

Synthesis of Dimethylamine by Zeolite Rho: A Rational Basis for Selectivity

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Received April 20, 1990; revised July 2, 1990

The sorption of trimethylamine by zeolite rho was studied to provide a rational basis of catalyst selectivity for the methylamines synthesis reaction from ammonia and methanol. Sorption kinetics, obtained for the range 150–250°C, yield an activation energy of 9 kcal/mole. Mass spec data indicate that trimethylamine is both physisorbed and chemisorbed with relative amounts of 10 and 90%, respectively. The physisorbed entity desorbs intactly while, above 300°C, the chemisorbed trimethylamine pyrolyzes forming mono- and dimethylamines plus some residue. For a given zeolite rho sample, the yield of trimethylamine in the methylamines synthesis reaction was found to correlate with the quantity of physisorbed trimethylamine. For zeolite rho catalysts, an activation energy of 42 kcal/mole was determined for the appearance of trimethylamine in the product stream. © 1990 Academic Press, Inc.

INTRODUCTION

Methylamines are made commercially by the reaction of methanol and ammonia over amorphous alumina-silica catalysts. The product stream over such nonselective catalysts proceeds toward the thermodynamic distribution of monomethylamine (MMA), dimethylamine (DMA), and trimethylamine (TMA), 17, 21, and 62 wt%, respectively. Because market demand favors both mono- and dimethylamines, we explored the possibility of finding a catalyst selective for these products (1–6). It was found that zeolites with medium or large pores produce nearly an equilibrium product distribution, where TMA is the dominant species (2). A wide range of selectivities toward DMA was found for small pore zeolites, for example, mineral chabazites (3).

Zeolite rho was found to provide very high selectivity to DMA as well as very high catalytic activity (4). This combination of selectivity and activity is unusual and permits the reaction to be run at 325°C instead

of 400°C using conventional amorphous silica-alumina catalysts or the chabazites noted above. Unlike the chabazite study where a relationship between alcohol absorption and catalytic selectivity was found, no such correlation was observed for zeolite rho (4). Although not providing a rationale for catalytic selectivity, sorption measurements of alcohols were invaluable in examining the synthesis of zeolite rho and how it evolves to become a superior catalyst, and in distinguishing various rho preparations and their treatment conditions (7). A study of the adsorption and desorption of ammonia by the zeolite rho framework did not yield conclusive results regarding the origin of selectivity for the amines synthesis reaction (8). Ammonia sorbed readily into and from the rho framework, but neither amount correlated with catalytic selectivity.

The absence of any strong correlation of a sorption measurement with the catalytic selectivity for a zeolite rho sample prompted studies on the sorption of molecules larger than *n*-propanol, for example, isobutane and isopropanol. Below 100°C, these molecules show no appreciable sorption into the rho

¹ Contribution No. 5479.

framework. Following these experiments, we then examined the sorption of TMA by zeolite rho which this paper summarizes.

METHODS

Na,Cs-Rho was prepared using AlOOH (Catapal® SB), NaOH, CsOH, and Ludox® LS-30 according to the method described by Robson *et al.* (9). Following repeated ion exchanges at 90°C with 20% NH₄NO₃ solution, the filter cake was washed with distilled water and dried. Wet chemical analysis of the resultant NH₄-Rho preparations indicated a typical composition of (NH₄)_{9.6}Cs_{1.0}Al_{10.5}Si_{37.5}O₉₆. The NH₄-forms were calcined at conditions noted in the text to provide the different H-Rho catalysts. All of the samples used in this study are highly crystalline samples (>90%) according to X-ray diffraction results and have high methanol sorption capacities of 0.22–0.23 g/g dry sample (7). At room temperature, some samples of H-Rho were contacted with a stream of nitrogen which had first passed through trimethylphosphite, TMP. After 4 h of contact, the TMP supply was shut off and the sample left under flowing nitrogen for an additional 16 h. The TMP treatment did not alter the methanol sorption capacity of the samples (10).

