Role of Water in the Kinetic Modeling of Catalyst Deactivation in the MTG Process

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A kinetic model is proposed for deactivation by coke of a HZSM-5 zeolite catalyst used in the transformation of methanol into hydrocarbons in the 573−723 K range. The attenuating effect on coke deposition due to the presence of water in the reaction medium was quantified by a parameter that increases with reaction temperature. The slower deactivaton of the methanol dehydration step compared to the formation steps of olefin and gasoline lumps is taken into account. In view of the results, water content in the reaction medium is an efficient variable for controlling the results of activity−selectivity−deactivation. This model is not applicable for a temperature of 723 K when water content in the reaction medium is high, due to the fact that under these conditions the zeolite is subjected to irreversible deactivation.

Introduction

Rapid deactivation of the catalyst by coke is the principal inconvenience in the transformation of methanol into gasoline (MTG process) on a HZSM-5 zeolite catalyst. The operation strategy based on an adiabatic fixed bed that operates in cycles of reaction−regeneration was adopted in the MTG process at a time when the known technology of the fluidized bed with catalyst circulation was so limited that its industrial implementation was somewhat adventurous (Allum and Williams, 1988; Yurchak, 1988; Chang, 1991). Subsequent studies have revealed the great advantages of the fluidized bed, and so this technology has been proven to be the most suitable for this process (Chang and Silvestri, 1987; Ortega et al., 1998; Gayubo et al., 2000).

It is well known that catalyst deactivation is attenuated by feeding water with methanol; nevertheless, water also attenuates the steps of the main reaction and, consequently, process selectivity is modified and the yield of light olefins is increased at the expense of reducing the production of aromatics (Van den Berg et al., 1981; Chang, 1983; Benito et al., 1996a).

Due to the effect of water on the main reaction and on deactivation, control of water content in the reaction medium is an interesting way of improving the MTG process. Nevertheless, studies in the literature on the effect of water are qualitative and of poor application for reactor design. In a previous article, a kinetic model was proposed that quantitatively takes into account the effect of water on the kinetics of each reaction step in the MTG process in the range between 573 and 723 K (Gayubo et al., 2002). The aim of the present paper is to complete this study by considering the effect of water in the kinetic modeling of the catalyst deactivation.

When the mechanisms proposed in the literature for formation and growth of coke in HZSM-5 zeolites are analyzed (Guisnet and Magnoux, 1989, 1994, 2001; Meinhold and Bibby, 1990; Bibby et al., 1992), the attenuation of deactivation by coke caused by the presence of water can be attributed to the fact that water molecules compete with coke precursor compounds in the adsorption on strong acid sites (which are required for formation of oligomers constituting slightly developed coke, and also for generation of polyaromatic structures that make up developed coke). Our results in previous articles on coke deposition in the MTG process on a HZSM-5 zeolite (Benito et al., 1996b) and in the MTO process (methanol to olefins) on a SAPO-34 (Aguayo et al., 1999) support this hypothesis, which also explains the slower deactivation of the HZSM-5 zeolite attributable to water in the reaction transforming aqueous ethanol into hydrocarbons (Oudejans et al., 1982) and in the catalytic upgrading of vegetable oils (Sharma and Bakhshi, 1991).

On the other hand, the peculiarities of the coke deposited in the MTG process must be taken into account. Thus, because of the limitations on coke development due to the shape selectivity of the HZSM-5 zeolite, this coke is highly hydrogenated and unstable and, consequently, it may suffer thermal degradation or it may be swept out when a vacuum is created (Schulz et al., 1987; Sexton et al., 1988; Bibby et al., 1992; Dimon et al., 1993; Aguayo et al., 1994; Guisnet and Magnoux, 1994). Taking these characteristics into account, the

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physical action of the steam present in the reaction medium on the coke cannot be ignored. Furthermore, the role of water in attenuating coke formation is observed even when coke is highly developed (graphitic, filamentous), like that formed in the hydrogenolysis of cyclopentene on Ni/Al_2O_3 (Demicheli et al., 1994).

The analytical expressions proposed in the literature for deactivation kinetics in the MTG process do not explicitly take into account the attenuating effect of water, but they do take into account the effect of other reaction variables: temperature, time, and concentration of reaction components (Liederman et al., 1978; Schipper and Krambeck, 1986; Sedrán et al., 1990a,b). Benito et al. (1996a) have proposed a kinetic equation of deactivation dependent on concentration, where the importance of the concentration of lumps on coke deposition was ordered as follows: oxygenates (methanol + dimethyl ether) > aromatics > olefins. The more severe deactivation attained when oxygenate concentration increases is in agreement with the low water concentration in the reaction medium. Thus, for a given feed composition, an increase in oxygenate concentration in the reaction medium is a consequence of its lower conversion and, as water is formed in this first step, this results in lower water concentration. The longitudinal coke profile obtained in an isothermal fixed-bed reactor, which has a decreasing trend from reactant inlet (Benito et al., 1996b), is also in agreement with the increasing trend of the water content profile from the inlet to the outlet of the reactor.

The attenuating effect on deactivation attributed to water is also seen when the deactivation in fixed- and fluidized-bed reactors are compared (Aguayo et al., 1997). The reduced deactivation observed in a fluidized bed is explained because particle contact (in a mixed regime) with a stream rich in steam gives way to an efficient delay in deactivation, as compared to that observed in a fixed bed, where the catalyst deactivated near the inlet of the reactor produces less water and, consequently, cannot benefit from this attenuating effect of water.

The aforementioned attenuating effect takes place under operating conditions that are not sufficiently severe for the water in the reaction medium to induce irreversible deactivation by dealumination of the HZSM-5 zeolite. Of the hydrotreating variables (temperature, water concentration in the gas phase, time), temperature is the most important, as it has been determined that above 773 K dealumination is significant (Yarlagadda et al., 1986; de Lucas et al., 1997), which in turn affects the water adsorption capacity of the acid sites (Bolis et al., 1980; Yarlagadda et al., 1986). Steam attacks Al-O-Si bonds and provokes rearrangement of the aluminosilicate structure (Jacob, 1977; Aukett et al., 1986). Consequently, a decrease in the number of Bronsted sites and generation of Lewis sites corresponding to AlO^+ species (de Lucas et al., 1997) occurs.

