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The Adsorption of Methanol and Water on H-ZSM-5[1]

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The adsorption of water and methanol on H-ZSM-5 has been characterized by temperature-programmed desorption (TPD), thermogravimetric analysis, and transmission infrared spectroscopy. For water, adsorption of the first molecule at the cation site occurs with a heat of adsorption of 12.1 kcal/mol. The heat of adsorption drops rapidly when more than one water molecule per cation is adsorbed and all additional water can be removed by evacuation at room temperature. For methanol, TPD shows adsorption in two desorption states. The higher temperature state corresponds to one molecule adsorbed at each cation site, while the lower temperature state is more weakly adsorbed and may not be associated with the cation. No reaction products were observed during desorption, indicating that methanol was the only species present on the surface. In the coadsorption of water and methanol, methanol vapor was found to rapidly displace adsorbed water, while water could not displace adsorbed methanol. However, deuterium-exchange experiments indicate that water is not blocked from approaching the cation sites by adsorbed methanol. Possible implications of these results on reactions carried out in the presence of water are discussed.

INTRODUCTION

Water adsorption on zeolites has been studied extensively in order to understand the hydroxyl groups and to determine the nature of the acidity of these materials (*1*). Most of this work was done on zeolites with relatively high alumina contents, but very little work has been published with the high silica zeolites like ZSM-5. These are usually considered hydrophobic (*2*); and therefore, the adsorption of water is often not considered.

However, there is evidence that the presence of water does have a significant effect on reactions carried out over ZSM-5. For example, Oudejans *et al.* (*3*) have found that the product distribution for ethanol conversion over H-ZSM-5 can be favorably changed by the presence of water in the feed. In another reaction, the conversion of small olefins to higher molecular weight products is enhanced by the presence of large quantities of water (*4*). (Mole ratios of water to olefin are reported to be 0.5 to 15.) In a third reaction water in the feed has been found to be beneficial for dewaxing (*5*). Part of the reason for the improved reaction characteristics in the presence of water may just be the gasification of coke deposits by steam. However, water should not have increased the reactivity of the catalyst in these reactions or changed the product distribution for the ethanol conversion.

In this paper, we will report our study of the adsorption of water and methanol on H-ZSM-5 using temperature-programmed desorption (TPD), transmission infrared spectroscopy, and thermogravimetric analysis (TGA). Our results indicate that water does preferentially interact with the hydrogen cations, which are the Brønsted acid sites in the zeolites, and that water could be present at the cation sites, even at reaction temperatures. However, methanol is very effective in displacing adsorbed water and we conclude that water is unlikely to affect the reactive sites on H-ZSM-5 during reaction. Changes in reaction chemistry due to

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water are likely due to interactions between water and adsorbed intermediates.

EXPERIMENTAL

The infrared and TPD experiments were completed in the same experimental apparatus shown schematically in Fig. 1. A 1.6-cm-diameter wafer was supported inside a gold-plated, copper tube. The gold plating was necessary for preventing desorption from the sample holder during TPD. The sample holder could be heated or cooled by contact with a second tube which could be heated with a cartridge heater or used as a liquid-nitrogen reservoir. A Chromel–constantan thermocouple was attached to the inner sample tube for measuring the temperature. Tests to determine whether there was sample heating due to the infrared beam showed that temperature differences between the sample and the sample holder were always less than 5 K.

The sample was evacuated with a liquid-nitrogen-trapped, mechanical pump. Both infrared and TPD spectra indicated that the sample would remain clean for several hours under this vacuum. Adsorption of methanol and water was accomplished by exposing the sample to the equilibrium vapors from a liquid held in a temperature bath. For the low water pressures, a $CaCl_2$ solution was used to prevent freezing. Exposure times were usually just a few seconds since adsorption was very rapid. Longer exposures resulted in no changes.

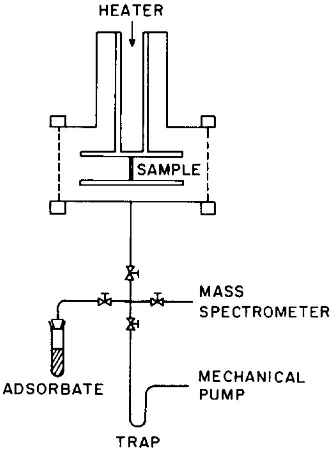

FIG. 1. The experimental apparatus for TPD and infrared measurements.

