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Regeneration of a HZSM-5 zeolite catalyst deactivated in the transformation of aqueous ethanol into hydrocarbons

A.T. Aguayo *, A.G. Gayubo, A. Atutxa, B. Valle, J. Bilbao

Departamento de Ingeniería Química, Universidad del País Vasco, Apartado 644, 48080-Bilbao, Spain

Abstract

A study has been made of coke combustion for regenerating a HZSM-5 catalyst deactivated in the transformation of aqueous ethanol into hydrocarbons (BTG process). Combustion activation energy decreases with the H/C ratio of the coke and this ratio decreases with aging prior to combustion. Consequently, the prior aging of the coke is required in order to reproduce the combustion kinetics (activation energy $\approx$29.50 kcal/mol). By conducting experimentation following reaction–regeneration cycles, activity recovery has been studied by following the composition of the products obtained in the reaction cycle subsequent to each partial regeneration of the catalyst. The acidity of the partially regenerated catalysts has been determined by differential adsorption and TPD of ammonia. It has been proven that a catalyst subjected to severe deactivation during the reaction and regeneration steps undergoes a slight hysteresis in the activity–coke relationship, whereas there is no hysteresis in the acidity–coke relationship, except in the first cycle of reaction–regeneration in which there is a slight irreversible loss of acidity with no bearing on the kinetic results.

Keywords: Regeneration; HZSM-5 zeolite; BTG process; Reactivation; Acidity

1. Introduction

The catalytic transformation of bioethanol (aqueous ethanol), which is the liquid product obtained by biomass fermentation, is an interesting avenue for valorization of natural hydrocarbons (vegetable biomass, agroforest residues and sugar industry wastes), given that costly operations for eliminating the water and pure ethanol forthcoming are avoided (partial elimination of water is sufficient) [1], and subsequently light olefins (raw material for petrochemistry) and C_5–C_{10} hydrocarbons (useful as fuel) are obtained.

In the reaction scheme of the BTG (bioethanol to gasoline) process (Fig. 1), ethylene is the primary product. The first step in the transformation of bioethanol into ethylene is the process called BETE (bioethanol to ethylene), which requires a lower temperature than the BTG process and a catalyst of lower acidity. Using a HZSM-5 zeolite and a temperature above 350 °C, bioethanol is completely transformed into ethylene at the reactor inlet and, subsequently, via oligomerization, isomerization and cracking steps, C_3–C_{10} hydrocarbons are obtained. The reaction conditions (space time, temperature) and, particularly, water content have a major incidence on product distribution [2–4] and on catalyst deactivation. The water in the reaction medium attenuates the deactivation by coke when the reaction temperature is moderate [2], but above 450 °C zeolite dealumination is significant [5].

In a previous paper [6], the main aspects of the deactivation of a HZSM-5 catalyst in the BTG process have been studied. These aspects are the deposition rate and nature of the coke and the limit operating conditions in order to avoid the deterioration of active site acidity. Given the rapid deactivation of the catalyst, the industrial viability of the process is conditioned by catalyst regeneration. In this paper, the regeneration of this catalyst by coke combustion with air has been studied and the two kinetic tools required for the design of the regenerator have been determined. These tools are: (1) the kinetic equation of coke combustion; (2) the reactivation kinetics (activity recovery with

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* Corresponding author.
E-mail address: iqpagura@lg.ehu.es (A.T. Aguayo).

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Notation

a_o, a	activity at the end of regeneration and at the beginning of regeneration, respectively
A_r, k_r	frequency factor and kinetic constant of coke combustion (Pa^{-1} s^{-1})
C_c	coke content (wt.%)
E_r	activation energy for coke combustion (kcal mol^{-1})
F_{Eo}	mass flow of ethanol in the feed (g h^{-1})
P_{O_2}	partial pressure of oxygen (Pa)
R	constant of gases (kcal mol^{-1} K^{-1})
t	time on stream (min)
T_c	combustion temperature (°C)
t_c	combustion time (min)
W	catalyst weight (g)
X_i	mass fraction of i component in the reaction medium, by mass unit of organic components
X_{Eo}	mass fraction of ethylene in the reaction medium, by mass unit of organic components, at zero time on stream
X_{Wo}	water/ethanol mass ratio in the feed

regeneration time). Furthermore, acidity recovery of the catalyst throughout regeneration is monitored.

