ELSEVIER

Catalysis Today 37 (1997) 71-102

CATALYSIS TODAY

Methylamines synthesis: A review[1]

David R. Corbin*, Stephan Schwarz, George C. Sonnichsen

DuPont Company, Central Research and Development, Experimental Station, Wilmington, DE 19880-0262, USA

Abstract

Monomethylamine (MMA), dimethylamine (DMA) and trimethylamine (TMA) are major industrial chemical intermediates. Generally, these compounds are prepared by reaction of methanol and ammonia over a dehydration catalyst such as silica alumina. While thermodynamics favors TMA formation, market demand is for DMA. This has led to the development of highly DMA selective zeolite-based catalysts. In this article, the history of, the reported routes to, the design of new catalysts for, and the mechanism of the synthesis of methylamines are discussed.

Keywords: Zeolite; Catalysis shape-selective;; Methylamine synthesis

1. Background

1.1. Introduction

With worldwide production of approximately 1.8×10^9 lbs/year, monomethylamine (MMA), dimethylamine (DMA) and trimethylamine (TMA) are major industrial chemical intermediates. They are used in such areas as pesticide production, solvent production, and water treatment. Thermodynamics favors the production of TMA while the largest worldwide demand is for DMA. This has led to major research efforts in the design of new, selective catalysts. Although the amines are prepared primarily from reaction of methanol (MeOH) and ammonia (NH_3) over a dehydration catalyst, numerous other starting materials and routes have been studied. It is the purpose of this article to review the history of, the reported routes to, the design of new catalysts for, and the kinetics and thermodynamics of the synthesis of methylamines.

1.2. Thermodynamics

The synthesis of methylamines from methanol and ammonia is described the following equilibrium reactions [1]:

		$\Delta G°$(kcal/g mol)
Amination	$MeOH+NH_3\rightarrow MMA+H_2O$	−4.13
	$MMA+MeOH\rightarrow DMA+H_2O$	−7.24
	$DMA+MeOH\rightarrow TMA+H_2O$	−8.39

---

*Corresponding author.

[1] Contribution Number 7447

PII S0920-5861(97)00003-5

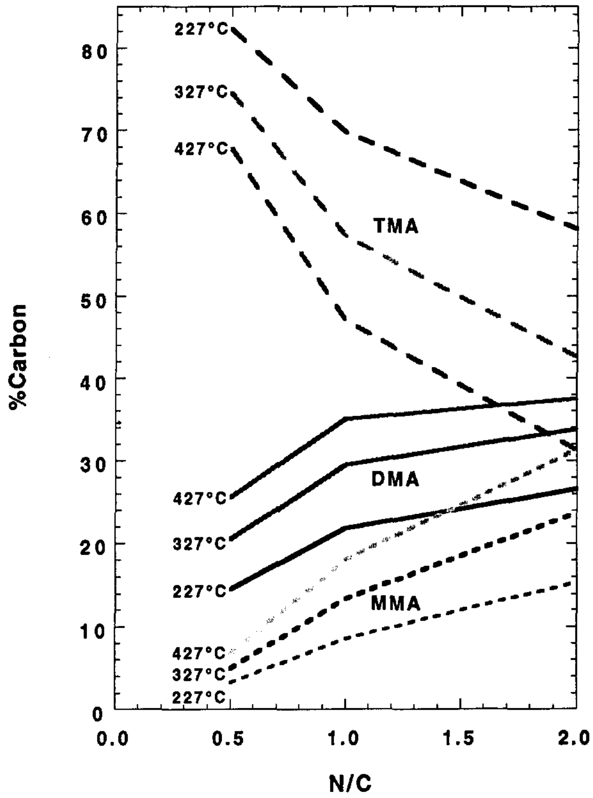

Fig. 1. Thermodynamic equilibrium in methylamines synthesis.

Disproportionation	$2MMA \rightarrow DMA+NH_3$	−3.11
	$MMA+DMA \rightarrow TMA+NH_3$	−4.15
	$2DMA \rightarrow TMA+MMA$	−1.15
DME formation	$2MeOH \rightarrow DME+H_2O$	−3.95
Also	$DME+NH_3 \rightarrow MMA+MeOH$	−0.28

DME (dimethylether) will undergo the same reactions as methanol with NH_3, MMA and DMA.

Fig. 1 [1] shows how the thermodynamic equilibrium is governed by temperature and N/C (molar ratio of NH_3 to MeOH). TMA is clearly the main product when equilibrium is approached. At 400°C and N/C=1, the M/D/T molar split (MMA/DMA/TMA molar ratio) is 17/21/62. At high MeOH conversion where equilibrium is approached, TMA is the major product; however, world demand is very different with DMA being the most desired product. The demand for methylamines is summarized in Table 1.

Table 1
Methylamines demand [179]

Region	1991 consumption of methylamines (10^6 lb)			Mass ratio	Mole ratio
	MMA	DMA	TMA	MMA/DMA/TMA	MMA/DMA/TMA
US	62	143	46	25/57/18	34/53/13
Western Europe	59	191	62	19/61/20	26/59/15
Japan	10	79	10	10/80/10	14/78/8
Equilibrium				10/18/72	17/21/62

1.3. Historical perspective

In 1884, the synthesis of methylamines in batch mode from methanol (MeOH) and ammonia (NH_3) using zinc chloride as a dehydrating agent was first reported [2,3]. It was not until 1909 that Sabatier and Mailhe reported amination of alcohols in the vapor phase [4]; however, they did not report the use of methanol. The actual first use of MeOH is attributed to Smolenski and Smolenski [5] who used an alumina catalyst. They reported not only MMA, DMA and TMA, but also olefins and ethers (from the side reaction of methanol). Other early studies [6–8] led to patents, the first of which was granted to DuPont [9] followed shortly thereafter by ones to commercial solvents corporation [10].

Commercial Solvents Corporation first made methylamines commercially in Terre Haute, Indiana, in the middle 1920s for use by the tanning industry for dehairing of animal skins [11,12]. The process that was commercialized by them and others was and is still today essentially the contact of gaseous methanol and ammonia over a dehydrating catalyst (e.g., alumina, silica–alumina) at elevated temperatures followed by the collection and separation of the products, MMA, DMA and TMA. Soon after, Rohm and Haas, and then DuPont in 1929, followed with their own commercial operations [13].

Today, worldwide production of methylamines is approximately 1.8×10^9 lb/year [14–24] with primary uses in pesticide production, solvent production and water treatment as summarized in Table 2.

2. Commercial practice

Most methylamines processes currently use amorphous silica–alumina catalysts for the exothermic reaction, which takes place at approx. 390–430°C and approx. 20 atm. Adiabatic fixed bed plug flow reactors are reported for this purpose [25]. The product distribution obtained approaches equilibrium; DMA production is enhanced by recycling TMA which can be costly. Various reference books [1,26] contain brief process descriptions. A simplified process diagram is given in Fig. 2.

Various purification trains and processes have been discussed [27–33].

A new process has been reported by Nitto process [34] that makes use of a modified mordenite zeolite catalyst which minimizes TMA formation through product shape selectivity. The pore size of the microporous mordenite catalyst is modified to an effective size smaller than TMA such that only DMA and MMA can escape the catalyst. This process has been commercialized in Japan [35] with capacity estimated at about 100 MM lb/year.

Two kinds of modified mordenites have been described, an acid- and steam-treated one and a $SiCl_4$-modified one [34]. The former reduces TMA production to about 17 mol% (at N/C=1.9, 320°C, 18 atm), while the latter can reduce TMA to 1% (at N/C=1, 380°C, 1 atm).

Table 2
Major applications of methylamines [17]

MMA	Pesticides	37%
	N-Methylpyrrolidone	35%
	Alkylalkanolamines	15%
	Others	13%
DMA	Solvents (dimethylformamide, dimethylacetamide)	41%
	Water treatment	20%
	Dimethylaminoethanol	12%
	Fatty tertiary amines	10%
	Others	17%
TMA	Choline chloride	70%
	Others	30%

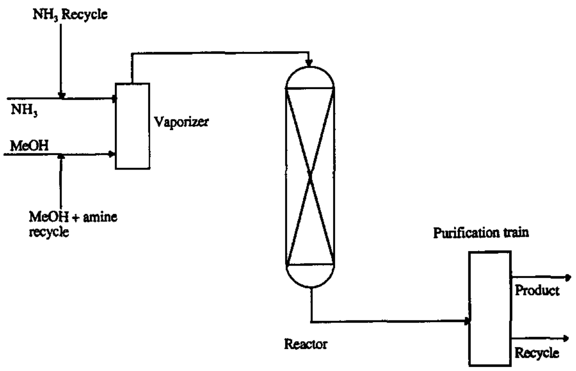

Fig. 2. Simplified methylamines process diagram.

Nitto has claimed a two reactor process, one containing the mordenite and the other a more conventional γ-Al_2O_3 catalyst [36,37]. Nitto also claims [38] that catalyst life is improved by restricting the concentration of aldehydes (poison to zeolites) in the zeolite bed to less than or equal to 0.15 g/h/kg cat. Other processes have been reported [25,39] including a fluidized bed process [40] which makes use of attrition resistant zeolites rho or chabazite, spray-dried with kaolin, bentonite, α-Al_2O_3 or TiO_2.

3. Non-zeolitic catalysts

3.1. *Non-silica–alumina catalysts*

As summarized in Table 3, a variety of catalysts for the vapor phase methanol–ammonia reaction have been reported in the open literature, including aluminas, silicas, zirconia, thoria and phosphates. These data include patent literature showing that many other materials that perform dehydration chemistry have been used for methylamines synthesis; even crushed building tile was reported [10]. Among the more exotic reports are a photocatalytic Pt/titania [41] system where at MeOH conversion of $<0.1\%$ only TMA is produced and a heteropoly acid [42] catalyst that suppresses TMA completely at 477°C and $N/C=2$. Interestingly, a 1935 patent to DuPont mentions zeolites as possible supports for aluminas [43].

It was recognized early on that a high N/C ratio favored MMA formation [9]. The temperature range employed was, as expected, large 250–500°C. The first process using higher than atmospheric pressures was patented by IG Farben [44], with pressures >50 atm being used. However, separation of methylamines by distillation under pressure was already mentioned by Martin and Swallen [10].

3.2. *Silica–alumina catalysts*

As stated in the section on commercial processes, silica–alumina (SA) is currently the most widely used catalyst for methylamines synthesis. It is usually made by coprecipitation [45–47]. Heinsohn [48] used SA with approx. 87 wt% silica. Leonard [49] has reported a steamed, metal-doped SA with 85–90 wt% silica. Brake [50] has found that reduced coking and improved rates are obtained by using a high alumina (94 wt%) SA catalyst.

When a SA (46.9 wt% SiO_2) was compared to a boron phosphate and an SA–boron phosphate hybrid [51], SA was found to be the preferred catalyst; it had a higher selectivity to amines. Leaching of phosphate was observed from the phosphate–SA hybrid. Schmitz [52] showed that at the same conditions, conversion and selectivity to amines increased with increasing surface area and acidity. He also showed that montmorillonite with the same acidity as SA is less active and less selective to amines.

Table 3
Summary of non-silica/alumina methylamines catalysts

Catalyst	Reference
Alumina	[5]
Blue oxide of tungsten, thoria, silica gel, alumina, zirconia	[6]
Thoria on pumice	[7]
Alumina gel (from aluminum ethoxide)	[9]
Alumina, thoria, silica gel, kaolin, blue oxide of tungsten (in decreasing order of activity)	[8]
Various aluminas	[10]
Indianite, Blue clay, crushed building tile, doucil, Putnam clay	[10]
Phosphate and supported phosphoric acid catalysts	[180]
Preferred are partially dehydrated alumina trihydrate, aluminum silicate	[181]
Alumina gel, silica gel	[44]
Alumina or boric anhydride on silica gel, aluminum phosphate; other supports mentioned are alumina gel, zeolites	[43]
Phosphoric acid on pumice, ammonium and aluminum phosphates	[182]
Alumina on activated carbon	[183]
Alumina or thoria on charcoal	[184]
Alumina gel	[185]
Phosphate catalysts	[186]
Clay	[185]
Alumina	[187]
Preferred are dehydrated alumina trihydrate, aluminum silicate	[188]
Alumina on silica	[189]
Aluminum phosphate, kaolinite	[190]
Any dehydrating catalyst, phosphates preferred	[191]
Alumina	[192]
Harshaw alumina	[11]
Magnesium-, cadmium-, lead-, nickel-, iron-, boron phosphates; boron being preferred	[193]
Acid activated montmorillonites	[194]
Lanthanum hydrogen phosphate	[195]
Pt/Titania	[41]
Heteropolyacids	[42]

A way to improve DMA selectivity of SA catalysts was found by Foley et al. [53,54], who showed that a carbon molecular sieve hybridized with a commercial SA exhibited enhanced selectivity towards MMA and DMA, the molar ratio of (MMA+DMA)/TMA increased from 1.05 to 3.30 at a MeOH conversion of ~95%.

Comparing data on SA catalysts [29,49–51,55,56] to others based on silica and alumina like boehmite/kaolin composites [57,58], clay [59] or straight alumina [11] show clearly that these kinds of equilibrium catalysts cannot meet the amine selectivity the world demands.

4. Zeolite catalysts

4.1. Background

Zeolite molecular sieves represent a large fraction of the approximately 500 materials listed in the *Handbook of Molecular Sieves* [60]. The primary building blocks of zeolites are $\{SiO_4\}^{4-}$ and $\{AlO_4\}^{5-}$ tetrahedra. As a result of the difference in charge between these tetrahedra, the total framework charge is negative and hence must be balanced by cations, typically protons, alkali, or alkaline earth metal ions. Generally in the protonic or acid form, these materials behave as solid acids and as such are excellent candidates as catalysts for methylamines synthesis. In addition, the $\{SiO_4\}^{4-}$ and $\{AlO_4\}^{5-}$ tetrahedra are linked to form channels and cages or cavities of discrete size. The numbers of tetrahedra in the openings to these channels and cages determine the dimensions of the zeolite pore openings. Generally, zeolites are classified by the size of the largest pore opening. For example, "small-pore" zeolites are those containing 8-membered ring openings, "medium-pore" 10-membered rings and "large-pore" 12-membered ring openings. The pore openings to these channels and cages generally range from 3 to 9 Å and allow for molecular sieving.

