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Reactions on ZSM-5-Type Zeolite Catalysts

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Catalytic reactions and sorption measurements have been carried out with ZSM-5 and silicalite catalysts which are distinguished by variation in skeletal heteroatom concentration. The catalysts were used in both the hydrogen-exchanged and sodium-exchanged forms. Sorption measurements were made with the hydrocarbons *n*-hexane, 3-methylpentane, and 2,2-dimethylbutane, and with the bases ammonia, *n*-butylamine, *t*-butylamine, and 4-methylquinoline. Catalytic reactions were carried out on both unpoisoned and base-poisoned catalysts using methanol, propylene, and 3-methylpentane reactants. In addition, the behavior of ethylene and ethanol reactants was also explored. The ease of base sorption and hydrocarbon sorption has been assessed in terms of effective molecular size in relation to the channel size of the catalyst, and this factor is also used as a basis for explaining the effectiveness of bases for poisoning the catalytic reactions. Temperature-programmed desorption (TPD) measurements with ammonia have been used to assess the energetic distribution of sorption sites for bases, and very strong binding sites with a TPD maximum for ammonia at about 780°K have been identified as the probable sites used in the conversion processes. The main features of the catalytic conversion process are discussed. It is concluded that sorbed C_3,C_4 olefinic residues are general intermediates leading to aromatic formation. Under most circumstances, ethylene was relatively unreactive, and it is inferred that a sorbed C_2 residue, which is related to ethylene by sorption and desorption, is an unlikely general intermediate. A mechanism is suggested for the formation of sorbed C_3,C_4 olefinic residues, and for initial carbon–carbon bond formation from methanol. Catalyst self-poisoning was observed with all catalysts except hydrogen-exchanged ZSM-5.

INTRODUCTION

A process was recently reported (*1*) for the conversion of methanol to gasoline-range hydrocarbons, using a novel zeolite catalyst ZSM-5. More recently, Chang and Silvestri (*2*) described the reactions of a number of oxygen-containing compounds, including methanol, over a ZSM-5 catalyst, and reported that all of them were deoxygenated to a mixture of hydrocarbons containing a large proportion of aromatic compounds, up to about C_{11} irrespective of the reactant. This behavior was attributed to the size-selective character of this zeolite and to the presence of extremely strong acidic sites.

The present work, which is part of a more extensive program to study the properties of this type of zeolite, is concerned with the dependence of the nature of the reaction upon (i) the size of the reactant molecule, and (ii) the concentration of acidic sites in the zeolite.

In studying the effect of reactant molecular size, we have preferred to use hydrocarbons rather than oxygen-containing

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molecules, since we know (*3*) that the main feature of the methanol/ZSM-5 reaction, that is the formation of aromatic products, is also found using suitable hydrocarbon reactants. For mechanistic purposes, hydrocarbon reactants have an advantage in removing some interpretative ambiguities.

In order to study the effect of changing the acid site concentration in the catalyst, while maintaining the essential skeletal structure constant, we have studied (i) ZSM-5 with varying levels of Na^+ exchange, (ii) the catalytic properties of silicalite containing low but non-zero concentrations of aluminium and boron [silicalite is a new crystalline form of silica (*4*) which has a skeletal structure very similar to that of ZSM-5], and (iii) the effect of poisoning by adsorbed ammonia and 4-methylquinoline on the catalytic behavior of ZSM-5.

Further, to obtain quantitative data on the size-selectivity of ZSM-5 and silicalite, we have measured the sorption of some substances of varying molecular size.

EXPERIMENTAL

The preparation of the ZSM-5 was based on methods given in the patent literature (*5*). A sealed Pyrex tube containing 3.05 g of precipitated silica (BDH), 2.35 g of aluminium hydroxide gel (Ajax, 10.5 wt% Al_2O_3), 20 cm^3 of 0.9 *M* tetrapropylammonium hydroxide (TPA-OH) (prepared from aqueous tetrapropylammonium bromide and silver oxide), and 0.31 g of sodium hydroxide (BDH AR grade), was heated at 443°K for 6 days. The Pyrex tube was extensively attacked, and the TPA-OH was extensively decomposed during the reaction to give propylene. After reaction the product was filtered, washed with water at room temperature, and heated in air at 810°K to oxidize the organic matter. At this stage the product contained Na 1.74 ± 0.01 wt%. The material was then converted into the ammonium form by repeated exchange with 1 *M* NH_4NO_3 solution at room temperature; the ammonium-ZSM-5 was washed with water at room temperature, and heated in air at 770°K to decompose the ammonium ions and thus produce the protonated form of ZSM-5. The product, which is designated ZSM-5–H, gave on analysis (wt%): Na, 0.38 ± 0.01; Al, 3.14 ± 0.01; B, 0.10 ± 0.01; Zr, 0.15 ± 0.1; Ti, 0.01 ± 0.01; Fe, 0.03 ± 0.03; total other heavy metals, 0.02 ± 0.02. Na and Al analyses were by atomic absorption spectroscopy, B by wet analytical methods, and the remainder by emission spectroscopy. The sodium form of the zeolite, designated ZSM-5–Na, was prepared from the protonated form by repeatedly exchanging with 1 *M* $NaNO_3$ solution, washing with water at room temperature, and heating in air at 770°K; it contained Na 2.03 ± 0.01 wt% by atomic absorption spectroscopy.

Silicalite was made by the same general procedure as described above, except that the containing tubes were made of fused silica, and the alumina and sodium hydroxide were omitted.

The silicalite sample, designated SL–O, contained (wt%): Na, 0.09 ± 0.01; Al, 0.17 ± 0.01; B, 0.10 ± 0.01; Zr, 0.03 ± 0.03; Ti, 0.01 ± 0.01; Fe, 0.06 ± 0.06; total other heavy metals, 0.04 ± 0.04; Mg + Ca, 0.07 ± 0.07. From this material, hydrogen-exchanged (SL–H) and sodium exchanged (SL–Na) forms were prepared by methods similar to those described above for ZSM-5. SL–H and SL–Na contained (wt%) Na 0.02_4 ± 0.01 and 0.22 ± 0.01, respectively. The analytical methods were the same as for ZSM-5.

Reactions were carried out in a stainless-steel flow reactor at a total pressure of 1 atm, and generally at 673°K. Prior to reaction the catalyst (0.1 to 0.2 g) was heated in a flow of oxygen for 8 hr at 673°K, and then in a flow of hydrogen for 16 hr at 673°K. The hexanes were fed by saturating a hydrogen stream through a bubbler containing the hydrocarbon liquid at 273°K.

