Selective Synthesis of Dimethylamine over Small-Pore Zeolites

IV. Effects of SiO$_2$ and Al$_2$O$_3$ Coatings

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Al$_2$O$_3$ and SiO$_2$ coatings are effective in increasing dimethylamine (DMA) and decreasing trimethylamine (TMA) selectivities of small-pore zeolites H–RHO and H–ZK-5 used as methylamine catalysts. The H–RHO catalysts typically contain chabazite or chabazite and pollucite impurities. SiO$_2$ is more effective than Al$_2$O$_3$ for improving DMA selectivity. SiO$_2$ coatings from monosilicic acid (MSA) reduce dimethyl ether (DME) yields over shallow-bed nitrogen (SBN)-calcined H–RHO, whereas Al$_2$O$_3$ coatings and SiO$_2$ coatings [from tetraethylorthosilicate (TEOS)] do not. Correlations between thickness of SiO$_2$ (TEOS or MSA) coatings and DMA selectivity as well as a decrease in the *n*-hexane rate of sorption suggest a physical hindrance to egress of TMA from RHO channels and cages to the product stream. Coating deep-bed calcined H–pollucite with either Al$_2$O$_3$ or SiO$_2$ from TEOS reduces activity and increases DMA selectivity through deactivation of nonselective surface sites. Improvement of DMA selectivity by coating *DB-calcined* H–RHO catalysts occurs primarily from (i) H–RHO port constriction and (ii) deactivation of external acid sites of H–RHO and H–pollucite and secondarily from deactivation of H–chabazite. Improvement of DMA selectivity by coating *SBN-calcined* H–RHO catalysts occurs primarily from (i) H–RHO port constriction and (ii) further deactivation of external acid sites of H–RHO and amorphous H–chabazite and secondarily from the deactivation of H–pollucite. SiO$_2$ coatings on H–ZK-5 increased DMA selectivity and decreased DME yields, but reduced activity. © 1989 Academic Press, Inc.

INTRODUCTION

Zeolites H–RHO, H–ZK-5, and chabazite are highly selective and active catalysts for dimethylamine (DMA) synthesis from the reaction of methanol and ammonia (*1–6*). H–RHO and H–ZK-5 are unusual in that they provide DMA selectivities similar to global market demands of 50 to 70% at operating temperatures of 325°C. Product selectivities depend strongly on the method and temperature of calcination of the acidic H–RHO from the ammonium precursor (*4*) and on the nature and quantity of impurities present (*5*). In part I of this series (*4*), it was shown that DMA selectivities of 60–70% could be attained over H–RHO by shallow-bed calcination in N$_2$ or steam with low di-

methyl ether (DME) yields. Steaming was found to deactivate pollucite, the most TMA selective impurity (*5*).

An alternate method of providing methylamine selectivities similar to market demand is to deposit coatings of SiO$_2$ and Al$_2$O$_3$ on the surface of these zeolites (*7, 8*). This paper discusses the effect of coatings on the catalytic properties of H–RHO, H–ZK-5, and two impurities frequently found in RHO preparations, chabazite and pollucite.

EXPERIMENTAL

RHO-A was prepared according to the procedure described earlier (*4*). After four 1-h exchanges in 10% aq NH$_4$NO$_3$ at 80°C the bulk composition was [NH$_4$]$_{10}$Na$_{.32}$Cs$_{.48}$Al$_{10.8}$Si$_{37.2}$O$_{96}$, where the ammonium content is assumed to comprise the differ-

ence between Al and the alkalies. Chabazite content was estimated to be ~10% by volume on the basis of SEM photographs. Another sample, RHO-B, contained, in addition to chabazite, significant quantities of pollucite and small amounts of P_c. NH_4–RHO-B was prepared by four 1-h exchanges in 10% aq NH_4NO_3 at 80°C. H–RHO samples used as coating precursors were made by calcination of NH_4–RHO by either dry shallow-bed (SBN) or deep-bed (DB) calcination as described earlier (4).

K,Cs–ZK-5 was prepared according to the procedure of Robson (9, Example 3). H–ZK-5, used for the coating experiments, was prepared by eight 4-h exchanges in 10% aq NH_4NO_3 at 80°C followed by DB calcination at 450°C for 20 h.

The preparation of the H–chabazite and H–pollucite coating substrates is described in Ref. (5).

The zeolites were coated with SiO_2 using monosilicic acid (MSA) and tetraethylorthosilicate (TEOS) solutions or with Al_2O_3 using solutions of basic aluminum chloride.

I. Al_2O_3 COATINGS

Typically, 0.13 g of an aqueous solution of $[Al_2(OH)_5Cl]_x$ (Chlorhydrol, Reheis Chemical), containing 24 wt% Al_2O_3, was added dropwise at 25°C to a slurry of 3 g of hydrated zeolite in 30 ml distilled H_2O to give a final pH of 4.86. About 31.2 mg of Al_2O_3 (1.04 wt%) was made available to the zeolite surface but only a small fraction of this amount was actually deposited. The slurry was then centrifuged to recover the treated zeolite and the solid residue was washed with H_2O to remove excess aluminum chloride. After washing, the coated zeolite was vacuum-dried and DB-calcined at 500 or 550°C in air for 3 h.