TPD spectra were analyzed by leaking desorbing gases into a separate, ion-pumped vacuum system with a mass spectrometer. With methanol, we searched carefully for other products besides methanol; however, we did not observe any other gases desorbing from the sample. In all cases, the TPD spectra obtained monitoring total pressure were identical to spectra obtained monitoring methanol at mass 31. The heating rate for all of the spectra was constant at approximately 30 K/min.

The zeolite samples were obtained as an NH_4-ZSM-5 powder from Mobil Oil Company. Mobil reported the sample to have particle sizes less than 0.5 μm and a silica-to-alumina ratio of about 70. X-Ray diffraction of these samples agreed with published spectra for ZSM-5, as did water uptake measurements (*7*). We also checked the silica-to-alumina ratio using TGA of NH_3 and found the ratio to be 67, in excellent agreement with the reported values. For the TPD and infrared experiments, 30 to 35 mg were pressed into the 1.6-cm-diameter wafers without further treatment.

For the TGA experiments, a Cahn microbalance was used to measure the uptake of a 130-mg sample. The adsorption techniques and vacuum system were essentially identical to the TPD–ir apparatus just described.

RESULTS

To convert the NH_4-ZSM-5 to the hydrogen form, it was necessary to heat the sample above 750 K. The conversion could be monitored very easily using the infrared spectrum. Figure 2 shows the differences between the hydrogen and ammonium forms of ZSM-5. Bands indicative of the ammonium ion were observed at 1450 cm^{-1} and between 3200 and 3400 cm^{-1} (*8, 9*). With heating, these peaks disappeared, followed by the growth of a new hydroxyl

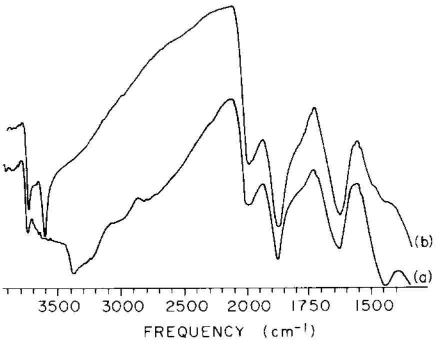

FIG. 2. Transmission infrared spectra for NH_4-ZSM-5 and H-ZSM-5. Comparison of these two spectra show that the 3605-cm^{-1} peak is due to the hydrogen cation, while bands at 1450 and 3200–3400 cm^{-1} are due to the ammonium cation.

stretch at 3605 cm^{-1}. This hydroxyl group has already been identified as being due to the hydrogen cation (*9–12*). The 3735-cm^{-1} peak is almost certainly due to hydroxyl groups which terminate the crystal edges. A peak at this frequency is observed on almost all zeolites and silica gels (*1*). The disappearance of ammonia as a function of temperature was also monitored. Decomposition of the ammonium cation occurs between 500 and 700 K, in basic agreement with TPD studies of NH_3 from H-ZSM-5 (*12, 13*).

All results in this paper will be for H-ZSM-5. We will first discuss the results for water and methanol individually, then the coadsorption of the two.

Water Adsorption

Figure 3 shows the effect of adsorbed water on the infrared spectrum. Here, the clean H-ZSM-5 is compared to the same surface after water has been adsorbed at room temperature, followed by evacuation. While water does not completely desorb with evacuation at room temperature, the water coverage in this spectrum is low, approximately 0.6 g/100 g of zeolite (~0.7 water molecule/cation) as determined by TGA. Even at this low coverage, there is substantial interaction between the water molecules and the cation hydroxyl group at 3605 cm^{-1}. The ir transmission at 3605 cm^{-1} is actually higher in the presence of water. From the quantity of water adsorbed and the fact that the hydroxyl peak is so strongly affected at this low coverage, one can see that all of the water molecules are adsorbed near a cation. There is no interaction between the water and the 3735-cm^{-1} hydroxyl group, as would be expected if these hydroxyls are due to silanol groups terminating the crystal. This peak remains sharp and with unchanged intensity.

Along with decreasing the absorbance at 3605 cm^{-1}, water causes a new peak at 3690 cm^{-1}. A peak at 3690 cm^{-1} has been frequently observed on other zeolites with monovalent cations and, in those cases, it has been ascribed to adsorption on the cation (*1*). For a hydrogen cation, adsorption of water on the cation results in a hydronium ion, which is an entirely reasonable assignment for this peak. When the sample is heated to desorb water, the 3690-cm^{-1} peak disappears at the same rate that the 3605-cm^{-1} peak reappears. Water is completely desorbed from the sample by 373 K under vacuum.

