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Catalyst deactivation by coking in the MTG process in fixed and fluidized bed reactors

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Abstract

The validity of a kinetic model for describing the deactivation of a catalyst based on a HZSM5 zeolite has been studied by carrying out reaction in fixed and fluidized bed reactors. The kinetic model takes into account that activity is dependent on the concentration of the lumps of oxygenates, of light olefins and of the remaining products and shows that coke formation capability follows this order. The difference between the deactivation kinetic constants calculated for the fixed and fluidized bed reactors is explained by the effect of the steam produced in the reaction, where coke stripping attenuates deactivation. Future improvements in the deactivation kinetic model must take into account coke stripping by the steam produced in the reaction.

Keywords: MTG process; HZSM5 zeolite; Deactivation kinetics

1. Introduction

The uniform microporous structure of the ZSM5 zeolite (in its acidic form, HZSM5) is responsible for high shape selectivity, which explains the high yield to gasoline in the MTG process (Methanol to Gasoline).

The HZSM5 zeolite has high resistance to dealumination under steam atmosphere which means that irreversible deactivation due to steam (formed in an important proportion as product) is insignificant up to temperatures around 500°C. This quality of the HZSM5 zeolite justifies its use as a catalyst in other processes, such as BETE [1] or in the transformation into hydrocarbons of the methanol plus water stream, which is a byproduct originated in the MtBE (Methyl *tert*-Butyl Ether) production in refineries [2,3].

The deactivation by coking is lower than that of amorphous silica/alumina and that of zeolites with a higher pore size, such as faujasite, mordenite and zeolites X and Y [4]. This lower deactivation is due to the steric hindrance of HZSM5 zeolites, which limits the condensation of aromatic rings in the internal channels of the crystals [5,6]. On the other hand, pore blockage does not occur so easily as with microporous zeolites [7]. However, the deactivation by coking is fast enough to condition the global economy of the MTG process, which is carried out in an adiabatic fixed-bed reactor under reaction–regeneration cycles [8,9]. An alternative is the operation in fluidized bed reactor with catalyst circulation, in which the catalyst is regenerated in an external unit [10]. The thermal stability of the HZSM5 allows for complete recovery of its activity after coke combustion in air stream at 550°C, which is

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carried out subsequent to thermal equilibration treatment [11].

Of the nature and location of the coke [4,6,12–16], it is concluded that the coke deposited over HZSM5 zeolite is more hydrogenated than the coke deposited over other acidic catalysts, which can be due to the effect of both the low activity for hydrogen transfer of the HZSM5 zeolite and the confined space of its pores.

Coke is heterogeneously distributed along the interior of the channels of the zeolite and the intersections between straight channels and zig-zag channels [13,15,17]. The internal coke deposited into the channels is soluble in pyridine, slightly developed and, finally, has a high H/C ratio corresponding to nonaromatic (oligomers) and monoaromatic structures, either methylated or not. The internal coke that partially blocks the channel intersections is slightly soluble, more developed, with a lower H/C ratio, and its heavier structures are made up of biaromatics. Due to the high degree of crosslinking the porous structure, pore blockage is only appreciable by N_2 adsorption, when the catalyst activity is very low [18]. Only in this situation is the access to the channels blocked by externally deposited coke.

Due to the low molecular weight of coke, it is unstable when it is subjected to thermal and sweeping treatments with an inert gas, which are stages prior to regeneration by coke combustion. Consequently, in order for coke combustion to be reproducible, a standard equilibration treatment of the catalyst with coke is required [11].

One of the consequences of catalyst deactivation due to coke, in addition to the decrease of methanol conversion with time on stream, is the evolution of selectivity. Although, the effect of the structure and of the composition of the HZSM5 zeolites on the selectivity of the MTG has been studied in the relevant literature [19,20], there are few studies on the evolution of selectivity with deactivation. The results obtained in pilot plants operating with an adiabatic fixed bed reactor [8,21], are difficult to interpret as these reactors have a pronounced temperature profile. The results obtained in isothermal fluidized bed reactor [10,22] show that, as a consequence of deactivation, the yield to gasoline decreases and the production of light olefins (primary products and intermediates in the reaction scheme) increases.

There are few papers concerning the kinetic modelling of deactivation, knowledge of which is necessary for the design of the reactor and for interpreting the evolution of selectivity with deactivation. The kinetic models proposed in the literature are simplified and empirical, and consider deactivation in an approximate way. The effect of concentration of reactants and/or products is not taken into account [8,10,23,24], although the need for considering the effect of concentration over the deactivation kinetics by coke deposition is clearly established in the literature [25–27].