The methylamines reactor operation, data acquisition, and analysis, have been previously described in detail (3). The reactor was a U-tube device immersed in a nitrogen-fluidized sand bath whose temperature was controlled by a microprocessor. A 1:1 methanol to ammonia feed to the reactor was controlled by a syringe pump. Products and reactants were measured by gas chromatography.

A Du Pont Instruments series 99 Thermal Analyzer (TGA) was used to record the adsorption and desorption processes of TMA by zeolite rho. The weighing sensitivity is ±20 μg for a sample size of 40–60 mg. A sample is activated in the TGA after being heated to 400°C and maintained at 400°C for 16 h under flowing helium. Afterward, the temperature is reduced to a constant value

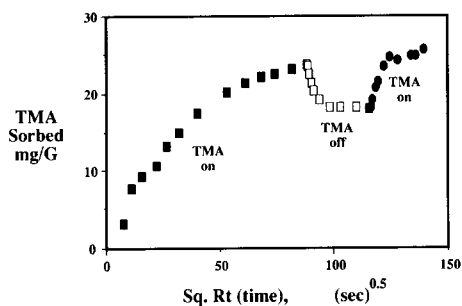


FIG. 1. Protocol for the TMA sorption experiments under isothermal conditions.

(typically 200°C) for the sorption measurements following this protocol:

The helium stream is shut off and, under isothermal conditions, the sample is exposed to TMA at 200 Torr (remainder helium; 1 Torr = 133.3 N m⁻²) for 1–2 h. Upon reaching a steady value for weight gain, the TMA stream is shut off and the sample is swept by flowing helium to monitor the desorption process as shown in Fig. 1. After a steady value has been achieved, the sample is again exposed to TMA. In this manner, the first exposure provides information about the combined chemisorption and physisorption process, the desorption process yields the chemisorbed amount, and finally, the physical adsorption amount is obtained by subtraction. The desorption-adsorption cycle could then be repeated yielding somewhat reproducible values (±10%).

From the exit port of the TGA, the TMA/He effluent was bubbled through two columns filled with sulfuric acid solutions to scrub out the TMA.

For the TMA desorption experiment, a Hewlett-Packard mass selective detector, Model 5970B, was used to monitor the effluent stream from the TGA. A sample of zeolite rho, in a cell containing a vacuum stopcock, was heated under vacuum to 425°C, where it was maintained for 16 h. The sample, after cooling to room temperature, was weighed and then put back onto the vacuum manifold. The sample was heated

to 200°C and exposed to 300 Torr of TMA after which it was cooled to room temperature. At 100°C during the cool-down, the sample was evacuated to remove excess TMA and evacuation was continued to room temperature. The sample had gained 7.87% TMA on a dry weight basis. Using a plastic glove bag with a nitrogen purge, a portion of the sample was removed from the cell and loaded into the TGA/mass spec (MS). The apparatus was then purged with helium and heated to 100°C to remove water adsorbed during the transfer process and reduce the background. The sample was then ramped at 300°C/h under flowing helium to a temperature of 700°C. Weight loss data, total MS ion counts, as well as selective m/z counts at 31 (MMA), 45 (DMA), and 59 (TMA) were obtained for the entire desorption process.

A description of the *in situ* X-ray powder diffraction apparatus and procedures for studying thermally and chemically induced transformations has been described previously (11). The theta-theta vertical mode goniometer was automated for angular slew and step control. Reactor chamber temperature and precursor partial pressure were controlled via microprocessors and mass flow controllers. For the experiment, a sample was dehydrated to 300°C under vacuum in the apparatus and then cooled to room temperature when it was exposed to ~100 Torr of ammonia. Individual ASCII files of 8000 steps were obtained for each isothermal data set. Cell parameters were refined using a modified least-squares program after correcting peak positions using a silicon internal standard.

