Catalysis Today 154 (2010) 264–270

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Silicalite-1 deactivation in vapour phase Beckmann rearrangement of cyclohexanone oxime to caprolactam

Alberto Cesana*, Stefano Palmery, Roberto Buzzoni, Guido Spanò, Franco Rivetti[1], Lino Carnelli

Eni S.p.A. – Strategies and Development Department – Research Centre for Non-Conventional Energies – ISTITUTO ENI DONEGANI, via Fauser, 4, I-28100 Novara, Italy

ARTICLE INFO

Keywords:
Beckmann rearrangement
Cyclohexanone oxime
Caprolactam
Silicalite-1
Catalyst deactivation
Kinetics catalyst deactivation

ABSTRACT

Defective silicalite-1 is an efficient and selective catalyst in gas phase Beckmann rearrangement. A kinetic study of catalyst decay applied to Beckmann reaction of cyclohexanone oxime into ε-caprolactam performed with silicalite-1 as catalyst was carried out with reference to time on stream theory. Information about kinetic deactivation constant was obtained. Kinetic deactivation expressions based on the Wojciechowski model were developed by regressing the experimental data over the silicalite-1 catalyst. The kinetic reaction constant for fresh catalyst k^o, the catalyst site deactivation constant k_d, the sites deactivation reaction order m and the deactivation reaction order n' with respect to cyclohexanone oxime were determined. It was established that k_d was independent from residence time and only was affected by temperature and cyclohexanone oxime concentration. The model suggested a deactivation rate established on a second order reaction kinetic both for active centre and cyclohexanone oxime concentration.

1. Introduction

The Beckmann rearrangement of cyclohexanone oxime (CEOX) to ε-caprolactam (CPL) is a key step in the manufacture of nylon 6 fibers and resins. Current CPL manufacturing processes produce large amounts of ammonium sulfate as a by-product: up to 4.4 kg/kg, of which 1.6 are generated in oleum catalyzed Beckmann rearrangement step. Several efforts were spent in past years in order to carry out the manufacture of CPL without any ammonium sulfate production. An outstanding industrial breakthrough was reached when Eni and Sumitomo Chemical joined their results. A new, groundbreaking process was thus set up merging titanium silicalite-1 catalyzed ammoximation of cyclohexanone to CEOX [1,2] and vapour phase Beckmann rearrangement of CEOX to CPL [3] on silicalite-1 catalyst. The combined process is substantially free of inorganic by-products, converting cyclohexanone to CPL with >98% yield and affording an increase of atom efficiency [4,5] from 29% to 75% with a corresponding reduction of E-factor [6] from 4.5 to 0.32.

High silica MFI zeolite [7], exhibiting a weak acidity, is the most suitable catalyst in vapour phase Beckmann rearrangement [8–10]. Besides, use of methanol is crucial in successfully performing the reaction with the highest conversion and selectivity [3,11]. Methanol is decisive to maintain the catalyst active site in the methylated silanol form which is essential in the reaction pathway [3].

Despite these strategies an unavoidable, fast catalyst deactivation occurs. This leads to a quick drop of conversion. However catalyst activity is always easily restored in a regeneration stage in which coke deposited on catalyst is burnt at high temperature in air or oxygen. As a consequence, continuous industrial operation requires smart design to overcame this downside, e.g. swing fixed bed reactors or, preferably, a fluid bed reactor with continuous catalyst make up and regeneration [12]. As deactivation proceeds along with time on stream it makes evident that it is extremely important to reveal every feature about the deactivation mechanism and a strong effort is worth to be spent to improve knowledge about catalyst decay, to get any chance to cut it down.

The decline of deactivation rate allows longer reaction runs between regenerations in a fixed bed reactor or decrease the quantity of catalyst to draw out from a fluidized bed reactor to send to regeneration stage, makes the oxidiser smaller with a valuable effect on costs and, in both case (PFR and FBR), allows a better exploitation of catalyst increasing the reactor productivity. In any case catalyst cannot be indefinitely exploited and unload of the exhausted catalyst bed should be planned or continuous purge and make-up of fresh catalyst in a fluid bed reactor should be taken into account.

