Journal of Catalysis 264 (2009) 130–137

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

A new approach to the modeling of deactivation in the conversion of methanol on zeolite catalysts

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ARTICLE INFO

Article history:
Received 8 January 2009
Revised 18 February 2009
Accepted 8 March 2009
Available online 1 May 2009

Keywords:
Conversion of methanol to hydrocarbons
Zeolite
Methanol to gasoline
ZSM-5
Deactivation
Kinetic model
Catalyst lifetime
Conversion capacity

ABSTRACT

The deactivation of a zeolite catalyst in the conversion of methanol to hydrocarbons is described as a reduction of the effective amount of catalyst with time on stream. With the assumptions that the conversion of methanol is a first-order reaction, and that the loss of active catalyst is proportional to the conversion, an expression for the conversion with time on stream is obtained, which describes the experimental data well. This expression contains the rate constant, that characterizes the activity, and a deactivation coefficient that describes the deactivation behavior as parameters. It is shown that active catalysts show a more sudden decrease in conversion, and that the deactivation rate determines the time at which the decrease in conversion is observed. If the initial conversion is close to 100%, the lifetime to 50% conversion does not depend on the activity, and the deactivation coefficient is directly derived from the experimental data, by dividing the measured lifetime to 50% conversion by the applied contact time. The lifetime to all other conversion levels is dependent on both deactivation and activity, which implies that a catalyst lifetime to breakthrough of methanol does not scale with the deactivation rate. Likewise, it is shown that the conversion capacity is a good characterization of the deactivation, and this can be readily calculated as the product of the space velocity of methanol (WHSV) and the lifetime to 50% conversion. The amount of converted methanol at other conversion levels depends on the deactivation, the activity, and applied contact time (space velocity), and is therefore less appropriate to use as a characterization of the deactivation behavior.

1. Introduction

The methanol to gasoline (MTG) reaction is the conversion of methanol over a zeolite-based catalyst to light olefins (C_2–C_4) and liquid products in the boiling point range of gasoline, which typically occurs in the temperature range of 300–400 °C. In the TIGAS (Topsøe Integrated GASoline) process, the MTG reaction is combined with the methanol synthesis, and in this way an efficient process converting synthesis gas to gasoline is obtained [1,2].

The MTG reaction can be regarded as a sequential reaction, consisting of the following steps [3]:

$$\text{Methanol} \rightleftarrows \text{DME} \rightarrow \text{light olefins} \rightarrow \text{gasoline products}$$

and this is known to occur on a variety of zeolites [4]. The ZSM-5 zeolite, however, is the most commonly applied one, since it appears to be superior for this reaction. The MTG reaction over a ZSM-5-based catalyst is, like many other hydrocarbon reactions over zeolite catalysts, always accompanied by coke formation, which leads to deactivation of the catalyst. The deactivation by coke formation occurs through blocking the access to the active acid sites, either by deposition of carbonaceous compounds directly on the acid sites itself and in the micropore channels of the zeolite (internal coke), or by blocking the entrance to the micropores, thereby preventing the diffusion of methanol molecules into the zeolite structure (external coke) [5–11]. Loss of activity due to the coke formation is, in principle, reversible, and the catalytic activity can be restored by a regeneration that removes the deposited coke. A common procedure is to burn off the coke with oxygen at 500–600 °C [7,8,12,13]. Regenerated catalysts often show a somewhat lower activity than fresh ones, possibly due to dealumination of the zeolite, which typically occurs at elevated temperatures (>500 °C) in the presence of water.

As a consequence of the deactivation, the total amount of methanol that can be converted over a ZSM-5 catalyst is limited, and it is therefore important to know the deactivation behavior of the catalyst. To characterize catalyst deactivation, it is required to describe how the catalytic activity decreases during the catalyst lifetime. Different approaches for such a description have been developed. The approach often encountered in the literature is based on a description of carbon formation as a function of contact time, e.g. by the empirical Voorhies equation [11,14,15]. The catalyst activity is then related to the carbon content in the catalyst, using (semi-) empirical relations, resulting in the description of

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doi:10.1016/j.jcat.2009.03.004

the activity as a function of time [15–19]. The percolation model describes the coke formation in the zeolite channels and the accessibility of the active sites in more detail, from which then the activity is derived [20–23]. Clearly, in these approaches, catalyst deactivation is directly related to the formation of coke, and deactivation by dealumination is not included as such. The advantage of these models is that the catalyst deactivation is related to the chemistry of carbon formation in the zeolite channels, which is helpful in the design of zeolite structures with a stable activity for MTG.

Another approach is to describe the change in catalytic activity with time, and incorporate this in a kinetic model. This yields a phenomenological description, and is independent of the cause of deactivation. Usually, the activation is defined by the ratio of the rate expression after a given time on stream and that for the fresh catalyst, which results essentially in a time-dependent rate constant [24]. The deactivation often depends on parameters, such as conversion, current activity, or certain product concentrations, and is typically described by similar expressions as a reaction rate, based on rate constant and an activation energy for deactivation. The deactivation is then characterized by one or more rate constants and activation energies [25–29].

