Reactivation of the HZSM-5 Zeolite-Based Catalyst Used in the MTG Process

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The recovery of the acidic structure and activity during the regeneration step by coke combustion of an HZSM-5 zeolite-based catalyst used in the methanol-to-gasoline (MTG) process in reaction–regeneration cycles was studied. The reactivation kinetics (activity vs. coke combustion time) was determined as a function of temperature and time on stream of the reaction step. The validity of the reactivation kinetic model was proven by using it for the simulation of the cyclic operation under conditions of catalyst partial reactivation, together with the kinetic model for the MTG process.

Introduction

After the discovery of the capacity of HZSM-5 zeolites (due to shape selectivity) for the transformation of methanol into hydrocarbons with boiling points within the range of gasoline (MTG process) or of light olefins (MTO process), serious attention has been paid to these processes in the literature (Chang, 1983, 1984; Tabak and Yurchak, 1990). Besides, the increasing demand of ethers for use in gasoline reformulation has increased interest in the transformation into hydrocarbons of the methanol stream (with water) that is the resulting byproduct of MtBE (methyl *tert*-butyl ether) production (Harandi and Owen, 1989a,b).

Although a great deal of effort has gone into minimizing the deactivation of the HZSM-5 zeolite, by studying the preparation of the catalysts and the operating conditions (Guisnet and Magnoux, 1994 Aguayo et al., 1994a; Benito et al., 1996a), the rapid deactivation of the catalyst by coke deposition is unavoidable and, consequently, it is necessary to reactivate the catalyst by burning coke in air or in air diluted with N_2.

In order to cover the gaps existing in the literature concerning this subject, previous articles (Benito et al., 1996b; Ortega et al., 1997) have studied the combustion of the coke deposited in the HZSM-5 zeolite in the MTG process. It has been proven that coke combustion presents peculiar characteristics due to the highly hydrogenated nature of the coke and to its location in the internal channels of the zeolite crystals (Ortega et al., 1997). As a result of these studies the tools needed for the design of the regeneration step have been obtained: the kinetics of combustion; the conditions for equilibration of the coke prior to combustion, in order for combustion to be reproducible; the combustion heat.

In this article, the recovery of catalyst activity during coke combustion is studied. This is a subject that has only been briefly studied in the literature, and it is of great interest for those processes in which the catalyst is sensitive to regeneration step conditions, which usually happens with acid catalysts. It has been proven that HZSM-5 zeolite has an acidic structure and activity that are very sensitive to temperature and coke combustion time (Benito et al., 1996b). By using air as the combustion gas, a combustion temperature of 823 K is considered to be the minimum needed for complete recovery of the catalyst activity in an indefinite number of successive reaction–regeneration cycles. Higher temperatures obviously accelerate the reactivation, but this effect is accompanied by a slight deterioration in the total acidity of the catalyst, because of the dehydroxilation of Bronsted sites.

Knowing the reactivation kinetics, which relate the recuperation activity to the coke combustion time, allows us to establish precisely the minimum combustion time for the recovery of the activity corresponding to fresh catalyst. In this way, in addition to minimizing the down time in the reaction–regeneration cycle, thus optimizing cost reduction, we can avoid an unnecessary thermal treatment time during which the catalyst can deteriorate.

The calculation method used in this article for the simulation of the reactor operation under the reaction–regeneration cycles is an extension of a reaction with a complex kinetic scheme with parts, like the one for the MTG process, of the methodology developed in a previous article (Gayubo et al., 1993a) in which the reactivation of a silica-alumina catalyst used in the isomerization of cis-butene to 1-butene and trans-butene was studied.

Experimental Studies

Catalysts

The ZSM5 zeolite has been synthesized with a Si/Al ratio of 42, by following the method detailed in an earlier article (Benito et al., 1994), according to Mobil patents (Argauer and Landolt, 1972; Chen et al., 1973), from sodium silicate, aluminum sulphate, and tetra-*n*-propylammonium nitrate. The final catalyst, as it is used in the reactor, is obtained by physically mixing, in high humidity, the zeolite (25 wt. %) with a binder (bentonite, 30 wt. %) and an inert (α-alumina supplied by Martinswerk and calcined at 1,373 K, 45 wt. %).

The surface acidic strength distribution and the total acidity have been studied by measuring the differential adsorption heat of NH_3, by combining differential scanning calorimetry (Setaram DSC 111) and FTIR spectrophotometry (Nicolet 740) in order to measure the heat from neutralizing the acidic sites with the former and the amount of base chemically absorbed with the latter (Aguayo et al., 1994b). Once the sample is saturated at 523 K, we use temperature-programmed desorption (TPD) of the base to obtain the total acidity measurement, by following an increase of 5 $K \cdot min^{-1}$ between 523 K and 873 K, with an He flow of 20 $cm^3 \cdot min^{-1}$, and using FTIR spectrophotometry for measuring the desorption products. It has been proven that the acidity measured with NH_3 is an index of the catalyst activity in the MTG process (Gaybo et al., 1996a). NH_3 is more suitable than organic bases for acid titration of microporous catalysts deactivated by coke, since the organic base desorption is hardly quantifiable because partial desorption of coke components also takes place.