TABLE 1

Sorption of Nitrogenous Bases at 293°K

Sorbate	Equilibration pressure/kPa	Sorbate uptake/mmol g^{-1a}		
		ZSM-5-H	ZSM-5-Na	SL-H
Ammonia	101 ($p/p_0 \approx 0.12$)	1.60	1.56	0.85
n-Butylamine	6.5 ($p/p_0 \approx 0.5$)	1.37 (1.45)	0.97 (1.16)	1.00 (1.53)
t-Butylamine	7.8 ($p/p_0 \approx 0.5$)	0.09_3 (0.27_5)	0.06_2 (0.153)	0.030 (0.067)
4-Methylquinoline	0.003 ($p/p_0 \approx 0.9$)	0.02	—	—

[a] Values in parentheses arc sorptions in equilibrium with base vapor; other values are sorptions after subsequent evacuation.

The hydrogen flow was varied to obtain the same feed rate of 3.5×10^{-7} mol sec^{-1} (throughout, mol ≡ g mol) for each of the hexanes. When necessary, the flow rate was also varied to obtain reactions at varying space velocities. In comparative experiments using propylene, ethylene, methanol, and ethanol as reactants, the feed conditions were: propylene or ethylene 3.3×10^{-6} mol sec^{-1} in a flow of hydrogen diluent, and methanol or ethanol 5.2×10^{-6} mol sec^{-1} without diluent.

The reactor effluent was analyzed by gas chromatography (GC) and by GC/mass spectrometry. For normal analyses, a 6 m × 3 mm silicone OV101 GC column was used in a temperature-programmed mode. The C_1–C_3 products were analyzed in more detail using a 0.6 m × 3 mm Porapak Q column.

Sorption measurements were carried out using a Sartorius microbalance connected to a vacuum/gas handling system. Prior to gas sorption, the samples (0.1 g) were outgassed in vacuum (10^{-3} Pa) at 720 to 770°K for several hours. Sorption was carried out at 293°K.

Temperature-programmed desorption measurements were made using the technique and apparatus previously described (*7*). A heating rate of 30°K min^{-1} was used, with a sweep gas (helium) flow rate of 20 cm^3 min^{-1}.

RESULTS

Catalyst Characterization

(*i*) *Structure.* Both the silicalite and ZSM-5 materials as prepared were free-flowing powders, just off-white in color. The as-prepared material was dried, ground, and sieved. For catalysis, powder of particle size 100 to 200 ASA sieve was used; for adsorption studies, powder of particle size 40 to 80 ASA sieve was used.

Both silicalite (SL-O) and the ZSM-5-Na were examined by transmission electron microscopy/diffraction and by X-ray diffraction in a Guinier camera. Both materials gave powder diffraction patterns with similar rings with similar intensities. The data were fitted to orthorhombic unit cells, and the Guinier data gave the following unit cell dimensions: silicalite (SL-O): $a = 20.119$ Å (20.1 Å); $b = 19.925$ Å (19.9 Å); $c = 13.419$ Å (13.4 Å); ZSM-5-Na: $a = 20.067$ Å (20.06 Å); $b = 19.936$ Å (19.80 Å); $c = 13.396$ Å (13.36 Å). Standard deviations were: a, ±0.005 Å; b, ±0.004 Å; c, 0.003 Å. Literature values are given in parentheses for silicalite (*4*) and ZSM-5 (*6*).

The ZSM-5 crystals were lath-shaped with sides parallel to (100) and (010), terminated at one end by a pair of {101} planes making a point. Silicalite crystals were generally larger, doubly terminated, and frequently consisted of an inter-

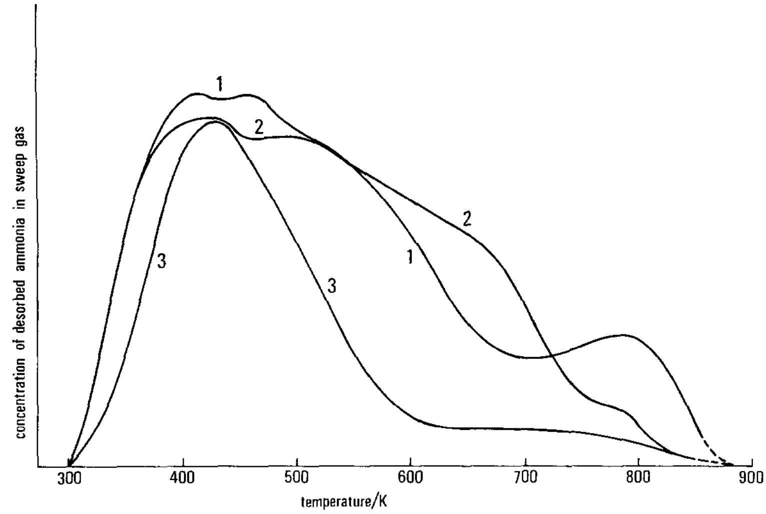


FIG. 1. Temperature-programmed desorption profiles for ammonia from ZSM-5-H (curve 1), ZSM-5-Na (curve 2), SL-H (curve 3). Ammonia initially sorbed at 293°K, 1 atm. Heating rate 30°K min^{-1}. Sweep gas (helium) flow rate 20 cm^3 min^{-1}. Sample masses: each 0.4 g.

penetrating pair. Electron diffraction patterns obtained by tilting crystals to make ⟨010⟩ parallel to the electron beam gave reciprocal lattice sections which were very similar for the two materials. Tilting about ⟨001⟩ confirmed that the unit cell was orthorhombic. These observations are consistent with the structures reported for ZSM-5 (*6*) and silicalite (*4*), and confirm that the two compounds have essentially the same skeletal structure.

(*ii*) *Sorption of nitrogeneous bases.* Measurements were made using ammonia, *n*-butylamine, *t*-butylamine, and 4-methylquinoline. As will be argued in the discussion, *t*-butylamine and 4-methylquinoline do not readily penetrate the pores of ZSM-5 or silicalite and are sorbed mainly on the external surface; on the other hand, the pore structure is easily accessible to penetration by ammonia and *n*-butylamine.

The sorption of *n*-butylamine, *t*-butylamine, and 4-methylquinoline was measured gravimetrically by equilibrating the sorbed sample in the base vapor at 293°K until no further mass increase was observed ($\leqslant$5 min) followed by evacuation to constant mass at 293°K. The equilibrium pressures for the various bases are listed in Table 1 together with the measured uptakes at equilibrium with base vapor and after evacuation.