In this article, it will be shown that catalyst deactivation in MTG also can be described as a loss of the effective amount of active catalyst in the reactor during catalyst operation, instead of a decrease in the rate constant, also resulting in a phenomenological description of the deactivation. The rate at which the effective amount of active catalyst decreases is then a direct measure for the catalyst deactivation. This approach is similar to the concept of an effective space velocity, which was proposed previously by Dahl and Kolboe [30,31] and Sapre [32], as a reduced amount of active catalyst results in an effectively lower contact time or higher space velocity.

To measure the catalyst deactivation experimentally, the conversion with time on stream is followed under constant process conditions. The deactivation rate is then derived from a model that describes the observed decrease in conversion in terms of a loss of active catalyst. In this article, experimental data for a few selected ZSM-5 zeolites, showing different deactivation behavior, are presented. The deactivation rates determined in this way can, in principle, be used for further study of the influence of catalyst properties, e.g. acidity, particle size, or of process conditions, e.g. temperature, pressure, feed composition, on the catalyst deactivation. The scope of the present article, however, is confined to the derivation of a deactivation model, and the procedures that can be used to extract information on the deactivation behavior from the experimental data, with the aim to develop a method for the characterization of catalyst deactivation.

The model that is derived here is based on the assumptions that the conversion of methanol is a first-order reaction, and that the deactivation rate is proportional to the total conversion of methanol and DME. The rate constant and the deactivation rate appear as the parameters to be determined. Since the deactivation is regarded as a reduction of the amount of active catalyst, or of the number active sites, rather than a reduction of the intrinsic activity of an active site, the rate constant does not change with time in the model. Although this seems to be a severe simplification, it turns out that it describes the observed conversion of methanol with time on stream well, and, in addition, a surprisingly easy method to extract the deactivation rate from the experimental data is found. The experimentally determined deactivation rates and rate constants are used to calculate the catalyst lifetime and the conversion capacity. The model gives a clear insight on how the catalytic activity, the space velocity, and the deactivation behavior affect the measured conversions, the catalyst lifetime, and the conversion capacity of the catalyst.

2. Experimental

To measure the deactivation, the total conversion of methanol to hydrocarbons, i.e. the hydrocarbon yield calculated on a C-atom basis, is measured as a function of time. Though it does not include the conversion of methanol to DME, this is referred to as "conversion" throughout this paper; methanol and DME are assumed to be in equilibrium and treated as one kinetic species. The deactivation measurements have been performed in a 10-channel parallel reactor setup, using steel reactors with an inner diameter of 3 mm. About 150 mg of a ZSM-5 zeolite sample (150–300 μm sieve fraction) was loaded in each reactor, and one channel was left empty to measure the feed composition. The deactivation measurements were performed at 350 °C and 15 bar, using a feed of 14 mol% methanol in N_2 at a total flow rate of 350 Nml/min. The methanol (>99.9%, Aldrich Chromasolv®) was supplied by evaporation in the N_2 stream using a syringe pump (ISCO 500D, dual pump system). The flow through each channel lies between 8.5% and 11.5% of the total flow; the different flow in each reactor is accounted for in the analysis of the data.

The methanol and DME concentrations of the reactor exit gas were followed with a mass spectrometer, which is connected to the reactors via a channel selector valve (Valco, 10-position valve SC configuration). The total conversion of methanol X (hydrocarbon yield) was then determined from the intensities of the $m/e = 32$ and $m/e = 46$ signals for the respective reactor channels and the empty channel (feed) as follows:

$$X = 1 - \frac{y_{\mathrm{MeOH}} + y_{\mathrm{DME}}}{y^0_{\mathrm{MeOH}}} = 1 - \frac{I_{32} + B' I_{46}}{I_{32,\mathrm{feed}}} \tag{1}$$

The sensitivity factor B' is determined from the measured intensities at complete deactivation for hydrocarbon formation. At this point, the exit gas usually consists of methanol and DME in equilibrium. The factor B' is then determined as

$$B' = \frac{I_{32,\mathrm{feed}} - I_{32,\mathrm{deact}}}{I_{46,\mathrm{deact}}} \tag{2}$$

The $m/e = 32$ and $m/e = 46$ signals were chosen, since there is no contribution of any of the hydrocarbon products, and no interference between methanol and DME at these masses.

3. The deactivation model

The motivation to describe the catalyst deactivation as a loss of active catalyst is the characteristic change in product distribution of the MTG reaction over a ZSM-5 catalyst with time. The top panel in Fig. 1 shows these changes in product distribution as a function of time on stream at 350 °C using a feed of methanol in N_2.[1] Initially, a high selectivity for gasoline at full conversion of methanol is obtained (A). At some point, the selectivity for propylene (and ethylene) increases, and the gasoline production decreases (B). Note that the conversion is still 100% at this point, but this is a clear sign that the methanol breakthrough has almost been reached. In the next phase, the methanol breakthrough is observed, and first methanol and then DME are observed in the product stream, and the conversion gradually decreases (C). Finally, no hydrocarbons are formed any more, and methanol typically is in equilibrium with DME (D). In some cases, a deactivation for DME formation is also observed, which results in a further increase of the methanol and reduction of DME in the product stream.

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[1] This product distribution was determined by on-line GC on an FID detector. The sensitivity factors per C atom for methanol and DME are 0.778 and 0.667, respectively; for all other compounds a C-atom based sensitivity factor of 1 is used.