In an earlier article (Benito et al., 1996b), it was shown that there is an unavoidable loss of catalyst activity after the first regeneration step. Therefore, in order to obtain reproducible results in an operation in reaction–regeneration cycles, the catalyst must be subjected to an equilibration treatment consisting of the following successive steps: (1) a thermal equilibration (stripping with N_2 at 823 K for 1 h); (2) a reaction–règeneration cycle (reaction conditions: $T = 623$ K, $t = 2$ h; combustion conditions: $T = 823$ K, $t = 20$ min). This treatment ensures reproducible results of conversion in the second and successive reaction cycles. Up to ten cycles have been carried out in order to prove the reproducibility of the results. In a previous article (Ortega et al., 1997) I have also proven that, for a particle size between 0.15 and 0.5 mm, coke combustion is not limited by the internal diffusion of oxygen.

Reaction – regeneration equipment and product analysis

The automated equipment has been described in earlier articles (Arandes et al., 1990; Gayubo et al., 1993b,c). The equipment, which is computer controlled, allows for uninterrupted reaction–regeneration cycles, where the length of time and flow rates regimes and temperatures can be programmed in for each of the steps (reaction, stripping, combustion, conditioning between steps). A fixed-bed reactor of 0.007-m internal diameter, which has a coil to preheat the gases, is used and both are in an oven of electric resistances, whose design minimizes the inertia to the computer-controlled temperature response. Temperature is measured by means of three thermocouples introduced in the bed, one at the middle point of the bed axis, the second at the outlet of the bed axis, and the last on the inside of the bed wall. The products pass through a ten-port valve that allows a sample to be sent to the Hewlett-Packard 5890 Series II chromatograph. The chromatograph has an HP 3390-A integrator, which is provided with a card enabling the results of the analysis to be sent to a computer by means of an RS-232-C interface. The feed-reaction-analysis system is controlled by a computer routine. Calculation of the weight fraction of the lumps of oxygenates (methanol and dimethyl ether), of light olefins (ethylene, propylene, and butenes), and of the rest of the products is carried out using a program in FORTRAN, which is based on the composition of each individual product obtained in the chromatographic runs (Benito et al., 1996a).

The kinetic experiments have been carried out under the following conditions:

Reaction Step. Catalyst particle size, between 0.15 and 0.5 mm; gas linear velocity at the entrance of the reactor, 20 $cm \cdot s^{-1}$; temperature, 573, 598, 623 and 648 K; contact time, between 0.01 and 0.1 (g of catalyst) h (g of methanol)$^{-1}$; partial pressure of methanol in the feed, 88 kPa, corresponding to 0.4 (g of methanol)$\cdot min^{-1}$ and 37 (cm^3 of He) min^{-1}; time on stream, between 2 and 8 h.

Regeneration Step. A stripping with He (100 $cm^3 \cdot min^{-1}$) is carried out prior to combustion. The stripping time is 30 min: first, the temperature is increased (10 K min^{-1}) from the reaction temperature up to the combustion temperature) (823 K), and then this temperature is maintained constant. With this treatment coke equilibration is achieved before combustion, so that the H/C ratio reaches a stable value, close to unity, for which combustion is reproducible. Subsequently, coke combustion is carried out with an air flow of 100 $cm^3 \cdot min^{-1}$ and combustion times of up to 40 min.

A thermoanalyzer (Setaram TAG 24) was used to determine the coke content remaining in the catalyst corresponding to each partial combustion time, following an identical process for coke combustion to that in the reactor: prior stripping with He followed by combustion with air at 823 K. Because the H/C ratio and coke content are different depending on the longitudinal position along the reactor (Benito et al., 1996c), a representative sample of the whole bed was taken.

Kinetic Model for the MTG Process

Kinetic modeling of the main reaction

Several authors have studied the kinetic modeling of the reaction at zero time on stream for the MTG process (Chen and Reagan, 1979; Chang, 1980; Mihail et al., 1983; Schipper and Krambeck, 1986; Sedrán et al., 1990; Gayubo et al., 1996b). In this work a model based on Schipper and Krambeck's (1986) was used, which fits well the experimental results of conversion at zero time on stream in both a fixed-bed reactor and a fluidized-bed reactor (Aguayo et al., 1997). The kinetic model has three segments: oxygenated (methanol and dimethyl ether), light olefins (ethylene and propylene), and gasoline (rest of hydrocarbons):

$$\text{MeOH} \rightleftharpoons \text{dimethyl ether (DME) (in equilibrium)}$$

$$\text{MeOH/DME (A)} \xrightarrow{k_1} \text{light olefins (C)}$$

$$2\mathrm{C} \xrightarrow{k_2} \text{products (G)}$$

$$\mathrm{A}+\mathrm{C} \xrightarrow{k_3} \mathrm{G}$$

$$\mathrm{C}+\mathrm{G} \xrightarrow{k_4} \mathrm{G}.$$

Light olefins (C) can polymerize to form products in the gasoline boiling range (G), or can be methylated to higher olefins that are grouped in the gasoline segment. The products (G) can react with light olefins to produce additional gasoline.

