

## A Novel Thermic Effect in the H-ZSM-5/Methanol/Dimethyl Ether System

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Since the ZSM-5 zeolite was discovered in 1972 and the subsequent discovery in 1976 of its unique properties as a catalyst for formation of medium-sized hydrocarbons from methanol, a large amount of work has been devoted to the H-ZSM-5/methanol/dimethyl Ether (DME) system. Much of the literature is referenced in Refs. 1–3. In spite of this effort and the considerable amount of information about the reaction behaviour which has been gained, details concerning the reaction mechanism still remain disputed, and much fundamental information on the system has still to be obtained.

While carrying out thermal analysis studies on the adsorption/desorption of methanol and DME on H-ZSM-5 a very unexpected thermic effect has been observed. The effect is connected with a sudden appearance of hydrocarbon-forming activity of the catalyst. It is believed that the phenomenon will be of decisive influence for a full understanding of the reactions taking place when methanol/DME is transformed to hydrocarbons in the MTG process. The work was carried out with the goal of obtaining further insight into the mechanism of the hydrocarbon-forming reactions, and is a continuation of previous work, which led to the proposal of a new reaction mechanism.<sup>4,5</sup>

### Experimental

The experiments were carried out in a modified Stanton Redcroft STA 785 apparatus. This instrument can best handle 5 to 50 mg samples. It is

so constructed that weight changes and heat effects can be measured simultaneously for one sample. Typically, measurements were carried out on 30 mg catalyst samples. Weighing sensitivity is 0.1 to 1  $\mu\text{g}$ ; heat sensitivity is 1 to 10  $\mu\text{W}$ . The experiments can be carried out in any atmosphere. One can work isothermally, or in a temperature program mode. The experiments reported here were performed under gas-flow conditions using highly purified nitrogen as carrier gas. A small dose of methanol or DME was added to the carrier gas which transported the adsorbent to the catalyst. Typically, a quantity leading to 1 or 2% weight increase was used. The system was thereafter left in the nitrogen carrier gas stream. Samples of the effluent were taken at intervals for analysis.

### Results and discussion

The following discussion will concentrate on one single experiment which is considered representative for the results obtained until now. The main outcome of this experiment, which concerns adsorption/desorption of DME, is displayed in Fig. 1.

From Fig. 1 it is seen that during the first part of the desorption period (the initial 80 min are not shown) there is no hydrocarbon-forming activity (insets). After 135 min from the start of desorption a sudden, very pronounced event takes place. This sudden phenomenon is above all evidenced by the DSC curve, which jumps from zero to 2.2 mW and very rapidly falls again

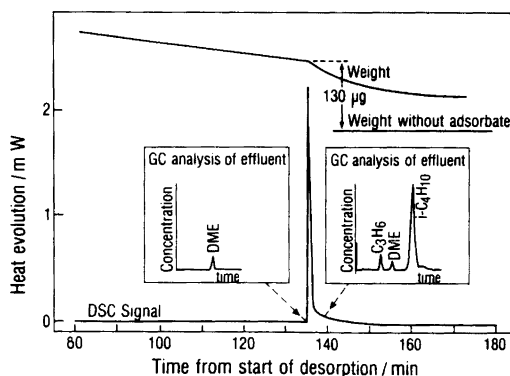


Fig. 1. Weight and heat changes during desorption of dimethyl ether from H-ZSM-5 (30 mg) in a nitrogen stream. The temperature was constant (185 °C) from desorption start to 60 min, thereafter increasing at 0.3 K min<sup>-1</sup> to 220 °C at 180 min. Gas chromatographic analyses of effluent carrier gas samples taken immediately before and shortly after the exothermic phenomenon are shown in insets.

almost to the initial zero, followed by a slower final full decline to zero which is reached after 6 to 7 min. A pronounced break in the weight curve is clearly seen to take place simultaneously. The rate of weight loss jumps from 1.0 µg min<sup>-1</sup> to ca. 6.6 µg min<sup>-1</sup>. Samples of the carrier gas leaving the instrument were analyzed by gas chromatography at intervals during the experiment. The chromatograms of sample No. 14, taken immediately before the event, and of sample No. 15, shortly after, are shown in the insets. The pre-event chromatogram shows only a small DME peak, whereas the post-event chromatogram shows a significant content of isobutane and propene (possibly also some propane, although the peaks are not well separated). Very small quantities of C<sub>1</sub> and C<sub>2</sub> species are also evidenced. The DME peak, which was the only one present in the pre-event case, is still present but considerably smaller. There was also evidence that some C<sub>5</sub> hydrocarbon (apparently isopentane) was formed. This is not shown in the chromatogram because it was eluted much later and appeared only as a broad baseline disturbance under the peaks in the subsequent chromatogram. The other chromatograms recorded prior to the event were all qualitatively similar to the one shown, displaying gradually diminishing DME peaks. The chromatograms recorded fol-

lowing the appearance of the exothermic peak were also qualitatively similar to the one shown, with quite rapidly diminishing peak heights, as would be expected from the rapidly decreasing weight curve. The DME peak diminished much faster than those for the other compounds and was virtually absent 6 or 7 min after the event.