In catalysis this molecular sieving ability is referred to as size or shape selectivity. At least three types of shape selectivity over zeolite catalysts have been described [61]:

- Product selectivity – molecules smaller than the pore openings can exit from the framework into the product stream while larger molecules are retained within the framework.
- Transition state selectivity – certain reactions are prevented because the corresponding transition state requires more space than is available within the framework of the zeolites.
- Reactant selectivity – only those components of the feed stream that are small enough to enter the pores can react while larger ones are excluded.

In the case of methylamines synthesis, if the pore size of an acid zeolite is small enough to hinder the egress of TMA (0.39×0.54×0.61 nm) and still allow easy exit of MMA (0.37×0.39×0.44 nm) and DMA (0.39×0.47×0.60 nm) [62], the final product distribution should be skewed towards the smaller MMA and DMA due to "product selectivity".

A listing of the numerous molecular sieves that have been investigated as methylamines catalysts is given in Table 4 with their respective pore sizes. In addition, illustrations of the frameworks of three of the most studied zeolites, mordenite, rho and chabazite are given in Fig. 3.

Table 4
Zeolites reported as methylamines catalysts [60,196]

Catalyst	Structure type	Pore size (Å)		
		8-Membered ring	10-Membered ring	12-Membered ring
H–Y, RE–Y	FAU			7.4
Mordenite	MOR	2.6×5.7		6.5×7.0
H-Offretite	OFF	3.6×5.2		6.4
H-T	OFF/ERI	3.6×5.2 3.6×5.2		6.4
H-ZSM-5	MFI	5.4×5.6 5.1×5.5		
FU-1			5.0–5.2[a]	
NU-85	EUO/NES		4.1×5.7 4.7×6.0	
Clinoptilolite	HEU	2.6×4.7 3.3×4.6	3.0×7.6	
Ferrierite, H-ZSM-21	FER	3.5×4.8	4.2×5.4	
ZSM-11	MEL		5.3×5.4	
5A	LTA	4.1		
NU-3	LEV	3.6×4.8		
Chabazite, SAPO-34	CHA	3.6×3.7		
H-Rho	RHO	3.6		
H-ZK-5	KFI	3.9		
H-Erionite	ERI	3.6×5.2		
H-Phillipsite	PHI	3.6 3.0×4.3 3.2×3.3		

[a] Estimated values.

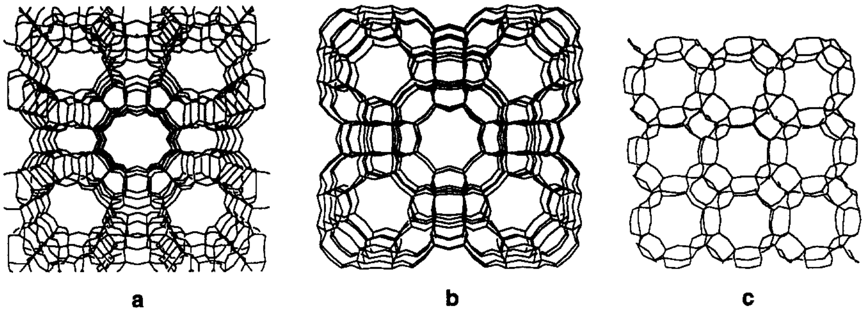

Fig. 3. Structures of zeolites (a) mordenite, (b) rho and (c) chabazite.

In the review of catalytic work in this area given below, the following definitions will be used throughout unless otherwise specified:

$$\text{MeOH conversion} = 100 \times \left(1 - \frac{(\text{mol MeOH})_{\text{in product}}}{(\text{mol MeOH})_{\text{in feed}}}\right),$$

$$\text{N/C} = \frac{\text{mol NH}_3}{\text{mol MeOH}},$$

$$\text{Selectivity to DMA} = 100 \times \left(\frac{2(\text{mol DMA})}{\text{mol MMA} + 2(\text{mol DMA}) + 3(\text{mol TMA})}\right),$$

$$\text{Selectivity to DME} = 100 \times \left(\frac{(\text{mol DME})}{\text{mol MMA} + \text{mol DMA} + \text{mol TMA} + \text{mol DME}}\right).$$

In Tables 5–12 literature data on various zeolites is compared at similar MeOH conversions by selecting appropriate WHSVs (weight hourly space velocities) and/or reaction temperatures.

4.2. *Large-pore zeolites*

4.2.1. *Faujasite*

Very high TMA selectivities were observed by all groups reporting the use of faujasite (e.g., HY, NaY, NaX, CaX and RE-X), as a methylamines catalyst. For example, workers at DuPont [63] showed H–Y to be very selective for TMA (95% at 94% MeOH conversion) with significant DME production (24%). The data are summarized in Table 5.

4.2.2. *Mordenite*

In 1981, Weigert [64] reported that mordenite among other zeolites was a selective catalyst for MMA production. This was followed by efforts by various groups showing the effects of zeolite modification by cation exchange, steaming, extrusion, coating and $SiCl_4$-treatment on catalyst performance. The results are summarized in Table 6.

4.2.2.1. Effect of ion exchange. Weigert [64] reported that Ca-mordenite showed promise for this chemistry. Later studies reported mordenite to show selectivity toward DMA in the Mg- [56,65], Mg,H- [56,65,66] and La,H- [56,65] exchanged forms, especially in the highly exchanged forms. Weigert [67] and Ashina [68] showed certain levels of Na^+ or Na^+/K^+ appeared necessary for decreasing TMA selectivity. Keane [69] showed mordenite in the H^+-form to be relatively unselective.

Table 5
Summary of Faujasite-based catalysts

Catalyst	Temperature (°C)	WHSV (g MeOH/g cat per h)	N/C	P (atm)	MeOH conversion (%)	MMA (C%)	DMA (C%)	TMA (C%)	DME (%)	Reference
HY	300	0.93	1	1	94	1	4	95	33.1	[63]
HY	380	0.156[a]	1	1	>90	15.5	25.5	59.0	11.1	[75]
Fau	400	1.28	1.9	18	96.1	21.9	28.3	49.8	[b]	[197]
NaY	400	2.78	0.69	1	90.0	10.7	18.3	71.0	[b]	[64]
CaX	400	2.50	0.81	1	93.0	12.2	22.6	65.2	[b]	[64]
NaX	400	3.13	0.7	1	84.0	6.3	10.7	83.0	[b]	[64]
REX	332	1.39	0.82	1	89.0	8.2	18.2	73.6	[b]	[64]
13X	400	1.25	1	1	72.7	6.6	13.0	80.4	3.3[c]	[65]
SK-40	400	1.25	1	1	10.3	17.3	11.8	70.9	14.7[d]	[65]

[a] Initial rate of MeOH consumption=mol MeOH/g cat per h, WHSV=0.52–5.2 g MeOH/g cat per h.
[b] 2–3 mol% DME.
[c] 1.6 mol% of total products are olefins.
[d] 2.1 mol% of total products are olefins.

4.2.2.2. Effect of steaming. Studies [70–72] of the effect of steaming on catalyst performance showed decreased TMA levels in Na,H-, Na,K- and H-mordenite samples.

4.2.2.3. Effect of extrusion. A non-alumina binder combined with a "gelatinizer" (e.g., NH_4NO_3) used with Na, H-mordenite gave low TMA (<4%) and good DMA selectivity (approx. 60%) at N/C=1 [71,72]. Similarly, a dealuminated H-mordenite with a non-alumina binder exhibited very high MMA selectivity (>80%) at N/C=3 [73].

4.2.2.4. $SiCl_4$-treatment. Segawa et al. [74–78] showed that excellent selectivity (<1% TMA at N/C=1 and MeOH conversions >90%) could be obtained using H-mordenite formed when Na-mordenite is treated with $SiCl_4$.

4.2.2.5. TEOS-treatment. Treatment of hydrated H-mordenite with tetraethylorthosilicate (TEOS) has been shown to give catalysts with TMA selectivities <5% [79–81]. The preferred mordenite crystals have c/a or c/b >2 [82].

4.2.3. Offretite

Groeb et al. [83] found H-offretite to show some selectivity but low activity for this chemistry. Zeolite T, an intergrowth of offretite and erionite, will be discussed later.

4.3. Medium-pore zeolites

4.3.1. H-ZSM-5

Gier et al. [84] showed H-silicalite to be relatively inactive and non-selective (see Table 7). Kotowski [85] reported high MMA+DMA selectivity at 88% MeOH conversion with low DME and olefin formation but poor activity. High MMA selectivity (>80%) and TMA selectivity of <6% were reported for a ZSM-5 extrudate (alumina binder, unspecified Si/Al) at N/C=3 [73]. All other studies showed TMA selectivity greater than 25% at N/C between 1 and 3.

4.3.2. FU-1

The structure of FU-1, a high-silica zeolite (Si/Al=5–100), is not known; however, its adsorption [60,86] and catalytic [87] properties indicate it to be most likely a medium-pore zeolite with an effective pore size smaller than that of the MFI (ZSM-5) framework. Dewing et al. [86] estimate the pore size to be on the order of 5.0–5.2 Å for H-

Table 6
Summary of mordenite-based catalysts

Catalyst	Temperature (°C)	WHSV (g MeOH/g cat per h)	N/C	P (atm)	MeOH conversion (%)	MMA (C%)	DMA (C%)	TMA (C%)	DME (%)	Reference(s)
(a) *Effect of ion-exchange*										
H-Mor	325	2.0	1	1	90	7.2	10.4	82.5		[69]
Zeolon	400	1.25	1	1	85.5	9.5	31.7	58.8	1.0[a]	[56,65]
H-Zeolon	400	1.25	1	1	86	18.7	44.9	36.4	1.0	[56,65]
Na-Zeolon	400	1.25	1	1	85.5	10.8	36.2	53.0	1.1[b]	[56,65]
Mg-Zeolon	400	1.25	1	1	90.9	21.1	54.7	24.2	0.2	[56,65]
Mg,H-Zeolon	400	1.25	1	1	75.9	18.4	56.8	24.8	0.6[c]	[56,65]
La,H-Zeolon	400	1.25	1	1	94.5	20.7	58.9	20.4	0[d]	[56,65]
Cu-Zeolon	400	1.25	1	1	82.1	16.1	22.1	61.8	3.9[e]	[56,65]
Na-Mor	[f]	[f]	1	1	90	42.1	42.1	15.8	[g]	[67]
Na,H-Mor (4.2% Na)	358	1.79	0.87	1	65	50	45.9	4.1	[g]	[64]
Na,H-Mor (2.7% Na)	358	1.92	0.88	1	56	17.3	36.4	46.4	[g]	[64]
H-Mor	358	1.92	0.71	1	98	7.8	36.9	55.3	[g]	[64]
Ca-Mor	325	1.56	0.94	1	93	24.2	36.4	39.4	[g]	[64]
Ca-Mor	325	1.25	0.94	1	83	37.5	45.5	17.0	[g]	[64]
Ca-Mor	375	2.08	0.99	1	90	31.5	45.7	22.8	[g]	[64]
Sr-Mor	400	1.53	0.74	1	93	15.3	41.2	43.5	[e]	[64]
Cr-Mor	400	1.29	1.2	1	92	19.5	26.0	54.5	[e]	[64]
Na,H-Mor (4.1% Na)	350	0.64	1.9	18	83.7	42.1	37.2	20.7	[h]	[68]
K,H-Mor (3.8% K)	350	1.29	1.9	18	87.6	32.9	30.4	36.7	[h]	[68]
H-Mor	310	1.97	1.9	18	87.6	19.6	26.5	53.9	[h]	[68]
Li,H-Mor (0.3% Li)	320	1.02	1.9	18	93.2	16.5	27.8	55.7	[h]	[68]
Ca,H-Mor (1.5% Ca)	330	0.96	1.9	18	89.1	19.1	30.6	50.3	[h]	[68]
Na,H-Mor (2.1% Na)	360	0.65	1.9	18	89.2	29.2	53.7	17.1	[h]	[68]
Na,H-Mor (0.4% Na)	360	1.29	1.9	18	90.3	26.2	41.8	32.0	[h]	[68]
Na,K,H-Mor (2.0% Na, 3.7% K)	340	0.89	1.9	18	82.2	31.3	59.9	8.7	[h]	[68]
Na,Ca,H-Mor (0.7% Na, 1.0% Ca)	320	0.65	1.9	18	90.3	31.8	45.3	22.9	[h]	[68]
H-Mor	320	0.64	1.95	10	93			58[i]	[g]	[66]
H,Mg-Mor (20% Mg exchange)	320	0.64	1.95	10	92			35[i]	[g]	[66]
H,Mg-Mor (50% Mg exchange)	320	0.64	1.95	10	92			16[i]	[g]	[66]
H,Mg-Mor (96% Mg exchange)	320	0.64	1.95	10	91			9[i]	[g]	[66]
Mor, natural	400	1.79	1.9	18	96.7	26.5	36.8	36.7	[j]	[197]
Mor, natural	400	1.92	1.9	18	95.8	26.9	37.5	35.6	[j]	[197]

Table 6
(Continued)