The kinetic equations that describe the rate of formation at zero time on stream are as follows:

$$-r_{\mathrm{A}_0} = -\frac{dX_\mathrm{A}}{d\tau} = k_1 X_\mathrm{A} + k_3 X_\mathrm{A} X_\mathrm{C} \tag{1}$$

$$r_{\mathrm{C}_0} = \frac{dX_\mathrm{C}}{d\tau} = k_1 X_\mathrm{A} - k_2 X_\mathrm{C}^2 - k_3 X_\mathrm{A} X_\mathrm{C} - k_4 X_\mathrm{C} X_\mathrm{G} \tag{2}$$

$$r_{\mathrm{G}_0} = \frac{dX_\mathrm{G}}{d\tau} = k_2 X_\mathrm{C}^2 + k_3 X_\mathrm{A} X_\mathrm{C} \tag{3}$$

where the best fit kinetic constants are (Aguayo et al., 1997):

$$k_1 = 0.315 \times 10^7 \exp(-65{,}710/\mathrm{RT}) \tag{4}$$

$$k_2 = 0.155 \times 10^3 \exp(-25{,}310/\mathrm{RT}) \tag{5}$$

$$k_3 = 0.154 \times 10^7 \exp(-56{,}430/\mathrm{RT}) \tag{6}$$

$$k_4 = 0.141 \times 10^3 \exp(-20{,}900/\mathrm{RT}) \tag{7}$$

Deactivation kinetic model

A kinetic equation for deactivation of the separate functions (Szépe and Levenspiel, 1971), depending on the concentration of the three sections of the reaction scheme, which are possible coke precursors, has been proven (Benito et al., 1996a; Aguayo et al., 1997), considering only deactivation by coke deposition:

$$-\frac{da}{dt} = (k_{d_\mathrm{A}} X_\mathrm{A} + k_{d_\mathrm{C}} X_\mathrm{C} + k_{d_\mathrm{G}} X_\mathrm{G})a. \tag{8}$$

In Eq. 8, the individual contribution to deactivation by each of the sections is differentiated. Activity was considered the same for describing the decrease of individual reaction rates:

$$a = \frac{r_i}{r_{i_0}} = \frac{\left(\dfrac{dX_\mathrm{A}}{d\tau}\right)_t}{\left(\dfrac{dX_\mathrm{A}}{d\tau}\right)_{t=0}} = \frac{\left(\dfrac{dX_\mathrm{C}}{d\tau}\right)_t}{\left(\dfrac{dX_\mathrm{C}}{d\tau}\right)_{t=0}} = \frac{\left(\dfrac{dX_\mathrm{G}}{d\tau}\right)_t}{\left(\dfrac{dX_\mathrm{G}}{d\tau}\right)_{t=0}}. \tag{9}$$

The theory that the acidic site deterioration of the catalyst affects each of the individual steps of the kinetic scheme equally is based on the verification made in a previous work (Gayubo et al., 1996a). There it was shown that the same acidic sites take part in the individual steps by which light olefins form and on their transformation into hydrocarbons of gasoline in the boiling point range. It has also been proven that methanol is in equilibrium with dimethyl ether until almost total deactivation (a situation where light olefin production is very small).

The best fit kinetic constants are (Aguayo et al., 1997):

$$k_{d_\mathrm{A}} = 0.165 \times 10^9 \exp(-108{,}140/\mathrm{RT}) \tag{10}$$

$$k_{d_\mathrm{C}} = 0.121 \times 10^6 \exp(-79{,}130/\mathrm{RT}) \tag{11}$$

$$k_{d_\mathrm{G}} = 0.603 \times 10^8 \exp(-109{,}850/\mathrm{RT}). \tag{12}$$

Calculation of the activity recovered in the regeneration step

The activity (defined by Eq. 9) corresponding to a partially reactivated catalyst has been determined from the experimental measurement of the product stream composition by analyzing the mass fraction of the portions of oxygenates (methanol and dimethyl ether), X_A. As an example of the method for calculating activity, the evolution with time on stream of activity, a, and of the mass fraction of the oxygenates segment, X_A, have been plotted together in Figure 1 for the given operating conditions [reaction temperature, 623 K; contact time, 0.03 (g of catalyst) h (g of methanol)$^{-1}$]. In Figure 1 when the mass fraction of oxygenates at the beginning of the reaction step is $X_{\mathrm{A}_0} = 0.74$, the activity corresponding to the partially reactivated catalyst is $a_0 = 0.85$.