RESULTS AND DISCUSSION

While ammonia adsorption into the zeolite rho framework readily proceeds at or below 100°C (8), the amount of TMA sorbed is too small and the rate too slow to be easily monitored using the TGA set-up. Higher temperatures were needed to perform TMA sorption experiments. Furthermore, it was found that, unlike the sorption of alcohols discussed earlier (3), TMA left an apprecia-

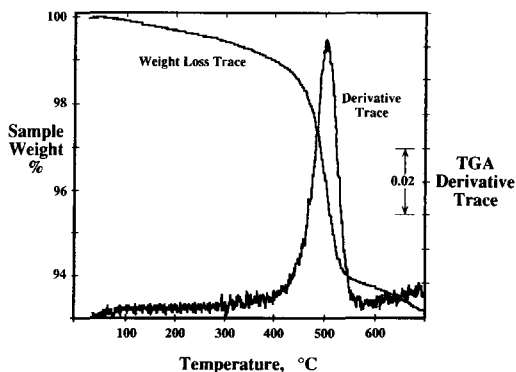


FIG. 2. TGA weight loss and derivative traces for a zeolite rho sample containing 7.87% (dry sample weight basis) TMA.

ble residue on the samples even after prolonged heating at 425°C under vacuum. For that reason, a fresh 50 mg batch of sample was used for each experiment. Sorption curves, similar to that shown in Fig. 1, were obtained for samples of zeolite rho for the temperature range 150–250°C. The sorption rates for the initial exposure to TMA for a sample were then used to produce an Arrhenius plot, $\ln(\text{rate})$ vs $1/T$, such that an activation energy of 9 ± 2 kcal/mole was obtained for the sorption of TMA into zeolite rho.

Of major concern was the possibility of reaction of the TMA within the rho framework during TGA sorption experiments. For this reason, TMA was sorbed into a sample of zeolite rho which was then loaded into the TGA/MS. Shown in Fig. 2 are the TGA weight loss and derivative traces for the desorption experiment. The traces are relatively uneventful until 450–550°C where almost 70% of the sorbed material desorbs. The derivative trace is asymmetrical with a leading edge starting at ~350–400°C. Continued heating to 700°C does not return the sample to its original weight (92.7%) indicating that some residue persists within the framework. Shown in Fig. 3, for the desorption process, is a comparison of the TGA derivative trace with that of the total mass spec ion counts. Both show a major event

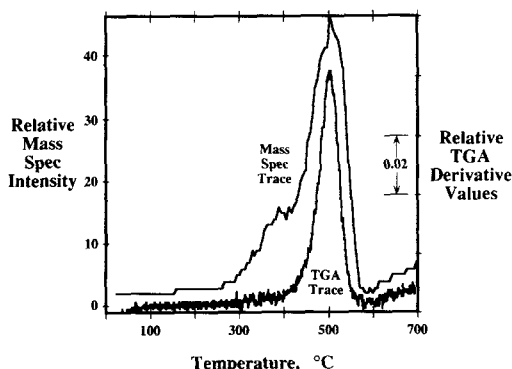
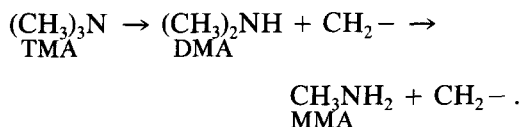


FIG. 3. Comparison of the TGA derivative with the counts from mass spectrometry for the desorption process of a TMA-loaded zeolite rho sample.

at $\sim 500^{\circ}\text{C}$ but the MS trace has a more apparent shoulder in the $300\text{--}400^{\circ}\text{C}$ region. As shown in Fig. 4, selective ion monitoring for the parent species MMA, DMA, and TMA suggest a complex desorption process. While the traces for MMA and DMA have a single peak, the TMA trace has two. The lower temperature peak for TMA corresponds to physically absorbed TMA as suggested by the analysis associated with Fig. 1 while the higher temperature peak is assigned to chemisorbed TMA. From examination of the data in Fig. 4, it is apparent that, below 300°C , TMA desorbs from the rho framework with no apparent degradation. Above 300°C , some DMA is evident in the desorption stream and by 400°C , MMA makes its appearance. The presence of MMA and DMA in the effluent stream indicates that TMA pyrolyzes within the rho framework to produce the other amines via the sequence



The CH_2- fragmentation products account for the residue remaining within the framework after calcination in a nitrogen or vacuum atmosphere at 600°C and above. In the presence of ammonia, TMA reacts to pro-

duce MMA and DMA; this is the basis of the recycle process which we seek to eliminate. The combined TGA/MS data suggest that the TMA sorption measurements, if performed at 200°C , should be fast enough to monitor using the TGA system and free of side reactions such as pyrolysis.

