SHAPE-SELECTIVE MORDENITE-CATALYZED AMINATION OF ETHANOLAMINE TO ETHYLENEDIAMINE

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Summary

Hydrogen mordenite and dealuminated hydrogen mordenites catalyze the reaction of ethanolamine with ammonia to form ethylenediamine at low pressure. Selectivity to ethylenediamine depends on the degree of mordenite dealumination; best results are obtained with a moderately dealuminated catalyst. Self-amination of ethanolamine leads to *N*-(amino-ethyl)ethanolamine, the major byproduct.

Introduction

Ethylendiamine (EDA) is an important organic intermediate with many uses. Major industrial applications of EDA include: (a) broad spectrum fungicides [1–5]; (b) chelating agents [6–12]; (c) epoxy curatives [13]; (d) hot melt adhesives [14–19]; (e) corrosion inhibitors [20–22]; and (f) lubricating oil and fuel additives [23–26].

Classically, EDA is made by amminolysis of ethylene dichloride [27–31]. Disadvantages of this process include coproduction of sodium chloride [28], corrosion associated with chlorine-based technology [27–29], and a relatively inflexible product mixture which typically contains significant amounts of higher polyethylene polyamines [30, 31]. Reductive amination of ethanolamine (EA) has been investigated extensively as a route to EDA [32–47]. Most processes involve high pressure reactions (>1500 psig) with ammonia and hydrogen over mixed metal [38, 39] or modified nickel [33–35, 37, 41–47] or cobalt [34, 36, 37, 41, 47] catalysts. Good selectivities (up to 80 wt.%) to EDA are typically obtained by inclusion of large stoichiometric excesses of ammonia (mole ratio ammonia/EA > 10/1). Despite claims [41, 42] that rhenium-promoted catalysts possess enhanced selectivity for conversion of EA to EDA, a 20/1 molar feed ratio of ammonia/EA is preferred.

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Acid-catalyzed amination of EA with ammonia has been reported [48, 49]. Low selectivities (≤40%) were obtained over silica–alumina or phosphoric acid on silica–alumina at high temperatures (≥300 °C) [48]. Use of lanthanum acid phosphate under similar conditions (reaction temperatures up to 300 °C) provided somewhat better selectivity to EDA (up to 50 wt.%) [49]. We now report that EDA is obtained in good selectivity by shape-selective acid-catalyzed amination of EA with mordenite catalysts.

Experimental

EA was purchased from Aldrich Chemical Co. Ammonia (high purity; >99.9%) was obtained from Air Products and Chemicals, Inc. Catalysts were commercially available: silica–alumina (Davison 970); HY (Linde LZY62); rare earth-exchanged Y (Linde SK-500); H-mordenite (Norton Z-900H); and dealuminated H-mordenite (Union Carbide LZ-M-8; Si/Al ratio 10.0). Unless otherwise specified, all chemicals were ACS reagent grade; all were used without further purification.

H-mordenite was dealuminated in either of two ways. A mixture of Norton Z-900H (80 g), 37% aqueous hydrochloric acid (50 ml, 0.5 mol); ammonium chloride (110 g, 2.06 mol) and deionized water (2 l) was heated under reflux for 1 h. After cooling and filtration, the catalyst was washed with deionized water (2 l) under reflux for 1 h. Filtration and drying (80–90 °C/50 mmHg) provided a catalyst with Si/Al molar ratio of 6.9 (by XRF). This catalyst is designated 'catalyst A'. The above procedure was repeated, with dealumination being carried out with 1.5 l of deionized water. A catalyst ('catalyst B') with a Si/Al ratio of 9.2 was obtained. All reactions of ethanolamine and ammonia were carried out in a 20 cm^3 fixed bed stainless steel tubular reactor [50, 51]. Temperature was controlled with an ECS 6401 Time Proportioning Control Module. Feeds were metered to the reactor as liquids using Isco Model 314 high pressure syringe pumps. Pressure was maintained with a Grove Model SD-91LW back-pressure regulator, and monitored with a Validyne Model DP 15–62 pressure transducer. Pressure and temperature readings were continuously recorded with a strip chart recorder.

Typically, the reactor was charged with crushed vicor (5 cm^3 of −12 to −18 mesh particles) followed by a mixture of the catalyst (5 cm^3 of −12 to −18 mesh particles) and crushed vicor (5 cm^3 of −12 to −18 mesh particles). The catalyst charge was overlaid with an additional 2 cm^3 of vicor (−12 to −18 mesh particles. Catalysts were heated (90 °C) in the reactor under nitrogen (10–20 sccm at 1 atm) for 16–18 h. The temperature was then raised to the desired level over 3 h. Nitrogen was shut off; ammonia was introduced, and the back-pressure regulator set to 150 psig. Ethanolamine (which also contained 6 wt.% diethylene glycol dimethyl ether as an internal standard for the GLC analyses) was then introduced to obtain the desired feed ratio. Performance of each catalyst was evaluated over 24 h.

