added. The last EPT prediction with effective core potentials is 1.966 eV; combined with the calculated neutral relaxation energy, this results in an adiabatic ionization energy of 1.966 − 0.480 = 1.486 eV.

VI. Conclusions

Adiabatic ionization energies calculated with EPT and MBPT are in excellent agreement with photoelectron spectroscopy. Vertical ionization energies, nuclear relaxation energies, and accompanying geometries are generated as by-products of these calculations. In the case of the germyl anion ionization energy, the vertical and adiabatic calculations supplement the upper bound measured with photodetachment spectroscopy. The best all-electron calculations of vertical ionization energies are 0.51 eV for CH_3^-, 1.79 eV for SiH_3^-, and 2.01 eV for GeH_3^-. All-electron adiabatic counterparts are 0.19 eV for CH_3^-, 1.31 eV for SiH_3^-, and 1.39 eV for GeH_3^-. Effective core potential calculations give vertical ionization energies of 1.88 and 1.97 eV for SiH_3^- and GeH_3^-, respectively. Adiabatic effective core potential results are 1.46 eV for SiH_3^- and 1.49 eV for GeH_3^-.

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In Situ FTIR Studies of Methanol and Dimethyl Ether in ZSM-5

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Abstract: In situ infrared spectra are reported of methanol and dimethyl ether in H-ZSM-5 and Na-ZSM-5. Methanol reacts with internal acidic hydroxyl groups at 523 K to form a methoxy species, the appearance of which correlated with the onset of hydrocarbon formation. Dimethyl ether is protonated at lower temperatures but forms the same methoxy species at 473 K. The methoxy species methylates benzene and alkenes at 523 K. The implications of these observations for the mechanism of hydrocarbon formation are discussed.

The interaction of methanol and dimethyl ether with the acid zeolite ZSM-5 has obvious importance in the complex chemistry associated with methanol conversion to gasoline over this catalyst.[1] In particular, elucidation of the mechanism by which the first carbon–carbon bonds are formed from methanol or dimethyl ether requires a detailed knowledge of the species adsorbed in the zeolite at this point in the reaction. There have, however, been few spectroscopic studies of methanol and dimethyl ether in ZSM-5. Ono and Mori[2] first reported infrared evidence for formation of methoxy species from CD_3OH and showed that desorption of this species was accompanied by cleavage of C–D bonds. Infrared spectra of methoxy species have also been described by Kubelkova et al.,[3,4] and NMR evidence for formation of methoxy from methanol has been presented.[5] Other infrared studies have shown the growth of complex spectra due to adsorbed reaction products after heating ZSM-5 in the presence of methanol.[6,7]

In none of the previous spectroscopic studies were spectra recorded of the catalyst under reaction conditions. With a reaction sequence as complex as that in methanol conversion to gasoline, spectra recorded at room temperature after cooling the catalyst from reaction temperatures will in general contain contributions from adsorbed reaction products which may obscure species initially formed. We have accordingly undertaken an in situ infrared study of the interaction of methanol and dimethyl ether with ZSM-5 under reaction conditions with the particular objective of identifying species formed initially when methanol and dimethyl ether first encounter a fresh catalyst. By using an in situ infrared cell which functions as a pulsed microreactor we have been able also to correlate infrared spectra with reaction products detected downstream from the catalyst. A preliminary account of this work has appeared elsewhere;[8] in this paper a more complete description and analysis of the spectra is presented and the implications of these results for the mechanism of methanol to gasoline conversion are discussed.

Experimental Section

A ZSM-5 zeolite with Si:Al = 26 was provided by Mobil Research and Development Corp. in the ammonium-exchanged form. A second ZSM-5 with Si:Al = 15 was prepared in the sodium-exchanged form by the method of Grose and Flanigen[9] and subsequently proton exchanged. Both zeolites were fully characterized by X-ray diffraction, scanning electron microscopy, ^{29}Si and ^{27}Al NMR spectroscopy, elemental analysis, and surface area determination (500 ± 20 m^2 g^{-1}). Na-ZSM-5 was prepared by ion exchange of H-ZSM-5 with NaBr solution and shown by infrared spectroscopy to contain no acidic protons. All reagents used were spectroscopic or AR grade.

The in situ infrared experiments employed a cell similar to that described by Katzer et al.[10] Zeolite samples were pressed into self-supporting wafers (7–10 mg cm^{-2}), mounted in the cell, and activated by heating in flowing nitrogen (400 mL min^{-1}) to 673 K. Gas and liquid samples were injected into the cell by syringe (typically 1–5 μL of liquid or 1 mL of gas) or via an evacuated gas dosing system. Reaction products were either collected in a liquid nitrogen trap downstream from the cell and analyzed off-line by gas chromatography or analyzed on-line via a gas-sampling valve.

All infrared spectra were recorded on a Nicolet 5DX spectrophotometer at 4-cm^{-1} resolution. Typically 400 interferograms (1s per scan)

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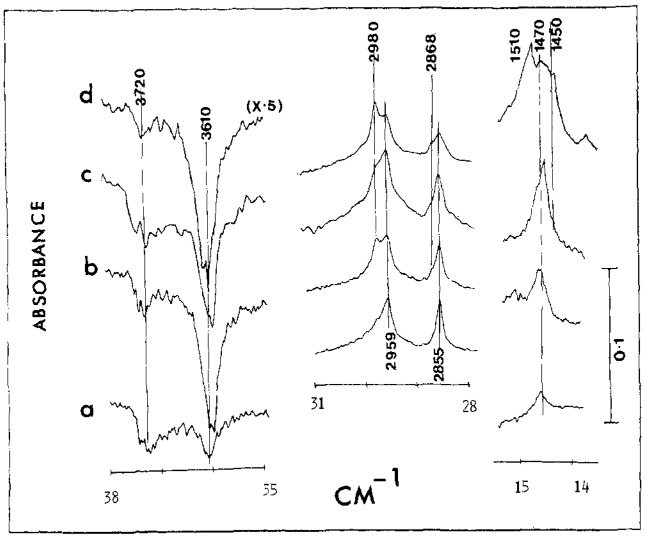

Figure 1. Difference spectra recorded after injecting a 2-μL pulse of methanol onto H-ZSM-5 (3.6 Al per unit cell) at (a) 473 K, (b) 523 K, (c) 573 K, (d) and H-ZSM-5 (6 Al per unit cell) at 523 K.

were averaged. Reference spectra of all zeolite catalysts after activation were recorded at each reaction temperature prior to introducing reactants. Gas chromatographic analyses employed a Shimadzu GC8 instrument (2-m octene on Poropak column for C_1–C_5 hydrocarbons and a 3-m Ovasil column for analysis of benzene and toluene).