The results of a typical TMA sorption experiment at 200°C are shown as Fig. 1. The weight gain upon the initial exposure to TMA is 23.76 mg/G ; a portion of this is chemisorbed TMA and the remainder is physisorbed. After the initial sorption process looks basically complete, the TMA stream is shut off and the sample is purged with pure helium. The amount desorbed at 200°C in flowing helium is 5.79 mg/G and is assigned to physically bound TMA with the difference, $23.76 - 5.79$, 17.97 mg/G being the chemisorbed amount. After equilibrium is reached, the TMA stream is turned back on to monitor the readsorption process.

Table 1 summarizes the TMA sorption data for a variety of samples that were also examined as catalysts in the methylamines synthesis from methanol and ammonia. The table is arranged in order of increasing TMA yield using the normalized methylamines distribution produced in the synthesis reaction at 90% methanol conversion at 325°C and 1 atm. Shown in Fig. 5 is a plot of the

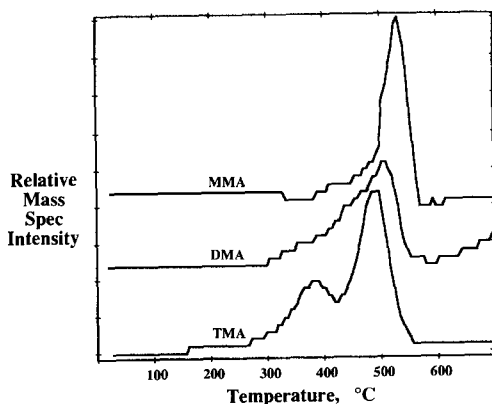


FIG. 4. Selective ion monitoring of the desorption process from a TMA-loaded sample.

TABLE 1

Zeolite Rho: TMA Sorption vs Reactor Yield Data

Calcination conditions ^a		Reactor TMA yield ^b (%)	Total TMA adsorbed ^c	TMA chemisorbed ^d (mg/G)
Temp. (°C)	Time (h)			
600	4	4.0	129.9	118.8
600	4 (Steam)	7.0	42.0	26.5
700	10	16	38.3	24.5
550	6	20	99.1	68.3
600	4	21	104.2	82.5
500	17	24	107.1	81.0
550	10	30	112.6	85.6
600	4	34	110.3	79.3

^a Calcinations generally performed under dry, flowing nitrogen except where noted.

^b Normalized methylamines product distribution at 90% methanol conversion at 325°C and 1 atm.

^c The amount of TMA (mg) adsorbed at 200°C by 1 g of dried sample. Sorption times are in excess of 1 h.

^d The amount of TMA desorbed (at 200°C) from a sample following the adsorption measurement. Desorption was generally carried out for at least 1 h.

TABLE 2

Zeolite Rho: TMA Sorption vs Reactor Yield Data

Calcination conditions ^a		TMA yield ^b (%)	TGA sorption data	
Temp. (°C)	Time (h)		TMA adsorbed ^c (mg/G)	TMA desorbed ^d (mg/G)
700	TMP ^e	0.4	18.2	4.2
400	TMP ^e	0.4	24.6	5.7
600	TMP ^e	0.6	27.2	3.2
600	4	4.0	129.9	11.1
600	4 (Steam)	7.0	42.0	15.5
700	10	16	38.3	13.8
550	6	20	99.1	30.8
600	4	21	104.2	21.7
500	17	24	107.1	26.1
550 ^f	10	30	112.6	27.0
600	4	34	110.3	31.0

^a Calcinations generally performed under dry, flowing nitrogen except where noted.

^b Normalized methylamines product distribution at 90% methanol conversion at 325°C and 1 atm.

^c The amount of TMA (mg) adsorbed at 200°C by 1 g of dried sample. Sorption times are in excess of 1 h.

^d The amount of TMA desorbed (at 200°C) from a sample following the adsorption measurement. Desorption was generally carried out for at least 1 h.