Analyses were carried out on a Varian Model 3700 gas chromatograph equipped with a capillary injection port for use with fused-silica columns, Model 8000 autosampler and a flame ionization detector. Separations were effected with a fused-silica DB-5 wall coated open-tubular column (30 m × 0.32 mm; 1.0 μm film thickness). Quantitation was based on use of diethylene glycol dimethyl ether as an internal standard. The autosampler was controlled, and integrations were performed by a Varian VISTA 402 chromatography data system. Identities of major products were confirmed by GC–MS.

Results and discussion

Treatment of EA with ammonia in the presence of H-mordenite provided significant conversions at temperatures of at least 300 °C (molar feed ratio of ammonia/EA = 12/1 or 16/1; 150 psig; 0.15 h^{-1} LHSV, based on EA; see Table 1, runs 1, 2). However, selectivities to EDA were low (<35 wt.%). In an attempt to improve selectivity by modification of catalyst

TABLE 1

Production of EDA over mordenite catalysts[a]

Run	NH$_3$/EA[b]	Catalyst (Si/Al)[c]	T (°C)	LHSV (h^{-1})[d]	Conversion (%)[d]	Selectivity[e]				
						EDA[f]	C[g]	NC[h]	AEEA[i]	UNK[j]
1	12	H-mordenite (6.0)	300	0.15	24	30	31	5	24	10
2	16	H-mordenite (6.0)	300	0.15	20	30	30	6	25	9
3	8	A (6.9)	300	0.15	26	57	15	2	17	9
4	16	A (6.9)	300	0.15	27	59	17	3	12	9
5	8	A (6.9)	300	0.30	17	58	11	3	23	5
6	16	A (6.9)	300	0.30	15	56	12	2	20	10
7	9	A (6.9)	300	0.30	15	56	12	2	12	8
8	12	A (6.9)	310	0.22	30	64	14	3	11	8
9	8	A (6.9)	325	0.30	23	56	16	4	15	9
10	16	A (6.9)	325	0.30	27	62	16	3	11	8
11	8	B (9.2)	325	0.30	25	49	22	5	14	10
12	16	B (9.2)	325	0.30	23	54	19	5	11	11
13	13	LZM8 (10.0)	280	0.30	21	42	15	2	21	20

[a] All reactions carried out at 150 psig.
[b] Mole ratio ammonia/EA.
[c] See Experimental for catalyst preparation; Si/Al ratios determined by XRF.
[d] Based on EA.
[e] Feedstock-free, water-free, weight-normalized basis from GLC analysis of reactor effluent.
[f] Ethylenediamine.
[g] Summation of GLC analyses of piperazine, 1,(2-aminoethyl)piperazine and higher cyclic oligomers.
[h] Summation of GLC analyses of diethylenetriamine and triethylenetetramine.
[i] Aminoethylethanolamine.
[j] Summation of GLC analyses of unidentified components (none >0.3 wt.%).

structure, a moderately dealuminated H-mordenite was prepared. Amination of EA with this catalyst provided EDA in good selectivity (57–64 wt.%) under virtually identical conditions (300–325 °C; molar feed ratio of ammonia/EA = 8/1–16/1; 150 psig; 0.15–0.30 h^{-1} LHSV, based on EA; see Table 1, runs 3–10). Similar results were obtained with a more extensively dealuminated mordenite at 325 °C (see Table 1, runs 11, 12). Formation of aminoethylethanolamine (AEEA) and cyclic polyethylene amines (primarily piperazine and 1-(2-aminoethyl)piperazine) was suppressed by the modified mordenite catalysts. The most extensively dealuminated mordenite had the highest activity (see Table 1, run 13). Reaction at 280 °C was required to obtain a conversion comparable to those found with less dealuminated catalysts.

To assess the degree of steric control in the mordenite reactions, comparative aminations were carried out with amorphous silica–alumina, and large pore acidic (HY) and rare earth-exchanged (REY) zeolites (275–300 °C; molar feed ratio of ammonia/EA = 16/1; 150 psig; 0.15 h^{-1} LHSV, based on EA; see Table 2). Uniformly poor selectivities (<15 wt.%) to EDA were obtained at conversions comparable to those observed with mordenite catalysts.

Amination of EA is catalyzed by a variety of solid acids. Selectivities obtained in the control experiments clearly show that H-mordenite, and especially dealuminated H-mordenites, are required for selective production of EDA from EA and ammonia. High conversions of EA were obtained with

TABLE 2

Amination of EA with acidic catalysts[a]

Run	Catalyst	T (°C)	Conversion (%)[b]	Selectivity[c]				
				EDA[d]	C[e]	NC[f]	AEEA[g]	UNK[h]
1	silica–alumina	275	40	8	37	8	10	37
2	silica–alumina	300	73	10	34	12	1	43
3	HY	300	37	8	43	3	14	32
4	REY	300	46	13	37	7	7	36
5[i]	A	300	27	59	17	3	12	9

