Kinetic modeling of deactivation profiles in the methanol-to-hydrocarbons (MTH) reaction: A combined autocatalytic–hydrocarbon pool approach

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Catalyst deactivation in the methanol-to-hydrocarbons (MTH) reaction was modeled using two approaches and compared with experimental data obtained over ZSM-5 and ZSM-22. In the first approach, the methanol conversion with time on stream was calculated using an autocatalytic reaction model, with the assumption that deactivation is proportional to methanol conversion. The model predicts a linear dependence of the catalyst lifetime to 50% conversion on the contact time, with a slope that characterizes the deactivation behavior. In the second model, a dual-cycle reaction mechanism was constructed, with the assumption that only reaction between methanol and aromatic species leads to coke formation. The active sites on the catalyst are gradually covered with autocatalytic species, and subsequently with coke, leading first to an induction period and later to deactivation; thereby, offering an explanation to how deactivation rates close to zero may be obtained at less than 100% initial conversion.

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1. Introduction

The conversion of methanol to hydrocarbons (MTH) over zeolite- or zeotype-based catalysts represents a flexible route for the production of light alkenes, referred to as the methanol-to-olefins (MTO) process, and gasoline, by the methanol-to-gasoline (MTG) process, from carbon sources such as natural gas, biomass, coal, and CO2. The best known catalysts for the conversion of methanol to hydrocarbons are ZSM-5 and SAPO-34, which are both applied in industrial processes [1,2]. However, many other zeolite structures are known to be active for MTH, and, in fact, the zeolite structure influences the product distribution and deactivation behavior. The hydrocarbons formed in the MTH reaction range from light alkenes and alkanes to aromatic compounds and result from a complex reaction network [2], which involves methylation and decomposition of adsorbed alkenes and aromatics; this is called the “hydrocarbon pool mechanism.” The presence of the adsorbed hydrocarbon fragments is therefore crucial for the reaction to occur.

Besides the desired hydrocarbon products and adsorbates, coke deposits are generally formed in the catalyst's internal channels and the outer surface [3], which lead to deactivation of the zeolite catalyst. The internal coke deposits consist of molecules that have grown too big to diffuse out of the catalyst pores, e.g., hexamethylbenzene in ZSM-5 [4] and can be regarded as an undesired by-product of the reaction. On the external surface of the catalyst, graphite-like coke is typically found [3]. The high stability of the ZSM-5 catalyst is ascribed to the 3-dimensional structure of the channel system in this zeolite, which makes it more difficult to block for access to the active Brønsted acid sites, resulting in a longer catalyst lifetime [5]. Deactivation as a consequence of coke deposition is reversible, in contrast to deactivation due to degradation of the zeolite material, and the catalytic activity can be restored by burning off the deposits by a treatment in a few percent of oxygen at 500–600 °C. Industrial MTG plants contain several reactors in parallel, such that the reactors can be regenerated one by one, without interruption of the production.

Clearly, catalyst deactivation is an important issue, and knowledge about the influence of the zeolite structure on deactivation requires a well-defined characterization of the deactivation. One approach to achieve this is by modeling of the catalyst deactivation. Many studies have been devoted to the MTH reaction mechanism during the past three decades, contributing to the generalized reaction scheme shown in Scheme 1. Based on this insight, a few studies have recently appeared which target the quantification of the alkene-based versus the aromatic-based reaction cycles [6,7]. However, less attention has been devoted to the mathematical description of catalyst behavior with time on stream, which obviously must reflect the deactivation behavior. A few models describing catalyst deactivation appeared in the literature in the 1980s and 1990s and were reviewed by Keil in 1999 [8]. All those models...
consider methanol a main contributor to coke formation. This is in line with experimental observations of used SAPO-34 and ZSM-5 catalysts, which show no coke deposits in the very first part of the bed, followed by a deactivated, coked zone, and finally an active zone [3,9–11]. Still, deactivation is modeled as a function of methanol conversion. Some models are based on methanol conversion alone, with a positive correlation between conversion level and deactivation rate, while others also take the contribution of individual product groups into account (see [8] and refs. therein). A satisfactory fit of experimental data can generally be obtained.

In 2009, Janssens presented a different approach to model catalyst deactivation for the MTH reaction, by describing catalyst deactivation as a reduction of the effective amount of catalyst in the reactor with time. This approach is based on the observation that the changes in product distribution, especially an enhanced yield of propene and ethene shortly before the breakthrough of methanol, resemble the development of the product distribution one would expect with a continuously increasing space velocity [12]. The change in effective catalyst mass is then a direct measure for the deactivation rate of the catalyst. To calculate the conversion with time on stream, it was assumed that the MTG reaction is first order in methanol, and that the deactivation rate is proportional to the conversion, which corresponds to a constant selectivity for coke formation. With these assumptions, it follows that the ratio of the catalyst lifetime to 50% yield of hydrocarbons and the applied contact time (W/F weight-to-flow ratio) is a direct measure for the deactivation rate, independent of the activity. This provides an easy and well-defined characterization of catalyst deactivation, which was later applied to relate the deactivation of a large number of ZSM-5-based catalysts with the presence of internal silanol groups inside the zeolite channels [13].

