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Kinetics of catalyst deactivation. An example: methylnaphthalene transformation

E. Rombi*, R. Monaci, V. Solinas

Dipartimento di Scienze Chimiche, via Ospedale 72, 09124, Cagliari, Italy

Abstract

The progressive deactivation of various HNaY zeolite catalysts (Si/Al=2.4), during methylnaphthalene isomerisation, was studied at 573–663 K. The activity decay was expressed as a function of time-on-stream (t-o-s) and of coke content (C_c). In both cases very simple exponential equations, whose parameters depend on the degree of decationation of the zeolite and temperature were satisfactorily used to fit the experimental data. Coke analysis was performed on the most acidic catalyst (HNaY-98) at T=633 K and the composition of the coke soluble in methylene chloride was determined. The influence of temperature and ion-exchange degree on the coke deposition rate was also examined. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Catalyst deactivation; Coke formation; 1-Methylnaphthalene transformation

1. Introduction

Most of the catalytic reactions of organic compounds are accompanied by the formation of heavy by-products, referred to as ''coke'', which form a deposit on the surface and provoke deactivation. ''Coke'' can be defined as ''carbonaceous compounds (polyaromatics and non-polyaromatics) formed during the reaction and responsible for deactivation'' [1].

The deactivation rate depends obviously on the relative rate of formation of these by-products, a rate which can be different from one catalytic system to another. Coking and deactivation depend also on the characteristics of the active sites and on the operating conditions such as reaction time, temperature [2–7], pressure and nature of reactant [4,8–11]. They also depend on the mode of deactivation: the deactivating effect of coke is more pronounced when deactivation is due to pore blockage than when it is due to site coverage [1,12,13].

Whatever be the catalytic system, it is important to limit the deactivation rate. To obtain this result it is essential to understand what is the mode of coke formation as well as the mode of deactivation.

Owing to their great activity, to their particular selectivity (shape selectivity) and to their high thermal stability, acid zeolites are more and more used in catalytic industrial processes [14].

The formation of heavy products, which generally remain in the pores, is mainly responsible for zeolite deactivation. On this type of catalysts coke formation is a shape selective reaction [15,16]: pore, channel and cavity dimensions control its rate and selectivity. Coking and deactivation rates as well as coke com-

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*Corresponding author. Tel.: +39-70-6758602; fax: +39-70-6758605
E-mail address: rombi@vaxca1.unica.it (E. Rombi)

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position also depend on the strength and density of the active sites. It is sometimes difficult to discriminate between the effects of pore structure and acidity.

2. Modes of zeolite deactivation by coke deposition

There are four possible modes of deactivation of zeolites by coke (Fig. 1):

1. Diffusional limitation of reactants by adsorption of small coke molecules on the active sites.
2. Blockage of the access to the sites of the cavities (or of the channel intersections) in which the coke molecules are located.
3. Blockage of the access to the sites of channels and cavities containing coke molecules (coke molecules growth).
4. Blockage of the access to the sites of channels and cavities not containing coke molecules (steric effects of the coke molecules growth).

To discriminate among these contributions and to identify the occurrence of more than one of them, it is necessary to have information on the kinetics of deactivation as well as on coke composition and location.

Various spectroscopic techniques such as IR [2–4,9,17–22], UV–Vis [23], CP/MAS-^{13}C NMR spectroscopy [5,24–28], and EPR [6,7,29–31] have been used to characterise the chemical nature of coke, while its location, inside the micropores or on the outer surface, was investigated by XPS [32], electron microscopy [33], XRD [34] and adsorption measurements [1,8,29,30,35–37].

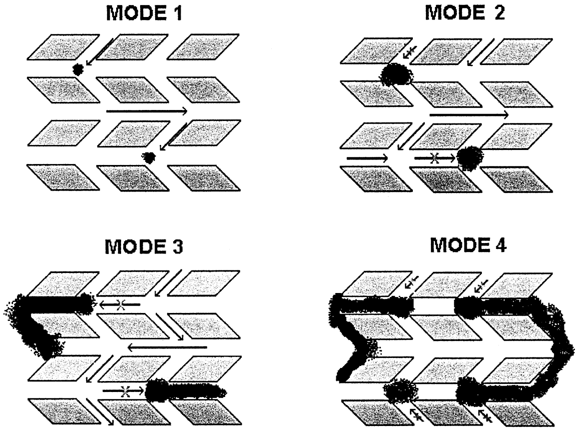


Fig. 1. Modes of zeolite deactivation by coke deposition.