In this paper a kinetic model of deactivation proposed in a previous paper [28] has been used for interpreting the results in integral fixed and fluidized bed reactors, which allows for comparing the performance of these reactors from the point of view of deactivation. Unfortunately, the information in the literature concerning these subjects is scattered, as it corresponds to different reaction conditions. In this work, we tried to analyse deactivation under reaction conditions that are delimited and similar to those of the industrial operation. Thus, the results will be of great interest for the global comprehension of catalyst deactivation in the MTG process.

2. Experimental

The catalyst has been prepared [29] from a HZSM5 zeolite, synthesized by following the methods proposed by Mobil. The zeolite has been subjected to an agglomeration process with bentonite (Exaloid), using fused alumina (Martinswerk) as inert charge. The properties of the HZSM5 zeolite are: Si/Al, 42; ratio Bronsted/Lewis, 2.9; pore volume, 0.65 $cm^3 g^{-1}$; micropore volume, 0.17 $cm^3 g^{-1}$ (99% of diameter <0.7 nm); apparent density, 0.94 $g cm^{-3}$; BET area, 420 $m^2 g^{-1}$; crystallinity, 97%; crystal size, 6.3 μm. The catalyst properties are: particle size, between 0.3 and 0.5 mm; pore volume, 0.43 $cm^3 g^{-1}$; apparent density, 1.21 $g cm^{-3}$; BET area, 124 $m^2 g^{-1}$. Prior to use the catalyst is calcined at 570°C for 2 h (in order for the experimental results to be reproduced under reaction–regeneration cycles).

The reaction has also been carried out in an automated isothermal fixed bed integral reactor of 0.7 cm internal diameter [30], and in a fluidized bed reactor of

3.0 cm internal diameter, under the following conditions: temperature in fixed bed reactor, in the 320–380°C range (at higher temperatures, an isothermal bed is not guaranteed); temperature in fluidized bed reactor, in the 360–420°C range; contact time, between 0.01 and 0.15 (g of catalyst) h (g of methanol)$^{-1}$; time on stream, up to 10 h; partial pressure of methanol in the feed (diluted with helium), 88 kPa. The products are analysed by gas chromatography. The calculation of the weight fraction of the lumps defined in the different kinetic models is carried out by means of a program in FORTRAN, on the basis of the composition of each individual product obtained in the chromatographic runs [31]. Subsequent to the reaction the catalyst bed was subjected to sweeping with helium (100 cm^3 min^{-1}) for 30 min.

3. Kinetic modelling of deactivation

As has been previously mentioned, the effect of composition upon deactivation has not been taken into account in the literature. Liederman et al. [10] introduce an exponential function for activity vs. time on stream, considering both the effect of deactivation and of methanol dilution with an inert upon the kinetics of the process. Although Chang [32] did not take into account catalyst deactivation in his kinetic model for the MTG process, Sedran et al. [24] have used that model, considering that the kinetic constants of the individual steps, k_i, are the mean values for a range of time on stream. The kinetic constants are defined as the product of their value for a zero level of coke deposited, k_{i0}, by the activity, f

$$k_i = k_{i0}f. \tag{1}$$

Sedran et al. [23] have proposed different kinetic models that take into account the distribution of olefins in the MTG process. The deactivation is quantified by means of an empirical equation that relates the decrease of the kinetic constants to the cumulative amount of hydrocarbons produced per catalyst mass unit, $\bar{H}_c/W$,

$$k_i = k_{i0}\exp\left(-\beta_i\frac{\bar{H}_c}{W}\right). \tag{2}$$

Schipper and Krambeck [8] defined catalyst activity for a given time on stream, β, as the product of two activity terms, which correspond to the remaining activity due to irreversible deactivation (by deterioration of acidic structure), α, and to the remaining activity due to reversible deactivation (by coke deposition), a,

$$\beta = \alpha a. \tag{3}$$

The expression proposed by Schipper and Krambeck [8] for total deactivation is

$$\frac{d\beta}{dt} = \alpha[-k_d(\alpha a)^d - K_\alpha\alpha^{h-2}(\alpha a)]. \tag{4}$$