Even though a description of catalyst deactivation based on a first-order reaction and a deactivation rate proportional to the conversion may work well in a number of cases, these assumptions obviously put limitations on the validity of the model. First, it is well known that the conversion of methanol to hydrocarbons is autocatalytic [2,14–16], which implies that the rate of the reaction increases with the concentration of the products. The effect of this on the observed decline in hydrocarbon yield with time on stream is not straightforward, as a lower yield of hydrocarbons results in a slower conversion of methanol, which may enhance the observed deactivation. On the other hand, the lower rate of methanol conversion also results in a lower rate of coke formation, and this will delay the deactivation of the catalyst. To elucidate the effect of an autocatalytic reaction scheme, the equations for the conversion as a function of time on stream and a deactivation rate proportional to the conversion are derived for an autocatalytic reaction scheme. This shows how to derive a well-defined measure for the deactivation rate for an autocatalytic reaction.

The assumption that the deactivation rate is proportional to the methanol conversion implies that the formation of deactivating coke deposits follows the conversion of methanol. It is, however, conceivable that it takes some time to build up the hydrocarbon fragments in the zeolite channels; during this initial phase, the deactivation does not take place or will be slower compared to the methanol conversion. Furthermore, the product distribution on a deactivated catalyst may be different from that on a fresh catalyst, even if the conversion is the same. Such a selective deactivation is known for alkene production over SAPO-34, which has a cavity-window structure with 12-ring cavities, allowing containment of polycyclic aromatics as large as pyrene [17], but with narrow, 8-ring windows which allow only linear, light alkenes to diffuse out and become part of the reactor effluent. The observed increase in the ethene-to-propene ratio appears to be due to an increasing diffusion hindrance, as the adsorbed hydrocarbon residues inside the cavities gradually grow bigger [18]. This results in an ethene and propene selectivity that depends on the deactivation history. For the conversion of methanol to hydrocarbons on a number of other zeolites and zeotypes, including ZSM-11, IM-5, TNU-9 [5], ZSM-5 [11], ZSM-22, ZSM-23, EU-1 [19], SAPO-5 [20], such a selective deactivation could not be determined and the deactivation seems to occur simply as a loss of active sites with time on stream in these cases.

In order to obtain further insight in the deactivation by coke formation in a more realistic way, we present a kinetic model for the conversion of methanol to alkenes, aromatics and coke, which essentially is an extension of the dual-cycle model proposed earlier (Scheme 1). In our model, the formation of coke leads to a loss of active sites, giving rise to catalyst deactivation. The model is capable of describing the build-up of the hydrocarbon phase in the zeolite channels and can therefore produce situations with a deactivation rate that is not proportional to the methanol conversion. Furthermore, the model also indicates where coke deposition occurs and how the adsorbed coke profile develops with time on stream. It can be shown that the reaction zone not always is a front moving from the inlet to the exit of the reactor, but also can grow against the flow direction, as has recently been observed experimentally by operando X-ray diffraction for SAPO-34 [21].

2. Modeling of deactivation for an autocatalytic reaction

2.1. Catalyst lifetime in an autocatalytic reaction

Based on a description of catalyst deactivation as a reduction of the effective amount of catalyst in the reactor with time, it could be
shown that, for a high initial conversion, catalyst deactivation is conveniently characterized by the ratio of the catalyst lifetime to 50% conversion (hydrocarbon yield) and the contact time (weight-to-flow ratio W/F) applied, if the reaction is first order with a deactivation rate that is proportional to the conversion [22]. As the conversion of methanol to hydrocarbons is known to be autocatalytic, we now derive a similar expression for the catalyst lifetime for an autocatalytic reaction. (Throughout this paper, the term conversion refers to the hydrocarbon yield, implying that DME, which is in equilibrium with methanol, is not considered as converted methanol.) An autocatalytic reaction consists of a slow initiation step, followed by a fast reaction step dependent on the concentration of the reaction products. The reaction scheme is as follows:

\[ M \rightarrow PM \rightarrow P \]

where \( M \) is the reactant (methanol) and \( P \) is the product. The rate expression for \( M \), according to this scheme, becomes:

\[
\frac{dM}{d\tau} = -k_1M - k_2MP
\]  

(2)

Using the mass balance \( M_0 + P_0 = M + P \), and introduction of the conversion \( X = (M_0 - M)/M_0 \) leads to the following expression for the conversion:

\[
\frac{dX}{d\tau} = (1-X)(k + k_2M_0X)
\]  

(3)

where \( k' = k_1 + k_2P_0 \). The exact analytical solution, using the condition that \( M = M_0 \) at \( \tau = 0 \) [23] becomes:

\[
X = \frac{\exp((k + k_2M_0)\tau) - 1}{\exp((k + k_2M_0)\tau) + \frac{E}{q}} = \frac{E - 1}{E + q}
\]  

(4)

\( M_0 \) and \( P_0 \) are the initial concentrations of the reactant (methanol) and product, respectively, and \( \tau \) is the applied contact time or catalyst weight-to-flow ratio (W/F). For convenience, the following substitutions are made: \( \exp((k + k_2M_0)\tau) = E \) and \( \frac{E}{q} = q; \) this implies that \( E = \exp(k(1 + q)\tau) \). For \( q \neq 0 \), Eq. (4) results in an S-shaped development of the conversion with contact time, which is typical for an autocatalytic reaction.