In order to draw Figure 1, the activity of the catalyst and the corresponding mass fraction of the oxygenates segment were calculated by solving the deactivation equation (Eq. 8) and the mass conservation equations of the segments (defined in the previously described kinetic scheme) in an isothermal plug-flow reactor without radial gradients:

$$\frac{dX_i}{dt} = \frac{(1-\epsilon)}{\epsilon} \rho \frac{RT}{PM} r_{i_0} \frac{m}{m_t} a - \frac{u}{Z} \frac{dX_i}{d\xi}. \tag{13}$$

Equation 13 was solved by orthogonal collocation (Villadsen and Michelsen, 1978). In Eq. 13, the composition values

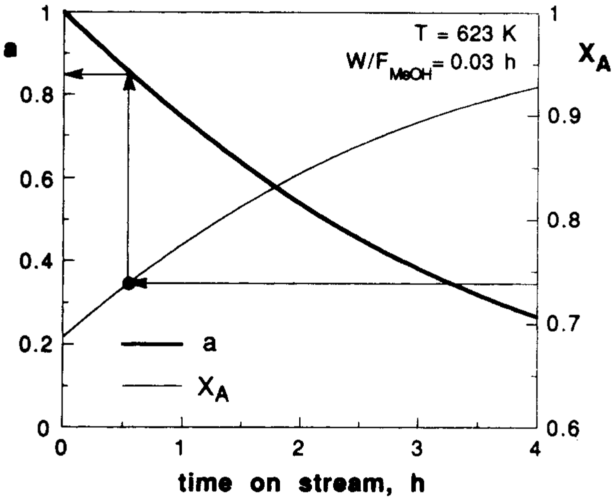

Figure 1. Procedure for calculating the activity recovered, using values of initial-weight fraction of oxygenates.

are expressed as the weight fraction of the segments on a water-free basis, X_i, in order to simplify the treatment of the data. In a previous paper (Benito et al., 1996a) the calculation of the variables needed for the resolution of Eq. 13 has been detailed; gaseous linear velocity, u; water mass flow; partial pressure of the water free products; molecular weight of the lumps.

Results

Acidity recovery

In Figure 2, the differential adsorption heat of NH_3 at 523 K was plotted for different states of the catalyst: equilibrated catalyst (totally reactivated), deactivated [temperature, 648 K; contact time, 0.075 (g of catalyst) h (g of methanol)$^{-1}$; time on stream, 12 h], and two states of partially reactivated catalyst (for combustion times of 10 and 20 min). The results of Figure 2 reflect the acidic strength distribution of the catalyst in the different states. It can be observed that as coke combustion progresses, acidic sites of different strengths are recovered in the same proportion.

For the whole range of conditions studied, it has been proven that after total combustion of the coke, the acidic structure corresponding to the equilibrated catalyst is recovered, which means that the irreversible deactivation due to the steam is negligible, this steam being a product in the reaction and regeneration steps.

The results of total acidity have been plotted against combustion time in Figure 3. It can be seen that as combustion evolves, the acidic site release rate is attenuated. After burning for 60 min, the total acidity corresponding to the equilibrated catalyst, 0.50 mmol NH_3 (g of zeolite),$^{-1}$ has not yet been recovered. These results correspond to coke combustion following first-order kinetics with respect to the remaining coke content in the catalyst (Ortega et al., 1997).

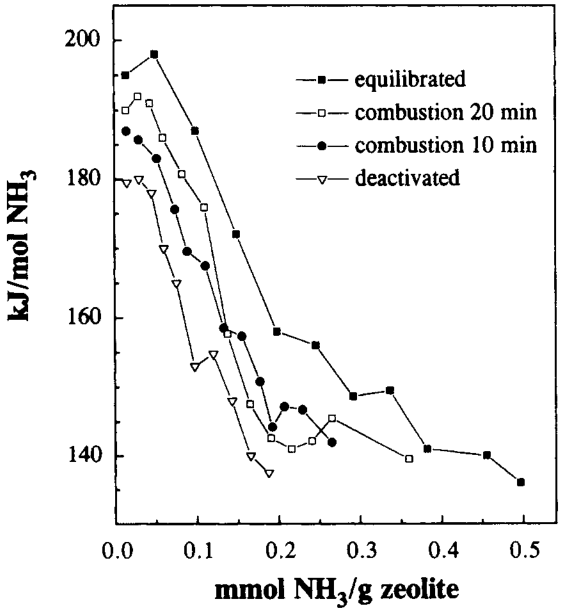

Figure 2. Acidic strength distribution of the equilibrated catalyst, deactivated catalyst (at 648 K and for a contact time of 0.075 h for 12 h) and the catalyst partially reactivated for two different combustion times.

