

# Steric aspects in methylamine and dimethylether synthesis over acidic mordenites

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## Abstract

Mechanistic and steric aspects of direct amination of methanol over Brønsted acidic mordenites were investigated using in situ infrared (IR) spectroscopy and kinetic studies. It was found that the rate of formation of the primary product monomethylamine is linearly correlated to the total concentration of available methyl groups from methylammonium ions rather than the acid site concentration. This indicates scavenging of methyl groups by ammonia and amines is likely to be the major pathway for amine formation. Differences in selectivity to the different amines, i.e., mono-, di- and trimethylamine, are related to differences in hindrance for the diffusion of the larger molecules. Higher concentration of alkylammonium ions in the pores and higher substitution of sorbed molecules suppress formation of trimethylamine. The selectivity to dimethyl ether seems also to be controlled by such steric factors. Lowering the effective available space for formation and transport retards dimethyl ether formation or leads to more dimethyl ether reacting to amines. A concerted bimolecular mechanism involving weakly sorbed methanol species is proposed to be the main pathway for ether formation. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Methylamine; Dimethylether; Acidic mordenite; IR spectroscopy

## 1. Introduction

The industrial production of methylamines via the reaction of methanol with ammonia is usually carried out over amorphous solid acids, i.e., alumina or silica–alumina [1–3]. Under these conditions the products are close to the thermodynamic equilibrium, trimethylamine (TMA) being the main product. However, the most interesting products from a commercial point of view are the lower substituted amines, especially dimethylamine (DMA) [3]. This has

been the incentive for research efforts to obtain nonequilibrium mixtures of methylamines in the amination of methanol by using shape-selective catalysts, such as zeolites [1–15] or carbon modified silica aluminas [16].

In this respect small pore zeolites, like chabazite, RHO and ZK-5, have been studied extensively [4–6]. Abrams et al. [7,8] showed that the distribution of methylamines over a series of Brønsted acidic, small pore zeolites can be correlated to their microporous volume indicating that the formation of these amines is governed by (i) the retention of bulky TMA molecules inside the pores and (ii) transition state selectivity due to steric constraints.

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Also medium-pore zeolites show greater selectivity toward the lower substituted amines, especially (partially) alkali-exchanged [9,10], steam-treated [11,12] and silylated samples [13,14]. Preferential adsorption of methanol is responsible for the high selectivity toward monomethylamine (MMA) over alkali-exchanged zeolites [9,15]. Over the modified acidic mordenites diffusional constraints suppress the release of TMA from the pores, increasing the selectivity toward the lower methylated products [13]. The reported selectivities on Brønsted acidic mordenites, however, vary substantially and a more detailed understanding of the processes inside the pores on a molecular level is required for catalyst design. We report, therefore, here on the crucial parameters that influence the selectivity to a particular amine and to dimethylether, an unwanted side product from methanol.

## 2. Experimental

### 2.1. Catalysts

Brønsted acidic mordenites with a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 10 (HMOR10), 15 (HMOR15) and 20 (HMOR20) were obtained from the Japanese Catalysis Society [17]. The adsorption/desorption curves were measured on a Micromeritics ASAP 2400 porosimeter. The surface area and the micropore volume were calculated from these curves with, respectively, the BET and Harkins–Jura method. The amount of extra framework aluminum (EFAL) was determined by  $^{27}\text{Al}$  MAS NMR using a Varian Unity WB 400 spectrometer with RT CP/MAS probe head. The concentration Brønsted acid sites was calculated from the amount of irreversibly adsorbed ammonia at 373 K (for details see Refs. [15,18]).

In order to obtain a material with a low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio containing less extra framework material than HMOR10 (believed to cause the reduction in micropore volume of HMOR10

compared to the other samples), HMOR10-E was prepared by suspending sodium mordenite ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 10$ ) in a hot 0.01-M EDTA solution and refluxing for 16 h. The suspension was filtered, washed, dried and subsequently three times ion-exchanged in a 1-M ammonium nitrate solution. After filtration, the residue was repeatedly washed with hot water until nitrate was not detected in the effluent.

A fraction of HMOR20 was silylated on the outside of the crystals. For this, 1 g of the activated mordenite was suspended in 25 ml *n*-hexane at room temperature. Tetraethoxysilane (TEOS) was added, the amount of which was calculated to result in a weight gain of 4% based on conversion of TEOS to  $\text{SiO}_2$ . After 1 h of stirring at room temperature, the solvent was removed by evaporation and the remaining HMOR20-M was calcined in synthetic air for 2 h at 773.