II. SiO_2 (TEOS) COATINGS

Samples of dry H–RHO were exposed to 100% humidity for 3 days and picked up ~26.0% water. Typical TEOS-zeolite slurries were prepared by rapidly adding 35 ml of solutions of TEOS in toluene containing 0.347, 0.68, and 1.36 g TEOS, respectively, to ~5.4 g of the humidified samples and agitating for 4 days at 25°C. The SiO_2 made available to the three samples corresponded to 2.5, 4.9, and 9.8% SiO_2 by weight of dry H–RHO, respectively. The samples were then dried and DB calcined at 500 or 550°C for 3 h.

III. SiO_2 (MSA) COATINGS

A dilute solution of MSA was prepared by mixing an aqueous solution of sodium metasilicate (30 g $Na_2SiO_3 \cdot 9H_2O$ in 100 ml 0.1 N NaOH) with 0.025 N H_2SO_4 in the presence of the H^+ form of Dowex HCR-W2H-H^+ cation exchange resin. The resin (15 g) was added to 100 ml of the acid solution in a beaker at about 5°C followed by addition of 5 ml of the MSA solution by intermittent jets of about 0.3 ml each to give a solution of pH 2.15 containing 3 mg SiO_2/ml.

In a typical coating procedure, the pH of a dispersion of 11.84 g of hydrated H-zeolite in 500 ml H_2O was adjusted to 10.5 by the addition of NH_4OH. While heating this slurry to 60°C, 164 ml of the above MSA solution at 5°C was added dropwise. This slurry was then cooled to 25°C and allowed to settle for 64 h. After washing and drying, the product was DB calcined at 500 or 550°C for 3 h.

Pore constriction was determined from sorption measurements of methanol, n-propanol, and n-hexane using a technique described earlier (10). Geometric selectivity index (GSI) defined as (McOH sorption/ n-PrOH sorption) is used as a measure of pore constriction (2, 3).

X-ray photoelectron spectroscopy (XPS) was used to determine the approximate thickness of the oxide coatings. XPS data were obtained using a Physical Electronic 560 ESCA/SAM spectrometer and Mg$K\alpha$ radiation (1253.6 eV). The sample chamber was held at ~5 × 10^{-8} Torr. Spectra were recorded using PHI's Version 6A MACS software on a PDP-11 computer.
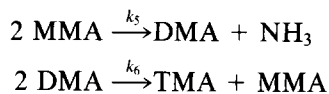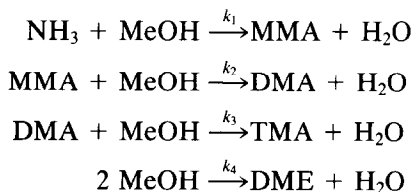
Atomic ratios of Si to Al were determined from the Si $2p$ and Al $2p$ peak areas. Area sensitivity factors, provided by Physical Electronics, were calculated using theoretical photoelectron cross sections, the kinetic energy dependence of the analyzer, and an average value for the dependence of electron escape depth on kinetic energy. NBS Standard No. 70a, a potassium feldspar, was used as a reference sample to monitor consistency of results. To correct for interference of the Cs $4d$ with the Al $2p$ peak in H–RHO, the Cs $4d$ contribution to the Al $2p$ peak was subtracted out, after calculating the contribution from Cs $3d_{5/2}$ peak area.

Coating thicknesses, t, were estimated using the relation proposed by Niwa et al. (*11, 12*),

$$t = d(n - n_0)/(n + 1),$$

where n is the Si/Al atomic ratio of coated sample, n_0 is the Si/Al atomic ratio of uncoated sample, and d is the electron penetration depth assumed to be 20 Å.

To determine catalytic behavior of the coated zeolites, samples were evaluated in a U-tube reactor at temperatures of 250–400°C using a methanol : ammonia mixture at a molar ratio of 1 : 1. Feed rate and reactor temperature were varied to obtain as wide a range of reactant conversion as possible. Multiple data were obtained under each condition to ensure stable reactor operation; i.e., the reactor was lined out and the catalyst showed constant activity. No catalyst deactivation was observed over normal runs of ~8 h. Details are given in Ref. (*4*). The data were fit to a second-order reaction mechanism described in Keane *et al.* (*1*), using the scheme

$$NH_3 + MeOH \xrightarrow{k_1} MMA + H_2O$$

$$MMA + MeOH \xrightarrow{k_2} DMA + H_2O$$

$$DMA + MeOH \xrightarrow{k_3} TMA + H_2O$$

$$2\ MeOH \xrightarrow{k_4} DME + H_2O$$

$$2\ MMA \xrightarrow{k_5} DMA + NH_3$$

$$2\ DMA \xrightarrow{k_6} TMA + MMA$$

The bulk analysis on the reactor effluent was fit to these reactions. Accuracies of individual rate constants were ±10%. The rate constant of the first reaction, k_1, was set to 1. Thus, relative rate constants were measured against k_1. Because our goal was to maximize DMA yield at the expense of TMA, the reactor was operated such that kinetics controlled the product distribution.

The reactions of primary importance in this regime were k_1, k_2, and k_3, the series methylation of ammonia, but the disproportionation reactions, k_5 and k_6, also contributed to the reactor effluent. Typically, $k_2 > 1$, whereas k_5 and $k_6 = 0.1$. Thus, the disproportionation reactions contribute less than 10% of the total reaction products. Therefore, these secondary reactions do not play a major role in determining reactor effluent until the methanol is nearly exhausted and the reaction approaches equilibrium.