^e Samples were calcinated at the temperatures noted and then treated with TMP, trimethylphosphite.

^f The control (untreated) sample used for the TMP treatments.

total amount of TMA sorbed on the initial exposure vs the reactor yield. Similar scatter was found in the studies using ammonia as the titrant (8). Also included in Table 1 are the chemisorbed amounts of TMA for the different samples. If all of the framework aluminums were titrated by TMA, a value of ~200 mg/G would be obtained but steric constraints (caused by the size of the zeolite rho framework compared to the size of the TMA molecule) limit the amount of TMA absorbed to ~120 mg/G. The data in Table

1 indicate that the chemisorbed amounts of TMA are equivalent to titration of 3–6 framework aluminums which agrees with a previous NMR study (12).

Included in Table 2 are the amounts of TMA desorbed, mg/G, in the TGA experiment. The amounts of TMA desorbed directly relate to the TMA yield as shown by Fig. 6. This correlation suggests that the

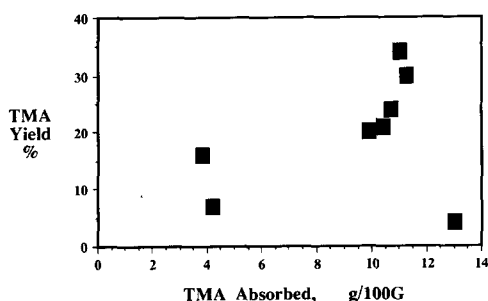


FIG. 5. TMA reactor yield at 90% methanol conversion versus the total amount of TMA sorbed (wt%) at 200°C in a TGA experiment for a given rho sample.

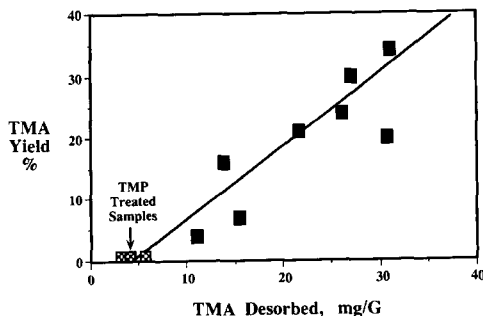


FIG. 6. TMA reactor yield at 90% methanol conversion versus the amount of TMA desorbed (wt%) at 200°C in a TGA experiment for a given rho sample.

appearance of TMA in the product stream is related to an amount in excess of that required to titrate the accessible acid sites. This is a unique observation with respect to zeolite catalysis for which size and shape selective control are the norms. This observation explains why TMA or DMA reactor selectivity did not correlate with the selective absorption of alcohols as was the case for mineral chabazites.

The desorption process, in these experiments, is monitoring the TMA that is physisorbed; that is, the amount that can be adsorbed and desorbed at 200°C through several cycles. For an external surface area of the zeolite rho particles of 20–40 m²/G, a monolayer coverage of TMA would correspond to 5–10 mg/G assuming 40 Å² per TMA molecule. For untreated samples of zeolite rho, this range is much less than the observed weight changes. Furthermore, the range represents an upper limit for the TMA physisorbed on the surface. In all probability, the same fraction, ~10%, of total TMA that is physisorbed compared to the total amount absorbed, physisorbed + chemisorbed, is physisorbed on the surface. If this assumption is correct, then the amount of TMA physisorbed on the external surface of the zeolite particles is less than 1 mg/G. Therefore, almost all of the TMA that is desorbed must be coming from within the zeolite framework.