Under the experimental conditions of this paper, only reversible deactivation takes place. A kinetic model proposed in a previous work has been used [28], which takes into account the effect of concentration of the lumps on the deactivation by coke

$$-\frac{da}{dt} = (k_{dA}X_A + k_{dC}X_C + k_{dD}X_D)a, \tag{5}$$

where A denotes oxygenates (methanol and dimethylether); C, light olefins (ethylene and propylene) and D, lump of the rest of hydrocarbons. Activity, a, refers to reaction rate [28]

$$\begin{aligned} a = \frac{r_i}{r_{i0}} &= \frac{(dX_A/d(W/F_{M0}))_t}{(dX_A/d(W/F_{M0}))_{t=0}} \\ &= \frac{(dX_C/d(W/F_{M0}))_t}{(dX_C/d(W/F_{M0}))_{t=0}} \\ &= \frac{(dX_D/d(W/F_{M0}))_t}{(dX_D/d(W/F_{M0}))_{t=0}}. \end{aligned} \tag{6}$$

The hypothesis that only reversible deactivation (by coking) occurs is based on the experimentation carried in a previous paper [33] where the catalyst recuperates its activity after successive cycles of reaction–regeneration (by combustion of the coke with air at 550°C). This result shows that the acid structure does not suffer irreversible deactivation (by steaming) throughout the reaction and regeneration steps.

Eq. (5) takes into account the effect on deactivation of the concentration of the three lumps of the kinetic model at each longitudinal reactor position. The preferable deposition of coke at the reactor inlet (where X_A value is higher) is known from literature [18,34], but under the reaction conditions, light olefins and aromatics contained in the lump of the remaining products cannot be ignored as possible coke precursors.

For the zero time on stream kinetics of the MTG process, the following scheme has been adopted:

$$A \xrightarrow{k_1} C$$

$$2C \xrightarrow{k_2} D$$

$$A + C \xrightarrow{k_3} D$$

$$C + D \xrightarrow{k_4} D$$

The selection of this kinetic scheme (in which the steps are considered elementary), instead of others [32,35] that have also been proven to be valid [36] is due to its application possibilities in a wide range of operating conditions, especially of temperature.

4. Deactivation in fixed and fluidized bed reactors

For the analysis of kinetic data and calculation of the kinetic parameters, a rigorous methodology has been applied [30,36,37], which consists of solving the mass conservation equation in the reactor, for each of the lumps, and assuming plug flow.

In order to calculate the kinetic scheme parameters of the MTG process, the following equation must be solved:

$$\frac{\mathrm{d}X_i}{\mathrm{d}\xi} = \frac{Z(1-\epsilon)}{u\epsilon}\rho\frac{RT}{P\bar{M}}\frac{m}{m_t}r_{i0} - \frac{X_i}{u}\frac{\mathrm{d}u}{\mathrm{d}\xi}. \qquad (7)$$

For the calculation of the deactivation kinetic parameters the equation to solve is

$$\frac{\partial X_i}{\partial t} = -\frac{u}{Z}\frac{\partial X_i}{\partial \xi} + \frac{(1-\epsilon)}{\epsilon}\rho\frac{RT}{P\bar{M}}r_{i0}\frac{m}{m_t}a. \qquad (8)$$

Given this methodology, the main requirements in a study of this nature are fulfilled [27,38,39]: (a) activity is defined referring to the reaction rates corresponding to the different states of the catalyst, but it is calculated for the same value of temperature and composition; (b) the real past history of the catalyst is rigorously taken into account.

The results of composition at the reactor exit corresponding to zero time on stream have been equal for both reactors when they operated with the same value of space time and temperature. Nevertheless, deactivation is appreciably lower in the fluidized bed reactor. Fitting the results of composition for zero time on stream vs. space time and those of composition vs. time on stream to the kinetic model, the following values for the kinetic parameters have been obtained.

For the main reaction (MTG process) (320–420°C):

$k_1 = 0.315 \times 10^7 \exp(-15720/RT)$,
$k_2 = 0.155 \times 10^3 \exp(-6055/RT)$,
$k_3 = 0.154 \times 10^7 \exp(-13500/RT)$,
$k_4 = 0.141 \times 10^3 \exp(-5000/RT)$.

For the deactivation in fixed bed reactor (320–380°C):

$k_{da} = 0.165 \times 10^9 \exp(-25870/RT)$,
$k_{dC} = 0.121 \times 10^6 \exp(-18930/RT)$,
$k_{dD} = 0.603 \times 10^8 \exp(-26280/RT)$.