After we recognized the minor contribution of the secondary reactions, we operated the reactor to facilitate data collection for k_1, k_2, and k_3. As noted above, the reactions of prime importance were the DMA formation rate, k_2, and the TMA formation rate, k_3. Thus the ratio of these two rate constants, k_2/k_3 was a measure of DMA selectivity independent of initial feed composition, catalyst activity, and methanol conversion in the range examined. In general, for RHO-zeolite k_2 is nearly constant and increases in k_2/k_3 result from decreases in k_3. Therefore, k_2/k_3 and k_3 were used to monitor coating effects. Values of $k_2/k_3 > 1$ indicate DMA selectivity while values of $k_2/k_3 < 1$ indicate a product closer to the equilibrium value (*1*).

Space velocities, which correlate to catalyst activities, were obtained from the reactant feed rates and catalyst charge. Space velocity data under the reactor conditions, 90% MeOH conversion, 325°C, 1 : 1 NH$_3$ to

MeOH feed composition, and 1 atm, were used to compare catalyst activities.

RESULTS

I. RHO

A. Al_2O_3 Coatings

Samples calcined under SBN and DB conditions at increasing temperatures were coated with Al_2O_3. Table 1 shows that TMA selectivities of the SBN samples decreased from 10 to ~5% and were independent of calcination temperature in the range 500–700°C. Al_2O_3 coatings did not affect the DME yields.

Although starting from a higher initial TMA value, similar relative decreases in TMA selectivities were noted for the DB-*calcined* samples: TMA decreased from 19% in the uncoated sample to ~10% for the coated samples. The absence of a decrease in MeOH sorption capacities of the coated 500 and 600 DB samples implies that the Al_2O_3 was deposited at the surface of the zeolite particles and did not enter the zeolite pores.

The gradual decrease in TMA selectivity and increase in DME yield with calcination temperature were observed before (4) and are not attributed to the Al_2O_3 coating.

Coating impure H–RHO-B containing pollucite and P_c with 1% Al_2O_3 under opti-
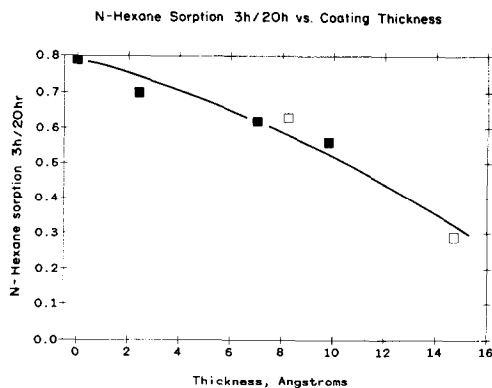
FIG. 2. Three-hour n-hexane sorption/20-h n-hexane sorption vs SiO_2 coating thickness on DB-calcined H–RHO. (■) TEOS coating; (□) MSA coating.

mum conditions reduced TMA from 23 to ~10%. This is almost equivalent to the best Al_2O_3-coated "pure" RHO sample free from pollucite and P_c.

B. SiO_2 Coatings

1. TEOS. TEOS coatings reduce TMA in *SBN-calcined* H–RHO from 10 to 6% and did not reduce the level of DME yields. The TEOS coating on *DB-calcined* H–RHO reduced the TMA yield from 22 to 10%. As in the case of the Al_2O_3-coated samples the absence of a decrease in MeOH sorption capacity of the DB-*calcined* samples with 2.5, 4.9, and 9.8% TEOS implies that the SiO_2 resulting from TEOS resides on the exterior of the zeolite particles rather than in the zeolite pores.

The effect of increasing SiO_2 thickness on catalytic properties is shown in Fig. 1. There are strong correlations between coating thickness and k_3 and k_2/k_3.

The increased thickness of the oxide layers also affects the rates of adsorption of n-hexane and n-propanol as shown in Table 1 and Fig. 2. Increased DMA selectivities are also accompanied by reduced n-hexane sorption as shown in Fig. 3. The MeOH capacities do not generally differ significantly from values of ~22–24% for "pure" RHO (4). However, the ratio of the amount of the larger molecule n-hexane sorbed af-

FIG. 1. DMA and TMA selectivity vs SiO_2 coating thickness on DB- and SBN-calcined H–RHO. (■, ▲) TEOS coating; (□, △, ○) MSA coating.

k₂/k₃ vs. N-Hexane Sorption 3h/20h for SiO₂-coated RHO

FIG. 3. DMA selectivity vs 3-h n-hexane sorption/ 20-h n-hexane sorption for SiO₂-coated RHO. (■) SiO₂ coating; (□) Al₂O₃ coating.