For water adsorption, one should also see a bending mode at 1640 cm^{-1}. However, there is a strong band due to the zeolite framework near this same frequency which apparently masks this peak. There may be a slight broadening of this frame-

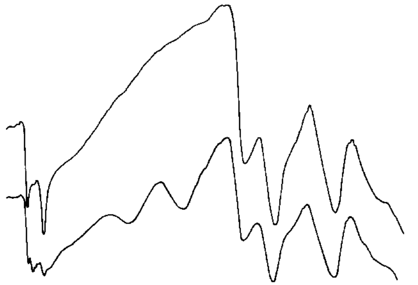

FIG. 3. Transmission infrared spectra for H-ZSM-5 with and without adsorbed water at 300 K. The 3605-cm^{-1} peak is severely attenuated, even though the water coverage is ~0.7 molecules/cation.

work band, but this is not readily apparent. We observed a general decrease in transmission below 2000 cm^{-1} when water was adsorbed; therefore, it is unlikely that subtraction techniques would be useful for studying this bending mode.

Infrared spectra taken while holding the sample at a fixed water pressure and various temperatures are reported in Fig. 4. In this experiment, adsorption was rapid and equilibrium was quickly established. These infrared spectra are identical to those obtained during desorption under vacuum. The shape of the spectra apparently change only with the quantity of water adsorbed on the sample; therefore, the ir spectrum can be used to measure water coverage. This coverage was calibrated by TGA for an equilibrium uptake of 7.5 Torr water. These results are shown in Table 1.

Since the infrared spectrum appears to be a function only of coverage, we obtained the heat of adsorption of the water by measuring the equilibrium infrared spectra as a function of vapor pressure and sample temperature. The Clausius–Clapeyron plots for 0.7 water molecules per cation and 2.0 molecules per cation are given in Fig. 5. For each point on Fig. 5, the sample was held in the water pressure indicated and the infrared spectrum was taken at various temperatures until it matched the spectrum obtained at the coverage of interest. These plots indicate that the heat of adsorption for the first molecule at the cation site is approximately 12.1 kcal/mol. For a coverage of 2.0 molecules per cation, the adsorption energy has decreased to 8.2 kcal/mol. For the ZSM-5 structure without any cations, Flanigen *et al.* (*14*) reported that the initial heat of adsorption was only 6 kcal/mol. Our results were reproducible to better than 1.0 kcal/mol and we believe the numbers we report are this accurate; therefore, the difference between our results on H-ZSM-5 and those reported by Flanigan *et al.* is the attraction between the water and the cat-

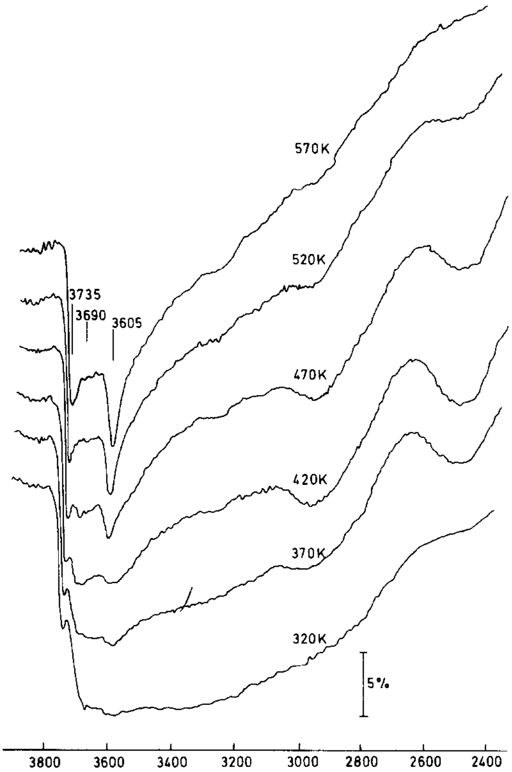

FIG. 4. Transmission infrared spectra for the H-ZSM-5 sample in equilibrium with 19 Torr of water at the temperature indicated.