2. Experimental

The catalyst has been prepared by agglomerating 25% weight of HZSM-5 zeolite (prepared following Mobil patents [7] with an atomic ratio of Si/Al = 24) with bentonite (30%) and using inactive alumina (45%) as inert charge. The calcination temperature (570 °C) is suitable for obtaining a stable acid structure for reaction–regeneration cycles [8]. The physical properties of the catalyst, determined by N_2 adsorption–desorption in a Micromeritics ASAP 2000, are: surface area, 131 m^2 g^{-1}; pore volume, 0.43 cm^3 g^{-1}; apparent density, 1.21 g cm^{-3}; real density, 2.53 g cm^{-3}. The contribution of pores of different size to the total pore volume is: $d_p < 10^{-3}$ μm (micropores), 8.1%; 10^{-3} μm < $d_p < 10^{-2}$ μm (mesopores), 14.7%; 10^{-2} μm < d_p < 2 μm (macropores), 77.2%. The Brönsted/Lewis site ratio, determined by FT-IR analysis (Nicolet 740 provided with a Spectra Tech chamber) of adsorbed pyridine is 2.9.

The reaction–regeneration runs have been carried out in automated reaction equipment [5] provided with an isothermal fixed-bed reactor of 316 stainless steel of 9 mm internal diameter and 1 m length. The reactor is connected, by means of a thermostated line, to Hewlett-Packard 6890 chromatograph, in order to analyse the reaction products. The analysis of products is carried out by means of a system made up of three columns: (1) HP-1 semicapillary column for splitting the sample into two fractions: (a) volatile hydrocarbon components (C_{4-}) and polar components (ethanol, water and diethyl ether); (b) remaining products (C_{5+}). (2) SUPEL-Q Plot semicapillary column for individually separating out both volatile components and polar components, which will subsequently be analysed by TCD and FID. (3) PONA capillary column for separation of C_{5+} hydrocarbons, which will be analysed by FID. The results of reaction component concentration, expressed as wt.% by organic mass unit, are determined from the chromatographic results by means of a program written in FORTRAN. This program carries out both the carbon atom and the mass balances by calculating, from the stoichiometry of its formation, the water formed along time on stream.

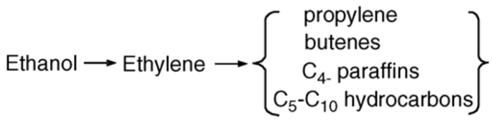

Fig. 1. Simplified kinetic scheme of the transformation of bioethanol on a HZSM-5 zeolite catalyst.

The results of the evolution of product distribution with time on stream for a given set of experimental conditions are shown as an example in Fig. 2. Deactivation is caused by the deposition of coke and, in order to recover catalyst activity, regeneration by coke combustion is required.

Three sets of reaction–regeneration runs have been carried out at atmospheric pressure. The conditions of the reaction step, corresponding to three levels of deactivation, are set out in Table 1. Subsequent to the reaction step, the bed is subjected to sweeping with N_2 following a temperature ramp up to 550 °C. The N_2 stream is maintained for 30 min at this temperature prior to coke combustion with air (40 cm^3 min^{-1}). Combustion has been carried out for: 15, 30, 60 and 120 min (complete coke combustion).

The acidity of the partially regenerated catalysts and the kinetics of coke combustion have been determined in a SDT

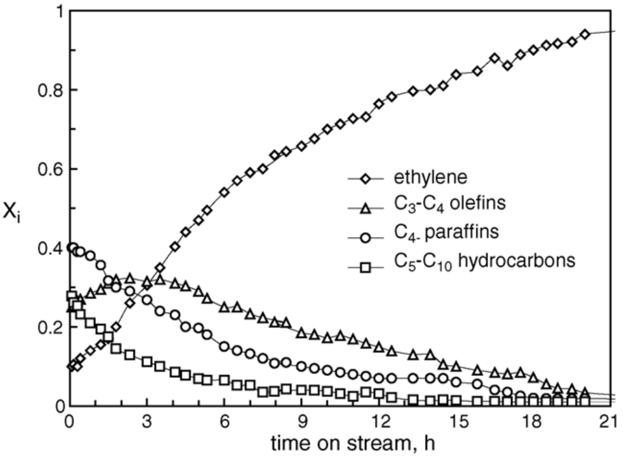

Fig. 2. Evolution with time of the product distribution in the transformation of aqueous ethanol. Temperature = 450 °C, space time = 0.387 (g of catalyst) h (g of ethanol)$^{-1}$; water/ethanol mass ratio in the feed = 1.