With respect to the discussion whether the MTH reaction proceeds by a direct C–C bond formation from methanol or DME, or is always initiated by a low concentration of impurities in the methanol or zeolite [24], we note that the kinetic behavior of the autocatalytic reaction scheme depends on \( k' \), the sum of \( k_1 \) and \( k_2P_0 \). Here, \( k_1 \) represents the rate of C–C bond formation by methanol and/or DME, independent of other hydrocarbon species, and \( P_0 \) represents the initial hydrocarbon concentration. According to Eq. (4), the conversion in the autocatalytic reaction scheme develops identically in the case that \( k_1 = 0 \) and \( P_0 = 0 \) (reaction by hydrocarbon impurities) or \( k_1 \neq 0 \) and \( P_0 = 0 \) (direct C–C bond formation). This means that the kinetics of the autocatalytic reaction cannot distinguish between these two opposing mechanisms, and that the rate of C–C bond formation can be modeled exactly by assuming an appropriate low concentration of hydrocarbon impurities.

To calculate the conversion with time on stream for an autocatalytic reaction, it is assumed that the deactivation rate is proportional to the conversion, which is the same assumption as made in Ref. [22] with first-order reaction:

\[
\frac{dW}{dt} = -a'X
\]  

(5)

where \( W \) is the effective amount of catalyst, \( t \) is the time on stream, and \( a' \) is a deactivation constant (g/h). Division of both sides by the flow \( F \) (in mol/h) then yields an analogous expression in terms of a time-dependent contact time \( \tau \):

\[
\frac{d\tau}{dt} = -aX
\]  

(6)

where \( a = a'/F \) is a deactivation constant in g/mol. The conversion with time on stream is then found from Eqs. (3) and (6):

\[
\frac{dX}{d\tau} = -aX(1 - X)(k' + k_2M_0X)
\]  

(7)

The exact analytical solution of Eq. (7), using the initial conversion; at \( \tau = 0 \), \( X = X_0 \),

\[
\ln \left( \frac{X(1 - X)}{X_0(1 - X)} \right) + q \ln \left( \frac{X(1 + qX)}{X_0(1 + qX)} \right) = -ak'(1 + q)t
\]  

(8)

It is straightforward to see that Eq. (8) reduces to the expression for a first-order reaction for \( q = 0 \) [22], i.e., for large values of \( k' \) or for \( k_2 \rightarrow 0 \), which are the cases where the contribution of the self-accelerating step becomes negligible.

As \( X_0 \) in Eq. (8) cannot be equal to 1, \( X \) and \( X_0 \) are eliminated using (Eq. (4)) to yield:

\[
\ln \left( \frac{E - 1}{E_0(1 - E)} \right) + q \ln \left( \frac{E_0(1 - E)}{E_0(1 - E)} \right) = -ka(1 + q)t
\]  

(9)

where \( E \) and \( q \) are defined as in Eq. (4); \( E_0 \) is the exponential term at \( \tau = \tau_0 \), \( \tau_0 \) is the contact time applied in the experiment; \( \tau \) is the effective contact time, which decreases with time on stream as deactivation occurs. Eq. (9) relates the effective contact time \( \tau \) and the time on stream \( t \).

From Eq. (9), the catalyst lifetime to the 50% conversion level can be derived. For \( X = 0.5 \), we find that \( E = q = 2 \) from Eq. (4). Furthermore, for high initial conversions, it follows that \( E_0 \approx 1 \), leading to the approximation \( \ln(E_0 - 1) \approx k(1 + q)\tau_0 \). Introduction of these expressions in Eq. (9) results in the following relation for the catalyst lifetime to 50% conversion and the contact time \( \tau_0 \):

\[
\tau_0 = \frac{1}{a} \left( \ln(q + 1) + q \ln \left( \frac{q + 1}{q} \right) \right) = \frac{(\tau_0 - \tau_{crit})}{a}
\]  

(10)

Eq. (10) shows that the lifetime to 50% conversion is a linear function of the contact time. A plot of the lifetime to 50% conversion has a slope equal to \( 1/a \), independent of the rate constants (catalyst activity), exactly as in the case for the first-order reaction. (In fact, the lifetime to an arbitrarily chosen conversion level depends linearly on the applied contact time \( \tau_0 \) with a slope \( 1/a \); only the value for \( \tau_{crit} \) is affected by this choice.) However, the deactivation constant is no longer just the ratio of the contact time and the deactivation constant. To obtain the correct value for the deactivation constant, the actual contact time has to be adjusted by the second term in the brackets, which we define as the critical contact time \( \tau_{crit} \). Physically, the critical contact time is the contact time (or weight or volume-to-flow ratio \( \tau = W/F \)) needed to reach a product concentration level where the autocatalytic reaction is dominating the overall reaction rate. The critical contact time only depends on the rate constants and initial concentrations of the reactant \( M_0 \) and products \( P_0 \) and is thus constant for given reaction conditions. Once the deactivation rate, \( a \), is known, it follows that the conversion capacity of the catalyst, \( R_0 \) (in gMeOH/gcat), is:

\[
R_0 = \frac{M_{MeOH}y_{MeOH}}{a}
\]  