Results and Discussion

Methanol in H-ZSM-5. After activation in flowing nitrogen at 523 K infrared spectra of H-ZSM-5 showed two bands in the ν(OH) region at 3720 and 3610 cm^{-1}. The 3610-cm^{-1} band is due to the acidic hydroxyl groups within the zeolite channels.[11,12] The 3720-cm^{-1} band has been variously assigned to silanol groups associated with silica impurities[11] or to hydroxyl groups terminating the zeolite lattice at the external surface.[12] We prefer the latter assignment; certainly the 3720-cm^{-1} band is due to hydroxyl groups outside of the zeolite channels, since it is perturbed by molecules too large to enter the channels. Exposure of the activated zeolite to methanol vapor at room temperature produced intense infrared bands characteristic of hydrogen-bonded methanol,[13] and the 3610-cm^{-1} band was broadened and shifted to lower frequency by ca. 200 cm^{-1}. The methanol hydrogen bonded to acidic hydroxyl groups could be removed by subsequent evacuation at 423 K, as reported by Ison and Gorte.[13]

Hydrogen bonding was not observed when pulses of methanol were added to H-ZSM-5 in flowing nitrogen at temperatures of 373 K or above. Figure 1 shows difference spectra obtained from a series of experiments in which pulses (2 μL) of methanol were added to freshly activated H-ZSM-5 samples at various temperatures. In each case the spectrum of the activated zeolite recorded at the same temperature was subtracted from that of the zeolite after addition of methanol. Negative features in the resulting difference spectra thus correspond to species lost from the zeolite and positive features to species formed. At 473 K, for example (Figure 1a), methanol interacts with both types of hydroxyl groups, as seen from the negative features at 3720 and 3610 cm^{-1}, and new bands appeared in the ν(CH) and δ(CH) regions. The interaction does not involve hydrogen bonding, since no new bands appeared in the ν(OH) region. The fraction of the acid hydroxyl groups interacting with methanol was however small (less than 10% of the total), although a 2-μL pulse corresponds to ca. 6 methanol molecules per acid site, and injection of further methanol caused no further change in the spectra. The frequencies of the ν(CH) and δ(CH) bands formed at 473 K (2959, 2855, and 1470 cm^{-1}) correspond closely to those of methoxy groups formed from methanol chemisorbed on silica gel surfaces. Morrow[14] reports the formation of methoxy groups to be accompanied by a decrease in the intensity of the 3750-cm^{-1} band due to isolated silanol groups, implying an esterification reaction

$$\mathrm{SiOH + CH_3OH \rightarrow SiOCH_3 + H_2O}$$

although others[15] have proposed that methoxy groups are formed from reaction of methanol with strained siloxane bridges on dehydroxylated silica surfaces

$$\mathrm{SiOSi + CH_3OH \rightarrow SiOCH_3 + SiOH}$$

The observed decrease in the ν(OH) band in Figure 1 is not consistent with this alternative, and the existence of strained siloxane bridges on the external surface of ZSM-5 has not been demonstrated. We thus attribute the decrease in the 3720-cm^{-1} band and the new bands at 2959, 2855, and 1470 cm^{-1} to an esterification reaction of methanol with silanol groups external to the zeolite channels. At this temperature, under the experimental conditions employed (single pulses of methanol in flowing nitrogen), only a small fraction of the internal acidic hydroxyl groups interact with methanol.

At 523 K, on the other hand, a much larger fraction of the internal hydroxyls interact with methanol (Figure 1b). The decrease in the 3610-cm^{-1} band is accompanied by the appearance of new bands at 2980 and 2868 cm^{-1} in the ν(CH) region (the latter as a shoulder on the high-frequency side of the 2855-cm^{-1} band) and a poorly resolved shoulder can be resolved on the low-frequency side of the δ(CH) band at 1470 cm^{-1}. On standing in flowing nitrogen at 523 K the new bands decayed slowly over a period of several hours. The extent of the reaction with external silanol groups, as judged by the loss in intensity of the 3720-cm^{-1} band and the intensities of the 2959-, 2855-, and 1470-cm^{-1} bands, was no different at 523 K from that at 473K.

Similar spectra were obtained on adding methanol to a fresh catalyst at 573 K (Figure 1c), but at this temperature the new bands decayed more rapidly. At 623 K and above (not shown) chemisorbed methanol could be detected only if the spectrum was measured immediately following injection of methanol. The spectrum in Figure 1d was measured following injection of methanol at 523 K into a ZSM-5 sample containing 6 Al per unit cell. Comparison with the corresponding spectrum from ZSM-5 containing 3.6 Al per unit cell (Figure 1b) shows that the second chemisorbed species (2980, 2868, and ca. 1450 cm^{-1}) is formed to a greater extent in the zeolite containing more aluminum. There is a correspondingly larger change in the 3610-cm^{-1} band due to acidic hydroxyls in the higher aluminum content zeolite as well. The additional band at 1510 cm^{-1} in Figure 1d is due to strongly adsorbed aromatic products such as xylenes.[6] This band and other new bands (e.g., at 2935 cm^{-1}) grew in intensity when further pulses of methanol were injected at 523 K or above. The 2980-, 2868-, and 1450-cm^{-1} bands were unchanged, however, on injection of further methanol.

