Conversion of Methanol to Dimethylether over ZSM-5 by DRIFT Spectroscopy

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A diffuse reflectance infrared study of the dehydration of methanol to dimethylether over ZSM-5 catalyst is presented. Between 125° and 200°C, dimethylether is formed and a possible stable intermediate in the nucleophilic attack on surface methoxide groups by methanol is observed on the acid form of the zeolite. This species occupies two OH sites in close proximity. In contrast to the deactivated zeolite, the acid form of ZSM-5 shows an increase in the concentration of terminal silanol groups as the temperature is increased above 100°C and a concurrent increase in reflectivity in the region of the lattice overtone and combination modes.

Index Headings: **DRIFT spectroscopy; ZSM-5; FT-IR.**

INTRODUCTION

The concern over air quality has continued to grow. A major contributor to increasing levels of pollutants is transportation fuel emissions. The use of methanol in automobiles has been proposed as a means of reducing air pollution in congested metropolitan areas. Before it can replace gasoline and other fuels, however, the problems associated with cold starting and cold drivability of methanol-fueled vehicles must be satisfactorily resolved. One such solution may be the use of dimethylether as an additive to methanol. Along with its high volatility, dimethylether has the advantage of being able to be produced directly from the dehydration of methanol.

A possible route for the *in situ* dehydration of methanol involves the use of ZSM-5 catalyst (Mobil Co.). The proton-exchanged form of ZSM-5 zeolite has been successfully employed for the conversion of methanol to gasoline-range products.[1] Studies on the mechanism of this reaction have established the first step in the reaction as the conversion of methanol to dimethylether;[2,3] this is followed by conversion to higher hydrocarbons at temperatures around 350°C.

Although the methanol-to-gasoline reaction has been studied extensively, few studies have focused on the lower-temperature dehydration reaction. This paper presents the results of an *in situ* diffuse reflectance study of the dehydration of methanol to dimethylether over ZSM-5 at temperatures between 22° and 200°C.

EXPERIMENTAL

Two zeolites were studied: ZSM-5 and Silicalite. The ZSM-5 was obtained from Mobil Corp. in a dried ammonium form. The acid form, H-ZSM-5, was obtained by calcining the zeolite in air at 500°C for two hours. The decomposition of the organic template was accompanied by a color change from gray to white. The Na and Fe ion-exchanged forms were prepared by repeated washings of H-ZSM-5 with 1 M solutions of NaCl or $FeCl_3$ in an ultrasound bath at 60°C. The Silicalite SP-115 (Union Carbide), a silicon-rich zeolite isomorphous with ZSM-5, was calcined in the same manner as ZSM-5.

ICP analyses gave Si/Al ratios of 40 for each of the ZSM-5 zeolites, and 3.8 for the Silicalite. The high aluminum content in the latter may be due to extra-framework material. The Al/Na ratio in Na-ZSM-5 is 1.1, indicating that the charge on the tetrahedral aluminum is almost completely balanced by sodium. The remaining aluminum may either be non-tetrahedral or be balanced by hydrogen ions. The Al/Fe ratio in Fe-ZSM-5 is 0.5. Iron is in excess of what is needed to balance the charge on aluminum and is therefore partially or wholly incorporated elsewhere in the zeolite. Mossbauer spectroscopy indicates the presence of a single iron species which is trivalent and in the high-spin state.

Infrared spectra were collected on a Nicolet 60 SXB dry-air purged spectrophotometer with a TGS detector using a Spectra-Tech (Collector) diffuse reflectance attachment. Single-beam spectra were ratioed against KBr reference spectra collected at the same temperature as the sample. A Spectra-Tech controlled environmental chamber was used to collect spectra between 22° and 200°C and to allow reactant gases to pass over the sample. The temperature controller was calibrated to the actual sample temperature by inserting a thin thermocouple directly into a sample and monitoring the sample temperature at different controller settings. Spectra were normally collected on neat samples. To look at framework vibrations, the samples were diluted to less than 0.5% by weight in KBr to eliminate *restrahlan* effects. The spectra are plotted in absorbance units which are sufficient for qualitative purposes. Integrated areas have been calculated from Kubelka-Munk plots.

Gaseous reactants were introduced directly into the sample environmental chamber at 2 mL/min. Liquid reactants were introduced by bubbling a stream of dry nitrogen through the liquid and into the sample chamber. Samples were equilibrated for ½ h at each temperature or reactant condition prior to collection of spectra or samples for GC-MS analysis. Excess reactant was evacuated from the sample chamber.