Experimental Studies

The automated reaction equipment and the conditions for product analysis have been detailed in a previous article (Gayubo et al., 2002). A fixed-bed reactor of 0.007-m interior diameter provided with a coil to preheat the gases is used. Temperature is measured by means of three thermocouples introduced in the bed, one at the center of the bed axis, another at the outlet of the bed axis, and the third on the inside of the bed wall. The products pass through a 10-port valve that allows for a sample to be sent to the Hewlett-Packard 5890 Series II chromatograph. The feed-reaction-analysis system is controlled by a computer run by means of a program in Fortran.

Table 1. Properties of the HZSM-5 Zeolite and of the Catalyst

	HZSM-5 Zeolite	Catalyst*
Si/Al ratio	27	
Bronsted/Lewis ratio	2.9	
Crystallinity	97 %	
Crystal size, μm	6.3	
Particle size, mm		0.3−0.5
Apparent density, $kg \cdot m^{-3}$	940	1210
BET surface area, $m^2 \cdot g^{-1}$	420	124
Pore volume, $cm^3 \cdot g^{-1}$	0.65	0.43
Micropore volume, $cm^3 \cdot g^{-1}$ (99% of diameter < 0.7 nm)	0.17	
Pore volume distribution of the catalyst, vol %		
$d_p < 10^{-3}$ μm 8.1		
10^{-3} to 10^{-2} μm 14.7		
10^{-2} to 2 μm 77.2		
Zeolite acidity measurements	NH_3	*tert*-butylamine
Total acidity, mol of base kg^{-1}	0.51	0.46
Temperature peaks in the TPD	695 K	577 K

*Composition: zeolite, 25 wt %; bentonite, 30 wt %; alumina, 45 wt %.

The ZSM-5 zeolite has been synthesized with a Si/Al ratio, Si/Al = 24, from sodium silicate, aluminium sulfate, and tetra-*n*-propylammonium bromide, and has been cation-exchanged to HZSM-5 by using ammonium nitrate. The method used was detailed in a previous article (Benito et al., 1996c), following Mobil patents (Argauer and Landolt, 1972; Chen et al., 1973). The zeolite was subjected to an agglomeration process with bentonite (Exaloid), using fused alumina (Martinswerk) as inert charge. The properties of the HZSM-5 zeolite and of the catalyst are given in Table 1. The physical properties of the catalyst (BET surface area, pore volume, pore-volume distribution) were determined by N_2 adsorption−desorption in an ASAP 2000 (Micromeritics). The crystal size was determined in a Mastersizer (Coulter). The zeolite acidity measurements were obtained by temperature programmed desorption (TPD) of NH_3 and *tert*-butylamine carried out in an SDT 2960 thermobalance (TA Instruments) connected on-line to a Thermostar (Balzer Instruments) mass spectrometer. The Bronsted/Lewis ratio was measured by FTIR spectrometry from the intensity of the adsorption bands at 1,550 and 1,455 cm^{-1}. Prior to use, the catalyst was calcined at 843 K for 2 h (in order for the experimental results to be reproducible under reaction-regeneration cycles) (Benito et al., 1996d).

The experiments were carried out under the following conditions: temperature (±2 K), 573, 598, 613, 653, 673 and 723 K (the isothermicity of the bed was achieved by diluting the catalyst with inert alumina); space time, between 0.004 and 0.37 (kg of catalyst) h (kg of methanol)$^{-1}$ (space time was changed by modifying the catalyst mass); time on stream, 1 h; water/methanol ratios in the feed, 0 and 1, in weight; catalyst particle size, between 0.3 and 0.5 mm; gas linear velocity at the entrance of the reactor, 0.2 m s^{-1}.

Kinetic Modeling for Zero Time on Stream (Fresh Catalyst)

The kinetic scheme for the MTG process shown in Eqs. 1–8 was proposed in a previous article (Gayubo et al., 2002). This scheme incorporates the following innovations into models, made up of lumps, that were proposed in the literature (Chen and Reagan, 1979; Chang, 1980, 1983; Schipper and Krambeck, 1986; Sedrán et al., 1990a; Gayubo et al., 1996, 1997a; Aguayo et al., 1997): (1) methanol and dimethyl ether are taken into account separately due to their different reactivity. These reactions are irreversible and occur at a high rate, which means that methanol and dimethyl ether are only present in the reaction medium at the reactor inlet. (2) The hydrocarbon cracking step is taken into account because temperature in the adiabatic reactor is sufficiently high for cracking to contribute to increasing the selectivity to light olefins (ethene and propene). Equation 8 is established separately from Eq. 4 with the aim of identifying the cracking of the G lump.

$$2M \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} D + W \tag{1}$$

$$M \xrightarrow{k_2} C \tag{2}$$

$$D \xrightarrow{k_3} C \tag{3}$$

$$2C \xrightarrow{k_4} G \tag{4}$$

$$M + C \xrightarrow{k_5} G \tag{5}$$

$$D + C \xrightarrow{k_6} G \tag{6}$$

$$C + G \xrightarrow{k_7} G \tag{7}$$

$$G \xrightarrow{k_8} 2C. \tag{8}$$

The net rate equations at zero time on stream for the formation of three of the four components (methanol, dimethyl ether, and light olefins) of the kinetic scheme shown in Eqs. 1–8, when the steps are assumed to be elemental and by expressing the concentration of the components as the weight fraction by mass unit of organic components, X_i, are:

$$(r_M)_o = \left[\frac{dX_M}{d(W/F_{Mo})}\right]_o = \frac{-k_1 X_M^2 + (k_1/K) X_D X_W - (k_2 + k_5 X_C) X_M}{1 + k_{Wo} X_W} \tag{9}$$

$$(r_D)_o = \left[\frac{dX_D}{d(W/F_{Mo})}\right]_o = \frac{+k_1 X_M^2 - (k_1/K) X_D X_W - (k_3 + k_6 X_C) X_D}{1 + k_{Wo} X_W} \tag{10}$$

In Eqs. 9–11 the attenuating effect of water in the steps of the kinetic scheme has been taken into account by incorporating a term depending on water concentration in the reaction medium, $k_{Wo} X_W$, in the denominator of the kinetic equations.