Reaction products desorbing from the zeolite following injection of a pulse of methanol were trapped downstream from the infrared cell and analyzed by gas chromatography. No hydrocarbon products were detected following injection of methanol onto fresh catalysts at temperatures below 473 K. At 473 K traces of C_2–C_4 hydrocarbons (ca. 0.01% of the total hydrocarbon yield at 623 K) were measured. Injection of methanol onto a fresh catalyst at 523 K (corresponding to the infrared spectrum in Figure 1b) gave a 20-fold higher hydrocarbon yield with the composition shown in Figure 2a. (The total hydrocarbon yield is expressed as a percentage of the total hydrocarbon yield obtained when methanol was injected onto a fresh catalyst at 623 K.) At 573 K, the hydrocarbon yield was further increased (Figure 2b). A noteworthy feature of the product distributions obtained from the first pulses of methanol injected onto fresh catalysts at 523 and 573 K is the high proportion of methane formed. This declined

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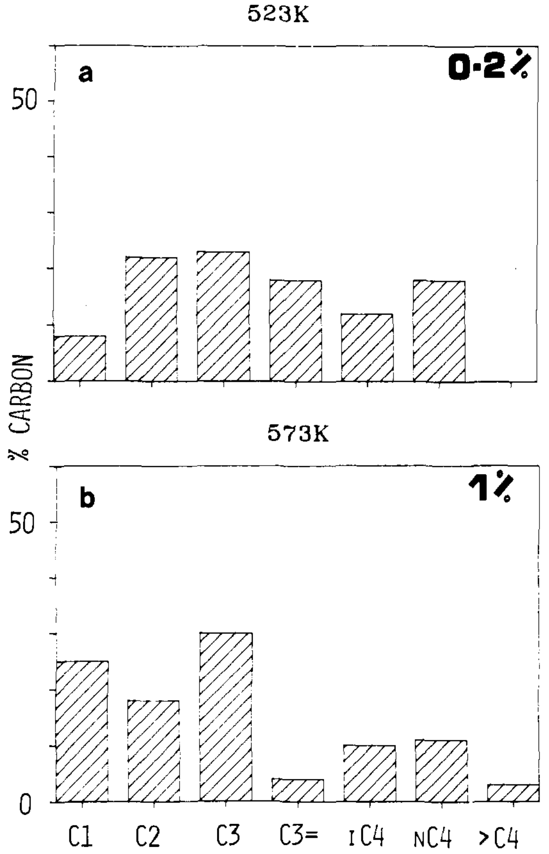

Figure 2. Hydrocarbon products from a single pulse of methanol onto H-ZSM-5 (3.6 Al per unit cell) at the temperature indicated: C1 = methane, C2 = ethane + ethene, C3 = propane, $C3^=$ = propene, C4 = butane. Total hydrocarbon yield is expressed relative to that at 623 K.

steadily when further pulses of methanol were injected at the same temperature, and the proportion of propene correspondingly increased. At 623 K (not shown) propene was the major hydrocarbon product from the first pulse of methanol, with only traces of methane being formed at this temperature.

Infrared experiments similar to those described above were carried out with methanol-d_3 (CD_3OH). The frequencies of the ν(CD) bands corresponding to the ν(CH) bands in Figure 1 are listed in Table I. The formation of zeolite OD groups on injection of methanol-d_3 was observed at temperatures of 573 K and above (ν(OD) bands at 2728 and 2650 cm^{-1}). Ono and Mori[2] observed formation of OD groups when methanol-d_3 was desorbed from H-ZSM-5 at 512 K and correlated this with the formation of hydrocarbon products. Our experimental conditions are quite different (flow cell, in situ measurement of spectra), but a similar correlation is found between the onset of significant hydrocarbon formation and the cleavage of C–D bonds. Furthermore, the in situ measurements show that hydrocarbon formation also correlates with the appearance of the second chemisorbed methanol species in the infrared spectra at 523 K and above. The nature of this species and its role in initial carbon–carbon bond formation are discussed further below.

Methanol in Na-ZSM-5. The infrared spectrum of Na-ZSM-5 after dehydration at 673 K showed only a single weak ν(OH) band at 3720 cm^{-1} corresponding to silanol groups external to the zeolite channels. Injection of methanol onto dehydrated Na-ZSM-5 at 473 K gave the difference spectrum shown in Figure 3a. Aside from the weak 1641-cm^{-1} band due to traces of H_2O in the methanol, all of the new bands appearing at this temperature can be attributed to molecularly adsorbed CH_3OH. The observed frequencies are compared with those of matrix-isolated[16] CH_3OH in Table I. Some frequency shifts are seen relative to the free molecule, but this is consistent with an interaction between CH_3OH and Na^+ cations. The breadth of the 3610-cm^{-1} band and the fact that it is not observed at higher temperatures (e.g., 573 K, Figure 3c) rules out assignment of this band to new zeolite hydroxyl groups formed by dissociative chemisorption of CH_3OH. The spectra of Figure 3 are completely accounted for in terms of adsorption of intact CH_3OH into the pores of Na-ZSM-5, the extent of which decreases with increasing temperature. A similar conclusion (i.e., no dissociative chemisorption) was reported by Salvador and Kladnig[17] from their study of methanol in zeolite NaY. Only traces of light hydrocarbon products (principally propene) were detected following injection of methanol into Na-ZSM-5 at 573 K.