GC-MS analyses (Finnegan-MAT 4600) were obtained on gas samples collected at the entrance and exit to the environmental chamber.

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TABLE I. Mole percent conversion of methanol to dimethylether.

	Temperature, °C					
Zeolite	22	100	125	150	175	200
H	1%	1%	23%	44%	74%	52%
Na					3%	
Fe					68%	
Non-calcined					<1%	
Silicalite					1%	

RESULTS AND DISCUSSION

The mole percent conversions of methanol to dimethylether are reported in Table I. No other hydrocarbons, CO, or CO_2 were detected. For H-ZSM-5, the conversion to dimethylether is at a maximum at 175°C. At this temperature, Fe-ZSM-5 is also active for methanol dehydration, but Na-ZSM-5 and Silicalite are not.

OH Groups. Surface OH groups are generally considered to be both the adsorption sites and active sites in zeolite catalysts. Figure 1 shows the OH region of H-ZSM-5 at temperatures between 22° and 200°C. The band at 3745 cm^{-1}, appearing at all temperatures, is well established as being due to terminal silanol groups.[4,5] At room temperature there is a band at 3676 cm^{-1} which has been variously assigned in ZSM-5 as amorphous or poorly crystallized phases,[6] hydroxyl groups on extra-framework aluminum,[7] and water-perturbed silanols.[8] At 100°C, this band disappears and a new band appears at 3700 cm^{-1}, which in turn decreases in intensity at higher temperatures. A band at 3700 cm^{-1} was observed in a previous study of ZSM-5 and was found to increase in intensity as the Si/Al ratio increased and was therefore thought to be some kind of silanol group.[9] At the same time that the 3700-cm^{-1} band appears, a second new OH group appears at 3550 cm^{-1}. This band is more apparent in the subtraction spectra (not shown). Bands near 3550 cm^{-1} have been assigned to Si-OH-Al bridging groups in ZSM-5,[7] in HY zeolite,[10] and in X and Y zeolites.[11] At 125° to 150°C, a band at 3605 cm^{-1} appears. This has been previously assigned as being due to a bridged Si-OH-Al type structure and is thought to be the active site in the conversion of methanol to gasoline-range products.[6,8,12] In addition to these hydroxyl groups on the zeolite there is molecular water, which gives a very broad band near 3300 to 3200 cm^{-1} that disappears upon heating of the zeolite (observed in the subtraction spectra, not shown). Similar results are obtained for Fe-ZSM-5.

The OH groups in Na-ZSM-5, on the other hand, undergo fewer changes with temperature (Fig. 2). In addition to the room-temperature OH bands at 3740 and 3676 cm^{-1} seen for H-ZSM-5, Na-ZSM-5 has a band at about 3600 cm^{-1}. Upon heating, the 3740-cm^{-1} band becomes more distinct, and the band near 3600 cm^{-1} appears to shift to lower frequency, collapsing above 150°C. Silicalite (not shown) shows only a shoulder at 3740 cm^{-1} and a broad band near 3540 cm^{-1} at higher temperatures.

The integrated band areas of the OH groups at 3740, 3700, and 3605 cm^{-1} in H-ZSM-5 and the 3740-cm^{-1} group in Na-ZSM-5 are plotted against temperature in Fig. 3. There is a steady increase in the area of the band at 3740 cm^{-1} with temperature, which may be due initially to surface water desorption and, at higher temperatures, to desorption of water imbedded more deeply in the zeolite or to the creation of new silanol sites. The area of the band at 3605 cm^{-1} increases steadily after it appears at 125°C. Coincident with the increase in the 3605-cm^{-1} band area is a decrease in the band area at 3700 cm^{-1}, which is at a maximum at 100°C. In contrast, only the OH band area at 3740 cm^{-1} increases with temperature in Na-ZSM-5. This increase, unlike that for H-ZSM-5, levels off above 150°C. An increase in silanol band area has been linked to an increase in surface area.[13]

