Temperature Programmed Surface Reaction Studies of the Methanol to Gasoline (MTG) Conversion over ZSM-5

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The methanol to gasoline conversion over ZSM-5 has been studied by the Temperature Programmed Surface Reaction (TPSR) technique. The technique is able to delineate the two steps in the process: the dehydration of methanol to dimethyl ether and the subsequent conversion of dimethyl ether to hydrocarbons. The activation barriers associated with each step was evaluated from the TPSR profiles and are 108 kJ/mol and 195 kJ/mol respectively. The methanol desorption profile shows considerable change with the amount of methanol molecules adsorbed per Brönsted site of the zeolite. The energy associated with the desorption process, $(CH_3OH)_nH^+-ZSM\text{-}5 \rightarrow (CH_3OH)_{n-1}H^+-ZSM\text{-}5+CH_3OH$, shows a spectrum of values depending on n. The spectrum is not continuous and has a gap for $n=1$. The trend is similar to that for the corresponding gas-phase reaction, $(CH_3OH)_nH^+ \rightarrow (CH_3OH)_{n-1}H^+ + CH_3OH$. The present investigation highlights the importance of the protonated methanol cluster, $(CH_3OH)_nH^+-ZSM\text{-}5$, in the primary step of the MTG process, the formation of dimethyl ether. The reaction is compared with the corresponding gas phase ion-molecule reaction of $CH_3OH_2^+$.

1. Introduction

The methanol to gasoline (MTG) conversion by the Mobil process – in which H-ZSM-5 (HZSM5) a high silica alumino-silicate zeolite catalyzes the dehydration of methanol to yield a mixture of aliphatics and aromatics has attracted keen interest because of its simplicity and industrial potential. The reaction has been exhaustively investigated both experimentally [1 – 13] and by means of quantum chemical calculations [14]. The importance of the Brönsted sites of the HZSM5 has been reasonably well established [12] and there is considerable experimental evidence to show that within the zeolite, methanol exists in the protonated form probably as a protonated cluster [6].

In this paper we demonstrate how the temperature-programmed surface reaction (TPSR) technique is able to follow the primary steps of the MTG process as well as to give quantitative information on activation barriers and heats of desorption associated with these steps. It has thus been possible to establish a close parallelism between the reaction of methanol over HZSM5 and the corresponding gas phase ion-molecule reactions involving $CH_3OH_2^+$.

The TPSR experiment is essentially a temperature-programmed desorption (TPD) experiment carried out under reactive conditions [15] using a mass spectrometer to detect the species evolving as a function of temperature. In addition to simple desorption processes, the evolution of the products of a surface reaction may be observed in a TPSR run. The technique is, in principle, capable of delineating the various steps of a heterogenous catalytic process as well as give information on surface intermediates [13, 15]. The temperature at which the evolution of a species is a maximum is a measure of the activation barrier for its formation or its heat of desorption from the surface. The two may be distinguished by contrasting the temperatures at which the products desorb when adsorbed separately on the catalyst with the temperature at which they appear in the TPSR experiment. Just as heats of desorption, ΔH_{des}, may be determined in a TPD experiment, the activation barriers, E_{act}, for the formation of a species, may be determined from the TPSR, once it has been ascertained that the rate of evolution of the species is not controlled by desorption. The usual procedure for determining ΔH_{des} from a TPD experiment, by noting the change in the peak temperature for varying rates of heating, is unsuitable for determining E_{act}, and we have adopted a "single curve" fitting technique [13, 16].

The TPSR studies compliment the earlier NMR [9] and IR [4] spectroscopic studies. In contrast to these experiments which probe the reactants, intermediates and products in the adsorbed state, within the cavities and channels of the zeolite, the TPSR experiment probes these molecules as they exit from the zeolite channel [17]. The TPSR of methanol over ZSM-5 for various adsorbed concentrations have been studied. The technique is clearly able to delineate the two main steps in the MTG process: the dehydration of methanol to dimethyl ether and the conversion of dimethyl ether to hydrocarbons. The activation barriers associated with each of these steps has been evaluated from the TPSR profiles.