Table I. Vibrational Frequencies of Species Derived from Methanol

species	ref	$cm^{-1\,a}$	assignment
CH_3OSi (external)	this work	2959 (2240)^b	$\nu(CH_3)$ asymm
		2855 (2079)^b	$\nu(CH_3)$ symm
		1470	$\delta(CH_3)$
CH_3OSi on SiO_2	14	(3000)^c (2252) 2958 (2218)	$\nu(CH_3)$ asymm
		2858 (2082)	$\nu(CH_3)$ symm
		1472 1464	$\delta(CH_3)$
CH_3OAl (internal)	this work	2980 (2203)^b	$\nu(CH_3)$ asymm
		2868 (2100)^b	$\nu(CH_3)$ symm
		ca 1460	$\delta(CH_3)$
$CH_3OH{:}Na^+$	this work	3610	$\nu(OH)$
		2994^c 2884	$\nu(CH_3)$ asymm
		2855	$\nu(CH_3)$ symm
		ca 1470	$\delta(CH_3)$
CH_3OH (matrix isolated)	16	3667	$\nu(OH)$
		3005^c 2961	$\nu(CH_3)$ asymm
		2847	$\nu(CH_3)$ symm
		1473 1466 1451	$\delta(CH_3)$

^{a} ±2 cm^{-1} in this work. ^{b} ν(C–D) in parentheses. ^{c} Degeneracy of asymmetric $\nu(CH_3)$ modes is lifted in lower symmetry environments.

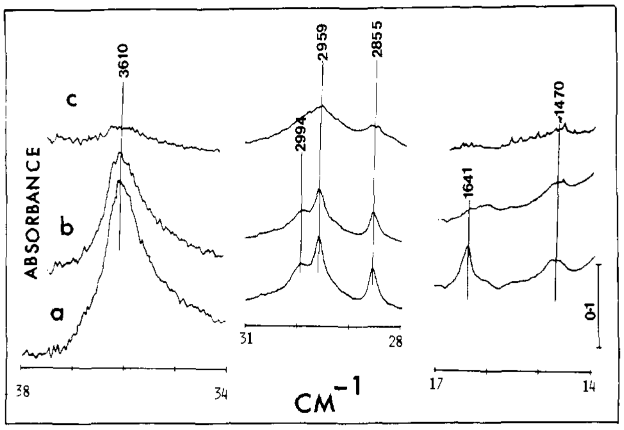

Figure 3. Difference spectra recorded after injecting a 2-μL pulse of methanol onto Na-ZSM-5 (6 Al per unit cell) at (a) 473 K, (b) 523 K, and (c) 573 K.

Dimethyl Ether in H-ZSM-5. Exposure of H-ZSM-5 to dimethyl ether at room temperature produced a complex spectrum showing evidence of hydrogen bonding to both internal and external zeolite hydroxyl groups (loss of intensity in both the 3720- and 3610-cm^{-1} bands, and appearance of a new broad band at ca. 3300 cm^{-1}). From closer examination of the ν(CH) region of the spectrum a distinction could be made between two forms of hydrogen-bonded dimethyl ether, one which was removed more rapidly on outgassing attributed to dimethyl ether on the external surface and a second to dimethyl ether adsorbed within the zeolite

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Table II. Vibrational Frequencies of Species Derived from Dimethyl Ether

species	ref	cm$^{-1\,a}$	assignment
CH_3OCH_3 (solution)	18	2985 2918	$\nu(CH_3)$ asymm
		2880	combination
		2813	$\nu(CH_3)$ symm
CH_3OCH_3 (physically adsorbed on external surface)	this work	2980 2920	$\nu(CH_3)$ asymm
		2878	combination
		2813	$\nu(CH_3)$ symm
CH_3OCH_3 (physically adsorbed on internal surface)	this work	2997 2943	$\nu(CH_3)$ asymm
		2896	combination
		2831	$\nu(CH_3)$ symm
$CH_3O^+HCH_3$	this work	3011 2973	$\nu(CH_3)$ asymm
		2947	combination
		2844	$\nu(CH_3)$ symm
CH_3OAl (internal)	this work	2980	$\nu(CH_3)$ asymm
		2868	$\nu(CH_3)$ symm
$CH_3OCH_3{:}Na^+$	this work	2998 2951	$\nu(CH_3)$ asymm
		2903	combination
		2840	$\nu(CH_3)$ symm
$(CH_3)_3N$	20	2970 2944	$\nu(CH_3)$ in phase
		2878 2818 2768	$\nu(CH_3)$ out of phase
$(CH_3)NH^+$	21	3026 2964	$\nu(CH_3)$ in phase
		2948 2920 2878	$\nu(CH_3)$ out of phase

[a] This work ±2 cm^{-1}.

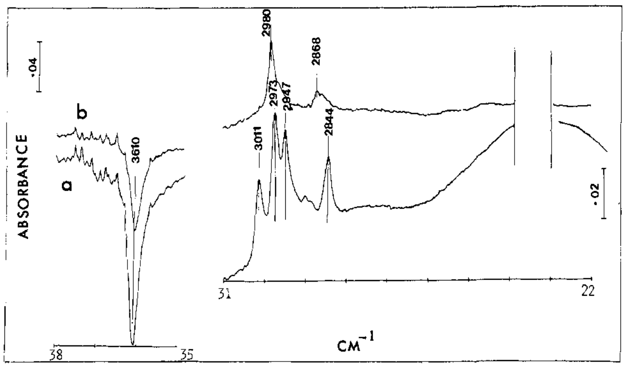

Figure 4. Difference spectra recorded after injecting a 1-mL pulse of dimethyl ether onto H-ZSM-5 (3.6 Al per unit cell) at (a) 373 K and (b) 473 K.

channels. The vibrational frequencies of the external species were identical with those of dimethyl ether in solution,[18] while the ν(CH) vibrations of the internal species were shifted significantly to higher frequencies (Table II).