In this experiment the temperature was 185 °C during the adsorption, and was kept constant until 60 min after the start of desorption; thereafter it was increased at a rate of ca. 0.3 K min<sup>-1</sup> to 220 °C at 180 min. The thermic effect took place at about 207 °C. The very low rate of temperature increase was chosen in order to operate under quasi-isothermal conditions. The observed heat evolution/activation is not a simple temperature effect. The phenomenon has also been observed in strictly isothermal runs, where a temperature-dependent time delay after sorbate (methanol, DME) cut-off was observed (25, 13 and 3 min at 210, 220 and 240 °C, respectively).

The phenomenon leading to the thermic effect and the break in the weight curve takes place very rapidly once it starts. The clearest evidence of the rapidity of the transformation is given by the DSC curve, which displays the heat evolution in the sample. Separate experiments have shown that the time needed to go from zero heat evolution to the peak and start a decline is about 20 s. The time needed for the DSC signal to change from the initial zero value of the pre-event to 50% of the peak value has been measured as only 3 s. When interpreting this result one must take into account that the first effect of a sudden heat evolution must be a temperature rise of the catalyst/adsorbate system (much less than 1 K). Consequent to the heating of the catalyst particles there is a heating of the aluminium pan containing the sample, and then the measuring system which is actually the support of the catalyst-containing aluminium pan. Because of the finite, and not very high, heat conductivity of the catalyst sample, the time needed to heat it must be shorter than the time measured on the recorder for the DSC curve, which reflects the sample-holder/support temperature. Indeed, it appears plausible that the main heat evolution takes place within only a few seconds, possibly less than one second.

The relaxation time of the system (sample plus instrument) after a momentaneous energy input

is not known, but it seems reasonable that essentially all of the rapidly declining heat curve for the first 50 to 60 s after the onset of the heat evolution is due only to a relaxation effect – it would correspond to a relaxation time of 8–10 s.

Separate reactor experiments using a replacement technique in which the adsorbate in the zeolite was displaced by ammonia immediately prior to the onset of hydrocarbon formation have shown that until a substantial hydrocarbon formation actually starts, all, or essentially all, of the catalyst adsorbate consists of  $C_1$  entities: presumably  $(CH_3)_2OH^+$  and  $(CH_3)_3O^+$ .<sup>6</sup> This result is also corroborated by Forester and Howe,<sup>3</sup> who using IR spectroscopy have presented strong evidence that only  $C_1$  entities are present in the zeolite at temperatures which are too low (in their case ca. 200 °C) for gas phase hydrocarbon formation.

Although further details of the processes taking place remain to be elucidated one may be tempted to adopt as a working hypothesis the following: *At some point in time which depends on coverage and possibly on temperature, a sudden transformation takes place which within a second or so transforms the  $C_1$  entities into  $H_2O/H_3O^+$  and a hydrocarbon mixture – probably in a protonated state.*

Whether the hydrocarbon distribution found in the gas phase over the catalyst is the same as in the initially formed adsorbate on the surface is at present totally unknown. From general knowledge concerning alkene reactions over protonated zeolites at around 200 °C it will not be surprising if considerable reconstruction is going on, however. The very weak exothermicity which is observed for 3 to 6 min after the appearance of the sharp exothermic peak might suggest that such a process takes place. It is probably also significant that the main hydrocarbons observed are isobutane and isopentane, which are the hydrocarbons most easily formed in cationic cracking reactions.

The reactions described here, taking place over H-ZSM-5, are not restricted to that catalyst alone. Similar behaviour was observed with an H-Y catalyst. No other catalysts have so far been investigated by the experimental technique outlined here. Results previously obtained on time-dependent activation for hydrocarbon formation strongly suggested that fundamentally similar reaction mechanisms are at work in all

protonated zeolite/methanol/DME systems.<sup>5</sup> From such a point of view one would expect the behaviour of other protonated zeolites to exhibit broad similarity to what has been found here.

A detailed discussion is not warranted at present, but attention should be drawn to the very recent work of Forester and Howe.<sup>3</sup> They investigated the adsorption/desorption of methanol/DME by IR spectroscopy, using an experimental set-up which in broad outline was similar to the one employed here. On admitting a small quantity of DME at 200 °C they found traces of hydrocarbons, notably propene, in the effluent carrier gas. The IR spectra indicated that  $CH_3OSi$  species were formed on the catalyst.

Fig. 1 indicates that the weight during the desorption run levels off at a higher value than the adsorbent-free value. In this experiment and others, a residual excess weight of 20–40  $\mu g$  remained even after many hours flushing with nitrogen. The work of Forester and Howe strongly indicates that the remaining excess weight is due to  $CH_3OSi$  species which have been formed (variously being called methoxide species or adsorbed methyl cation in the literature). They suggested this species to be the primary source of catalytic activity. The results reported here would rather suggest it to be a fragment remaining after the true catalytic process, although it is, as shown by Forester and Howe, a quite reactive species in itself.

Further studies of these reaction systems employing other methods are currently being undertaken. A detailed report of this work will be published later.

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SHORT COMMUNICATION

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