The values calculated for the kinetic parameters are (Gayubo et al., 2002):

$$k_1 = 88.73(\pm 7.89) \exp\left[\frac{-53{,}100(\pm 4{,}000)}{R}\left(\frac{1}{T} - \frac{1}{673}\right)\right] \tag{12}$$

$$k_2 = 11.98(\pm 2.16) \exp\left[\frac{-102{,}400(\pm 7{,}100)}{R}\left(\frac{1}{T} - \frac{1}{673}\right)\right] \tag{13}$$

$$k_3 = 9.95(\pm 3.29) k_2 \tag{14}$$

$$k_4 = 9.42(\pm 3.07) \exp\left[\frac{-38{,}450(\pm 13{,}800)}{R}\left(\frac{1}{T} - \frac{1}{673}\right)\right] \tag{15}$$

$$k_5 = 34.82(\pm 6.80) \exp\left[\frac{-89{,}450(\pm 6{,}300)}{R}\left(\frac{1}{T} - \frac{1}{673}\right)\right] \tag{16}$$

$$k_6 = 7.62(\pm 1.60) k_5 \tag{17}$$

$$k_7 = 6.89(\pm 4.90) \exp\left[\frac{-27{,}600(\pm 16{,}300)}{R}\left(\frac{1}{T} - \frac{1}{673}\right)\right] \tag{18}$$

$$k_8 = 0.60(\pm 0.10) \exp\left[\frac{-127{,}500(\pm 57{,}300)}{R}\left(\frac{1}{T} - \frac{1}{673}\right)\right] \tag{19}$$

$$k_{Wo} = 1.0(\pm 0.3). \tag{20}$$

It should be noted that a detailed study on the inclusion in the denominator of the kinetic equations of other terms, corresponding to adsorption of the lumps of the kinetic scheme, has been carried out. Nevertheless, in spite of the increase in the kinetic parameters, the quality of the fitting to the experimental results hardly improved. This result is evidence

$$(r_C)_o = \left[\frac{dX_C}{d(W/F_{Mo})}\right]_o = \frac{+k_2 X_M + k_3 X_D - k_4 X_C^2 - (k_5 X_M + k_6 X_D) X_C - k_7 X_C X_G + k_8 X_G}{1 + k_{Wo} X_W}. \tag{11}$$

that the inhibiting effect of the components of the kinetic scheme is of minor importance compared to the inhibiting effect of water, which is due to the fact that the mechanism of water adsorption−desorption on the active sites is slower than the mechanisms of adsorption−desorption corresponding to the reaction steps.

Deactivation Kinetic Modeling

The kinetic model proposed for deactivation by coke is based on a previous one whose applicability has been proven in an isothermal integral fixed-bed reactor (Benito et al., 1996a) and in a fluidized-bed reactor (Aguayo et al., 1997):

$$-\frac{da}{dt} = (k_{dA}X_A + k_{dC}X_C + k_{dG}X_G)a, \tag{21}$$

where A = oxygenates (methanol + dimethyl ether); C = olefins; G = the remaining hydrocarbons (which are the main components of the gasoline lump, C_5-C_{10}, with a high aromatic content).

When Eq. 21 is compared with other kinetic models previously proposed in the literature (Schipper and Krambeck, 1986; Sedrán et al., 1990a) for deactivation, it has the advantage of taking into account the effect of the composition of the reaction medium.

The contributions made in this article are: (1) deactivation kinetics for the methanol dehydration step was considered to be different from the other steps of the kinetic scheme in Eqs. 1−8; and (2) the attenuating effect of water on deactivation by coke was taken into account.

The deactivation of the methanol dehydration step is significantly slower than the deactivation of the subsequent steps in the kinetic scheme due to the fact that dehydration occurs by the action of weak acid sites and because a small site density suffices (Spivey, 1991). Consequently, in the MTG process on a HZSM-5 zeolite, methanol dehydration occurs without its rate being affected when the catalyst is completely deactivated for formation of olefins and gasoline (Benito et al., 1996a).

Taking this fact into account, the deactivation of the dehydration step has been quantified by means of an activity, a_D, that is different from the activity of the other steps in the kinetic scheme, a. These activities have been defined by means of the following expressions:

$$a_D = \frac{(r_i)_l}{(r_{io})_l} = \frac{(r_i)_{l'}}{(r_{io})_{l'}} \tag{22}$$

$$a = \frac{(r_i)_j}{(r_{io})_j} \quad \text{for } j = 2,\ldots,8, \tag{23}$$

where j is the number corresponding to the reaction step in the kinetic scheme in Eqs. 1−8.

Consequently, the net rate equations for the formation of the components of the kinetic scheme in Eqs. 1−8 are given by the following expressions, as a function of catalyst activity:

$$r_M = \frac{dX_M}{d(W/F_{Mo})} = \frac{a_D\left[-k_1X_M^2 + (k_1/K)X_DX_W\right] - a(k_2 + k_5X_C)X_M}{1 + k_{Wo}X_W} \tag{24}$$

$$r_D = \frac{dX_D}{d(W/F_{Mo})} = \frac{a_D\left[k_1X_M^2 - (k_1/K)X_DX_W\right] - a(k_3 + k_6X_C)X_D}{1 + k_{Wo}X_W} \tag{25}$$

$$r_C = \frac{dX_C}{d(W/F_{Mo})} = (r_C)_o a. \tag{26}$$

By taking the effect of water explicitly into account in the deactivation kinetics, an equation based on a previous one by Benito et al. (1996a) (see Eq. 21) is proposed by adding a term in the denominator, k_WX_W, in order to quantify the attenuation in deactivation caused by water in the reaction medium, X_W:

$$-\frac{da}{dt} = \frac{k_{dA}X_A + k_{dC}X_C + k_{dG}X_G}{1 + k_WX_W}a. \tag{27}$$

In Eq. 27 the content of the oxygenate lump, X_A, is calculated by summing the concentrations of methanol and dimethyl ether ($X_M + X_D$).

On the other hand, the activity from methanol dehydration, a_D, is calculated by relating it to the activity for hydrocarbon transformation steps, a, by means of the following expression:

$$a_D = a^n. \tag{28}$$

In these equations the deactivation for all the reaction steps depends on the same variables (concentration of components, temperature, and time on stream) and follows a similar kinetics, although a_D decreases with time on stream more slowly than a. Equation 28 relates both activities in a simplified form.