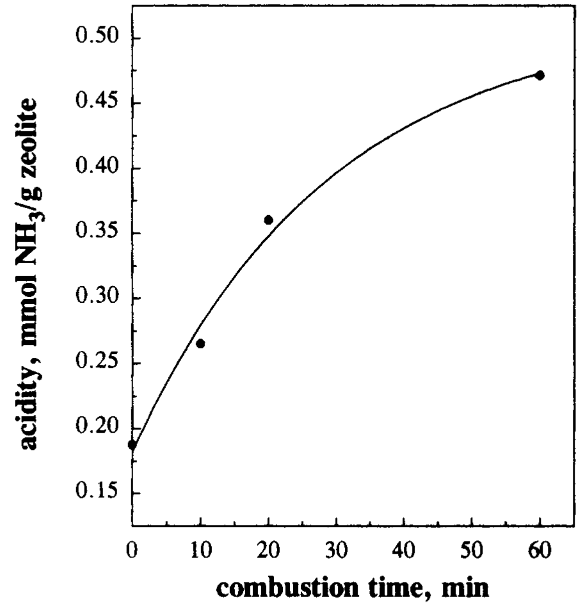

Figure 3. Evolution of total acidity of the catalyst as a function of the combustion time.

Activity – coke-content relationship

As can be seen in Figure 4, the activity–coke-content relationship during a reaction–regeneration cycle shows a noticeable hysteresis.

The activity–coke-content relationship was determined by calculating the activity from the measurement of the composition of the reaction products, as was previously indicated, and analyzing the corresponding coke content by thermogravimetry.

The evolution of coke content with time on stream throughout the reaction step was studied in an earlier article

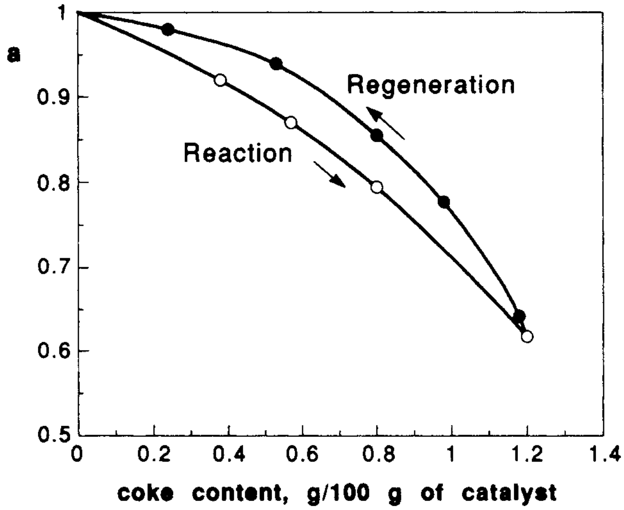

Figure 4. Activity–coke-content relationship during a reaction–regeneration cycle.

(Benito et al., 1996c), where it was proven that the coke content under different reaction conditions (temperature and time on stream) and for a contact time of 0.052 (g of catalyst) h (g of methanol)$^{-1}$ fits the following expression:

$$C_c = 1.96 \times 10^8 t^{0.43} \exp(-12{,}206/T). \qquad (14)$$

The results of Figure 4 show that by eliminating the first coke fractions, a noticeable activity recovery is achieved. This result, together with the uniform recovery of sites with different acidic strengths, which is evident in Figure 2, must be attributed to selective coke combustion and not to selective release of sites of greater acidic strength. The so-called selective coke combustion consists of preferent combustion of the more hydrogenated components (which are also more effective in the deactivation). Simultaneous with coke combustion, transformation of the remaining coke by pyrolysis occurs, reducing the coke H/C ratio and, consequently, the capacity of the coke for adsorption and the deactivation of the acidic sites. On the other hand, the fact that combustion is carried out in a fixed bed contributes to the hysteresis of Figure 4, so that partial reactivation of a catalytic bed in which there is a decreasing longitudinal profile for coke yields to the preferred catalyst reactivation near the reactor inlet.

The explanation of the hysteresis shown in Figure 4 on the basis of the preferent combustion of the external coke that partially blocks the pores is not consistent, as the experimental determination of the porous structure under different deactivation states and the deactivation kinetic model show that deactivation below a reaction temperature of 673 K is due to site coverage and not to pore blockage, up to a state of almost total catalyst deactivation. Coke deposition under these circumstances occurs within the internal channels of the crystals and in the intersections between channels, and the external coke is only important once the pores have been blocked (Benito et al., 1996c). The kinetic model of deactivation follows this scenario.

Reactivation equation

The recovery of catalyst activity depends on the operating conditions, on the stripping steps (with He), and on the combustion of the remaining coke. Because both steps are carried out under a given temperature and flow conditions, the variables that control the regeneration step are the length of time of stripping, t_s, and of combustion: t_c:

$$a_0 = f(t_s, t_c) \qquad (15)$$

Nevertheless, in an earlier article (Ortega et al., 1997) it was proven that the stripping treatment, with He at 823 K, of the catalyst deactivated at 598 K and at higher temperatures, has a negligible effect on the elimination of coke, and that activity recovery after this treatment is also negligible.