2. Experimental

HZSM5 was prepared by ammonium exchanging Na-ZSM-5 (Si/Al = 30) followed by calcination at 823 K in flowing air for 5 h. The TPD/TPSR experiments were carried out in a modified GC-MSD system (HP 5890-5970B). In the TPSR experiment, the reactants (methanol or dimethylether) were adsorbed on the catalyst (HZSM5) which was then heated at a constant heating rate of 10 K/min in a flow of He (flow rate 10 ml/min) to a maximum temperature of 673 K. The evolved products in the mass range m/e 10 to m/e 250 were analyzed 'on-line' using a quadrapole mass spectrometer. The output of the experiment is a temperature profile for each evolved mass frag-

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ment (counts vs temperature for each evolved *m/e*). In a typical TPSR run, a weighed amount (5 – 10 mg) of the zeolite was placed in a thin-walled stainless steel tube. The tube occupied the same position as the column in the GC oven and was connected to the He gas cylinder, via the injection port using the gas plumbing provided in the GC. The temperature of the oven was controlled to ± 1 K by the control circuit in the GC, which also provided variable linear rates of heating.

The zeolite was flushed in He for at least 2 h prior to the TPSR experiment. Methanol and dimethylether were adsorbed by injecting known volumes directly upstream into the He flow with the zeolite maintained at 300 K. The heating schedule was started only after all free (non-adsorbed/desorbed) adsorbate was purged, as determined by the mass spectrometer.

The amount of methanol adsorbed on the zeolite, before the initation of the heating schedule was calculated in the following way. A known amount of methanol, e.g. 2 µl, was injected with no catalyst in the reactor tube and the temperature of the oven kept constant at 300 K. He flow rates and pressures were identical to those in a TPSR run. The area under the *m/e* 31 profile (counts vs time) was computed. This provided an internal calibration or conversion constant between the *m/e* 31 counts and the volume of methanol. The experiment was repeated for different volumes of injected methanol. In the TPSR experiment, a known volume of methanol was injected with a weighed amount of zeolite in the reactor tube. The volume of the unadsorbed/desorbed methanol at 300 K was obtained by integrating the *m/e* 31 profile and multiplying it with the conversion constant (at 300 K, the only species observed in the mass spectra were the mass fragments of methanol). The volume of methanol adsorbed at 300 K was hence obtained as the difference between the volume injected and the unadsorbed/desorbed volume. This value is expressed as the number of methanol molecules adsorbed per Brönsted site of the zeolite.

Data analysis. The heats of desorption, ΔH_{des}, and the activation barrier, E_{act}, were obtained by fitting the theoretical rate expressions to the experimental TPD and TPSR evolution profiles [16]. The theoretical expressions were derived under the assumption that (i) there is no temperature gradient across the catalyst, (ii) the gas phase temperature is the same as the solid phase temperature and (iii) mass transfer effects are negligible. Under the present experimental conditions – low heating rates, high He flow rates and small amounts of the catalyst (< 10 mg) – the above assumptions are not too drastic. Assumption (iii) was verified by repeating the experiment with different amount of catalyst as well as by changing the flow rate [13]. In the present experiments it was found that the evolution of species irrespective of whether they were rate controlled by ΔH_{des} or E_{act} was first order in the evolved species.

The theoretical expression for a first order process was used to obtain ΔH_{des} and E_{act}. The expression for such a process is [13, 18]

$$\frac{\mathrm{d}C_{\mathrm{N}}}{\mathrm{d}T_{\mathrm{N}}} = C_{\mathrm{N}} E_{\mathrm{m}} \left(\exp \left[E_{\mathrm{m}} \left(1 - \frac{1}{T_{\mathrm{N}}} \right) \right] - \frac{1}{T_{\mathrm{N}}^2} \right) . \tag{1}$$

C_N is the normalized gas phase concentration of the evolving species, $E_m = \Delta H_{\text{des}}/R T_m$ for a desorption process while for a reaction profile, $E_m = E_{\text{act}}/R T_m$. T_m is the temperature at the peak maximum. The theoretical profile C_N vs T_N was obtained by numerical solution of the above equation. The only variable in the fitting is either ΔH_{des} or E_{act} depending on the nature of the evolution process.

In the present study, the temperature profiles, irrespective of whether they were for desorption or for reaction process, were found to be first order with respect to the evolving species. Second or higher order rate process, with respect to the evolving species, was never encountered.