Catalyst deactivation is a consequence of coke deposition on the zeolite micropores. The effect of the MTG process operating conditions on the nature and composition of the coke has been the subject of numerous articles (Bibby et al., 1992; Aguayo et al., 1994; Benito et al., 1996b). The coke is slightly developed, highly hydrogenated, partially soluble in dichloromethane and composed of polyaromatic structures made up of two or three rings.

Figure 1 shows the attenuating effect of water on coke deposition. The results correspond to 673 K and to the 6-h time on stream. These results correspond to catalyst samples deactivated in the reactor's product outlet zone in experiments carried out under different values of space-time that have been obtained by the weight difference prior and subsequent to the combustion of the coke with air at 823 K in an SDT

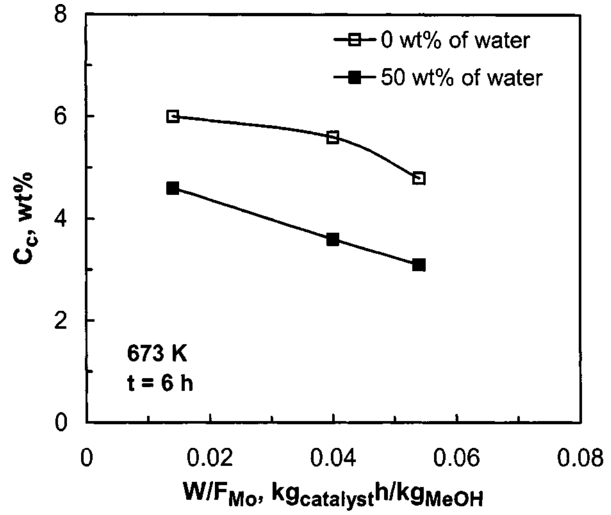

Figure 1. Influence of feeding water with methanol on the coke content in the catalyst for different values of space time: 673 K, time on stream = 6 h.

2960 thermobalance (TA Instruments). Prior to combustion, the deactivated catalyst samples were subjected to a sweeping treatment in the He stream (1 h; 5×10^{-7} $m^3\cdot s^{-1}$ at 823 K). It was seen that coke deposition decreases by more than 25% when methanol is diluted 1:1 in weight with water.

The concentration evolution with time in the stream at the reactor outlet for each lump of the kinetic scheme in Eqs. 1–8 has been calculated by solving the set of mass conservation equations in the reactor (plug flow), in the transient regime. The expression for each component is

$$\frac{\partial X_i}{\partial t} = \frac{(1-\epsilon)}{\epsilon}\rho\frac{RT}{PM}\frac{m_O}{F_{Mo}}r_i - \frac{u}{z}\frac{\partial X_i}{\partial \xi}. \quad (29)$$

In order to solve Eq. 29, the following boundary conditions are taken into account at the reactor inlet

$$X_M(\xi = 0,t) = 1 \quad (30)$$

$$X_D(\xi = 0,t) = X_C(\xi = 0,t) = X_G(\xi = 0,t) = 0 \quad (31)$$

$$a(\xi = 0,t) = a(X_{io},t). \quad (32)$$

The activity at the reactor inlet, $a(X_{io},t)$, is calculated with the following equation, which has been deduced by integrating Eq. 27 with the concentrations at the reactor inlet (Eqs. 30 and 31)

$$a(X_{io},t) = \exp\left(-\frac{k_{dA}X_{Ao} + k_{dC}X_{Co} + k_{dG}X_{Go}}{(1 + k_W X_{Wo})}t\right). \quad (33)$$

Also, in order to solve Eq. 29, the following initial conditions are taken into account:

$$X_i(\xi,t = 0) = (X_i)_{t=0} \quad (34)$$

$$a(\xi = 0,t) = 1. \quad (35)$$

The longitudinal composition profile along the reactor of each lump at zero time on stream, $X_i(\xi,t = 0)$, is calculated by solving the mass conservation equation (Eq. 29) under this condition.

For solving the set of Eqs. 29–35, a calculation program in Fortran, which uses the subroutine LSODE of the DSSP library, was developed. The kinetic parameters that best fit the experimental results are those that minimize the error objective function (EOF)

$$\text{EOF} = \frac{\sum_{i=1}^{n_l}\sum_{j=1}^{n_{\exp}}\left(X_{i,j} - X_{i(\text{calc}),j}\right)^2}{n_l n_{\exp}}, \quad (36)$$

where $X_{i(\text{calc}),j}$ are the calculated values of weight fractions for the i lump by the mass unit of the organic components for the value of time on stream, at the experimental point j (corresponding to the given value of space-time and temperature); $X_{i,j}$ are the experimental values; n_l is the number of lumps; and $n_{\exp}$ is the number of experimental points. The calculation is given in previous articles (Benito et al., 1996a; Gayubo et al., 1996).

The water/organic component ratio in mass in the reaction medium, X_W, is

$$X_W = \frac{m_W}{m_O}. \quad (37)$$

The water–mass flow in the reaction medium, m_W, is the sum of the water flow obtained as a product, m_{Wf}, and the water flow in the feed, m_{WO}

$$m_W = m_{Wf} + m_{Wo} = m_O\frac{m_{Wf}}{m_O} + m_{Wo}. \quad (38)$$

On the other hand, the following global mass balance is observed

$$m_T = m_O + m_W. \quad (39)$$

Combining Eqs. 38 and 39:

$$m_W = \frac{m_T\frac{m_{Wf}}{m_O} + m_{Wo}}{1 + \frac{m_{Wf}}{m_O}}. \quad (40)$$

In Eq. 40, the relationship between mass flows of water formed and of organic components is calculated by taking into account the stoichiometry of methanol dehydration (first step in the scheme in Eqs. 1–8) and of hydrocarbon formation (with a general formula $(CH_2)_n$) from the lump of oxygenates

$$\frac{m_{Wf}}{m_O} = 18\left(\frac{X_D}{46} + \frac{X_C + X_G}{14}\right). \quad (41)$$