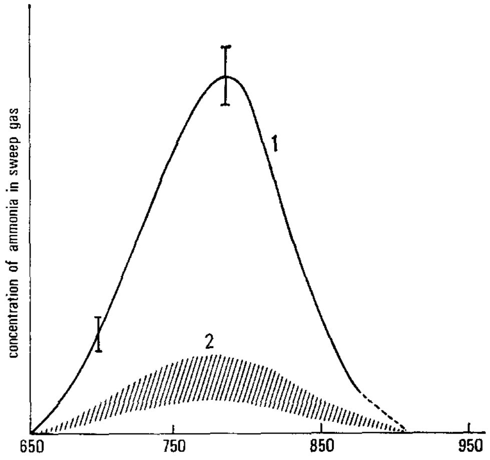


FIG. 2. Temperature-programmed desorption profiles for ammonia from ZSM-5-H (curve 1), and from ZSM-5-Na and SL-H (within hatched area labeled 2). Ammonia initially sorbed at 653°K, 1 atm. Heating rate 30°K min^{-1}. Sweep gas (helium) flow rate 20 cm^3 min^{-1}. TPD commenced at 653°K. Sample masses: each 0.4 g. Error bars are indicated on curve 1, while the hatched area 2 indicates the limits within which the profiles for ZSM-5-Na and SL-H are found.

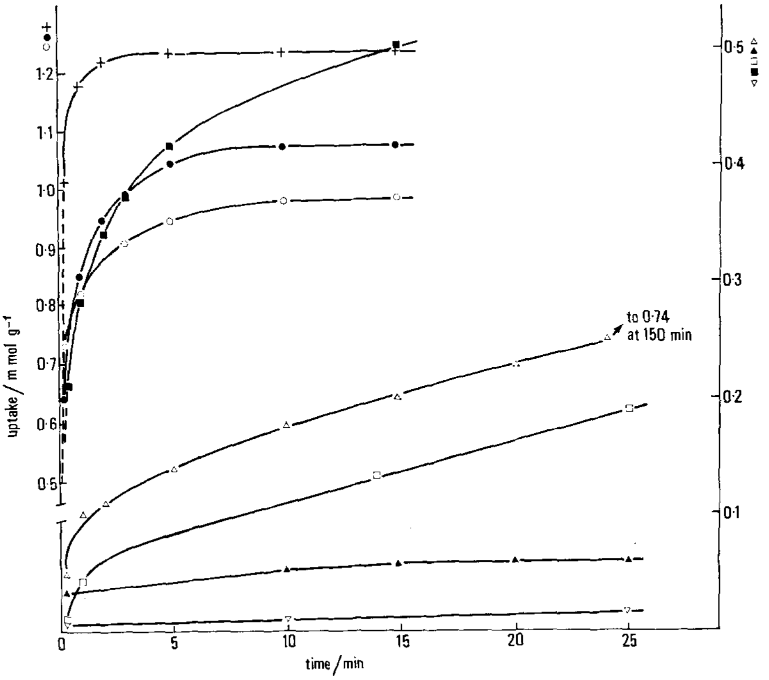


FIG. 3. Variation of sorption with time. 293°K, $p/p_0 = 0.5$. +, *n*-hexane/ZSM-5-H; ○, 3-methylpentane/ZSM-5-H; ●, toluene/ZSM-5-H; △, *o*-xylene/ZSM-5-H; ■, 2,3-dimethylbutane/ZSM-5-H; ▲, 2,2-dimethylbutane/ZSM-5-H; □, *o*-xylene/ZSM-5-Na; ▽, 2,2-dimethylbutane/SL-O.

The ammonia sorption values were obtained from temperature-programmed desorption (TPD) measurements (*vide infra*). The ammonia was sorbed prior to TPD at 293°K by equilibrating the sample in ammonia at a pressure of 1 atm. After this initial ammonia sorption, the sample was equilibrated in sweep gas (helium) at 293°K until no further desorption occurred, and the TPD profile was begun at 293°K. The values for the ammonia sorption which are recorded in Table 1 correspond to the entire amount of ammonia which was desorbed between 293 and 873°K (cf. Fig. 1). The ammonia sorption measured in this way is equivalent to that which would be measured gravimetrically after evacuation, and this is so identified in Table 1. TPD measurements with the bases other than ammonia were not possible because of decomposition reactions of the base molecules over the acidic catalysts at elevated temperatures.

The ammonia TPD profiles are shown in Fig. 1 for the temperature range 293 to 873°K with ammonia initially sorbed at 293°K.

With all three samples, ZSM-5-H, ZSM-5-Na, and SL-H, the main TPD profile maximum occurred in the region of 410 to 460°K, but there were nevertheless considerable differences between the individual profiles in this region: In particular, this low-temperature peak from SL-H was rather narrower than that from either of the ZSM-5 samples. Furthermore, the ZSM-5-Na profile was characterized by a pronounced shoulder at about 670°K, while the ZSM-5-H sample was characterized by a well-defined and substantial high-temperature peak at 790°K which was only vestigial with the other two samples.

TABLE 2

Comparative Sorption

	Sorbate uptake/mmol g^{-1}[a]			Effective[b] molecular size/nm
	ZSM-5–H	ZSM-5–Na	SL–O	
n-Hexane	(F)[c] 1.23	(F) 1.23	(F) 1.28	0.43[d]
3-Methylpentane	(F) 0.98	(S)[e] 0.76	(F) 0.93	0.55_8[f]
2,2-Dimethylbutane	(S) 0.051	(S) 0.025	(S) 0.015	0.62[d]
2,3-Dimethylbutane	(S) 0.50	(S) 0.23	(S) 0.083	0.61[g]
Toluene	(F) 1.07	(S) 0.31	(F) 0.96	0.58_5[h]
p-Xylene	(F) 0.95	(S) 0.27	(F) 0.83	0.58_5[h]
o-Xylene	(S) 0.15	(S) 0.10	(S) 0.16	0.68[i]
Mesitylene	(S) 0.11	(S) 0.02	—	0.75[d]

[a] At 293°K, $p/p_0 = 0.5$, $t = 10$ min.

[b] The effective molecular size is defined as the maximum van der Waals molecular dimension in a direction normal to the channel axis, and with the molecule in such a configuration relative to the channel axis as to maximize the ease of entry into the channel.

[c] F indicates that $\geqslant 95\%$ of equilibrium sorption was reached in $\leqslant 10$ min.

[d] Breck (*8*).

[e] S indicates failure to achieve the criteria which specify F.

[f] Barrer (*9*).

[g] Estimated by scaling to the value for 2,2-dimethylbutane, using density data and molecular scale models.

[h] Taken as the same value for benzene [Breck (*8*)], assuming a molecular orientation with the methyl group on the channel axis.

[i] Taken as the same value as for *m*-xylene [Breck (*8*)].

Dissection of the high-temperature portion of the profiles was obtained by carrying out the ammonia sorption at 653°K and then starting the desorption at that temperature. This procedure largely eliminates the low-temperature portions of the profiles which overlap and partly obscure the high-temperature features. The results, shown in Fig. 2, clearly demonstrate the greatly enhanced importance of the high-temperature peak with ZSM-5–H.