TABLE 1

Temp (K)	Uptake	
	(g H_2O/100 g H-ZSM-5)	Molecules/cation[a]
306	4.50	5.3
309	3.89	4.5
317	3.36	3.9
325	2.75	3.2
328	2.52	2.9
339	1.87	2.2
353	1.34	1.6
363	1.11	1.3
382	0.92	1.1
393	0.69	0.8
409	0.53	0.6
433	0.31	0.4
453	0.15	0.2
473	0.08	0.1
493	0.00	0.0

Notes. The equilibrium uptake of water on H-ZSM-5. The vapor pressure was 7.5 Torr.

[a] Assumes silica-to-alumina ratio of 70.

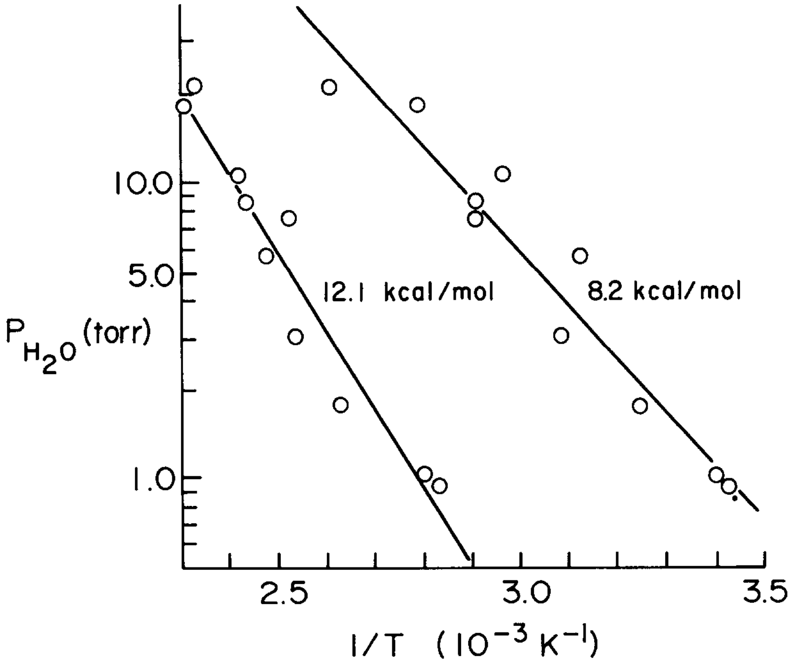

FIG. 5. Clausius–Clapeyron plots for water at 0.7 and 2.0 molecules/cation. Coverages were measured by matching infrared spectra which were calibrated by TGA.

ions. That there will be an attraction even for the second water molecule near the cation is entirely reasonable since Chen (*2*) reported that as many as four water molecules could be associated with a hydrophilic center.

Methanol Adsorption

When 80 Torr of methanol was exposed to H-ZSM-5 at 300 K, followed by evacuation, the adsorbate could be characterized by the TPD spectrum shown in Fig. 6. As we stated earlier, methanol was the only species we observed in desorption. Two desorption features are evident in this spectrum. The first desorbs at about 400 K and the size of this peak was dependent on the time of evacuation prior to heating. While diffusion into the pores was fast enough so that the TPD spectrum did not depend on exposure time, the coupling between desorption and diffusion made removal of the methanol in this first peak very slow at room temperature. The spectrum in Fig. 6 was taken from a sample which had been evacuated for 80 min before beginning the desorption. Spectra taken after shorter evacuation times displayed more desorption below 400 K.

The second desorption feature was present as a shoulder on the first peak and was centered at about 450 K. From the TGA and infrared data which will be discussed shortly, we found that this feature corresponds to the desorption of a single molecule of methanol from each cation site.

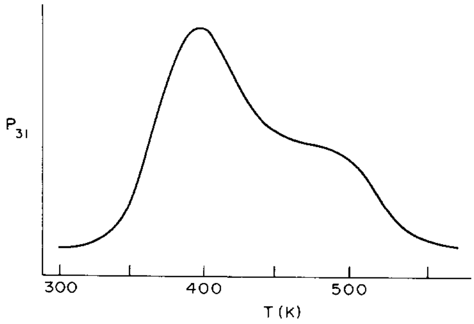

FIG. 6. TPD spectrum of methanol from H-ZSM-5. Methanol was the only product observed during desorption.