The hydrogen-bonded dimethyl ether species were not observed when pulses of dimethyl ether were added to H-ZSM-5 at 373 K or above. Figure 4a shows a difference spectrum recorded following injection of dimethyl ether onto H-ZSM-5 (3.6 Al per unit cell) at 373 K. At this temperature, only the internal hydroxyl groups react with dimethyl ether, producing the intense negative peak at 3610 cm^{-1}. This was accompanied by the appearance of broad intense positive peaks at ca. 2300 and 1600 cm^{-1} (not shown), and 4 new bands in the ν(CH) region. We attribute these changes to protonation of dimethyl ether to form a dimethyloxonium species.

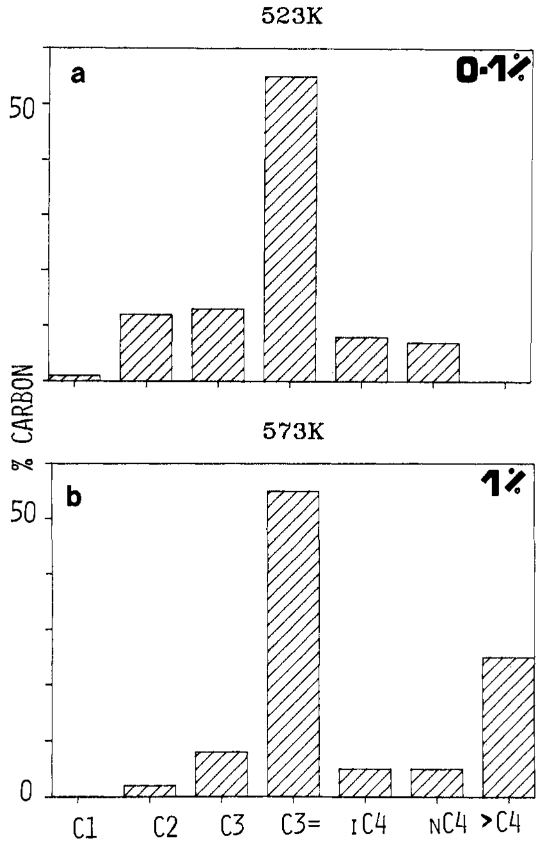

Figure 5. Hydrocarbon products from a single pulse of dimethyl ether on H-ZSM-5 (3.6 Al per unit cell) at the temperatures indicated. See legend for Figure 2.

The extent of proton transfer from the zeolite to the oxygen of dimethyl ether can be estimated from the observed stretching and bending frequencies of the O–H–O group. Pimentel[19] has proposed that the extent of proton transfer from a donor XH to a base B depends on the proton affinity difference between X$^-$ and B and has recorded correlations between the proton affinity difference and the X–H–B stretching and bending frequencies for acid–base complexes in low-temperature matrices. Taking the 2300-cm^{-1} band to be the ν_s[19] O–H–O stretching vibration and the 1600-cm^{-1} band to be the bending mode, we estimate the proton affinity difference between the conjugate base of the zeolite acid site and dimethyl ether to be comparable to that for adducts of HCl and HBr with trimethylamine in which the proton transfer is regarded as complete,[19] i.e., the chemisorbed dimethyl ether should be viewed as a dimethyloxonium ion hydrogen bonded to an oxide ion (the conjugate base site) of the zeolite lattice. Support for this description of complete proton transfer from the zeolite to dimethyl ether comes from examination of the ν(CH) frequencies (Table II); these are shifted upwards by between 26 and 67 cm^{-1} relative to the neutral molecule in solution. Similar differences exist between the ν(CH) frequencies of neutral $(CH_3)_3N$[20] and protonated $(CH_3)_3NH^+$ (Table II).[21]

No hydrocarbon products were detected following formation of protonated dimethyl ether at 373 or 423 K. Injection of dimethyl ether onto a freshly activated catalyst at 473 K gave the quite different infrared spectrum in Figure 4b. This again shows reaction of dimethyl ether with internal hydroxyl groups, but the species formed has vibrational frequencies identical with those of the second form of chemisorbed methanol, viz., 2980, 2868, and ca. 1460 cm^{-1}. Closer examination of the ν(CH) region revealed the presence of small amounts only of the CH_3OSi species formed from methanol at lower temperatures. Injection of dimethyl ether at 523 K gave similar spectra, but at 573 K only traces of adsorbed species were detected following injection of a single pulse of dimethyl ether.

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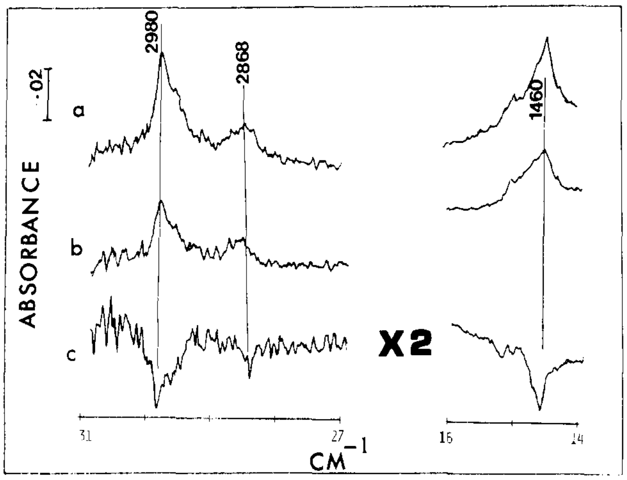

Figure 6. Difference spectra of H-ZSM-5 (3.6 Al per unit cell) at 523 K: (a) after injection of 1 mL of dimethyl ether and standing in flowing nitrogen for 30 min; (b) immediately following injection of 2 μL of benzene; (c) 2 × ((b) − (a)).

Hydrocarbon products were first detected following injection of dimethyl ether at 473 K (traces of ethene and propene which increased on addition of a second pulse). The product distributions obtained following injection of a single pulse of dimethyl ether at 523 and 573 K onto fresh catalysts are shown in Figure 5. Propene is seen to be the major initial product, and the total hydrocarbon yield increased 10-fold between 523 and 573 K (total hydrocarbon yield is expressed as a percentage of that at 623 K).