---

* Corresponding author. Tel.: +39 0321 44 7536; fax: +39 0321 44 7506.
E-mail address: alberto.cesana@eni.com (A. Cesana).

[1] Retired.

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.03.038

Nomenclature

CEOX	cyclohexanone oxime
CPL	ε-caprolactam
X	conversion
τ	residence time
WHSV	weight hourly space velocity
p	partial pressure
$k(t)$	kinetic rate constant at time t
k^o	initial kinetic reaction constant
k_d	deactivation constant
m	deactivation reaction order
n	order of the main reaction
f	mass transfer efficiency factor
$\langle\tau\rangle$	average residence time of the bubble in the bed
H	bed height
V_{br}	bubble relative linear velocity
g	gravitational acceleration
D_e	bubbles average diameter
ε	bed void grade
ε_{mf}	minimum fluidization void grade
δ	bed fraction containing bubbles
ν	linear velocity
ν_{mf}	minimum fluidization linear velocity
SSR	sum of squares of residuals

2. Experimental

2.1. Preparation of silicalite-1

Silicalite samples were synthesized according with the EniChem patent dealing with the hydrothermal synthesis of TS-1 [13] in the absence of Ti source [7]. Tetra-propyl-ammonium-hydroxide (TPAOH) was charged into a Pyrex reactor, flushed with nitrogen and tetra-ethyl-orthosilicate (TEOS) was added dropwise, stirring and flushing with nitrogen. The solution was loaded in a autoclave inside a PTFE vessel. Hydrothermal synthesis was then carried out at 413 K for 24 h with a stirring rate of 80 rpm. The suspension was centrifuged, separating the solid product which was washed with distilled water until the washing water reached pH ~7. The product obtained was filtered, dried at room temperature, and calcined in an oxidising atmosphere (air) at 823 K for 4 h at a heating rate of 50 K/h.

2.2. Catalyst characterization

Silicalite-1 quality, used in the experiments, was verified by means of XRD, FT-IR, BET, and ICP-AES analysis.

2.3. Reaction test

The vapour phase reaction has been carried out at atmospheric pressure both in a continuous flow fixed bed and in a fluidized bed reactor. The fixed bed reactor was a down-flow glass reactor, with an internal diameter equal to 11.5 mm, length 200 mm, and sheath for thermocouple with outer diameter 4 mm. A porous glass septum was placed at the bottom of the reactor; catalyst (typically 0.5–2 g, sieved at 42–80 meshes) was diluted with granular quartz up to a volume of 2 cm^3 and loaded between two layers of quartz.

The fluidized bed reactor was a stainless steel reactor with an internal diameter of 27.5 mm and a length of 350 mm. It was heated by immersion into a sand bath. A stainless steel porous septum on the bottom allowed the gas to flow into the reactor and also supported the catalyst. CEOX was vapourized along with solvents and carrier gas in a heater located ahead the reactor.

The reaction was carried out at temperature between 623 and 653 K. The catalyst was dried for 1 h with N_2 at reaction temperature. The catalyst was also pretreated for at least 30 min with the mixture used to dissolve the CEOX and made up of toluene, methanol and water in a molar ratio equals to 1:1:0.018. The cyclohexanone oxime was supplied dissolved into the above mentioned mixture of solvents by an HPLC pump, preheated, mixed with N_2 stream as a carrier gas and vapourized into CEOX evaporator vessel, in the case of fluid bed, or straight into the upper layer of quartz of the fixed bed reactor. The reactor effluent was cooled by a heat exchanger and collected in a flask. An automatic valves system provided samples at definite periods. Products were analyzed by a gas-chromatograph (Hewlett-Packard 5890) equipped with a capillary column (30 m × 0.58 mm, 0.5 μm film thickness, SE 54 phase) calibrated with known standards.

