Methanol-to-gasoline (MTG) conversion over ZSM-5. A temperature programmed surface reaction study.

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The conversion of methanol to gasoline over zeolite ZSM-5 has been studied by temperature programmed surface reaction (TPSR). The technique is able to monitor 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 were evaluated from the TPSR profiles and are 25.7 and 46.5 kcal/mol respectively. The methanol desorption profile shows considerable change with the amount of methanol molecules adsorbed per Brønsted site of the zeolite. The energy associated with the desorption process, $(CH_3OH)_nH^+\text{-ZSM5} \rightarrow (CH_3OH)_{n-1}H^+\text{-ZSM5} + CH_3OH$, shows a spectrum of values depending on n.

Keywords: temperature programmed surface reaction; methanol to gasoline; ZSM-5

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 aliphatic and aromatic hydrocarbons has attracted keen interest because of its simplicity and industrial potential. The reaction has been investigated both experimentally [1–13] and by means of quantum chemical calculations [14]. The importance of the Brønsted 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) is able to follow the primary steps of the MTG process. The TPSR experiment is essentially a temperature programmed desorption (TPD) experiment carried out under reactive conditions [13,15,16] using a mass spectrometer to detect the species evolving as a function of temperature. The technique is in principle capable of monitoring the various steps of a heterogeneous catalytic process as well as giving 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 in principle be determined from the TPSR.

The present 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.

2. Experimental

HZSM5 was prepared by ammonium exchanging Na-ZSM5 (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 dimethyl ether) 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 quadrupole mass spectrometer. The output of the experiment is a temperature profile for each evolved mass fragment (counts vs. temperature for each evolved m/e).

The zeolite was flushed in He for at least 2 h prior to the TPSR experiment. Methanol and dimethyl ether 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.

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The amount of methanol adsorbed on the zeolite was determined prior to the initiation of the heating schedule and is expressed as the number of methanol molecules adsorbed per Brønsted site.

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 [16,17]. 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 processes, with respect to the evolving species, were never encountered.

3. Results and discussion

Fig. 1 shows a typical TPSR of methanol adsorbed on HZSM5 catalyst. The profiles are for an initial concentration of three methanol molecules adsorbed per Brønsted site of HZSM5. 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 nor shape of the 557 K peak was found to change. The products of the dehydration of methanol – dimethyl ether (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 a shoulder at 463 K and a peak at 540 K. The DMR 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 aliphatic hydrocarbons (fig. 1). The hydrocarbons detected were propane (*m/e* 44), butane (*m/e* 58), and pentane (*m/e* 72) along with trace amounts of methane and ethane. The profiles and peak temperatures for the hydrocarbons are identical. (In fig. 1, the profile shown is for *m/e* 43, which is a mass fragment common to the higher aliphatic hydrocarbons.) 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. As in the case of aliphatic hydrocarbons, the aromatic hydrocarbon profiles are identical.

By comparing the temperature profile of water, aliphatic and aromatic hydrocarbons in fig. 1 with the desorption profiles obtained from TPD measurement of these species under identical experimental conditions, it was concluded that the profiles in fig. 1 were reaction profiles and not desorption profiles. The DME profile, on the other hand, reflects 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) and was independently verified by TPSR experiment on