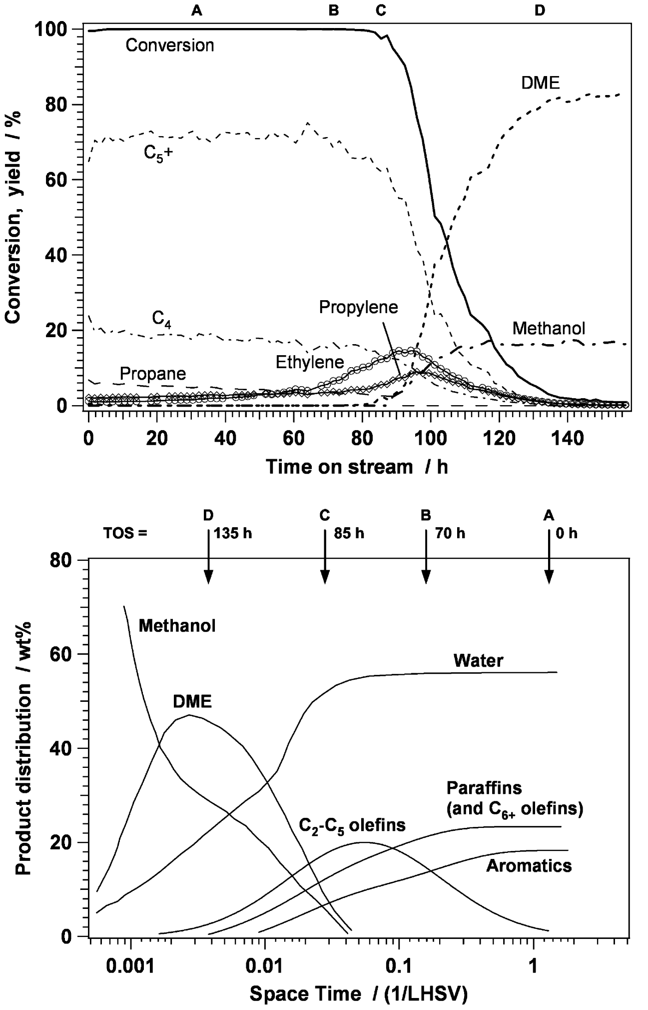

Fig. 1. Top panel: typical measured product distributions in the conversion of methanol to gasoline (350 °C, 15 bar, feed: 14% methanol in N_2, total flow 116 Nml/min, 500 mg ZSM-5 catalyst (Si/Al ≈ 70), WHSV = 2.8 g_{MeOH}/g_{cat}) with time on stream. Bottom panel: product distribution with different contact times, reproduced from Ref. [3]. Four different stages are distinguished: (A) complete conversion, (B) increase yield of ethylene and propylene, decrease of gasoline (C_5+) yield, (C) breakthrough of methanol, (D) methanol/DME equilibrium. The trend in product distribution with time on stream is reversed to that observed with contact time, suggesting that the catalyst deactivation is equivalent to a continuously decreasing contact time or a loss of active catalyst.

The bottom panel of Fig. 1 shows the variations in product distribution with contact time [3]. If we compare this product distribution with that observed during a catalyst life cycle, it looks as if the contact time, i.e. the ratio of amount of catalyst and flow (W/F), is continuously decreasing. This is indicated by the arrows shown in Fig. 1. In the procedure by Sapre [32], this observed decrease in contact time is corrected by reducing the flow in such a way that the conversion is kept constant; the required change in flow is then used as a measure of the catalyst deactivation. In this article, the deactivation has been measured under constant flow conditions, and the decrease in contact time is attributed to a decrease in the catalyst amount. Because no catalyst is physically removed from the reactor, this is then interpreted as a reduction of the effective amount of active catalyst. Consequently, a model describing how the effective space time, or effective amount of active catalyst varies during the catalyst life time also describes the catalyst deactivation in MTG. The rate at which the effective amount of active catalyst decreases is then the catalyst deactivation rate, which can be expressed in g_{cat}/h. This description of catalyst deactivation is equivalent to a description of deactivation by a time-dependent rate constant. An easy way to see this, without a formal derivation, is that the rate equations always contain the product of the rate constant and contact time, and therefore equivalent mathematical expressions are obtained with a time-dependent correction factor for either rate constant or contact time.

To derive an expression for the measured conversions as a function of time on stream, the deactivation rate is combined with a kinetic model. The general equations can be derived as follows. First, the deactivation rate is written as a change in the amount of catalyst with time:

$$\frac{dW}{dt} = -r_D \tag{3}$$

where W is the effective amount of catalyst, t is the time on stream, and r_D is the catalyst deactivation rate (in g_{cat}/h). With the definition of the contact time $\tau = W/F$, Eq. (3) becomes

$$\frac{d\tau}{dt} = -r'_D \tag{4}$$

Eq. (4) defines the deactivation rate r'_D (in g_{cat}/ mol_{gas}). As, by choice, the deactivation is a positive number, the minus sign indicates a loss of amount of catalyst. The deactivation rate r'_D represents the loss of active catalyst per mol of gas passed through the reactor, which could be interpreted as a “deactivation efficiency”; in this article, we will refer to this as deactivation rate as well.