Table 1
Conditions of the reaction step in the reaction–regeneration cycles

Deactivation level	Temperature (°C)	Time (h)	Space time (g of catalyst) h (g of ethanol)$^{-1}$	Water in the feed (made up of ethanol + water) (wt.%)
Slight	350	6	0.709	75
Moderate	450	6	0.219	6
Severe	450	56	0.827	6

2960 thermobalance (TA Intruments) that allows for the simultaneous measurement of mass and enthalpy variations. The thermobalance is on-line with a Thermostar mass spectrometer (Balzers Instruments).

The kinetics of coke combustion has been determined by dynamic experimentation, following a temperature–time sequence. Once the deactivated catalyst has been stabilized at 300 °C in a helium stream, the oxidant stream is fed (25% oxygen in helium) and heating is started at a rate of 3 °C min^{-1} up to 550 °C. This temperature is maintained for 1 h in order to complete coke combustion. During this time, the values of temperature, mass, temperature difference with a reference sample and the intensity in the mass spectrometer of the peaks corresponding to the masses 18 (water), 28 (CO), and 44 (CO_2) are registered. From the latter values, the atomic H/C ratio of the coke corresponding to each sample of deactivated catalyst is determined. Regeneration temperature has been established at 550 °C, in order to ensure that temperature at any point in the reactor is lower than the calcination point (570 °C), which will provoke partial deterioration of the acid sites.

In order to measure surface acidity, the sample has been subjected to an in situ sweeping with He at 500 °C for 30 min, and temperature is stabilized at 150 °C. A NH_3 stream is then introduced until the sample is saturated and the physisorbed NH_3 is subsequently desorbed by sweeping with He at 150 °C, which allows for determining the total acidity (total amount of chemisorbed base). Subsequently, the chemisorbed ammonia is desorbed at programmed temperature (TPD) by heating the sample at a rate of 5 °C min^{-1} up to 550 °C and the intensity of the peak corresponding to the mass 15 of NH_3 (which is not masked by the possible desorption of water, as happens with the main peak 17) is monitored in the mass spectrometer.

3. Results

3.1. Coke combustion kinetics

Combustion of the coke deposited on the catalyst subjected to different operating conditions has been studied in the transformation of aqueous ethanol: temperatures of 350, 400 and 450 °C; varying space time, up to 0.827 (g of catalyst) h (g of oxygenate)$^{-1}$; feed consisting of mixtures of ethanol/water with different water content, and of pure diethyl ether and ethylene.

The results of coke content remaining in each catalyst sample, C_c, which have been obtained throughout the dynamic experiments in thermobalance, have been fitted to a first order kinetics with respect to oxygen and to the coke content in the catalyst, as is widely accepted in the literature [9–11]:

$$-\frac{dC_c}{dt} = k_r C_c P_{O_2} = A_r \exp\left(\frac{-E_r}{RT}\right) C_c P_{O_2} \qquad (1)$$

The kinetic parameters (frequency factor, A_r, and activation energy E_r) of best fitting have been calculated by minimizing (by means of the Solver tool included in the spreadsheet Excel 7.0 for Windows) the sum of residuals between the experimental data of weight loss rate and those calculated using Eq. (1), as is shown in Fig. 3. It has been proven that the kinetic parameters corresponding to the combustion of the cokes studied fulfill the compensation effect (also named isokinetic effect, theta rule or linear relationship of the free energy) [12], which implies the fulfillment of a linear relationship between the logarithm of the frequency factor and the activation energy.