Numerous papers concerning coking and deactivation on protonic zeolites with different pore systems can be found in the literature [1,28,35,38–42]. The obtained results confirm that coking is a shape-selective reaction: both its rate and its selectivity, in terms of nature and distribution of the coke components, depend on the pore structure. The coking rate is greater when:

1. the space available for the formation of precursors is larger than their volume (steric constraints during the formation of the bulky intermediates of coking are less pronounced), and
2. the coke precursors diffuse more slowly from the pores to the gas phase.

The deactivating effect of coke depends very much on the zeolite. When the pore system is constituted of non-interconnecting channels, as in mordenites, deactivation occurs through pore blockage (Mode 4); coke has therefore a great deactivating effect. When the pore system is constituted of interconnecting channels, of large or intermediate size, with or without cavities, like in Y or ZSM-5 zeolites, respectively, deactivation occurs initially through limitation of the access to the active sites (Mode 1) and then blockage of the access to the sites of the channel intersections or cavities in which the coke molecules are situated (Mode 2). At high coke contents situation of mode 3 can also occur. Interconnected pore network indeed offers a much larger number of access paths to active sites through which molecules can diffuse randomly, coke has therefore a moderate deactivating effect. Zeolites having large cavities with small apertures (trap cavities), like for example Erionite, are highly sensitive to deactivation. The molecules of coke are preferentially formed in the cages close to the outer surface and block the access to the active sites of the inner cages. The deactivation is thus very rapid.

It is worth to point out once more that coking and deactivation do not depend only on the zeolite pore structure, but also on the operating conditions and on the number and strength of the active sites.

In the following, the study of the HNaY zeolites deactivation during the 1-methylnaphthalene (1MN) to 2-methylnaphthalene (2MN) isomerisation reaction is reported as an example of the influence of temperature, time-on-stream and surface acidity on the catalytic activity decay.

3. Apparatus and procedure

The isomerisation runs were carried out in a continuous, fixed bed, quartz-glass microreactor, 10 mm in diameter, fitted with axial thermowell and thermostated to ±1 K by a PID temperature controller. The catalyst was activated in situ by heating at 773 K for 12 h in flowing nitrogen. After the temperature was lowered to the chosen value, a mixture of carrier gas (H_2) and 1MN at a molar ratio R_H=10 was fed at atmospheric pressure and WHSV=6 (g_{1MN}/g_{cat} h). A high value of R_H means avoiding a too fast deactivation of catalyst. 0.5 g of fresh catalyst were charged for each run. Usually the analytical samples (collected in traps cooled to 193 K) were taken after 15, 30, 45, 60, 90, 120 and 180 min on-stream.

4. Activity decay with time-on-stream

Experimental data have been collected on the whole set of catalysts (Table 1) at temperatures ranging from 543 to 663 K.

The typical trend of conversion (y_t) vs. time-on-stream (t) is shown in Fig. 2. A very simple approach for the analysis of these data can be the following [44]. For a given value of time factor, as in the present case, the rate of reaction is expressed by

$$r_0 = L_0 \Phi(P,T) \tag{1}$$

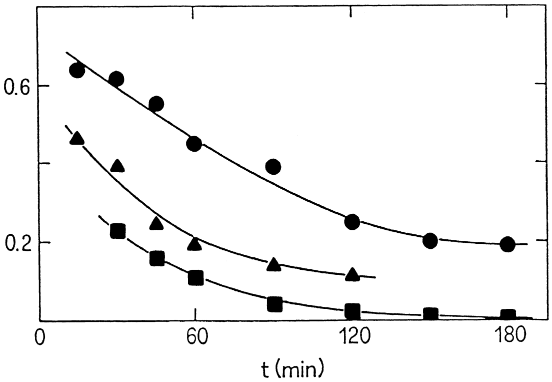


Fig. 2. Typical trend of conversion vs. time-on-stream: (●) HNaY-98, 633 K; (■) HNaY-98, 543 K; (◆) HNaY-55, 633 K.

