Letter

Methanol Reactions on ZSM-5 and Other Zeolite Catalysts: Autocatalysis and Reaction Mechanism

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Several aspects of the reactions leading to hydrocarbon formation from methanol or dimethyl ether (DME) over an H-ZSM-5 catalyst still remain unclear. In particular, the formation of the first C–C bond has been widely debated and several mechanisms proposed. Among proposed mechanisms are: Carbene or carbenoid intermediacy, trimethyloxonium ion rearrangements via ylides, and carbenium ion attack on methanol (or DME).[1] The reaction is also claimed to be autocatalytic. The first-formed alkene is then considered to be alkylated by methanol, thereby yielding a higher homolog and so on, followed by alkene interconversion.[1]

New experimental results in our laboratory have lead to new views on the reaction mechanism, and they also indicate that there is no general autocatalysis. There is an activation process taking place in the catalyst which renders it active for formation of C–C bonds from C_1. Alkenes are activating agents, but once activated, the C–C bond formation no longer requires their presence.

An H-ZSM-5 zeolite which has been heated to 500 °C in air is inactive for C–C bond formation from methanol at temperatures below 250 °C. We have found that addition of e.g. 1 ml of butene (STP) per g of catalyst at 220 °C *prior to* methanol admission leads to a catalyst which is active for C–C bond formation at 220 °C. The activity is observed even if the reaction system is flushed with nitrogen for 24 h at 200–250 °C after butene addition (hydrocarbon partial pressure in the effluent falls to zero) before admitting methanol.

In this active state, the fractional conversion of oxygenates to hydrocarbons, and thus also the concentration of alkenes over the catalyst, was found to vary in inverse proportion to the feed rate. Hence, the rate of formation (mol s^{-1}) of hydrocarbons does not depend on the concentration of alkenes in the system. It has previously been reported that an increase in reaction rate with increasing conversion is observed, and this has been taken as proof that the reaction is autocatalytic.[2,3]

Furthermore, in this active state, addition of alkenes to the feed does not lead to increased conversion of oxygenates to hydrocarbons. In contrast to earlier reports,[4] the reaction exhibits normal Arrhenius behaviour when this activation procedure has been employed. The activation energy for the hydrocarbon-forming reactions is 135 kJ mol^{-1}. At 220 °C and a methanol partial pressure of 120 mbar, about 5 % of the methanol is converted to (mainly) C_2–C_4 hydrocarbons when employing a feed rate WHSV = 1 h^{-1} and protonated ZSM-5 catalysts with atomic ratio Si:Al ≈ 50. The reaction is essentially zero order with respect to oxygenate partial pressure. Heating the catalyst to 500 °C in air or oxygen destroys its activity.

The used "C–C active" catalyst invariably contains adsorbed hydrocarbons (5–10 % *w/w*) retained to >300 °C in a nitrogen stream, whereas the "C–C inactive" catalyst retains less than 0.1 % of adsorbate at 250 °C. Fairly extensive experiments on temperature-programmed desorption indicate that there are several distinct spe-

cies of zeolite/adsorbed molecule complex. In some cases, up to 70 % (w/w) of the desorbate is aromatic, with a predominance of p-xylene.

It was found that addition of alkene to the (methanol) feed transformed a "C–C inactive" H-zeolite into a "C–C active" catalyst. During this activation period the system behaves in the same manner as would be observed for an auto-catalytic reaction, and previous reports of auto-catalysis[2,3,4] are thereby easily explained on this basis. A quantitative treatment of the phenomenon has been carried out.

Completely analogous results have been obtained with an H-ZSM-11 catalyst in the temperature range 200–275 °C. The activation energy for the hydrocarbon formation was determined also in this case to be 135 kJ mol^{-1} and the reaction rate showed a zero order dependence on methanol partial pressure. No sign of true auto-catalysis was observed with the "C–C active" catalyst. Preliminary experiments with protonated natural erionite show that this catalyst is also inactive for C–C bond formation until a considerable quantity of hydrocarbon is adsorbed on the catalyst. Again, autocatalysis was not observed.