The physico-chemical properties of the catalysts are summarized in Table 1.

### 2.2. Kinetic measurements

The catalytic experiments at high methanol conversions (> 30%) were performed in a continuous-flow fixed-bed tubular quartz reactor. Gas flows (ammonia, helium) were adjusted using mass-flow controllers and methanol (MeOH) was introduced into the system via a syringe pump. The reactor effluent was stored in sample loops (500  $\mu\text{l}$ ) of a multiposition valve and subsequently analyzed by gas chromatography using a packed column (3 m stainless-steel column packed with 25% carbowax 400 and 2.5% KOH on acid washed Chromosorb W) for separation, as described in Ref. [9]. Typically, the reaction was carried out at 633 K after activation of the catalyst (10–150 mg) in flowing helium at 823 K for 1 h. A partial pressure of  $5 \times 10^3$  Pa of each reactant (nitrogen to carbon (N/C) ratio = 1) was applied, balanced with helium to  $10^5$  Pa.

For the in situ infrared (IR) spectroscopic studies, the plug flow reactor was replaced by

Table 1  
Physico-chemical properties of the investigated mordenite samples

Catalyst	Specific area (m <sup>2</sup> /g)	Microporous volume (cm <sup>3</sup> /g)	Si/Al	EFAL (%)	Brønsted acid sites (mol/g)
HMOR20	390	0.13	10	n.d.	$1.3 \times 10^{-3}$
HMOR15	350	0.15	7.5	11	$1.7 \times 10^{-3}$
HMOR10-E	280	0.10	6	n.d.	$2.0 \times 10^{-3}$
HMOR10	130	0.05	5	8	$2.1 \times 10^{-3}$
HMOR20-M	350	0.15	10.4	10	$1.1 \times 10^{-3}$

n.d. = Not detected (< 5%).

an IR cell, which approximates a continuously stirred tank reactor with a reactor volume of 1.5 cm<sup>3</sup> (for details see Ref. [17]). This experimental setup allows simultaneous analysis of the sorbed products inside the zeolite pores and the products in the gas phase. The spectra recorded during the reaction were fitted in the spectral range between 1700 and 1350 cm<sup>-1</sup> via a multicomponent fit with reference spectra. These spectra were obtained by sorbing the individual reactants and products in a vacuum system at reaction temperature and a partial pressure of 1 Pa. Under these conditions reactive sorption of the methylamines (with exception of TMA) could be suppressed. Due to the low amount of sample possible in this reactor (< 5 mg pressed into self-supporting wafers) the methanol conversion could only be varied between 5 and 20% in these experiments, by varying the total flow rates from 20 ml/min to 3 ml/min (for details, see Ref. [19]).

Additionally, pressure transient response experiments were performed in the same system. The experiments were carried out by switching from pure carrier gas (He) to a gas stream containing the reactants by means of a dead volume free switching valve. For the steady state isotopic transient experiments, the reactant stream containing methanol and ammonia was replaced by a stream containing deuterated methanol (CD<sub>3</sub>OH) and ammonia in the same concentration.

The reported conversions are based on the methanol consumption. To compare the activities in methylamine synthesis for the different

catalysts, the rates of formation of the products were calculated at conversions lower than 5%. Due to the sequential nature of the amination reactions, only the primary products (i.e., MMA and dimethylether (DME)) were present in significant concentrations in the product stream under these conditions (product selectivity > 85%). The selectivities over the different catalysts were compared at intermediate (35%) and high (85–90%) methanol conversion. The total amine selectivity describes the molar ratio between the sum of methylamines and all reaction products (including DME as by-product). The selectivity towards each methylamine is given as the molar ratio between the concentration of this amine and the sum of all methylamines formed.

### 3. Results

Using the in situ IR cell the gas-phase concentrations and surface concentrations (obtained by quantitative evaluation of the IR spectra) of the reactants and products of the amination of methanol were measured as a function of methanol conversion over different mordenite catalysts. The conversions were varied by changing the space velocities for the different runs. It was found that at low methanol conversions (up to 20%) the concentration of the sorbed species remains constant (see Fig. 1).