Catalyst	Temperature (°C)	WHSV (g MeOH/g cat per h)	N/C	P (atm)	MeOH conversion (%)	MMA (C%)	DMA (C%)	TMA (C%)	DME (%)	Reference(s)
Ca,Na-Mor, synthetic	400	1.92	1.9	18	96.1	26.5	36.3	37.1	[j]	[197]
H,Na-Mor, synthetic	400	2.55	1.9	18	96.3	24.7	34.6	40.7	[j]	[197]
(b) *Effect of steaming*										
H-Mor unsteamed, natural	320	4.13	1.9	18	86.6	18.5	24.4	57.0	[h]	[70]
H-Mor steamed, natural	320	4.07	1.9	18	57.7	37.5	43.7	18.8	[h]	[70]
H-Mor unsteamed, synthetic	310	2.18	1.9	18	89.6	19.6	26.6	53.9	[h]	[70]
H-Mor steamed, synthetic	310	1.99	1.9	18	89.1	26.2	52.2	21.6	[h]	[70]
Na,K-Mor unsteamed, natural	320	1.37	1.9	18	91.5	28.6	57.1	14.3	[h]	[70]
Na,K-Mor steamed, natural	320	1.37	1.9	18	89.5	29.7	62.6	7.7	[h]	[70]
(c) *Effect of extrusion*										
Na,H-Mor steamed extrudates	390	2.08	1.1	?	90.9	35.1	60.5	3.6	0.67	[72]
Na,H-Mor steamed extrudates, no gelatinizer	390	1.56	1.1	?	91.4	18.5	67.3	11.9	1.92	[72]
Na,H-Mor steamed extrudates, less Na	430	2.08	1.1	?	88.0	15.2	66.0	16.6	2.10	[72]
Na,H-Mor steamed extrudates, Al_2O_3 binder	390	6.19	1.1	?	88.8	21.7	50.6	17.5	6.12	[72]
H-Mor, dealuminated, non-Al_2O_3 binder	425	1.23	3	1	95.1	82.2	16.5	1.2	[g]	[73]
(d) *Effect of $SiCl_4$ treatment*										
H-Mor	380	0.0445[k]	1	1	>90	26.6	25.7	47.7	19.0	[75]
Na-$SiCl_4$-Mor	380	0.00121[k]	1	1	>90	39.9	59.0	1.1	2.8	[75]
H-$SiCl_4$-Mor	380	0.0388[k]	1	1	>90	33.3	65.3	1.4	0.5	[75]
$SiCl_4$-H-Mor	380	0.0862[k]	1	1	>90	18.2	24.2	57.6	48.6	[75]
H-Mor (Si/Al=10)	380	0.52	1	1	94.1	31.4	31.0	37.6	7.6	[74–78,198]

Table 6
(Continued)

Catalyst	Temperature (°C)	WHSV (g MeOH/g cat per h)	N/C	P (atm)	MeOH conversion (%)	MMA (C%)	DMA (C%)	TMA (C%)	DME (%)	Reference(s)
H-Mor (Si/Al=15)	380	0.52	1	1	88.4	27.3	29.4	43.3	16.4	[74–78,198]
H-Mor (Si/Al=20)	380	0.52	1	1	86.4	26.6	25.8	47.6	20.6	[74–78,198]
H-Mor (Si/Al=10)/$SiCl_4$	380	0.52	1	1	98.9	35.8	61.7	2.5	0.8	[74–78,198]
(e) *Effect of TEOS treatment*										
TEOS-H-Mor (hydrated)	310	0.45	1.8	2	90	21.9	76.5	1.6	[g]	[79]
TEOS-H-Mor (unhydrated)	310	0.375	1.8	2	90	15.7	69.2	15.1	[g]	[79]
TEOS-H-Mor (c/a >2)	310	0.5	2	2	93	20.8	75.4	3.8	[g]	[82]
TEOS-H-Mor (c/a<2)	310	0.5	2	2	93	20.6	68.4	11.0	[g]	[82]
H-Mor	360	0.4	1	1	90	8.5	21.3	70.2	15	[81]
TEOS-H-Mor	360	0.4	1	1	90	19.5	75.8	4.7	2	[81]

[a] 0.6 mol% to others ($C_2^=$).
[b] 0.8 mol% to others ($C_2^=$).
[c] 0.1 mol% to others ($C_2^=$).
[d] 0.7 mol% to others ($C_2^=$).
[e] 1.0 mol% to others ($C_2^=$).
[f] For all T's, P's, WHSV's.
[g] No DME quoted.
[h] 2–3 mol% DME.
[i] mol% TMA; MMA and DMA were lumped together.
[j] 1–2 mol% DME.
[k] Initial rate of MeOH consumption=mol MeOH/g cat per h, WHSV=0.52–5.2 g MeOH/g cat per h.
Tetraethylorthosilicate (TEOS).

FU-1. Although it is believed to have a smaller pore size than ZSM-5, improved selectivity over the MFI framework was not observed (see Table 8).

4.3.3. *NU-85*

NU-85, an intergrowth [60] of zeolites EU-1 (EUO) and NU-87 (NES), both medium-pore zeolites, showed a TMA selectivity of 54.5% at 99% methanol conversion in the acid form [88] (see Table 8).

4.3.4. *Clinoptilolite*

Hutchings et al. [89] found they could activate a naturally occurring clinoptilolite zeolite by first treating it with sodium hydroxide followed by aqueous HCl treatment. The resulting catalyst was highly selective for MMA (89.6%) and showed no TMA produced at 99% methanol conversion and high N/C (=3). Other studies showed that at lower N/C ratios, H-clinoptilolite, steamed and unsteamed, was not very selective for DMA (30–40% TMA was formed) [70]. These studies are summarized in Table 8.

4.3.5. *Ferrierite*

Weigert showed TMA selectivity of 17% for a ferrierite catalyst [64] (see Table 8). H-ZSM-21, a synthetic ferrierite, has also been studied [90].

Table 7
Summary of MFI-based catalysts

Catalyst	Temperature (°C)	WHSV (g MeOH/g cat per h)	N/C	P (atm)	MeOH conversion (%)	MMA (C%)	DMA (C%)	TMA (C%)	DME (%)	Reference(s)
H-Silicalite (Si/Al=125)	400	0.93	1	1	97	9	22	69	5.9	[84]
H-ZSM-5 (Si/Al=42.5)	460	2.9	2	5	88	55.4	23.4	21.1	2.3	[85]
H-ZSM-5 (Si/Al=12.5)	380	0.03[a]	1	1	>90	10.9	21.5	67.5	20.6	[74–78]
H-ZSM-5 (Si/Al=?)	400	3.13	2	3	98	17.7	26.7	55.6	7.4	[199]
H-ZSM-5 (Si/Al=?, non-Al_2O_3 binder)	425	1.23	3	1	96.7	83.9	10.1	5.9	[b]	[73]
H-ZSM-5 (Si/Al=?)	480	3.32	1.7	3	87.8	39.6	24.9	35.5	[b]	[95]
H-ZSM-5 (Si/Al=?)	450	IR cell, 20 ml/min	3	1	72.7	42.1	28.6	29.3	2.2[c]	[83]
H-ZSM-5 (Si/Al=?)	290	1.19	1	1	81	1.3	5.0	93.8	[d]	[64]
Na-ZSM-5 (Si/Al=?)	397	1.67	0.96	1	93	11.5	22.9	65.6	[d]	[64]
H-ZSM-5 (Si/Al=?)	400	1.25	1	1	88.6	6.5	21.8	71.7	0	[65]

[a] Initial rate of MeOH consumption=mol MeOH/g cat/h, WHSV=0.52–5.2 g MeOH/g cat/h.
[b] No DME quoted.
[c] 8.2 mol% of total products were hydrocarbons.
[d] 2–3 mol% DME.

4.3.6. H-ZSM-11

Although zeolite ZSM-11 has been studied for methylamines synthesis, comparison to other zeolites is difficult because MMA and DMA selectivities were combined in the report [90].

4.4. Small pore zeolites

4.4.1. Zeolite A

Tompsett et al. [91,92] studied various cation-exchanged forms of zeolite A as methylamines catalysts and found Ca-exchange with removal of essentially all alkali cations to result in the best selectivity to MMA and DMA. In addition, it was found that addition of a binder – especially a clay binder – decreased the selectivity. Pressure studies showed that methanol conversion and DMA selectivity were not greatly affected but MMA selectivity increased and TMA selectivity decreased at low pressure. These results are summarized in Table 9(a) and (b). Studies by other groups as summarized in Table 9(c) do not show this degree of selectivity.

4.4.2. NU-3

Tompsett and Whittam [93] reported the use of the small pore zeolite NU-3, a synthetic zeolite with the levyne structure type for the selective synthesis of MMA and DMA (see Table 8).

Table 8
Summary of miscellaneous catalysts

Catalyst	Temperature (°C)	WHSV (g MeOH/g cat per h)	N/C	P (atm)	MeOH conversion (%)	MMA (C%)	DMA (C%)	TMA (C%)	DME (%)	Reference(s)
(a) *Offretite*										
H-Offretite	450	IR cell, 20 ml/min	3	1	75	31.9	33.6	34.5	9.3[a]	[83]
(b) *FU-1*										
H-FU-1	400	0.62	1.5	20	94.2	18.5	26.8	54.7	0[b]	[46, 200–202]
H,Na-FU-1	400	0.64[c]	1.5	19.0	95.5	28	31.7	40.2	0[b]	[201,203]
(c) *NU-85*										
H-NU-85	330	0.86	2	1[d]	99	19.2	26.3	54.5	[e]	[88]
(d) *Clinoptilolite*										
H,Na-Clinop, natural	400	0.074	3	1	96.6	89.6	10.4	0	[e]	[89]
H-Clinop, natural	350	1.36	1.9	18	88.2	24.7	36.0	39.3	[f]	[70]
H-Clinop, natural, steamed	350	1.37	1.9	18	85.1	27.0	40.7	32.3	[f]	[70]
(e) *Ferrierite*										
H-Fer	400	0.12	1	1	94	13	28	59	4.5	[94]
Fer,Natural	422	0.74	1.2	1	83	31.4	51.4	17.1	[e]	[64]
Ca-Fer	400	1.32	0.83	1	83	22.0	48.0	30.0	[e]	[64]
(f) *NU-3*										
H-NU-3	360	0.68	1.5	1	87.0	83.2	16.2	0.6	1.9	[93]
(g) *Erionite*										
H-Eri	400	0.46	1	1	98	18	31	51	0	[94]
H-Eri, natural	380	2.71	1.9	18	87.0	25.7	32.0	42.3	[f]	[70]
H-Eri, steamed	380	2.56	1.9	18	84.1	27.0	37.3	35.7	[f]	[70]
Ca-Eri	357	1.47	0.97	1	84	17.2	34.5	48.3	[f]	[64]
Ca-Eri	422	2.00	0.75	1	91	12.3	26.2	61.5	[f]	[64]
E-5	400	1.25	1	1	43.2	25.7	40.2	34.0	1.6	[65]
(h) *Zeolite T*										
H-T	430	3.32	1.7	3	84.5	41.4	31.4	27.2	[e]	[95]
H-Na,K-T	355	0.5	1[g]	1	88[g]	21.3	34.0	44.7	12.6[g,h]	[96,97]

[a] 21.9 mol% of total products were hydrocarbons.

[b] Assumed zero.

[c] Quoted SV assumed to read "mol MeOH/g cat per h".

[d] Assumed 1 atm.

[e] No DME quoted.

[f] 2–3 mol% DME.

[g] NH_3/DME feed.

[h] 3.5 mol% of total products were hydrocarbons.

Table 9
Summary of zeolite A-based catalysts

Catalyst	Temperature (°C)	WHSV (g MeOH/g cat per h)	N/C	P (atm)	MeOH conversion (%)	MMA (C%)	DMA (C%)	TMA (C%)	DME (%)	Reference(s)
(a) *Effect of ion-exchange*										
Na-A	380	0.35	2	1	34[a]	32.1	28.6	39.3	0[b]	[91,92]
La-A	360	0.70	1.5	1	91[a]	19.1	25.1	55.8	0[b]	[91,92]
Mg-A	360	0.70	1.5	1	99.3[a]	15.4	26.9	57.7	0[b]	[91,92]
Ce-A	360	0.70	1.5	1	88[a]	19	24	57	0[b]	[91,92]
Ca-4A	380	0.35	2	1	98.5[a]	28.8	40.9	30.3	0[b]	[91,92]
5A	380	0.35	2	1	99[a]	30.8	50.5	18.7	0[b]	[91,92]
Ca-5A	380	0.70	1.5	1	98.5[a]	27.8	59.3	13	0[b]	[91,92]
(b) *Effect of binder*										
5A without binder	380	0.31	2	1	99	30.8	50.5	18.7	[c]	[91,92]
5A with binder	380	[d]	[d]	1	90.2	23.1	30.1	46.8	[c]	[91,92]
Clay-bound 5A	360	0.63	[d]	1	82	32.9	41	26.1	[c]	[91,92]
(c) *Other studies*										
5A, Japanese reference catalyst	400	0.18	2	1	100[a]	2	9.4	88.6	0[b]	[198]
5A, Linde	400	0.93	1	1	96[a]	9	20	73	7.1	[138]
4A, Linde	400	0.12	1	1	86[a]	8	15	76	16.6	[138]
5A, Ca-4A	325	0.40	1	1	90[a]	11.9	17.7	70.4	0[b]	[69]
5A, conventional	400	1.25	1	1	54[a]	13.2	17.6	69.2	14.6	[56]
4A, conventional	400	0.51	2.3	18	85.5	27.5	29.5	42.9	[e]	[197]
Ca,Na-A, Ca-4A	400	2.08	0.68	1	95.0	12.1	19.9	68.1	[e]	[64]

[a] Assumed molar.
[b] Assumed zero.
[c] No DME quoted.
[d] Not given in reference.
[e] 2–3 mol% DME.

4.4.3. *Erionite, zeolite T*

Erionite has been studied by several groups as a methylamines catalyst [39,64,65,70,94]. This catalyst showed some selectivity, but low activity. Similar results were obtained with zeolite T, an intergrowth of zeolites offretite and erionite [95–97] (see Table 8).

4.4.4. *Chabazite*

Abrams et al. [94] claimed various chabazites as selective methylamines catalysts. For naturally occurring samples they found that the selectivity varied from source to source as shown in Table 10(a) and (b).