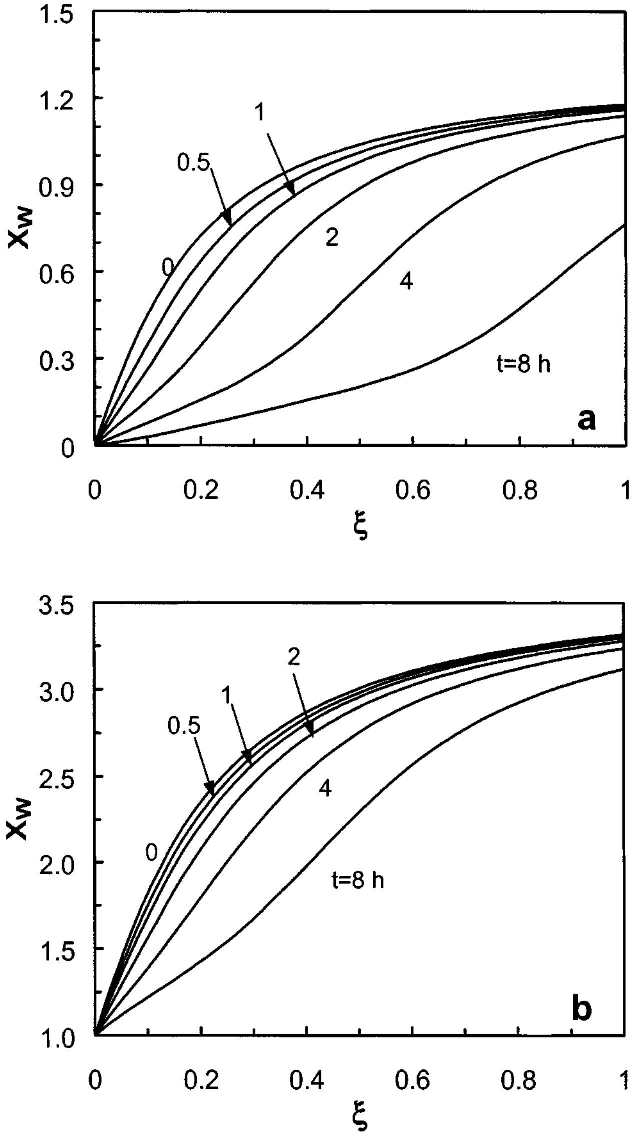

Figure 2. Evolution with time on stream of water concentration in the reaction medium along the reactor: 673 K, 0.104 (kg of catalyst) h (kg of methanol)$^{-1}$; (a), $X_{Wo} = 0$; (b), $X_{Wo} = 1.0$.

Given the importance of water content in the reaction medium, as an example of the results obtained, Figure 2 shows the evolution with time on stream of the water-concentration profile in the reaction medium along the reactor. The results correspond to 673 K, to a space time of 0.104 (kg of catalyst) h (kg of methanol)$^{-1}$, and to two contents of the water in the feed, $X_{Wo} = 0$ (Figure 2a) and $X_{Wo} = 1.0$ (Figure 2b). These data show the wide range of water concentrations in the reaction medium used for establishing the kinetic model.

It must be pointed out that attenuation of deactivation by water has a temperature limit (around 723 K), for which it has been proved that an important water concentration in the reaction medium causes irreversible deactivation by catalyst dealumination, as was pointed out in the literature (Yarlagadda et al., 1986; Benito et al., 1996d; de Lucas et al., 1997). When reaction-regeneration experiments were carried out in cycles following the methodology described in previous articles (Benito et al., 1996d; Gayubo et al., 1997a), it was proved that the catalyst completely recovers the activity corresponding to the fresh catalyst, except at a reaction temperature of 723 K, when water content in the reaction medium is higher than $X_W = 1.0$. Consequently, in order to calculate the kinetic parameters, all the results corresponding to 573–673 K were used, but for 723 K, only those corresponding to water content in the reaction medium lower than $X_W = 1.0$ (obtained for $X_{Wo} = 0$ and low values of space time).

In order to reduce the correlation between the estimations of the frequency factor and activation energy, reparameterization was carried out (Kittrell et al., 1965; Agarwal and Brisk, 1985). Thus, the parameters to optimize are the kinetic constants at the reference temperature, 673 K, and the activation energies. The 95% confidence intervals of the estimated parameters were obtained by nonlinear regression using the Marquardt algorithm (Marquardt, 1963). By using this procedure, the confidence intervals of the constants involved in the formation/disappearance of each lump were confirmed independently, with the goal of accurately analyzing the selectivity to each individual component in the kinetic scheme.

The calculated values are

$$k_{dA} = 1.639(\pm 0.022)\exp\left[\frac{-89{,}500(\pm 5{,}900)}{R}\left(\frac{1}{T}-\frac{1}{673}\right)\right] \tag{42}$$

$$k_{dC} = 0.138(\pm 0.043)\exp\left[\frac{-72{,}050(\pm 8{,}800)}{R}\left(\frac{1}{T}-\frac{1}{673}\right)\right] \tag{43}$$

$$k_{dG} = 0.075(\pm 0.028)\exp\left[\frac{-8{,}850(\pm 7{,}950)}{R}\left(\frac{1}{T}-\frac{1}{673}\right)\right] \tag{44}$$

$$k_W = 2.392(\pm 0.061)\exp\left[\frac{-57{,}400(\pm 3{,}600)}{R}\left(\frac{1}{T}-\frac{1}{673}\right)\right] \tag{45}$$

$$n = 0.25(\pm 0.01). \tag{46}$$

It must be pointed out that the procedure followed in calculating the kinetic model for deactivation takes into account the "past history" of the catalyst at each reactor point. This consideration is required when the deactivation is dependent on the composition of the reaction medium (Megiris and Butt, 1990a,b; Gayubo et al., 1994).

In Eq. 45 it is observed that constant k_W, which quantifies the attenuating effect of water in deactivation, increases as the temperature is increased. This is due to the nature of coke in this process, which is slightly aromatic and consists of oligomers, so that as the temperature is increased, the increase in the oligomers' volatilization rate favors the role of water in the attenuation of their evolution on the active catalyst sites. These results are in agreement with the discussion

Table 2. Constants of the Deactivation Kinetic Model at Different Temperatures

	573 K	598 K	613 K	653 K	673 K	723 K
k_{dA}, h^{-1}	0.100	0.220	0.342	1.004	1.639	4.957
k_{dC}, h^{-1}	0.015	0.027	0.039	0.093	0.138	0.337
k_{dG}, h^{-1}	0.005	0.010	0.016	0.046	0.075	0.224

in Dimon et al. (1993) about the effect of temperature on the steps of coke formation on the HZSM-5 zeolite from propene. They are also in agreement with the mechanisms of coke growth on the HZSM-5 zeolite (Guisnet and Magnoux, 2001) and with the recent results on the effect of water on coke deposition on SAPO-34 in obtaining olefins from methanol (Wu and Anthony, 2001).