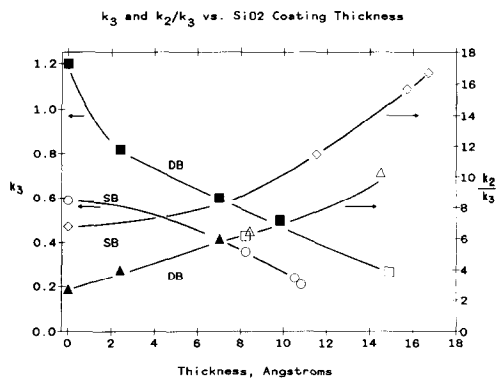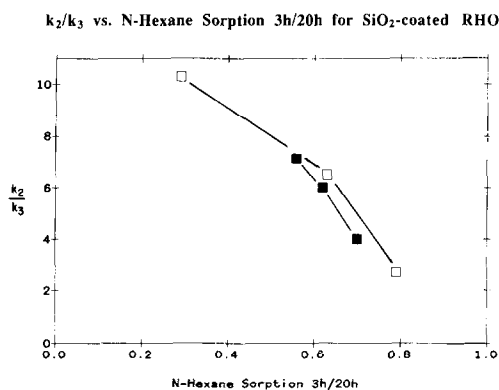ter 3 vs 20 h (n-hex 3/20) decreases regularly as the coating thickness increases as illustrated in Fig. 2.

2. Monosilicic acid. MSA coatings applied to *SBN-calcined* samples changed DMA and TMA selectivities slightly. The increase in DMA selectivity is similar to the increase found on increasing calcination temperature of SBN samples. DME yields were reduced from ~6 to ~3%. This contrasts with Al₂O₃ and TEOS coatings where DME was not reduced.

MSA coatings applied to *DB-calcined* samples were quite effective in reducing TMA from the control value of 22 to ~7%. DME was reduced slightly from 2.1 to 1.5%. As with TEOS coatings, no decrease in MeOH sorption capacities was noted after coating with 4.9 and 9.8% MSA. In addition, there is a good correlation between MSA coating thickness and k_3 and k_2/k_3 (Fig. 1).

C. Activities

No apparent relationship between activity and coating was observed. Whereas the DB series showed some decrease in activity, the SBN-calcined series showed little or no change, even when the coatings resulted in low TMA selectivities.

II. CHABAZITE

Coatings of Al₂O₃ and SiO₂ do not decrease TMA selectivity of *DB-calcined* chabazite, but do decrease activity slightly. As previously shown (5), *SBN-calcined* chabazite becomes amorphous and practically inactive with product selectivity close to the equilibrium distribution. Coating these samples with either Al₂O₃ or SiO₂ reduced the activity even further.

III. POLLUCITE

Of the impurities commonly present in RHO, pollucite is the most reactive and nonselective (5). Although generally not visible in XRD patterns of good RHO preparations, pollucite may nevertheless be present in quantities sufficient to reduce DMA selectivities. H–pollucite is highly nonselective, producing ~75% TMA, and is active at 325–350°C with SV = 1.1 h⁻¹ (5). Coating a DB-calcined control sample with Al₂O₃ or TEOS reduced TMA selectivity from 78 to 52 and 28%, respectively, while simultaneously decreasing activity from 1.1 to 0.33 and 0.08 h⁻¹, respectively. SiO₂ (TEOS) was clearly more effective in deactivating this nonselective zeolite than Al₂O₃.

As shown previously (5), pollucite loses much of its crystallinity and activity after *SBN calcination.* Coating SBN-*calcined* samples with Al₂O₃ and TEOS did not greatly affect TMA selectivity but decreased activity slightly.

IV. ZK-5

Although no reference sample of uncoated H–ZK-5 calcined twice at 450°C was prepared, the sample coated with Al₂O₃ serves as a reference for the SiO₂-coated ZK-5 because no change in DMA selectivity over that of the uncoated sample is observed.

Coating DB-calcined H–ZK-5 with Al₂O₃ had only little effect on TMA selectivities and DME yields. Sorption capacity of uncoated ZK-5 (12.8%) is anomalously low