4.4.4.1. Effect of ion exchange. The acid forms, in some cases, showed better selectivity and activity. In addition, they found, at least for one chabazite, back-exchange of alkali-metal cations into the acid form of the zeolite led to enhanced selectivity and an apparently much more active catalyst as shown in Table 10(a) and (b).

4.4.4.2. Effect of coating and HCl treatment. Treatment of the external surface with tetraethylorthosilicate [98,99,100–102], gave improved selectivities as shown in Table 10(d). Also, HCl(g) treatment [103] lead to enhanced selectivity for both the mineral and H-forms of the zeolite as shown in Table 10(e).

4.4.4.3. Synthetic forms. Shannon et al. (1988) showed that synthetic chabazites were selective for DMA synthesis (56.1%), even though DME selectivity was high (14.3%). Starting with a different synthesis method, the K^+- and Na^+- forms are preferred, with uncalcined samples more active than calcined ones. Low TMA (4%) selectivity was obtained at N/C=3 using uncalcined Na-chabazite at 90% MeOH conversion (see Table 10(f)) [104–106].

The silicoaluminophosphate (SAPO) isostructural with chabazite, SAPO-34, was first reported in 1984 [107,108]. Studies of this material as a methylamines catalyst showed it to be less active than the aluminosilicate variety (see Table 10(g)) [109–111].

Table 10
Summary of chabazite-based catalysts

Catalyst	Temperature (°C)	WHSW (g MeOH/g cat per h)	N/C	P (atm)	MeOH conversion (%)	MMA (C%)	DMA (C%)	TMA (C%)	DME (%)	Reference(s)
(a) *Effect of zeolite source*										
Cha (Naples)	400	0.46	1	1	96	20	55	24	1	[94]
Cha (Durkee)	400	0.23	1	1	97	21	45	34	5	[94]
Cha (Christmas)	400	0.46	1	1	98	16	33	51	4	[94]
Cha (Bowie)	400	0.93	1	1	95	13	23	64	3	[94]
H-Cha (Naples)	350	0.46	1	1	98	23	59	18	0	[94]
H-Cha (Durkee)	400	0.93	1	1	98	16	51	33	4.9	[94]
H-Cha (Christmas)	400	1.86	1	1	98	16	41	43	5.0	[94]
(b) *Effect of zeolite source*										
Nova Scotia, Canada	400	0.46	1	1	69	23	50	27	0	[138]
Durkee, OR, USA	400	0.46	1	1	84	27	53	20	4.0	[138]
Beaver Divide, WY, USA	400	0.46	1	1	94	18	34	49	1.1	[138]
Pyamid Lake, NV, USA	400	0.46	1	1	94	19	44	37	1.0	[138]
Naples, Italy	400	0.46	1	1	96	20	55	24	0.9	[138]
Bowie, AZ, USA	400	0.46	1	1	98	13	23	64	2.2	[138]
Christmas, AZ, USA	400	0.46	1	1	98	16	33	51	4.1	[138]
Bear Springs, AZ, USA	400	0.46	1	1	99	12	24	64	2.2	[138]
Wikeiup, AZ, USA	400	0.46	1	1	99	13	25	62	1.1	[138]
(c) *Effect of cation exchange*										
Cha (Durkee)	400	0.23	1	1	97	21	45	34	4.7	[94]
H-Cha (Durkee)	400	0.93	1	1	98	16	51	33	4.9	[94]

Table 10
Summary of chabazite-based catalysts

Catalyst	Temperature (°C)	WHSW (g MeOH/g cat per h)	N/C	P (atm)	MeOH conversion (%)	MMA (C%)	DMA (C%)	TMA (C%)	DME (%)	Reference(s)
Na,H-Cha (Durkee)	400	2.79	1	1	97	20	61	19	0.9	[94]
K,H-Cha (Durkee)	400	2.79	1	1	98	19	63	18	0.9	[94]
Cs,H-Cha (Durkee)	400	2.55	1	1	97	26	60	14	5.2	[94]
(d) *Effect of surface treatment*										
H-Cha (Durkee)	400	0.91	1	1	98	16	51	33	4.7	[98,99, 100–102]
H-Cha (Durkee)/ TEOS	400	0.23	1	1	97	17	58	25	5.3	[98,99, 100–102]
(e) *Effect of HCl treatment*										
Cha (Durkee)	400	0.23	1	1	97	21	45	34	4.7	[103]
Cha (Durkee)/ HCl	400	0.93	1	1	95	26	59	15	5.3	[103]
H-Cha (Christmas)	400	1.86	1	1	98	16	41	43	5.0	[103]
H-Cha (Christmas)/ HCl	400	1.86	1	1	97	23	60	17	0.9	[103]
(f) *Synthetic forms*										
H,K,Cs-Cha	325	1.0	1	1	93	15.3	56.1	28.6	14.3	[120]
K,H-Cha	300	0.434	3.5	18	97.3	36.0	54.8	9.3	[b]	[104–106]
K-Cha uncalcined	350	0.217	3.5	18	86[a]			6[a]	[b]	[104–106]
Na-Cha uncalcined	350	0.217	3.5	18	90[a]			4[a]	[b]	[104–106]
Na,K-Cha uncalcined	350	0.217	3.5	18	96[a]			20[a]	[b]	[104–106]
Na-Cha uncalcined	350	0.434	3.5	18	76[a]			4[a]	[b]	[104–106]
Na-Cha calcined	350	0.434	3.5	18	73[a]			4[a]	[b]	[104–106]
Na-Cha calcined, steamed	350	0.434	3.5	18	34[a]			1[a]	[b]	[104–106]
(g) *SAPO-34*										
SAPO-34	325	1	1	1	74.0	44.4	45.1	10.6	20.0	[109]
(h) *Other reports*										
Cha	400	2.69	1.9	18	87	25.4	31.7	42.9	[b]	[197]

[a] TMA in wt%; DMA and MMA not given.

[b] No DME quoted.

Tetraethylorthosilicate (TEOS).

4.4.5. *Rho*

Although the hypothetical structure of zeolite rho was first reported in the mid-1960s [112,113], it was not until the mid-1970s that Robson et al. [114,115] reported the synthesis of this small-pore zeolite from a Na/Cs/Al/Si/O gel. In the 1980s, the use of zeolite H-rho as a methylamines catalyst was studied in great detail.

4.4.5.1. *Effect of calcination conditions.* As with other zeolite-based catalysts, calcination configuration and atmosphere were shown to have significant effects upon catalyst performance (see Table 11(a)) [63,116–119]. In Fig. 4(a) and (b), the effect of calcination temperature and atmosphere on the catalytic selectivity and activity is shown for a particular sample of NH_4-rho. In a nitrogen atmosphere, with increasing calcination temperature (300–800°C), decreasing amounts of TMA are observed in the product stream. With this increasing selectivity with increasing calcination temperature, catalytic activity also increases and then falls at 800°C. This effect appears to be pushed to lower temperatures on addition of steam during calcination, i.e., the selectivity improvement is more dramatic and the activity begins to decrease at temperatures greater than 700°C.

Table 11
Summary of rho-based catalysts

Catalyst	Temperature (°C)	WHSV (g MeOH/g cat per h)	N/C	P (atm)	MeOH conversion (%)	MMA (C%)	DMA (C%)	TMA (C%)	DME (%)	Reference(s)
(a) *Effect of shallow-bed calcination temperature*										
H-Rho (1.0 Cs/uc)/ 400°C, 31 h	325	1.8	1	1	90	13.9	53.6	32.5	4.9	[118]
H-Rho (1.0 Cs/uc)/ 500°C, 16 h	325	1.4	1	1	90	15.6	60.2	24.2	3.7	[118]
H-Rho (1.0 Cs/uc)/ 600°C, 4 h	300	1.5	1	1	90	15.8	75.7	8.5	6.2	[118]
H-Rho (1.0 Cs/uc)/ 700°C, 4 h	325	1.3	1	1	90	15.0	73.3	11.7	6.3	[118]
(b) *Effect of Cs-content*										
H-Rho (0.62 Cs/uc)	300	1.86	1	1	90	13	50	37	3	[204]
H-Rho (1.61 Cs/uc)	300	1.86	1	1	91	13	42	45	4	[204]
H-Rho (4.40 Cs/uc)	300	0.46	1	1	90	16	42	42	6	[204]
H-Rho (0.50 Cs/uc)	350	3.71	1	1	92	13	53	34	4.3	[204]
H-Rho (0.87 Cs/uc)	350	2.79	1	1	91	12	54	34	9.2	[204]
H-Rho (1.62 Cs/uc)	375	3.25	1	1	90	12	49	39	5.0	[204]
H-Rho (2.67 Cs/uc)	375	1.86	1	1	90	12	44	44	4.3	[204]
(c) *Effect of coating (liquid phase)*										
H-Rho	300	1.86	1	1	88	24	44	32	1.0	[98–102]
H-Rho/H_2SiO_3	300	0.93	1	1	84	27	58	15	1.0	[98–102]

Table 11
(Continued)

Catalyst	Temperature (°C)	WHSV (g MeOH/g cat per h)	N/C	P (atm)	MeOH conversion (%)	MMA (C%)	DMA (C%)	TMA (C%)	DME (%)	Reference(s)
H-Rho	300	1.39	1	1	92	18	60	22	2.0	[98–102]
H-Rho/TEB	300	0.35	1	1	92	14	79	7	3.9	[98–102]
H-Rho	300	0.93	1	1	95	16	64	20	13.7	[98–102]
H-Rho/TMP	300	0.93	1	1	91	19	79	3	12.3	[98–102]
H-Rho	300	1.86	1	1	95	15	48	36	1.0	[98–102]
H-Rho/$\{Al_2(OH)_5Cl\}_x$	300	1.86	1	1	92	15	75	10	4.9	[98–102]
H-Rho/$NaAlO_2$	300	2.79	1	1	91	15	60	24	2.1	[98–102]
(d) *Effect of hydrogen level on effectiveness of coating*										
H-Rho	300	1.86	1	1	89	20	39	41	1.1	[98–102]
H-Rho (2.1%H_2O)/TEOS	300	0.93	1	1	93	20	57	23	0	[98–102]
H-Rho (8.2%H_2O)/TEOS	300	0.93	1	1	96	21	71	8	0.9	[98–102]
H-Rho (12.1%H_2O)/TEOS	300	0.93	1	1	97	20	74	6	0	[98–102]
H-Rho (14.7%H_2O)/TEOS	300	0.93	1	1	96	21	75	4	0	[98–102]
(e) *Effect of coating (vapor phase)*										
H-Rho	300	1.39	1	1	95	17	46	38	5.0	[98–102,121]
H-Rho/HMDS	300	1.39	1	1	88	19	63	19	3.0	[98–102,121]
H-Rho/$(CH_3)_2SiCl_2$	325	2.79	1	1	88	18	65	17	3.0	[98–102,121]
H-Rho/$SiCl_4$	325	2.79	1	1	92	17	57	26	3.0	[98–102,121]
H-Rho/$(CH_3)_3SiCl$	325	2.79	1	1	91	18	61	21	5.0	[98–102,121]
H-Rho/TMP	325	2.79	1	1	88	17	72	11	3.0	[98–102,121]
H-Rho	300	1.86	1	1	95	15	48	36	1.0	[98–102]
H-Rho/$(CH_3)_3Al$	300	1.16	1	1	88	20	72	8	2.9	[98–102]
(f) *Effect of starting zeolite on coating*										
H-Rho	300	1.39	1	1	95	17	46	38	5.0	[98–102,121]
H-Rho/TMP	325	2.79	1	1	88	17	72	11	3	[98–102,121]
H-Rho (poorly crystalline)	400	2.79	1	1	89	18	56	12	17	[98–102,121]
H-Rho (poorly crystalline)/TMP	400	1.86	1	1	92	16	76	8	14	[98–102,121]
H-Rho	325	1.86	1	1	91	16	54	30	4	[98–102,121]
H-Rho/TMP	300	0.93	1	1	93	14	86	0.4	5	[98–102,121]

TMP=Trimethylphosphite.
TEB=Triethylborate.
TEOS=Tetraethylorthosilicate.
HMDS=Hexamethyldisilazane.

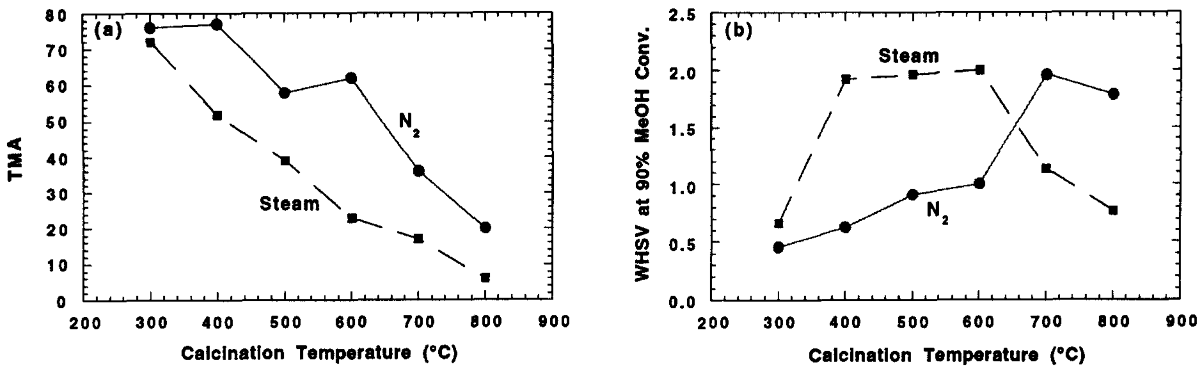

Fig. 4. Effect of calcination temperature and atmosphere on (a) TMA selectivity and (b) catalyst activity.

