Reactions of Silane with Zeolitic Water

By **Richard M. Barrer** * and **Jean-Christian Trombe**, Physical Chemistry Laboratories, Chemistry Department, Imperial College, London SW7 2AY

A study has been made of reactions of SiH_4 with regulated amounts of zeolitic water in zeolite Na-Y and in Na-mordenite. Between 60 and 200 °C the reaction proceeds more readily in the three-dimensional channel system of zeolite Y than in the one-dimensional channels of mordenite. Nevertheless, a very small deposition of Si (*ca.* 0.25 wt. %) within mordenite channels reduces the uptakes and rates of sorption of O_2 and N_2 to very low values, while in the modified Na-Y the capacity shown to these gases and to water is decreased only by small amounts, proportionally to the extents of reaction between silane and zeolitic water. This striking difference implies that in mordenite the reaction products are concentrated near the entrances to the channels. Lightly grinding the modified mordenite crystals causes an extremely large increase in the sorption rates of O_2 and N_2. The reaction products formed within the zeolites are not displaced by outgassing at 360 °C, and evidence has been obtained that they are condensation–polymerisation type molecules, probably of low molecular weight.

CHEMICAL modification of zeolites has been effected by reactions of H-zeolites with $SiMe_4$ [1] and with SiH_4.[2,3] After chemisorption of silane there can be profound changes in sorption and molecular-sieve properties of the parent zeolite such as H-mordenite. Another possibility is that SiH_4 will react with intracrystalline zeolitic water with deposition of siloxane-type compounds which change the properties of the zeolite. It is the purpose of the present work to investigate this possibility for a zeolite with a three-dimensional and one with a one-dimensional channel system.

Monosilane (SiH_4) is thermally stable up to 400 °C,[4] but its decomposition can be catalysed at lower temperatures by reduced Ni. In a quartz vessel it is not decomposed by pure water, but even trace amounts of alkali are sufficient to catalyse its decomposition.[5,6] Stock and Somiesky [7] reported that, in the presence of water vapour, 5—20% of the initial dose of SiH_4 was decomposed in the first 24 h at 25 °C. The hydrolytic oxidation of silane, catalysed either by acids or bases, gives in the first stage a short-lived monosilanol which soon condenses to disiloxane [5,8] [equations (1) and (2)].

$$SiH_4 + H_2O \longrightarrow SiH_3(OH) + H_2 \qquad (1)$$

$$2SiH_3(OH) \longrightarrow H_3SiOSiH_3 + H_2O \qquad (2)$$

Hydrolytic oxidation can, however, proceed further. Transient silane-di- and -tri-ols, $SiH_2(OH)_2$ and $SiH(OH)_3$, can form, although starting with SiH_4 they have not been isolated because they condense with loss of water to higher-molecular-weight compounds as soon as they are formed.[8] The remaining Si–H bonds of disiloxane or higher-molecular-weight compounds are less prone to hydrolytic scission than are these bonds in SiH_4.[8] However, starting with SiH_4, the final result of scission of all Si–H bonds, in whatever condensation polymer they may exist, must be to yield $4H_2$ per original SiH_4.

EXPERIMENTAL

The silane contained *ca.* 4% of hydrogen. Before each run the silane was purified by freezing at −196 °C and pumping off the uncondensable residual gas.

The apparatus included the volumetric unit already described [2] in which the gases were continuously circulated through a bed of zeolite heated to an appropriate temperature. There was provision for adding metered doses of water vapour to the zeolite and for measuring the H_2 and SiH_4 reacted or chemisorbed as well as the SiH_4 physically sorbed. A second unit comprised a McBain–Bakr silica spring balance, also with provision for continuous circulation of the gas past the sorbent in the balance case. A trap for freezing out condensable gas and a manometer were included, together with means for adding doses of water vapour to the zeolite, the amount being adjusted as desired through the measurement of weight change in the zeolite. Measured doses of silane could be admitted, as required, to this system, and the freezing-out arrangements allowed one to measure both unchanged SiH_4 and H_2.

The zeolite (*ca.* 0.3 g) was suspended in a small glass bucket by an intermediate silica fibre from the silica spring. Before each experiment the zeolite was outgassed at temperatures rising to 360 °C and at this temperature for at least 16 h. Distilled water was sorbed and the amount adjusted by outgassing at temperatures not less than 100 °C. The zeolite was then brought to the desired experimental temperature, and SiH_4 admitted. The weight changes due to reaction of zeolitic water with silane were then followed as extensions of the silica spring. At various times, *t*, the pressure and known volumes of the apparatus served to give the amounts of gaseous $H_2 + SiH_4$, and the H_2 was obtained after freezing out SiH_4. The physically sorbed SiH_4 was also obtained in this step since the freezing removed it from the zeolite and the weight change was measured. In this step it was assumed that for small uptakes of reaction products or of water the amounts sorbed remain nearly constant because of the rectangular nature of the isotherms. The silane reacted at time *t*, and bound as reaction products within the zeolite, was taken as the

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[1] J. C. McAteer and J. J. Rooney, *Adv. Chem. Ser.*, 1973, **121**, 258.