For different mordenite samples the concentration of the sorbed species, NH<sub>3</sub> until TET (tetramethyl ammonium ions), as measured with

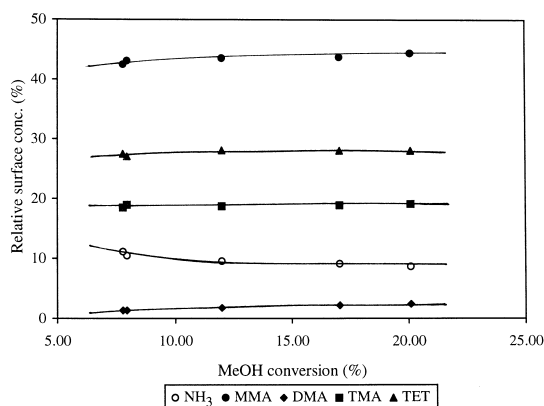


Fig. 1. Relative surface concentrations of sorbed species in HMOR15 as function of methanol conversion.

in situ FTIR, are given in Table 2. For these zeolites, the rate of formation of MMA and DME (the main by-product in direct methanol amination) at low methanol conversion are compiled in Table 3. A direct correlation between concentrations of chemisorbed molecules and their rates of formation is not observed.

From Tables 1 and 3 and Fig. 2, where the rate of MMA formation is plotted against the total amount of methyl groups from sorbed

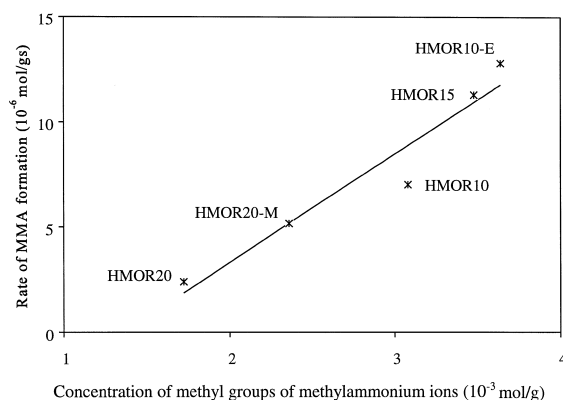


Fig. 2. Dependence of the reaction rates to MMA on the concentration of methyl groups of sorbed methylammonium ions.

species, it can be seen that the rate of MMA formation is not proportional to the acid-site concentration, but rather to the total concentration of methyl groups from sorbed species. Note, however, that the straight line intercept with the  $x$  axis at a positive value indicates that not all methyl groups participate in the reaction. It is also evident, when comparing Table 3 with Table 1 and Fig. 2, that the rate of DME formation is independent of the acid site concentration and the concentration of methyl

Table 2

Concentration of sorbed species on investigated mordenites under differential reaction conditions

Catalyst	Chemisorbed species ( $10^{-4}$ mol/g)					Relative concentration (%)				
	NH <sub>3</sub>	MMA	DMA	TMA	TET	NH <sub>3</sub>	MMA	DMA	TMA	TET
HMOR20	2.5	6.4	2.7	0.2	1.2	19	50	21	2	9
HMOR15	1.7	7.1	0.2	3.1	4.5	10	43	1	19	27
HMOR10-E	4.4	6.4	2.0	2.8	4.4	22	32	10	14	22
HMOR10	4.1	10	2.3	1.6	2.8	20	48	11	8	13
HMOR20-M	1.1	4.0	0.8	2.0	3.1	10	36	8	18	29

$$p_{(\text{MeOH})} = 5 \times 10^3 \text{ Pa}, p_{(\text{NH}_3)} = 5 \times 10^3 \text{ Pa}, T = 633 \text{ K.}$$

Table 3

Reaction rates to MMA and DME over mordenites under differential reaction conditions

Catalyst	Conversion (%)	Rate ( $10^{-6}$ mol/(g s))		Turnover frequency ( $10^{-3}$ /s)	
		MMA	DME	MMA	DME
HMOR20	5	2.4	2.2	1.9	1.7
HMOR15	4	11	1.4	6.7	0.8
HMOR10-E	8	13	3.0	6.4	1.5
HMOR10	9	6.8	1.1	3.2	0.5

$$p_{(\text{MeOH})} = 5 \times 10^3 \text{ Pa}, p_{(\text{NH}_3)} = 5 \times 10^3 \text{ Pa}, T = 633 \text{ K.}$$

groups from methylammonium ions sorbed inside the zeolite pores.