4.4.5.2. Effect of cation exchange. Cation exchange can also affect the catalytic performance of zeolite rho [63]. In forming the acid form of zeolite rho from Na, Cs-rho, the removal of cesium by ammonium exchange is not trivial. Residual Cs^+ can have a significant effect upon activity and selectivity as shown in Table 11(b).

4.4.5.3. Effect of impurity phases. Typical preparations of zeolite rho can contain a variety of impurities including unreacted gel, chabazite, P_c, pollucite and several phases of unknown structure [115,120]. The presence of these impurities can have a dramatic effect upon the catalytic properties of H-rho [120]. Although none of these phases after exchange and calcination is as active or selective as H-rho for synthesis of DMA from methanol and ammonia, these phases may convert DMA to TMA. Generally, calcination under shallow-bed conditions converts these phases into relatively inactive amorphous aluminosilicates while deep-bed calcination was found to be much less severe and permitted chabazite and pollucite to exist as active phases. Pollucite is believed to be one of the primary causes of lower DMA selectivity for samples calcined in deep-bed configurations.

4.4.5.4. Effect of surface treatment. Treatment of H-rho with various silicon, aluminum, phosphorus and boron compounds (usually alkoxides) led to enhanced selectivity [98,99,100–102,121]. The deposition can be accomplished either in the liquid or vapor phase (see Table 11(c)). In the liquid phase deposition, the degree of hydration of the zeolite can be critical to the amount of oxide/hydroxide deposited on the external surface of the zeolite and hence the catalyst selectivity (see Table 11(d)). Vapor phase treatments generally lead to much lower loadings of the deactivating species (see Table 11(e) and (f)). Characterization (infrared and sorption) studies showed these treatments deactivated the non-selective acid sites on the external surfaces of the zeolite rho crystallites and on the non-selective impurity phases, and in some cases (especially for liquid phase deposition), narrowed the zeolite pore openings.

4.4.5.5. Effect of framework flexibility. Abrams and co-workers [62,122] showed the reaction selectivity imposed by zeolite rho is related to the physisorbed amount of TMA for a given sample. In other words, TMA is related to the amount of TMA in excess of that necessary to titrate the accessible acid sites. It is also reported that NH_3, MMA, DMA and TMA strongly interact with zeolite such that the framework distorts [62,122–125]. This extreme framework flexibility, as illustrated in Fig. 5, is unique to this zeolite [126].

4.4.6. ZK-5

The synthesis of zeolite ZK-5 from $Na/Al/Si/O/\{(CH_3)_2(CH_2CH_2)_3N_2\}O$ gel was first reported by Kerr [127–129]. Later, Robson [130] disclosed a preparation of K, Cs-ZK-5 from a K/Cs/Si/Al/O gel. Gier et al. [69,84,119,131,132] studied the use of H-ZK-5 prepared from this latter procedure in methylamines synthesis. Unlike studies of the synthesis of zeolite Na, Cs-rho where significant amounts of impurity phases crystallize and affect catalyst performance, the K, Cs-preparation of zeolite ZK-5 showed the route to be very clean – only weak lines in neutron diffraction patterns indicated possibly a small amount of offretite formed.

4.4.6.1. Effect of ion exchange. Complete removal of residual cesium on ion exchange is difficult. Studies showed that Cs plays an important role: higher DME is observed for samples with higher Cs content and most deep-bed calcined samples with 1 Cs/uc showed higher DMA selectivity than those with 4 Cs/uc [69,84,119,131,132] (see Table 12(a)).

4.4.6.2. Effect of calcination conditions. As shown in Table 12(b) for deep-bed calcined samples, calcination temperature affected selectivity and activity significantly. Maximum selectivity to DMA was observed at 450–500°C compared with 600°C for zeolite H-rho. Deep-bed calcination led to improved DMA selectivity with increasing temperature of calcination while shallow-bed calcination led to considerable structural damage with decreased selectivity and activity. However, shallow-bed calcination (Table 12(a)) with steam showed less damage and enhanced selectivity. Stagnant deep-bed calcination (Table 12(a)) gave catalysts with lower activity but very high DMA selectivity and significantly more conversion to DME. Overall, H-ZK-5 prepared from K, Cs-ZK-5 showed good DMA selectivity but was less active and less thermally stable than zeolite H-rho.

4.4.6.3. Effect of surface treatment. The selectivity of H-ZK-5 can be improved by surface treatment [98,99,100–102]. In Table 12(c), the effect of treatment of H-ZK-5 with TEOS is shown. With enhanced selectivity, there is some loss of activity. Coatings of H-ZK-5 have also been studied by Fetting et al. [133,134] who showed at N/C=2, H-ZK-5 (made from K, Cs-ZK-5) modified with TMOS yields ~10% TMA and ~5% DME at 90% MeOH conversion (see Table 12(d)). At N/C ~1, TMA was >10% with DME >40% at MeOH conversion of 84%.

4.4.6.4. Effect of synthesis route. In 1991, Verduijn [135] reported the preparation of ZK-5 from an aluminosilicate synthesis gel containing only K^+ and a small amount of Sr^{2+} with no Cs^+. Corbin and Schwarz [136] studied this zeolite in the acid form as a methylamines catalyst and found it to have certain advantages over the Robson material: (1) it required fewer NH_4^+ ion exchanges required in catalyst preparation; (2) without the costly Cs^+ in the synthesis, the catalyst would be expected to be significantly less expensive; and (3) although less active, it showed significantly improved selectivity to MMA and DMA (see Table 12(e)) compared to both H(Cs)-ZK-5 and H-rho. The Verduijn preparation results in larger crystallites (3–4 vs. 1 μm), higher Si/Al ratio (4.1 vs. 3.3) and higher surface Si/Al compared to the bulk Si/Al. Each of these characteristics results in fewer acid sites on the external surface which would be more accessible to the reactants and less selective to MMA and DMA than the internal acid sites [137].

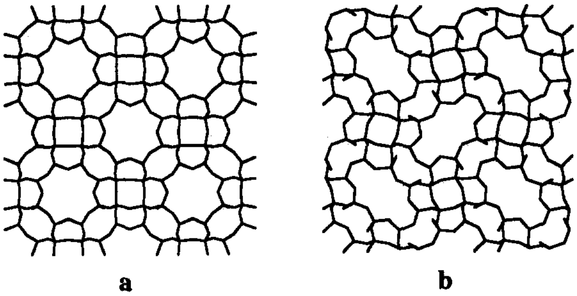

Fig. 5. Illustration of the extremes of the framework flexibility of zeolite rho. (a) centrosymmetric form (dehydrated H-rho) and (b) non-centrosymmetric form (dehydrated Ca-rho).

Table 12
Summary of ZK-5-based catalysts

Catalyst	Temperature (°C)	WHSV (g MeOH/g cat/h)	N/C	P (atm)	MeOH conversion (%)	MMA (C%)	DMA (C%)	TMA (C%)	DME (%)	Reference(s)
(a) *Effect of bed configuration and residual Cs content*										
H-ZK-5(4Cs/uc)/500°C,DB	325	1.1	1	1	94	13.9	53.6	32.5	24.4	[132]
H-ZK-5(4Cs/uc)/500°C,SDB	350	0.4	1	1	95	13.9	77.8	8.3	19.3	[132]
H-ZK-5(1.1Cs/uc)/500°C,DB	350	0.7	1	1	92	12.2	68.8	19.0	3.8	[132]
H-ZK-5(1.1 Cs/uc)/500°C,SB	400	0.16	1	1	93	15.4	46.2	38.5	6.8	[132]
H-ZK-5(1.1 Cs/uc)/500°C,SBST	375	0.27	1	1	93	25.9	66.7	7.4	5.7	[132]
(b) *Effect of deep-bed calcination temperature*										
H-ZK-5/450°C	325	1.2	1	1	98	12.2	43.9	43.9	15.3	[132]
H-ZK-5/500°C	325	1.1	1	1	94	13.9	53.6	32.5	24.4	[132]
H-ZK-5/600°C	325	0.8	1	1	98	12.0	78.3	9.8	28.3	[132]
(c) *Effect of surface treatment: TEOS*										
H-ZK-5	325	0.46	1	1	99	16	32	52	7.2	[98–102]
H-ZK-5/TEOS	350	0.46	1	1	98	22	73	6	0.8	[98–102]
(d) *Effect of surface treatment: TMOS*										
H-ZK-5/550°C	400	3.13	2	3	98.44	29.7	34.7	35.6	3.01	[133,134]
H-ZK-5/0.5%TMOS	400	3.13	2	3	92.84	22.7	55.5	21.8	7.44	[133,134]
H-ZK-5/1%TMOS	400	3.13	2	3	89.46	28.4	57.4	14.3	4.75	[133,134]
H-ZK-5/2%TMOS	400	3.13	2	3	90.05	30.5	58.7	10.8	4.38	[133,134]
H-ZK-5/3%TMOS	400	3.13	2	3	75.85	39.6	53.6	6.8	2.74	[133,134]
H-ZK-5/4%TMOS	400	3.13	2	3	56.91	55.1	40.3	4.6	2.81	[133,134]
H-ZK-5/5.9%TMOS	400	3.13	2	3	50.56	58.2	37.7	4.1	2.71	[133,134]
H-ZK-5/8%TMOS	400	3.13	2	3	36.16	73.4	23.4	3.2	2.41	[133,134]
H-ZK-5/10%TMOS	400	3.13	2	3	16.63	86.4	11.0	2.6	5.69	[133,134]
H-ZK-5/2%TMOS	400	0.10	0.92	3	83.57	69.7	17.1	13.2	46.8[a]	[133,134]
H-ZK-5/2%TMOS	400	3.13	1.0	3	39.0	40.6	46.0	13.4	14.4[b]	[133,134]
(e) *Effect of ZK-5 synthetic route*										
H(Sr)-ZK-5/500°C	325	1.85	1	200	90	24.8	73.3	1.9	0	[136,137]
H(Cs)-ZK-5/500°C	325	5.88	1	200	90	19.2	58.8	22	1	[136,137]
H(Cs)-ZK-5/500°C	300	1.85	1	200	90	17.4	72.1	10.5	1	[136,137]

[a] 28.3 mol% of total products are olefins.

[b] 0.9 mol% of total products are olefins.

4.5. *Comparison of zeolites*

In Fig. 6(a), a plot of the TMA selectivity vs. activity is given for all the various zeolites and a representative SA catalyst [138]. Those zeolite catalysts exhibiting the lowest TMA selectivity are plotted in Fig. 6(b). Clearly, selectivity improvements may be made by choosing appropriate small pore zeolites, with or without surface modification depending on the desired final product distribution, or a larger pore zeolite (mordenite) that has been modified by either ion exchange or surface passivation/pore mouth narrowing.

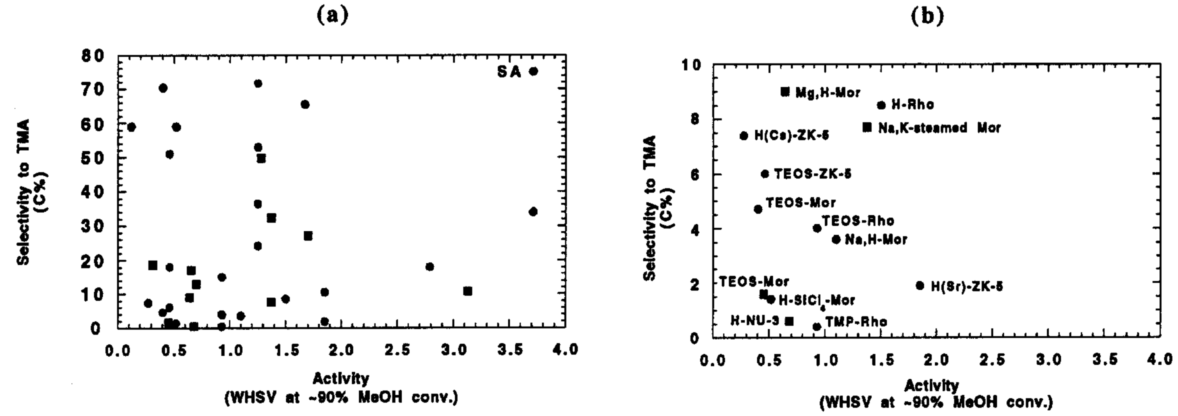

Fig. 6. Plots of activity vs. TMA selectivity (●, N/C=1; ■, N/C=1.5–2.0) for (a) all zeolite-based catalysts and (b) the most selective zeolite-based catalysts.

5. Kinetics

5.1. N/C ratios

There seems to be general agreement over a variety of catalysts, such as H-M, Na-M, H-ZSM-5, Na,H-Y and ZK-5/TMOS, that methanol conversion increases as the NH_3 partial pressure increases [67,76,134,139].

5.2. Reaction order

A number of different reaction orders for methanol have been found, from first order at low conversions [140], to zero and negative [67,139]. In several cases, adsorption terms were included in the kinetics. Dingerdissen et al. [141] found a good fit for NH_3 and methanol conversions assuming the same adsorption for all species. Low pressure data with Na mordenite or Na,K erionite was fit to Langmuir–Hinshelwood kinetics [142]. Schmitz found NH_3 pressure could not be represented by a Langmuir isotherm [52]. The reaction is first order in ammonia over both Na-M [67] and H-zeolites [139,143]. As total pressure is increased, inhibition of the reaction is often observed [67,139,142]. Disproportionation reactions were found to be important with ZSM-5 and ZK-5/TMOS [134,139], but not with Na mordenite, SiO_2/Al_2O_3 [67] or rho [69].