and

$$r_t = L_t \Phi(P,T) \tag{2}$$

for fresh (t=0) and fouled (time t) catalyst, respectively. P is the reactant partial pressure and L_0 and L_t are the number of active sites per unit mass of fresh and fouled catalyst, respectively. If the rate of the main reaction is much higher than the rate of deactivation, we can write

$$\frac{L_t}{L_0} \cong \frac{y_t}{y_0}, \tag{3}$$

y_t and y_0 being the conversion on fouled and fresh catalyst, respectively. Let us assume that deactivation follows the mechanism

$$\mathrm{MN} + \sigma \Leftrightarrow \mathrm{MN}\sigma \tag{4}$$

$$\mathrm{MN}\sigma \rightarrow \mathrm{D}\sigma \ \text{(r.d.s.)} \tag{5}$$

Table 1
Main characteristics of the catalysts employed

Catalyst[a]	Na^+ content (mg/g of catalyst)	Surface acidity[b] (mmol/g of catalyst)		
		$H_0 \leq -1.5$	$H_0 \leq 3.2$	$H_0 \leq 6.8$
HNaY-98	1.6	0.13	1.00	2.00
HNaY-67	30.3	0.07	0.94	1.88
HNaY-55	41.1	0.0	0.65	1.46
HNaY-45	51.0	0.0	0.47	1.01
HNaY-30	64.3	0.0	0.10	0.16

SiO_2/Al_2O_3 molar ratio 4.74 (by atomic absorption spectrometry).

[a] Figures represent the % ion-exchange degree with respect to the original Na form.

[b] Surface acidity was measured as previously reported [43] by titration with n-butylamine. Hammett acidity function, H_0, as defined in [45].

where MN is the methylnaphthalene, σ an active site, MNσ the adsorbed MN and σ is the deactivated site by which the coking reaction is initiated. If θ_{MN} is the fraction of active sites covered by MN and θ_{V} is the fraction of vacant sites, the fraction θ_t of non-deactivated sites at time t is

$$\theta_t = \frac{L_t}{L_0} = \theta_{\mathrm{V}} + \theta_{\mathrm{MN}}. \tag{6}$$

The rate of the surface deactivation reaction (5) is expressed by

$$\frac{\mathrm{d}\theta_{\mathrm{D}}}{\mathrm{d}t} = k_{\mathrm{D}}\theta_{\mathrm{MN}}, \tag{7}$$

k_{D} being the rate constant and θ_{D} the fraction of deactivated sites. If the adsorption process (4) is at equilibrium, we have

$$\frac{\theta_{\mathrm{MN}}}{P_{\mathrm{MN}}\theta_{\mathrm{V}}} = b_{\mathrm{MN}}, \tag{8}$$

where b_{MN} is the adsorption equilibrium constant and P_{MN} is the partial pressure of MN. As a consequence,

$$\frac{\mathrm{d}\theta_{\mathrm{D}}}{\mathrm{d}t} = k_{\mathrm{D}}b_{\mathrm{MN}}P_{\mathrm{MN}}\theta_{\mathrm{V}} \tag{9}$$

and

$$\theta_{\mathrm{V}} = \frac{\theta_t}{1 + b_{\mathrm{MN}}P_{\mathrm{MN}}}. \tag{10}$$

But

$$\frac{\mathrm{d}\theta_{\mathrm{D}}}{\mathrm{d}t} = -\frac{\mathrm{d}\theta_t}{\mathrm{d}t}, \tag{11}$$

so that by combining Eqs. (9)–(11), we have

$$-\frac{\mathrm{d}\theta_t}{\mathrm{d}t} = \frac{k_{\mathrm{D}}b_{\mathrm{MN}}P_{\mathrm{MN}}\theta_t}{1 + b_{\mathrm{MN}}P_{\mathrm{MN}}} = \beta\theta_t, \tag{12}$$

where

$$\beta = \frac{k_{\mathrm{D}}b_{\mathrm{MN}}P_{\mathrm{MN}}}{1 + b_{\mathrm{MN}}P_{\mathrm{MN}}}. \tag{13}$$