3. Results and Discussion

Fig. 1 shows a typical TPSR of methanol adsorbed on HZSM5 catalyst. The profiles shown are for an initial concentration of 3 methanol molecules adsorbed per Brönsted site of HZSM5, prior to the initiation of the temperature programme. (When the initial adsorbed concentration of methanol is less than 1 per Brönsted site the resulting TPSR profiles are different (Fig. 4) and are discussed in a latter section.) Methanol desorption shows two peaks – a broad asymmetric profile with a peak temperature of 423 K and a smaller peak at 557 K. The low temperature desorption profile was found to change considerably with the amount of methanol initially adsorbed whereas neither the position or shape of the 557 K peak was found to change as long as the initial adsorbed concentration was greater than 1 methanol per Brönsted site. The products of the dehydration of methanol – dimethylether (DME), *m/e* 45, and H_2O, *m/e* 18 (Fig. 1) – start appearing above 400 K. Water shows a well defined evolution profile with a peak at 463 K. DME shows

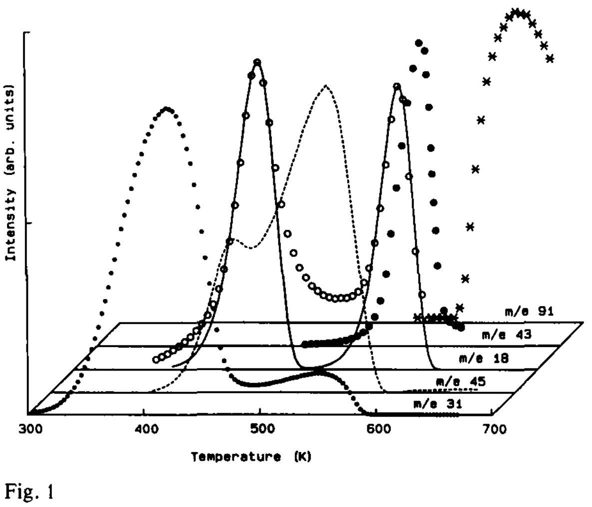


Fig. 1
TPSR of methanol over HZSM5. The profiles are for methanol (*m/e* 31) (○ ○ ○), dimethylether (*m/e* 45) (– – –), H_2O (*m/e* 18) (○ ○ ○), C_3-C_5 aliphatic hydrocarbon (*m/e* 43) (● ● ●) and aromatic hydrocarbons (*m/e* 91) (∗∗∗). The solid line is the fitted profile for H_2O evolution using Eq. 1

a shoulder at 463 K and a peak at 540 K. The DME profile shows a sharp drop in intensity at temperatures above 540 K. This temperature region coincides with the appearance of a second water peak and hydrocarbons (Fig. 1). The hydrocarbons detected were aliphatic viz propane (*m/e* 44), butane (*m/e* 58), and pentane (*m/e* 72) along with trace amounts of methane and ethane (Fig. 1). The profiles and peak temperatures for the hydrocarbons are identical and coincides with that for the second water peak (in Fig. 1, the profile shown is for *m/e* 43 which is a mass fragment common to the higher aliphatic hydrocarbons. Similarly the aromatic hydrocarbons are represented by *m/e* 91). At still higher temperatures (>585 K) aromatic hydrocarbons are observed (*m/e* 91 profile in Fig. 1). The observed aromatic hydrocarbons were benzene (*m/e* 78), toluene (*m/e* 92) and small amounts of xylene (*m/e* 106). Since the maximum temperature that could be attained with the present set-up was 673 K, the complete desorption profile for the aromatic hydrocarbons could not be recorded. It may be seen, however, that as in the case of aliphatic hydrocarbons, the aromatic hydrocarbon profiles are identical to each other.

Attempts were made to detect some of the species, e.g. CO, ethylene, formic acid, formaldehyde etc., which have been implicated by various mechanistic schemes [2, 9]. Their detection was found to be extremely difficult since the mass fragments of these small molecules are common to those of methanol, H_2O and the alkanes. Thus, for example, the CO mass fragments 28 and 16 are present in the mass spectra of alkanes, while *m/e* 12 occurs in the spectra of methanol and DME. The presence of CO may, however, be indirectly ruled out since the intensities of the temperature profiles of *m/e* 12 can be accounted for using the ratios of *m/e* 12:31 for methanol and 12:45 for DME. In a similar way, the presence of formic acid can be ruled out since the *m/e* 44 fragment may be fully accounted for by the presence of propane. It is not, however, possible to infer on the presence or absence of ethylene (*m/e* 28) and formaldehyde (*m/e* 18) since the intensities of these fragments are very low compared to the same fragments from hydrocarbons and water.

The above experimental result clearly shows the ability of the present technique to follow the MTG process on HZSM5 catalyst. There are clearly two main steps involved in the process, 1) the formation of DME from methanol and 2) the conversion of DME to aliphatic and aromatic hydrocarbons. The TPSR unfortunately does not provide any clue to the mechanism of formation of the first C – C bond.