(*iii*) *Sorption of various hydrocarbons.* The sorption of a number of hydrocarbon molecules of varying size and shape was examined at 293°K. These were chosen to have a carbon number $\geqslant 6$, and cover the reactants of interest in the present work, as well as to correspond to an important range of products formed over ZSM-5 catalysts.

Uptake/time curves showed an initial rapid sorption which was complete in the first 10–20 sec, followed by a much slower uptake component which occurred over a period of a few minutes to several tens of minutes. According to the nature of the slow uptake component, the sorbate/sorbent systems fall into two well-defined categories—either $\geqslant 95\%$ of equilibrium sorption was reached in $\leqslant 10$ min, or the uptake was continually increasing with time after several tens of minutes. Examples of the two sorts of behavior are shown in Fig. 3, while Table 2 lists the various sorbate/sorbent systems according to this classification. In making this classification, it was convenient to use uptakes measured at $p/p_0 = 0.5$; the equilibrium isotherms shown in Fig. 4 show that, at least with these sorbate/sorbent systems, $p/p_0 = 0.5$ is a satisfactory reference criterion by comparison with $p/p_0 = 1$, since the equilibrium isotherms are nearly parallel to the pressure axis in the region $0.5 \leqslant p/p_0 \leqslant 1$.

Since we were unable to achieve sorption equilibrium with the slow sorbate/sorbent

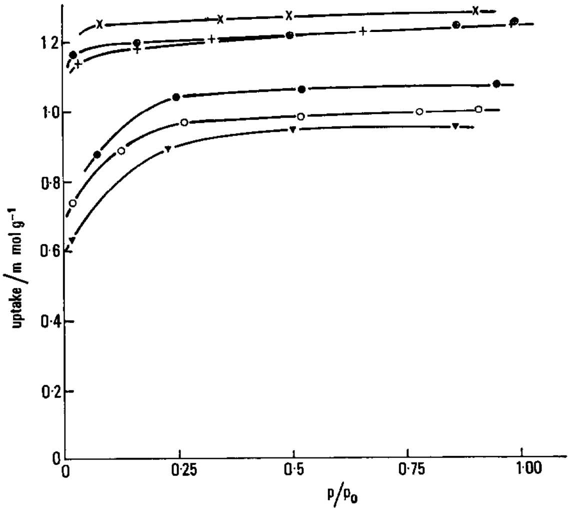


Fig. 4. Sorption isotherms, 293°K. +, *n*-hexane/ZSM-5-H; ○, 3-methylpentane/ZSM-5-H; ●, toluene/ZSM-5-H; ▼, *p*-xylene/ZSM-5-H; ⊕, *n*-hexane/ZSM-5-Na; ×, *n*-hexane/SL-O.

systems (designated S in Table 2), it is useful to compare the magnitudes of the various sorbate uptakes at the arbitrary time of 10 min and at $p/p_0 = 0.5$. These data are also given in Table 2. The values for the nonequilibrium uptakes give a semiquantitative indication of the relative ease of molecular penetration into the sorbent pores.

Catalytic Reactions

(*i*) *Comparative reactions of hexanes.* The reactions of *n*-hexane, 3-methylpentane, and 2,2-dimethylbutane were studied over ZSM-5-H catalyst. The results are contained in Table 3, which also summarizes the experimental conditions.

The composition of the reaction products from hexane reactants varied with reactant

TABLE 3

Comparative Reactions of Hexanes over ZSM-5-H[a]

	Product composition/mol%		
	n-Hexane	3-Methylpentane	2,2-Dimethylbutane
C_1, C_2 aliphatics	9.5	14.8	29.7
C_3 aliphatics	37.2	27.3	23.2
C_4 aliphatics	19.2	16.7	4.5
C_5 aliphatics	4.6	4.1	—
Toluene	5.2	7.4	8.8
m + *p*-Xylene	12.6	14.9	18.8
o-Xylene	4.8	6.7	8.7
Trimethylbenzenes	6.9	8.1	6.3
Reactant conversion/mol%	49.6	29.7	9.2
Fraction of reactant converted to aromatics/mol%	50.9	60.1	69.8
Fraction of aromatics in products/mol%	29.5	37.1	42.6

[a] Conditions: reaction temperature, 673°K ; feed rate, 3.50×10^{-7} g mol sec^{-1}; catalyst, 0.1 g.

space velocity: The proportion of aromatics increased and the proportion of cracked products (carbon number $\leqslant 5$) decreased as the space velocity decreased. This is illustrated in Fig. 5 for the reaction of 3-methylpentane.

Analysis of the cracked products showed that they contained a relatively large proportion of olefins at low conversions (high-space velocities), and that this proportion of olefins decreased as the conversion increased (as the space velocity decreased). This behavior is illustrated in Fig. 6 for the reaction of 3-methylpentane. Olefins with carbon number >3 were relatively minor products, but the analytical resolution was insufficient for these to be separately estimated.

(*ii*) *Comparative reactions over ZSM-5 and silicalite catalysts.* Three reactants, methanol, propylene, and 3-methylpentane, were used in order to assess the behavior of the various catalysts with a range of reactant types.

The main numerical results are summarized in Table 4 for the initial conversions and product distributions. The activity of the catalysts with time varied. The behavior of ZSM-5-H was constant over the time-scale of the measurements (up to about 12 hr), while the behavior of silicalite SL-H was also constant over a period up to about 6 hr. By contrast, the reaction rates over ZSM-5-Na and SL-O decreased fairly rapidly with time. For instance, over these latter two catalysts, the propylene conversion decreased by a factor of about 1.4 during 8 hr reaction, and the conversion of methanol decreased to near zero during about 5 hr reaction (both at 673°K). In most cases, the nature of the reaction products also changed during the course of catalyst deactivation. Thus, after 8 hr reaction over ZSM-5-Na or SL-O, the products from propylene consisted mainly of C_4 and C_5 aliphatics, with only about 5 mol% aromatics, and the proportion of aromatics in the products from methanol also decreased substantially during 5 hr reaction.

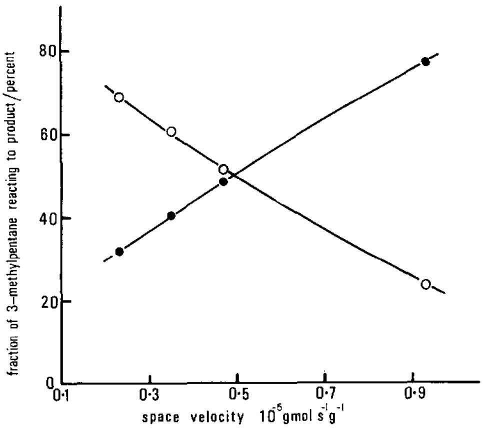


FIG. 5. Fraction of aromatics (-O-) and cracked products (-●-) formed from the reaction of 3-methylpentane over ZSM-5-H catalyst as a function of space velocity. Reaction temperature 673°K. Cracked products defined as having carbon number $\leqslant 5$.