By integrating Eq. (12), we have

$$\theta_t = \frac{L_t}{L_0} = \exp(-\beta t) \tag{14}$$

and recalling Eq. (3), we have

$$\frac{y_t}{y_0} = \exp(-\beta t). \tag{15}$$

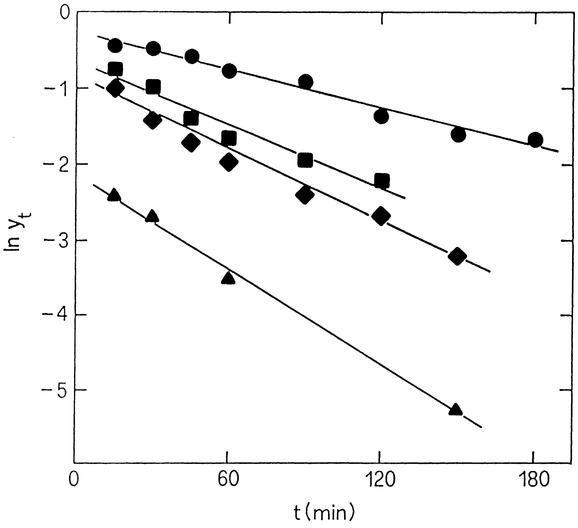


Fig. 3. Fitting of experimental data to Eq. (15): T=633 K; (●) HNaY-98, (■) HNaY-55, (◆) HNaY-30.

In this approach, the same adsorption equilibrium constant was attributed to the two MN isomers, and the deactivation reaction has been assumed to have started by either of the two, indifferently. In other words, from the point of view of coke formation, the isomers were considered to be a single substance so that MN≅ constant.

In Fig. 3 the results of the linear plot from Eq. (15) concerning the variously decationated Y zeolite catalysts at T=633 K are reported as an example (similar trends are obtained for the same samples at different temperatures). From the straight lines (least square procedure) drawn through the experimental points of the plots, the values of β shown in Table 2 were calculated. It can be noted that the values of β decrease with increasing ion-exchange degree, i.e. the surface acidity; since the value of β denotes a slower deactivation rate, the lower the surface acidity, the faster is the deactivation. This is likely due to the different number of active sites. For a given catalyst, β values decrease with increasing temperature, thus indicating that activity decay is more pronounced when operating at lower values of this parameter. This suggests that if the unconverted feed does not react (or scarcely reacts) and if it is strongly adsorbed under the catalytic conditions, it may contribute to deactivation and in a more general way it may be considered as “coke”.

Table 2
Values of parameter β (Eq. (15))

Zeolite	T (K)	$10^2\beta$ (min^{-1})
HNaY-98	633	0.83±0.06
	603	1.38±0.24
	573	1.86±0.13
	543	2.68±0.08
HNaY-67	603	1.74±0.27
HNaY-55	633	1.40±0.17
	603	1.95±0.14
	573	2.53±0.14
HNAY-45	633	1.53±0.01
HNaY-30	663	1.75±0.05
	633	2.16±0.1
	603	2.31±0.00
	573	(3.23)

In addition, the plot of ln β vs. $1/T$ (Fig. 4), from the equation $\beta = A\,\mathrm{e}^{(E_a/RT)}$, shows that the slopes increase with increasing degree of ion exchange. In other words, the less acidic is the catalyst surface, the less the deactivation rate depends on temperature.

In spite of the very simple approach followed, one can see that Eq. (15) interprets our data quite satisfactorily. Of course, owing to the complex nature of the parameter β, the data of Table 2 cannot give any reliable information on the true mechanism of catalyst deactivation. As pointed out by many authors [12,13,46,47], the most convenient way to throw light on the mechanism is to follow the coke formation rate by measuring in some way the growing amount of coke deposited with time.

4.1. Determination of coke amount

The amount of coke formed was determined as follows: at the end of the reaction, the mass of fouled catalyst was cleaned up and dried in situ by a nitrogen stream (20 cm^3/min for 24 h) at the reaction temperature. The coke was then burnt off in oxygen (20 cm^3/min) at a temperature rising (3 K/min) from 353 to 923 K. The CO_2 evolved was trapped in $Ba(OH)_2$ solution and determined by titration with HCl. Table 3 shows the results obtained at a reaction temperature of 633 K for the HNaY-30, HNaY-55 and HNaY-98 catalysts.