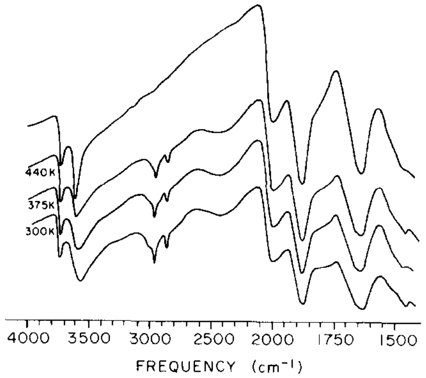

FIG. 7. Infrared spectra for H-ZSM-5 after exposure to methanol, followed by evacuation and heating to the indicated temperature. Heating to 375 K, a temperature high enough to remove the first desorption state in TPD, did not cause a return of the 3605-cm^{-1} peak due to the cation.

Figure 7 summarizes the infrared data for methanol adsorbed on H-ZSM-5. For these experiments, the sample was exposed to methanol vapors, evacuated, and heated to the temperature indicated until desorption stopped. As with water, methanol did not interact with the silanol groups at 3735 cm^{-1}; but it interacted strongly with the hydrogen cation at 3605 cm^{-1}, leading to a broad band between 3450 and 3650 cm^{-1}. The methyl stretches between 2850 and 2950 cm^{-1} are clearly visible, and a band at approximately 1450 cm^{-1} is also apparent due to the methyl deformation.

When the sample was heated to 375 K to remove the first TPD feature, the only change in the infrared spectrum was that the broad band between 3450 and 3650 cm^{-1} decreased in intensity. There is still no indication of anything but adsorbed methanol in the pores. There is also no return of the hydroxyl group at 3605 cm^{-1}, indicating that there is at least one methanol molecule near each cation. When the sample was further heated to 440 K, a temperature high enough to remove about half of the second desorption peak in TPD, the 3605-cm^{-1} peak began to reappear. At this temperature, some of the cations are no longer associated with a methanol molecule. Further heating returned the sample to the clean H-ZSM-5 form.

TGA was also used to characterize methanol adsorption. Following adsorption, the sample was evacuated and the TPD spectrum monitored by the weight loss. The data are shown in Table 2. At room temperature, more methanol is adsorbed in the zeolite than can be explained by adsorption of one molecule at each cation site. At 400 K, a temperature just high enough to remove the first desorption state, the coverage is approximately one methanol per cation. Since the infrared spectrum indicates that each cation is interacting with a methanol molecule, this is conclusive evidence for the strongly bound state in TPD being caused by the adsorption of just one molecule on each cation site.

Coadsorption of Methanol and Water

With both water and methanol adsorp-

TABLE 2

Temp (K)	Uptake	
	(g CH_3OH/100 g H-ZSM-5)	Molecules/cation[a]
307	3.83	2.5
320	3.53	2.3
333	3.07	2.0
337	2.80	1.8
353	2.30	1.5
362	2.00	1.3
378	1.53	1.0
385	1.30	0.9
401	1.15	0.8
406	1.04	0.7
414	0.92	0.6
423	0.84	0.6
449	0.46	0.3
459	0.38	0.3
467	0.35	0.2
475	0.31	0.2
490	0.23	0.2
498	0.15	0.1
566	0.00	0.0

Note. These TGA results were taken after exposure to methanol, followed by evacuation for 10 min at 307 K. The heating rate was 10 K/min.

[a] Assumes silica-to-alumina ratio of 70.

tion, our results show that there is an interaction with the cation site. To see whether the adsorption of water would change the adsorption properties of methanol, we attempted to coadsorb the two species. However, we found that water would not remain on the surface in the presence of methanol. When we adsorbed water and then methanol, followed by evacuation, we found that water had been forced out of the zeolite pores. The TPD and infrared spectra were identical to those we obtained for pure methanol adsorption. Bolis *et al.* reported that water did prevent ethylene from adsorbing on H-ZSM-5; however, this is not the result we observe with methanol (*15*).

When we adsorbed methanol and then water, we again found that the TPD and infrared spectra were identical to the pure methanol case. While methanol was very effective in displacing adsorbed water, water could not displace methanol and would not remain adsorbed in the presence of methanol. When one takes into account that all of the water remaining on the zeolite after evacuation is associated with the cation, it is not surprising that methanol, which is much more strongly adsorbed, would prevent water from remaining on the surface.

To determine whether adsorbed methanol could prevent water from approaching the cation sites, we performed a deuterium exchange with D_2O and adsorbed CH_3OH. In Fig. 8, the first spectrum was taken after methanol was exposed to the sample, followed by 10 min evacuation. The sample was then exposed to 17 Torr of D_2O for 5 s, followed by evacuation. The infrared spectrum after D_2O adsorption shows that complete exchange has occurred between the deuterium and all of the hydroxyl groups. There was no exchange with the methyl groups as expected. That the exchange was rapidly completed indicates that adsorbed methanol did not prevent water from diffusing into the pores and interacting with the methanol and the cation sites.