For the purpose of evaluating the relative contribution of the different lumps of the kinetic scheme to the formation of the coke that causes catalyst deactivation, the values of the different constants of the deactivation kinetic model (calculated with Eqs. 42–44) are shown in Table 2 for three temperatures.

The following is observed: $k_{dA} > k_{dC} > k_{dG}$. Consequently, the main precursor of the coke deposited in the catalyst is the lump of oxygenates, followed by the lump of light olefins, whereas the remaining lump of hydrocarbons (lump of gasoline) makes a smaller contribution to deactivation. This result is in agreement with Figure 1, where it is observed that as space time is increased (with the consequent decrease in oxygenates), coke content in the catalyst decreases when either pure methanol or methanol diluted with water is fed in. We see that the relative importance of the contribution of the light olefins lump to deactivation is less important as the temperature is increased. Thus, at 573 K the k_{dA}/k_{dC} ratio is 6.7, whereas at 723 K this ratio is 14.7. The higher activation energy for k_{dA} and k_{dG} can be attributed to the grater stability of the coke that grows from the lumps of oxygenates and gasoline. This latter lump contains aromatics, which are precursors of the coke fraction composed of di- and tri-aromatics.

In Figures 3–5, the experimental results of deactivation (points), which were obtained under different experimental conditions, and were chosen as an example, are compared with the results calculated using the kinetic model (lines). These figures permit to analyze the effect on deactivation of three main variables: temperature, space time, and water content in the feed.

In Figure 3 it is observed that as the temperature is increased from 613 K (Figure 3a) to 673 K (Figure 3b), oxygenate (reactant) concentration increases more rapidly and the concentration of the lumps corresponding to olefins and gasoline-range hydrocarbons decreases more sharply with time on stream. When Figure 3b is compared with the results for a lower value of space time (Figure 4), it is observed that as space time is increased, deactivation attenuates. Nevertheless, the attenuating effect on deactivation is greater when water is fed in, as is proven by comparing the results of Figure 3b (for $X_{Wo} = 0$) with those of Figure 5 (for $X_{Wo} = 1$ and for the same values of the other operating conditions).

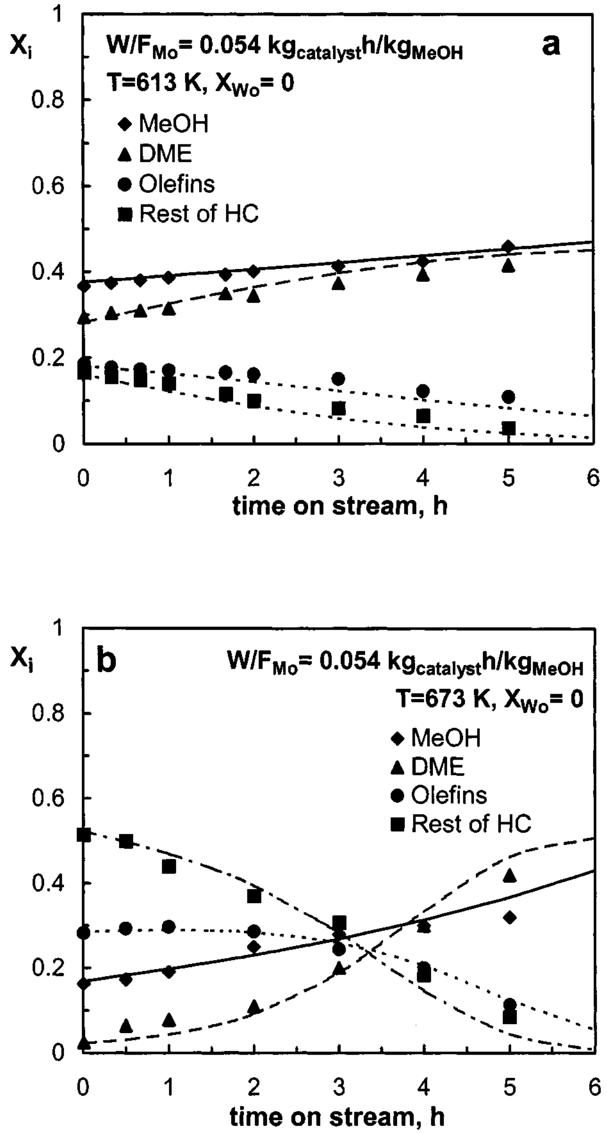

Figure 3. Comparison of the evolution with time on-stream of experimental results (points) of mass fraction of the components of kinetic scheme, by mass unit of organic components, with those calculated using kinetic parameters (lines), for 0.054 (kg of catalyst) h (kg of methanol)$^{-1}$ and $X_{Wo} = 0$: (a), 613 K, (b), 673 K.

The results of composition evolution at the reactor outlet with time on stream shown in Figures 3–5 are a consequence of the effect of the operating variables on activity. Figure 6 shows the effect of temperature on the decrease in activities a and a_D with time on stream. It is observed that as the temperature is increased, the decrease in both activities is more pronounced. It is also observed that for low values of time on stream, the activities are greater for the highest temperature studied, 673 K, which is explained by the combined effect of temperature on the deactivation kinetic constants and on water content in the reaction medium. For low values of time on stream, the attenuating effect on deactivation caused by water is more important.

For a shorter space time (Figure 7), due to a decrease in water content in the reaction medium, the decrease in activities with time on stream is more pronounced.