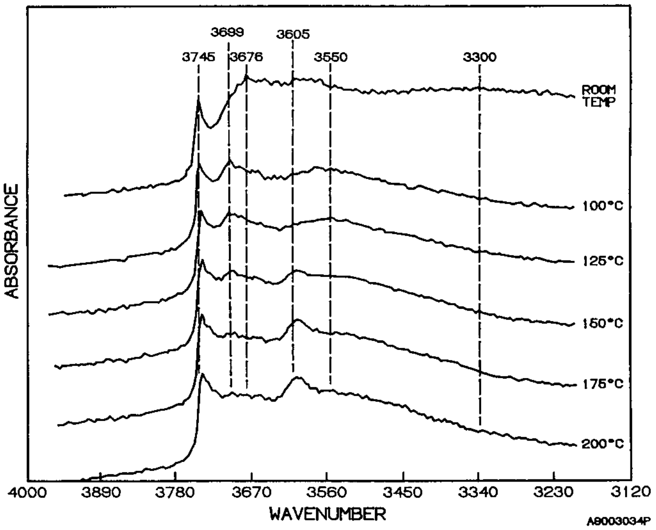


FIG. 1. OH region in H-ZSM-5, 22° to 200°C.

Adsorption of methanol, or another hydrocarbon, onto the zeolite surface OH groups can be seen from the negative peaks in the subtraction spectra. Figure 4 shows the subtraction spectra for methanol adsorbed on H-ZSM-5 between 22° and 200°C. At room temperature, the only adsorption site appears to be the OH group at 3685 cm^{-1}. At 150°C, this site shifts to 3700 cm^{-1} and a second adsorption site, at 3605 cm^{-1}, appears. The onset of conversion of methanol to dimethylether occurs at about 125°C (Table I). The terminal silanol OH groups at 3740 cm^{-1} and the OH groups at 3550 cm^{-1} are un-

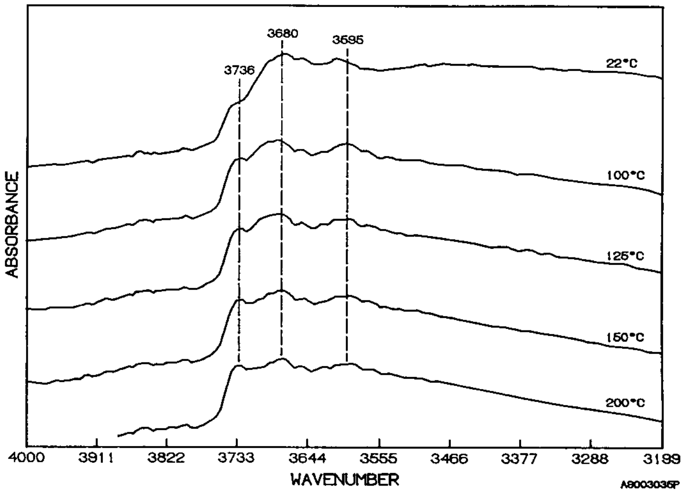


FIG. 2. OH region in Na-ZSM-5, 22° to 200°C.

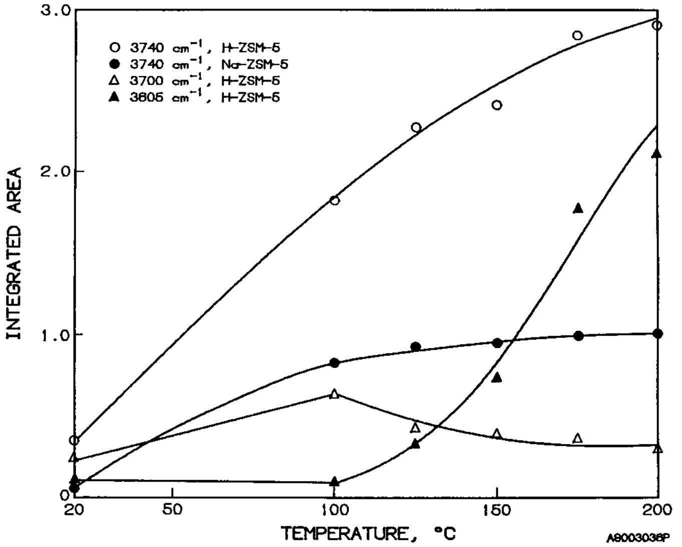


FIG. 3. Integrated OH peak area vs. temperature.

perturbed by methanol adsorption. In Na-ZSM-5, the only site of adsorption at any temperature between 100° and 200°C is the OH group at 3700 cm^{-1}. Similarly, Silicalite shows adsorption only near 3700 cm^{-1}.