[2] R. M. Barrer, R. G. Jenkins, and G. Peeters, in ' Molecular Sieves-II,' Amer. Chem. Soc. Symp. Ser. 1977, no. 40, p. 250.

[3] R. M. Barrer, E. F. Vansant, and G. Peeters, *J.C.S. Faraday I*, 1978, 1871.

[4] Von Wartenburg, *Z. anorg. Chem.*, 1913, **79**, 71.

[5] D. T. Hurd, ' The Chemistry of the Hydrides,' Wiley, New York, 1952, p. 109.

[6] A. Stock, ' Hydrides of Boron and Silicon,' Cornell and Oxford University Presses, 1933, p. 25.

[7] A. Stock and C. Somiesky, *Ber.*, 1918, **51**, 989.

[8] A. G. McDiarmid, *Adv. Inorg. Chem. Radiochem.*, 1961, **3**, 207.

difference between the initial dose of silane and the amount of physically sorbed plus gaseous silane at that time.

The zeolites used were Na-Y and Na-mordenite (Zeolon). Sorption on the parent and modified mordenites was studied using pure O_2 and N_2 gases.

TABLE 1

Reaction of SiH_4 with zeolitic water in Na-Y

				Amount/mmol			Uptake in wt. %	
Initial wt. % of water	Treatment	θ_c/°C	t/h	H_2 formed	SiH_4 reacted	$H_2 : SiH_4$	from volumetric data	experimentally observed
		60	18	Not measurable				
5.8_5	Silanation	100	68	0.99_0	0.32_4	3.0_6	3.5_7	3.3_1
			91.5	1.11_8	0.37_4	2.9_9	4.1_2	3.9_4
			112	1.20_0	0.40_0	3.0_0	4.4_1	4.2_8
		160	22	1.47_3	0.48_3	3.0_5	5.3_2	5.1_6
			44.5	1.51_9	0.51_5	2.9_5	5.6_8	5.4_0
			116	1.62_0	0.55_5	2.9_2	6.1_2	5.9_6
		200	27.5	1.68_4	0.58_0	2.9_0	6.3_9	6.3_6
			45.5	1.72_0	0.60_3	2.8_5	6.6_5	6.5_2
	SiH_4 pumped off, H_2O added	200	2	0.31_6				
			22	0.36_7		3.4_6		
4.7_9	Silanation	100	20	1.01_6	0.37_1	2.7_4	3.5_5	3.3_6
			43	1.25_7	0.44_5	2.8_2	4.2_6	4.2_9
			67.5	1.36_6	0.48_0	2.8_5	4.6_0	4.7_0
			112.5	1.44_9	0.51_9	2.7_9	4.9_7	5.1_3
			231	1.55_0	0.58_2	2.6_6	5.6_2	5.7_6
	SiH_4 pumped off, H_2O added	200	20	0.60_8		3.7_1		
	Outgassed	350	4					
	New dose of SiH_4	100	42	0.19_5	0.12_2	1.6_0	1.2_7	1.1_1
			65	0.24_0	0.15_2	1.5_8	1.5_8	1.4_0
3.2_8	Silanation	100	20	0.81_0	0.31_9	2.5_7	2.9_1	2.6_4
			42.5	0.99_6	0.38_3	2.6_0	3.4_7	3.2_8
			113	1.10_2	0.43_8	2.5_2	3.9_9	3.8_5
			135	1.13_3	0.45_2	2.5_1	4.1_2	4.0_6
	SiH_4 pumped off,	100	19	0.26_9				
	H_2O added	200	23	0.468		3.5_4		
2.0_1	Silanation	100	21	0.50_2	0.20_1	2.4_3	2.0_0	1.8_0
			56.5	0.58_2	0.23_6	2.4_6	2.2_8	2.0_6
			92	0.60_3	0.25_0	2.4_1	2.4_2	2.2_2
			112.5	0.62_0	0.25_7	2.4_1	2.4_8	2.3_3
	SiH_4 pumped off, H_2O added	200	20	0.29_6		3.5_6		

RESULTS

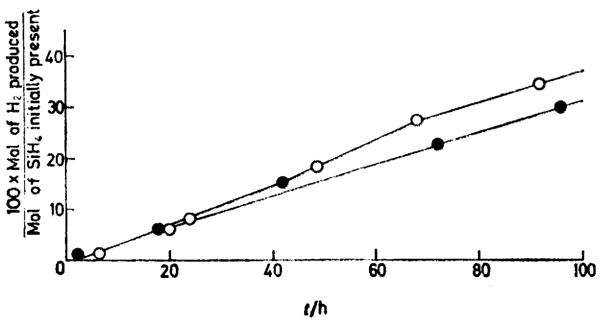

FIGURE 1 Reaction of SiH_4 with H_2O in the volumetric unit in the absence of zeolite. Comparable amounts of SiH_4 gas and H_2O vapour were initially introduced. The reaction is expressed as the ratio H_2 formed : SiH_4 initially present. At 25 °C (○), $p(H_2O) = 17._6$ and $p(SiH_4) = 23.3$ Torr; at 60 °C (●), $p(H_2O) = 12._6$ and $p(SiH_4) = 15._6$ Torr