A correlation thus exists between the onset of hydrocarbon formation and the first appearance of the species responsible for the infrared bands at 2980, 2868, and 1460 cm^{-1} in the case of dimethyl ether as well. Furthermore, the temperature range in which the hydrocarbon yield increases dramatically corresponds to that in which this species disappears from the infrared spectrum (i.e., does not survive long enough for its spectrum to be recorded).

Dimethyl Ether in Na-ZSM-5. Injection of dimethyl ether into Na-ZSM-5 at temperatures between 423 and 523 K produced a single set of infrared bands attributable to dimethyl ether interacting with Na$^+$ cations in the zeolite channels. The ν(CH) frequencies of this form of chemisorbed dimethyl ether are shifted to higher frequency from those of the molecule in solution much less (Table II) than those of the protonated species formed in H-ZSM-5, and the concentration detected decreased with increasing temperature. No hydrocarbon products were observed from dimethyl ether in Na-ZSM-5 between 423 and 623 K.

Methylation Experiments. The correlations observed between hydrocarbon formation over H-ZSM-5 and the appearance of a particular adsorbed species common to methanol and dimethyl ether prompted us to investigate the ability of this species to methylate hydrocarbons. Methylation of aromatics by methanol over H-ZSM-5 is well known,[1] and Ono and Mori[2] reported that toluene could be formed by passing benzene over H-ZSM-5 pretreated with methanol. Furthermore, methylation of alkenes by methanol has been shown to be an important route to higher hydrocarbons in methanol conversion.[22]

Methylation experiments were undertaken by injecting a pulse of methanol or dimethyl ether into H-ZSM-5 at 523 K and waiting 30 min for any reaction products to desorb. Spectra scanned successively after this delay period showed no changes. A pulse of the substrate to be methylated was subsequently injected, the spectrum recorded again, and products trapped downstream analyzed by gas chromatography. Figure 6 shows spectra obtained in such an experiment with benzene. Injection of dimethyl ether in this case gave the spectrum in Figure 6a, which contains the 3 bands described above (after standing in flowing nitrogen for 30 min at 523 K the band intensities were significantly less than immediately after injection). Injection of benzene caused an immediate further reduction in intensity of all 3 bands (Figure 6b), which can be seen clearly in the difference spectrum (Figure 6c). At the same time, toluene was detected downstream. In blank experiments with H-ZSM-5 not exposed to dimethyl ether no conversion of benzene occurred at 523 K.

Table III. Summary of Methylation Experiments

substrate	infrared bands of CH_3OAl reduced	methylation products
benzene	yes	toluene
ethene	yes	propene
cyclopentene	2980-cm^{-1} band reduced; others obscured by new bands due to oligomerization products	methylcyclopentene
propene		no unique methylation products detected
1-hexene		

Similar results were obtained with catalysts pretreated with methanol. In this case only the second chemisorbed species was reduced on addition of benzene; the infrared bands of the $SiOCH_3$ species formed on the external surface of the zeolite were unchanged.

Table III summarizes the results of methylation experiments attempted with other substrates. Injection of a single pulse of ethene at 523 K onto fresh catalysts which had not been pretreated with methanol or dimethyl ether gave no new infrared bands and no reaction products were detected downstream from the infrared cell (oligomerization of ethene at this temperature was found to require exposure to either multiple pulses or a static constant pressure of ethene). Injection of a single pulse of ethene at 523 K onto catalysts pretreated with methanol or dimethyl ether gave propene as a reaction product and caused a reduction in the intensities of the 2980-, 2868-, and 1460-cm^{-1} bands similar to that seen with benzene.

Single pulses of propene and 1-hexene reacted with fresh catalysts at 523 K, forming C_6 aliphatic hydrocarbons and benzene in the case of propene, and ethene, propene, benzene, and $\geq C_6$ aliphatics in the case of 1-hexene. No different products were detected when these molecules were injected into catalysts pretreated with methanol or dimethyl ether; the infrared spectra were then partially obscured by bands of strongly adsorbed oligomerization products, but the 2980-cm^{-1} band from adsorbed methanol or dimethyl ether was nevertheless seen to decrease in intensity on injection of propene and 1-hexene.

Cyclopentene also reacted with fresh catalysts (single pulse injected at 523 K), forming ethene, propene, C_6 aliphatics, toluene, and higher aromatics. Methylcyclopentene was detected as an additional product when cyclopentene was injected onto catalysts pretreated with methanol or dimethyl ether, and the 2980-cm^{-1} band was again seen to decrease in intensity.

Identification of the Reactive Methylating Species. The above experiments have shown clearly that the species formed from both methanol and dimethyl ether in H-ZSM-5 with vibrational frequencies of 2980, 2868, and 1460 cm^{-1} is not only implicated in the formation of the first carbon–carbon bonds from methanol or dimethyl ether but also methylates other molecules. The simplicity of its vibrational spectrum further suggests that this species contain only a single methyl group. In contrast, the trimethyloxonium cation $(CH_3)_3O^+$, which has been proposed as a key intermediate in the conversion of methanol and dimethyl ether, shows 6 infrared-active ν(CH) frequencies.[21] The observed species thus cannot be trimethyloxonium. Furthermore, the 2980-, 2868-, and 1460-cm^{-1} bands cannot be due to reaction products formed subsequent to carbon–carbon bond formation. Alkenes adsorbed in H-ZSM-5 at various temperatures form a common oligomeric species with a characteristic pattern of 3 ν(CH) bands at 2960, 2930, and ca. 2870 cm^{-1};[23] this pattern was not detected from single pulses of methanol or dimethyl ether. Adsorbed benzene and toluene also did not give the same bands as those formed from methanol or dimethyl ether.