For the deactivation in fluidized bed reactor (360–420°C)

$k_{dA} = 0.163 \times 10^8 \exp(-23700/RT)$,
$k_{dC} = 0.526 \times 10^4 \exp(-14570/RT)$,
$k_{dD} = 0.121 \times 10^8 \exp(-24130/RT)$.

In Figs. 1 and 2 some results are shown as an example for illustrating the validity of the calculated kinetic parameters for the simulation of the corresponding reactor. In these figures the lump composition calculated by the kinetic model (lines) and the experimental results (points) obtained are shown. Each plot corresponds to a temperature and a space time value. The fitting for the other conditions is also adequate.

As an example of the different deactivation in the fixed and fluidized bed reactors, the results of Fig. 1(d) (fixed bed at 380°C and W/F_{M0}=0.0261 (g of catalyst) h (g of methanol)$^{-1}$) and Fig. 2(b) (fluidized bed at 380°C and W/F_{M0}=0.0272 (g of catalyst) h (g of methanol)$^{-1}$) can be compared.

It is noteworthy that, in the kinetic study, two characteristics of the fluidized bed reactor have been taken into account:

1. *Attrition.* The catalyst mass loss due to attrition (2.71 wt% h^{-1}) has been taken into account, as it implies an important contribution to total deactivation. In the mathematical solving of Eq. (8), attrition has been considered as catalyst mass (or space time) reduction.
2. *Uniform activity for the whole catalyst mass.* This is a consequence of mixed regime for the solid.