5.3. Adsorption

IR measurements of methanol alone [144,145] show both protonated methanol and methoxy species. When methanol and ammonia are coadsorbed, methanol is more strongly adsorbed with sodium zeolites, though the difference diminishes at pressures of 10^3 Pa or higher [142]. On the hydrogen form, ammonia and the methylamines are more strongly adsorbed and covers all Brønsted acid sites [134–145]. Methanol is adsorbed on preadsorbed ammonium ions [143]. Several groups [145,146] have made microcalorimetric measurements of amines adsorption with H-ZSM-5 and H-mordenite. The results along with the gas phase proton affinities are tabulated in Table 13. Lee et al. [146] have noted the heats of adsorption correlate with the gas phase proton affinities which they offer as proof that the heats of adsorption arise mainly from proton transfer. The lower than predicted ΔH_{ads} of TMA is ascribed to a lack of bidentate hydrogen bonding with the lattice. Ab initio calculations also predict ammonium ion stabilization by hydrogen bonding to the anionic cluster [147,148] and NMR measurements on MMA adsorbed on H–Y are also consistent with hydrogen bonding to the lattice [149]. Other NMR measurements show a dynamic system, rapid rotation of the ammonium ions in rho zeolite [150], both chemisorbed and physisorbed species [151–153] and rapid exchange between these species [154]. NMR measurements of a sealed tube of methanol, ammonia and zeolite that had been heated to 275°C showed the three amine products, DME and tetramethyl ammonium ions [155]; at temperatures greater than 400°C, decomposition products were observed.

6. Mechanism

6.1. Hydrogen zeolites

The only species seen with IR measurements of the H-zeolite catalysts in the presence of methanol and ammonia are protonated ammonia or amines which cover all Brønsted acid sites [134–145]. This has led to a number of mechanisms, all of which invoke ammonium or methylammonium ions as being involved.

Chen and coworkers [145], based on the relative strengths of adsorption, propose that weakly adsorbed methanol reacts with strongly adsorbed ammonia or methylamines (ammonium ions or methylammonium ions) (Fig. 7). This reaction pathway is very unlikely, as ammonium ions are not at all nucleophilic and are unlikely to displace a hydroxyl group from methanol.

Fetting et al. [134] and Mochida et al. [65] propose protonation of the methanol by an ammonium ion, followed by displacement of the protonated hydroxyl group by the nitrogen of the resulting hydrogen-bonded ammonia (Fig. 8).

The most probable mechanism for methylamine formation is the S_N2 attack of a protonated methanol by weakly adsorbed ammonia. The source of the proton can be either the ammonium ion (Fig. 9) or the zeolite hydrogen (Fig. 10). They are equivalent as a proton sources since ammonia, methanol and their protonated forms are all in equilibrium. After the displacement, the resulting methylammonium ion would be of very high energy unless it were stabilized by hydrogen bonding to the lattice. Another possibility that will not develop such a charge separation is a six membered transition state for the S_N2 displacement (Fig. 11). Normally, an S_N2 transition state is linear, but calculations show that where solvation is poor and ion pairing is expected, it can be bent [156,157].

Higher amines are formed when the attacking group is MMA or DMA and DME is formed when the attacking group is methanol. Since the amino group is a much better nucleophile than hydroxyl, mainly methylamine is formed.

Disproportionation reactions occur in an analogous manner. Now the amino group of a methylamine is protonated and the attacking group is ammonia or a methylamine (Fig. 12).

Without ammonia present, these catalysts produce DME. The most likely mechanism is the one proposed by Fetting et al. [134] where methanol displaces the oxygen from another methanol molecule whose oxygen has been activated either by protonation of the hydroxyl group (Fig. 13) or by coordination with a Lewis acid site (Fig. 14).

Table 13
Adsorption enthalpies on H-ZSM-5 and H-Mordenite

Compound	H-ZSM-5 [146] $-\Delta H$ (kJ/mol)	H-ZSM-5 [139] $-\Delta H$ (kJ/mol)	H-Mordenite [146] $-\Delta H$ (kJ/mol)	H-Mordenite [139] $-\Delta H$ (kJ/mol)	Proton affinity [139] PA (kJ/mol)
NH_3	145	151	160	158	857.7
CH_3NH_2	185	204	200	219	895.8
$(CH_3)_2NH$	205	245	225	207	922.6
$(CH_3)_3N$	205	155	220	140	938.5
$(CH_3)_2O$		91		87	807.9
CH_3OH		79		99	773.6
H_2O		61		75	723.8

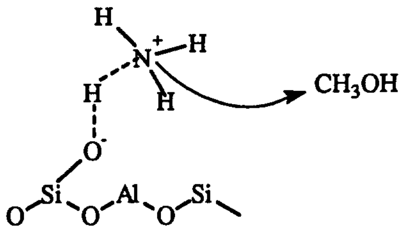

Fig. 7. Weakly adsorbed MeOH reaction with strongly adsorbed ammonia.

The protonated DME that is formed can be stabilized by hydrogen bonding to the lattice. Another possibility that minimizes charge separation is again a cyclic transition state (Fig. 15). Chen et al. [145] have observed methoxyl species by IR and suggested that these may be the reactive intermediate for DME formation (Fig. 16).

6.2. *Alkali zeolites*

On sodium zeolites, methanol is more strongly adsorbed than ammonia. Kogelbauer et al. [142] propose that DME formation takes place from sodium-coordinated methanol molecules first by proton transfer from one methanol to another, making sodium methoxide and protonated methanol, followed by attack of the anion on the protonated methanol, displacing water (Fig. 17). This mechanism seems unlikely because of the energetics of making an acid–base pair.

More likely is an analogous mechanism to that previously discussed for H-zeolites. The methanol oxygen is activated as a leaving group by interaction with the sodium cations allowing methylamine formation by an S_N2 attack of methanol by ammonia, followed by proton transfer [142]. The ammonium ion formed can be stabilized by the lattice (Fig. 18). A cyclic transition state (Fig. 19) is less likely, because NaOH would be formed. Higher amines can be formed by attack on MMA or DMA in a similar manner and DME when the attacking group is methanol. This mechanism for DME formation is consistent with the observation of Kogelbauer et al. [142] that aluminum-rich zeolites make more DME vs. MMA because the methanol oxygen is made more nucleophilic by increased hydrogen bonding with lattice oxygen atoms which have a greater negative charge at higher aluminum concentrations.

7. Synthesis from CO/CO_2

There are a number of reports (Table 14) on the synthesis of amines using CO or CO_2 as the carbon source. Usually the reactants are $CO/H_2/NH_3$ or $CO_2/H_2/NH_3$ except for Enders [158,159] who reports low conversions to

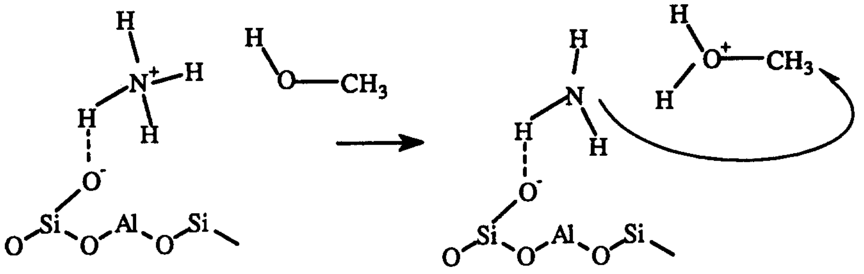

Fig. 8. Protonation of MeOH by ammonium ion.

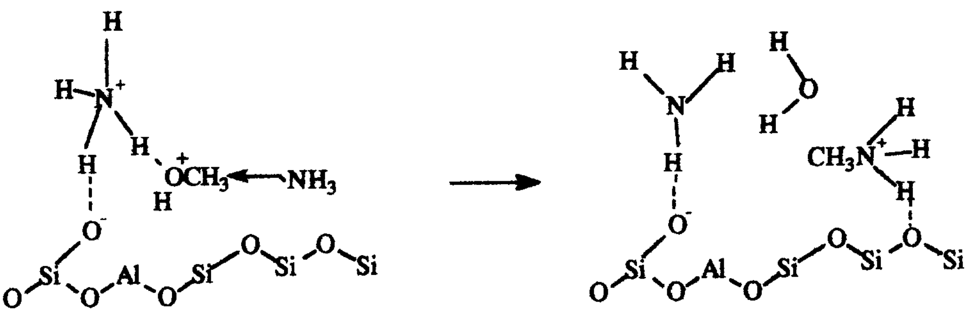

Fig. 9. S_N2 attack of protonated MeOH by weakly adsorbed ammonia. (a) H^+ source=NH_4^+ ion.

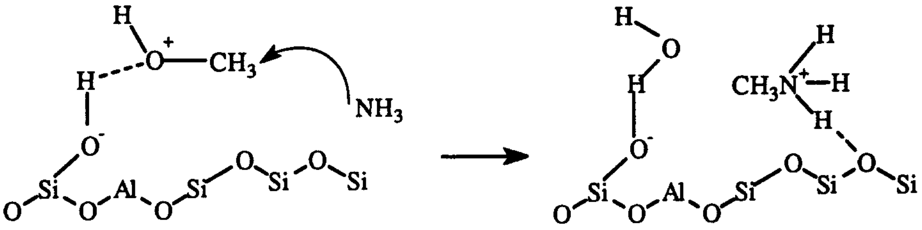

Fig. 10. S_N2 attack of protonated MeOH by weakly adsorbed ammonia, (b) H^+ source=zeolite proton.

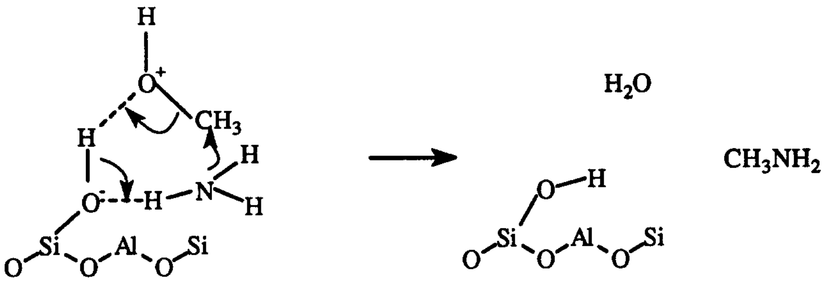

Fig. 11. Six membered transition state for S_N2 displacement.

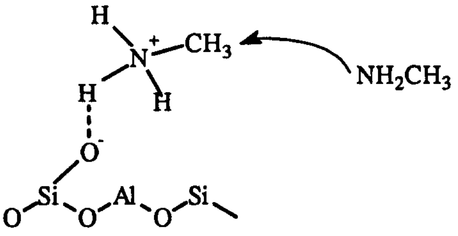

Fig. 12. Disproportionation mechanism (products not shown).

MMA and DMA from $CO/H_2/N_2$ using Th, U and Zr catalysts. For $CO_2/H_2/NH_3$, two main classes of catalysts have been found effective, Fischer–Tropsch catalysts and methanol synthesis catalysts.

7.1. Fischer–Tropsch catalysts

Fischer–Tropsch type catalysts convert $CO/H_2/NH_3$ to methyl- and higher alkyl-amines [160–163]. Kölbel and Trapper [164] have reported similar products using steam in place of hydrogen. Selectivities of nitrogen containing

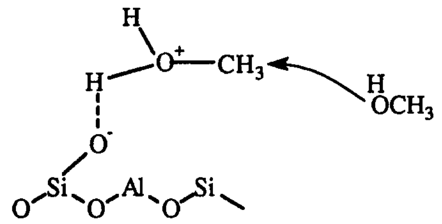

Fig. 13. DME formation by protonation of hydroxyl group.

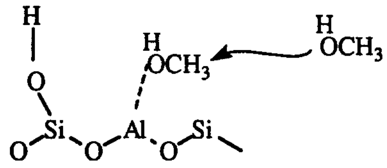

Fig. 14. DME formation by coordination with Lewis site.

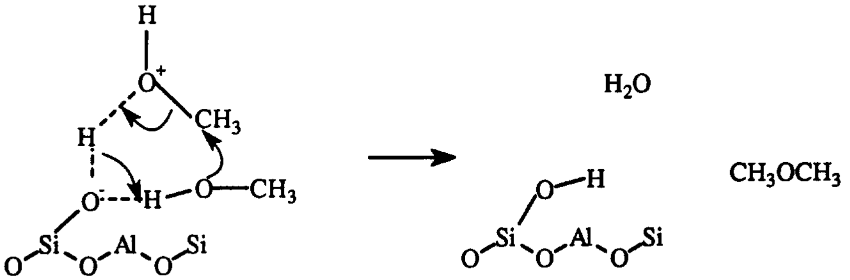

Fig. 15. Cyclic transition state for DME formation.

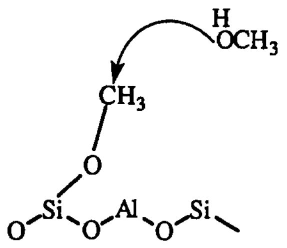

Fig. 16. Methoxyl species as intermediate.

products are not high, generally less that 35%. The amine products follow a Schulz–Flory distribution and are probably formed by ammonia intercepting the growing hydrocarbon chain [165,166].

7.2. *Methanol catalysts*

Methanol synthesis catalysts such as CuO/Cr_2O_3 [167,168], CuO/ZnO [169,170], ZnO/Al_2O_3 [171,172] and Pd or Pt/Al_2O_3 [167] make methylamines from $CO/H_2/NH_3$. Methylamines have also been formed from $CO_2/H_2/NH_3$

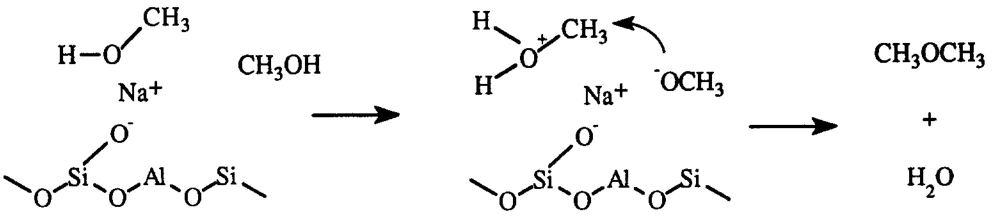

Fig. 17. Alkali zeolites: DME formation via methoxide.

