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NOTE

The Role of Eight-Membered Rings of Mordenite in Methanol Amination

For industrial manufacturing of methylamines, an amorphous silica alumina catalyst has been used for several decades. Such an amorphous catalyst is sufficiently active and stable for commercial methylamine production. On the other hand it suffers from disadvantages that might be overcome by employing shape selective zeolite catalyst. The amorphous catalysts give monomethylamine (MMA), dimethylamine (DMA), and trimethylamine (TMA) that are close to the thermodynamically equilibrium ratios. Nevertheless most methylamine markets need much larger amounts of MMA and DMA, and much smaller amounts of TMA than are given by the amorphous silica alumina catalyst. Energies consuming TMA and recycled ammonia are therefore essential to the conventional manufacturing process.

Since Hamilton (1) patented the concept of producing selective mono- and dialkylamines from alcohols and ammonia using zeolite catalysts, various types of zeolites have been proposed for selective MMA and DMA production. Among these candidates, modified mordenite is a particularly effective catalyst for the selective synthesis of MMA and DMA (2–4), and the large-scale industrial production of methylamines using mordenite was introduced in 1986 by Nitto Chemical Co. (5). Nevertheless, the reasons why mordenite is effective for selective MMA and DMA synthesis are not thoroughly clear.

The channel system of mordenite is formed by parallel elliptical 12-membered rings of 6.7 × 7.0 Å, and 8-membered rings of 2.9 × 5.7 Å. The parallel channels are interconnected via small side pockets of 2.9 Å. The porous structure is illustrated in Fig. 1.

For the diffusion of small molecules, mordenite has a two-dimensional channel system but for large molecules the channel system is one dimensional. It is known that severe pretreatment of mordenite by a concentrated acid can open the structure, creating defects that give a three-dimensional character to the large channels (6). For industrial manufacturing of methylamines, the mordenite catalyst is merely treated with a dilute acid; accordingly the mordenite catalyst still behaves as a two-dimensional system for small molecules and a one-dimensional system for large molecules.

Provided the reactant molecules—ammonia and methanol—preferentially enter mordenite through the 8-membered rings, while the products—methylamines—diffuse out through 12-membered rings, the occurrence of counterdiffusion limitations (7) is prevented in the selective methanol amination.

In order to confirm the absence of the counterdiffusion limitations mentioned above, we have attempted a computer-assisted study of diffusion of the reactant molecules through the eight-membered rings of mordenite.

The diffusion process is mainly governed by a steric hindrance in zeolite channel. In such a case, the energy barrier profile of the molecule passing through the sterically restricted part of the channel can be adequately approximated by the activation energy of diffusion.

The variation of the reactant versus mordenite interaction energy along the eight-membered rings pathway should provide information on the relative rates of diffusion of the different reactant molecules. The energy profile along the diffusion pathway can be obtained by means of molecular mechanics calculations based on the empirical parameters (8, 9). The parameters used in the calculations are installed in the computer software (10) and are listed in Table 1. The calculations were carried out using program Discover (10).

The diffusion path is defined by a pair of asterisks in Fig. 1. We use a minimization routine (10) that ensures that the diffusing molecule follows a minimum energy path along the mordenite channel. The diffusion path is decided automatically, so as to follow the minimum energy path. The reactant molecule was shifted along the channel of mordenite in the direction of diffusion in steps of 0.2 Å. For each step of the calculation the total energy of the reactant, including the interaction with mordenite, was minimized at each step. The reactant was allowed complete freedom to optimize the interaction with mordenite during the minimization, while the mordenite lattice was held fixed at the crystallographically determined geometry.

The series of energy minimization calculations provides a minimum energy profile for the diffusion of the reactant along the mordenite channel. The above-mentioned calculation does not take into account fluctuations in the size of mordenite pore during the lattice vibrations.

Figure 2 shows the calculated minimum energy profiles for the diffusion of ammonia, methanol, and MMA through the eight-membered rings of mordenite. The energy barrier

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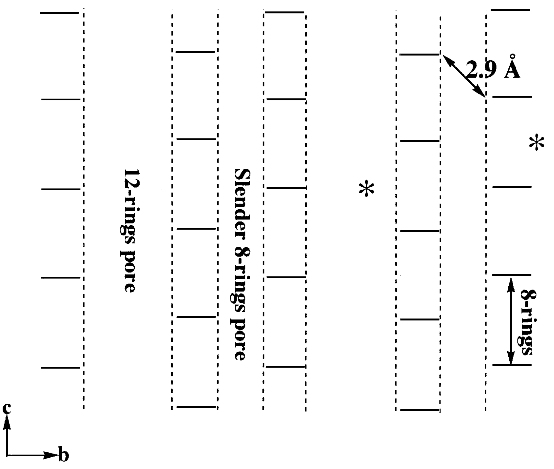

FIG. 1. Pore structure of mordenite. A pair of asterisks shows the diffusion path.

of ammonia diffusion was 15 kcal/mol, and this value is relatively high. The energy barriers of methanol and MMA diffusion were 55 and 57 kcal/mol, respectively.

It is evident that the diffusion of methanol and MMA is significantly impeded, and so methanol and MMA find it difficult to diffuse through the eight-membered rings of mordenite.

Although the estimated energy barrier of ammonia diffusion through the eight-membered rings is relatively high—15 kcal/mol—we tentatively conclude that ammonia can diffuse into mordenite through the eight-membered rings, and thus it can avoid counterdiffusion limitations in methanol amination.

This conclusion is supported by the evidence that analcime, which has six-membered rings with 2.6 Å aperture, adsorbs ammonia (11) and that the activation energy of methanol amination on mordenite catalyst is 25 kcal/mol (5). Furthermore, water can diffuse through analcime pores, and the activation energy for the diffusion is 17 kcal/mol (12).