The two results shown in Fig. 3 correspond to the combustion of the coke deposited on the same partially deactivated catalyst, but under two different states. One sample has been burnt without aging (not subjected to any treatment prior to combustion). The other sample has been subjected to an aging treatment consisting of a sweeping with He at 550 °C for 40 min. It is proven that the

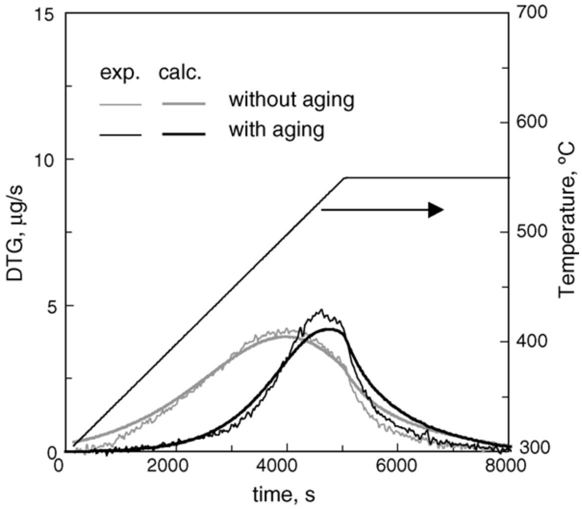

Fig. 3. Experimental results and those calculated with Eq. (1) for the combustion of the coke deposited under conditions of slight deactivation.

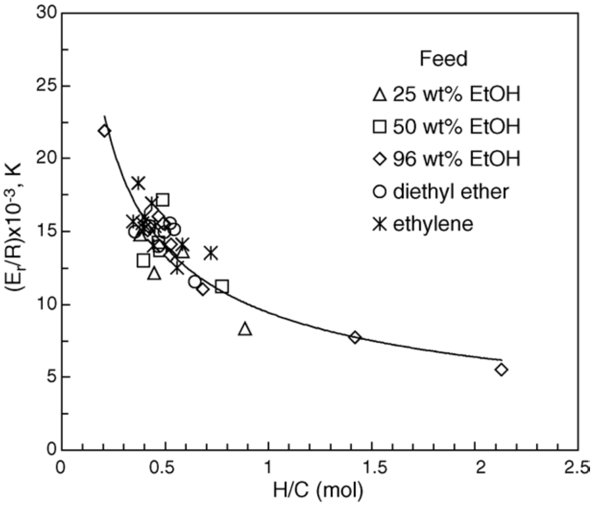

Fig. 4. Effect of the H/C ratio of the different coke samples on the activation energy of the combustion.

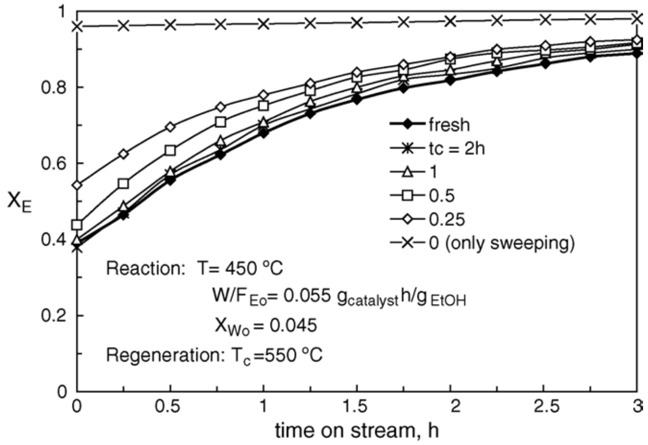

Fig. 5. Experimental results of ethylene mass fraction (by mass unit of organic components) vs. reaction time at 450 °C, 0.055 (g of catalyst) h (g of ethanol)$^{-1}$ and 94 wt.% of ethanol in the feed for the fresh catalyst and subsequent to different regeneration times. Reaction step in the first cycle: conditions for moderate deactivation in Table 1.

combustion of a non-aged coke starts at a very low temperature, 300 °C, given that it corresponds to a slightly evolved coke (highly hydrogenated). The aged sample requires a higher temperature to start coke combustion (≈400 °C), which is due to the fact that its H/C has decreased during aging to a value close to 0.5.

When the values of the activation energy corresponding to the combustion of the different coke samples and their H/C ratio are analysed (Fig. 4), lower activation energies are obtained for the more hydrogenated cokes. In general, when the samples are sufficiently aged, very similar values are obtained for the kinetic parameters (E_r/R between 13,000 and 16,000 K), independently of the reaction conditions (temperature, space time and composition of the feed), and a value close to 0.5 is obtained for the H/C ratio. It is noteworthy that, for a reaction time of 56 h, a very high value is obtained for the activation energy ($E_r/R = 21{,}900$ K), which corresponds to a very hard coke, with a highly graphitic structure, as confirms the low value of H/C ratio calculated for this sample (H/C = 0.21).