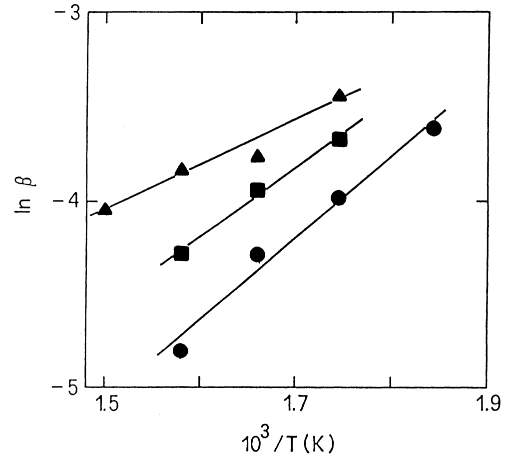


Fig. 4. Dependence of parameter β on temperature: (●) HNaY-98, (■) HNaY-55, (◆) HNaY-30.

4.2. Analysis of coke

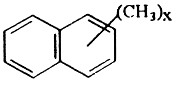
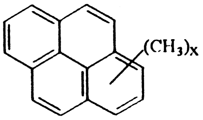
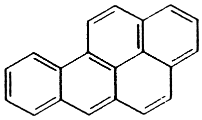
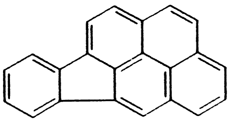
Various techniques have been used to recover the carbonaceous compounds trapped in the zeolite pores. The direct treatment of the coked zeolite by an organic solvent [48] or under an inert gas flow at high temperature [49] allows the recovery of a small part of the carbonaceous compounds. The inner coke can be

Table 3
Amount of coke (C_c) deposited on the catalysts at 633 K

HNaY-30			HNaY-55			HNaY-98		
t-o-s (min)	Coke (wt%)	A_R[a] (%)	t-o-s (min)	Coke (wt%)	A_R[a] (%)	t-o-s (min)	Coke (wt%)	A_R[a] (%)
15	1.32	72.9	15	1.99	66.7	15	7.28	84.8
30	1.77	58.3	30	3.09	56.4	30	8.60	81.2
45	2.14	29.2	45	4.58	35.3	45	9.99	72.4
60	2.43	25.5	60	5.02	26.9	60	10.79	58.8
90	3.28	7.3	90	5.50	19.9	90	11.43	50.6
120	3.34	3.6	120	6.02	15.4	120	11.97	32.9

[a] A_R: residual catalytic activity defined by the ratio between the initial activity A_0 (mmol$_{\mathrm{1MN\ reacted}}$/min g$_{\mathrm{cat}}$) and A_t the activity after a time t.

Table 4
Coke analysis after HF attack and CH_2Cl_2 extraction for HNaY-98 at different time-on-stream (T=633 K)

	t-o-s=1 h	t-o-s=6 h
% of coke	10.8	12
% of soluble coke	80	35
 $x = 0 \rightarrow 3$	60	45
 $x = 0 \rightarrow 3$	27	37
 + 	13	18

liberated by solubilising the zeolite in acid solutions [50–52]. To characterise the compounds responsible for the zeolite deactivation we used the technique developed by Guisnet and co-workers [50], by which the coked zeolite was treated at room temperature with a solution of hydrofluoric acid at 40% in order to dissolve the zeolite and to liberate the inner coke. The soluble coke components were analysed by classical methods such as GC, MS, etc., after extraction with CH_2Cl_2.

Analysis of coke was performed on the HY-98 zeolite after 1 and 6 h on-stream at T=633 K. The results are reported in Table 4.

The solubility of coke in methylene chloride strongly depends on time-on-stream: 80% of the coke formed after 1 h on-stream is soluble in CH_2Cl_2, but this percentage decreases to 35% after 6 h on-stream. The soluble coke is mainly composed by both the MN isomers, polyalkylated naphthalenes, pyrenic and indenopyrenic compounds; it becomes more aromatic in nature when increasing the reaction time. It can be reasonably assumed that the soluble coke molecules are intermediates in the formation of the insoluble coke, which is composed of higher polynuclear aromatics.