(11)

where \( M_{MeOH} \) is the molar weight of methanol and \( y_{MeOH} \) is the molar fraction of methanol in the feed gas.
2.2. Catalyst lifetime with an induction period – a dual-cycle kinetic model

The dual-cycle MTH mechanism (Scheme 1) is a natural starting point for addressing the early stages of the MTH reaction. The development of a kinetic model based on this scheme is straightforward. However, in order to limit the complexity of the model, some simplifications have been made. First, the debate about whether the MTH reaction is initiated by a slow reaction between two methanol molecules, eventually leading to the first C–C bond formation or, alternatively, that the reaction is initiated by a reaction between methanol and trace impurities in the feed, has been by-passed by assuming that $k_1 = 0$ while $P_0 \neq 0$ (see Section 2.1). Second, the overall rates of the alkene, versus the aromatic, cycles leading to alkene formation, have been modeled by letting propene ($Pr$) represent all alkenes, while trimethylbenzene ($T$) represents all polymethylbenzenes; thereby, assuming that propene or trimethylbenzene methylation, respectively, is the rate-limiting step of each reaction cycle. Trimethylbenzene is formed by a combination of three propene molecules. The hydrogen atoms which are released upon aromatization are represented by the formation of a corresponding number of alkanes (A). Coke is represented by an unspecified, C$_{10}$ aromatic species (C). An influence of product selectivity on deactivation rate is introduced by assuming that coke is formed exclusively by reaction between methanol and trimethylbenzene. This assumption is based on previous studies of MTH catalyst deactivation, showing that polymethylated benzene or polycyclic aromatics are the main coke species, as well as the direct participation of methanol in coke formation (see [2] and refs. therein). All reaction rates are assumed to be first order in each reacting species.

The accumulation of hydrocarbon pool species, eventually leading to an increase in methanol conversion, represents a modeling challenge. In the cavity-window structure of SAPO-34, for which a similar model was recently developed [21], the accumulation could conveniently be represented by trapped polymethylbenzene species in the cavities. In ZSM-5, however, no trapping of active species is observed, and the hold-up of such species is therefore represented by the assumption of a gas-adsorbate steady-state for propene and trimethylbenzene at each reactor segment, being maintained until the next time on stream segment, where a new gas-adsorbate steady-state is established. Such an assumption seems reasonable, taking into account the non-negligible proton space time ($s$) and the sites covered by some component: $N_{free} = N_{tot} - N_{Pr} - N_{T} - N_{C}$. Eq. (24) together with the adsorption constants leads to the familiar Langmuir terms in the kinetic expressions.

It is noted that the independent variable in Eqs. (16)–(20) is the space time $t$, while it is the time $t$ in Eq. (21). To solve this system, we first solve Eqs. (16)–(20) to yield a concentration profile of the gas-phase products over the whole reactor, using a standard Runge–Kutta algorithm [26], using 200 points over the whole reactor length. This step is followed by a single step time integration over a time interval $\Delta t = 0.1h$ to calculate the coke coverage as $\Delta C = 10k_5MT\Delta t$ (Eq. (21)) and adjust the coverage of the adsorbed propene and trimethyl benzene using the current gas-phase composition, equilibrium constants, and the number of free sites in Eqs. (22)–(24). This process is repeated 500 times to cover a time range of 50 h. The calculated conversion and product yield data with time for different contact times are derived from a single calculation by evaluation of the time dependence of these data at the appropriate positions in the reactor.

The stoichiometric coefficients are chosen such that the calculated amounts of the several components can be interpreted as the amount of carbon atoms present in that particular component. After completion of one integration step over space time and time, the number of carbon atoms does not change, which is easily verified from Eqs. (16)–(21); the differential equations thus merely describe how the carbon atoms in the system are redistributed over the different products and adsorbed phases.

Finally, it is stressed that the goal of the kinetic model here is to generate realistic situations to obtain insight in the chemical events that lead to deactivation, rather than to obtain a precise description of measured data. By combination with known effects of the zeolite structure on the activity and product selectivity for the conversion of methanol and hydrocarbons, this model can then sent the hydrocarbon pool present in the zeolite during the reaction.