TABLE 1

Data on Coated Zeolites

Treatment	t (Å)	T (°C)	Conv (%)	DME (%)	DMA (%)	TMA (%)	SV (h⁻¹)	k_2/k_3	MeOH (%)	PrOH 3 h	PrOH 20 h	PrOH 3/20	GSI	n-Hex 3 h	n-Hex 20 h	n-Hex 3/20
A. RHO																
Al₂O₃ Shallow-bed pure RHO																
600SB/no coat/500 DB		300	92	5.6	63	10	3.3	6.80								
500SB/1%Al₂O₃/500DB[a]		300	91	5.9	69	5	3.3	17.60								
600SB/1%Al₂O₃/500DB		300	89	6.1	64	6	3.7	12.70								
700SB/1%Al₂O₃/500DB		300	91	4.0	68	4	3.3	10.70								
Al₂O₃ Deep-bed pure RHO																
600DB/no coat/500 DB		300	91	4.6	54	19	5.3	2.90	23.0	18.9	19.3	0.97	1.2	11.2	12.6	0.89
500DB/1%Al₂O₃/500DB		300	95	1.4	61	12	4.5	4.60	24.5	12.9	18.3	0.71	1.3	1.7	2.7	0.58
600DB/1%Al₂O₃/500DB		300	91	3.3	61	10	4.8	6.10	23.5	17.5	18.1	0.97	1.3	11.5	13.0	0.89
700DB/1%Al₂O₃/500DB		300	92	8.2	64	8	3.8	8.50								
Al₂O₃ Deep-bed impure RHO																
550DB/no coat/550DB		300	92	1.9	47	22	5.0	2.27								
550DB/1%Al₂O₃/550DB		300	93	2.5	59	10	4.0	6.80								
550DB/5%Al₂O₃/550DB		300	87	2.4	59	6	4.0	9.63								
550DB/10%Al₂O₃/550DB		300	88	2.6	59	9	5.0	6.98								
550DB/15%Al₂O₃/550DB		300	93	1.5	63	7	4.0	8.79								
500DB/no coat/500DB		300	92	1.7	50	23		2.50								
500DB,0.2%Al₂O₃/500DB		300	89	2.6	62	13	6.7	6.00								
500DB,0.5%Al₂O₃/500DB		300	95	2.6	65	13	5.0	4.80								
550DB,1%Al₂O₃,,500DB		300	89	1.5	64	8	4.8	7.40								
SiO₂(TEOS)-shallow-bed																
600SB/no coat/500DB		300	92	5.6	63	10	3.3	6.80								
600SB/TEOS/500DB		300	89	6.3	64	6	3.1	11.67								
SiO₂(TEOS)-deep-bed																
500DB/no coat/500DB	0.0	300	93	2.1	51	22	4.5	2.69	22.0	15.7	16.2	0.97	1.4	7.0	8.9	0.79
500DB/2.5%TEOS/500DB	2.4	300	93	1.8	56	14	4.5	4.00	23.6	17.2	17.7	0.97	1.3	5.9	8.4	0.70
500DB/4.9%TEOS/500DB	7.0	300	94	3.3	61	13	5.0	6.00	24.1	15.5	16.9	0.92	1.4	5.1	8.3	0.62
500DB/9.8%TEOS/500DB	9.8	300	90	1.9	62	8	4.2	7.14	22.7	15.1	18.5	0.82	1.2	4.3	7.6	0.56
500DB/10%TEOS/500DB		300	94	3.1	64	10	3.7	7.20								
550DB/1%TEOS/550DB		300	94	4.3	65	11	6.3	9.60								
550DB/5%TEOS/550DB	18.6	300	89	4.0	71	3	5.0	26.70								
550DB/10%TEOS/550DB		300	93	4.0	70	4	4.2	22.70								
550DB/20%TEOS/550DB		300	95	3.9	72	5	2.9	15.10								

SiO_2(MSA)-shallow-bed																
600SB/no coat/500DB	0.0	300	92	5.6	63	10	3.3	6.80			16.2		1.4			
500SB/10%MSA/500DB	8.2	300	93	2.9	69	9	2.3	11.50			16.3	0.97	1.4	7.0	8.9	0.79
600SB/10%MSA/500DB	10.5	300	93	2.8	70	7	3.6	15.70			7.2	0.56	3.1	2.4	3.9	0.63
700SB/10%MSA/500DB	10.8	300	91	3.0	69	4	2.2	16.70			16.2	0.51	1.4	0.6	1.9	0.29
SiO_2(MSA)-deep-bed																
500DB/no coat/500DB	0.0	300	93	2.1	51	22	4.5	2.70	22.0	15.7						
500DB/4.9%MSA/500DB	8.2	300	89	2.0	62	10	3.6	6.50	23.0	9.1						
500DB/9.8%MSA/500DB	14.7	300	89	1.5	59	8	3.7	10.30	22.5	3.7						
500DB/no coat/500DB	0.0	300	93	2.1	51	22	4.5	2.70	22.0	15.7						
500DB/8.9%MSA/500DB		300	90	1.5	63	7	3.8	10.00								
700DB/8.9%MSA/500DB		300	95	6.7	69	5	2.6	16.70								
B. Chabazite																
600DB/no coat		325	93	15.0	53	18	1.1	2.75								
600DB/no coat		350	91	11.0	52	17	1.0	3.10								
600SB/no coat		375	90	10.0	32	44	0.24	1.40								
600SB/no coat		400	94	5.4	39	29	0.08	1.28								
600SB/SBST/no coat		375	87	21.0	28	49	0.20	1.10								
600DB/Al₂O₃/500DB		350	95	14.0	49	20	0.71	2.36								
600DB/TEOS/500DB		375	89	13.0	47	13	0.48	1.50								
600SB/Al₂O₃/500DB		425	~50				0.01	0.54								
600SB/TEOS/500DB							0.01	2.50								
C. Pollucite																
600DB/no coat		350	93	8.1	14	78	1.1	0.15								
600SB/no coat		400	89	11.0	22	53	0.12	0.50								
600SBST/no coat		400	89	4.8	31	37	0.12	0.70								
600DB/Al₂O₃/500DB		375	91	7.1	23	52	0.33	0.50								
600DB/TEOS/500DB		400	91	3.9	35	28	0.08	1.10								
600SB/Al₂O₃/500DB		400	94	10.0	22	59	0.09	0.54								
600SB/TEOS/500DB		400	93	5.7	24	53	0.09	0.64								
D. ZK-5																
Al_2O_3																
500DB/no coat	0.0	325	94	6.6	58	19	2.0									
450DB/1%Al₂O₃/450DB	0.4	325	90	8.5	62	20	1.5	1.76	19.9	1.6	12.8	0.12	1.5	13.2	13.7	0.96
450DB/5%Al₂O₃/450DB	7.0	325	95	6.1	64	16	1.2	6.16	19.4	2.1	5.2	0.41	3.7	13.3	13.6	0.98
SiO_2(TEOS)																
450DB/10%TEOS/500DB	8.2	375	94	0.7	61	2.0	0.23	23.50	19.1	0.0	0.0			8.4	13.1	0.65
SiO_2(MSA)																
450DB/1.25%MSA/500DB	0.0	325	92	8.2	53	20.0	1.1	2.30	20.0	3.6	11.1	0.32	1.8	14.0	14.2	0.98
450DB/10%MSA/500DB	6.7	350	87	1.2	57	3.0	0.43	11.60	19.5	0.5	0.8	0.61	24.3	13.0	13.6	0.95