As mentioned in the Introduction, the temperature profiles of the products (water, DME, alkanes, etc.) in the TPSR experiment (Fig. 1) could either reflect the heats of desorption or the activation barriers for their formation, depending on which is higher. To distinguish the two, the TPD of water, alkanes and aromatics adsorbed directly on HZSM5, under conditions similar to that for the TPSR experiment was recorded. Water adsorbed at 300 K on HZSM5 showed a desorption maximum at 423 K. This clearly implies that the first water peak in Fig. 1, at 463 K, is the reaction profile for the dehydration of methanol, and not the desorption profile for adsorbed water. Similarly, when aromatic hydrocarbons are adsorbed on HZSM5, they desorb at temperatures lower than 550 K. The desorption of benzene adsorbed on HZSM5 shows a peak maximum at 533 K which is considerably lower than the peak temperature (644 K) of the benzene profile in the TPSR of methanol (Fig. 1). In the case of alkanes, too, TPD studies came to the same conclusion. This conclusion may have also been arrived at from the fact that the aliphatic profiles are identical and coincident with the water profile. The DME profile in Fig. 1 reflects on the heat of desorption of adsorbed DME. This was concluded from the fact that the DME peak in the TPSR experiment appeared at a temperature higher than that for the water peak (463 K). This was independently verified by TPSR experiment on DME (Fig. 2) which is described in the following section. The small shoulder at 463 K in the DME profile may have been caused by the local heating of the catalyst by the heat liberated (10.9 kJ/mol) during the exothermic dehydration of methanol.

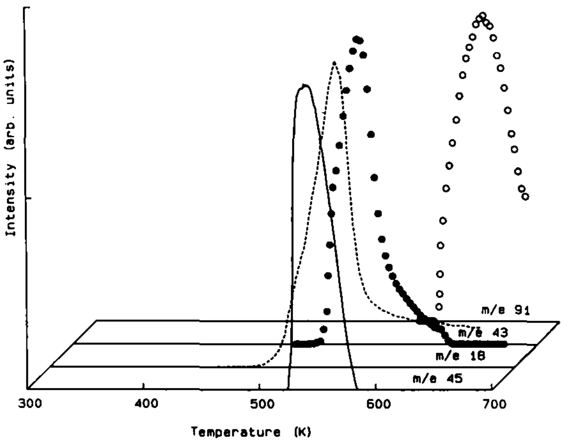


Fig. 2
TPSR of dimethylether over HZSM5. The profiles are for dimethylether (*m/e* 45) (———), H_2O (*m/e* 18) (– – –), C_3-C_5 aliphatic hydrocarbon (*m/e* 43) (● ● ●) and aromatic hydrocarbons (*m/e* 91) (○ ○ ○)

Since the H_2O profiles in the TPSR are the reaction profiles for the dehydration of methanol and the conversion of DME to hydrocarbons, it is possible to evaluate the activation energy for the two reactions by curve fitting the H_2O profiles. The fitted profiles using Eq. (1) are shown as the full line in Fig. 1. The activation energies obtained are: 107.6 kJ/mol for the dehydration of methanol to DME and ii) 195 kJ/mol for the conversion of DME to alkanes. The activation energy for the conversion of DME was also independently obtained by fitting the profiles for any of the aliphatic hydrocarbons, e.g. butane. The best fit was for a first order reaction (in butane). The activation barrier obtained was identical to that obtained by fitting the water profile. (Since the aromatic hydrocarbon profiles are incomplete, no attempt was made to fit them). The evaluation of the activation energies is one of the main strengths of the

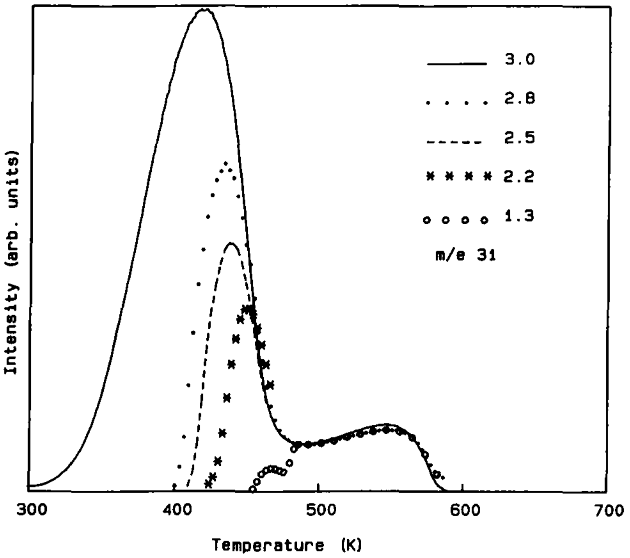


Fig. 3a
Desorption profiles for methanol (*m/e* 31) over HZSM5 for different amounts of methanol molecules adsorbed per Brönsted site. The profiles are on the same intensity scale