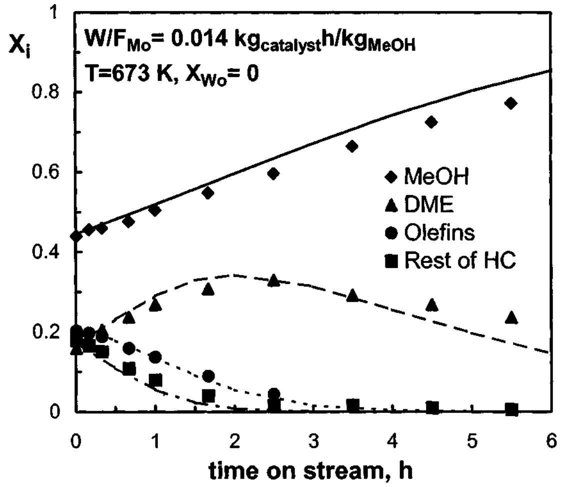

Figure 4. **Comparison of the evolution with time onstream of the experimental results (points) of mass fraction of components of kinetic scheme, by mass unit of organic components, with those calculated using kinetic parameters (lines), for 673 K, 0.014 (kg of catalyst) h (kg of methanol)$^{-1}$ and $X_{W_o} = 0$.**

In Figure 8 the effect of water content in the feed is analyzed for three operating conditions for which deactivation severity increases: Case 1: temperature, 598 K; space time, 0.054 (kg of catalyst) h (kg of methanol)$^{-1}$. Case 2: temperature, 613 K; space time, 0.054 (kg of catalyst) h (kg of methanol)$^{-1}$. Case 3: temperature, 673 K; space time, 0.014 (kg of catalyst) h (kg of methanol)$^{-1}$. As shown, the effect of water in the feed as an attenuating agent is more important when the other operating conditions correspond to severe deactivation.

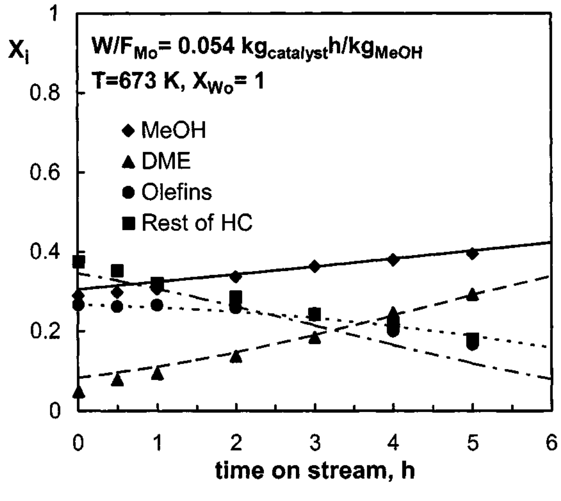

Figure 5. **Comparison of the evolution with time onstream of the experimental results (points) of mass fraction of the components of the kinetic scheme, by mass unit of organic components, with those calculated using the kinetic parameters (lines), for 673 K, 0.054 (kg of catalyst) h (kg of methanol)$^{-1}$ and $X_{W_o} = 1.0$.**

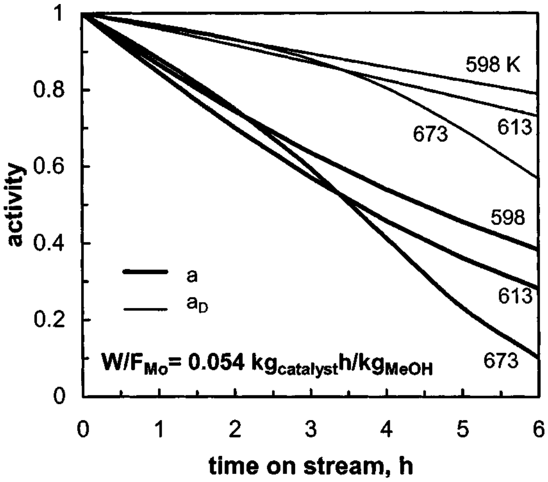

Figure 6. **Decrease with time onstream in the activities for methanol dehydration, a_D, and for the other steps of the MTG process, a, for different reaction temperatures, for 0.054 (kg of catalyst) h (kg of methanol)$^{-1}$ and $X_{W_o} = 0$.**

Discussion

In the literature there is an important gap in information about the kinetic model of MTG process deactivation, even though deactivation is an important factor in the design of the reactor, and this limits the technological development of the industrial process (Liederman et al., 1978; Schipper and Krambeck, 1986; Allum and Williams, 1988; Yurchak, 1988; Chang, 1991; Gayubo et al., 2000).

The contribution and limitations of this article are in line with the state of the literature on the development of kinetic models for complex catalytic processes, among which are those with great economic relevance, such as catalytic crack-

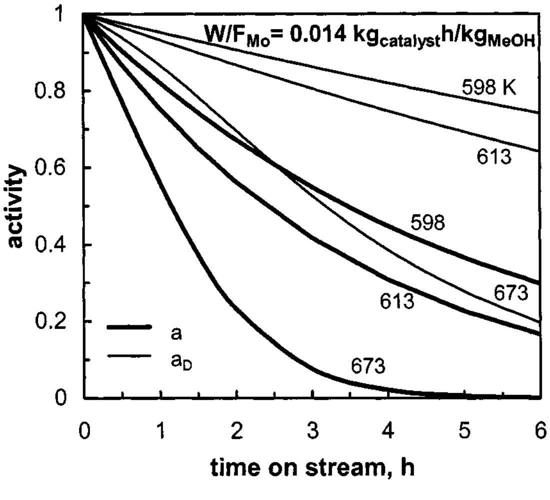

Figure 7. **Decrease with time onstream in the activities for methanol dehydration, a_D, and for the other steps of the MTG process, a, for different reaction temperatures, for 0.014 (kg of catalyst) h (kg of methanol)$^{-1}$ and $X_{W_o} = 0$.**

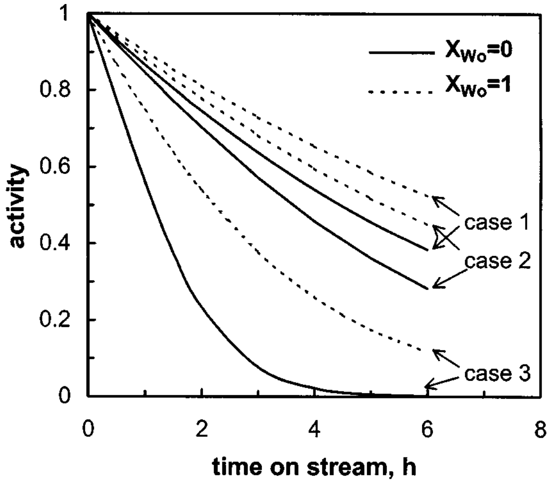

Figure 8. Decrease with time onstream in the activities for methanol dehydration, a_D, and for the other steps of the MTG process, a, for 3 operating conditions of increasing severity: Case 1. 598 K; 0.054 (kg of catalyst) h (kg of methanol)$^{-1}$; Case 2. temperature, 613 K; space time, 0.054 (kg of catalyst) h (kg of methanol)$^{-1}$; Case 3. temperature, 673 K; space time, 0.014 (kg of catalyst) h (kg of methanol)$^{-1}$.

ing in FCC units or reforming processes. The MTG process is a complex system made up of individual reactions, whose molar stoichiometry is undefined and changes with conversion and with time on stream (Mihail et al., 1983).