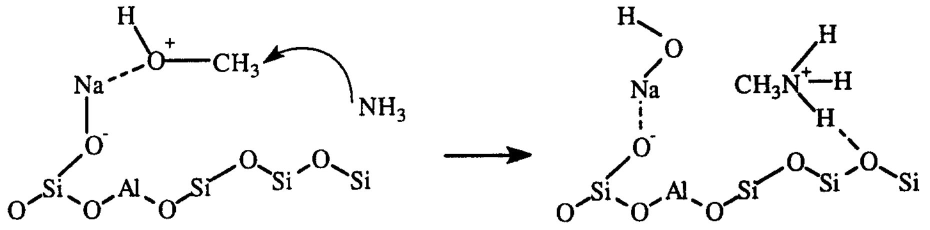

Fig. 18. Alkali zeolites: Ammonium ion stabilization by lattice.

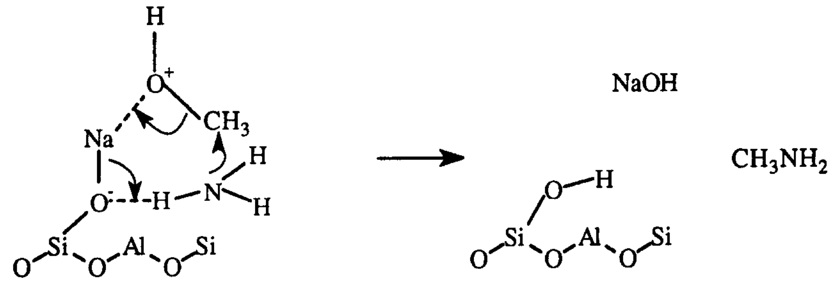

Fig. 19. Alkali zeolites: Cyclic transition state.

[173] with a Cu/Al_2O_3 catalyst or even from $CO/NH_3/CH_3NO_2$ using $Cu/ZnO/Al_2O_3$ [174] where the nitro group is first reduced, then alkylated. For methanol type catalysts, amine selectivities, defined as amine containing hydrocarbon products, not CO_2, are quite high, usually over 75% and 100% in some cases. Different amounts of MMA, DMA and TMA are made depending on the conversion and N/C ratio. Several authors have noted [172,173] that conversion to methylamines is greater than the amount of methanol formed under the same conditions if ammonia is not present. For the Cu or group VIII containing catalysts, it has been proposed that the ammonia or the amino group is reacting with an intermediate on the catalyst such as surface aldehydic species [170,173] in a mechanism similar to that proposed for the formation of amines from higher alcohols [175] which is catalyzed by the same type of catalyst [176]. Vlasenko et al. [172] who used a ZnO/Al_2O_3 catalyst, have proposed the alkylation of ammonia by methanol may be shifting the equilibrium towards products if the methanol formation is equilibrium limited. A different mechanism is likely with ZnO since it is not active in the conversion of higher alcohols to amines.

Table 14
Summary of methylamines synthesis from CO/CO_2

Feed	Catalyst	Amine products	% Amines in products	Reference(s)
Fischer–Tropsch catalysts				
$CO/H_2/NH_3$	K,Al promoted Fe	Alkylamines		[160]
$CO/H_2/NH_3$	Cu promoted Fe	Alkylamines	18	[205]
$CO/H_2/NH_3$	Ba,Al promoted Fe	Alkylamines	10–25	[161]
$CO/H_2/NH_3$	Ba,Al promoted Fe	Alkylamines	10–35	[163]
$CO/H_2/NH_3$	Ba,Al promoted Fe	Alkylamines	37	[166]
$CO/H_2O/NH_3$	Cu,K promoted Fe	Alkylamines	18	[164]
Methanol catalysts				
$CO/H_2/NH_3$	Ba,Cu chromite, Pd/SiO_2, Pt/Al_2O_3	TMA	99	[167]
$CO/H_2/NH_3$	Cu, Cr_2O_3/Al_2O_3	MMA, DMA, TMA	70–100	[168]
$CO/H_2/NH_3$	ZnO/Al_2O_3	DMA, TMA	100	[171]
$CO/H_2/NH_3$	ZnO/Al_2O_3	DMA, TMA	75–100	[172]
$CO/H_2/NH_3$	Cu/ZnO	MMA, DMA, TMA	80–100	[169]
$CO/H_2/NH_3$	Cu/ZnO	MMA, DMA, TMA	100	[170]
$CO_2/H_2/NH_3$	Cu/Al_2O_3	MMA, DMA, TMA	98	[173]
Other catalysts				
$CO/H_2/N_2$	Uranium hydride, Thorium hydride	MMA, DMA	50	[158]
$CO/H_2/N_2$	Zr, Zr/Ag	MMA, DMA	50	[159]
$CO/H_2/NH_3$	Ru	TMA, $HCONR_2$, R=H, Me	100	[206]
$CO/H_2/NH_3$	Mo/SiO_2	MMA, DMA	50	[177]
CO/NH_3	Zeolites H-ZSM-5, Y, Mordenite, etc.	MMA, DMA	50–100	[178]
$CO_2/H_2/CH_3NO_2$	$Co/Cu/ZnO/Al_2O_3$	MMA, DMA, TMA		[174]

7.3. *Other catalysts*

The formation of methylamines and amides has also been reported over $Rh/Fe/SiO_2$ [162]. Tatsumi et al. [177] have reported amine and nitrile formation over Mo/SiO_2 and Subrahmanyam et al. [178] claim synthesis of MMA and DMA from CO/NH_3 using zeolite catalysts.

8. Conclusions

Methylamines are still mainly produced using equilibrium catalysts, but the market demand is clearly driving research efforts towards selective zeolite catalysts. Fig. 6 shows that selectivity improvements may be made by choosing appropriate small pore zeolites, with or without surface modification depending on the desired final product distribution, or a larger pore zeolite that has to be modified by either ion exchange or surface passivation/pore mouth narrowing.

References

[1] A.B. Van Geysel, W. Musin, in: B. Elvers, S. Hawkins, G. Schulz (Eds.), Ullmann's Encyclopedia of Industrial Chemistry, vol. A16, 1990, p. 535.
[2] V. Merz, K. Gasiorowski, Berichte (1884) 623.

[3] W.D. Turner and A.M. Howald, J. Am. Chem. Soc., 42 (1920) 2663.
[4] P. Sabatier and A. Mailhe, Compt. Rend., 148 (1909) 898.
[5] E. Smolenski and K. Smolenski, Roczniki Chem., 1 (1921) 232.
[6] A.B. Brown and E.E. Reid, J. Phys. Chem., 28 (1924) 1067–1076.
[7] T.L. Davis and R.C. Elderfield, J. Am. Chem. Soc., 50 (1928) 1786.
[8] E. Briner and J. Gandillon, Helvetica Chim. Acta, 14 (1931) 1283–1307.
[9] H.R. Arnold, US 1 799 722 (1931).
[10] J. Martin, L.C. Swallen, US 1 875 747 (1932).
[11] Egly, R.S., Smith, E.F., Chem. Eng. Progr. 44 (1948) 387.
[12] L.W. Watts, M. Brennan, E.L. Yeakey, in: J.J. McKetta, W.A. Cunningham (Eds.), Encyclopedia of Chemical Processing and Design, vol. 3, 1977, p. 147.
[13] R. Williams Jr., J.R. Willner and J.J. Schaefer, Chem. Eng. News, 33 (1955) 3982.
[14] CEH Marketing Research Report on Alkylamines, 611.5030A, 1993.
[15] Directory of World Chemical Producers, 1995–1996.
[16] SRI Directory of Chemical Producers, 1994.
[17] Chemical Marketing Reporter 246 (1994) 45.
[18] Chem. Eng. News (1996) 12.
[19] Chem. Week 156 (1995) 6.
[20] Chem. Week 152 (1993) 25.
[21] Chem. Week 146 (1990) 33.
[22] Chem. Wkly. 37 (1991) 50–51.
[23] China Chem. Week 2 (1995) 2.
[24] Wencai, C., Fusheng, W., Chen, W., Ming, Z., Zhaonan, X., Youmin, T., Shiyou Huagong 19 (1990) 35–39.
[25] R.N. Cochran, M. Deeba, US 4 398 041 (1983).
[26] M.G. Turcotte, T.A. Johnson, in: J.I. Kroschwitz, M. Howe-Grant (Eds.), Kirk Othmer Encyclopedia of Chemical Technology, vol. 2, 1992.
[27] J. Ramioulle and A. David, Hydrocarbon Process. Int. Ed., 60 (1981) 113–117.
[28] Leonard Process Co., Hydrocarbon Process. 52 (1973) 150.
[29] H.D. Berrouschot, H.J. Derdulla, C. Eichner, I. Hacker, R. Holm, R. Kloss, M. Mahn, K. Rebbe, G. Schmidt, K. Weber, DD 134518 (1979).
[30] J.F. Olin, US 2 377 511 (1945).
[31] W. Tyerman, US 2 547 064 (1951).
[32] E.M. Nicholl, DE 2 053 709 (1971).
[33] E.M. Nicholl, US 3 720 715 (1973).
[34] W.S. Fong, PEP Review, 89-3-4 (1991).
[35] Jpn. Chem. Week 33 (1992) 2.
[36] Y. Ashina, NL 8 201 523 (1982).
[37] Y. Ashina, M. Fukatsu, US 4 485 261 (1984).
[38] Y. Ashina, T. Fujita, K. Niwa, T. Inagaki, Y. Nikaido, EP 342 999 (1989).
[39] Deeba, M., Ambs, W.J., Cochran, R.N., US Patent 4 434 300 (1989).
[40] K. Kourtakis, H.E. Bergna, G.C. Sonnichsen, D.R. Corbin, L.D. Brake, PCT Int. Appl. WO 9 518 675 (1995).
[41] B. Ohtani, H. Osaki, S. Nishimoto and T. Kagiya, Tetrahedron Lett., 27 (1986) 2019–2022.
[42] M. Nasikin, R. Nakamura and H. Niiyama, Chem. Lett., 2 (1993) 209–212.
[43] H.R. Arnold, US 1 992 935 (1935).
[44] IG Farben, FR 771 859 (1934).
[45] P.H. Emmett, Catalysis, Reinhold, New York, NY, 1960.
[46] D.G. Parker, A.J. Tompsett, DE 2 904 303 (1979).
[47] C.J. Plank, US 2 499 680 (1950).
[48] G.E. Heinsohn, US 4 374 273 (1983).
[49] J.D. Leonard, US 3 387 032 (1968).
[50] L.D. Brake, US 4 370 503 (1983).
[51] E.C. Novella and G.V. Una, Anales de Quimica, 65 (1969) 689.
[52] G. Schmitz, J. Chim. Phys. Phys. Chim. Biol., 77 (1980) 393–400.
[53] H.C. Foley, D.S. Lafyatis, R.K. Mariwala, G.D. Sonnichsen and L.D. Brake, Chem. Eng. Sci., 49 (1994) 4771–4786.
[54] H.C. Foley, G.C. Sonnichsen, L.D. Brake, R.K. Mariwala, D.S. Lafyatis, US 5 354 893 (1994).
[55] H. Uchida, S. Kuraishi, H. Ichinokawa and T. Hosoya, Tokyo Kogyo Test Facility Report, 50 (1955) 150.
[56] I. Mochida, JP Kokai 58-49340 (1983).