On the basis of these observations, and drawing on comparisons with results in the literature, assignments for the OH groups can be proposed. The band at 3740 cm^{-1} has been established as being due to terminal silanol groups. These groups are undisturbed by methanol adsorption at the temperatures investigated. The OH group which appears at 3676 cm^{-1} at 22°C shifts to 3700 cm^{-1} after water is desorbed and is an adsorption site for methanol on all of the zeolites, but is inactive for dehydration. It may be due to a silanol group made more acidic by proximity to an aluminum atom. The area of the band at 3605 cm^{-1} becomes significant at 125°C, the same temperature at which the dehydration reaction starts, and is an adsorption site in the active zeolites. This assignment agrees with earlier assignments for this OH group as an acidic OH bridging group, Si-OH-Al.

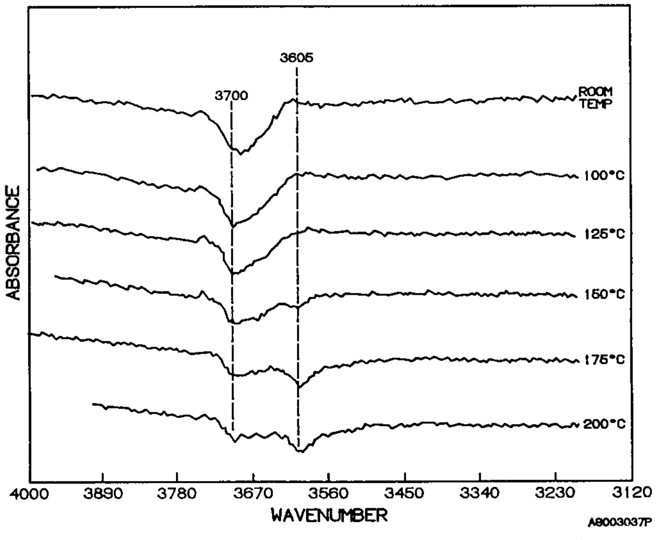


FIG. 4. OH region of methanol-adsorbed H-ZSM-5 after subtraction of initial H-ZSM-5 spectrum.

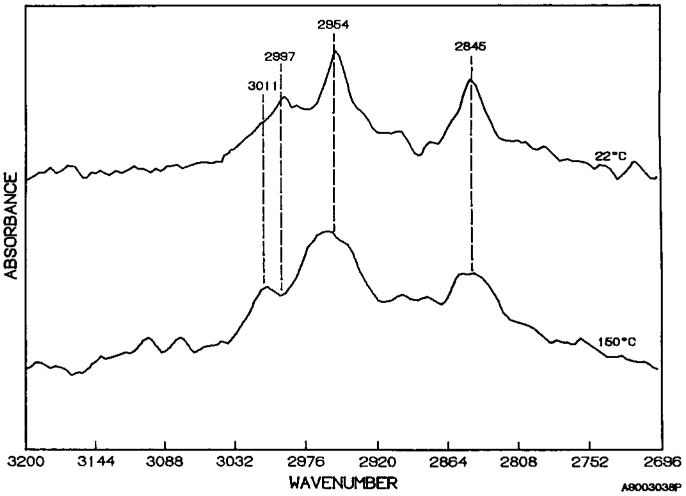


FIG. 5. C-H region of methanol adsorbed on H-ZSM-5 at 22° and 150°C.

Although a similar band appears near 3600 cm^{-1} in Na-ZSM-5, it is not an adsorption site in this zeolite. The band at 3550 cm^{-1} appears when water is desorbed, but is not perturbed by adsorption of methanol. The low frequency suggests that it is acidic or strongly hydrogen bonded, but because it is unaffected by adsorption, it may not be accessible.

Organic Fragments. The adsorbed organic fragment can also be examined by infrared. The spectra of the room-temperature and 150°C fragments present after methanol adsorption on H-ZSM-5 are shown in Fig. 5. The room-temperature spectrum, with bands at 2997, 2954, and 2845 cm^{-1}, corresponds to a surface methoxide group.[14-16] At the higher temperature, the 2997-cm^{-1} shoulder is lost and a new band appears at 3011 cm^{-1}. The band at 2954 cm^{-1} broadens and encompasses a high-frequency component at 2972 cm^{-1}, and the band at 2845 cm^{-1} broadens. In a study of dimethylether adsorption on alumina, a C-H band at 3036 cm^{-1} appeared above 75°C, in addition to other C-H bands.[17] This band was attributed to a second type of hydrogen on the adsorbed methoxy group arising from the reduced symmetry of the adsorbed species. Elsewhere, bands appearing above 3000 cm^{-1}, accompanied by graying of the zeolite, have been attributed to coke buildup.[6] In the present case, however, no graying is observed, and the 3011-cm^{-1} band appears soon after heating above 150°C in the presence of methanol.