Introducing the mass balance for a plug flow reactor $y_0 \frac{dX}{d\tau} = r$ – where r is an expression for the reaction rate, and y_0 is the concentration of the key reactant in the feed – and applying the chain rule for differentiation results in the basic equation for the conversion with time on stream:

$$\frac{dX}{dt} = \frac{dX}{d\tau}\frac{d\tau}{dt} \tag{5}$$

Eq. (5) is essentially the product of the expressions for the MTG reaction rate r, and for the deactivation rate $-r'_D$.

In principle, any expression for the deactivation rate and kinetic model can be introduced, and by solving the resulting differential equations, the conversion, and product compositions as a function of time on stream are found. In the present article, we determine the conversion as a function of time on stream, under the assumption that the deactivation rate is proportional to the conversion:

$$\frac{d\tau}{dt} = -aX \tag{6}$$

This assumption is motivated by the consideration that a certain fraction of the methanol that is consumed is transformed into coke product causing deactivation. The easiest assumption is that this fraction is constant, resulting in a proportional relation between conversion and deactivation.

It is furthermore assumed that the MTG reaction is a first-order reaction in the total (C-based) concentration of methanol + DME (y), leading to the familiar expression for the conversion:

$$\frac{dX}{dt} = k(1 - X) \tag{7}$$

According to Eq. (5), the conversion as a function of time on stream then becomes

$$\frac{dX}{dt} = \frac{dX}{d\tau}\frac{d\tau}{dt} = -kaX(1 - X) \tag{8}$$

Using the start condition that $t = 0$ at the conversion is equal to the initial conversion X_0, integration of Eq. (8) yields:

$$\ln\left(\frac{X}{1 - X}\cdot\frac{1 - X_0}{X_0}\right) = -kat \tag{9}$$

It is noted here that the initial conversion X_0 and rate constant are related through the rate expression for a first-order reaction. If we introduce $X_0 = 1 - \exp(-k\tau_0)$, the conversion with time on stream is written as

$$X = \frac{(\exp(k\tau_0) - 1)\exp(-kat)}{1 + (\exp(k\tau_0) - 1)\exp(-kat)} \tag{10}$$

Eq. (10). is the exact solution of Eq. (8), containing the rate constant k and the deactivation coefficient a as unknown parameters. The deactivation coefficient characterizes the deactivation behavior of the catalyst. The initial contact time τ_0 is the ratio of the total amount of fresh catalyst in the reactor and the total flow (W_0/F).

To give a feeling for the effects of the rate constant k and deactivation coefficient a on the observed deactivation behavior, the conversion with time on stream is calculated according to Eq. (10) for two different values of k and a, using a contact time $\tau_0 = 2$ g h/mol. The results are displayed in Fig. 2. It follows from Fig. 2 that for a given contact time, the position of the curves on the x-axis is determined by the deactivation rate, and that the activity affects the slope at which the conversion decreases from 1 to 0. As can be anticipated from Eq. (9), the point $X = 0.5$ is a special point: the curves for the same deactivation rate intersect here, indicating that, in this model, the lifetime to the 50% conversion level is independent of the activity.

Fig. 3 shows some examples of measured conversions with time on stream, for selected H-ZSM-5 samples with diverse activities and deactivation rates. Clearly, the measured conversions show different slopes and occur after different times on stream, corresponding to different combinations of activity and deactivation behavior. The solid lines represent calculated conversions according to Eq. (10), indicating that the model describes the experimentally observed conversions with time on stream well in all these cases.

To derive the values for the rate constant k and the deactivation coefficient from experimental data, the measured conversions can be fitted to Eq. (10). A faster method is to determine lifetime to two arbitrarily chosen conversion levels. From rearrangement of Eq. (10), the lifetime to a given conversion X can be written as

$$t = \frac{\ln(\exp(k\tau_0) - 1) - \ln\frac{X}{1-X}}{ka} \tag{11}$$

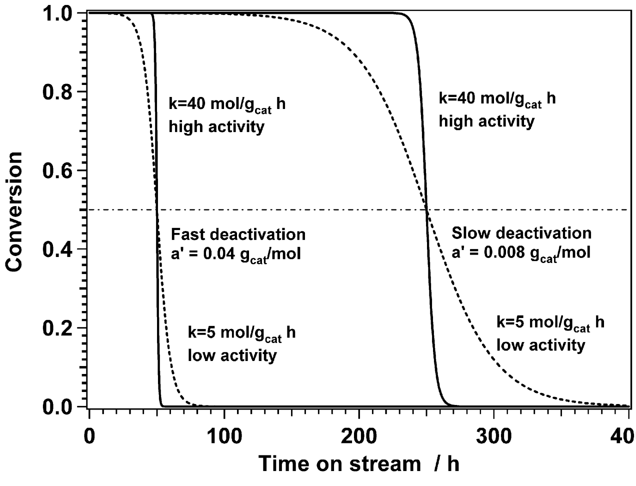

Fig. 2. Calculated conversion with time on stream for different combinations of activity and deactivation rates, according to Eq. (10), using $\tau_0 = 2$ g h/mol. Solid lines: high activity ($k = 40$ mol/g$_{cat}$ h). Dashed lines: low activity ($k = 5$ mol/g$_{cat}$ h). The curves intersect at a conversion of 0.5, indicating that the lifetime to this conversion level does not depend on the catalyst activity.

