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Effects of the Operating Conditions on Coke Deactivation of 5A Molecular Sieve in N-Decane Adsorption/Desorption

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Abstract. The influence of operating conditions (time-on-stream, temperature, pressure and paraffin feed concentration) on the deactivation of a 5A molecular sieve during the adsorption/desorption of *n*-decane has been studied using a cyclic operating procedure. After 10 adsorption/desorption cycles, the 5A molecular sieve used in this study showed the same deactivation level as an used industrial molecular sieve provided that the deactivation of the zeolite was due to coke deposition by site coverage and pore blockage. The temperature effect was studied in the range of 373–523 K, obtaining a minimum deactivation at 448 K. The pressure does not influence adsorption parameters in the range of 1–3 MPa, but it does affect the nature of the coke deposited on the zeolite. The influence of paraffin concentration can be considered negligible.

Keywords: 5A zeolite, coke deactivation, *n*-decane, liquid phase adsorption, adsorption/desorption cycles

Introduction

In addition to drying and purification processes, zeolite 5A has been widely used at industrial scale in several processes involving *n*-paraffins separation from kerosene by selective adsorption (Broughton, 1968). As a consequence of the operating conditions used ($T = 448$ K and $P = 2.1$ MPa), the presence of coke precursors in the kerosene and the high acidity of the 5A zeolite, the adsorbent is affected by a deactivation process mainly due to coke deposition on the zeolite surface. Thus, the zeolite gradually loses its adsorption capacity and should be replaced after a given time-on-stream (normally, 3–4 years).

From the studies so far reported, two major mechanisms of zeolite deactivation by carbon residue involving catalytic processes have been proposed: site coverage and pore blockage, where the latter is considered a more severe mechanism (Guisnet and Magnoux, 1989). Likewise, it has been shown that the deactivation of a zeolite by these residues not only depends on the nature of the feedstock and operating conditions, but also on the properties of the zeolite used, like its porous structure and acidity (Langner, 1981; Bhatia et al., 1989; Bibby, 1992; Uguina et al., 1993; Sotelo et al., 1993, 1994, 1996).

Although zeolite 5A should present low coking because of its pore opening (0.49 nm), the presence of large cavities in its structure of 1.14 nm in diameter, compensates this trend. Therefore, the formation of large molecules inside the cavities could restrain them from diffusing out of the particle. In addition they also could act as coke precursors, thus increasing the deactivation rate of this zeolite.

The objective of this work is to study the deactivation of 5A zeolite during the adsorption/desorption of *n*-paraffins. With this aim, a cyclic procedure designed to reach a fast deactivation of the zeolite was employed (Díaz, 1997). The influence of the operating conditions during the adsorption step, such as time-on-stream,

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temperature, pressure and paraffin feed concentration have been analysed. Furthermore, the influence of these variables on the nature of the coke deposition has also been analysed.

Experimental

Materials

A commercial molecular sieve 5A was used in this study, in the form of spherical beads of 0.7 mm average diameter, with an acidity of 1.07 meq $NH_3 \cdot g^{-1}$, a surface area of 566 $m^2 \cdot g^{-1}$ and a pore volume of 0.23 $cm^3 \cdot g^{-1}$. A sample of this molecular sieve from a commercial unit taken after three years-on-stream was used as deactivation reference. n-Decane (n-C_{10}) and iso-octane (i-C_8) used in this study as representatives of a model feed stream were of high purity grade ($\geq$99.5%).

Characterisation

Carbon, hydrogen and nitrogen contents in fresh and deactivated solid samples, dried at 373 K for 12 h, were measured in a Leco CHN-600 analyser. The crystallinity was determined from the XRD spectra obtained in a Siemens-Kristalloflex D500 diffractometer with Cu Kα radiation and Ni filter. Thermogravimetric analyses were performed in a Mettler TA3000 system, using inert (N_2) and oxidant (air) atmospheres with a volumetric flow rate of 60 $Nm^3 \cdot min^{-1}$ and a heating rate of 5°C$\cdot min^{-1}$ up to 748 K. Finally, the soluble carbon residues of the spent sample were extracted according to the procedure previously described (Magnoux, 1987; Guisnet, 1989) and analysed by gas chromatography and IR spectroscopy (Conley, 1979; Silverstein, 1980).