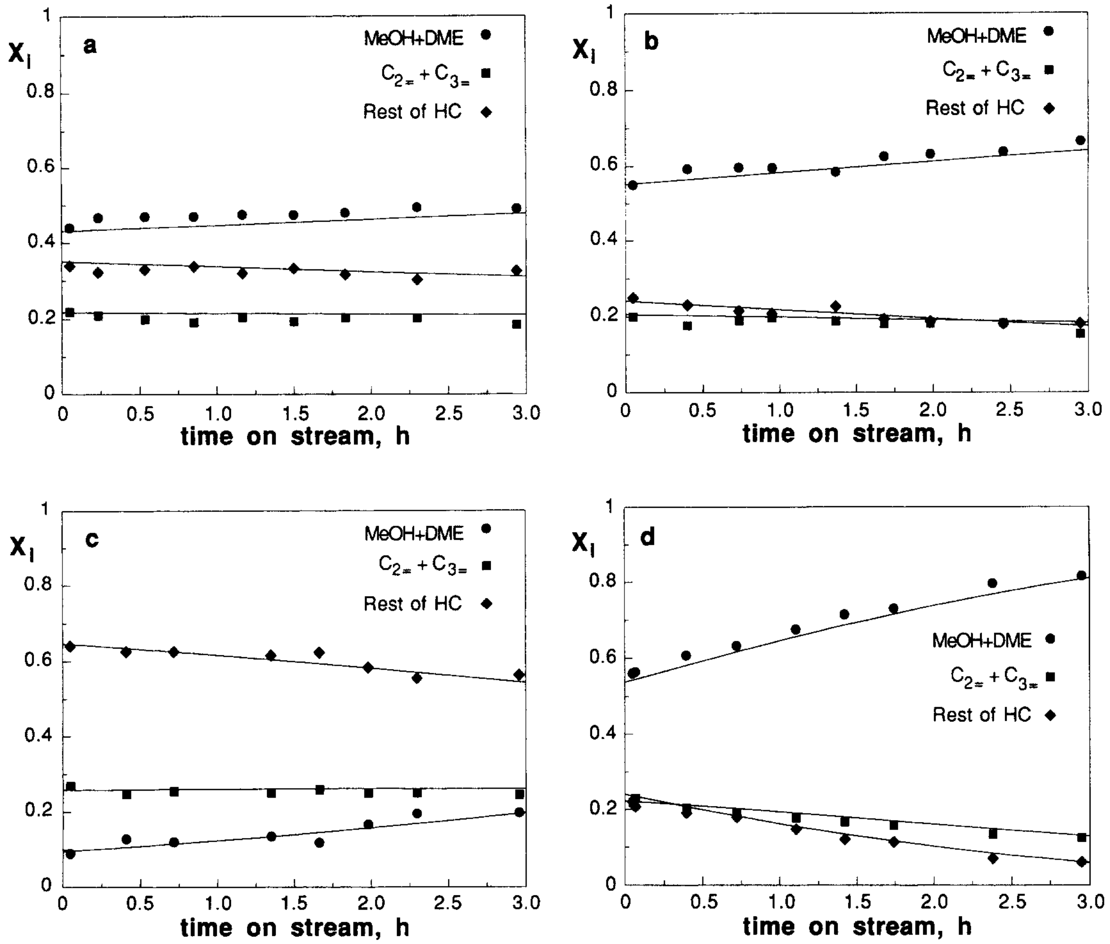

Fig. 1. Results of the evolution of lump composition with time on stream corresponding to the fixed bed reactor. The lines have been calculated with the kinetic model and the points are experimental. Plot a: temperature=320°C; space time=0.1125 (g of catalyst) h (g of methanol)$^{-1}$. Plot b: 340°C; 0.0545 (g of catalyst) h (g of methanol)$^{-1}$. Plot c: 360°C; 0.1234 (g of catalyst) h (g of methanol)$^{-1}$. Plot d: 380°C; 0.0261 (g of catalyst) h (g of methanol)$^{-1}$.

This uniformity for each time on stream has been taken into account in the mathematical solving of Eq. (8). As an example of the way the evolution of activity with time on stream has been taken into account, the longitudinal profiles of activity in the fixed bed reactor for different values of time on stream have been plotted in Fig. 3. In Fig. 4 the evolution of activity (uniform along the position in the bed) through time on stream has been plotted. The results of Figs. 3 and 4 have been calculated for the same value of temperature (380°C) and of space time (0.0272 (g of catalyst) h (g of methanol)$^{-1}$).

Analysing the results, the following order of the values of the deactivation kinetic parameters is observed:, $k_{dA} \gg k_{dD} > k_{dC}$ which shows the higher potential capacity of the oxygenate lump for coke forming, while the capacity for degradation to coke of the aromatics contained in lump D and of the light olefins (lump C) is appreciably lower. This result explains the experimental fact observed by different authors that coke is preferably deposited at the inlet zone of the bed, while coke content is low in the zone near the exit of the bed, when excessive amount of catalyst is used (so that the catalyst is in contact with a stream without oxygenates).