This leads to the following rates of formation for each species:

$$\frac{dM}{dt} = -3k_3MPr^* - 3k_3MT^* - k_5MT$$

$$\frac{dPr}{dt} = 3k_3MPr^* + 3k_3MT^* - 18k_3Pr^*$$

$$\frac{dA}{dt} = 9k_3Pr^*$$

$$\frac{dT}{dt} = 9k_3Pr^* - 9k_3MT^*$$

$$\frac{dC^*}{dt} = 0$$

$$\frac{dC^*}{dt} = 10k_5MT$$

Furthermore, the amount of adsorbed propene ($Pr^*$) and trimethyl benzene ($T^*$) are assumed to be in equilibrium with the gas-phase products, determined by equilibrium constants for adsorption of propene ($K_p$) and trimethyl benzene ($K_T$) as follows:

$$K_p = \frac{Pr^*}{PrN_{free}}$$

$$K_T = \frac{T^*}{TN_{free}}$$

The number of free sites is evaluated as the difference between the total sites and the sites covered by some component:

$$N_{free} = N_{tot} - N_{Pr} - N_{T} - N_{C^*}$$

In these equations, $M$ indicates methanol, $Pr$ indicates propene (or alkenes in general) in the gas phase, $A$ indicates alkanes (which are considered inert), and $T$ indicates trimethyl benzene (aromatics) in the gas phase. For the adsorbed species, we have $Pr^*$ for adsorbed propene (alkenes), $T^*$ for adsorbed trimethyl benzene (aromatics), and finally $C^*$ for the adsorbed coke; these adsorbed species represent the hydrocarbon pool present in the zeolite during the reaction.
serve as a basis for the understanding of the influence of the zeolite structure on the deactivation behavior.

2.3. Experimental

The experimental data used to validate the models developed in this contribution have been published and discussed elsewhere, in Ref. [11] for the ZSM-5 (Si/Al = 50) tests, and in Ref. [19] for the ZSM-22 (Si/Al = 50) tests. The catalytic tests were carried out at atmospheric pressure and 350 °C for the ZSM-5 catalyst, and at 400 °C for the ZSM-22 catalyst, using a glass reactor with inner diameter 3 mm and 10 mm, respectively, for the two catalysts. Before each test, the reactor was heated to 550 °C under a flow of helium. The catalysts were calcined in situ at this temperature under a flow of pure oxygen for 1 h. The carrier gas, He, was saturated by methanol (BDH Laboratory Supplies, >99.8% chemical purity) at 20 °C, giving a methanol partial pressure of 13 kPa. The reactor effluent stream was analyzed on an on-line Agilent 6890A GC with a FID detector and automatic sampling (Supelco SPB-5 capillary column: 60 m, 0.530 mm i.d., stationary phase thickness 3 μm). Appropriate response factors for dimethyl ether and methanol were found by experiment. In the ZSM-5 tests, the absence of bypass was verified by observing that the methanol-to-dimethyl ether reaction was always at equilibrium.

In the ZSM-5 tests, the He flow was kept at 30 Nl/min, while the catalyst mass was varied between 8 and 40 mg, so that the lower and upper bounds of WHSV were 8.8 and 44.1 (g MeOH)/(g cat) h⁻¹. In the ZSM-22 tests, the catalyst mass was kept at 50 mg, while the He flow was varied to give WHSV from 2.05 to 4.05 (g MeOH)/(g cat) h⁻¹.

3. Results and discussion

3.1. The autocatalytic model and critical contact time

The characteristic feature of an autocatalytic reaction is that the conversion remains very low for low contact times, followed by a steep increase in conversion, resulting in an S-shaped curve. The physical interpretation of the critical contact time τ₀ in Eq. (10) is (approximately) the contact time at which the steep increase in hydrocarbon production occurs. This is evident from Eq. (10), as τ₀ → 0 for a pure first-order reaction, if evaluated at X = 0.5 [24], or for large values of q, when the conversion is essentially dominated by the accelerating step; these cases do not show a delay in the conversion with contact time. This is further illustrated in Fig. 1, which shows the typical S-shaped curve for the conversion in an autocatalytic reaction with contact time. At high conversion levels, the conversion can be approximated by an ordinary first-order reaction, which is transposed in the contact time (dashed line in Fig. 1). The fit is not perfect, since the second-order effects present in the autocatalytic reaction are not taken into account. The transposed line crosses the x-axis at a contact time which corresponds approximately to the critical contact time; this is the contact time at which the autocatalytic step starts to dominate the total reaction rate. In the example in Fig. 1, the critical contact time calculated from Eq. (10) was 0.36, which is close to the transposition of 0.38 required for the approximation by a first-order reaction at high conversion levels.

Although the critical contact time is closely related to an induction time, it has been shown that for ZSM-5, there is an autocatalytic effect for the methanol-to-hydrocarbon reaction that actually is determined by the contact time. Changing the contact time (flow) back and forth around the critical contact time several times results in the same S-shaped curve of the hydrocarbon yield [2]. This behavior is inconsistent with an induction time, as that would imply that the acceleration is observed in the first cycle only, when the hydrocarbon pool is established; in the following cycles, the reaction should show an ordinary first-order-like behavior governed by the activity of the autocatalytic step, and the conversion should show a steep decrease toward τ = 0. Therefore, we can actually speak of a “critical contact time”, below which only a minor conversion production of hydrocarbons can be expected.