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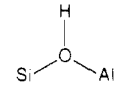
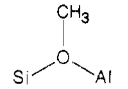
Table IV. ν(CH) Frequencies of Surface Methoxy Species

species	ref	cm^{-1}
CH_3OSi (H-ZSM-5, external)	this work	2959, 2855
CH_3OSi (on SiO_2)	14	3000, 2958, 2858
CH_3OAl (H-ZSM-5, internal)	this work	2980, 2868
CH_3^+, calculated	24	3090, 2903
CH_3^+, gas phase	25	3108
CH_3OAl (in HY)	17	2985, 2885
CH_3OZ (in HY)	3	2977, 2870
CH_3OAl (in AlHY)	3	2968, 2857

We therefore identify the species responsible for the 2980-, 2868-, and ca. 1460-cm^{-1} bands as a second type of methoxy group which is formed at acid sites within the zeolite channels. Salvador and Kladnig[17] reported a similar species to be formed in HY zeolite on chemisorption of methanol (Table IV). The ν(CH) frequencies are higher than those of the CH_3OSi species formed by chemisorption of methanol on SiO_2 and on the external surface of ZSM-5 but below those calculated or observed for "free" methyl carbenium cation.[24,25] We thus follow the suggestion of Ono and Mori[2] that the internal methoxy species should be regarded as an incipient methyl carbenium cation with a structure analogous to that of the internal hydroxyl group, which is an incipient proton, i.e., associated with an oxide anion bridging between a silicon and an aluminum in the zeolite lattice



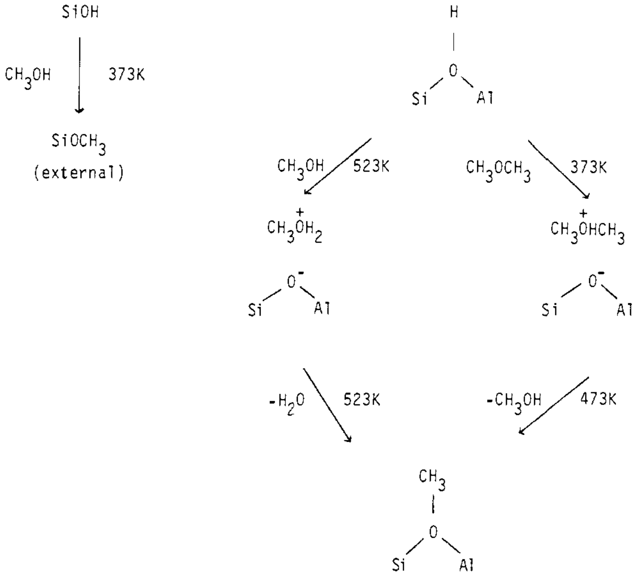


The reactivity of such a methoxy species will depend on the C–O bond strength which may vary between different zeolites just as the acid strength of the hydroxy species varies. The ν(CO) frequency of the methoxy species is obscured by the intense zeolite absorptions below 1300 cm^{-1}. (We have also not detected the second lower frequency δ(CH) band that would be expected for a methoxy species, possibly for the same reason.) Large variations in C–O bond strength will not necessarily cause correspondingly large shifts in ν(CH) frequencies. For comparison, the ν(CH) frequencies of the trimethyloxonium and trimethylammonium cations differ by only 5–15 cm^{-1}, although there is a large difference between the C–Y (Y = O or N) stretching force constants (4.80 mdyn $Å^{-1}$ in $(CH_3)_3NH^+$ and 4.05 mdyn $Å^{-1}$ in $(CH_3)_3O^+$).[21]

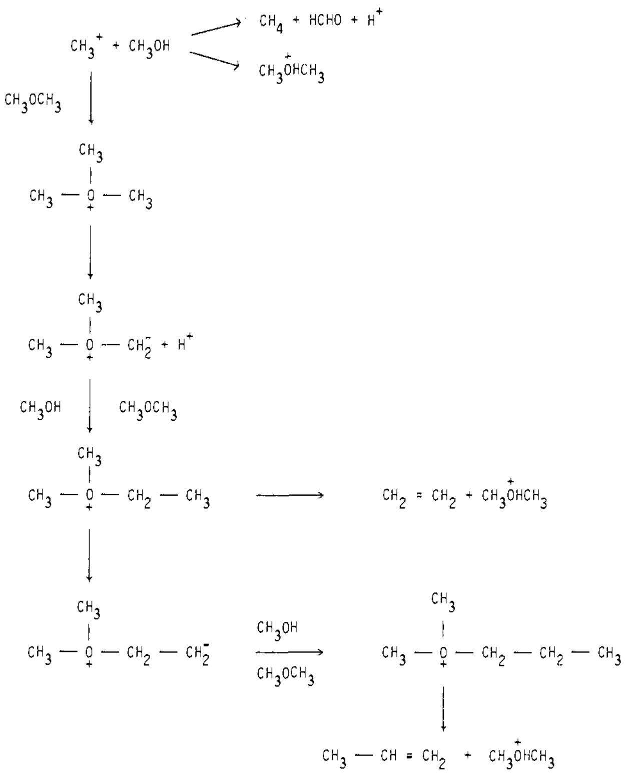
Kubelkova et al.[3,4] have reported the presence of a third type of methoxy group in H-ZSM-5 which they identify as $AlOCH_3$, formed by reaction of methanol with extra-framework Al^{3+} cations in the zeolite channels. In our case, ^{27}Al NMR and pyridine adsorption measurements have shown that there are negligible concentrations of extra-framework Al^{3+} in the zeolite samples used. Although the frequencies of the species identified by us as external $SiOCH_3$ are close to those of Kubelkova's $AlOCH_3$, the observed loss of external SiOH groups on chemisorption of methanol and the absence of Al^{3+} in our zeolites strongly support our assignment. The reactive methoxy species that we have identified may, however, correspond to the "CH_3OZ" species of Kubelkova et al.[3]