Experimental Set Up

Adsorption/desorption runs were carried out in a 318 stainless steel downflow fixed bed, with an internal diameter of 4.9 mm and 1.5 m length, placed in an oven and packed with 11 g of 5A zeolite. The temperature of the bed was measured and controlled with thermocouples at two axial positions; a back-pressure-regulator (BPR) was used to maintain constant pressure in the bed. A displacement pump was used to feed the adsorption mixture into the bed. The effluent was analysed by gas chromatography (GC), using a capillary column.

Operating Procedure

A cyclic procedure, combining adsorption and desorption steps, was used to study the deactivation of the adsorbent. The adsorption step was carried out in liquid phase, at high temperature (373–523 K) and pressure (1.1–3.1 MPa) feeding rate 6 $cm^3 \cdot min^{-1}$ of a mixture consisting of n-C_{10} and i-C_8. The concentration of n-C_{10} was varied in the range 2–9.6% by weight. Under these conditions, the ratio of volumetric flow/mass of adsorbent was more than fifty times larger than used in the commercial unit, thus providing an accelerated deactivation process suitable for laboratory studies. In all the cyclic runs, the duration of the adsorption step was kept constant at 70 min, which was 1.6 times longer than the saturation time required for the fresh 5A sample. The desorption of n-C_{10} was carried out by purging with pure He at 573 K for 16 hours. Under these conditions, practically all the n-C_{10} was desorbed.

The level of deactivation of the adsorbent was determined from the breakthrough curves of n-C_{10} obtained in each adsorption step, using the following parameters:

- *Breakthrough point* (t_b): time when the adsorbate (n-C_{10}) starts to break in the effluent stream.
- *Saturation time* (t_s): time when the adsorbate concentration in the effluent reaches the feed value.
- *Slope of the breakthrough curve* (S), defined as:

$$S = \frac{C_{90\%C_0} - C_{10\%C_0}}{t_{90\%} - t_{10\%}} \tag{1}$$

where C and C_0 are the concentration of n-decane (wt%) in the effluent and in the feed, respectively.

This parameter (S) is proportional to the diffusion time constant, D_c/r^2(D_c, is the effective diffusion coefficient; r, the length of the diffusional pathway (Ruthven, 1984)), and therefore proportional to the adsorption rate of the paraffin in the molecular sieve.

- *Adsorption capacity* (q): mass of adsorbate taken up by an unit mass of zeolite. The mass of n-paraffin adsorbed, m_{ads}, is calculated as:

$$m_{\text{ads}} = \rho_m Q_v \left[X_0(t_s - t_R) - \int_{t_b}^{t_s} X_j(t)\,dt \right] \quad (2)$$

where ρ_m is the density of the feed mixture (g·cm^{-3}); Q_v, the volumetric flow (cm^3·min^{-1}); X_0, the mass fraction of adsorbate in the feed; $X_j(t)$, the mass fraction of adsorbate in the effluent and t_R, the residence time (min).

- *Deactivation degree after "i" cycles* (DD$_i$): loss of adsorption capacity at cycle i related to the adsorption capacity of zeolite in the first cycle, wt%.

$$\text{DD}_i = \frac{q_1 - q_i}{q_1} \cdot 100 \quad (3)$$

where q_1 and q_i are adsorption capacity of the adsorbent in the first and ith cycle, respectively.

Results and Discussion

Characterisation of the Deactivated Reference Sample

Table 1 shows the XRD analysis and C, H and N content of the spent sample of 5A zeolite used to establish the deactivation level of reference, compared with the fresh sample.

It can be seen that there are no changes with respect to the crystallinity of the 5A zeolite during the time-on-stream in the industrial process (≅3 years). The higher carbon content of the spent sample was the major difference observed. The carbon content detected in the fresh sample come from organic compounds used in the agglomeration process; its atomic H/C ratio (38.8) clearly indicates that detected hydrogen does not only originate from these compounds, but also from adsorbed humidity and/or from the crystallised water in the zeolite.

Table 1. Characterisation of the 5A zeolite reference sample: crystallinity, carbon content and H/C atomic ratio.

Sample	Crystallinity (%)	H/C atomic ratio[a]	Coke content[b] (%)
Fresh	100	38.8	–
Spent	100	2.5	5.1

[a] Of the soluble coke.
[b] Weight loss at 570–700 K.