[57] K. Becker, H.D. Berrouschot, H. Blume, H.J. Derdulla, D. Koehler, M. Mahn, K. Rebbe, K. Weber, DD 108 275 (1974).
[58] R. Kloss, H.D. Berrouschot, K. Rebbe, K. Becker, H. Albrecht, I. Hacker, D. Pape, K. Klein, R. Koch, DD 149 213 (1981).
[59] J. Ramioulle, G. Schmitz, P. Lambert, GB 2 045 232 (1980).
[60] R. Szostak, Handbook of Molecular Sieves, Van Nostrand Reinhold, New York, NY, 1992.
[61] S.M. Csicsery, Zeolites, 4 (1984) 202.
[62] L. Abrams and D.R. Corbin, J. Inclusion Phenom. Mol. Recognit. Chem., 21 (1995) 1–46.
[63] D.R. Corbin, T.E. Gier, M. Keane, R.D. Shannon, G.C. Sonnichsen, US 4 806 689 (1989).
[64] F.J. Weigert, US 4 254 061 (1981).
[65] I. Mochida, A. Yasutake, H. Fujitsu and K. Takeshita, J. Catal., 82 (1983) 313–321.
[66] T. Kiyoura, K. Terada, JP 06 009 510 (1994).
[67] F.J. Weigert, J. Catal., 103 (1987) 20–29.
[68] Y. Ashina, T. Fujita, M. Fukatsu, J. Yagi, US 4 578 516 (1986).
[69] M. Keane Jr., G.C. Sonnichsen, L. Abrams, D.R. Corbin, T.E. Gier and R.D. Shannon, Appl. Catal., 32 (1987) 361–366.
[70] Y. Ashina, T. Fujita, M. Fakatsu, J. Yagi, US 4 582 936 (1986).
[71] Y.Z. Zhang, Z.L. Xu, J. Wang and Y.Y. Ke, Stud. Surf. Sci. Catal., 84 (1994) 1927–1933.
[72] Y. Zhang, X. Zhou, Z. Ke, CN 1 095 645 (1994).
[73] W. Kerui, Y. Xiuzhi and F. Yun, Shiyou Huagong, 16 (1987) 6.
[74] K. Segawa, A. Sugiyama, H. Tachibana, Y. Kurisu, JP 03 262 540 (1991).
[75] K. Segawa and H. Tachibana, J. Catal., 131 (1991) 482–490.
[76] K. Segawa, A. Sugiyama, H. Tachibana, Y. Kurusu, US 5 137 854 (1992).
[77] K. Segawa and H. Tachibana, Stud. Surf. Sci. Catal., 75 (1993) 1273–1283.
[78] K. Segawa, A. Sugiyama, H. Tachibana, Y. Kurusu, US 5 210 308 (1993).
[79] T. Kiyoura, K. Terada, EP 593 086 (1994).
[80] T. Kiyoura, K. Terada, US 5 382 696 (1995).
[81] C. Gründling, G. Eder-Mirth and J.A. Lercher, J. Catal., 160 (1996) 299–308.
[82] T. Kiyoura, S. Nakahara, EP 681 869 (1995).
[83] J. Groeb and F. Fetting, DECHEMA Monogr., 122 (1991) 35–54.
[84] T.E. Gier, R.D. Shannon, G.C. Sonnichsen, US 4 602 112 (1986).
[85] W. Kotowski, H. Dilcher, S. Zamorowska-Biernacik and J. Mazur, Przem. Chem., 68 (1989) 160–162.
[86] J. Dewing, F. Pierce and A. Stewart, Stud. Surf. Sci. Catal., 5 (1980) 39.
[87] D.G. Parker, Appl. Catal., 9 (1984) 53.
[88] J.L. Casci, M.D. Shannon, I.J.S. Lake, EP 462 745 (1991).
[89] G.T. Hutching, T. Themistocleous, R.G. Copperthwaite, EP 452 085 (1991).
[90] W.W. Kaeding, US 4 082 805 (1978).
[91] A.J. Tompsett, US 4 436 938 (1984).
[92] A.J. Tompsett, EP 76 034 (1983).
[93] A.J. Tompsett, T.V. Whittam, EP 107 457 (1984).
[94] L. Abrams, R.D. Shannon, G.C. Sonnichsen, US 4 737 592 (1988).
[95] C. Herrmann, F. Fetting and C. Plog, Appl. Catal., 39 (1988) 213–226.
[96] A. Martin, B. Luecke, W. Wieker and K. Becker, Catal. Lett., 9 (1991) 451–459.
[97] A. Martin, H. Berndt, U. Wolf and B. Luecke, Catal. Lett., 13 (1992) 359–371.
[98] H.E. Bergna, D.R. Corbin, G.C. Sonnichsen, AU 8 656 884 (1986).
[99] H.E. Bergna, D.R. Corbin, G.C. Sonnichsen, US 4 683 334 (1987).
[100] H.E. Bergna, D.R. Corbin, G.C. Sonnichsen, US 4 752 596 (1988).
[101] H.E. Bergna, D.R. Corbin, G.C. Sonnichsen, US 4 683 334 (1989).
[102] H.E. Bergna, M. Keane Jr., D.H. Ralston, G.C. Sonnichsen, L. Abrams and R.D. Shannon, J. Catal., 115 (1989) 148.
[103] D.R. Corbin, J.B. Parise, G.C. Sonnichsen, unpublished.
[104] F.C. Wilhelm, T.R. Gaffney, G.E. Parris, B.A. Aufdembrink, CA 2 126 834 (1995).
[105] F.C. Wilhelm, G.E. Parris, B.A. Aufdembrink, T.R. Gaffney, US 5 399 769 (1995).
[106] F.C. Wilhelm, T.R. Gaffney, G.E. Parris, B.A. Aufdembrink, EP 632 012 (1995).
[107] B.M. Lok, C.A. Messina, R.L. Patton, R.T. Gajek, T.R. Cannan and E.M. Flanigen, J. Am. Chem. Soc., 106 (1984) 6092.
[108] B.M. Lok, C.A. Messina, R.L. Patton, R.T. Gajek, T.R. Cannan, E.M. Flanigen, US 4 440 871 (1984).
[109] K.D. Olson, S.W. Kaiser, US 4 874 896 (1989).
[110] K.D. Olson, S.W. Kaiser, W.T. Reichle, A.R. Doumaux, Jr., D.J. Schreck, J.H. McCain, PCT Int. Appl. WO 8 905 810 (1989).
[111] K.D. Olson, S.W. Kaiser, EP 324 267 (1989).
[112] P.B. Moore and J.V. Smith, Mineral. Mag., 33 (1964) 1008.
[113] W.M. Meier and G.T. Kokotailo, Z. Kristallogr., 121 (1965) 211.

[114] H.E. Robson, D.P. Shoemaker, R.A. Ogilvie and P.C. Manor, Advan. Chem. Ser., 121 (1973) 106–115.
[115] H.E. Robson, US 3 904 738 (1975).
[116] L. Abrams, D.R. Corbin, R.D. Shannon, EP 251 597 (1988).
[117] L. Abrams, D.R. Corbin, R.D. Shannon, US 4 814 503 (1989).
[118] R.D. Shannon, M. Keane Jr., L. Abrams, R.H. Staley, T.E. Gier, D.R. Corbin and G.C. Sonnichsen, J. Catal., 113 (1988) 367–382.
[119] L. Abrams, T.E. Gier, R.D. Shannon, G.C. Sonnichsen, EP 183 423 (1986).
[120] R.D. Shannon, M. Keane Jr., L. Abrams, R.H. Staley, T.E. Gier, D.R. Corbin and G.C. Sonnichsen, J. Catal., 114 (1988) 8–16.
[121] D.R. Corbin, M. Keane Jr., L. Abrams, R.D. Farlee, P.E. Bierstedt and T. Bein, J. Catal., 124 (1990) 268–280.
[122] L. Abrams, D.R. Corbin and M. Keane Jr., J. Catal., 126 (1990) 610–618.
[123] C. Weidenthaler, R.X. Fischer, L. Abrams, A. Hewat, Acta Cryst., submitted.
[124] C. Weidenthaler, R.X. Fischer, L. Abrams, Acta Cryst., submitted.
[125] C. Weidenthaler, R.X. Fischer, L. Abrams, A. Hewat, Acta Cryst., submitted.
[126] D.R. Corbin, L. Abrams, G.A. Jones, M.M. Eddy, W.T.A. Harrison, G.D. Stucky and D.E. Cox, J. Am. Chem. Soc., 112 (1990) 4821–4830.
[127] G.T. Kerr, Science, 140 (1963) 1412.
[128] G.T. Kerr, Inorg. Chem., 5 (1966) 1539–1541.
[129] G.T. Kerr, US 3 247 195 (1966).
[130] H.E. Robson, US 3 720 753 (1973).
[131] JP 61 254 256 (1986).
[132] R.D. Shannon, M. Keane Jr., L. Abrams, R.H. Staley, T.E. Gier and G.C. Sonnichsen, J. Catal., 115 (1989) 79–85.
[133] F. Fetting, U. Dingerdissen, O. Witzel, M. Hesse, DE 4 105 188 A1 (1991).
[134] F. Fetting and U. Dingerdissen, Chem.-Eng.-Technol., 15 (1992) 202–212.
[135] J.P. Verduijn, US 4 994 249 (1991).
[136] D.R. Corbin, S. Schwarz, US 5 344 989 (1994).
[137] S. Schwarz, D.R. Corbin, G.C. Sonnichsen, in preparation.
[138] G.C. Sonnichsen, unpublished.
[139] D.T. Chen, L. Zhang, J.M. Kobe, C. Yi and J.A. Dumesic, J. Mol. Catal., 93 (1994) 337–355.
[140] C. Herrmann, E. Nagy and F. Fetting, Chem. Ing. Tech., 59 (1987) 227–228.
[141] U. Dingerdissen, E. Nagy and F. Fetting, Chem. Ing. Tech., 63 (1991) 625–628.
[142] A. Kogelbauer, C. GrŸndling and J.A. Lercher, J. Phys. Chem., 100 (1996) 1852.
[143] A. Kogelbauer, C. Grundling and J.A. Lercher, Stud. Surf. Sci. Catal., 84 (1994) 1475–1482.
[144] A. Kogelbauer and J.A. Lercher, J. Chem. Soc. Faraday Trans., 88 (1992) 2283.
[145] D.T. Chen, L. Zhang, C. Yi and J.A. Dumesic, J. Catal., 146 (1994) 257–267.
[146] C. Lee, D.J. Parrillo, R.J. Gorte and W.E. Farneth, J. Am. Chem. Soc., 118 (1996) 3262.
[147] E.H. Teunissen, F.B. van Duijneveldt and R.A. van Santen, J. Phys. Chem., 96 (1992) 366.
[148] E.H. Teunissen, R.A. van Santen and A.P.J. Jansen, J. Phys. Chem., 97 (1993) 203.
[149] C.P. Grey and B.S.A. Kumar, J. Am. Chem. Soc., 117 (1995) 9071.
[150] A.J. Vega and Z. Luz, J. Phys. Chem., 91 (1987) 365.
[151] Z. Luz and A.J. Vega, J. Phys. Chem., 90 (1986) 4903.
[152] Z. Luz and A.J. Vega, J. Phys. Chem., 91 (1987) 374.
[153] A.J. Vega and Z. Luz, Zeolites, 8 (1988) 19.
[154] H. Kao and C.P. Grey, J. Phys. Chem., 100 (1996) 9071.
[155] H. Ernst and H. Pfeifer, J. Catal., 136 (1992) 202–208.
[156] S. Harder, A. Streitwieser, J.T. Petty and P.V.R. Schleyer, J. Am. Chem. Soc., 117 (1995) 3253.
[157] A. Streitwieser, personal communication, 1995.
[158] E. Enders, US 3 646 148 (1972).
[159] E. Enders, D. Huellstrung, US 3 636 153 (1972).
[160] A. Clark, US 2 518 754 (1947).
[161] A.N. Bashkiriv, Y.B. Kagan and G.A. Kliger, Doklady Akad. Nauk. SSSR, 109 (1956) 774.
[162] W.J. Bartley, US 4 250 116 (1981).
[163] P.M. Brown, J.M. Maselli, US 3 726 926 (1973).
[164] H. Kölbel, J. Trapper, in: Symp. Chem. Oil Coal, p. 189 and 190, Cent Fuel Res. Inst., Dhanbad, India, 1969.
[165] G. Henrici-Olivé and S. Olivé, J. Mol. Catal., 4 (1978) 379.
[166] G.A. Kliger, L.S. Glebov, T.P. Popova, E.V. Marchevskaya, V.G. Beryezkin and S.M. Loketv, Catalysis, 111 (1988) 418.
[167] K. Nozaki, US 3 410 904 (1968).
[168] A.N. Kurtz, US 3 444 203 (1969).
[169] K. Klier, R.G. Herman, G.A. Vedage, EP 127 874 (1984).

[170] G.A. Vedage, R.G. Herman and K. Klier, Chem. Ind. (Catal. Org. React.), 33 (1988) 149–176.

[171] V.M. Vlasenko, M.T. Rusov, V.L. Chernobrivets and G.E. Yuzefovich, Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 46 (1969) 23.

[172] V.M. Vlasenko, M.T. Rusov, V.L. Chernodrivets and G.E. Yuzefovich, Katal. Katal., 9 (1972) 48–55.

[173] S.V. Gredig, R.A. Koeppel and A. Baiker, J. Chem. Soc. Chem. Commun., (1995) 73–74.

[174] J. Wang, R. Oukaci, I. Wender and D.G. Blackmond, J. Catal., 153 (1995) 100–107.

[175] A. Baiker, in: J.R. Kosar, T.A. Johnson (Eds.), Catalysis of Organic Reactions, vol. 53, Marcel Dekker, New York, NY, 1994, p. 81.

[176] A. Baiker and J. Kijerski, Catal. Rev., 27 (1985) 653.

[177] T. Tatsumi, S. Kunitomi, J. Yoshiwara, A. Muramatsu and H. Tominaga, Catal. Lett., 3 (1989) 223–226.

[178] M. Subrahmanyam, S.J. Kulkarni and A.V.R. Rao, J. Chem. Soc. Chem. Commun., (1992) 607–608.

[179] T. Gibson, W.K. Johnson, M. Jaekel, Y. Ishikawa, CEH Marketing Research Report on Alkylamines, 611.5030A (1993).

[180] FR 734 404 (1932).

[181] L.C. Swallen, J. Martin, US 1 926 691 (1933).

[182] DRP 617 990 (1935).

[183] H.R. Arnold, T.L. Williams, US 2 017 051 (1935).

[184] W.A. Lazier, US 2 017 069 (1935).

[185] P. Herold, K. Smeykal, US 2 068 132 (1937).

[186] C.E. Andrews, US 2 073 671 (1937).

[187] K. Smeykal, US 2 090 953 (1937).

[188] L.C. Swallen, J. Martin, US 2 092 431 (1937).

[189] C.H. Greenewalt, US 2 098 289 (1937).

[190] E.B. Punnett, US 2 113 241 (1938).

[191] C.E. Andrews, L.U. Spence, US 2 153 405 (1939).

[192] E.F. Smith, US 2 456 599 (1948).

[193] W. Richarz, M. Lutz and A. Guyer, Helvetica Chim. Acta, 27 (1959) 2212.

[194] J. Ramioulle, G. Schmitz, P. Lambert, DE 3 010 791 (1980).

[195] J.E. Wells, V. Eskinazi, US 4 582 904 (1986).

[196] W.M. Meier and D.H. Olson, Zeolites, 12 (1992) 1–195.

[197] Y. Ashina, M. Fukazu, Kokai 57-169444 (1982).

[198] K. Segawa, A. Sugiyama, M. Sakaguchi, K. Sakurai (Eds.), Shape-Selective Reactions for Methylamine Synthesis from Methanol, Kodansha, 1988.

[199] F. Fetting, T. Petry and U. Dingerdissen, Chem. Ing. Tech., 63 (1991) 492–495.

[200] BE 873 851 (1979).

[201] D.G. Parker, A.J. Tompsett, US 4 205 012 (1980).

[202] D.G. Parker, A.J. Tompsett, GB 2 019 394 (1979).

[203] BE 875 674 (1979).

[204] D.R. Corbin, M. Keane, Jr., unpublished.

[205] W. Rottig, DE 904 891 (1954).

[206] J.A. Marsella, G.P. Pez, Prepr. – Am. Chem. Soc., Div. Pet. Chem. 31 (1986) 22–25.