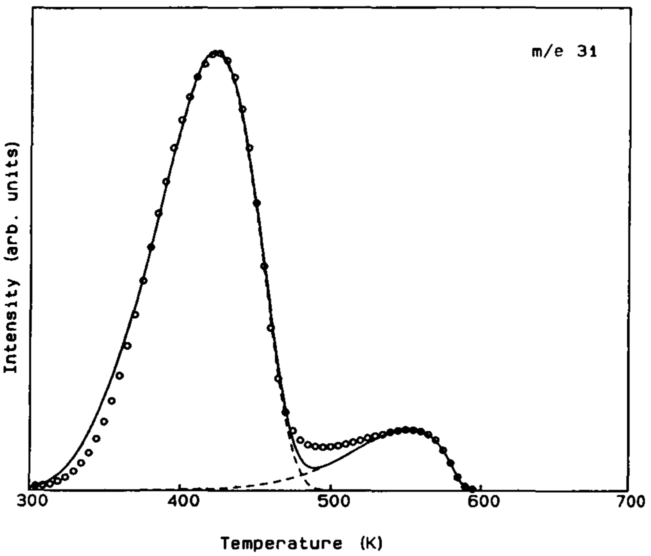


Fig. 3b
A representative fit to the experimental methanol desorption profile. The initial adsorbed concentration was 3 methanol molecules per Brönsted site. The fit was obtained using two first order desorption profiles (Eq. 1) with $E_\alpha = 41.8$ kJ/mol and 111.8 kJ/mol. The dashed lines are the individual profiles

TPSR technique. As opposed to the determination of the activation barriers for the overall MTG process, the TPSR technique is able to evaluate the barriers associated with each of the steps that make-up the overall process.

An as yet unexplained feature of the TPSR profiles (Fig. 1) is the origin of the high temperature (557 K) coverage-independent methanol peak. It could either be a product of the reaction of DME or desorption from a site with higher binding energy. The question may be resolved from the TPSR experiment for DME. Fig. 2 shows the TPSR of DME adsorbed on HZSM5 at 300 K. A comparison with the TPSR of methanol (Fig. 1) shows the absence of a methanol peak at 557 K; the product profiles, however, are identical (obviously the first methanol peak and the water peak at 463 K will not be present). This clearly indicates that the 557 K methanol peak in Fig. 1 results from the desorption of methanol from a site with higher binding energy.

Coadsorption of methanol and DME caused no change in the TPSR profiles. Neither did pre- or post-adsorption of methanol make any difference to the product profiles. Thus it is highly unlikely that adsorbed methanol is involved in the second step of the MTG process, i.e. the conversion of DME to hydrocarbons.

As mentioned earlier the TPSR profiles show considerable change with the amount of methanol adsorbed initially. For concentrations greater than one methanol per Brönsted site, the product (water, DME and hydrocarbon) profiles are identical to that in Fig. 1; the methanol desorption profiles, however, are quite different. The methanol desorption profiles for varying concentrations are shown in Fig. 3 (the profiles are on the same intensity scale). For initial methanol concentrations less than one per Brönsted size, no methanol desorption was observed. The reaction profiles, too are different (Fig. 4) and are discussed in a later section.

It may be seen from Fig. 3 that the high temperature peak at 557 K is saturated at low coverages. Increasing the amount of methanol adsorbed makes no difference either to the intensity or to the temperature of desorption. This, however, is not true for the low temperature peak. With increasing amount of injected CH_3OH, there is an increase in intensity, a shift in the peak temperature to lower values and a marked broadening of the profiles. The desorption energy of the high temperature peak was obtained by curve fitting (Fig. 3b) to a first order desorption process. The