[a] Coating levels are nominal quantities. The actual amounts can be lower if all the oxide in solution is not deposited on the zeolite.
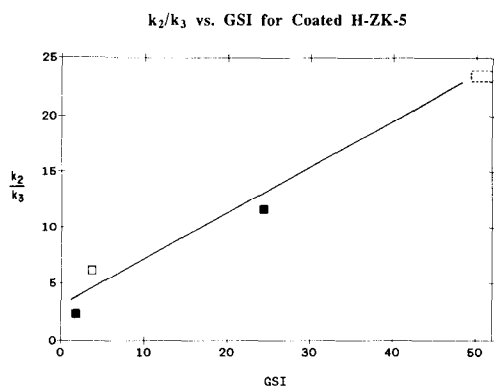
k₂/k₃ vs. GSI for Coated H-ZK-5

FIG. 4. DMA selectivity vs GSI for coated H–ZK-5. (■) TEOS coating; (□) MSA coating.

relative to values obtained for RHO (15.7, 18.9%) and relative to n-hexane (13.7%). After coating, sorption capacity for n-propanol after 20 h is decreased even further to 5.2%, giving an increase in GSI from 1.5 to 3.7 (see Fig. 4). Sorption capacity for n-hexane, however, remained unchanged, suggesting a stronger interaction between the zeolite and n-propanol than n-hexane.

The SiO_2 (TEOS) coating of H–ZK-5 reduced the TMA selectivity from 20 to 2% and the DME yield from 8.5 to 0.7%. The effectiveness of the TEOS coating is reflected in the lack of n-propanol sorption and reduced n-hexane sorption. Coating a sample with SiO_2 from a solution calculated to yield a deposit of 1.25% SiO_2 was relatively ineffective and changed neither TMA selectivity nor DME yield. However, a thicker SiO_2 coating from MSA was as effective as the SiO_2 coating from TEOS; TMA selectivity and the DME yield were reduced from 20 to 3% and 8.5 to 1.2%, respectively. As in the case of the TEOS coating, n-propanol sorption capacity was reduced considerably. Effective SiO_2 coatings, however, greatly reduce H–ZK-5 activity.

DISCUSSION

I. PREVIOUS WORK ON COATINGS

Coating zeolites with oxides to reduce pore openings and obtain separation of gas mixtures or catalytic shape selectivity is a recent development. Barrer and Trombe (13) used silanes and boranes to coat mordenite and observed different sieving properties. Thijs et al. (14) used diborane (B_2H_6) and silane (SiH_4) sorption followed by oxidation with CH_3OH to coat H–mordenite with methoxy groups. Further oxidation with O_2 at 400°C removed methoxy groups formed during reaction with CH_3OH. Oxidation of silane or borane with H_2O produced B–OH or Si–OH groups that effectively reduced the mordenite port size to less than 4 Å.

Niwa et al. (11, 12) coated H–mordenite by vapor deposition of tetramethylorthosilicate and calcination at 400°C in flowing O_2. XPS studies indicated the development of coatings with thicknesses of 2–8 Å. Sorption studies showed that 1.4% SiO_2 reduced the effective diameter of the mordenite channels from 6.7 × 7.0 to ~6 Å and 2.7% SiO_2 reduced the effective diameter to ~5 Å. On the basis of unchanged zeolite acidity, as measured by NH_3 adsorption, the authors concluded that SiO_2 was deposited only at the external surface of the zeolite crystallites. They also concluded that this would enhance shape selectivity in certain reactions. Later experiments (12) where coated Pt–mordenite was used in hydrocracking of paraffins confirmed their conclusion as only the smaller octane isomers could be cracked on 3.2 and 3.4% SiO_2-coated zeolites. At 3.7% SiO_2 loading, not even octane could be cracked.

II. COATING OF SMALL-PORE ZEOLITES FROM SOLUTION

Our results on the small-pore zeolites H–RHO and H–ZK-5 show that solution deposition of SiO_2 and Al_2O_3 produces coatings sufficiently thick to improve shape selectivity in the methylamine reaction. Figure 1 shows that SiO_2-coated H–RHO behaves similarly to the coated H–mordenite of Niwa et al. (11, 12) insofar as thicker coatings progressively reduce selectivities of reactants or products with molecular dimen-

sions similar to those of pore openings. On the basis of the sorption rate changes of n-propanol and n-hexane, the order of effectiveness of these coatings was TEOS > MSA 10% > Al_2O_3 > MSA 1%.

Coating of zeolite RHO reduces the acidity of the external surface which would be expected to be nonselective. Use of Hammett indicators shows a shift in surface pK_a of zeolite H–RHO from about −5 to −8 to greater than about +4 on TEOS treatment (7). External surfaces of both RHO and impurity phases are involved but we do not know the relative importance of each.