Adsorption of methanol on Fe-ZSM-5 results in the same fragments observed on H-ZSM-5. Methanol adsorption on Na-ZSM-5 or Silicalite at 22° or 200°C, however, results only in the surface methoxide fragment observed on H-ZSM-5 at 22°C.

In order to identify the nature of the 150°C fragment on H-ZSM-5, other hydrocarbons were adsorbed at different temperatures. Ethylene does not adsorb at 22°C, and above 150°C, only a broad envelope is observed between 3000 and 2800 cm^{-1}. Adsorption of ethylene oxide at 22° or 200°C results in the same broad feature. Adsorption of dimethylether at room temperature results in a C-H spectrum similar to that of gas-phase dimethylether, indicating that the ether adsorbs intact. At 150°C, however, the C-H bands shift and broaden and become

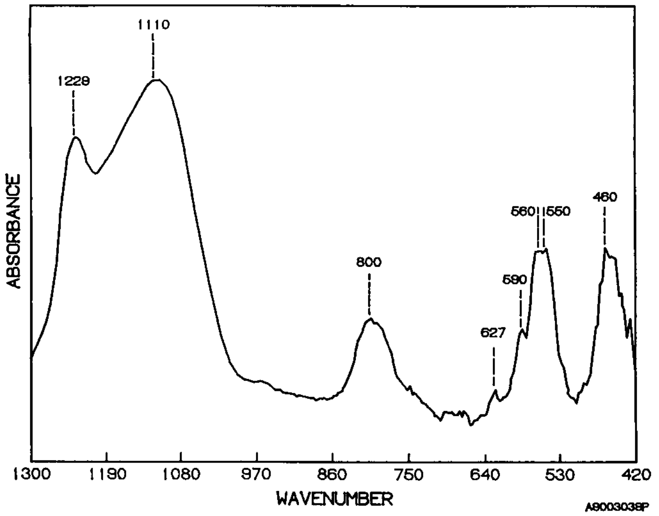


FIG. 6. Framework vibrations in KBr-diluted H-ZSM-5.

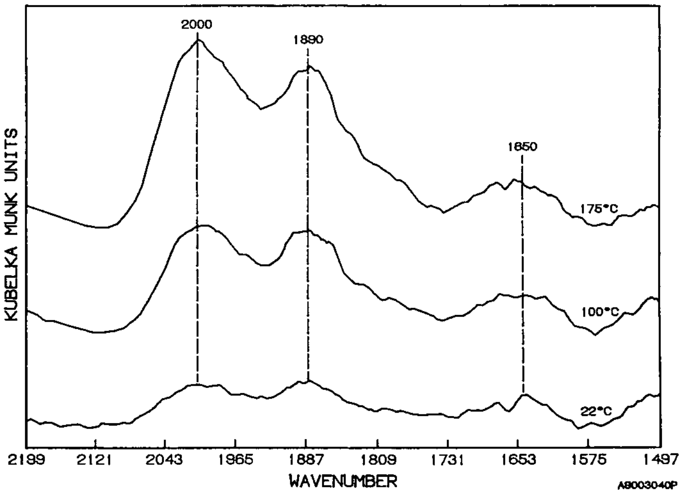
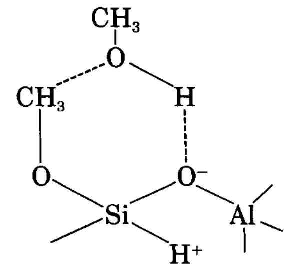


FIG. 7. Combination/overtone region of lattice modes of H-ZSM-5 at 22°, 100°, and 175°C.

identical to those observed for methanol adsorbed at these temperatures. On Na-ZSM-5, adsorption of dimethylether between room temperature and 200°C results in the same dimethylether fragment observed on H-ZSM-5 at room temperature.