Table 2. IR spectra of carbon residues present in spent 5A zeolite.

Wavelength (cm^{-1})	Link type	Absorbance (a.u.)[a]
2855.8	$-CH_2-$	0.7
2932.4	$-CH_2-$	1.2
2964.8	$-CH_3$	0.6
2981.0	C=C[b]	0.7
3035.9	C=C[b]	0.3

[a] a.u. arbitrary units.
[b] Olefinic and/or aromatic.

The carbon residues of the spent sample were totally soluble in CCl_2H_2 and CCl_4, and their GC analyse (Díaz, 1997) showed boiling points ranging between 448 and 553 K, the main individual components being β, γ C_{10}–C_{16} olefins as well as some aromatic compounds. The IR spectra of the soluble carbon residues confirmed that only olefinic and/or aromatic C=C links were detected, besides the paraffinic C—C links corresponding to the adsorbed paraffins (Table 2). These soluble carbon residues were responsible for the zeolite deactivation in an industrial process.

Finally, the TG analysis of N_2, Fig. 1, showed a two step weight loss of 16%. The weight loss detected at temperatures below 498 K was related to the desorption of both, the paraffins adsorbed in the zeolite pore system and the less evolved carbon residues physically adsorbed and/or retained on its external surface. On the other hand, the weight loss observed in the range of 570–700 K was assigned to the pyrolysis of the heavier carbon residues (further referred as "coke") deposited on the zeolite surface (internal + external), as it was observed in a previous study dealing with the regeneration of the 5A molecular sieve (Bonilla, 1992).

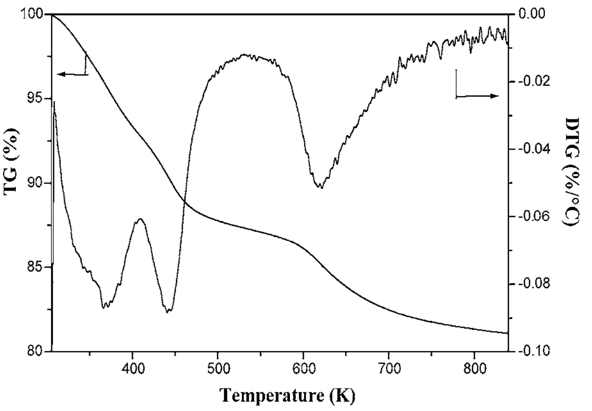

Figure 1. Thermogravimetric analysis of the deactivated 5A zeolite sample in N_2 atmosphere.

These results led us to set the desorption temperature of the cyclic operating procedure to 573 K, in order to ensure the complete desorption of the n-C_{10} as well as of that the carbon residues physically adsorbed on the zeolite surface, avoiding the pyrolysis of the heavier fraction.

Variation of the Adsorption Parameters with Time-On-Stream

Figure 2 shows the n-C_{10} breakthrough curves obtained in cycles 1, 5, 10 and 20 of a cyclic adsorption/desorption experiment carried out at 448 K and 2.1 MPa. The feed stream was introduced at 6 $cm^3 \cdot min^{-1}$ of n-C_{10}/i-C_8 mixture (2 wt% of n-C_{10}). As expected, the adsorption capacity and the breakthrough point of the n-C_{10} curves decrease with the number of adsorption/desorption cycles due to the deactivation of the adsorbent. The breakthrough point of the curves corresponds to the residence time of the experimental set up (8 min) in cycle 12.

The deactivation of the adsorbent can be better understood by following the evolution of the adsorption/desorption parameters calculated from the breakthrough curves (slope of the breakthrough curve (S), adsorption capacity (q) and deactivation degree (DD_i)), with respect to the number of cycles, as it is shown in Fig. 3.