The evolution of the coke in the aging treatment by using a stream of inert gas or hydrogenating gas has been studied in the literature [13,14]. This aspect is especially important in those processes in which the operating conditions (such as low temperature and high water content in the reaction medium) or the shape selectivity of the catalyst favour a slightly evolved coke. The composition of these cokes is significantly altered (aging) by the sweeping treatment prior to combustion, which is usually required in the studies carried out either in thermobalance, laboratory scale or industrial reactors. Consequently, combustion is very different depending on prior treatment. In order to avoid this problem, coke combustion studies must be carried out subsequent to an aging treatment that equilibrates its structure. Thus, the results will be reproducible and applicable to the industrial stage of regeneration.

In view of the results obtained, for a sufficiently aged coke, average values of combustion kinetic parameters may be established: $A_r \approx 11.31$ Pa^{-1} s^{-1}; $E_r/R \approx 14{,}800$ K. This value of activation energy is not very high, although it is slightly higher than that previously obtained for a catalyst based on HZSM-5 zeolite used in the MTG process [15,16], which is explained by the fact the H/C ratio obtained for the coke in this process (≈0.5) is lower than that corresponding to the MTG process (≈1.0) [15]. This difference is a consequence of the higher reaction temperature in the BTG process.

3.2. Activity recovery during regeneration

Activity recovery of the catalyst has been studied by means of reaction–regeneration cycles carried out using different regeneration times, according to the procedure developed by Gayubo et al. [17]. In each series of cycles, the reaction conditions are maintained constant and the catalyst is subjected to combustion for different times at 550 °C. As an example of the results, the effect of combustion time, t_c, on the initial composition of ethylene in the reaction step subsequent to combustion, X_{Eo}, is shown in Fig. 5.

The activity recovered, a_o, is determined from the ethylene composition in the product stream for zero time on stream, X_{Eo}. Accordingly, as is schematically shown in Fig. 6, the composition–time and activity–time relationships [6] are used, which are the numerical solutions of the mass conservation equation for ethylene in the reactor and of the kinetic equation for deactivation, respectively. The values of the activity recovered, a_o, as a function of the combustion time of the coke, t_c, for the three catalysts with different level of initial deactivation, are shown in Fig. 7. The set of curves has been fitted to the following empirical equation, which allows for verifying the activity recovered, a_o, starting from

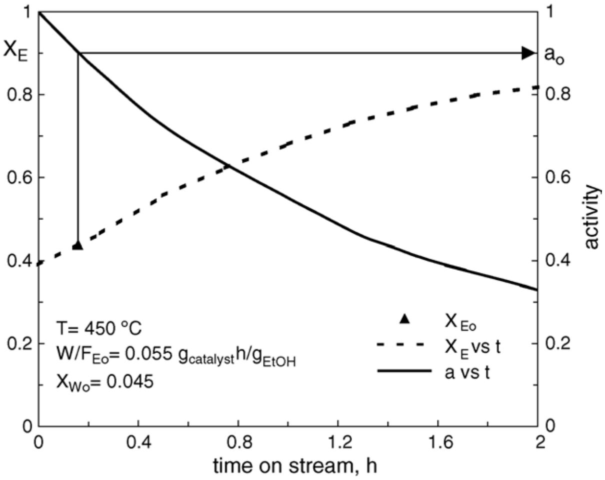

Fig. 6. Procedure for calculation of the activity recovered, a_o, for a given combustion time, from the composition of ethylene in the product stream at zero time on stream, X_{Eo}.

a given activity, a, subsequent to a given combustion time, t_c:

$$a_o = 1 - (1 - a)\exp[-((4.0a - 2.0)10^{-4}t_c + (0.240a - 0.037)t_c^2)] \tag{2}$$

Furthermore, the coke content remaining in the partially regenerated catalyst samples has been determined by using the thermobalance. Fig. 8 shows the values of the activity recovered vs. the coke content remaining in the regeneration, for three initial levels of catalyst deactivation. This figure also shows (solid line) the average trend of the relationship activity–coke obtained during the reaction step (during catalyst deactivation) [6]. It is observed that the reactivation of a catalyst with a slight deactivation follows the same activity–coke trend as that obtained for the reaction step. Nevertheless, for the catalysts subjected to moderate and severe deactivation, a slight hysteresis in the relationship activity–coke (a different evolution compared to that of the reaction step) is observed. Thus, for the same coke content, the activity initially recovered in the regeneration is slight higher than the activity in the reaction step. The hysteresis significantly attenuates for low coke contents; that is, when the catalyst is considerably regenerated.