Water vapour and silane gas at comparable partial pressures were mixed in the volumetric apparatus in the absence of zeolite, and the H_2 formed was determined as a function of time at 25 and 60 °C. Figure 1 shows that a slow reaction took place. However, in the presence of zeolite there are, for the small uptakes of water considered (<6% by weight), only low equilibrium pressures of water vapour. In zeolite Na-Y at 25 °C the pressure is *ca.* 0.1 Torr * for 8% uptake of water.[9] Accordingly, reaction outside the zeolite should be limited.

Results of the reaction of silane in the presence of Na-Y containing initially controlled amounts of zeolitic water are recorded in Tables 1 and 2 and in Figure 2(*a*) and 2(*b*). The sample in Table 2 referred to as Na-Y_L is Na-Y suspended at 25 °C for 24 h in 0.01N sodium hydroxide solution and then rapidly washed with distilled water, before the usual outgassing at 360 °C. However, no appreciable alkali-catalysed acceleration of reaction was observed (Table 2).

In Na-mordenite with small contents of zeolitic water the reactions with silane gave the curves of Figure 3. Of these Figure 3(*a*) and (*b*) were weight–time curves obtained in the gravimetric unit and 3(*c*) and (*d*) give the evolution of H_2 and consumption of SiH_4 measured in the volumetric unit. Reactions in the volumetric unit, because of the smaller gas-phase volume (*ca.* 0.12 dm^3) and the larger amounts of zeolite (between 0.5 and 1 g), could be followed more precisely than corresponding volumetric measurements in the gravimetric unit (*ca.* 0.90 dm^3). The weight changes shown in Figure 3(*a*) and (*b*) are small. When the temperature is increased there is an initial decrease in weight which may be due to desorption of physically sorbed silane, and possibly of small amounts of reaction product or water [Figures 2(*a*) and 3(*a*)]. In the case of Figure 3(*c*) and (*d*)

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* Throughout this paper: 1 Torr = (101 325/760) Pa; 1 mmHg ≈ 13.6 × 9.8 Pa.

[9] D. W. Breck, 'Zeolite Molecular Sieves,' Wiley, New York, 1974, p. 614.

the zeolite was outgassed not at 360 °C but at 200 and 100 °C respectively, the temperatures selected for reaction.

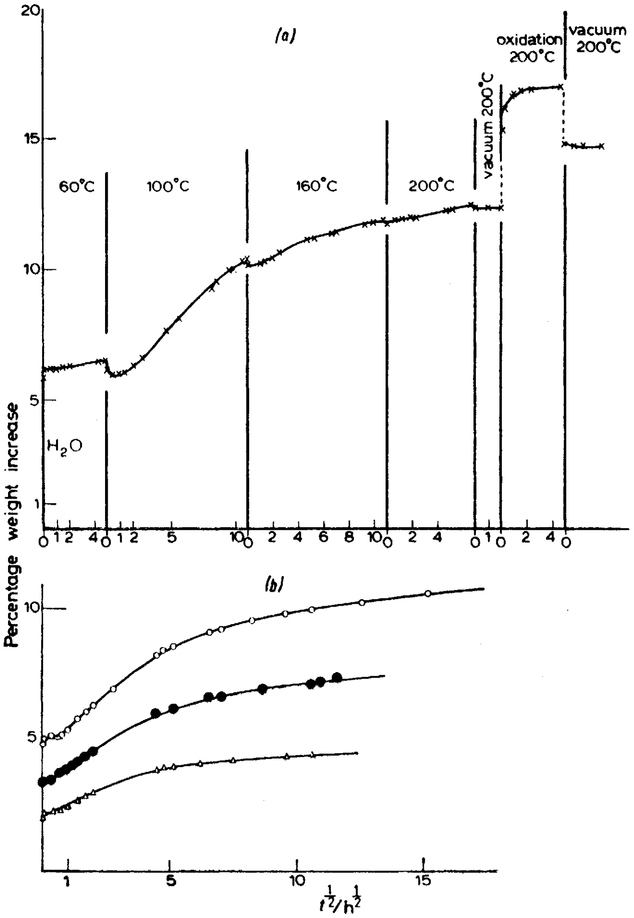


FIGURE 2 (*a*) Reaction of SiH_4 with water in Na-Y initially containing 5.85% by weight of water. (*b*) The same reaction in Na-Y samples initially containing 4.7_9 (○), 3.2_2 (●), and 2.0_1 wt.% H_2O (△)

The water capacity of the zeolites before and after treatments with silane are reported in Table 3 and isotherms for O_2 and N_2 at −196 °C are shown for Na-Y in Figure 4(*a*) and (*b*) and for Na-mordenite in Figure 5(*a*). Kinetics of sorption in modified Na-mordenite, before and after light grinding, are illustrated in Figure 5 (*b*).