From cycle 1 up to cycle 12, a decrease of the breakthrough curve slope is observed. This decrease is attributed to the steric hindrance caused by the coke deposited inside the particles by a site coverage mechanism. This coke reduces the available porosity inside the particles and the diffusion coefficient of the paraffin, D_c. From cycle 12 to 15 the decrease of the slope is attenuated, although after cycle 16 the slope even increases again. Since the slope of the breakthrough curve is proportional to the inverse of diffusional time, D_c/r^2, a possible explanation of this increase can be given in terms of a reduction of the effective diffusion length, r, caused by a pore section reduction which is enough to avoid the diffusion of the paraffin. This idea is supported by the fact that the decrease in adsorption capacity, q_i, is accentuated from cycle 16. Figure 3 also shows the evolution of the deactivation degree with time-on-stream, that reach a value of 80% in cycle 20.

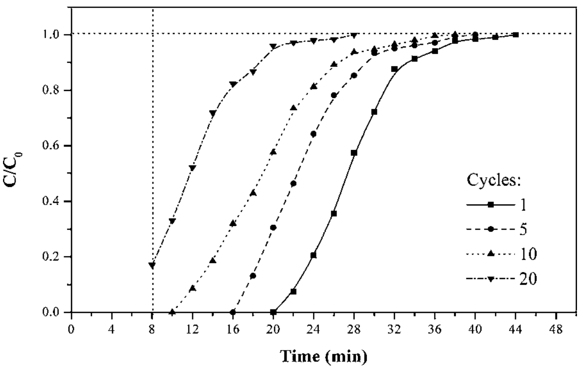

Figure 2. Breakthrough curves of n-C_{10} in the cyclic adsorption/desorption experiment. Operating conditions: $T = 448$ K, $P = 2.1$ MPa and 2 wt% of n-C_{10} in i-C_8.

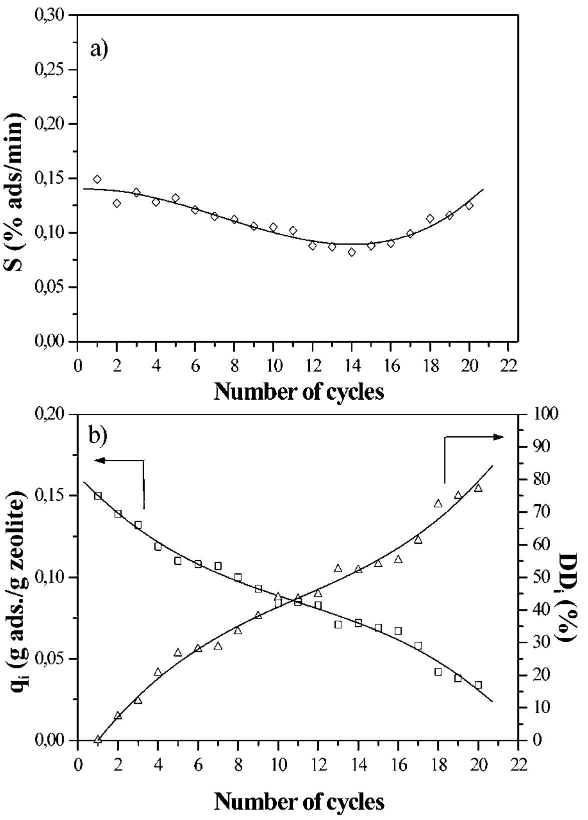

Figure 3. Variation of the adsorption parameters with time on-stream at 448 K: (a) Slope of breakthrough curve (S) vs number of cycles, (b) Adsorption capacity (q) vs number of cycles.

The H/C atomic ratio of the carbon residues (paraffins + coke) in the zeolite after 1, 10 and 20 adsorption/desorption cycles and the coke content of these deactivated samples (weight loss in the range 550–700 K) are summarised in Table 3. As expected, the coke content increases with time on stream, along with its heavier character.

Table 3. Characterisation of the deactivated samples after a number of adsorption/desorption cycles using 2 wt% of n-C_{10} in the feed.

Experimental conditions			H/C of the soluble coke	Coke content
T (K)	P (MPa)	No. of cycles	(atomic ratio)	(ww%)[a]
448	2.1	1	3.5	1.73
448	2.1	10	3.1	4.29
448	2.1	20	2.9	4.54
373	2.1	10	3.3	3.46
448	2.1	10	3.1	4.29
523	2.1	10	2.7	6.95
448	1.1	10	2.9	5.77
448	2.1	10	3.1	4.29
448	3.1	10	3.4	4.81

[a] Weight loss at 570–700 K.