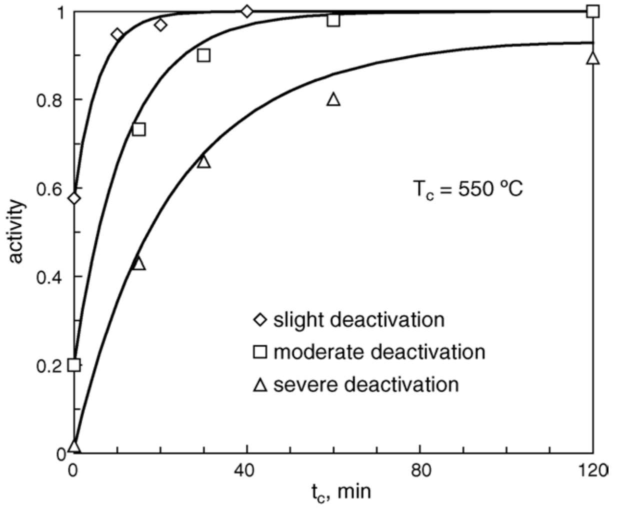

Fig. 7. Activity recovery as a function of combustion time for catalysts with different level of deactivation. Lines: calculated with Eq. (2). Points: experimental.

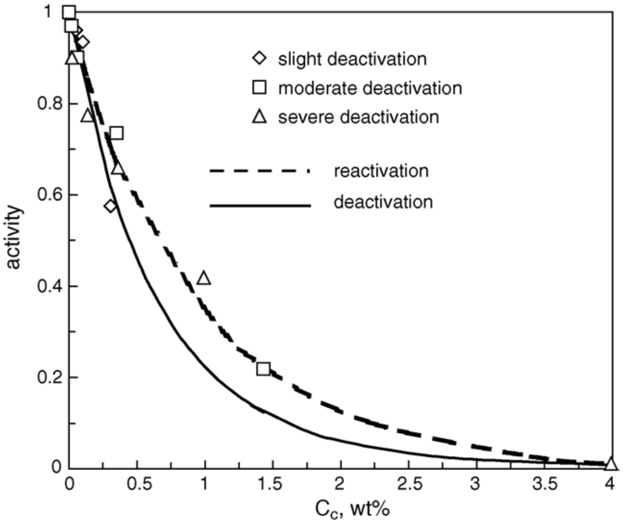

Fig. 8. Hysteresis in the activity–coke content relationship for reaction–regeneration cycles.

These hysteresis phenomena in the activity–coke content relationship have also been observed in the MTG [18] process, where the hysteresis is more pronounced due to the higher coke content. This coke blocks the pores in the MTG process, thereby hindering the onset of reactivation.

3.3. Acidity recovery during regeneration

Acidity recovery is shown in Figs. 9 and 10. Fig. 9 displays the total acidity (total amount of ammonia

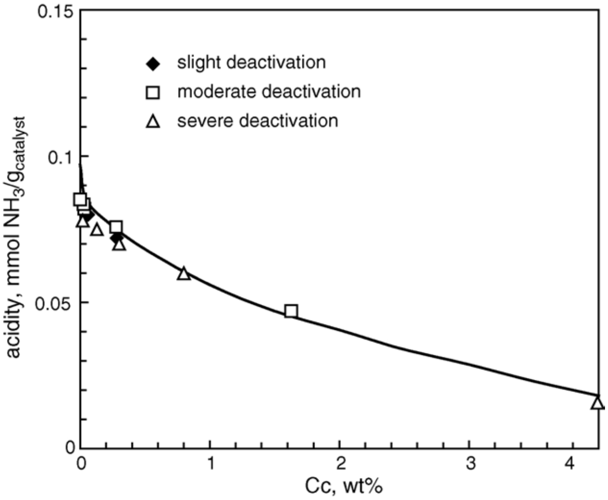

Fig. 9. Acidity–coke relationship during the reactivation of catalysts with different level of deactivation.