TABLE 3

Saturation capacities after reaction of SiH_4 with zeolitic water in Na-Y

Material	Percentage weight loss observed on outgassing at 360 °C [a]	Difference in percentage weight loss	Reduction in weight loss as a percentage of weight loss of parent Na-Y	Reduction of sorption capacity as percentage of sorption for Na-Y [b]	
				O_2	N_2
Na-Y parent material	25.6_7				
Na-Y $+2.0_1$ wt. % H_2O [c]	22.1_8	3.4_9	$13._6$	$14._3$	$14._2$
Na-Y $+3.2_2$ wt. % H_2O [c]	20.2_8	5.3_9	$21._0$	$24._1$	$24._2$
Na-Y $+4.7_9$ wt. % H_2O [c]	18.6_7	7.0_0	$27._3$		

[a] After storing over saturated $Ca[NO_3]_2$ at room temperature. [b] At −196 °C and 50 mmHg. [c] Silanated according to Table 1.

DISCUSSION

Reaction in Na-Y.—The weight increases in Na-Y after reaction between SiH_4 and zeolitic water experimentally observed and determined from volumetric data are not very different, estimates from the volumetric measurements being a little larger (Table 1). The close correspondence indicates either that the reaction is almost wholly between intracrystalline SiH_4 and H_2O, or that products of any simultaneous reaction external to the crystals are sorbed into the zeolite. There can also be a small amount of reaction with terminal silanols on external surfaces of crystals.[2] Table 2, line 1, shows the very minor extent of such reaction in well outgassed Na-Y as compared with the amount of reaction when the crystals contained zeolitic water.

TABLE 2

Reaction of SiH_4 with zeolitic water

Material	Amount of water in wt.%	Conditions (t/h, θ_c/°C)	Percentage weight increase	
			partial	total
Na-Y	0	92, 160		0.3_2
Na-Y	2.8_9	72, 25	0.9_3	
		70, 50	1.5_2	
		288, 60	1.6_4	
		30, 100	0.5_7	
		18 (supplementary), 100	0.00	
		24, 200	0.03	4.6_9
Na-Y	5.2_7	30, 60	0.7_0	
		119 (supplementary), 60	2.0_8	
		90, 100	2.7_0	
		24, 160	0.09	5.5_7
		4, 300	−0.05	
		19 (high vacuum), 300	−0.21	5.3_1
Na-Y_L	5.3_3	23, 60	0.5_3	
		75, 100	4.5_1	
		26, 160	0.2_0	5.2_4

Some examples of possible reactions are indicated in Table 4 together with characteristics that may be compared with experiment. In Table 4, $H_2 : SiH_4$ denotes the ratio of H_2 evolved during the reaction to SiH_4 consumed, $H_2 : H_2O$ is the ratio of H_2 evolved to H_2O consumed, and in the last column the increase in weight is given in terms of x, the initial amount of water in the zeolite (assuming all this water to have reacted). From Table 1 the experimentally observed ranges in these three quantities were (at the end of the run but before final oxidation by a new addition of excess of water): (*a*) $2.4_1 \leqslant H_2 : SiH_4 \leqslant 2.8_5$, (*b*) $2.0 \leqslant H_2 : H_2O \leqslant 2.2_5$, and (*c*) weight increases from 1.1_1x to 1.2_6x. In (*b*) the ratio $H_2 : H_2O$ denotes H_2 produced over zeolitic water initially in the zeolite. This water is assumed to be used up at the end of the run. Comparison of these values with those given in Table 4 excludes all the reactions not involving condensation and certain of those which do. However, some condensation processes are possible, for example a mixture of reactions (v) and (vi) of Table 4, which give respectively $H_2 : SiH_4$ ratios of 2 and 3 : 1, $H_2 : H_2O$ ratios of 2 : 1, and weight increases of 1.55x and 0.96x. These values thus span the experimental values. Reactions (v) and (vi) lead respectively to ring siloxanes or to silasesquioxanes such as (I) and (II).