As indicated by Eq. (10), the critical contact time and deactivation constant a can be derived from a plot of the catalyst lifetime to 50% conversion as a function of the applied contact time. Fig. 2 shows such experimental data measured for a ZSM-5 catalyst (Si/Al = 50) at 350 °C [11] and contact times τ between 0.1 and 0.5 g h/mol (WHSVMeOH between 8.8 and 44.1 g h/mol), and for a ZSM-22 (Si/Al = 50) catalyst at 400 °C and τ between 1 and 2 g h/mol (WHSVMeOH = 2–4 g h/mol) [19]. In both measurements, the methanol partial pressure was 13 kPa (13%). The first feature that is apparent from the graphs is that a linear dependence of the critical contact time on τ₀ is observed for both sets of experiments, in agreement with the autocatalytic model Eq. (10). The τ₀,5 values for ZSM-5 far exceed those of ZSM-22, in spite of a 10-fold longer initial contact time for ZSM-22, which is reflected in the values for the deactivation constant a for these catalysts. From the slopes in the graphs, we find a value for the deactivation constant of a = 0.0192 g/mol, for ZSM-5, which corresponds to a conversion capacity of 219 gMeOH/gcat. Likewise, we find a value of a = 0.4199 g/mol, corresponding to a conversion capacity of 9.9 gMeOH/gcat for the ZSM-22, indicating a clearly faster deactivation of ZSM-22. This difference in deactivation constant reflects the superior stability of ZSM-5 compared to ZSM-22 and demonstrates the usefulness of a modeling approach for characterization of catalyst deactivation.

The second feature is that the line for the ZSM-5 data set crosses the x-axis close to the origin, while the line for ZSM-22 crosses the x-axis at τ = 0.7 g h/mol. According to Eq. (10), this means that the critical contact time for ZSM-5 is negligible in our measurement, while it is only close to the contact times used in the measurements with ZSM-22. It is noted that both catalysts were calcined in air in situ before the measurement of the catalyst lifetime, in order to remove any trace of hydrocarbons in the zeolite before testing. Therefore, the difference in critical contact time for ZSM-5 and ZSM-22 suggests a significantly higher rate constant of the methanol conversion reaction(s) in ZSM-5 compared to ZSM-22. In line with this suggestion, Hill et al. recently reported alkene methylation rates using dimethyl ether as methylaing agent over ZSM-5, Beta, Mordenite and ferrierite at 345–430 K and found significant
differences. For instance, ferrierite, which is a combined 10- and 8-ring structure with MTH product spectrum similar to that of ZSM-22 [16], was reported to have a rate constant for propene methylation which was 0.03 times that of ZSM-5, and with similar activation energy (57 ± 2 versus 62 ± 3 kJ/mol, respectively) [27]. The reason for the reported rate difference is yet to be found.

From Eq. (10), it follows that the approximation for deactivation constant as the ratio of the applied contact time and lifetime to 50% conversion \( \alpha = \tau_{0t} / \tau_{05} \), as derived for a first-order reaction [22] at high initial conversion, also is valid for an autocatalytic reaction if \( \tau_{crit} \) is negligible, which means that the catalyst lifetime to 50% conversion should be measured at a contact time well above the critical contact time (corresponding to a sufficiently low space velocity) to evaluate the deactivation behavior. This means that the analysis derived for a first-order reaction would produce a good estimate of the deactivation constant \( \alpha \) for the ZSM-5 zeolite, but a quite poor estimate would be found for the ZSM-22 catalyst.

A fitted plot of the calculated conversion with time on stream according to Eqs. (8) or (9) to the full set of experimental data for ZSM-5 taken at different contact times is shown in Fig. 3 (experimental data taken from Ref. [11]). The value for the deactivation constant \( \alpha \) used in the calculation is the one determined in Fig. 2, while the values for \( k_1 \) and \( q \) are manually adjusted to approximate the experimental data, without further optimization. As a general trend, the shape of the curves produced by the autocatalytic model is fair in the cases with a full initial conversion. These curves show a plateau at full conversion followed by rather steep deactivation, and finally, tailing of the conversion versus time on stream curves at conversions lower than 20%.

According to the autocatalytic model, the critical contact time depends on the values of \( k' \) and \( q \), and thus the rate constants \( k_1 \) and \( k_2 \), as well as the initial concentrations of methanol and hydrocarbon products. In principle, these values could be determined from the critical contact time, and to obtain the calculated curves in Fig. 3, we have used \( k = 6 \) and \( q = 5 \). The value of the factor \( q = 5 \) is lower than the \( k_2/k_1 \) ratio of 50 estimated by Chen and Reagan [14]. We note that the exponential factor \( E = k' (1 + q) \tau \) (Eq. [9]), so a change in the value of \( k' \) can be compensated with an opposite change in the factor \( q \). Therefore, the values of the parameters \( k' \) and \( q \) can change significantly, while only a modest change in the conversion with time on stream is observed. This is illustrated in Fig. 4, which shows the experimentally measured decay in conversion together with the calculated curves for \( q = 5 \) and \( k' = 6 \) and \( q = 30 \) and \( k' = 1.3 \). All curves in the graph are quite close together, which means that it is difficult to extract reliable data on the values of \( k' \) and \( q \) from the measured conversions with time on stream during deactivation. Furthermore, the autocatalytic model also shows that a difference in measured \( k'/k_2 \) ratio can be a consequence of other parameters, such as different amounts of hydrocarbons adsorbed in the zeolite, or just the activity.