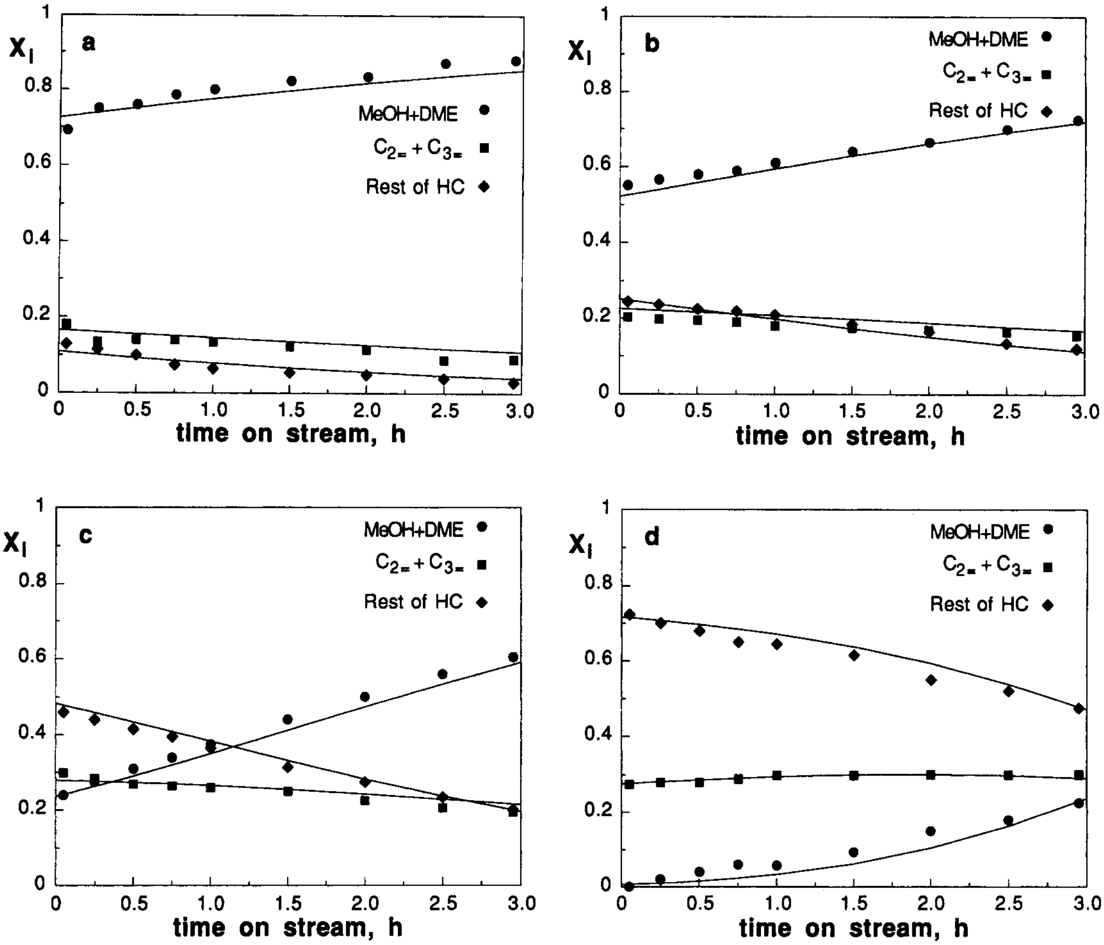

Fig. 2. Results of the evolution of lump composition with time on stream corresponding to the fluidized bed reactor. The lines have been calculated with the kinetic model and the points are experimental. Plot a: temperature=380°C; space time=0.0148 (g of catalyst) h (g of methanol)$^{-1}$. Plot b: 380°C; 0.0272 (g of catalyst) h (g of methanol)$^{-1}$. Plot c: 400°C; 0.0383 (g of catalyst) h (g of methanol)$^{-1}$. Plot d: 420°C; 0.8698 (g of catalyst) h (g of methanol)$^{-1}$.

The deactivation kinetic model corresponds to a deactivation in parallel with the main reaction, as the preferable coke precursor is the reactant (oxygenates). This parallel deactivation can explain the evident result of this and other papers that the deactivation in fluidized bed is lower than in fixed bed due to the homogenization of bed activity, which avoids the inconvenience of preferable deactivation at the inlet zone of the reactor (a characteristic of the fixed bed reactor with parallel deactivation).

Nevertheless, the difference in the values obtained in this paper for the kinetic parameters of deactivation in fixed and fluidized bed, cannot be explained if the kinetic model of deactivation, Eq. (5), is correct, as the uniformity of activity in the fluidized bed reactor has already been taken into account in the calculation of the kinetic parameters. Having proven that the kinetic model of deactivation is valid when the results of the fixed and fluidized bed reactors are fitted with the kinetic parameters corresponding to each reactor, our explanation is based on the fact that some factor has not been taken into account in the deactivation kinetic model and that this factor has a different effect on both reactors. The non-considered factor is the presence of steam (product) in the reaction medium. The attenuation of deactivation by steaming is cited

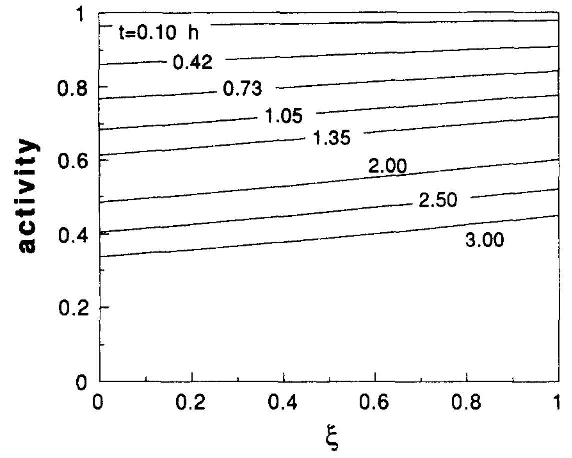

Fig. 3. Evolution of activity profile along the fixed bed reactor with time, calculated for 380°C and for a space time of 0.0272 (g of catalyst) h (g of methanol)$^{-1}$.

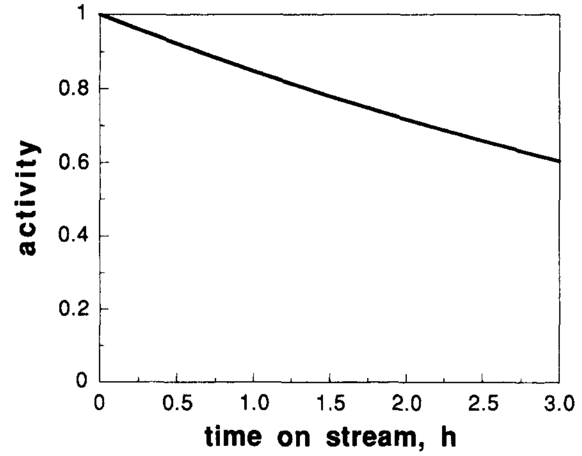

Fig. 4. Decrease in catalyst activity with time on stream in the fluidized bed reactor, calculated for 380°C and for a space time of 0.0272 (g of catalyst) h (g of methanol)$^{-1}$.