Contrary to this result, Schulz et al. (1995) proved that the coke deposited on a HZSM-5 zeolite during the transformation of methanol into hydrocarbons at temperatures below 563 K is almost totally eliminated by stripping with an inert at temperatures higher that the reaction's. In order to explain the difference in the results of coke volatility, the effect of the reaction conditions, especially of temperature, must be considered for the following: (a) the structure of coke, which has a higher molecular weight and lower H/C ratio as the reaction temperature increases; the coke is therefore less volatile; (b) the volatility of coke components, which will be volatilized at high reaction temperatures, and they will consequently not be present in the final stripping step with an inert. The volatilization of the coke components will limit its evolution by condensation–cyclation–aromatization, which means an attenuation of the effect of temperature in these coke growing steps. Schulz et al., (1991) have proven this effect of attenuation in coke deposition in the 623–673 K range.

The aforementioned explains why an important portion of the coke deposited in the isomerization of *cis*-butene over a silica-alumina catalyst at 493 K is removed by stripping with an inert gas (Gayubo et al., 1993a), while, on the other hand, elimination of the coke deposited at 798 K over a chromia-alumina catalyst used in the dehydrogenation of butene to butadiene is not noticeable (Royo et al., 1994).

Stripping with He, although it does not remove the coke deposited within the zeolite at 598 K and higher temperatures, has the effect of coke equilibration by reducing the H/C ratio up to an equilibrium value close to unity (Ortega et al., 1997). Including this result, the conditions for stripping with He have been fixed in this article: $t_s = 30$ min, corresponding to a temperature increase from the reaction temperature to the combustion temperature; and a period of stabilization at 823 K. This treatment ensures that the remaining coke has a similar H/C ratio (H/C $\approx$ 1), independent of the conditions in the reaction–regeneration cycles. When these conditions are adhered to, the evolution of coke combustion products (CO, CO_2, and H_2O) is reproducible (Ortega et al., 1997).

Table 1 contains the results of the mass fraction of the oxygenates portion (methanol and dimethyl ether) for zero time on stream, which were obtained in the reactivation experiment. These results correspond to different operating conditions in the reaction step (temperature, 598, 623 and 648 K; time on stream, 2, 4 and 8 h) and to different combustion times at 823 K (5, 10, 20, and 40 min). From these mass fraction results the activity of the catalyst corresponding to

Table 1. Activity Recovered in Different Reaction–Regeneration Cycles

T (K)	t(h)					
623	2	t_c (min)	5	10	20	40
		X_{A_0}	0.737	0.718	0.701	0.687
		a_0	0.855	0.917	0.960	—
623	4	t_c (min)	5	10	20	40
		X_{A_0}	0.771	0.738	0.707	0.696
		a_0	0.755	0.850	0.945	0.980
623	8	t_c (min)	5	10	20	40
		X_{A_0}	0.849	0.794	0.737	0.701
		a_0	0.527	0.694	0.855	0.960
598	2	t_c (min)	5	10	20	40
		X_{A_0}	0.828	0.824	0.816	0.813
		a_0	0.930	0.950	0.988	—
648	2	t_c (min)	5	10	20	40
		X_{A_0}	0.637	0.621	0.567	0.540
		a_0	0.770	0.802	0.909	0.960

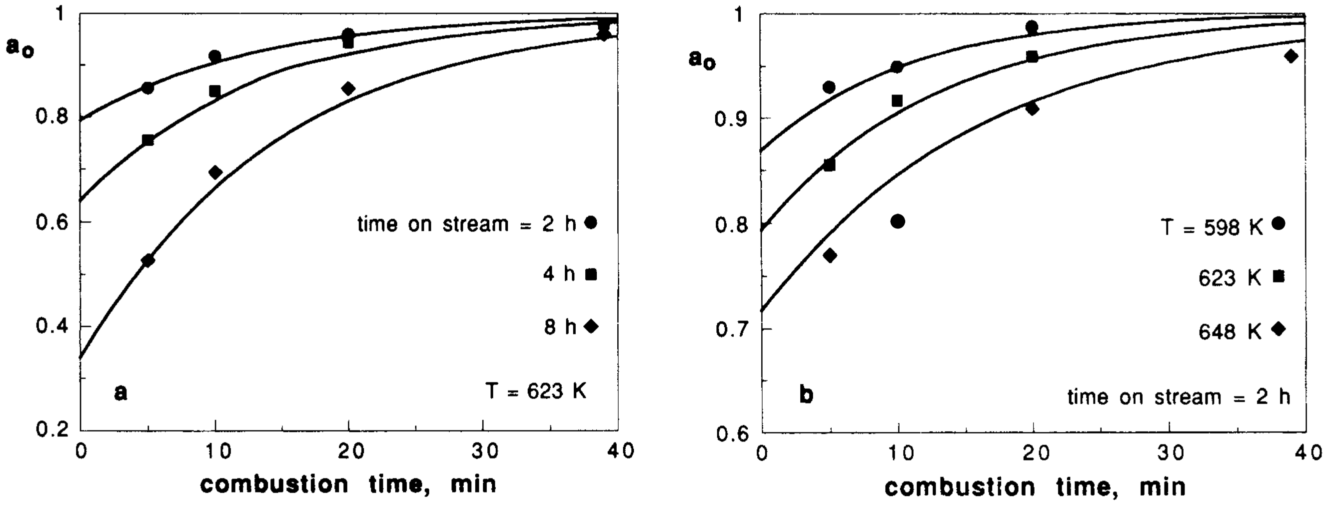

Figure 5. Experimental (points) vs. calculated (curves) values of activity vs. combustion time.

each of the reactivation states (a_0 in Table 1) has been calculated by resolving the mass conservation equation (Eq. 13) together with Eq. 8.