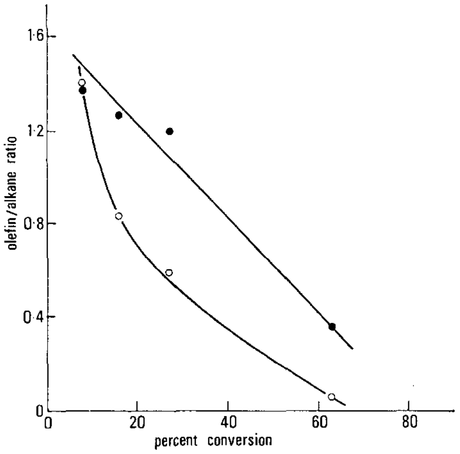


FIG. 6. Olefin/alkane ratio as a function of reactant conversion. Reaction, 3-methylpentane over ZSM-5-H catalyst at 673°K. ●, ethylene/ethane; O, propylene/propane.

Results ancillary to those recorded in Table 4 were obtained over an aerosil silica catalyst at 673°K. Propylene gave zero conversion, while methanol gave a conversion of about 12 mol%, with methane and ethylene being the main products, together with a small amount of dimethyl ether.

TABLE 4

Comparative Reactions on ZSM-5 and Silicalite Catalysts[a]

Reactant	Methanol					Propylene					3-Methylpentane		
Catalyst	SL–O	SL–Na	SL–H	ZSM-5–Na	ZSM-5–H	SL–O	SL–Na	SL–H	ZSM-5–Na	ZSM-5–H	SL–O	ZSM-5–Na	ZSM-5–H
Initial conversion/mol%	90	50	100	100	100	94	0	90	94	85	0	0	28
	Initial product composition/mol%												
C_1, C_2 aliphatics	28.0	Main product dimethyl-ether, some propane, no aromatics	Trace	28.2	2.9	1.3	← No reaction →	4.4	Trace	12.2	← No reaction →	← No reaction →	18.3
C_3 aliphatics	22.0		14.5	19.0	10.3	Trace[b]		—	Trace[b]	Trace[b]			47.0
C_4 aliphatics	10.7		12.4	18.1	8.4	18.0		41.6	10.8	30.3			19.8
C_5 aliphatics	15.0		6.8	8.2	Trace	10.1		9.7	8.7	4.5			4.9
C_{6+} aliphatics	10.0		21.3	5.6	Trace	25.5		18.0	27.3	5.2			Trace
Benzene	Trace		—	Trace	Trace	3.3		—	4.5	Trace			Trace
Toluene	Trace		2.5	1.6	4.9	4.8		2.4	9.8	10.1			2.2
Xylenes	10.8		16.9	9.3	18.5	14.4		10.8	28.6	26.7			5.3
C_{9+} aromatics	3.5		25.6	9.1	55.0	22.6		13.1	10.3	11.0			2.5

[a] Conditions: reaction temperature, 673° K; catalyst mass, 0.2 g; for details of feed rates, see text.

[b] Propane.

(*iii*) *Reactions over catalysts poisoned with nitrogenous bases.* Two nitrogenous bases were used in poisoning experiments: 4-methylquinoline which, for steric reasons, does not penetrate the pores of ZSM-5, and ammonia which does penetrate the pores.

In these experiments, a steady-state reaction was first established in the absence of poison, and the degree of reactant conversion was measured. Then a known quantity of poison was injected as a single dose into the feed stream, and the new degree of reactant conversion was measured. The reactants used were *n*-hexane and 2,2-dimethylbutane, and the catalyst was ZSM-5–H.

In the case of poisoning by 4-methylquinoline, the conversion of the poisoned reactions was constant with time for a period of at least several hours at 723°K, and the results are contained in Table 5. Desorption of the 4-methylquinoline poison is apparently extremely slow under reaction conditions. In the case of poisoning by ammonia, although immediately after introduction of the poison dose the conversion fell to near zero, the conversion subsequently recovered slowly, presumably because of desorption of the ammonia. The results are shown in Fig. 7.

In all cases, the product distribution was the same for the poisoned as for the unpoisoned reactions.

(*iv*) *Catalysis with other reactants.* The reactions of ethylene and of ethanol were studied over ZSM-5–H catalyst at 673°K. The behavior was irreproducible, but low reactivity was the usual occurrence. However, with occasional catalyst samples there was an initial level of activity comparable to that normally found with methanol or propylene. When reaction did occur, the product distribution generally resembled that from methanol or propylene. Although high reactivity of ethylene or ethanol was observed only occasionally, we were not able to find any consistent pattern in the behavior and, in particular, no correlation with catalyst history could be seen. Nevertheless, the behavior of ethylene and ethanol was mutually consistent: A catalyst sample which gave high ethylene reactivity always gave high ethanol reactivity, and low reactivity was also always coupled in the same way.

TABLE 5

Reaction Poisoning by 4-Methylquinoline with ZSM-5–H Catalyst[a]

	Reactant conversion/mol%	
	Unpoisoned	Poisoned
n-Hexane	97.6	95.3
2,2-Dimethylbutane	34.5	3.6

[a] Conditions: reaction temperature, 723°K; catalyst mass, 0.2 g; feed rate, 3.50×10^{-7} mol sec^{-1}; poison, 4-methylquinoline, 5.0×10^{-5} mol.

Some reactions with propylene/methanol and ethylene/methanol mixtures were also studied over ZSM-5–H catalyst in the temperature range 523 to 673°K. No synergistic effects were found either in terms of reactivity or product distribution, and the mixtures behaved as though the reactant components were acting independently.

DISCUSSION

(*i*) *Catalyst Structure*

Our X-ray data show that the unit cell dimensions of silicalite SL–O and zeolite ZSM-5–Na are almost identical. From this, and from the previous structural studies (*4*, *6*), it is clear that the basic skeletal channel sizes must also be closely similar. That is, the "free" channel cross-section dimensions given previously for silicalite (*4*) are also representative of ZSM-5: These values are 0.54 ± 0.02 nm (for nearly circular cross-sectioned zig-zag channels) and 0.57–0.58 × 0.51 to 0.52 nm (for elliptical cross-sectioned straight channels).