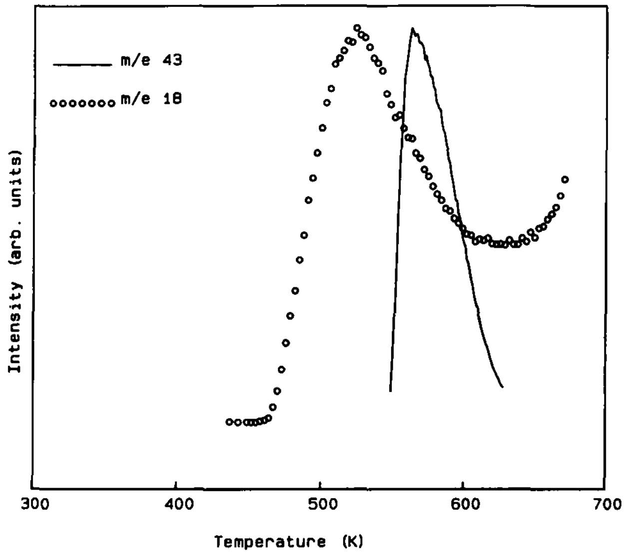


Fig. 4
TPSR of methanol over HZSM5 for an initial adsorbed concentration of 0.8 methanol molecule per Brönsted site. The profiles are for H_2O (*m/e* 18) and for C_3-C_5 aliphatic hydrocarbons (*m/e* 43)

desorption energy was 111.8 kJ/mol. The extraction of desorption energies from the low temperature peak is, however, problematic since desorption energies are now coverage dependent and surface reaction, to DME, at higher temperatures (>400 K) may lead to the depletion of adsorbed methanol, in addition to desorption. Nevertheless, an attempt was made to fit the low-temperature methanol profile to obtain at least an approximate ΔH_{des}. A representative fit using two first order desorption processes with $\Delta H_{des} = 111.8$ kJ/mol and 41.9 kJ/mol respectively is shown in Fig. 3b. The desorption energies were found to vary from 40 kJ/mol for the three methanols per Brönsted site to 60 kJ/mole for lower concentrations and peak temperature from 422 to 466 K.

A possible explanation for the two features observed in the desorption profile is that the higher desorption energy peak corresponds to the methanol adsorbed directly on the Brönsted sites. Since these sites are few in number (depending on the Si/Al ratio), the amount of methanol adsorbed on such sites is easily saturated. The low temperature peak corresponds to methanol molecules adsorbed/interacting with the methanol adsorbed directly on the Brönsted sites, thus forming a protonated cluster. As '*n*' (number of methanol molecules in the cluster) increases, the binding energy decreases and a spectrum of energies would be observed corresponding to the following process.

$$(CH_3OH)_nH^+ - \text{ZSM-5} \xrightarrow{\Delta H_n} (CH_3OH)_{n-1}H^+ - \text{ZSM-5}$$

$$+ CH_3OH_{(g)} \xrightarrow{\Delta H_{n-1}} \ldots$$

with $\Delta H_n < \Delta H_{n-1} < \ldots << \Delta H_1$.

The TPD results show that there is a gap in the spectrum, corresponding to the last step, i.e. the desorption of methanol directly adsorbed on the Brönsted site. This is the peak at 557 K. A similar trend has been observed for the gas phase reaction [19]

$$(CH_3OH)_nH^+ \rightarrow (CH_3OH)_{n-1}H^+ + CH_3OH \ldots$$

The ΔH_f values for various values of '*n*' are [19, 20] ($n = 1$, 762; $n = 2$, 139; $n = 3$, 89.6; $n = 4$, 67.4; $n = 5$, 56.5; $n = 6$, 52.3; $n = 7$, 49.8 and $n = 8$, 50.2 (all values are in kJ/mol). It may be seen that there is a substantial difference in ΔH_f between $n = 1$ and for larger *n*'s. The effect is similar to that observed for methanol adsorbed on the Brönsted sites on HZSM5.

For initial concentrations of less than one methanol per Brönsted site, the only species observed in the TPSR are H_2O and the aliphatic hydrocarbons (Fig. 4). No DME is observed. The water profile shows two peaks which are poorly resolved. In analogy with the earlier explanation, the first peak (≈ 500 K) may be attributed to dehydration of methanol and the second to the formation of the hydrocarbons. The peak temperature of the hydrocarbon profile is similar to that of the higher methanol concentrations (Fig. 1). No DME is observed, probably because at the temperature at which it is formed gets converted to hydrocarbons. This is probably the reason why the water peaks are poorly resolved. The point to note is that the formation of DME as inferred from the water peak now occurs at a temperature (>500 K) higher than in the earlier TPSR experiments (Fig. 1). In other words, the activation barrier for the dehydration of methanol adsorbed directly on a Brönsted site is higher than that for the protonated methanol cluster.