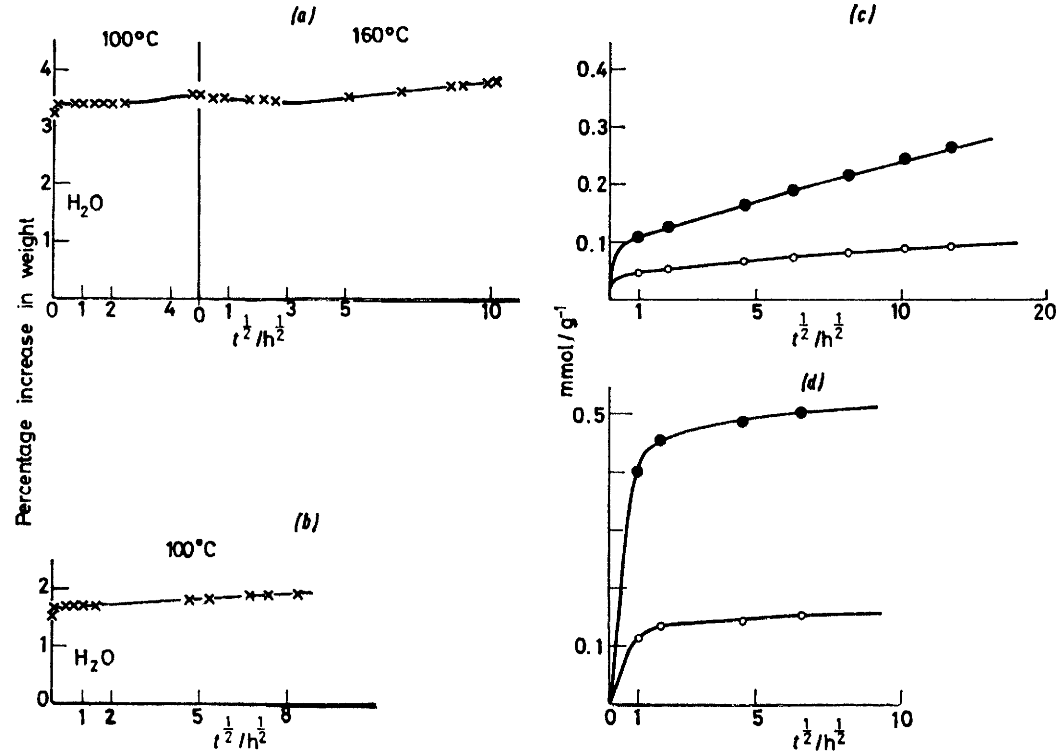


FIGURE 3 (*a*) and (*b*) reaction of SiH_4 with water in Na-mordenites containing initially 3.2 and 1.5 wt.% H_2O respectively. (*c*) and (*d*) reaction of SiH_4 with water in the volumetric unit and in mordenites containing respectively *ca.* 0.35 wt.% H_2O at 200 °C and *ca.* 2.4 wt.% H_2O at 100 °C. The consumption of SiH_4 (○) and evolution of H_2 (●) are shown

TABLE 4

Some possible reactions of SiH_4 and H_2O

		Reaction	$H_2 : SiH_4$		$H_2 : H_2O$		Increase in weight as a function of x *	
Without condensation	(i)	$SiH_4 + H_2O \longrightarrow SiH_3(OH) + H_2$	1		1		1.67x	
	(ii)	$SiH_4 + 2H_2O \longrightarrow SiH_2(OH)_2 + 2H_2$	2		1		0.78x	
	(iii)	$SiH_4 + 3H_2O \longrightarrow SiH(OH)_3 + 3H_2$	3		1		0.48x	
	(iv)	$SiH_4 + 4H_2O \longrightarrow Si(OH)_4 + 4H_2$	4		1		0.38x	
With condensation	(v)	$nSiH_4 + nH_2O \longrightarrow (H_2SiO)_n + 2nH_2$	2		2		1.55x	
	(vi)	$2nSiH_4 + 3nH_2O \longrightarrow (H_2Si_2O_3)_n + 6nH_2$	3		2		0.96x	
	(vii)	$nSiH_4 + 2nH_2O \longrightarrow (SiO_2)_n + 4nH_2$	4		2		0.66x	
		n	0	∞	0	∞	0	∞
	(viii)	$(n + 2)SiH_4 + (n + 1)H_2O \longrightarrow H_3Si(OSiH_2)_nOSiH_3 + (2n + 2)H_2$	1	2	2	2	3.33x	1.56x
	(ix)	$(n + 2)SiH_4 + (2n + 3)H_2O \longrightarrow (HO)H_2Si[OSiH(OH)]_nOSiH_2(OH) + (3n + 4)H_2$	2	2	1.33	2	1.04x	0.72x
	(x)	$(2n + 2)SiH_4 + (3n + 3)H_2O \longrightarrow (HO)H_2Si\{OSiH[OSiH_2(OH)]\}_n\text{-}OSiH_2(OH) + (5n + 4)H_2$	2	2.5	1.33	1.67	1.04x	1.00x

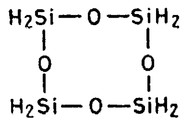
* x = Initial amount of H_2O.