For the data sets starting at a conversion level below 100%, the experimental data can also show a plateau of rather stable methanol conversion. Such a plateau cannot be reproduced by the autocatalytic model. This becomes immediately clear from Eq. (7), which only results in \( \tau_{crit} = 0 \) for \( X = 1 \) or \( X = 0 \); a conversion below 100% thus always results in a non-zero slope of the conversion with time. In order to reproduce this initial behavior, a counterbalancing parameter, such as a parallel build-up of reactive species, must be introduced.

3.2. The dual-cycle model

The dual-cycle model is, in principle, capable of describing the build-up of the reactive species in the zeolite, along with the deactivation. Fig. 5 shows a set of the calculated conversion with time on stream for different contact times, using the following values for the parameters: \( k_2 = 9.5 \), \( k_3 = 0.63 \), \( k_4 = 0.03 \), \( k_5 = 1.2 \), \( N_{ref} = 0.5 \), \( M_0 = 1 \), \( P_0 = 10^{-4} \), \( K_0 = 4 \), \( K_7 = 25 \), together with the full set of experimental conversion versus time on stream data over ZSM-5. At the
longest contact times, an S-shaped curve is observed, with full initial conversion and rather rapid decline in conversion, followed by tailing of the conversion versus time on stream curve at low conversions. At shorter contact times, the kinetic model produces an initial, rapid increase in conversion, followed by a maximum, which can extend over some time, and finally, a decay of the conversion with parallel slopes at all space times applied, in agreement with the experimental data. Although a better fit could certainly be obtained if taking into account a higher fraction of adsorbed alkene species, gradually converting to more alkenes and aromatics, which will eventually lead to coke formation. Such counter-flow alkene and aromatic accumulation is the origin of the modeled plateaus at less than 100% conversion in the conversion versus time on stream plots in Fig. 5, and is therefore a main feature of the dual-cycle model. The existence of such a phenomenon is yet to be verified for ZSM-5. However, a recent time- and space-resolved operando X-ray diffraction study of the MTH reaction over SAPO-34 showed a direct correlation between an initial increase in product formation and a counter-flow accumulation of hydrocarbon species in the catalyst [21]. Recently, similar studies were performed for ZSM-5 (Si/Al = 140; 350 °C) as the MTH catalyst. A gradual increase in channel occupancy was observed throughout the 140 min duration of the experiment, being initially more rapid in the middle and final segments of the reactor compared to the initial segment; and gradually more important in the first segment due to leveling off of the curves for the two later segments. A constant, incomplete methanol conversion was observed throughout the experiment [28]. Although no conclusive evidence of a correlation between accumulation of active species and methanol conversion could be drawn from the cited study, at least it illustrates the feasibility of a slow build-up of active species in the ZSM-5 structure, on a time-scale similar to that predicted by the kinetic model.

An interesting aspect of the induction period observed in the dual-cycle model is the definition of a critical contact time and its influence on a catalyst’s methanol conversion capacity. According to the autocatalytic model, the conversion capacity is inversely proportional to the fraction of the catalyst bed in which the product concentration is below the critical limit. It follows directly that the critical contact time found from multiple lifetime tests could be used to determine \( k' \) versus \( k_2 \), i.e., the relative rates of direct (or impurity-induced) versus autocatalytic methanol conversion. In the dual-cycle model, however, the critical contact time varies with time on stream, due to the accumulation of reactive intermediates in the pre-autocatalytic zone. The conversion capacity will therefore only be limited by the (initial) critical contact time in cases where the rate of product accumulation in the first part of the catalyst bed is slow compared to catalyst deactivation, corresponding to a high \( a/k \) ratio in the autocatalytic model. If \( a/k \) is low, however, the reaction front will progress both in the flow and counter-flow directions, eventually leading to a negligible apparent critical contact time.

The dual-cycle model also offers a possibility to check the basic assumption that the deactivation rate is proportional to the conversion, as used in the autocatalytic model. If we assume that the amount of deactivated catalyst is equal to \( W_0 C \), where \( W_0 \) is the amount of fresh catalyst, and \( C \) is the coke coverage, then the effective amount of catalyst becomes proportional to \( 1 - C \), and

![Image](image_url)
the rate of deactivation ($\frac{d\alpha}{dt}$ in Eq. (6)) can then be found by the rate of coke accumulation. Division by the conversion then gives an estimate for the deactivation constant $a$. Fig. 8 shows the conversion, the relative amount of active catalyst, the deactivation rate, and the estimated deactivation constant as calculated from the coke profiles shown in Fig. 6. From this figure, we find that the deactivation rate is not proportional to the conversion over the whole conversion range. In the low conversion range (<25%), it actually is rather constant, but at higher conversion levels, the dual-cycle model predicts that the deactivation constant actually increases with conversion, indicating that the deactivation is faster than predicted by the assumed proportional relation to the conversion. This means that in the deactivation measurements, we can expect that the deactivation rate decreases more than assumed in the autocatalytic model, leading to somewhat longer lifetimes than predicted, which is consistent with the observed differences between the calculated and measured conversion shown in Fig. 3.