Since kinetic models are the tools for reactor design, a balance should be reached between the simplicity required for simulating the industrial reactor and the rigor required for considering the real mechanisms involving individual reactions. Furthermore, the rigor required in the kinetic modeling of deactivation (of great importance in the operation of the industrial reactor) must be in agreement with that adopted for the main reaction, which undoubtedly implies an additional difficulty, compounding the inherent difficulties involved in the kinetic study of deactivation.

The cause of the main gaps in the kinetic modeling of the MTG process lie in the simplifications of the kinetic scheme and of the mathematical expressions used for the kinetic equations, as well as in the definition of component concentrations. Consequently, future articles must be centered on the following objectives:

- The proposal of kinetic schemes in which "lumps" are defined according to their reactivity in each reaction step. Thus, just as the separation of methanol and dimethyl ether, whose difference in reactivity is widely accepted, has proved to be a significant improvement in the kinetic scheme, so olefin quantification should be performed by considering ethylene, propylene, and butenes separately, as their reactivities are different. Likewise, the lump of gasoline-range hydrocarbons should be substituted for the lumps of heavy olefins, naphthenes, paraffins and aromatics within the C_5–C_{10} range. In addition to considering the different reactivities of these fractions, their identification in the kinetic scheme means that the quality of the gasoline can be quantified by means of indicators, such as the research octane number (RON).
- Consider reaction mechanisms for deriving the kinetic equations, in order to avoid the present empiricism. Nevertheless, the proposed Langmuir–Hinshelwood–Hougen–Watson (LHHW) -type equations suffer from the high number of kinetic parameters involved (equilibrium constants for the adsorption of each component).

In addition, the realism of the kinetic model of deactivation proposed in this article is on the same level as that of the kinetic model for the main reaction, on which it is based. In view of the previous comments, future modifications of this model will allow researchers to improve the kinetic model of deactivation, which has a high level of empiricism and in which kinetic equations based on LHHW postulates can be introduced. Nevertheless, at the present state of this subject, we consider it more important to consider the selective deactivation, using different activities for each step in the kinetic scheme and, consequently, using different equations of deactivation for each step.

The concept of selective deactivation, which has been used in this article in order to differentiate the deactivation in the methanol dehydration step from the deactivation of the other steps, already has been introduced in other reactions with kinetic schemes simpler than the one studied here, for example, skeletal isomerization of butenes on chlorinated aluminas (Gayubo et al., 1997b).

Conclusions

It has been proved that water attenuates deactivation by coke in the transformation of methanol into dimethyl ether and in the transformation of both these oxygenate compounds into hydrocarbons. This effect may be caused by attenuating the growth of coke on acid sites, which is due to the fact that water and oligomers (intermediate products that will end up as coke) compete for adsorption.

A deactivation kinetic model has been proposed which, in addition to the effect of the composition of the lumps of the kinetic scheme, includes the attenuating effect of water concentration in the reaction medium by means of a kinetic constant that increases with temperature. The deactivation of the dehydration step is quantified by means of an activity that differs from that of the other steps of the kinetic scheme of the MTG process. Thus, the slower deactivation for the dehydration step is taken into account. The kinetic model predicts that the attenuating effect of water on all the steps is more pronounced as the deactivation increases, that is, when the temperature is higher and space time is lower.

This kinetic model is an interesting tool in order to progress in the design of reactors, of both fixed and fluidized beds. In addition, the attenuating effect on the deactivation of water may also occur in other similar reactions carried out on different zeolites and on acid catalysts in general.

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Notation

A, C, D, G, M, W = oxygenates (methanol + dimethyl ether), light olefins, dimethyl ether, gasoline range hydrocarbons, methanol, and water, respectively

a = activity for all the steps of the kinetic scheme in Eqs. 1–8, except for methanol dehydration

a_D = activity for methanol dehydration, step 1 in Eqs. 1–8

EOF = error objective function

F_{Mo} = mass flow of methanol in the feed, $kg \cdot h^{-1}$

k_i = kinetic constant of step i in kinetic scheme, h^{-1}

k_{dA}, k_{dC}, k_{dG} = kinetic constant for deactivation by coke due to oxygenates, light olefins, and gasoline range hydrocarbons, respectively, h^{-1}

k_W = parameter that quantifies the attenuation in deactivation due to the presence of water in the reaction medium

k_{Wo} = parameter that quantifies the resistance to formation of component i in the corresponding reaction step, due to the presence of water in the reaction medium

M = average molecular weight of organic components, $kg \cdot mol^{-1}$

m_O, m_T, m_W = mass flow rate of organic components, total, and that of water, respectively, $kg \cdot h^{-1}$

m_{Wo}, m_{Wf} = mass flow rate of water in the feed and produced in the reaction, $kg \cdot h^{-1}$

n = coefficient in Eq. 28

P = partial pressure of organic components, Pa

R = constant of gases, $J \cdot mol^{-1} \cdot K^{-1}$

$(r_i)_j, (r_{io})_j$ = reaction rate for formation of component i in reaction step j of the scheme in Eqs. 1–8, for any time on stream and for zero time on stream, $kg \cdot h^{-1}$ (kg of catalyst)$^{-1}$

T = temperature, K

t = time on stream, h

u = linear gas velocity, $m \cdot h^{-1}$

W = catalyst weight, kg

X_i = weight fraction of component i, by mass unit of organic components

X_{io} = weight fraction of component i, by mass unit of organic components, at the reactor inlet

X_W = water/organic component mass ratio in the reaction medium

X_{Wo} = water/methanol mass ratio in the feed

Z = total length of the reactor, m

z = longitudinal coordinate of the reactor, m

Greek letters

ϵ = bulk porosity

ρ = catalyst density, $kg \cdot m^{-3}$

ξ = dimensionless longitudinal coordinate of the reactor (z/Z)

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