[40] and, with this aim, the feeds to be treated with HZSM5 zeolites are mixed with water [41–43]. Similarly, the resistance of these zeolites to high contents of steam is known; nevertheless, there are no actual studies that explain the cause of deactivation attenuation due to steam and which quantify this attenuation.

In this paper, coke deposition in the fixed bed reactor has been studied carrying out reactions by feeding different proportions of methanol diluted with water. In Fig. 5, coke content in the lower and upper half of the bed has been plotted against methanol concentration in the feed (in wt%), at 380°C, space time 0.1236 (g of catalyst) h (g of methanol)$^{-1}$ and time on stream 3 h. The results show the pronounced attenuation of coke deposition due to steam, which can be attributed to the stripping of the evolving coke. This explanation agrees with the nature of the coke in this process (highly hydrogenated, unstable, with low molecular weight, liable to transformation by thermal and sweeping treatments) [18,44]. It has also been proven that there is no irreversible deactivation by zeolite dealumination within the temperature range studied and that the catalyst used in the experiments in Fig. 5 recuperates its activity after successive cycles of reaction–regeneration (by combustion of the coke with air at 550°C). It can be observed in Fig. 5 that when the steam concentration is higher than 50 wt% at the reactor inlet, coke deposition in the lower and upper half of the bed is similar.

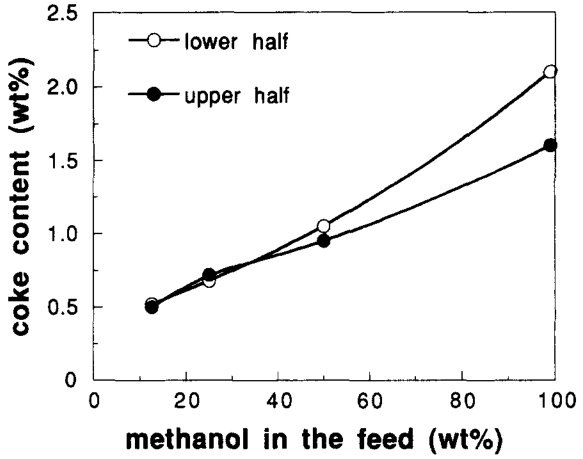

Fig. 5. Effect of the content of methanol in the feed (made of methanol plus water) on the coke content within the catalyst, in the lower and upper halves of the fixed bed reactor. Temperature=380°C; space time=0.1236 (g of catalyst) h (g of methanol)$^{-1}$; time on stream=3 h.

The stripping of the coke with the steam produced in the reaction can explain the different coke deposition observed in the fixed and fluidized bed reactors when no steam is fed. In Fig. 6 coke content has been plotted against time on stream. The results correspond to runs carried out at 380°C and for a space time of 0.1236 (g of catalyst) h (g of methanol)$^{-1}$. In the fixed bed reactor, coke content within the catalyst has been measured in the lower and upper halves. It can be observed that coke content in the fluidized bed reactor

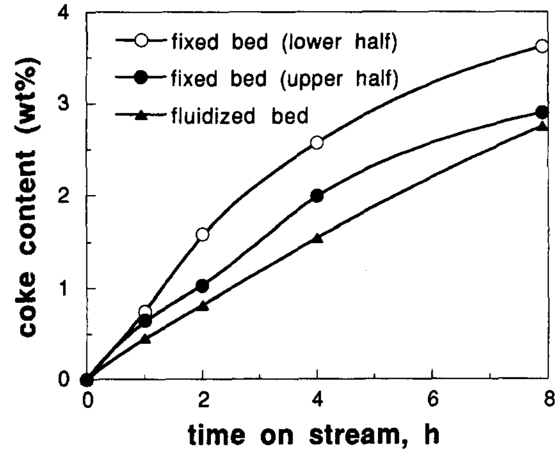

Fig. 6. Evolution with the time on stream of the coke content on the catalyst, in the fluidized bed reactor and in the lower and upper halves of the fixed bed reactor. Temperature=380°C; space time=0.1236 (g of catalyst) h (g of methanol)$^{-1}$.

is appreciably lower than that corresponding to both halves of the fixed bed reactor, which can be explained by the mixing regime in the fluidized bed reactor, as it allows the whole catalyst amount to be subjected to the stripping with the steam produced in the reaction.