It is immediately clear that the term $\ln(X/(1 - X))$ in Eq. (11) becomes 0 for $X = 0.5$. The lifetime to this conversion level becomes:

$$t_{0.5} = \frac{\ln(\exp(k\tau_0) - 1)}{ka} \approx \frac{\tau_0}{a} \tag{12}$$

The approximation in Eq. (12) is valid for $\exp(k\tau_0) \gg 1$, which very often is the case. The error introduced by this approximation is less than 1% for $(\exp(k\tau_0) - 1)/k\tau_0 > 0.99$ or $X_0 > 0.967$. Eq. (12) shows that $t_{0.5}$ for active catalysts, indeed is independent of the activity, as indicated in Fig. 2, and that the value for the deactivation coefficient is obtained by division of the applied contact time τ_0 by the measured $t_{0.5}$. Once a is known, the value for the rate constant k is found by solving Eq. (11) for another conversion level; for the curves shown in Fig. 3, a conversion level of 0.8 was chosen, since this point usually lies on the steep descent in the experimental curves, thereby making the determination of the time on stream more accurate, compared to, e.g. the 95% conversion level. In addition, the methanol + DME concentration is then clearly distinguishable in the data, resulting in a more accurate measurement of the conversion. Table 1 summarizes the relevant experimental parameters and the calculated values for the rate constant and deactivation coefficients for the measured curves shown in Fig. 3, as an example. The accuracy of the measurement of the deactivation coefficient is found from a series of 19 measurements for sample A in Fig. 3. The average value for the deactivation coefficient in this series was 16.72 mmol/g, with a standard deviation of about 9%, corresponding to a relative error of about 18% at a confidence level of 95% for a single measurement.

4. Discussion

4.1. Catalyst lifetime

The catalyst lifetime is obviously limited by catalyst deactivation, and is therefore often used to characterize catalyst deactivation [33,34]. In this section, the relation between the deactivation coefficient and the catalyst lifetime is explored. The lifetime is defined here as the time to reach a given conversion level, e.g. the breakthrough of methanol, and is calculated directly by Eq. (11). An important point to realize is that the measured lifetime depends on the catalyst activity and contact time τ_0 used. As an example, the time to methanol breakthrough is calculated by introducing $X = 0.98$ in Eq. (11), and applying the approximation for high activity $\exp(k\tau_0) \gg 1$:

$$t_{0.98} = \frac{\tau_0}{a} - \frac{\ln(49)}{ka} \tag{13}$$

This indicates that the time to breakthrough and contact time τ_0 are linearly related, with a slope of $1/a$. However, the time to breakthrough and contact time are not proportional, since the line does not pass through the origin of the plot; the graph intersects the x-axis at $\tau_0 = \frac{1}{k}\ln\frac{X}{(1-X)} = \frac{1}{k}\ln(49)$, as shown in Fig. 4.

The non-proportional behavior between the lifetime and the contact time is well illustrated by the data of Kaarsholm et al. [34], who have reported a lifetime to breakthrough of 40 h at a $\tau_0 = 1.25$ s, and a ten times lower lifetime (=4 h) at half the contact time, $\tau_0 = 0.63$ s for a phosphorus-modified ZSM-5 catalyst in the MTO (methanol-to-olefins) reaction. It is tempting to interpret this as a faster deactivation rate at lower contact times, but this observation is in fact entirely consistent with a *constant* deactivation coefficient a of 0.0172[2] and rate constant of 6.94 s^{-1} (see Fig. 4). Therefore, the strong decrease in life time to the breakthrough of methanol is not necessarily due to a higher value of the deactivation

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[2] Since the contact time τ_0 is given on volume catalyst/volume reactor basis, the dimension of τ_0 is s, and the deactivation coefficient a becomes dimensionless.