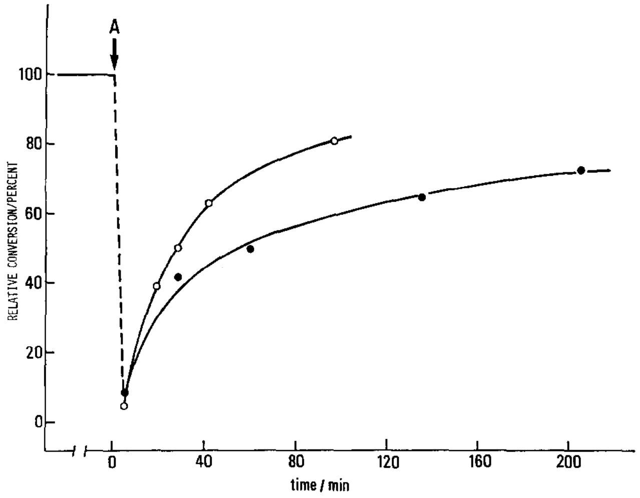


FIG. 7. Effect of ammonia poison on reaction of *n*-hexane (○) and 2,2-dimethylbutane (●) over ZSM-5-H catalyst. Reaction temperature 673°K; catalyst mass 0.1 g; feed rate 3.5×10^{-7} mol sec^{-1}. Ammonia dose (4.0×10^{-4} mol) introduced at point A at arbitrary zero time.

The aluminium content of our ZSM-5 (3.14 wt%) is almost identical with that recently reported by Derouane *et al.* (*10*) for their initial preparation (3.17 wt% aluminium calculated from their quoted SiO_2/Al_2O_3 molar ratio of 26.3/1). However, Derouane *et al.* (*10*) chose to convert their sample to the protonated form by treatment with HCl, and their analytical data reveal that this treatment also removed nearly half the aluminium, the SiO_2/Al_2O_3 molar ratio having increased to 43.6/1. It is expected that conversion to the protonated form via the ammonium exchanged form as in the present work obviates this aluminium loss (and this was confirmed by analysis).

(*ii*) *Hydrocarbon Sorption*

The results recorded in Table 2 and Fig. 3 show that the ease of hydrocarbon sorption depends on both the structure of the hydrocarbon and on the nature of the sorbent. The sorptive behavior of ZSM-5-H and SL-O was very similar when judged by the extent of hydrocarbon uptake and by the division of hydrocarbon/sorbent systems into fast and slow categories. This implies that the pore size and pore volume are very similar for ZSM-5-H and SL-O. On the other hand, the sorptive behavior of ZSM-5-Na was markedly different from that of the other two materials in that there were a number of hydrocarbons (3-methylpentane, toluene, *p*-xylene) which fell into the fast category with ZSM-5-H and SL-O, but into the slow category with ZSM-5-Na. We conclude that, as a result of the presence of sodium ions, the pores of ZSM-5-Na are appreciably more constricted than in ZSM-5-H or SL-O; this constriction is insufficient to affect the entry of a straight-chain hydrocarbon (cf. the behavior of *n*-hexane, Table 2) but is sufficient to impede the ingress of the rather large molecules, 3-methylpentane, toluene, and *p*-xylene.

Since the basic skeletal channel sizes are the same for SL-O and ZSM-5-Na, we conclude that the different hydrocarbon sorptive properties of ZSM-5-Na on the one hand, and ZSM-5-H and SL-O on the other, arise from the steric effect of the exchanged Na^+ cations; the size of the Na^+ cations influences the apparent "free" channel size in a manner that is superimposed on a constant basic skeletal channel geometry.

From the data in Table 2 it appears that, for ZSM-5–H and SL–O, the critical value for the effective molecular size separating fast and slow hydrocarbon sorption is >0.58 and <0.61 nm. This is rather larger than the estimate for the "free" channel cross-section dimensions given above, but we consider this disagreement to be no more than a manifestation of the uncertainty in the estimation of the van der Waals dimensions for the molecules and the channels.

With ZSM-5–Na the critical value for the effective molecular size separating fast and slow hydrocarbon sorption is substantially less than with ZSM-5–H or SL–O, and the value is >0.43 and <0.56 nm.

That the nature of the exchanged cation in ZSM-5 can have a large effect on the size of molecule which can penetrate its pores is important, because it is an effect which can, in principle, modify the catalytic activity of ZSM-5 in a manner that is additional to whatever effect the exchanged cation may have on the intrinsic activity of the active sites (e.g., by modifying the acidity, *vide infra*).

(*iii*) *Sorption of Nitrogenous Bases*

The extent of sorption of nitrogenous bases is given in Table 1. The data may be considered in relation to the effective molecular sizes of the base molecules, and to the criteria defined in the previous section for molecular penetration into the sorbent channels. For ammonia, *n*-butylamine, *t*-butylamine, and 4-methylquinoline we estimate the values for the effective molecular sizes (cf. definition in Table 2) to be 0.29, 0.43, 0.62, and 0.65 nm, respectively.

On this basis, we expect ammonia and *n*-butylamine to be able to penetrate readily the channels of all three sorbents, ZSM-5–H, ZSM-5–Na and SL–O, but we expect *t*-butylamine and 4-methylquinoline to penetrate only with difficulty. These expectations are in agreement with the data in Table 1 which show that the uptake of *t*-butylamine or 4-methylquinoline is more than an order of magnitude less than that of ammonia or *n*-butylamine, and we conclude that the entire pore volume is readily accessible to ammonia or *n*-butylamine but, under the conditions used to measure base uptake, sorption of *t*-butylamine or 4-methylquinoline is mainly confined to the external surface.

The differences in Table 1 between the magnitude of base uptake measured in equilibrium with base vapor, and that measured after pumping, are attributed to weakly sorbed base—possibly physically sorbed—which is removed on evacuation.

Referring to the gross sorption of ammonia and *n*-butylamine, the data in Table 1 show that the uptakes on ZSM-5–H, ZSM-5–Na, and SL–O vary by less than a factor of two. The factor is much smaller than the variation in concentration of skeletal heteroatom-generated acidic sites. Thus, using the analytical data given previously, we evaluate the following values for the concentration (C_A) of heteroatom acidic sites in the protonated form (mmol g^{-1}): ZSM-5–H, 1.10 ± 0.06; ZSM-5–Na, 0.37 ± 0.1; SL–H, 0.09 ± 0.06; SL–O, 0.06 ± 0.06; SL–Na 0.00 ± 0.06. In making these evaluations we assumed that every aluminium, boron, or zirconium atom (the last two as impurities) is a potential acidic site (the structure of ZSM-5 and silicalite is such that every skeletal atom is a "surface" atom, i.e., at a pore wall or the external surface), and that a fraction of these potential sites is exchanged by cations (mainly Na^+) and thus is nonprotonated. Within the limits of the model assumed, the errors in C_A are dictated by analytical accuracy.