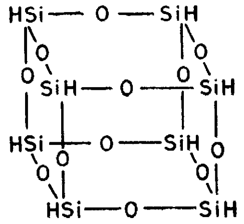
It has been noted above that at the end of a run (but before final oxidation with a fresh excess of water) the ratio $H_2 : H_2O$ equals, or is a little above, 2 : 1, which is the upper limit in many condensation reactions (Table 4). Ratios a little above 2 : 1 could result either from additional silanation of OH groups on external zeolite surfaces,[2] or from reactions of the type (3).

The total replacement of SiH by SiOH in all the reaction products would, in the absence of reaction (3),

$$\geqslant\text{SiH} + \text{H–SiH}_3 \longrightarrow \geqslant\text{Si–SiH}_3 + \text{H}_2 \qquad (3)$$

always give $H_2 : SiH_4 = 4 : 1$. The ratios after treatment with excess of water covered the range 3.4_6—$3.7_1 : 1$, indicating either incomplete replacement of


(I)


(II)

SiH by SiOH or some of reaction (3). The former possibility is more likely because the experimental temperatures were usually low for reaction (3) and because in previous work[2] exhaustive treatment with excess of water gave ratios nearer to 4 : 1.

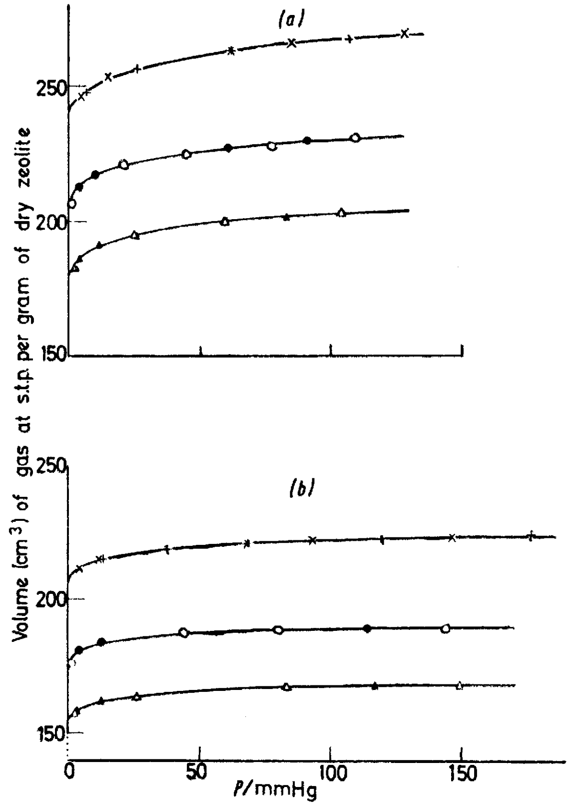


FIGURE 4 Sorption isotherms of O_2 (*a*) and N_2 (*b*) at −196 °C in Na-Y before and after silanation treatments. Outgassing at 360 °C. (+) and (×) denote sorption and desorption in the parent Na-Y, (○) and (●) denote sorption and desorption in silanated Na-Y initially containing 2.0_1% H_2O (Table 1), and (△) and (▲) denote sorption and desorption in silanated Na-Y initially containing 3.2_2% H_2O (Table 1)

The ratios $H_2 : SiH_4$ (Table 1) are larger the greater the initial water content of the zeolite. For the more heavily hydrated samples this ratio decreases slightly as reaction proceeds, but for the two least-hydrated samples $H_2 : SiH_4$ remained virtually constant at all stages prior to the final oxidation with excess of water. For the second sample of the Table, after reaction at 100 °C, oxidation of intracrystalline products with excess of water at 200 °C, and outgassing at 350 °C, a fresh dose of SiH_4 was found to react further. However, now the ratio $H_2 : SiH_4$ was only 1.58 : 1, a value more nearly characteristic of the reaction between SiH_4 and H-zeolites.[2,3] This may indicate reaction of SiH_4 with OH groups introduced into the condensed reaction products by the final oxidation with excess of water [equation (4)].

$$\geqslant\text{SiH} + \text{H}_2\text{O} \longrightarrow \geqslant\text{SiOH} + \text{H}_2 \qquad (4)$$