It must be pointed out that the difference between coke deposition in fixed and fluidized bed reactors is in agreement with the different values calculated for the deactivation kinetic parameters for both reactors. In the same way, the different coke amount deposited in the lower and upper halves of the fixed bed reactor is in agreement with the deactivation kinetic model.

The fact that the deactivation kinetic model, Eq. (5), is valid for each one of the two reactors can be explained by the steam content to be implicitly taken into account in the model, as it is reciprocally proportional to concentration of oxygenates, X_A. Nevertheless, the effect of coke stripping on deactivation would require the concentration of water to be taken into account as an independent term in the kinetic model. This term would attenuate the deactivation.

5. Conclusions

Eq. (5) can be used without great difficulty in a wide range of reaction conditions together with kinetic models for the MTG process at zero time on stream expressed in terms of lumps for simulation of the reactor under strategies that can be applied to the MTG process at a larger scale than the one studied in this work (adiabatic fixed bed reactor operating under reactor-regeneration cycles, or in isothermal fluidized bed with catalyst circulation). The use of Eq. (5) can provide a better approximation to practical reality with respect to the use of other empirical equations that do not take into account the effect of composition upon deactivation.

The effect of the composition of the lumps of the kinetic scheme on deactivation gives way to a slight advantage of the fluidized bed over the fixed bed when the catalyst attrition problem is avoided by means of a suitable catalyst preparation technique.

The difference observed between the values of the deactivation kinetic parameters for the fixed and fluidized bed reactors must be explained on the basis of some limitation of the kinetic model. In this paper experimental evidence has been obtained on the effect of steam produced in the reaction, whose coke stripping attenuates coke evolution and, consequently, catalyst deactivation decreases. Our proposal is that the development of the deactivation kinetic model must be directed towards the quantitative consideration of this effect on deactivation, which will presumably be more important as reaction temperature increases.

6. Notation

A, C, D	lump of oxygenates (methanol and dimethylether), of light olefins (ethylene and propylene), and of the rest of products, respectively
a	remaining catalyst activity due to coke deposition, referred to the reaction rate, Eq. (6)
d	deactivation order for coke deposition
F_{M0}	mass flow of methanol fed, (g of methanol) h^{-1}
f	remaining catalyst activity referred to the kinetic constant, Eq. (1)
$\bar{H}_c$	cumulative amount of hydrocarbons produced, g
h	irreversible deactivation order

K_α	kinetic constant for irreversible deactivation, h^{-1}
k_d	kinetic constant for deactivation by coke deposition, h^{-1}
k_{di}	kinetic constant for deactivation by coke formation for lump i, h^{-1}
k_i, k_{i0}	kinetic constant for formation of lump i for a given value of time on stream, and for the fresh catalyst, h^{-1}
k_1, k_2, k_3, k_4	kinetic constants for the different individual steps of the kinetic scheme, h^{-1}
$\bar{M}$	average molecular weight of the water free products, $g\ mol^{-1}$
m, m_t	mass flow of water free products and total mass flow, $g\ h^{-1}$
P	partial pressure of water free products, atm
R	constant of the gases, $cal\ mol^{-1}\ K^{-1}$ ($atm\ m^3\ mol^{-1}\ K^{-1}$ in Eq. (7))
r_i, r_{i0}	reaction rate of lump i formation, for a given value of time on stream, and for the fresh catalyst, (g of lump i) (g of total mass) h^{-1} (g of catalyst)$^{-1}$ (g of water free products)$^{-1}$
T	temperature, K
t	time on stream, h
u	gas linear velocity, $m\ h^{-1}$
W	catalyst mass, g
X_i	weight fraction of lump i, on a water-free basis
Z	total length of the reactor, m
z	longitudinal coordinate of the reactor, m

Greek letters

α	remaining catalyst activity due to irreversible deactivation, referred to the reaction rate
β	remaining catalyst activity due to coke deposition, referred to the reaction rate, Eq. (3)
β_i	deactivation coefficient, Eq. (2)
ϵ	bulk porosity
ρ	catalyst density, $g\ l^{-1}$
ξ	dimensionless longitudinal coordinate of the reactor (z/Z)

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