Finally, one adsorption-desorption cycle was performed with the spent industrial reference sample. The deactivation degree obtained (relative to the fresh one) was 30% (Díaz, 1997). Thus, taking into account the values of deactivation degree obtained in Fig. 3(b), a 10 cycles run was considered long enough to study the effect of the operating conditions. This effect is presented below.

Effect of Temperature

The influence of the temperature during the adsorption step on the deactivation of the 5A zeolite has been studied at 373, 448 and 523 K. In all cases, the adsorption step was performed in liquid phase, as the boiling point of the mixture n-C_{10}/i-C_8 (2 wt% and 2.1 MPa), is 530 K. The influence of the adsorption temperature on the evolution of adsorption parameters with the number of cycles is shown in Fig. 4.

For the fresh bed (cycle 1), the slope of the breakthrough curve increases with temperature, showing a higher diffusion rate of the adsorbate (n-C_{10}). Besides, since adsorption is an exothermic process, the adsorption capacity decreases with this variable.

Figure 4 also shows the variation of the adsorption parameters with the number of cycles. At 448 and 523 K, a continuous decrease of the slope (S) and bed adsorption capacity (q_i) and accordingly, an uniform increase of the deactivation degree (DD_i) with the number of cycles are observed. Besides, the higher deactivation degree after 10 cycles (52 wt%) is obtained at 523 K. This result can be attributed to the fact that coke formation is favoured with temperature (Langner, 1981; Magnoux et al., 1987; Menon, 1990; Magnoux et al., 1993).

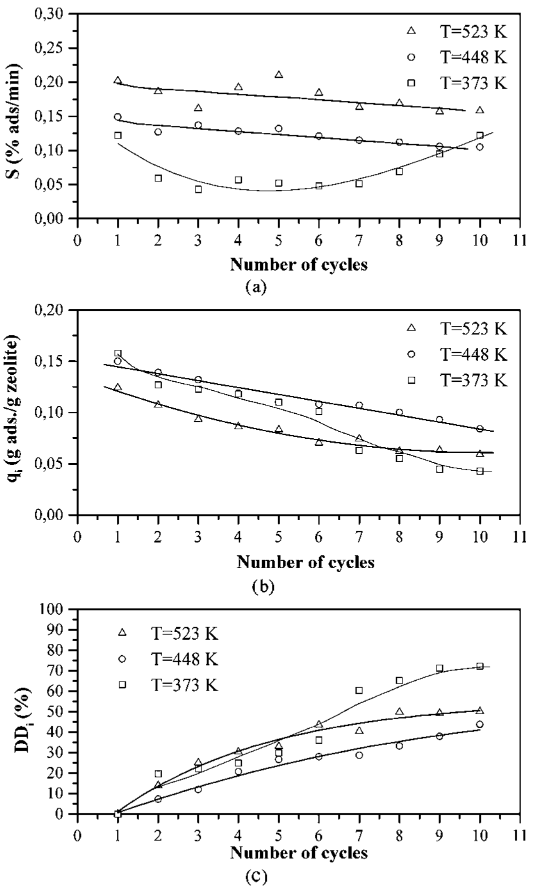

Figure 4. Effect of temperature on the adsorption parameters with reference to the number of cycles: (a) Slope of the breakthrough curve; (b) adsorption capacity; (c) deactivation degree.

However, considering only the effect of coke formation with temperature, the rapid decrease of adsorption parameters S and q_i at the lowest temperature (373 K) for the first cycles is unexpected. At this low temperature, the variation of these parameters must be attributed to the coupled effect of the low paraffin diffusivity and the coke deposition. When the diffusivity is low, small amounts of coke have a great impact on the adsorption parameters.