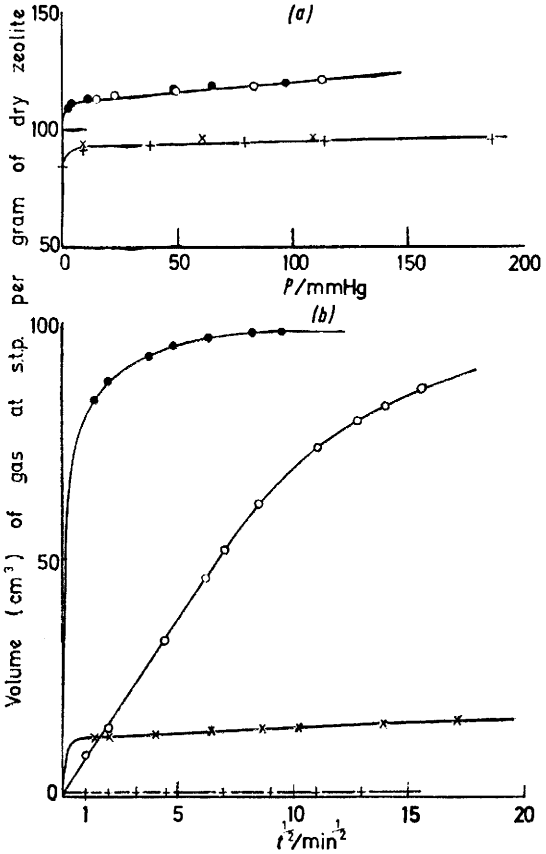


FIGURE 5 (*a*) Sorption isotherms at −196 °C in parent Na-mordenite outgassed at 360 °C: (+), (×) sorption and desorption points for N_2; (○), (●) sorption and desorption points for O_2. (*b*) Sorption kinetics at −196 °C in Na-mordenite outgassed and silanated at 200 °C and with 0.25 wt. % of added Si. Curves show rates for N_2 and O_2 respectively before, (+) and (×), and after grinding, (○) and (●)

Reactions in Na-*mordenite*.—The limited weight increase when SiH_4 reacted with zeolitic water in Na-mordenite is seen from Figure 3(*a*) and (*b*). The sample initially containing 1.5% by weight of water increased in weight by 0.20% in 70 h at 100 °C, while that containing initially 3.2% of water increased in weight by 0.19% after 23 h at 100 °C and by 0.35% after 92 h at 160 °C.

More extensive reaction occurred in the volumetric unit [Figure 3(*c*) and (*d*)]. This difference could arise because of non-equilibrium initial distributions of zeolitic water within the crystals. In the gravimetric unit the mordenite was completely outgassed at 360 °C, cooled to 100 °C, and then partially hydrated. In the volumetric apparatus the hydrated zeolite was outgassed at the same temperature as the subsequent silanation reaction. Initial non-equilibrium distributions in the gravimetric unit would thus give a greater concentration of water nearer the external surfaces of crystallites, and in the volumetric unit a greater concentration nearer the centres of the crystallites. Silane would thus enter the crystals in the volumetric unit more easily than in the gravimetric one. In the experiments of Figure 3(*c*) and (*d*), from the study of the dehydration behaviour of mordenite, the initial water contents should have been *ca.* 2.4% at 100 °C and *ca.* 0.3_5% at 200 °C. The run at 100 °C added 0.42% Si to the zeolite and that at 200 °C added 0.25% Si. The $H_2:SiH_4$ ratios were respectively 3.5 and 2.4 : 1 at the beginning and 3.3 and 2.8 : 1 at the end of the runs. The high values of these ratios at 200 °C could indicate condensation reactions (Table 4) involving SiH_4 and H_2O in mordenite as in zeolite Y. In the experiment at 200 °C the added percentage of Si compared with the initial amount of zeolitic water suggests that nearly all the water was consumed.

In the first stage of the runs of Figure 3(*c*) and (*d*), SiH_4 may diffuse inside the parallel non-intersecting channels of mordenite which have free cross-sectional dimensions of 6.7 × 7.0 Å, although some water and Na^+ ions are also in these channels. Reaction then deposits products in the channels which limit or slow down further penetration by SiH_4. Reaction will thus depend more and more not on migration of SiH_4 to water molecules but on migration of the small H_2O molecules to SiH_4, past the barriers created by the products. Accordingly, the overall result should be a concentration of reaction products near the entrances to the channels. In the three-dimensional channel system of zeolite Y this effect should be much less in evidence, because there are many ways for diffusing molecules to avoid obstructions by by-passing them, and because deposition of reaction products could occur in hexacosahedra rather than in the 12-ring windows. These differences between modified mordenite and modified zeolite Y are emphasised by their very different sorption behaviour as demonstrated below.

Sorption by the Modified Zeolites.—In the silane-treated zeolites Na-Y, isotherms of N_2 and O_2 are fully reversible but show somewhat reduced saturation capacities [Figure 4(*a*) and (*b*)]. For these small molecules the reaction products do not prevent diffusion but they occupy a fraction of the intracrystalline free volume. Table 3 gives the reductions in sorption capacity for H_2O, O_2, and N_2. These reductions for O_2 and N_2 are a little bigger than for water possibly because water at room temperature can enter the sodalite cages while at −196 °C O_2 and N_2 can not. The reduction in sorption capacity increases with the amount of water initially present in the parent Na-Y and hence with the amount of the intracrystalline silanation products.