4.3. *Mode of coke formation*

In Fig. 5 a simplified reaction scheme for coke formation is reported. The intermediate alkyldinaphthylmethane results from a nucleophilic attack of a naphthylmethylenic carbonium ion (formed by hydride transfer from MN's to a pre-existing carbocation or to a protonic site) to another molecule of MN's. It leads to naphthalene and DMN's through disproportionation or to indenopyrenic compounds through cyclisation. All these molecules can undergo further reactions leading to higher polynuclear aromatics.

4.4. *Coking and isomerisation rates*

The typical trend of 1MN conversion and of coke formation is shown in Fig. 6. It can be observed that the decrease of conversion occurs simultaneously with the increase of coke content (C_c, wt% on the catalyst) and that the rate of coke deposition is higher during the first minutes on-stream and tends to zero with increasing t.

Coke formation rate, r_c, has been expressed [53] as mole of 1MN transformed into coke h^{-1} g_{cat}^{-1}. Fig. 7(a) shows that for a given catalyst, r_c slightly increases with increasing temperature, but quickly decreases with time-on-stream, its value after 100 min being less than 20% of the value after 15 min. However, r_c strongly depends on the ion-exchange degree (i.e. on the surface acidity). This is shown in Fig. 7(b), where the behaviour of differently ion-exchanged zeolites at the same temperature is presented: the initial (after 15 min on-stream) coking rate of the most acidic catalyst (HNaY-98) is one order of magnitude higher than that for the less acidic one (HNaY-30), while the values after 120 min are very low and practically identical for all the catalysts. It is generally accepted [40,47] that coke formation is proportional to the rate of deactivation of the Brϕnsted acid sites and that strong centres deactivate more quickly than the weaker ones. This is in agreement with our titration data (Table 1): HNaY-98 catalyst possesses strong acid sites (0.13 mmol/g for $pK_a \leq -1.5$), which are

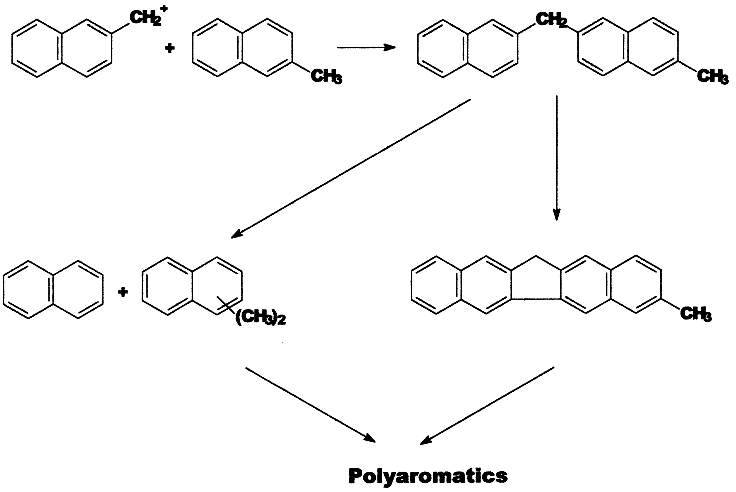


Fig. 5. Mechanism of coke formation.

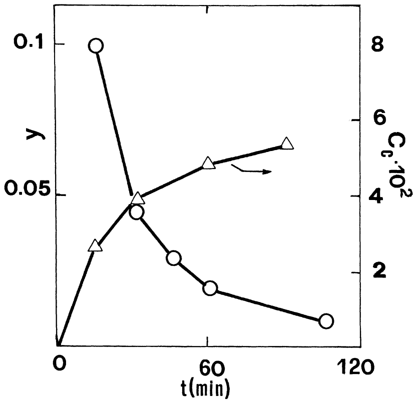


Fig. 6. Fractional conversion of 1MN and coke formation on HNaY-55 catalyst vs. time-on-stream at 573 K.

virtually absent in both HNaY-55 and HNaY-30, and are responsible for the high initial rate of coke formation.

