TMA formation as might be expected if the reaction truly exhibited shape selectivity.

Mechanism. DME is clearly a dead end rather than an intermediate on the path to methylamines with sodium mordenite. The reactivity of DME on mordenite is sufficiently low that it might be explained by formation of surface MeOH or methoxide from DME and surface hydroxyls present on the catalyst. This behavior of sodium mordenite is in marked contrast to typical acidic catalysts which can use MeOH and DME essentially interchangeably.

The two very different sets of rate constants imply different active sites for sodium mordenite versus typical acid catalysts. Since the sites on SiO_2/Al_2O_3 and hydrogen zeolites are generally assumed to be Brønsted acids (18), the active sites on sodium mordenite must be something different.

Not having done spectroscopic studies, we cannot definitely identify the sites. The effect of water on MMA disproportionation over Al_2O_3 may provide a clue. In a balanced equation, water can convert Lewis acid sites to Brønsted acid sites. Anhydrous alumina is postulated to have the Lewis sites, and therefore is selective to MMA disproportionation in the absence of water. Water, either explicitly added, or formed from the reaction of MeOH plus NH_3, transforms the alumina sites to their Brønsted forms which have the selectivity typical of acid catalysts in amines synthesis. Finally we must postulate that no Brønsted acid sites form on sodium mordenite, even in the presence of MeOH or water.

Reaction rates measure the product of the number of sites times their intrinsic activity. We have not studied the problem of differentiating a small number of very active sites from a majority of weakly active sites.

Methyl amines synthesis is much slower on selective sites such as sodium mordenite than on nonselective sites such as hydrogen mordenite. The presence of even small numbers of Brønsted acid, nonselective, sites masks the selective behavior. The behavior of DME is consistent with adsorption expectations, as DME is much less strongly adsorbed than MeOH, and the relationship with NH_3 reverses. The overall reaction is also slower than when MeOH is the carbon source.

CONCLUSIONS

Sodium mordenite is a selective catalyst for the formation of methylamine and dimethylamine relative to trimethylamine. Hydrogen mordenite, although having the same pore structure as sodium mordenite, is a very active, nonselective catalyst. Shape selectivity is not a critical factor in the methylamines selectivity with sodium mordenite. The pore structure of sodium mordenite is accessible to all three methylamines by both TGA and relative rate measurements.

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