In agreement with general literature reports all three of the above-mentioned zeolite catalysts were active catalysts for the methanol/DME reaction, no form of activation being required.

The experimental results can hardly be explained on the basis of any of the mechanisms for the C–C bond formation which have been proposed so far, with the exception of a reformulated carbene mechanism. On the basis of the results reported above and other experiments a new mechanism for the hydrocarbon formation from methanol or dimethyl ether is proposed: Alkenes, in particular those which form tertiary carbenium ions upon proton addition, exhibit a very pronounced proton affinity.[5] This affinity is considerably greater than that of water, alcohols or ethers, and the literature on ZSM-5/methanol[1] has not taken this fact into account. As a consequence of this high proton affinity there will be an essentially complete transfer of protons from their positions in the virgin H-zeolite to alkene molecules when they enter the zeolite pores. The situation can formally be described as shown in Scheme 1.

By this process the zeolite, which originally had only acidic character, can be expected also to exhibit basic character due to the resonance con-
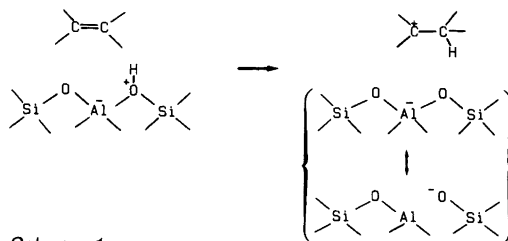
Scheme 1.
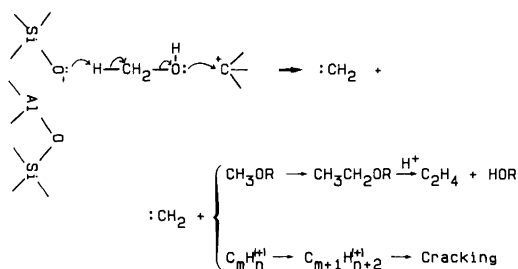
Scheme 2.

tribution of the structure with an $-O^-$ group. The acidic part of the system is then found on the carbenium ion. Together, the two regions constitute the dual acid/base center required for a carbene mechanism, and the main objection to this mechanism is thereby removed. The reasoning concerning acidity/basicity on part of the zeolite could also (more satisfactorily) be expressed in a terminology based on crystal field theory. As an evolution of earlier mechanism proposals,[1] the first step in the formation of hydrocarbons from methanol may then be formulated as shown in Scheme 2.

An alternative formulation in which a methyl cation, rather than simply a proton, is transferred to the zeolite oxygen is possible and this may well be the main route for formation of CH_4, which is always a (minor) product.

According to Scheme 2 an alcohol (or ether) is formed as an initial part of the reaction. This alcohol may, however, be protonated and will then rapidly eliminate water leaving a protonated alkene, whereby the catalytic cycle is continued.

The methylene radical will add very easily to the double bond in ethene, forming cyclopropane. Cyclopropane has not been found but ancillary experiments show that at 200 °C it is completely transformed into propene, which is a major reaction product.

This mechanism is in agreement with the recently reported observations by Olah and co-workers[6] that tungsten oxide supported on alumina, a system which is known to exhibit pronounced amphoteric properties, is also a rather efficient catalyst for C–C bond formation from methanol and other monofunctional methane derivatives. The fact that no activation of the H-zeolites appears to be necessary for hydrocarbon formation at higher temperatures, such as 350 °C, can be readily accounted for by assuming a slight hydrocarbon-forming ability also for the non-activated catalyst. The reaction rate at this stage may be many orders of magnitude lower than in the "C–C active" state but an accelerating activation will still take place. The first few molecules may be formed according to any of the mechanisms proposed in the literature, or by a mechanism basically similar to the one proposed here. The phenomenon has been studied in some detail and the results are in agreement with the general hypothesis stated above. A kinetic equation which can be quantitatively fitted to literature data on "autocatalysis" can be deduced from simple mechanistic considerations of the processes taking place in the non-activated catalyst.

Complete reports on this activation process and on the experimental work forming the basis for the mechanistic model proposed here, will be published later.

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