It is interesting to compare the isomerisation rate r_i, defined as mole of 1MN transformed into 2MN h^{-1} g_{cat}^{-1}, with the coking rate r_c.

Fig. 8 shows not only that r_i is always higher than r_c by one or two orders of magnitude, but also that the higher the temperature (Fig. 8(a)) and the higher the surface acidity (Fig. 8(b)), the lower is the r_c/r_i ratio. In other words, in spite of a marked increase of temperature and/or of surface acidity, isomerisation grows more quickly than coking. With the most acidic catalyst (HNaY-98) both r_i and r_c decrease with time-on-stream. However, within 30 min on-stream, the latter drops more quickly (from more than 23×10^{-4} to ca. 4×10^{-4} mol/h g_{cat}) than the former (from ca. 30×10^{-4} to ca. 23×10^{-4} mol/h g_{cat}). As a consequence, the r_c/r_i ratio becomes very low and remains practically unchanged due to a further slow decaying of both the rates with similar trends. These facts seem to confirm that deactivation does not occur through a pore blocking mechanism (Mode 4, Fig. 1).

4.5. *Coke deposition and deactivation rate*

If the activity decay is due to coke formation, then activity cannot be a simple function of time and the deactivation function should be referred to coke content rather than to time-on-stream. For the cracking of cumene on Y zeolite, the best deactivation function was found to be [54]:

$$\phi = \exp(-\alpha C_c), \qquad (16)$$

where $\phi = r_i/r_i^0$, r_i^0 being the value of r_i for fresh catalyst (t=0), and α is an empirical constant. By applying such an equation to our data, the plots shown in Fig. 9 were obtained. From the slopes of such straight lines, the values of α shown in Table 5 were calculated. One can notice that the value of α decreases with increasing temperature and surface acidity (a similar trend is shown by the parameter β of Eq. (15)). In other words, the lower the temperature and surface acidity, the less is the amount of coke

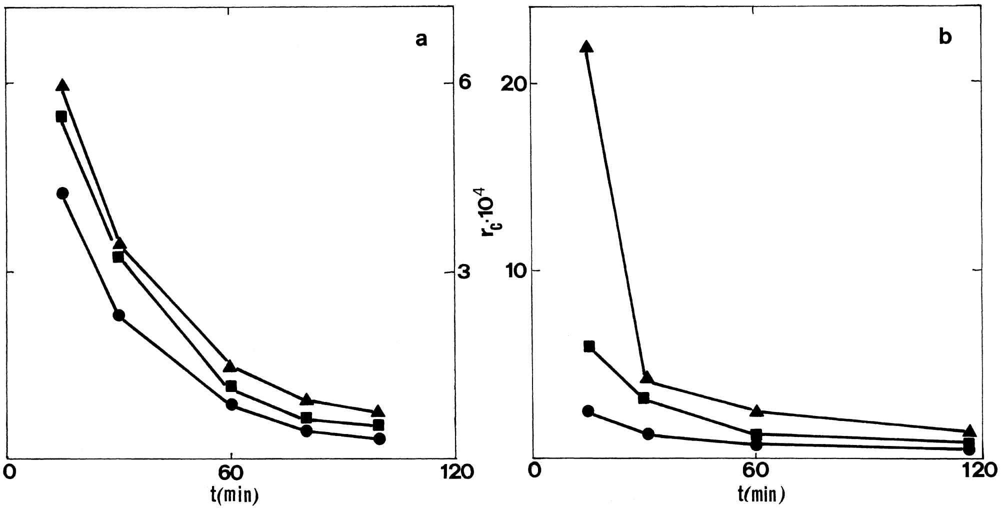


Fig. 7. Coking rate vs. time-on-stream. (a) HNaY-55 catalyst: (◆) 633 K, (■) 603 K, (●) 573 K; (b) T=633 K: (◆) HNaY-98, (■) HNaY-55, (●) HNaY-30.