Included in Table 2 are data for trimethylphosphite, TMP, treated samples. TMP was found to be extremely efficient in reducing the TMA yield over zeolite rho catalysts in the methylamines synthesis reaction (10). In a prior study using the sorption of alcohols at 25°C, we showed that the TMP treatment did not significantly affect the sorption process of *n*-propanol. From that observation, we concluded that TMP was effective in eliminating TMA as a product in the reactor, not by reducing the size of the zeolite rho pore openings but by eliminating unselective surface reactions. The data in Table 2 show a significant drop in the amount of TMA absorbed, 112.6 mg/G, by the control

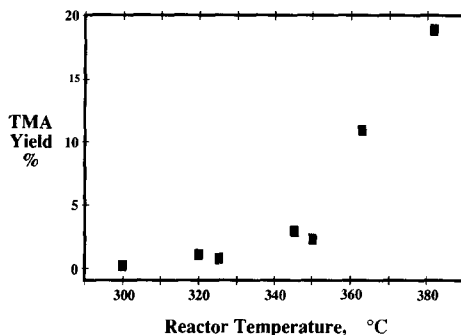


FIG. 7. The TMA reactor yield at constant methanol conversion versus reactor temperature for a sample of zeolite rho.

(an untreated zeolite rho sample) vs that sorbed by the TMP-treated samples, 18–27 mg/G. The reduction in sorption values suggest that the pore openings are slightly reduced in size by the TMP treatment. By raising the sorption temperature to 250°C, it was found that the TMP treated samples sorbed 70–90 mg/G of TMA. Using this new information, we now conclude that TMP surface treatments appear to be bifunctional in nature; TMP eliminates the activity of external surface sites and inhibits the TMA sorption process. Furthermore, the amount of TMA desorbed by the TMP-treated samples corresponds to a monolayer of TMA physisorbed on the external surface. This observation is reasonable as the TMP treatment virtually eliminates external surface acidity of zeolite rho thereby removing the chemisorption sites for TMA.

For several samples, we discovered that the amount of TMA desorbed in the TGA experiment increased with increase of the desorption temperature to 250°C. From this experiment, we concluded that raising the reactor temperature should provide an increase in TMA yield. As shown in Fig. 7 for a TMP-treated sample, the TMA yield does increase with temperature and provides us with the ability to fine tune the TMA yield by adjusting reactor conditions. Note: the amount of monomethylamine is nearly constant at a given methanol conversion for ev-

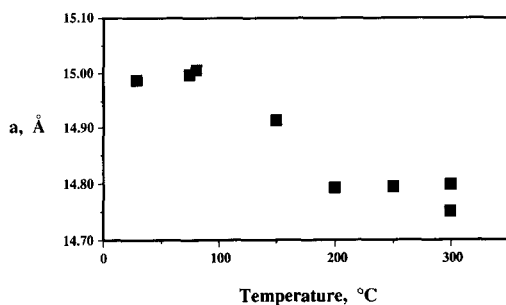


FIG. 8. Changes in the unit cell dimension upon heating an H-rho sample under 100 Torr of ammonia from room temperature to 300°C.

ery sample of zeolite rho examined. Therefore, the increase in TMA yield in the reactor comes at the expense of DMA. An Arrhenius plot for the rate constants for TMA yield as a function of $1/T$ yields an activation energy of 42 ± 4 kcal/mole which is the same for the reaction over a nonselective catalyst. Hence, on the basis of activation energies, it must be concluded that the rate limiting step for TMA synthesis from DMA is the same for both the nonselective and selective catalysts.

Shown in Fig. 8, is the change of unit cell dimension upon heating dehydrated zeolite H-rho under an ammonia atmosphere to 300°C. Normally, the response of the unit cell parameter of H-Rho is to expand $\sim 1\%$ upon heating from room temperature to 300°C (13). For the present study, the observed shrinkage of $\sim 1.6\%$ attests to the strong interaction between the framework and the adsorbed ammonia. After some time at 300°C, a methanol-ammonia mixture was introduced and the changes in unit cell dimension were monitored as a function of time as shown in Fig. 9. During the course of reaction, the unit cell dimension increases significantly paralleling the synthesis of TMA via the reaction sequence:



In-progress neutron diffraction studies of zeolite rho with adsorbed MMA, DMA, or TMA, indicate that the unit cell dimensions

increase in the order: $\text{MMA} < \text{DMA} < \text{TMA}$ (14). In effect, as the methylamines synthesis reaction proceeds, the unit cell responds to the amines present within and the cell size enlarges resulting in more physisorbed TMA. Because of the correlation shown in Fig. 6, more TMA should appear in the product stream as is observed under reactor conditions. Shutting off the methanol and cooling the sample down under ammonia produced a sample (loaded with amines) with a cell constant of ~ 15.05 Å, about 0.06 Å larger than the cell constant of the starting material. Based on examination by NMR, cooled reactor samples were found to contain predominantly TMA (15) which is consistent with this larger cell size.