Another result deriving from the coupled effect of diffusivity and coke deposition is the variation with temperature of the minimum of S showed in Figs. 3(a) and 4(a) (5th and 14th cycles for 373 and 448 K, respectively). At 373 K this combined effect is much stronger

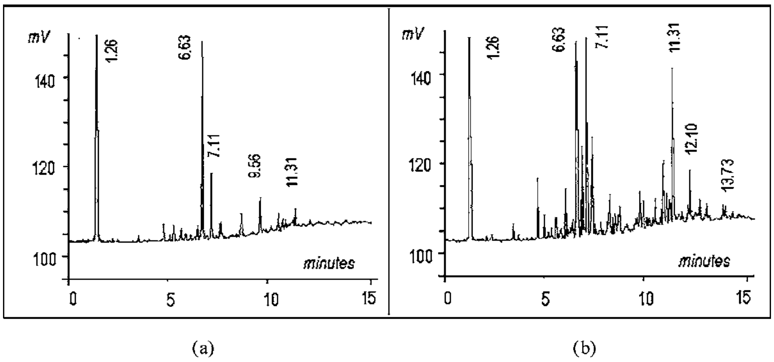

Figure 5. Chromatographic analysis of soluble coke deposited after 10 cycles at: (a) 373 K and (b) 523 K.

than at 448 K, explaining that the minimum of S takes place for a lower number of cycles.

The total C/H atomic ratio of the residues present in the deactivated samples and their coke content are also summarised in Table 3. The coke deposited on the sample deactivated at 523 K (6.95 wt%) is approximately 62 and 100 wt% larger compared to the one obtained at 448 K and 373 K, respectively. It can be seen that the coke content increases with the temperature of the adsorption step, as well as its heavy character (lower total H/C atomic ratio). The chromatographic analysis of the soluble residues of the experiments performed at 523 and 473 K, Fig. 5, also show a higher amount of coke with a heavier nature at the highest temperature. The formation of heavier coke at higher temperatures has also been observed by other authors (Menon, 1990; Magnoux et al., 1993; Uguina et al., 1994).

These results also support the fact that the deactivation effect at 373 K with low amounts of light coke deposited, should be a consequence of the lower n-C_{10} diffusion rate, previously commented. After 10 cycles, the lowest deactivation degree was obtained at 448 K, showing that the coupled effect of diffusivity and coke deposition is minimum at this temperature.

Effect of Pressure

Two additional experiments were performed at 448 K, at pressures of 1.1 and 3.1 MPa. In all cases, the adsorption step was carried out in the liquid phase, since the 2 wt% n-C_{10}/i-C_8 mixture used had a boiling point of 486 K at the lower pressure studied (1.1 MPa).

Since adsorption was developed in liquid phase, pressure did not affect the n-C_{10} adsorption in the first cycle, the differences in the slope of the breakthrough curves and the adsorption capacity being within the experimental error.

Figure 6 shows the variation of deactivation degree with the number of cycles at the three pressures studied.

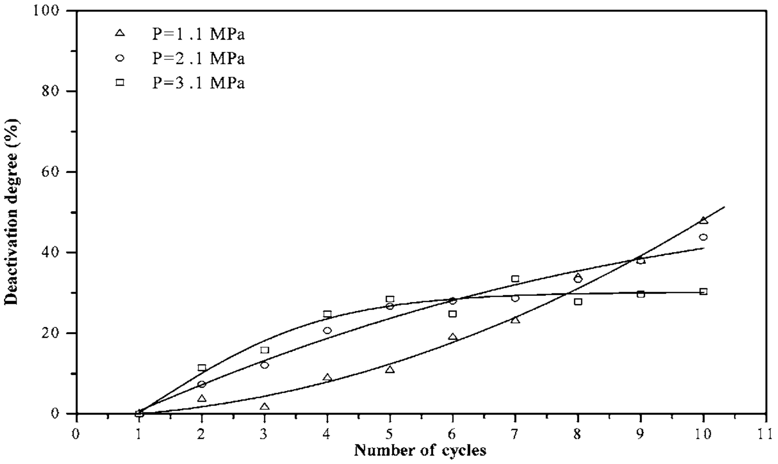

Figure 6. Effect of pressure: Variation of the deactivation degree with the number of cycles.