Conceivably, the changes in catalytic behavior of coated RHO and ZK-5 could also be affected by the deposition of Al or Si oxide species in the zeolitic pores. However, we believe this is unlikely for several reasons. First, the absence of a decrease in MeOH sorption capacity after coating with Al_2O_3, TEOS, or MSA argues against this possibility. Second, it is unlikely that the species in solution are sufficiently small to enter the ~3.9-Å channels of RHO or ZK-5 (7, 8). Third, MSA is rather unstable at the pH of 10.5 used for the application of the coating and is anticipated to react at the hydroxylated zeolite surfaces or polymerize to form even larger dimers or trimers. Fourth, after the first reaction the channel size should be restricted and decrease even further the possibility that new MSA could diffuse into the channel. Al hydroxide species in solution $(Al_2(OH)_5Cl)_x$ (7, 8) are even bulkier than the silica species and even less likely to enter the zeolitic channels.

Figure 3 shows the correlation between k_2/k_3 and GSI for coated H–ZK-5. This correlation suggests that coatings constrict the pore openings of H–ZK-5 and prevent TMA from exiting the zeolite cages to the product stream. A plot of n-hex 3/20 vs coating thickness (Fig. 2) reflects the increasing hindrance of the thicker oxide layers on H–RHO to passage of n-hexane. This hindrance is further reflected in the correlations of k_2/k_3 with n-hex 3/20 shown

in Fig. 4. Coatings on both H–ZK-5 and H–RHO provide a physical barrier for TMA egress from the large cages to the product stream.

As noted earlier the n-propanol vs n-hexane sorption results for H–ZK-5 are anomalous. The other small-pore zeolites RHO, chabazite, and CaA show 20-h n-propanol capacities that are 50–100% greater than n-hexane capacities (15) whereas ZK-5 shows approximately equal capacities for these two probe molecules. Typical n-PrOH sorption capacities for H–ZK-5 are ~12–15 g/100 g at 20 h whereas H–RHO capacities are ~20 g/100 g. In addition to anomalous n-PrOH capacities, ZK-5 also shows lower rates of n-PrOH sorption. All of the 3-h n-propanol sorption values for both uncoated and coated ZK-5 are significantly lower than the 20-h values while the n-hexane values remain more or less constant.

The size of the zeolite cages cannot be the source of this anomaly because the sizes of the α cages in both ZK-5 and RHO are similar. The most likely source of the hindered n-PrOH sorption is the presence of residual NH_4^+ ions and nonframework Al species (6) located close to or in the double eight-ring. An infrared spectrum with a weak band at 1400 cm^{-1} indicated that some residual NH_4^+ was present in the uncoated H–ZK-5 DB calcined at 500°C and a T–O stretching frequency of 1075 cm^{-1} indicated considerable dealumination (6).

The high degree of correlation evident in Figs. 1–3 can be explained by TMA hindrance from either a continuous oxide layer or a discontinuous layer of oxide islands. A continuous coating would grow progressively thicker with a consequent progressive narrowing of the ports. A discontinuous oxide "island" coating of ports would occur if islands of constant or varying thickness spread out over the zeolite external surface. With existing data we have no way to distinguish between these two mechanisms. The coating is probably discontinuous at very low levels of coating but the discontinuities could also predominate

at oxide coating levels sufficiently heavy to completely cover the surface.

III. EFFECTS OF COATINGS ON DME YIELDS

Table 1 shows that DME yields are generally not affected by coating. However, DME yields were significantly reduced by SiO_2 (MSA) coatings on SBN-calcined H–RHO and by SiO_2 and Al_2O_3 coatings on H–ZK-5. Apparently, DME is produced in the zeolite cages and on external surfaces. DME arising from nonframework Al located in the large zeolite cages (4), particularly in DB-calcined samples (10), is not affected by surface coatings. However, DME arising from external surface sites, apparently present on SBN-calcined H–RHO (4) or impurity phases such as chabazite (5), is suppressed by SiO_2 (MSA). Similarly, DME from surface sites on H–ZK-5 is suppressed by Al_2O_3 or SiO_2 coatings.

IV. EFFECTS OF COATINGS ON IMPURITIES

Table 2 summarizes the catalytic results on uncoated and coated H–RHO/H–chabazite mixtures, pure H–chabazite, and pure H–pollucite and shows the importance of pollucite in determining the catalytic behavior of typical H–RHO catalysts.

A. H–Chabazite

Coating DB-calcined H–chabazite has minimal effects on DMA selectivity but does reduce activity slightly. Coating amorphitized SBN-calcined chabazite deactivates any remaining nonselective surface sites. Because H–chabazite has somewhat lower activity than H–RHO, its presence as an impurity in coated H–RHO samples should not have much effect on selectivities.

B. H–Pollucite

Pollucite, which occasionally appears in RHO samples crystallized for longer than optimum time periods, reduces DMA selectivities of H–RHO to levels of 40–50% (5). However, SiO_2 and Al_2O_3 coatings can effectively increase DMA selectivities of pollucite-containing RHO to ~70%, probably by deactivation of surface Lewis sites on H–pollucite (5).

Coating *DB-calcined* H–pollucite simultaneously decreases activity and increases DMA selectivity. SiO_2 (TEOS) reduced activity by an order of magnitude. This reduction in activity probably occurs because of deactivation of surface sites rather than because of port constriction because MeOH is too large to enter the 2.6-Å ports of pollucite.