Reaction Pathways. The reactions occurring when methanol or dimethyl ether first contact a fresh H-ZSM-5 catalyst are summarized in Scheme I. Chemisorption of methanol on external SiOH groups occurs readily at 373 K. The low reactivity of the internal (acidic) hydroxyls at this temperature is consistent with the observations of Gorte et al.[13,26] that methanol adsorbed in H-ZSM-5 at room temperature mostly desorbs at ca. 400 K without reaction. We attribute the dramatic increase in the extent of reaction between methanol and acidic hydroxyls at 523 K to the protonation of methanol at this temperature. The in situ infrared spectra show no bands that can be assigned to protonated methanol; this species evidently eliminates H_2O immediately to form methoxy groups. The lifetime of protonated methanol has been proposed as the rate-controlling factor in methoxylation of zeolite HY,[17] while spectroscopic evidence for $CH_3OH_2^+$ formation in heteropolyacid catalysts has been presented by Highfield and Moffat.[27]

Scheme I, Formation of Methoxy Species



Scheme II. Possible Pathways for Hydrocarbon Formation



In contrast, dimethyl ether is protonated in H-ZSM-5 already at 373 K. This difference can be readily understood in terms of the 10 kcal mol^{-1} difference between the gas-phase proton affinities of methanol and dimethyl ether.[28] The protonated dimethyl ether is then observed as a stable species between 373 and 473 K. At 473 K or above it eliminates methanol to form the same internal methoxy species formed from methanol; the reaction with dimethyl ether is simpler in that only trace amounts of the external methoxy species are formed.

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Scheme II outlines possible pathways to the first hydrocarbon products formed from the reactive methoxy species (represented as CH_3^+ for simplicity). Hydrocarbon products are first detected over the temperature range in which this species first appears, but the dramatic increases in hydrocarbon yields above 523 K correspond to further reaction of CH_3^+. Our observation of methane as a major initial product from methanol only supports earlier suggestions[1,29] that methane need not necessarily result from cracking of higher hydrocarbons. We have not observed formaldehyde as an accompanying product but would not expect to do so under the conditions used. Novakova et al. have detected formaldehyde by mass spectrometry during initial conversion of methanol over H-ZSM-5.[29] Methane and formaldehyde are considered in Scheme II to arise from hydride abstraction from methanol by CH_3^+; the alternative pathway involves methylation of the oxygen in methanol to form a dimethyloxonium ion (protonated dimethyl ether), which is the reverse of the reaction forming CH_3^+ from dimethyl ether. We have not considered in Scheme II the possibility raised by Ono and Mori[2] of attack of CH_3^+ on the C–H bonds of methanol or dimethyl ether, since such chemistry would seem to be confined to superacid media.

Methylation of dimethyl ether by CH_3^+ would produce the trimethyloxonium cation, which is the starting point for the oxonium–ylide mechanisms for carbon–carbon bond formation proposed initially by Olah[30] and Van den Berg.[31] We have not at any point detected the trimethyloxonium cation spectroscopically in ZSM-5, although its vibrational frequencies in the solid state are now well-established.[21] Nevertheless, the methylating ability of the internal methoxy species (CH_3^+) that has been demonstrated here makes this pathway an attractive one. The immediate further reaction of the trimethyloxonium cation (deprotonation by the conjugate base of the zeolite acid site) would prevent its spectroscopic detection.

Ylide formation by proton abstraction also accounts for the spectroscopic observation of OD formation from CD_3OH (and the isotope exchange between D_2O and dimethyl ether reported by Mole[32]). Van den Berg[31] proposed that the oxonium ylide undergoes an intramolecular Stevens rearrangement to form protonated methyl ethyl ether, which eliminates ethene as a product. Olah et al. have subsequently shown, however, that in homogeneous solution intramolecular rearrangement of dimethyloxonium methylide does not occur; the preferred pathway is intermolecular methylation to ethyl dimethyloxonium ion.[33,34] This may eliminate ethene, as shown in Scheme II, or undergo further methylation to form propyl dimethyloxonium ion, resulting in propene as a final product. Our observation of high initial yields of propene from dimethyl ether suggests that the latter route is favored for dimethyl ether at least. For methanol, the situation is less clear in that high yields of propane are formed from the first pulse which cannot be accounted for in terms of Scheme II. The increase in propene yield in subsequent pulses (and in the initial pulse at 623 K) may be due to methylation of initially formed ethene or to a growing contribution from the propyl dimethyloxonium route; the question of whether ethene is an important initial product in the case of methanol[35,36] remains open.

It must be emphasized that our spectroscopic observations do not prove the mechanism outlined in Scheme II. The scheme does, however, provide plausible pathways to the observed products from the adsorbed species ($CH_3O^+HCH_3$ and CH_3^+) detected by the in situ FTIR technique. We emphasize also that this study relates to the *initial* interactions of methanol and dimethyl ether with freshly activated catalysts. Many authors have reported that methanol conversion over H-ZSM-5 is autocatalytic,[1] and the reactions proposed in Scheme II may be important only in the initial stages of the reaction. Our observation of the methylation of alkenes and benzene by CH_3^+ certainly supports suggestions[22,37] that methylation of initially formed products is an important route for chain growth, although we cannot at this point separate the relative contributions of methylation and alkene oligomerization under steady-state methanol conversion conditions. The in situ infrared technique is currently being applied to this phase of the methanol to gasoline process.

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Note Added in Proof. Since this manuscript was submitted Hutchings et al.[38] have proposed a surface bound oxonium methylide as the key intermediate in initial carbon–carbon bond formation. In the present study we cannot distinguish between this possibility and the trimethyloxonium pathway suggested in Scheme II.

Registry No. CH_3OH, 67-56-1; CH_3OCH_3, 115-10-6.

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