4. Concluding remarks

Past experience has shown that the autocatalytic nature of the MTH reaction makes catalyst stability comparisons a challenging task. As the initial reaction between two methanol molecules, or between methanol and trace impurities of C$_2$+ compounds, is slow compared to the autocatalytic reaction, stability studies are mainly performed at full initial conversion. The observed activity loss per unit time will strongly depend on the unknown initial activity of the catalyst, as well as the choice of contact time. Catalysts with high initial activity will typically yield similar methanol conversion capacities at a range of contact times [11], while less active catalysts will yield higher methanol conversion capacities at longer contact times [19]. The difficulty in performing reliable comparisons of catalyst performance, in particular when comparing contributions from different laboratories employing different protocols, constitutes a significant obstacle to the further advancement of the field.

A primary objective of this contribution has been to develop a test protocol which will facilitate representative stability comparisons that are independent of the initial catalyst activity. This goal has been met by developing the autocatalytic model, and the analytical expression derived thereof; in particular, the observation that a plot of time on stream to 50% conversion versus contact time would yield the critical contact time, while the slope of the $t_{50}$ versus contact time curve would yield the deactivation rate, independent of catalyst activity. The test protocol developed herein therefore consists of repeated stability tests under the same conditions but with different contact times; each of them with 100% initial conversion.

A second objective of this contribution has been to mathematically describe, and thereby model, some unexpected and hitherto little discussed observations occasionally made during catalyst stability studies, in particular the rather stable conversion level often observed at less than 100% initial conversion before a clear loss of activity sets in. The dual-cycle model was developed for this purpose and was shown to successfully reproduce this behavior by predicting a gradual accumulation of alkenes and aromatics in

Fig. 6. Left panel: measured conversion (see also Figs. 3 and 4) and yield of aromatics over ZSM-5 with time on stream at 350 °C at WHSV = 8.8 h$^{-1}$, methanol concentration 13% [11]. Right panel: calculated conversion (see also Fig. 4) and yields of aromatics, alkanes and olefins for WHSV = 8.8 h$^{-1}$, using the same parameters as in Fig. 4.

Fig. 7. Development of the coke profile with time on stream according to the dual-cycle model using the same parameters as in Fig. 4. A darker color indicates a higher coke coverage, as indicated in the color bar to the left.

Fig. 8. Calculated relative effective mass and deactivation constants according to the dual-cycle model, based on the assumption that the effective mass is proportional to $1 - \frac{C}{C_3}$, where $C$ is the total coke coverage shown in Fig. 6.
the catalyst, modeled as an adsorption-desorption equilibrium at the given conversion level in each reactor segment at each time on stream. Moreover, using the adsorption-desorption equilibrium as the only source of product hold-up in the catalyst, the catalyst would be rapidly depleted of product with a change in conversion due to changing reaction conditions (not shown). Hence, the model is also in agreement with previously published data for the MTH reaction over ZSM-5, where a conversion versus contact time pattern typical of an autocatalytic reaction is established under changing space velocities, irrespective of the test history [2]. The dual-cycle model demonstrates that the slope of the conversion versus time on stream curve represents the sum of site activation and deactivation and is therefore not directly correlated with the deactivation rate, unless the critical contact time is small compared to the applied contact time. In that case, the site activation term becomes negligible.

As a secondary goal, the kinetic description of the dual-cycle model has been used to reproduce the axial coke profile typically observed for a partially deactivated catalyst. By assuming that coke molecules are formed exclusively by the reaction between methanol and aromatic molecules, and not alkenes, the dual-cycle model successfully reproduces the white, uncoked zone observed at the inlet of the catalyst bed after testing, as well as the tailing of the conversion versus time on stream curves when complete deactivation is approached. It further reproduces the generally observed coke profile of the catalyst bed – a heavily coked zone (after the white zone) followed by gradually lighter grey segments. The dual-cycle model thereby clarifies the apparent self-contradiction of older models, which assumed that methanol was the main source of catalyst deactivation, while at the same time modeling deactivation as a function of methanol conversion (see Section 1).

It should be noted that the kinetic model based on the dual-cycle concept presented here probably overestimates the selectivity toward coke formation: The model assumes that each coke molecule is irreversibly adsorbed on one active site, thereby leading to deactivation of that site. However, it seems more likely that every coke molecule will serve as a diffusion barrier and block the access to several acid sites, in addition to the poisoning of the site of adsorption.

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