The effect of coating *SBN-calcined* H–pollucite was less marked because of the already low activity and because the coatings were not very effective in increasing k_2/k_3.

V. Increased DMA Selectivity of Coated H–RHO Catalysts

We believe the reaction of methanol and ammonia occurs mainly in the internal cages of RHO and ZK-5 zeolites. In these cages the reaction produces a mixture of methylamines that contains significant amounts of TMA. Examination of used TEOS-treated RHO zeolite by CP/MAS ^{13}C NMR shows approximately equal amounts of DMA and TMA (16). The MMA and

TABLE 2

Typical Methylamine Activities and Selectivities of Uncoated and Coated RHO and Impurities

	SV (h⁻¹)	DMA	TMA	k_2/k_3	SV (h⁻¹)	DMA	TMA	k_2/k_3
	DB-RHO + Chabazite				SB-RHO + Chabazite			
Uncoated	5.0	52	21	2.8	3.3	63	10	5.2
Al_2O_3	4.7	62	10	7	3.5	67	5	15
SiO_2(TEOS)	4.5	62	10	7	3.1	64	6	12
SiO_2(MSA)	3.6	60	9	10	3.6	69	7	16
	DB-Chabazite				SB-Chabazite			
Uncoated	1.10	52	17	3.0	0.20	35	35	1.35
Al_2O_3	0.70	49	20	2.4	0.01	—	—	0.5
SiO_2(TEOS)	0.50	47	13	1.5	0.01	—	—	2.5
	DB-Pollucite				SB-Pollucite			
Uncoated	1.10	14	78	0.15	0.10	22	53	0.50
Al_2O_3	.33	23	52	0.50	0.09	22	59	0.55
SiO_2(TEOS)	.08	35	28	1.10	0.09	24	53	0.65

DMA formed in the cages should readily diffuse out through the zeolite ports, but the egress of TMA would be hindered, either because of size limitations or because it is more tightly bound. Thus, the majority of the TMA remains in the interior of the zeolite where it reacts with excess ammonia to form MMA and DMA.

Coating either DB- or SBN-calcined H–RHO catalysts which contain H–chabazite and perhaps H–pollucite further enhances DMA selectivity with little or no change in activity. This increased DMA selectivity appears to have two sources: further port constriction and surface deactivation resulting from elimination of external acid sites from both H–RHO and the impurities pollucite and chabazite. Port constriction is evidenced by the high correlation among k_2/k_3, n-hex 3/20, and coating thickness as discussed in Section II.

In addition to providing port constriction, coating also reduces the surface acidity (7) and thereby the activity of H–RHO and the less DMA-selective impurity phases pollucite and chabazite. Coating pollucite is particularly effective as it masks the active surface of pollucite and inhibits it from contributing to the product stream.

ACKNOWLEDGMENT

REFERENCES

1. Keane, W., Sonnichsen, G. H., Abrams, L., Corbin, D. R., Gier, T. E., and Shannon, R. D., *Appl. Catal.* **32**, 361 (1987).
2. Gier, T. E., Shannon, R. D., and Sonnichsen, G. C., U.S. Patent 4,602,112 (July 22, 1986).
3. Abrams, L., Gier, T. E., Shannon, R. D., and Sonnichsen, G. C., Eur. Patent Appl. 183,423 (April 6, 1986).
4. Shannon, R. D., Keane, M., Abrams, L., Staley, R. H., Gier, T. E., Corbin, D. R., and Sonnichsen, G. C., *J. Catal.* **113**, 367 (1988).
5. Shannon, R. D., Keane, M., Abrams, L., Staley, R. H., Gier, T. E., Corbin, D. R., and Sonnichsen, G. C., *J. Catal.* **114**, 8 (1988).
6. Shannon, R. D., Keane, M., Abrams, L., Staley, R. H., Gier, T. E., and Sonnichsen, G. C., *J. Catal.* **115**, 79 (1989).
7. Bergna, H. E., Corbin, D. R., and Sonnichsen, G. C., U.S. Patent 4,683,334 (July 28, 1987).
8. Bergna, H. E., Corbin, D. R., and Sonnichsen, G. C., U.S. Patent 4,752,596 (June 21, 1988).
9. Robson, H. E., U.S. Patent 3,720,753 (March 13, 1973).
10. Fischer, R. X., Baur, W. H., Shannon, R. D., Staley, R. H., Vega, A. J., Abrams, L., and Prince, E., *J. Phys. Chem.* **90**, 4414 (1986).
11. Niwa, M., Kato, S., Hattori, T., and Murakami, Y., *J. Chem. Soc. Faraday Trans. 1* **80**, 3135 (1984).
12. Niwa, M., Kawashima, Y., and Murakami, Y., *J. Chem. Soc. Faraday Trans. 1* **81**, 2757 (1985).
13. Barrer, R., and Trombe, J. C., *J. Chem. Soc. Faraday Trans. 1* **74**, 2798 (1978).
14. Thijs, A., Peeters, G., Vansant, E., and Verhaert, I., *J. Chem. Soc. Faraday Trans. 1* **79**, 2821 (1983).
15. L. Abrams, unpublished data.
16. A. J. Vega and G. C. Sonnichsen, unpublished results.