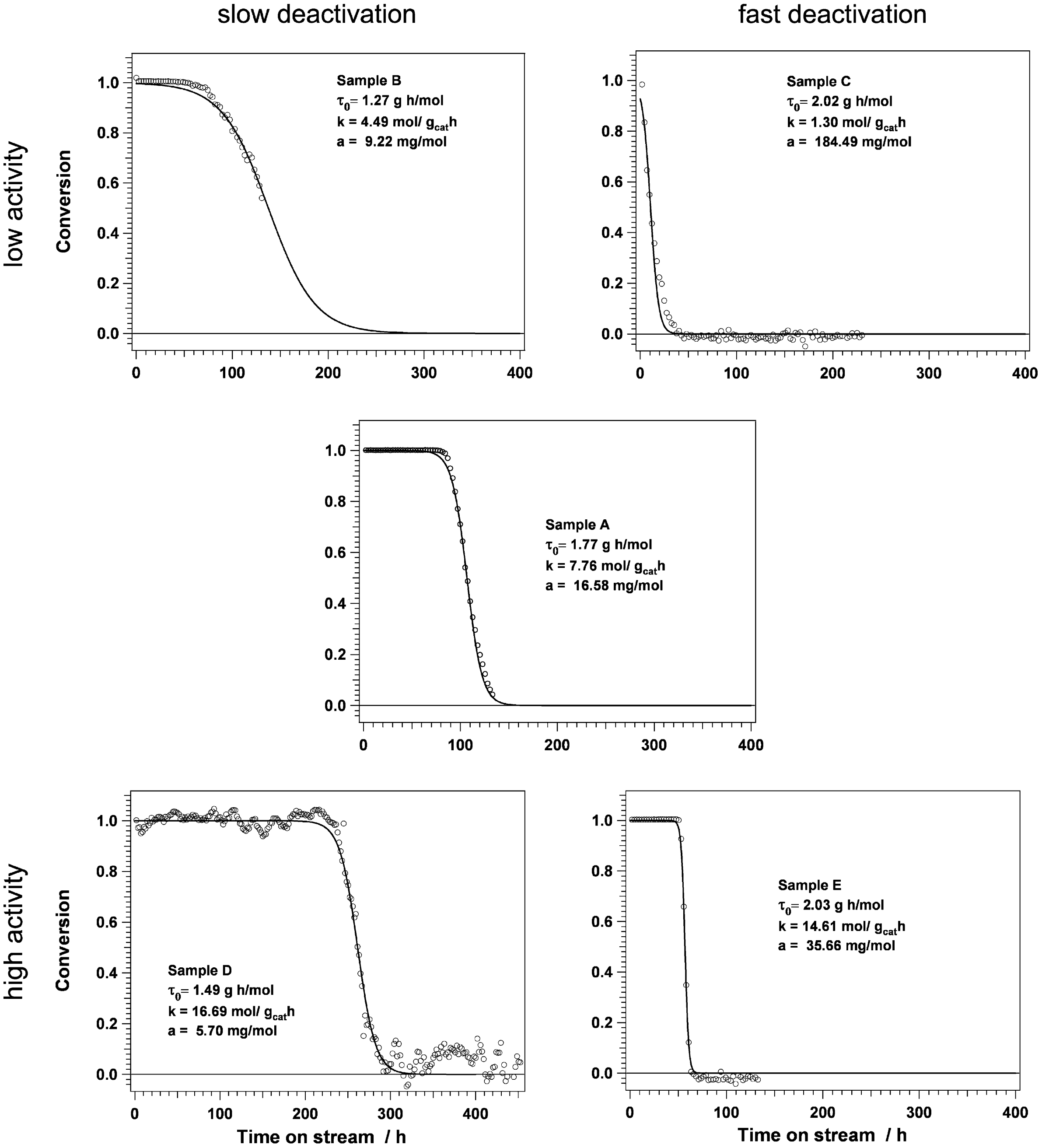

Fig. 3. Comparison of the calculated conversion levels with measured methanol conversions with time on stream on ZSM-5 catalysts at 350 °C and 15 bar g. The examples show cases with different combinations of low and high activity and deactivation rate.

Table 1
Calculated values of the rate constant, deactivation coefficient, and conversion capacity (g_{MeOH}/g_{cat}) for samples A–E shown in Fig. 3.

Sample	W_0 g	τ_0 g h/mol	y_{MeOH} (fract.)	WHS_{MeOH} g_{MeOH}/g_{cat} h	$t_{0.5}$ h	$t_{0.8}$ h	k mol/g_{cat} h	a mmol/g	R g_{MeOH}/g_{cat}
A	0.150	1.77	0.161	2.901	106.91	96.13	7.76	16.58	310.19
B	0.115	1.27	0.161	4.057	132.93	103.87	5.00	9.53	539.45
C	0.151	2.02	0.161	2.541	10.66	4.90	1.30	184.51	27.87
D	0.150	1.49	0.142	3.045	261.41	246.84	16.69	5.70	795.87
E	0.150	2.03	0.161	2.531	56.98	54.32	14.61	35.66	144.20

coefficient, indicating that the deactivation behavior of the catalyst has not changed. This also implies that a single measurement of the catalyst lifetime to breakthrough is not a sufficient characterization of the deactivation, since, for a given contact time, many combi-

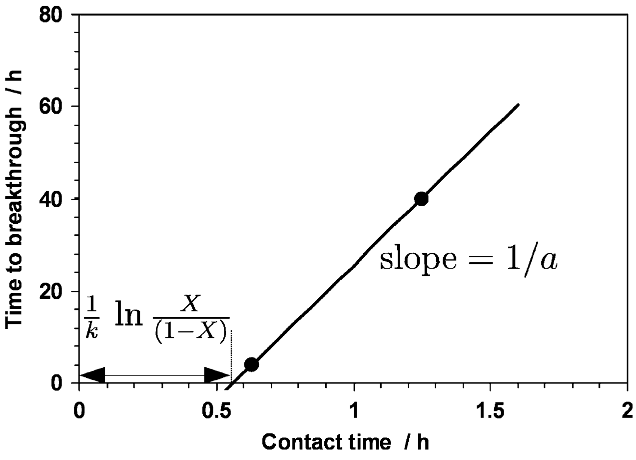

Fig. 4. Calculated catalyst lifetime to breakthrough of methanol (98% conversion) for $k = 6.94\ \mathrm{s}^{-1}$ and $a = 0.0172$. The line crosses the x-axis at $\tau_0 = 0.561$. The two data points indicate the life times reported in Ref. [34], showing that the decrease in lifetime by a factor of 10 when the contact time is decreased by a factor of 2 is consistent with a constant deactivation coefficient and catalyst activity.

nations of k and a result in that particular lifetime. Only if the rate constant is known, the deactivation coefficient can be derived from such an experiment, and a conclusion on the deactivation behavior can be drawn.