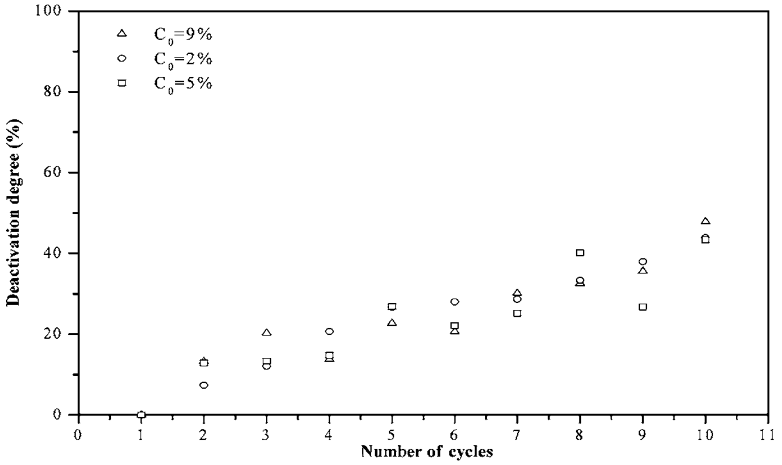

Figure 7. Effect of the paraffin concentration on the deactivation degree.

When the number of cycles performed is small (≤5), an increase of pressure seems to favour the deactivation of the zeolite. Nevertheless, an opposite influence is observed when the number of cycles is further increased. Thus, the effect of deactivation with the number of cycles increases at the lower pressure (1.1 MPa), whereas it slows down for the higher pressure (3.1 MPa).

To explain this result it must be taken into account the reaction mechanism that leads to the formation of the carbon residues from paraffins on the zeolite surface, in which dehydrogenation, oligomerization, cyclation, condensation and alkylation reactions in series and parallel take place (Bhatia, 1989). In this complex scheme, the condensation reactions are favoured at high pressures, leading to lighter coke residues, whereas the dehydrogenation reactions seem to be favoured at lower pressures, thus leading to heavier carbon residues. This explanation is confirmed by the coke content and its H/C ratio on the adsorbents at the three pressures, shown in Table 3. Thus, the coke content of the sample at 3.1 MPa (4.81 ww%) is lower than the corresponding one at 1.1 MPa (5.77 ww%), and its H/C atomic ratio clearly larger.

Effect of the Adsorbate Concentration

Mixtures with 9.7, 5.0 and 2.0 wt% of n-C_{10} in i-C_8 were used to study the influence of the feed adsorbate concentration on zeolite 5A deactivation. The evolution of the deactivation degree with the number of cycles, Fig. 7, was quite similar for the three concentrations studied, for which the differences observed were within the experimental error (6%). Therefore, the influence of this parameter on the zeolite deactivation by coke can be considered negligible.

Conclusions

The characterisation of industrially deactivated samples of the 5A molecular sieve used in a commercial process for n-paraffins separation, showed that the loss of adsorption capacity is due to coke deposition on the surface of the zeolite by both site coverage and pore blockage. A laboratory scale cyclic adsorption-desorption procedure leading to a fast deactivation by coke of this 5A molecular sieve used has shown to be useful for the deactivation studies. The deactivation levels of the zeolite after 10 adsorption-desorption cycles were similar to those found for the industrial spent adsorbent.

The temperature of the adsorption step is considered to be the main factor for the coke formation on the adsorbent surface (internal + external) in the range 373–523 K. Although the amount of coke and its heavy character increases with the temperature of the adsorption step, its deactivating effect after 10 cycles is higher at 373 K, due to the lower diffusion rate of the n-C_{10} at this temperature. As the temperature increases, diffusivity of paraffin is higher and the overall deactivation effect of the deposited coke is lower. A minimum deactivation degree was obtained at 448 K.

The adsorption pressure also affects the nature of the coke formed and therefore the deactivation degree of the zeolite. This influence has been explained considering the mechanism proposed in the literature for coke formation on small pore zeolites. The influence of these operating conditions can be useful to better understand the deactivation of 5A molecular sieves by coke deposition in alkane adsorption, which is also interesting for the industrial scale process.

Nomenclature

t_b	breakthrough point (min)
t_s	saturation time (min)
t_R	residence time (min)
S	slope of breakthrough curve (wt%·min^{-1})
m_{ads}	mass of paraffin adsorbed (g)
ρ_m	density of the feed mixture (g·cm^{-3})
X_0	mass fraction of adsorbate
$X_i(t)$	mass fraction in the effluent
Q_v	volumetric flow (cm^3·min^{-1})
q_i	adsorption capacity in the ith cycle (g·g^{-1})
DD_i	deactivation degree after i cycles (%)
D_c	effective diffusion coefficient (m^2·s^{-1})
r	length of the diffusional pathway (m)

Acknowledgments

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