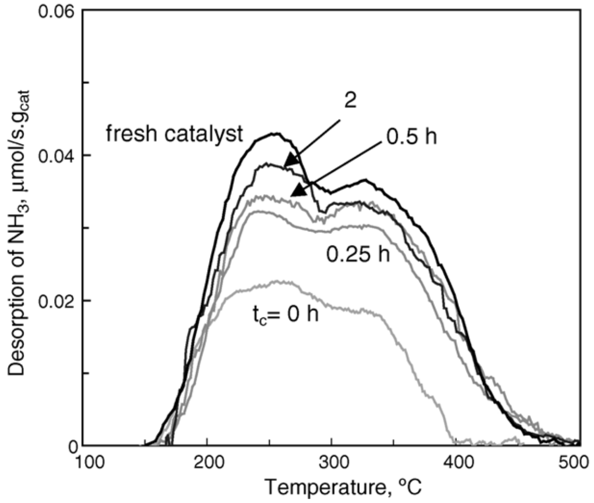

Fig. 10. TPD of ammonia for the fresh catalyst and at different states of regeneration subsequent to moderate deactivation conditions.

chemisorbed at 150 °C) of the catalyst under different states of regeneration against the coke content remaining in the catalyst subsequent to different combustion times at 550 °C. The results shown are those corresponding to the reactivation of three catalysts with different levels of initial deactivation (points) and the average trend of acidity–coke content obtained for catalyst deactivation (reaction step) (curve) [6]. The results of TPD of NH_3 for the partially regenerated catalysts, which were previously subjected to moderate deactivation conditions, are shown in Fig. 10.

As is observed in Fig. 9, during the reaction step (curve) there is initially a very fast loss of active sites and subsequently the acidity–coke relationship is almost linear. The recovery of the total acidity of the catalyst for the different coke contents in the regeneration is almost the same as the loss of acidity during the reaction, except for very low values of coke contents, which means that the catalyst does not recover the fraction of sites that have been lost rapidly during the initial reaction period.

As is qualitatively observed in Fig. 10, for the initial 15 min of coke combustion (in which approximately 80 wt.% of the coke is eliminated) regeneration is slightly selective for the strong acid sites (desorption peak at 335 °C). Subsequently, weak and strong acid sites are recovered in a similar proportion. In order to make a quantitative analysis, by means of deconvolution of the two peaks shown in Fig. 10, the areas corresponding to each individual peak have been calculated; strength acidity, As, (mmol of NH_3) (g of catalyst)$^{-1}$, and weak acidity, Aw, (mmol of NH_3) (g of catalyst)$^{-1}$. Thus, subsequent to 15 min regeneration, the increase in As (from 0.020 to 0.038 (mmol of NH_3) (g of catalyst)$^{-1}$) is 10% greater than the increase in Aw (from 0.027 to 0.034 (mmol of NH_3) (g of catalyst)$^{-1}$). Subsequently (between 15 min and 2 h regeneration), acid sites are recovered at the same rate, both strong sites (from 0.038 to 0.051 (mmol of NH_3) (g of catalyst)$^{-1}$) and weak sites (from 0.034 to 0.046 (mmol of NH_3) (g of catalyst)$^{-1}$).

It is also proven that the total area under the desorption curve (indicative of the total amount of NH_3 chemisorbed) for the catalyst regenerated for 2 h (0.088 (mmol of NH_3) (g of catalyst)$^{-1}$) at 550 °C is slightly lower than that of the fresh catalyst (0.097 (mmol of NH_3) (g of catalyst)$^{-1}$), which is evidence of a irreversible loss of a small fraction of acid sites, as is shown in Fig. 9. Nevertheless, it has been proven (Fig. 7) that this catalyst does recover the activity corresponding to the fresh catalyst. This result is explained by the fact that these sites are strongly acid and they are selectively lost at the beginning of the reaction. Consequently, they are not relevant in the determination of the global kinetics of the process and in the calculation of the activity values, given that they cannot be quantified in the experiments of deactivation, as they have been ignored in the extrapolations of composition to zero time on stream.