4.2. Methanol conversion capacity

Another consequence of the catalyst deactivation is that the amount of methanol that can be converted is limited. The maximum amount of methanol that can be converted per gram catalyst is referred to as the conversion capacity [35,36]. The assumption that the deactivation rate is proportional to the conversion implies that the amount of deactivated catalyst is proportional to the amount of converted methanol. Hence, the maximum amount of converted methanol is found from $W_0 = a'W_{\mathrm{MeOH,max}}$ and the conversion capacity can be written as

$$R_0 = \frac{W_{\mathrm{MeOH,max}}}{W_0} = \frac{1}{a'} = \frac{M_{\mathrm{MeOH}}y_{\mathrm{MeOH}}}{a} \tag{14}$$

where R_0 is the conversion capacity', $W_{\mathrm{MeOH,max}}$ is the maximum amount of converted methanol (g), W_0 is the initial amount of catalyst (g), and a' ($\mathrm{g_{cat}/g_{MeOH}}$) is the proportionality factor, which essentially is the deactivation coefficient as defined in Eq. (6); to arrive at the deactivation coefficient a (in $\mathrm{g_{cat}/mol_{gas}}$), the factor a' must be multiplied by the molar weight of methanol ($M_{\mathrm{MeOH}} = 32.04\ \mathrm{g\ mol^{-1}}$) and the mole fraction of methanol in the feed (y_{MeOH}). With the approximation for catalysts with high activity in Eq. (12), the conversion capacity becomes

$$R_0 = \frac{M_{\mathrm{MeOH}}y_{\mathrm{MeOH}}}{\tau_0}t_{0.5} = \mathrm{WHSV_{MeOH}}t_{0.5} \tag{15}$$

where $\mathrm{WHSV_{MeOH}}$ is the weight hourly space velocity of methanol. This means that according to the present model, the conversion capacity for active catalysts ($\exp(k\tau_0)) \gg 1$) can be found by multiplication of the space velocity of methanol by the measured time to reach 50% conversion. The conversion capacities for samples A–E in Fig. 3 calculated according to Eq. (15) are listed in the last column in Table 1.

The general expression for the amount of converted methanol per gram catalyst (R_X) at any conversion level can be found by integration of Eq. (10), as follows:

$$R_X = \frac{M_{\mathrm{MeOH}}y_{\mathrm{MeOH}}}{\tau_0}\int_0^{t'} X(t)\,dt \tag{16}$$

Substitution of the conversion and the time on stream (Eqs. (10) and (11)) results in the following (exact) expression for the amount of converted methanol as a function of the conversion:

$$R_X = R_0\left(1 + \frac{\ln(1-X)}{k\tau_0}\right) \tag{17}$$

where R_0 is the conversion capacity as given in Eq. (14), and X is the conversion level at which the amount of converted methanol is evaluated. R_X obviously becomes equal to the conversion capacity at $X = 0$. Eqs. (15) and (16) imply that for active catalysts, the integral $\int_0^\infty X(t)\,dt$ equals $t_{0.5}$. A graphic representation of this is given in Fig. 5: the area under the curve, which is calculated using Eq. (10), is equal to the area of the rectangle enclosed by $X = 1$ and $t_{0.5}$, as the areas of the hatched parts are equal.

Another method to find the conversion capacity is by linear extrapolation of a plot of the conversion as a function of the cumulative amount of converted methanol (R_X) to zero conversion [35,36]. Such an extrapolation requires that R_X depends linearly on the conversion for low conversions. As the term $\ln(1-X)$ in Eq. (17) can be approximated by $-X$, the amount of converted methanol at low conversions can be written as $R_X = R_0\left(1 - \frac{X}{k\tau_0}\right)$, which is indeed a linear dependence. Therefore, the extrapolation method to find the conversion capacity is consistent with the assumptions of a first-order reaction and a deactivation rate that is proportional to the methanol conversion. Bjørgen et al. found a conversion capacity of 165, 400, and $550\ \mathrm{g\ g^{-1}}$ for an untreated ZSM-5 zeolite, and two differently NaOH-treated zeolites, all measured at a WHSV of $8\ \mathrm{g_{MeOH}/g_{cat}}$. The $t_{0.5}$ derived from Fig. 5 in Ref. [35] are 21.8, 49.5, and 63.7 h. The conversion capacities according to Eq. (15) then become 174.4, 396.0, and $509.6\ \mathrm{g\ g^{-1}}$, which is close to the values obtained by the extrapolation method.

An important consequence from Eq. (14) is that the conversion capacity R_0 is independent of activity and contact time applied, and therefore it is a good characterization for catalyst deactivation. In contrast, the amount of converted methanol at other conversion levels R_X is less appropriate as a characterization for deactivation, since it depends on the activity and contact time. The conclusion that a treatment will affect the amount of converted methanol at 80% conversion in the same way as the conversion capacity [35] is only valid if the activity of the catalyst remains unchanged, as a consequence of this dependence.