Methanol also suffers from counterdiffusion problems. Weigert reported that the rate of methanol amination on mordenite is first order with ammonia and zero order with methanol (3). The counterdiffusion limitation of methanol has less influence on methylamine formation, because the rate of the reaction is zero order with methanol.

In order to estimate the contribution of the 8-membered rings path way of ammonia to the reaction, it is necessary to compare the counterdiffusion rate of ammonia in the 12-membered rings with the diffusion rate in the 8-membered rings. Concerning counterdiffusion, very little information is available, and we could not estimate the energy barrier for the counterdiffusion of ammonia in the 12-membered rings. Satterfield *et al.* reported that the counterdiffusion rate is many orders of magnitude less than the rate of diffusion of a single component in mordenite channel (13). As a consequence, the 8-membered rings path way can contribute to a considerable extent to the reaction.

Therefore, the evidence that ammonia diffuses through the eight-membered rings without counterdiffusion limitation makes mordenite well suited to methanol amination.

TABLE 1

Parameters Used in Molecular Mechanics Calculations

Charge parameters

NH_3		CH_3OH		CH_3NH_2		Zeolite	
n3	−0.4022	c3	−0.2700	n3	−0.500	sz	0.6000
hn	0.1400	h	0.1000	hn	0.1400	oz	−0.3000
hn	0.1400	h	0.1000	hn	0.1400		
hn	0.1400	h	0.1000	c3	−0.0800		
		oh	−0.3800	h	0.1000		
		ho	0.3500	h	0.1000		
				h	0.1000		

Bond length parameters

Atoms		R_0 (Å)	k_2 (kcal mol^{-1} $Å^{-2}$)
c	h	1.1050	340.6175
oh	ho	0.9600	540.6336
oh	c	1.4200	384.0000
n3	hn	1.0260	457.4592
c	n3	1.4700	356.5988

Bond angle parameters

Atoms			Theta o	k_2 (kcal mol^{-1} deg^{-2})
h	c	h	106.4000	39.5000
c	o	ho	106.0000	58.5000
o	c	h	109.5000	57.0000
hn	n3	hn	105.5000	36.0000
hn	n3	hn	105.5000	36.0000
c	n3	hn	110.0000	41.6000

Torsional parameters

Atoms		K phi	n	phi o
c	o	0.3900	3	0.0000
n3	c	0.8000	3	0.0000

Nonbonded parameters

Atom	A (kcal mol^{-1} $Å^{12}$)	B (kcal mol^{-1} $Å^{6}$)
h	7180.4660	32.87076
cg	1790340.7240	528.48190
o	272894.7846	498.87880
n3	2266872.4000	1230.55700
hn	0.00000001	0.00000
sz	3149175.0000	710.00000
oz	272894.7846	498.87880

Bond increments parameters

Atoms		Delta ij	Delta ji
n3	hn	−0.1400	0.1400
oh	ho	−0.3500	0.3500
c	oh	0.0300	−0.0300
c	n3	0.2200	−0.2200
c	h	−0.1000	0.1000
oz	sz	−0.1500	0.1500

Note. Atom types: h, hydrogen bonded to C; hn, hydrogen bonded to N; ho, hydrogen bonded to O; c3, Sp3 carbon in methyl group; n3, Sp3 nitrogen with three substituent; oh, oxygen in OH group; oz, oxygen stub for zeolite; sz, silicon stub for zeolite.

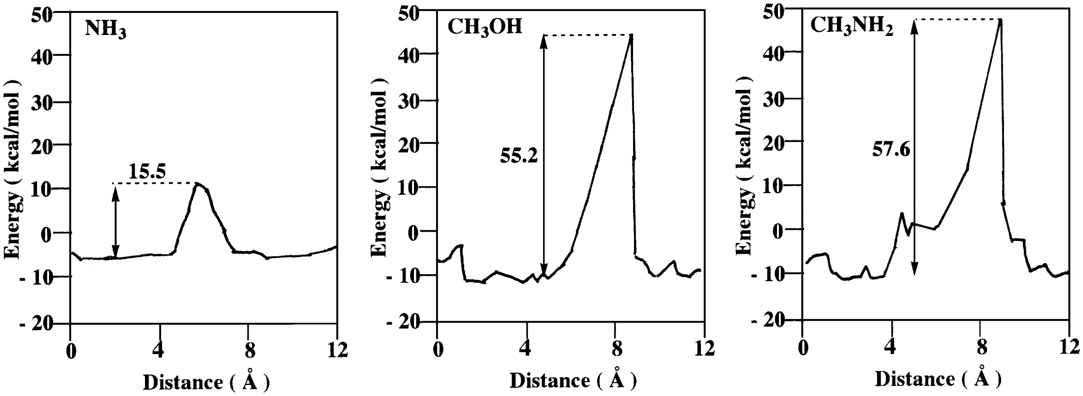

FIG. 2. Minimum energy profiles for diffusion of NH_3, CH_3OH, and CH_3NH_2. Energy zero corresponds to the empty mordenite plus the sorbate in the ideal gas phase.

Moreover, ammonia diffused into mordenite through the eight-membered rings enhances the disproportionation of TMA, the ammonia that makes mordenite suitable for methanol amination. The produced

$$(CH_3)_3N + NH_3 = (CH_3)_2NH + CH_3NH_2$$

TMA inside mordenite pores during methanol amination cannot diffuse to the outside of mordenite in selective DMA and MMA production.

In conclusion, ammonia can diffuse into mordenite through the eight-membered rings while methanol and MMA are difficult to diffuse through. That the ammonia diffuses into mordenite through the eight-membered rings without counterdiffusion limitation makes mordenite well suited to methanol amination.

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