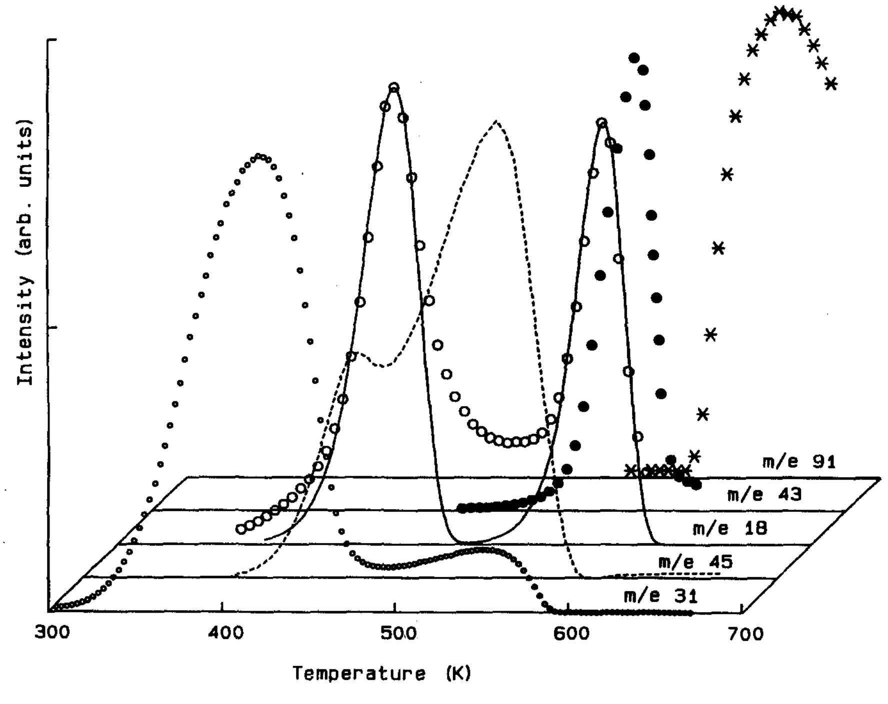

Fig. 1. TPSR of methanol over HZSM5. The profiles are for methanol (*m/e* 31) (o), dimethyl ether (*m/e* 45) (- - -), H_2O (*m/e* 18) (O), C_3–C_5 aliphatic hydrocarbon (*m/e* 43) (●) and aromatic hydrocarbons (*m/e* 91) (*). The solid line is the fitted profile for H_2O evolution (ref. [17]).

DME. The small shoulder at 463 K in the DME profile may have been caused by the local heating of the catalyst by the heat (2.6 kcal/mol) liberated during the exothermic dehydration of methanol.

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 best fit was obtained for an evolution process which was first order with respect to H_2O. The activation energies obtained are: 25.7 kcal/mol for the dehydration of methanol to DME and 46.5 kcal/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.

The methanol profiles in the TPSR show considerable change with amount of methanol initially adsorbed (fig. 2); the product (water, DME and hydrocarbons) profiles are identical. It can be seen from fig. 2 that the high temperature peak at 557 K is saturated at low coverages. In contrast the low temperature peak shows an increase in intensity, a shift in the peak temperature to lower values and a marked broadening of the profiles with increasing methanol concentration.

A possible explanation for the two features is that the higher desorption energy peak corresponds to the methanol adsorbed directly on the Brønsted 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 Brønsted 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.

$$(CH_3OH)_nH^+\text{-ZSM5} \xrightarrow{\Delta H_n} (CH_3OH)_{n-1}H^+\text{-ZSM5} + CH_3OH_{(g)} \xrightarrow{\Delta H_{n-1}} \cdots$$

with $\Delta H_n < \Delta H_{n-1} < \cdots \lll \Delta H_1$,

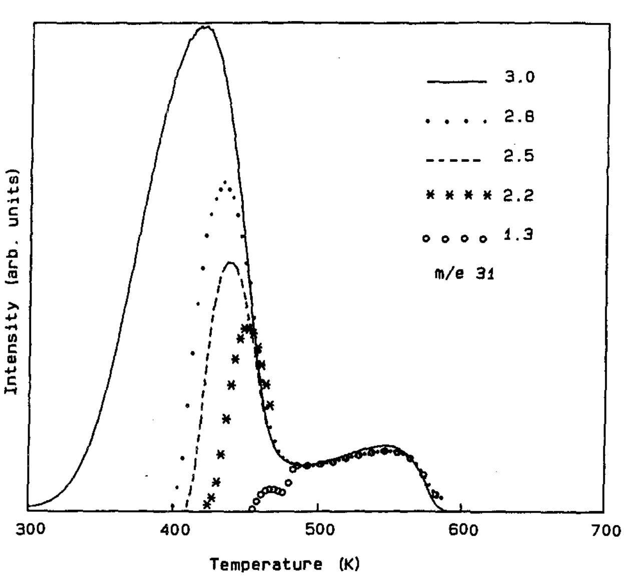

Fig. 2. Desorption profiles for methanol (m/e 31) over HZSM5 for different amounts of methanol molecules adsorbed per Brønsted site. The profiles are on the same intensity scale.

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 Brønsted site. This is the peak at 557 K. A similar trend has been observed for the gas phase reaction [18],

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

where there is a substantial difference in ΔH_f between $n = 1$ (182 kcal/mol) and for larger n ($n = 2$, 33.1; $n = 3$, 21.4; $n = 4$, 16.1; $n = 5$, 13.5; $n = 6$, 12.5, $n = 7$, 11.9 and $n = 8$, 12.0 all values are in kcal/mol) [18,19].

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 [20] 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 Anderson and Klinowski [9]. For example, at 423 K, the ^{13}C CPMAS NMR shows the presence of both DME and methanol. It can 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.

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 25.7 kcal/mol and 46.5 kcal/mol respectively.

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