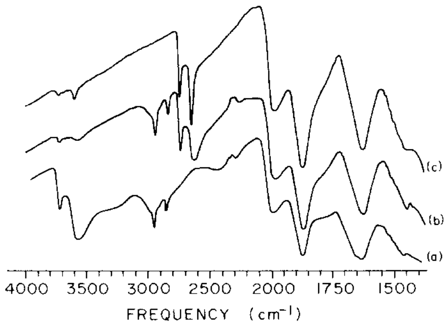

FIG. 8. Infrared spectra for H-ZSM-5 after the following treatment: (a) The sample was exposed to methanol followed by evacuation. (b) The sample in (a) was exposed to D_2O, resulting in complete deuteration of all hydroxyls. (c) The sample in (b) was heated to remove the CH_3OD.

DISCUSSION

Effect of Water on Reactions

The purpose of this study was to determine how water affected the reaction chemistry for several important reactions cited in the Introduction. The first way in which water could change the reaction chemistry is by modifying the acid sites in the zeolite. We have observed the formation of a hydronium ion in this study, and it is possible that this species is responsible for the reactivity of the zeolite in the presence of water. While water desorbs from the zeolite at 370 K under vacuum, extrapolation of the 0.7-molecule/cation curve in Fig. 5 shows that, in 1 atm of steam, this coverage of water on the zeolite would be present at 590 K. This is in the range of temperatures reported for dewaxing and olefin conversion (*4*, *5*); therefore, it is possible that hydronium ions could be present on the surface.

However, we observed that methanol was very effective in displacing water from the zeolite. We find similar results when other alcohols are coadsorbed with water (*6*). It seems unlikely, therefore, that hydronium ions could exist at these temperatures in a reactive environment. An alternative explanation is that water interacts with adsorbed intermediates. From the deuterium exchange with adsorbed methanol, we observe that water vapor can come in contact with adsorbed species. It would seem possible, therefore, that water could affect adsorbed intermediates like carbonium ions and change their reactivity. Since we did not observe any reaction under the conditions of our experiment, we were not able to observe such interactions.

Desorption Rates

In all cases, we observed that the adsorption of methanol and water was rapid at room temperature, in agreement with Doelle *et al.* (*16*). However, we did not find it to be reversible at room temperature, even though the heats of adsorption for water and for methanol in the low-temperature TPD peak are low. For methanol, the size of the low-temperature desorption state did decrease with prolonged evacuation, but the time constant for this desorption could be measured in hours at room temperature. The reason for the irreversibility of the low energy states is due to the coupling of desorption and diffusion processes. Gorte (*17*) showed that the effective desorption rate constant for desorption from a porous material into a vacuum is given by $\pi^2D/\alpha\rho R^2K$, where D is the diffusivity, $\alpha\rho$ is the specific area of the catalyst (cm^2/cm^3), R is the radius of the catalyst particle, and K is the ratio of adsorption to desorption rate constants. For our experimental configuration, assuming typical diffusivities and adsorption rates, the effective desorption rate constant is only 10^{-9} of the intrinsic rate constant. This explains why water, with a heat of adsorption of only 12.1 kcal/mol at the cation site, cannot be easily removed by evacuation at room temperature. For this reason also, we have not attempted to analyze the TPD curve in Fig. 6.

SUMMARY

The results of our studies show a clear preference for water adsorption near the cation sites on H-ZSM-5. For water, the heat of adsorption at these sites was approximately 12.1 kcal/mol, but dropped rapidly as additional molecules were added. While this adsorption energy is quite low, extrapolation of our results to high temperatures and pressures indicates that it may be possible for water to be present on the surface at reaction conditions; however, the rapid displacement of water by reactive molecules makes this unlikely.

Methanol also shows a preference for adsorbing near the cations in H-ZSM-5. This is shown by the desorption of methanol, which occurs in two clearly defined states, the second of which corresponds to one molecule per cation. While our results indicate that methanol is effective in displacing water from the cation sites, we did observe an isotopic exchange between water and the cation, even in the presence of adsorbed methanol, showing that water could be interacting with reaction intermediates.

ACKNOWLEDGMENTS

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