The appearance of the same fragment on H-ZSM-5 at 150°C from the adsorption of either methanol or dimethylether suggests either that both methanol and dimethylether rearrange to form the same adsorbed species or that the fragment forms from gas-phase dimethylether introduced directly or produced from methanol. The latter possibility was tested by adsorbing methanol onto H-ZSM-5 at room temperature, evacuating excess gas-phase methanol, and heating the adsorbed zeolite to 175°C under vacuum. The C-H stretching bands shifted from those corresponding to surface methoxide to those observed with methanol or dimethylether adsorption at the higher temperature. Cooling the sample back to room temperature leaves the high-temperature fragment in place. Subtraction spectra again show a single adsorption site at 3700 cm^{-1} at room temperature and two adsorption sites, at 3700 and 3605 cm^{-1}, at 175°C. Thus, rearrangement of the fragment appears to occur in the absence of gas-phase species and involves two different OH sites. These results suggest that these two OH sites are either adjacent or in close proximity.

The high-temperature fragment does not interfere with dimethylether production and appears only when dimethylether is present, either as a reactant or a product. It may be a stable intermediate in the formation of the ether such as:



Framework Vibrations. The framework vibrations of zeolites occur below 1300 cm^{-1} and are primarily due to internal vibrations of the silica and alumina tetrahedra and to the external motions of the rings with respect to the lattice. The spectrum of a KBr-diluted sample of H-ZSM-5 is shown in Fig. 6. The bands at 1229, 627, 590, and 550 cm^{-1} are due to the external vibrations of the double five-membered rings,[7,18,19] and those at 1110, 800, and 460 cm^{-1} are due to the internal vibrations of the SiO_4 tetrahedra. In Silicalite, an additional shoulder is seen at 1074 cm^{-1}.

The external modes are especially sensitive to structural changes such as the Si/Al ratio, the degree of crystallinity, and cation substitution. All of the zeolite samples gave identical spectra in this region regardless of cation substitution. The ratio of the infrared absorbances at 560 and 460 cm^{-1} has been correlated with the degree of crystallinity in zeolites.[18] For all of these samples, this ratio is about 1, indicating well-crystallized samples. In addition, this ratio remains unchanged after the sample has been heated to 200°C and when it is reacted with methanol, showing that no collapse of the crystal structure occurs under these conditions.

In addition to the fundamental framework modes, weak bands at 2000, 1880, and 1650 cm^{-1} appear in all of the zeolite spectra. Infrared bands near 2000, 1860, and 1630 cm^{-1} have previously been assigned as overtone and combination modes of fundamental lattice vibrations in silica[20,21] and in alumino-silicates.[22] Similar bands have been observed in the spectra of quartz, silica gel, and feldspar minerals in this laboratory. The band at 1650 cm^{-1} includes a contribution from molecular water. The areas of these bands show a marked difference in behavior between the active and inactive zeolites. As the temperature is increased, the areas of these bands in-

TABLE II. Integrated areas of Si-O overtone and combination modes.

	1650 cm^{-1}		1880 cm^{-1}		2000 cm^{-1}	
Zeolite	22°C	175°C	22°C	175°C	22°C	175°C
H	75	152	30	130	28	172
Na	121	89	64	83	80	109
Fe	8.6	29	12	33	16	55
Non-calcined	31	19	28	37	47	77
Silicalite	108	59	28	33	17	20

crease sharply in H-H (Fig. 7) and Fe-ZSM-5 but increase only moderately in Na-ZSM-5, Silicalite, and the noncalcined ZSM-5. The relative areas of these bands, determined from Kubelka-Munk spectra at 22° and 175°C, are shown in Table II. The decrease in the 1650-cm^{-1} band area in the inactive zeolites reflects the desorption of water. Adsorption of methanol at 175°C reduces the band areas to almost their initial levels. No such changes in intensity with temperature were observed in the fundamental framework modes on either the neat or diluted samples.

The behavior of these overtone and combination bands with temperature parallels that of the terminol silanol band. In H-ZSM-5, the area of the 3740-cm^{-1} band increases continually from 22° to 200°C. In Na-ZSM-5, the area of the 3740-cm^{-1} band increases only slightly above 100°C. The reflectivity of the zeolite in the frequency range of the lattice combination/overtone modes, therefore, may be partly a function of the concentration of surface OH groups, and thus site-related.

SUMMARY

Between 125° and 200°C several events occur on the active zeolites. A new OH group, at 3605 cm^{-1}, appears; the concentration of terminol silanol groups and the reflectivity of the zeolite in the region of the lattice overtone and combination modes increase; a new surface fragment, occupying two OH sites, is formed in the presence of methanol or dimethylether and may be a stable intermediate in the formation of dimethylether; and finally, dimethylether is formed. The major differences observed between the dehydration of methanol and the methanol-to-gasoline reactions are the involvement of two OH sites and the formation of an organic fragment that includes high-frequency C-H groups.

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