The selectivity in the methylamine synthesis of the different mordenite catalysts was compared at two methanol conversion levels (i.e., at 35% and 90%). The data are summarized in Table 4. Upon varying the conversion, similar trends were observed for all catalysts. With increasing conversion, the selectivity toward MMA decreased and the selectivity toward TMA increased. The selectivity toward TMA decreased in the order HMOR20 > HMOR15 = HMOR10-E > HMOR10. The silylated sample (HMOR20-M) showed a very low selectivity to TMA and DME (i.e., high total amine selectivity).

To further establish the independency of DME formation from the concentration of methyl groups, an isotopic transient experiment was performed. Three milligrams HMOR20 were activated, saturated with ammonia (50 mbar at 360°C for 30 min) and exposed to 50 mbar of CH<sub>3</sub>OH for 30 min. This treatment caused the acidic mordenite sample to be loaded with alkyl ammonium ions [18]. Then, the CH<sub>3</sub>OH-containing stream was switched to a CD<sub>3</sub>OH/NH<sub>3</sub> stream (50/50 mbar). The results are shown in Fig. 3. In this figure, the relative abundance of CH<sub>3</sub>OCH<sub>3</sub>, CH<sub>3</sub>OCD<sub>3</sub> and CD<sub>3</sub>OCD<sub>3</sub>, as well as CH<sub>3</sub>NH<sub>2</sub> and CD<sub>3</sub>NH<sub>2</sub> in the effluent gas are plotted vs. time on stream. CH<sub>3</sub>NH<sub>2</sub> was present long after the switch has been made,

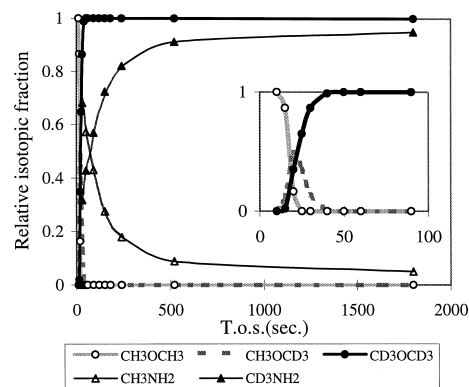


Fig. 3. Relative concentrations of CH<sub>3</sub>OCH<sub>3</sub>, CH<sub>3</sub>OCD<sub>3</sub>, CD<sub>3</sub>OCD<sub>3</sub> and CH<sub>3</sub>NH<sub>2</sub>, CD<sub>3</sub>NH<sub>2</sub> during isotopic transient experiment ( $p_{\text{reactant}} = 5 \times 10^3$  Pa,  $T = 633$  K).

whereas CH<sub>3</sub>OCH<sub>3</sub> and CH<sub>3</sub>OCD<sub>3</sub> disappeared after 40 s.

## 4. Discussion

### 4.1. Selectivity to amines

The mechanism for the direct amination of methanol by ammonia has been shown to consist of two major steps. A relatively fast step in which ammonium ions or methylammonium ions on the Brønsted acid sites are alkylated via nucleophilic substitution and a slower step in which methylamines are released into the gas phase by either adsorption-assisted desorption

Table 4  
Amine selectivities over investigated mordenite catalysts

Catalyst	WHSV (h <sup>-1</sup> )	Conversion (%)	Total	Amine selectivity (mol%)		
				MMA	DMA	TMA
HMOR20	2.3	35	76	55	20	25
	0.4	89	85	20	25	55
HMOR15	4.0	34	87	67	18	14
	0.8	93	95	28	25	47
HMOR10-E	6.5	33	79	71	17	12
	1.0	86	87	36	19	45
HMOR10	2.7	34	92	73	21	7
	0.5	89	95	40	36	24
HMOR20-M	2.8	35	96	67	30	3
	0.5	87	98	32	62	6

$p_{\text{(MeOH)}} = 5 \times 10^3$  Pa,  $p_{\text{(NH}_3\text{)}} = 5 \times 10^3$  Pa,  $T = 633$  K.

or by scavenging of methyl groups from adsorbed species by ammonia or free amines [18,20]. The rate of MMA formation is not directly correlated to the concentration of Brønsted acid sites, which was also reported by Chen et al. [21]. Note, however, that the rate of methylation seems to be proportional to the total concentration of methyl groups of adsorbed methylammonium ions which strongly suggests that the methyl scavenging mechanism is the major pathway.

Abrams et al. [8] already showed over a series of RHO zeolites that the yield to TMA decreased with the gravimetrically determined amount of physisorbed (but not chemisorbed) TMA inside the zeolite pores. A decrease in physisorbed TMA suggests diffusional constraints for the bulky TMA leading to disproportionation of TMA. Hence, under steady state the diffusion limitation is coupled to transalkylation reactions leading to lower amines. The amination process can be schematically represented by Scheme 1.