The intracrystalline free volume of Na-Y can be used like a specific-gravity bottle to estimate a mean density of the intracrystalline reaction products, assuming an intracrystalline free volume for water in Na-Y of 0.35 $cm^3\ g^{-1}$ of outgassed zeolite. Also referred to outgassed parent Na-Y, the weight gains, after the reactions of SiH_4 with zeolitic H_2O plus final oxidation of products with excess of water and outgassing at 360 °C, were: Na-Y + 2.0_1% $H_2O \longrightarrow$ 5.2% weight gain (A), Na-Y + 3.2_2% $H_2O \longrightarrow$ 9.0% weight gain (B), and Na-Y + 4.7_9% $H_2O \longrightarrow$ 13.8% weight gain (C). Thus 1 g of water-free Na-Y gives 1.052 g of (A), so that 1 g of (A) contains only a fraction 1/1.052 of the unit cells in 1 g of outgassed parent Na-Y. Accordingly, from the water uptakes of Table 3, in the same number of unit cells of (A) as there are in 1 g of outgassed parent Na-Y the water capacity is reduced in the ratio $(22.1_8 \times 1.052) : 25.67 = 0.909 : 1$. Therefore the volume occupied by 0.052 g of the reaction products in (A) is $0.35 \times 0.091 = 0.031\,9$ cm^{-3}, so that the density is 1.6_3 g cm^{-3}. Similarly, for (B) and (C) the densities were estimated as 18_5 and 2.2_9. These approximate densities appear to increase with the initial amount of zeolitic water which may indicate increasing proportions of oxygen to hydrogen in the products.

The modified Na-mordenite behaved very differently from the modified Na-Y. In unmodified parent Na-mordenite both O_2 and N_2 were quickly and reversibly sorbed at −196 °C [Figure 5(*a*)], but after the addition of only *ca.* 0.25% by weight of Si through reaction with zeolitic water there was a very great diminution in rate and amount of uptake [Figure 5(*b*), points (×) (for O_2) and (+) (for N_2)]. Penetration at −196 °C involves extremely slow activated diffusion. The great change for so small an uptake of Si (*ca.* 0.25%) supports the view given earlier that in the mordenite the reaction products of SiH_4 with zeolitic water were concentrated near the exits to the channels so that a limited deposition is enough to seal the channels.

Further evidence of this was sought by grinding the crystals for 5 min and then remeasuring the rate and amount of uptake. This resulted in a dramatic improvement [Figure 5, points (●) (for O_2) and (○) (for N_2)]. Grinding, by fracturing or eroding the crystals, provides new unblocked entry points into the mordenite channels. Also it reduces the average size of crystallites, and both factors need to be considered. The effect of reducing the average size is considered below.

For simplicity the crystals are idealised as spheres, number N_1 and radius r_1 before grinding and N_2 and r_2 after grinding. In the early stage of diffusion and at constant external pressure of sorbate vapour the amount, Q_t, which has entered the crystals at time t is given by

$$Q_t/Q_\infty = 2A(Dt/\pi)^{\frac{1}{2}}/V \qquad (5)$$

(5) where Q_∞ is the amount sorbed at equilibrium, A is the total external area, V the total volume of crystals, and D is the diffusion coefficient. Before (subscript 1) and after grinding (subscript 2) we have $4\pi r_1^2N_1 = A_1$, $(4/3)\pi r_1^3N_1 = V$, $4\pi r_2^2N_2 = A_2$, and $(4/3)\pi r_2^2N_2 = V$, where V is of course unchanged by grinding. Thus the gradients S_1 and S_2 of plots of Q_t/Q_∞ against $t^{\frac{1}{2}}$ before and after grinding are in the ratio $S_1 : S_2 = r_2 : r_1$. Comparison of the gradients of curves 1 and 3 then shows that if a change of crystallite size alone was the cause of the rate change, r_1 would need to be reduced by two orders of magnitude by the brief grinding. This is not expected and the main effect is therefore ascribed to the provision through grinding of new unblocked entrances to the channels.

Conclusions.—The differences in the extent of reaction between SiH_4 and zeolitic water in Na-Y and in Na-mordenite, as well as the major difference in the effect of the deposition of reaction products on the subsequent sorption of O_2 and N_2, appears to be due to the three-dimensional channel system in Na-Y and the one-dimensional system in mordenite. The controllable initial water content of the zeolite and extent of reaction with silane, as well as the stability to outgassing of the reaction products in the zeolite, makes the deposition of these products an interesting means of modifying zeolite sorbents and catalysts. It is also a method which will be sensitive to the geometry of the channel systems involved, and takes its place alongside the silanation of structural OH groups in H zeolites for like purposes. It differs from the latter in that the zeolite retains all the inorganic cations of the parent, and in that whole molecules are deposited rather than fragments chemisorbed. The new method can be employed for modifying zeolites the H forms of which are unstable (zeolites X and A are examples).

We thank the Royal Society and the C.N.R.S. for the award of grants which made possible the participation of J.-C. T. in this work.

[8/413 *Received, 6th March,* 1978]