The present results are in broad agreement with the earlier studies on the MTG process using different techniques. Ison and Gorte [1, 3] found two types of methanol from TPD and IR experiments. The peak temperatures they report agree with the present experiment. Quasi-elastic neutron scattering [21] and NMR [12] studies had shown the presence of two types of methanol – one which was strongly bound and the other a loosely bound, diffusive methanol. The former would correspond to the methanol species desorbing at 557 K, observed in the present studies, while the loosely bound diffusive methanol species to the low temperature desorbing methanol. There is reasonable agreement between the present experimental results and the recent NMR studies of Klinowski et al. [9]. For example, at 423 K, the ^{13}C CPMAS NMR shows the presence of both DME and methanol. It may be seen from Fig. 1 that the evolution of DME starts at $T > 400$ K. A major disagreement with the NMR results is in the temperature of formation of the aromatic hydrocarbons. The ^{13}C CPMAS NMR spectra of a sample heated to 573 K shows the presence of both aliphatic and aromatic hydrocarbons. The TPSR experiments, however, show the formation of the aromatic hydrocarbons at temperatures (>585 K) higher than that of the aliphatic hydrocarbons (from 523 K). The difference in temperatures is not due to a difference in the heats of desorption between aliphatic and aromatic hydrocarbons.

Primary Reaction Step: Comparison with Gas Phase Ion-Molecule Chemistry

Since the first step of the MTG process, the formation of the DME, is from the protonated methanol-zeolite cluster, it is instructive to compare this reaction with the corresponding gas phase 'ion-molecule' chemistry of $CH_3OH_2^+$. The comparison is shown in Fig. 5. All values are in kJ/mol. The upper portion of the figure shows the thermodynamics of the ion-molecule gas phase reaction $(CH_3OH)_2H^+$ giving $(CH_3OCH_3)H^+$. The thermodynamic data and the computed values of the activation barriers are from the work of Bowers et al. [22]. The lower part of the figure shows the corresponding sequence for the catalyzed reaction process. In constructing Fig. 5, it has been assumed that $\Delta H_{ads} = -\Delta H_{des}$. This is true only if there is no activation barrier for adsorption. In Fig. 5, the heats of formation of the reactants CH_3OH, H and HZSM5 have been equated to zero.

The heat of formation of CH_3OCH_3 from $2CH_3OH$ is -22.6 kJ/mol. In the gas phase, the species $CH_3OH_2^+$ is formed from CH_3OH and H^+. The processes involved in this reaction are the formation of H^+ ($\Delta H_f(H^+) =$

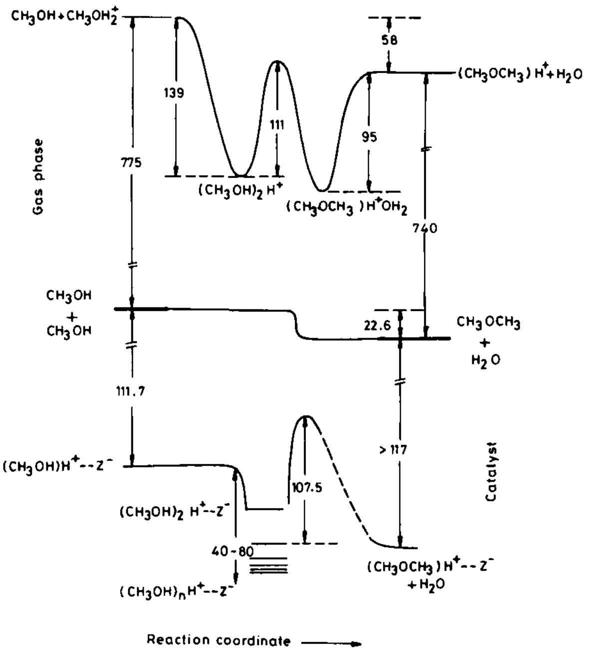
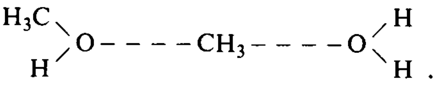


Fig. 5
One dimensional potential energy diagram for the primary step of the MTG process, $2CH_3OH \rightarrow CH_3OCH_3 + H_2O$. The top part of the figure is for the gas phase reaction and is taken from Ref. [21]. The bottom half is the reaction over HZSM5. All figures are in kJ/mol

1538 kJ/mol) [23] and the formation of protonated methanol. The energy which is the Proton Affinity of methanol, PA(CH_3OH), is equal to 762 kJ/mol [20]. Keeping the heat of formation of methanol and H as zero, the total relative heat of formation of $CH_3OH_2^+$ is

$$\Delta H_f CH_3OH_2^+ = \Delta H_f(H^+) - PA(CH_3OH) = 775.4\ \mathrm{kJ/mol}.$$

The heat of formation of $(CH_3OH)_2H^+$ is from Ref. [22]. The activation barrier is the calculated value assuming that the activated complex is



$$\mathrm{H_3C(H)O{-}{-}{-}{-}CH_3{-}{-}{-}{-}O(H)H}\,.$$

The ΔH_f for $(CH_3OCH_3)H^+OH_2$ is also a computed value. The heat of formation of $(CH_3OCH_3)H^+$ is given as the difference between ΔH_f for H^+ and the proton affinity for DME ($1538 - 795.5 = 742.5$ kJ/mol).