A catalyst with more severe steric constraints for diffusion of the higher substituted amines will lead to an increase of these higher substituted amines ( $\text{MeNR}^A\text{R}^B$ ) in the pores, thereby enhancing the rate of the back reaction (with constant  $k_{-3}$ ). The lower substituted amines ( $\text{HNR}^A\text{R}^B$ ) can diffuse out of the pores more easily, thereby retaining the driving force for their formation.

We observed an increase in selectivity to TMA with decreasing acid-site concentration which can be well explained by the model proposed above. A catalyst with a lower acid-site concentration will contain less adsorbed alkylammonium ions than a catalyst with a high concentration. Therefore, more void space in the

pores may exist under reaction conditions in the aluminum poor material (low Brønsted acid site concentration) than in an aluminum-rich material. This higher void space in the former material allows easier formation and diffusion of TMA out of the pores.

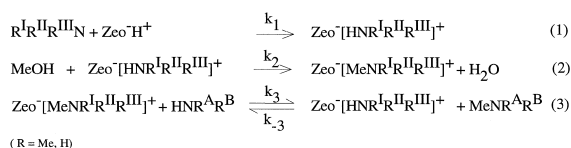
With HMOR20-M showing a very low TMA selectivity, TMA formed in the pores of the mordenite cannot leave the channels as the diameter of the pore mouth opening is smaller than the kinetic diameter of the TMA [13,20]. Fig. 2 shows that the silylation, which destroys all Brønsted acid sites at the external surface of the zeolite, did not decrease but increase the catalytic activity. This indicates that the contribution of Brønsted acid sites at the crystallite surface to the amination reactions is very small.

Another interesting feature of Fig. 2 is the positive intercept with the  $x$  axis indicating that in these materials the reaction would cease at a concentration of approximately 1.3 mmol methyl groups per gram zeolite. It is likely that the portion of inactive methylammonium ions present in the catalyst is adsorbed on sites which are located in the side pockets of the mordenite where they can be formed, but are effectively inaccessible for amination reactions.

#### 4.2. Selectivity to DME

DME is by far the most abundant byproduct in the direct amination of methanol. Its formation seems to be affected by several factors such as (i) the ammonia and methanol partial pressures, (ii) the concentration of the acid sites (iii) the modification of the outer zeolite surface by TEOS and subsequent hydrolysis (silylation). While it is conceptually easy to understand that with increasing ammonia and decreasing methanol partial pressure the rate and selectivity to form DME decreases the other two factors are more subtle to explain.

As it was observed that the silylation of the catalyst drastically reduced the DME formation, one tends to speculate that the DME formation



Scheme 1. Reaction steps in alcohol amination.

takes place at the outer surface of the zeolite. Silylation is known to eliminate the (weak) acid sites on the outer surface [22,23]. If only these sites at the outer surface were active for DME production, one would expect for the parent material a sympathetic variation of DME formation with acid site concentration (the variations in the concentration of the acid sites should be reflected at the surface of the zeolite crystals). In contrast, DME selectivity decreased with increasing concentration of acid sites. Thus, let us tentatively conclude that the contribution of external acid sites to DME formation is small. (Note in that context that the estimated concentration of acid sites on the outside of the parent material is approx. 0.1 mmol/g, based on the loss of acid sites during silylation, the increase of percentage inactive material and EFAL).

If one assumes the DME to be formed inside the pores, three possible pathways can be proposed: (i) Direct bimolecular reaction of two methanol over a Brønsted acid site, (ii) scavenging of methyl groups by methanol, similar to amination, and (iii) methanol coordinated to a weak sorption site (e.g., ammonium ion) reacts with another methanol molecule.

The first of the three possibilities can be ruled out as only (alkyl)ammonium ions have been observed in the materials studied and all sites have seen to be occupied. If (spectroscopically undetected) trace amounts of methoxy groups or free Brønsted acid sites would exist under reaction conditions, it is safe to assume that their concentration would be proportional to the concentration of tetrahedrally coordinated aluminum in the zeolite lattice. The results show clearly, however, that the rate of DME formation decreases as the concentration of aluminum in the lattice increases.