[a] All reactions carried out at 150 psig; molar feed ratio of ammonia/EA = 16/1; 0.15 h^{-1} LHSV, based on EA.
[b] Based on EA.
[c] Feedstock-free, water-free, weight-normalized basis from GLC analysis of reactor effluent.
[d] Ethylenediamine.
[e] Summation of GLC analyses of piperazine, 1-(2-aminoethyl)piperazine and higher cyclic oligomers.
[f] Summation of GLC analyses of diethylenetriamine, triethylenetetramine and higher noncyclic oligomers.
[g] Aminoethylethanolamine.
[h] Summation of GLC analyses of unidentified components (none >0.3 wt.%).
[i] Run 4 of Table 1.

silica–alumina; however, selectivity to EDA was poor ($\leq$10 wt.%; Table 2, runs 1, 2). Silica–alumina is a macroporous, amorphous solid. Consequently, EA amination is not subject to steric control, and self-condensation of EA to form AEEA and cyclic polyethylene amines [52] predominates over reaction of EA with the less basic and nucleophilic ammonia. Catalysis by the large pore zeolites HY (Table 2, run 3) and rare earth-exchanged Y (Table 2, run 4) provided lower conversions. Selectivities to EDA remained low, owing to the lack of steric constraints on EA amination within the Y zeolite intracrystalline structure.

In contrast to the catalysts examined in the comparative runs, H-mordenite provided better selectivities to EDA at similar conversions (Table 1; runs 1, 2). Best selectivities to EDA were obtained with dealuminated H-mordenites; moderately dealuminated H-mordenite was the most selective (*cf.* runs 3–10 *vs.* 1 and 2, 11 and 12, Table 1). Marginally lower selectivities to EDA were obtained with highly dealuminated mordenites (*cf.* runs 9, 10 *vs.* 11, 12, 13 Table 1), presumably as a result of the more open pore structure induced by the greater degree of dealumination.

The pore diameter of H-mordenite is sufficiently large to allow diffusion of EA into the zeolite. Owing to mordenite's narrow tabular structure, EDA is produced with improved selectivity, and cyclization of AEEA to piperazine and higher cyclic polyamines is retarded. However, byproducts such as cyclic polyamines can be formed non-selectively on the exterior of the catalyst. Partial dealumination of H-mordenite resulted in a moderate increase in catalyst activity and a significant increase in selectivity to EDA. As has been suggested previously [52–54], such improved activity and selectivity may result from an increase in effective micropore diameter by removal of amorphous alumina from the pores. Higher selectivity to EDA with dealuminated mordenite at the expense of cyclic and heavy byproducts is a clear indication of reduced residence time of reaction intermediates within the zeolite pores. In this instance, therefore, partial dealumination reduced diffusion resistance, but maintained micropore diameters within the limit required for selective formation of EDA. In contrast, extensive dealumination opened the pore structure to the degree that shape selectivity was compromised, and selectivity to cyclics increased (*cf.* runs 9 and 11, Table 1).

Improvement of H-mordenite activity for acid-catalyzed reactions via dealumination has been reported by several groups [52–54]. Specifically, higher activities for cumene cracking and n-decane/decalin hydrocracking were found with increasing Si/Al ratio of the mordenite catalyst. In addition, lower selectivity to coke formation during cumene cracking was observed [53, 54]. With dealumination, adsorptive capacities of mordenite for cumene [53, 54] and palladium on mordenite for hydrocarbons such as toluene and decalin [52] increased significantly, as did the rates of adsorption and desorption of both catalysts. Consequently, the enhanced activity and slower deactivation of the dealuminated catalysts were primarily results of improved diffusivity. Recently, the activity of a series of dealuminated mordenites for isomerization of *o*-dichlorobenzene has been correlated with the Si/Al

ratio [55]. A volcano-type relationship between the initial rate and alumi-num content of the zeolite was found. The maximum isomerization rate was observed with a partially dealuminated H-mordenite with $Si/Al = 9$. This value is within the range of Si/Al ratios with which best conversions and selectivities to EDA were observed.

With moderately dealuminated mordenite, selectivity to EDA was relatively insensitive to conversion (*cf.* runs 3, 4 *vs.* 5, 6, Table 1), a reflection of steric control of amination by the zeolite. Highest selectivities to EDA were obtained at 310–325 °C. As reaction temperature was increased to 350 °C, selectivity declined dramatically, owing to intervention of acid-catalyzed dehydration of EA. Finally, selectivities to EDA are insensitive to the ammonia/EA feed ratio, as long as molar feed ratios of at least 8/1 are used. However, inclusion of high concentrations of ammonia did not compensate for the lack of catalyst shape selectivity (*e.g., cf.* runs 1, 3–4, Table 2 *vs.* runs 3, 4, Table 1).

In summary, EDA is produced in good selectivity by shape-selective amination of EA with dealuminated mordenite catalysts at low pressure. Selectivity to EDA depends on the degree of mordenite dealumination; best results are obtained with a moderately dealuminated catalyst. In addition, AEEA and cyclic polyethylene amines, major byproducts of this process, are also useful industrial chemicals [50, 56].

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