The results in Table 1 have been fitted by linear regression (by using the complex algorithm of optimization) to the following equation:

$$a_0 = 1 - \alpha \exp(-\beta t_c), \qquad (16)$$

where α and β are functions of the operating conditions in the reaction step:

$$\alpha = -1.820 + 0.076t + 3.011 \times 10^{-3} T \qquad (17)$$

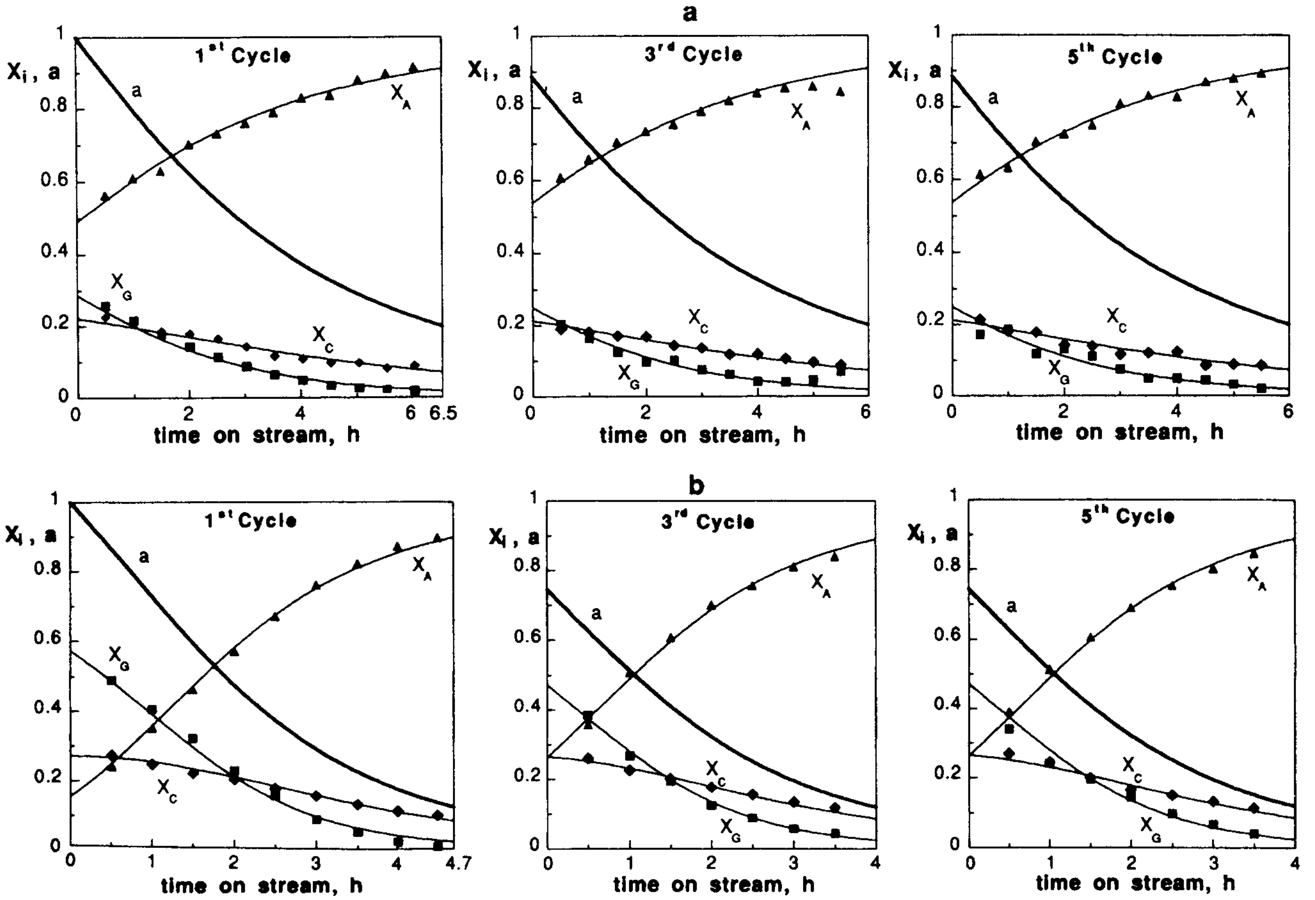

Figure 6. Evolution with time on stream of the weight fraction of lumps and of the activity during the first, third and fifth reaction cycle.