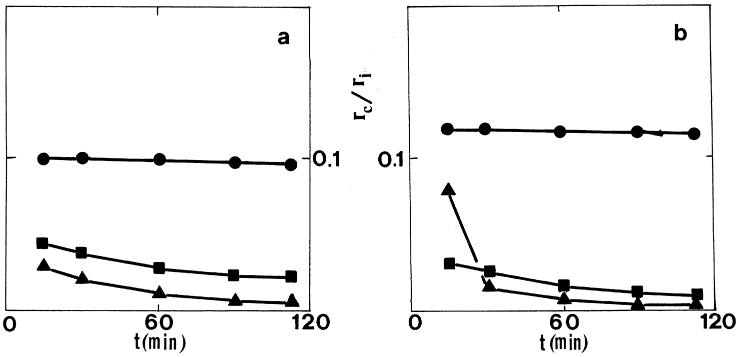


Fig. 8. Coking and isomerization rate vs. time-on-stream. (a) HNaY-55 catalyst: (◆) 633 K, (■) 603 K, (●) 573 K; (b) T=633 K: (◆) HNaY-98, (■) HNaY-55, (●) HNaY-30.

Table 5
Deactivation coefficient α (g_{cat}/g_{coke})

Catalyst	T (K)	α
HNaY-55	573	40
	603	36
	633	31
HNaY-30	633	55
HNaY-98	633	6

required for deactivating the active sites. As for the effect of surface acidity, this can be explained by considering that in zeolitic catalysts, both concentration and strength of acid sites decrease with decreasing the ion-exchange degree, a lower amount of coke can be reasonably sufficient to deactivate the catalyst. On the other hand, the effect of temperature is easily explainable by taking into account that the lower the temperature, the more strongly coke precursors are adsorbed on catalyst surface and the less easily they can move out of the zeolite pore system.

5. Conclusions

The information collected in the present work permits us to draw the following conclusions:

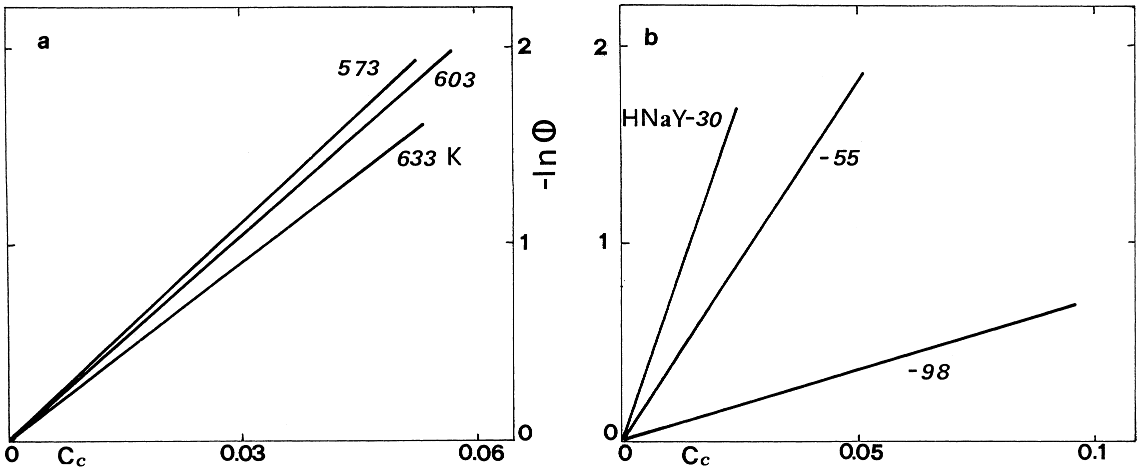


Fig. 9. Effect of coke on catalyst activity: (a) HNaY-55 catalyst, and (b) T=633 K.

1. The decay of catalyst activity with time-on-stream can be satisfactorily expressed by a very simple exponential equation, whose parameter b depends on the degree of decationation of the zeolite and on temperature. Deactivation rate decreases with increasing temperature and surface acidity.
2. Coke becomes more aromatic in nature when increasing reaction time and its composition also changes with the same parameter.
3. The coke formation is relatively fast, but, in any case, it is at least one order of magnitude slower than the main reaction.
4. The deactivation process seems to be due to a progressive blockage of the access to the sites of channels and cavities containing coke molecules.
5. The lower the reaction temperature and the less acidic the catalyst surface, the lower is the quantity of coke required for poisoning the catalyst.

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