Since the amount of base sorbed by ZSM-5–Na and SL–O is much greater than that attributable to C_A, we conclude that under these conditions much of the base sorption occurs in a mode that is unrelated to C_A, probably via a hydrogen-bonding interaction with generally distributed surface oxide and hydroxyl groups. Furthermore, in our ZSM-5 the skeletal heteroatom concentration was only 7.5% of the total (the balance being silicon), and the conclusion given above regarding the mode of base sorption therefore applies to this material also. On the other hand, we need to note that, for ZSM-5–H, the value of C_A (1.10 ± 0.06 mmol g^{-1}) is roughly comparable to the magnitude of base uptake (1.60 and 1.37 mmol g^{-1}) for ammonia and *n*-butylamine, respectively. We have to conclude that only a minor fraction of the sites represented by C_A are, in fact, strongly acidic.

Support for this model is provided by the ammonia temperature-programmed desorption profiles shown in Figs. 1 and 2. With all three sorbents, the main TPD peaks occur at 410 to 460°K. Although the profile for SL–H is distinguished from those for ZSM-5–H and ZSM-5–Na by having rather less weight in the region 500 to 600°K, the most decisive distinction is provided by the high temperature dissections shown in Fig. 2 for the region 650 to 900°K. These high-temperature peaks all occur at about 780°K, but the intensity of the ZSM-5–H peak is much larger than those from ZSM-5–Na or SL–H.

From the peak area one obtains a value of 0.31 ± 0.04 mmol g^{-1} for the ammonia sorption on ZSM-5–H corresponding to this high-temperature peak. On ZSM-5–Na and SL–O, the corresponding ammonia sorptions were in the region 0.05 ± 0.04 mmol g^{-1}, but were too small for reliable estimation to be possible. Nevertheless, the data are sufficient to show that the ammonia bound to ZSM-5–H in this mode exceeds that on ZSM-5–Na or SL–H by a factor of about 6, and this is roughly the magnitude of the variation in C_A for these substances (*vide supra*).

Accordingly, we propose that the strongly bound ammonia corresponding to these high temperature (780°K) TPD peaks is sorbed at strong acid sites, and the concentration of such sites in ZSM-5–H is thus estimated at 0.31 ± 0.04 mmol g^{-1}.

(*iv*) *Reactions over Catalyst Poisoned with Nitrogenous Base*

The data in Table 5 show that sorption of 4-methylquinoline onto ZSM-5–H catalyst drastically reduces the extent of conversion of 2,2-dimethylbutane, but *n*-hexane is almost unaffected. The amount of 4-methylquinoline added to the catalyst in the poisoning experiment was considerably in excess of the quantity indicated in Table 2 as being required for surface saturation.

Both 4-methylquinoline and 2, 2-dimethylbutane are of an effective molecular size which inhibits easy penetration into the catalyst channels. Thus, these poisoning results are fully consistent with the concept that 2,2-dimethylbutane reacts on the external surface of the catalyst which is also the part easily accessible to 4-methylquinoline, while *n*-hexane has rapid access to the channels in the catalyst.

In the case of ammonia poisoning, the (initial) decrement in the conversion was essentially the same for reactions of both 2,2-dimethylbutane and for *n*-hexane, and this agrees with the concept that ammonia has ready access to the channels of ZSM-5–H and to the external surface. The size of the ammonia dose, 4.0 mmol g^{-1}, was clearly more than sufficient to give surface saturation (cf. Table 2).

After the initial fall in conversion due to ammonia poisoning, the conversion recovered slowly. We propose that this recovery is due to ammonia desorption. The reaction temperature lies within (but near the lower end of) the temperature range of the high temperature ammonia TPD peak: Nevertheless, given the extent of the recovery period (up to 2–3 hr), the proposal of recovery by ammonia desorption is consistent with the TPD profile data.

(*v*) *Catalytic Reaction Processes*

Our results lead to the conclusion that olefins are intermediates in the formation of aromatic products. However, in contrast to Derouane *et al* (*10*), our results strongly support the concept that the main intermediates are olefins with carbon number $\geqslant 3$, and that ethylene is not generally an important intermediate. The arguments leading to these conclusions are as follows:

(a) Figure 5 shows that as the space velocity for the reaction of 3-methylpentane on ZSM-5–H decreased, the proportion of aromatic products increased and the proportion of cracked products (carbon number $\leqslant 5$) decreased.

(b) Figure 6 shows that, for the reaction of 3-methylpentane on ZSM-5–H, as the conversion increased (space velocity decreased) the olefin/alkane ratio decreased. Bearing in mind that alkane is very inert relative to olefin over this catalyst, this is equivalent to saying that the proportion of olefin in the cracked products decreased as the space velocity decreased. However, it is also apparent from Fig. 6 that the propylene/propane ratio falls much more quickly than does the ethylene/ethane ratio, and this suggests that ethylene is a much less important intermediate than propylene for subsequent conversion to aromatics.

(c) Although propylene reacts readily over ZSM-5–H to give aromatic products in substantial yield (cf. Table 4), ethylene is usually considerably less reactive.

The reactivity of ethylene (or ethanol) over ZSM-5–H was complicated by irreproducibility, in that low reactivity was the usual behavior, but with occasional catalyst samples a level of reactivity comparable to methanol or propylene was found. This situation was unique to these reactants; all other reactants showed no such variation from catalyst sample to catalyst sample. We suggest that occasional ZSM-5–H samples may possess some catalytic sites at which ethylene (or ethanol) is highly reactive, but these are either very easily poisoned or in most preparations are never present at all. The similar behavior of ethylene and ethanol in this respect suggests that ethanol reacts by way of initial dehydration to ethylene.

From Table 3 it is seen that over ZSM-5–H catalyst, the decreasing order of extent of conversion is *n*-hexane > 3-methylpentane > 2,2-dimethylbutane. This is a result of decreased ease of reactant entry into the catalyst channels with increased chain branching (increased effective molecular size), since this order agrees with that for ease of hydrocarbon sorption (cf. Table 2). However, it is opposite to the order expected if the extent of conversion were controlled by the intrinsic molecular reactivity for a process requiring carbonium ion formation. The increased intrinsic molecular reactivity of hydrocarbons with increased chain branching has been well demonstrated (*12–14*), and the modification of this order by the effect of molecular size in controlling reactant entry into catalyst channels has been previously observed (*12*) with the zeolites erionite, ferrierite, and offretite (for alkane isomerization and cracking). A similar size effect has also recently been reported by Chen and Garwood (*15*) for ZSM-5.