(a) Reaction temperature, 623 K; contact time, 0.052 h; combustion time; 20.7 min. (b) Reaction temperature, 648 K; contact time, 0.075 h; combustion time; 12.2 min.

$$\beta = (0.518 - 2.047\times 10^{-4} t^2 - 7.044\times 10^{-4} T). \qquad (18)$$

In order to show the validity of Eq. 16, we plotted the results of recovered activity against combustion time (Figure 5). The points are experimental results (Table 1), and the lines have been calculated with the reactivation kinetic equation proposed, Eq. 16. The results in Figure 5a correspond to one reaction temperature (623 K), and each curve corresponds to one length of time on stream (2, 4 and 8 h). The results of Figure 5b corresponds to one length of time on stream (2 h) and to different values of the reaction temperature (598, 623 and 648 K).

Simulation of the cyclic operation

The validity of the kinetic model for the MTG process has been proven by using it in the simulation of the reactor operation during reaction–regeneration cycles, in which the catalyst is partially reactivated. Catalyst activity is therefore $a_0 < 1$ at the beginning of the reaction step.

In order to show the suitability of the fitting, both the calculated (lines) and experimental results (points) of the activity and mass fraction of the segments of the kinetic model and plotted them against time on stream in the reaction step (Figure 6). The results correspond to the first, third, and fifth cycles for the following values of activity recovered: $a_0 = 0.88$ (Figure 6a) and $a_0 = 0.73$ (Figure 6b). The reaction conditions corresponding to the set values of a_0 were calculated by solving Eq. 13. These conditions are, for $a_0 = 0.88$ (Figure 6a): reaction temperature, 623 K; contact time, 0.052 (g of catalyst) h (g of methanol)$^{-1}$; combustion time, 20.7 min; for $a_0 = 0.73$ (Figure 6b): reaction temperature, 648 K; contact time, 0.075 (g of catalyst) h (g of methanol)$^{-1}$; combustion time, 12.2 min.

We can see in Figure 6 that the first cycle corresponds to a totally reactivated catalyst ($a_0 = 1$). This first cycle must be carried out for a slightly longer time on stream than do the subsequent cycles, with the aim of reaching the final activity, a_f, in the same time as in the steady-state operation. The time on stream needed to reach the final activity, a_f, from $a = 1$ is determined directly from the deactivation kinetics.

Conclusions

It has been proven that the reactivation of the catalysts by coke combustion occurs in homogeneous way in the acidic catalyst sites of different strength, whose release takes place in a uniform way. Nevertheless, the results show that coke combustion selectively affects coke components, depending on their H/C ratio, which explains the hysteresis in the activity–coke-content relationship in the reaction–regeneration cycles.

Reactivation kinetics is very dependent on the reaction conditions (temperature and time on stream). The kinetic equation obtained may be useful in designing the operation during the reaction–regeneration cycles in an adiabatic fixed-bed reactor, in order to economically optimize the cyclic operation, or simply to calculate the minimum time needed for total catalyst reactivation.

The economic optimization of the operation during the reaction–regeneration cycles does not necessarily correspond to the total recovery of the catalyst activity, $a_0 = 1$, in all positions in the reactor. Verifying the validity of both the kinetic scheme based on the one in Schipper and Krambeck (1986) and the kinetic deactivation model of Benito et al. (1996a) will be interesting, using the simulation of the industrial reactor under those conditions.

Acknowledgments

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Notation

a_0 = catalyst activity at the end of the regeneration step or at the beginning of the reaction step, referred to as the reaction rate
d = deactivation order
F_{M_0} = mass flow of methanol in the feed, (g of methanol)$\cdot$h^{-1}
$k_{d_A}, k_{d_C}, k_{d_G}$ = kinetic deactivation constants for the coke deposited from segments A, C and G, respectively, h^{-1}
$\overline{M}$ = average molecular weight of the water-free products, g$\cdot$mol^{-1}
m, m_t = mass flow of water-free products and total mass flow, g$\cdot$h^{-1}
P = partial pressure of water-free products, Pa
R = constant of the gases, J$\cdot$mol$^{-1}\cdot$K^{-1} (Pa$\cdot$m$^3\cdot$mol$^{-1}\cdot$K^{-1} in Eq. 13)
r_i, r_{i_0} = reaction rate of the formation of portion i, for a given value of time on stream, and for the fresh catalyst, (g of portion i) (g of total mass) h^{-1} (g of catalyst)$^{-1}$ (g of water-free products)$^{-1}$
u = linear gas velocity, m$\cdot$h^{-1}
W = catalyst mass, g
X_A, X_C, X_G = weight fraction on a water-free basis of segments A, C and G, respectively
X_i = weight fraction of segment i, on a water-free basis
Z = total length of the reactor, m
z = longitudinal coordinate of the reactor, m
ϵ = bulk porosity
ρ = catalyst density, g$\cdot l^{-1}$
τ = space time (W/F_{M_0}), (g of catalyst)$\cdot$h$\cdot$(g of methanol)$^{-1}$
ξ = dimensionless longitudinal coordinate of the reactor (z/Z)

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