The second route, i.e., the scavenging of methyl groups from methylammonium ions, would require that the rate of DME formation would vary in parallel to their concentration. Thus, a sympathetic variation of the rates of amination and DME formation should be observed. We clearly see that both conditions are

not fulfilled. Thus, we can conclude that the formation of DME during amination does not proceed via (i) reaction of two methanol molecules on an empty Brønsted site, (ii) reaction of methanol with methoxy groups formed by elimination of water from a methanol on a Brønsted acid site or (iii) direct scavenging of methyl groups from sorbed methylammonium ions by methanol.

The third route, i.e., the condensation of two methanol molecules to DME on weakly acidic sites, such as the ammonium ions or defect sites remains as the most probable possibility. Intuitively it is clear that a higher concentration of acid sites (leading to a higher concentration of alkylammonium ions in the pores) and a higher degree of methylation of the ammonium ions would diminish the space available for DME formation and reduce the rate.

However, one has also to consider that in a secondary reaction DME can also react with ammonia to amines, although with lower reaction rate than methanol [24]. In that case the decrease in DME selectivity could be caused by a lower concentration of acid sites (reducing the rate of formation) or by a longer residence time of DME inside the pores (favoring the rate of removal through amination). The concentration and degree of substitution of the sorbed methylammonium ions are directly related to this. A high concentration of highly substituted methylammonium ions will severely reduce the available effective pore volume for diffusion. So one would expect a relatively high rate of DME production for HMOR20, which has the highest available effective pore volume due to a lower acid-site concentration and relatively low degree of substitution of the methylammonium ions, and the lowest for HMOR10 and HMOR20-M, in accordance with our observations. Additionally one could speculate that a higher degree of substitution of the ammonium ions might hinder favorable coordination of two methanol molecules.

To support the above conclusions, we performed isotope transient experiments that allow

to relate the residence time of isotopically marked molecules and surface fragments to the observed overall kinetic results. The pores of a mordenite sample were preequilibrated with methylammonium ions and then exposed to a stream of  $\text{CD}_3\text{OH}/\text{NH}_3$ .  $\text{CH}_3\text{NH}_2$  was present in the effluent stream more than 30 min after the start consistent with earlier in situ IR experiments under comparable conditions [19] in which methylammonium ions in HMOR were depleted by a stream of 50 mbar ammonia. DME, however, was exclusively produced as  $\text{CD}_3\text{OCD}_3$  already after 40 s on stream suggesting that DME does not use the pool of methyl groups present in the form of methylammonium ions. This proves that direct scavenging of methyl groups by methanol is not a significant route to produce DME under the present reaction conditions. It is interesting to note that between 20 and 40 s on stream still some  $\text{CH}_3\text{OCD}_3$  is formed, although gas phase  $\text{CH}_3\text{OH}$  was not present. This effect tentatively attributed to the somewhat slower diffusion of DME out of the mordenite pores of the mordenite, compared to methanol.

## 5. Conclusions.

Brønsted acidic mordenites are highly active for the synthesis of methylamines via the reaction of methanol with ammonia. The catalytic activity is affiliated with the presence of methylammonium ions which are formed by a rapid reaction between (alkyl)ammonium ions and methanol. The rate-determining step seems to be the reaction between ammonia and these alkylammonium ions. A significant fraction of the methyl groups in the methylammonium ions, however, seem to react markedly slower. We speculate that these methyl groups are less accessible, e.g., from methylammonium ions in the mordenite side pockets.

Selectivities to the different methylamines and to DME differ drastically for the different mordenite samples investigated. Steric effects

play a large role in determining these selectivities. Selectivity to TMA and the selectivity to DME were concluded to be affiliated with the total available micropore volume for diffusion under reaction conditions. This volume is mainly determined by the concentration and degree of substitution of the sorbed alkylammonium ions. Silylation of the mordenite does not markedly decrease the intrinsic pore volume, as measured by nitrogen adsorption/desorption, but it drastically decreased the available pore volume for diffusion by increasing the concentration and substitution of the products in the pores. In general, zeolites with a fairly large pore volume and narrow pore openings (such as modified mordenites) seem to be ideally suited for the amination reaction, in which slow diffusion of unwanted bulky product and the reequilibration of the amines play a large role.

The formation of DME from methanol is concluded to be catalyzed by condensation over (alkyl)ammonium ions. Scavenging of methyl groups from methylammonium ions by methanol is concluded not to be a significant pathway. In addition to possible spacial problems, formation of DMA, similar to the higher substituted amines, is reduced by diffusional constraints allowing DME to react to form amines.

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