Moreover, this irreversible loss of a small fraction of sites takes place only during the first reaction–regeneration cycle, but is not observed in successive cycles. Consequently, from the second reaction–regeneration cycle, the total amount of sites present at the beginning of the reaction of the second cycle is recovered and this reproducibility in the results is maintained even after six cycles. Consequently, except for the first initial period of the first reaction–regeneration cycle, there is no hysteresis in the evolution of the acidity–coke relationship corresponding to the steps of reaction and regeneration of the catalyst subjected to a moderate deactivation.

The maximum acidity recovered by the catalyst subjected to 56 h of reaction at 450 °C with a feed containing 6 wt.% of water is slightly lower than that recovered by the catalyst subjected to only 6 h of reaction at 450 °C and, moreover, this catalyst subjected to severe deactivation does not recover the activity corresponding to the fresh catalyst (Figs. 7 and 8). This result may be due to the fact that under these reaction conditions (450 °C and a low water content in the reaction medium) there is an irreversible loss of sites by dealumination of the zeolite (due to the presence of steam at high temperature). This loss accumulates throughout the reaction, but under the conditions indicated it is only incipient, which means that it is not significant in a few reaction–regeneration cycles when the duration of the reaction step is 6 h, but it begins to be manifest subsequent to 56 h of reaction.

The ammonia TPD technique used for characterizing the acidity of the catalysts prepared with HZSM-5 zeolite and those partially deactivated with coke has been proven to be useful for explaining the results on deactivation in the MTG and MTO processes [19,20]. In these processes, this technique is suitable because the low molecular size of ammonia avoids diffusional restrictions within the micropores partially blocked by coke. Furthermore, in these processes and, particularly in the one studied in this paper, even very weak acid sites are significant, being measured by ammonia TPD. Nevertheless, quantification of these sites (in order to ascertain the catalytic capacity) in processes in which exclusively very strong sites are required would lead to error. The catalytic capacity in these latter processes would be overestimated by ammonia TPD [21].

4. Conclusions

The regeneration of the HZSM-5 catalyst used in the transformation of aqueous ethanol into hydrocarbons (BTG process) requires an aging treatment of the coke prior to combustion, in order to ensure a homogeneous and reproducible combustion independently of the reaction conditions and in order to avoid uncontrolled combustion of light components. The moderate value of the activation energy for the combustion of a sufficiently aged coke ($\approx 29.50\ \text{kcal mol}^{-1}$) is evidence of a relatively high reactivity of the coke deposited on the HZSM-5 catalyst in the BTG process.

By carrying out experimentation in reaction–regeneration cycles, a kinetic equation for reactivation has been calculated; that is, the relationship between activity recovered and the combustion time with air at 550 °C, Eq. (2). This equation is required for the design and optimization of a reactor that operates in reaction–regeneration cycles, in order to determine the activity recovered at the beginning of each reaction step.

There is a very rapid activity recovery of the catalyst in the first period of regeneration. When the deactivation level of the catalyst is relatively high (ethanol feed with a low content of water), there is a slight hysteresis in the activity–coke relationship corresponding to the reaction and regeneration steps. Consequently, in the first period of regeneration (high coke content), a higher activity level than that of the catalyst in the reaction step is recovered for a given coke content. Subsequently, the hysteresis is almost insignificant. This result notably differs from that previously found for the MTG process on the same catalyst. The difference between the results of both processes is explained by the lower coke content of the catalyst in the transformation of ethanol, which does not block the internal channels of the zeolite crystals.

Subsequent to the total elimination of the coke in the first reaction–regeneration cycle, the catalyst does not recover all the acid sites, although it does recover the activity corresponding to the fresh catalyst. This result is explained by the fact that the fraction of non-recovered sites is rapidly lost at the initial period of the reaction and is not quantified in the calculation of catalyst activity. There is no irreversible loss of acid sites in the subsequent six cycles of reaction–regeneration and no hysteresis is appreciated in the acidity–coke relationship. The reaction conditions at 450 °C with low water content in the reaction medium are the threshold from which there is irreversible loss of active sites by zeolite dealumination. Thus, for higher water contents in the reaction medium and higher temperatures, an irreversible loss of active sites in the successive cycles may take place.

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