In the case of the catalytic reaction, the proton is initially associated with the zeolite and later with the adsorbed methanol. The ΔH_f for $(CH_3OH)H^+ - ZSM\text{-}5^-$ is consequently the difference between the proton affinities of the zeolite and methanol besides an additional term, ΔH_{inter}, which is due to the interaction between the protonated methanol and the zeolite. $\Delta H_f\ (CH_3OH)H^+ - ZSM\text{-}5^- = PA(ZSM\text{-}5^- H^+) - PA(CH_3OH) - \Delta H_{inter} = \Delta H_{ads} = -111.8$ kJ/mol. This protonated methanol is solvated by neutral methanol mol1537ecules and shows a spectrum of adsorption energies from 40 to 60 kJ/mol corresponding to the process

$$(CH_3OH)_{(n-1)}H^+ - ZSM\text{-}5^- + CH_3OH \rightarrow (CH_3OH)_nH^+ - ZSM\text{-}5^-$$

The activation barrier for the formation of DME from this protonated cluster is 107.6 kJ/mol. It has not been possible to estimate the ΔH_f for $(CH_3OCH_3)H^+ - ZSM\text{-}5^-$ $[\Delta H_f = PA(H^+ZSM\text{-}5^-) - PA(CH_3OCH_3) - \Delta H_{inter}]$ since the desorption profile for DME (Fig. 1) is incomplete because of its reaction to hydrocarbons. The desorption, however, is an endothermic process. Since it occurs at a fairly high temperature, a conservative estimate of the lower bound of the desorption energy would be 117 kJ/mol.

Fig. 5 shows that, once the protonated cluster is formed, the activation energies for the formation of DME as calculated for the gas phase and as measured for ZSM-5 are comparable in magnitude, 111.8 kJ/mol and 107.6 kJ/mol respectively. The main difference between the gas phase and the catalytic processes lies in the energetics of the formation of the protonated methanol cluster. In the gas phase, the process is energetically expensive because of the high heat of formation of H^+ ($\Delta H_f = 1538$ kJ/mol). In the catalyst, since the proton affinity of ZSM-5 is less than that of CH_3OH, the process is exothermic (it may be re-emphasized that in Fig. 5 the energies have been computed with heat of the reactants equated to zero).

For the primary step of the MTG process the 'catalysis' is perhaps not in the lowering activation barriers, but in the lowered heat of formation of the active species, $(CH_3OH)_nH^+ - ZSM\text{-}5$, as compared to that in the corresponding gas phase reaction, $CH_3OH)_nH^+$.

4. Conclusions

The present study shows the ability of the TPD/TPSR technique to follow the MTG process. The technique is clearly able to delineate the two main steps, (i) the dehydration of methanol to dimethyl ether and (ii) the conversion of dimethyl ether to hydrocarbons. In addition, it was also possible to evaluate the activation barriers associated with each step. The activation barriers for the dehydration of methanol and the conversion of DME to hydrocarbons are 107.6 kJ/mol and 194.7 kJ/mol respectively.

Methanol desorption shows two peaks in the TPSR experiment. The profile appearing at lower temperatures shows a strong coverage dependence. The heat of desorption of the methanol desorbing at high temperatures (557 K) is 111.8 kJ/mol. The methanol desorption profiles can be interpreted as arising from the desorption process $CH_3OH)_nH^+ - ZSM\text{-}5^- \rightarrow CH_3OH + (CH_3OH)_{n-1}H^+ - ZSM\text{-}5^-$. The energy associated with this process shows a spectrum of energies corresponding to various values of n. The spectrum, however, is not continuous but has a gap for $n = 1$. The trend is similar to that for the corresponding gas-phase reaction, $(CH_3OH)_nH^+ \rightarrow CH_3OH + (CH_3OH)_{n-1}H^+$. It was found that it is the protonated cluster (for a restricted range of n) that is the active species. The activation energies for the formation of DME are similar to those of the corresponding gas-phase ion molecule reaction. However, while the heat of formation of the active species, $(CH_3OH)_nH^+ - ZSM\text{-}5^-$, is exothermic, the gas phase heat of formation of $(CH_3OH)_nH^+$ is strongly endothermic.

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