The reaction of 2,2-dimethylbutane over ZSM-5–H gives a high proportion of aromatic products, and the distribution of aromatic components closely resembles that from *n*-hexane (cf Table 3). Since the behavior of the latter, particularly the aromatic cut-off at trimethylbenzene, is channel controlled, we are forced to the conclusion that most of the 2,2-dimethylbutane reaction occurs via a primary reaction at the external surface of the catalyst (i.e., at channel entrances), and that the initial products are such as to allow relatively easy transfer into the pores where further reaction occurs. Since skeletal isomerization is much more facile than cracking at acidic sites (e.g., *12*), it is probable that the primary reaction is isomerization of 2,2-dimethylbutane to 3-methylpentane and 2,3-dimethylbutane: 3-methylpentane enters the catalyst channels easily (cf. Table 2); 2,3-dimethylbutane enters less easily than 3-methylpentane (*15*) but more easily than 2,2-dimethylbutane.

Since the reactions are diffusion controlled in the catalyst pores, it is not possible to evaluate true rates of reaction per catalytic site: Thus there are no suitable rate data available for comparison with C_A. Some facts are, however, obvious. When $C_A = 0$ (with SL–Na), the conversion of propylene and 3-methylpentane is zero, and methanol yields no aromatics but only some dimethyl ether as a significant product.

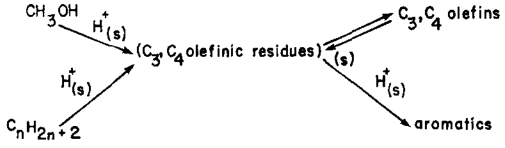
It was also observed that only ZSM-5–H was free from significant self-poisoning in the time scale of the measurements. This implies a rate of catalytic site deactivation that was significant only when the site concentration was sufficiently low. The behavior is thus at least qualitatively consistent with relative active site concentrations indicated by the values of C_A.

(*vi*) *Reaction Mechanism*

The high activity of ZSM-5–H for the conversion of methanol or hydrocarbons, and the fact that the reactions are poisoned by nitrogeneous base or Na^+, point strongly to an acid-catalyzed reaction mechanism [in agreement with earlier assumptions (*10, 2*)]; Brönsted acidity is most probably involved. Water produced in the methanol reaction would quench Lewis acidity.

For reasons which have been given in earlier sections, we have concluded that sorbed C_3 and C_4 olefinic residues are important intermediates in the formation of aromatics. We do not specify the precise nature of these residues in detail; the essential feature is that they may be formed from, or desorbed to, the corresponding olefins. Such residues are most easily formulated as sorbed molecular olefin itself, but this is not a necessary assumption.

Bearing in mind the general similarity of the aromatic product from the various reactants, we present the general reaction scheme



(1)

where $H^+_{(s)}$ indicates an acidic site on the catalyst. In this scheme it is understood that saturated hydrocarbon-cracked products are also formed but, being relatively inert, are not shown explicitly, and the connection between the C_3,C_4 olefinic residues and the corresponding olefins is shown to be reversible but not necessarily in sorption equilibrium.

The question arises how the olefinic residues are generated from the reactants. In the case of C_3 or C_4 olefin reactant, this does not require further comment. In the case of alkane reactant, the conversion is probably initiated by a hydride abstraction reaction: for instance, in the case of *n*-hexane

$$C_6H_{14} + H^+_{(s)} \rightarrow C_6H_{13}^+{}_{(s)} + H_2. \quad (2)$$

and

$$C_6H_{14} + R^+_{(s)} \rightarrow C_6H_{13}^+{}_{(s)} + RH. \quad (3)$$

Cracking reactions then generate, *inter alia*, olefinic products by conventionally accepted routes (cf. *13, 14*).

In the case of methanol reactant, the situation is more complex. Initial dehydration of methanol to dimethyl ether appears to be well established [cf. (*2*)], and our data suggest the following general reaction scheme for the formation of the products from the methanol reaction:

$$CH_3OH \rightarrow (CH_3)_2O \rightarrow (C_3,C_4 \text{ olefinic residues})_{(s)} \rightarrow \text{aromatics}. \quad (4)$$

This scheme is basically different from that postulated by Derouane *et al.* (*10*). It does not involve a sorbed C_2 residue such as $C_2H_5^+$ which is connected to gaseous ethylene by sorption and desorption, since in our experience ethylene is of relatively low reactivity on ZSM-5–H compared to higher olefins. Nevertheless, some ethylene is formed, possibly via a reaction path parallel to (4) of the type:

$$CH_3OH \rightarrow (CH_3)_2O \rightarrow (C_2 \text{ residue})_{(s)} \rightarrow C_2H_4. \quad (5)$$

The fact that ZSM-5–H yields relatively little ethylene compared to the less active and less acidic catalysts ZSM-5–Na and SL–O implies that in (4) the conversion of $(CH_3)_2O$ to sorbed C_3,C_4 residues involves reaction at an acidic site, while the conversion to ethylene by (5) does not involve an acidic site, or uses a different type of acidic site.

Returning to reaction (4), we have avoided writing a C_2-sorbed residue explicitly in the reaction scheme. However, if such an intermediate does exist, it must have the following characteristics: (i) it cannot be generated by ethylene sorption, otherwise ethylene would not be a relatively inert reactant; (ii) since relatively little ethylene product is generated, its steady-state concentration would presumably be low, implying very high reactivity for the formation of C_3,C_4 olefinic residues.

A probable route for the propagation of carbon–carbon bond formation is via protonation of dimethyl ether to $CH_3\text{–}\overset{+}{O}(H)\text{–}CH_3$, followed by cationic methylation of olefin as in (6)

$$CH_3\text{-}\overset{+}{O}(H)\text{-}CH_{3(s)} + X\text{-}CH{=}CH_{2(s)} \xrightarrow{-CH_3OH} X\text{-}\overset{+}{C}H\text{-}CH_2\text{-}CH_{3(s)} \xrightarrow{-H^+_{(s)}} X\text{-}CH{=}CH\text{-}CH_{3(s)}. \quad (6)$$

Formation of a carbonium ion, $H_2\overset{+}{C}\text{–}O\text{–}CH_3$ from dimethyl ether is possible from known carbonium ion chemistry (*17*, *18*), but work currently in progress in our laboratory using deuterium-containing reactant suggests that this species is not involved in the general propagation reaction.

The mode of *initial* carbon–carbon bond formation from dimethyl ether (or from methanol itself) is still quite uncertain. The possible generation of a carbenoid species, $CH_{2(s)}$ from methanol at an acidic site on H–Y zeolite, has been suggested by Salvador and Kladnig (*16*) and Venuto and Landis (*19*). Such a carbenoid species may be a precursor for initial carbon–carbon bond formation.

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