After assembling and reviewing all of the data, we still find it remarkable that the TMA found in the product stream depends on the physical and not chemisorbed amount. Although not intuitively obvious, this result might be explained on a size-exclusion basis. As we report, TMA tends to titrate the acid sites associated with the framework aluminum but does not titrate all of the sites. While the smaller amine precursors, MMA and DMA, can titrate virtually all of the acid sites, the larger, more basic TMA molecule can displace some of the smaller amine molecules but it is so large such that it is sterically inhibited from titrating all of the framework acid sites. Consequently, a portion of the sorbed TMA can

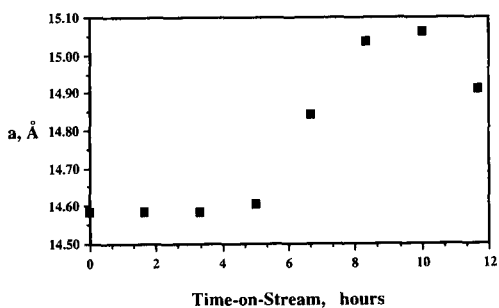


FIG. 9. Changes in unit cell dimension as a function of time of exposure of a rho sample to an ammonia-methanol mixture at 300°C.

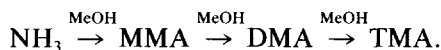
be considered physisorbed and capable of migration into the product stream. Because few TMA molecules can sorb and fit into the H-Rho framework, small differences in the framework geometry, the presence of cations, or the presence of extra-lattice alumina, ELA, may cause significant changes in the bonding of TMA in the framework. For example, calcination at progressively higher temperatures was observed to promote the dealumination of the H-Rho framework and the formation of ELA. In turn, the ELA could produce more accessible sites for strong bonding of TMA within the framework. Therefore, one might expect to measure less physisorbed TMA in samples with more framework dealumination. Indeed, lower TMA yields in the methylamines catalysis are observed as a function of framework dealumination.

CONCLUSIONS

Zeolite rho is a very active and selective catalyst for the synthesis of DMA from methanol and ammonia. Prior to this study, there was no way of predicting the catalytic performance for a given rho sample. Sorption measurements below 300°C show that TMA is ~90% chemisorbed to the rho framework with the remainder physisorbed. The initial rate of TMA sorption into the rho framework was used to calculate an activation energy of 9 ± 2 kcal/mole for the temperature range 150–250°C. The activation energy for conversion of DMA to TMA over zeolite rho is the same as for nonselective catalysts (~42 kcal/mole) suggesting that the reaction mechanism is the same for both catalysts. Since the activation energy for the rate-determining step was so much higher than that controlling sorption, another factor must be involved in determining the selectivity for rho catalysts. It was determined that the reaction selectivity imposed by zeolite rho was related to the physisorbed amount of TMA for a given sample; that is, the appearance of TMA in the product stream is related to an amount in excess of

that required to titrate the accessible acid sites.

The reaction of methanol with ammonia proceeds via the step-wise process:



The lattice parameter of the rho framework enlarges in the order $\text{NH}_3 < \text{MMA} < \text{DMA} < \text{TMA}$ upon absorption of those molecules. Thus, as the amine synthesis reaction proceeds toward completion, this event sequence occurs:

- more TMA is generated within the framework
- the unit cell enlarges providing more space within the framework
- more TMA can fill that space and be physisorbed
- more TMA appears in the product stream as a result.

This event sequence shows that the product spectrum can vary in a predictable fashion as the zeolite responds to changes in composition of the molecules within its framework.

ACKNOWLEDGMENTS

The authors thank Galen Stucky for valuable discussions, Glover Jones for performing the X-ray diffraction study, Mick McCann for the TGA/MS scans, and Brian Arters for performing the TMA/TGA sorption studies.

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