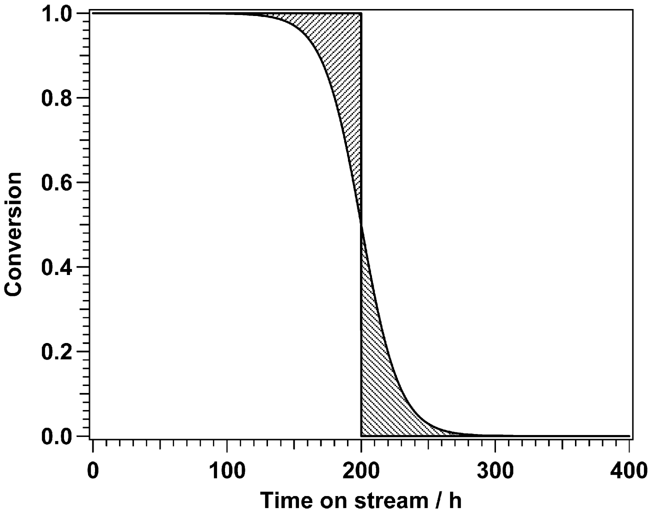

Fig. 5. Calculated conversion as a function of time on stream, using $k = 7\ \mathrm{mol/g_{cat}\ h}$, $a = 0.01$ g/mol, $\tau_0 = 2$ g h/mol. The area under the curve represents the conversion capacity, and is equal to the area of the rectangle enclosed by $X = 1$ and $t = t_{0.5}$, as the areas of the hatched parts are equal.

4.3. Final remarks

The procedures derived to determine the deactivation coefficient a (Eq. (12)) and the conversion capacity R_0 (Eq. (15)) from experimental data rely on the fact that the lifetime to 50% conversion only depends on the deactivation coefficient and not on the activity or contact time. This is, however, not a general property, but depends on the chosen expressions for the deactivation and reaction rate. A different kinetic expression for the reaction or for the deactivation rate leads to a different expression for the lifetime, instead of Eq. (11), which will generally be dependent on both the activity and the deactivation. Nevertheless, there may exist some special points in models based on other assumptions that are not dependent on the activity, similar to the lifetime to 50% conversion in the model discussed here. These points can form the basis for a fast and accurate determination of the deactivation behavior, independent of catalyst activity and applied contact time.

The assumption that the conversion of methanol on a ZSM-5 zeolite is first order is in fact quite rigorous. There seems to be consensus that the conversion of methanol proceeds via a hydrocarbon-pool mechanism, in which carbocations and hydrocarbon fragments adsorbed on the zeolite play a crucial role [4,30,31,37–43], and that the reaction is autocatalytic [29,44–49], showing an induction time. This indicates that the reaction shows a more complicated kinetic behavior than that assumed here. For this reason, the rate constants derived from deactivation model presented here should be used carefully. They probably give a good qualitative indication of the activity, and distinguish between high activity, moderate activity and low activity. It is also noted that a different choice for either the kinetic model or the deactivation rate may affect the values of both the rate constant and the deactivation coefficient. Nevertheless, the model presented here is capable of describing the observed conversion with time on stream well, despite the severe simplification of the kinetics, and clearly defines the conditions used for the determination of the activity and deactivation. This makes it possible to compare the activity and deactivation behavior of a wide variety of zeolites in the conversion of methanol to hydrocarbons on the same basis.

5. Conclusions

The deactivation of a ZSM-5 catalyst in the conversion of methanol to hydrocarbons can be described as a loss of effective amount of catalyst with time, or equivalently, a reduction of the effective contact time. The rate at which the effective amount of catalyst decreases with time is then a measure for the catalyst deactivation rate. Combining this with a rate equation for the conversion of methanol results in an expression for the conversion as a function of time. If it is assumed that the conversion of methanol to hydrocarbons is a first-order reaction, and that the deactivation rate is proportional to the methanol conversion, a good description of the experimentally determined conversion with time on stream is obtained for the methanol conversion on ZSM-5 zeolite at 350 °C. The model contains the first-order rate constant, which is a measure of catalyst activity, and a deactivation coefficient, which characterizes the deactivation behavior, as parameters.

Active catalysts show a more sudden decrease in conversion with time on stream, and the deactivation rate determines the time at which the decrease in conversion is observed. To extract the values for the activity and deactivation coefficient from the experimentally measured conversions with time on stream, the catalyst lifetime to two distinct conversion levels is determined, and the equation for the conversion with time on stream obtained in the model is solved for the rate constant and deactivation parameter. As a consequence of the assumptions that the reaction is first order and that the deactivation rate is proportional to the conversion, the lifetime to the 50% conversion level ($t_{0.5}$) is independent of the activity, if the initial conversion is close to 100%. In these cases, the deactivation coefficient is readily evaluated from the experimental data as the ratio of $t_{0.5}$ and the initial contact time.

The catalyst lifetime to the breakthrough of methanol depends not only on the deactivation rate, but also on the catalyst activity and chosen contact time or space velocity. Under the assumptions of the deactivation model presented in this article, the time to breakthrough depends linearly on the contact time; the slope is equal to the inverse of the deactivation coefficient, the intersection with the x-axis depends on the activity. The deactivation coefficient cannot be determined from a single lifetime measurement to catalyst breakthrough.

The assumptions that the reaction is first order and that the deactivation rate is proportional to the conversion also result in a conversion capacity that depends only on the deactivation rate. Therefore, the conversion capacity is a good characterization of the catalyst deactivation in the present model. For active catalysts, the conversion capacity is calculated as the product of the weight hourly space velocity (WHSV) of methanol and the lifetime to the 50% conversion level. The amount of methanol converted at the breakthrough, or other conversion levels of methanol, depends on the activity and contact time as well, and is therefore less appropriate as a characterization of catalyst deactivation.

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