Regeneration step was carried out purging reactant with N_2. Temperature was increased at 723–763 K and, when the desired temperature was reached, air was fed at a GHSV = 39,000 h^{-1}. A continuous IR analyser measured the concentration of CO_2 in the effluent gas. After few hours air was purged with N_2 from the reactor and the regenerated catalyst was ready for the next reaction cycle. Reaction–regeneration step was managed by a computer-aided system.

3. Results and discussion

Catalysts aging takes place in different ways, both chemical and physical reason can be present. Poisoning, fouling, sintering or structure alteration are the main causes of catalysts deactivation. Although Beckmann rearrangement is based on acid catalyst, poisoning by basic compounds is not an actual threat, in fact in some cases even mild bases have no impact on catalyst activity, e.g. pyridine, NH_3 [14,3].

The breakdown of zeolite structure is far away to happen in the usual condition of Beckmann reaction. Actually worn out catalysts from Beckmann runs show a completely maintained crystalline structure and a fully restored surface area after regeneration process, hence the silicalite structure is well maintained after reactions/regeneration cycles and sintering cannot represent a significant manner of deactivation. More likely a structural change into silicalite-1 framework affects catalyst decay. Since silicalite is a defective zeolite the number, nature and position of defects inside the structure are mainly variable as function of synthesis parameters, calcinations condition and post-synthesis treatment. Moreover the nature of defects influences their resistance to the destruction, e.g. defects migration, defects change from one type to another. Usually these kinds of changes in the framework are sluggish and always achieve either a loss of active sites or make them less active or less selective. Therefore they are generally associated to the irreversible catalyst decay that takes place very slowly. Instead the deactivation rate is very speedy and it is not due to the abovementioned phenomena that, even though exist, are disguised by a massive deactivation.

Actually the strongest deactivation effect in Beckmann reaction is played by coking. Coke cuts down reaction rate hampering the reagents to reach catalyst active sites; that takes place both straight on active site or in its surrounding or blocking whole pore at the entrance. The aim of present research is to study the kinetic of catalyst deactivation arising from coke build up over silicalite catalyst during Beckmann rearrangement of CEOX.

3.1. Silicalite-1 characterization

The product employed in current experimentation is a high silica MFI zeolite. Silicalite samples synthesized according with EniChem patent present consistent peculiarities and samples belonging to Enichem were in the past intensely studied and characterized in several works. All the silicalite samples prepared in this way show a much lower Na and Al content and a higher OH defect density [15–18] than silicalites synthesized following the original way [19]. The high purity and the presence of internal hydroxyl nests affect the long-range structural order, since the sample shows orthorhombic symmetry unlike the non-defective silicalite, which has a monoclinic symmetry. Moreover, high defective silicalite has smaller crystal size than regular silicalite, the former yielding a powder with grains about 220–260 nm large, whereas the latter has grains in the 2000 ± 3500 nm range.

3.2. *Kinetic model of catalyst decay*

The modelling of the catalyst aging due to coke build up is basically established on two common approach: one follows a more rigorous way established on a mechanistic approach and associates decay ultimately to the amount of coke accumulated on the catalyst [20,21], the other one, in order to make the matter more straightforward, relates the catalyst activity to the time on stream [22].

The former implies the exact knowledge of coke, or coke precursor, concentration in the time; hence it demands to draw out in an easy manner, from time to time, catalyst samples from the reactor and also it requires a large characterization effort to measure the coke concentration on each catalyst sample whereas time on stream method allows to straight relate time versus conversion in an easy and effortless way. Even if a method for collecting sample was realized in our testing bench scale fluid bed reactor, however it implies a complicate managing of the runs because of several stops required for catalyst sampling. Moreover it is quite unfeasible to collect samples of catalyst in a bench scale fixed bed reactor. The only way to take catalyst samples from a fixed bed reactor relies on turning to a different strategy, carrying out an apart run for each definite aging time. In this manner several runs performed in the same conditions, having just a different duration make achievable samples of aged catalyst for different periods as if they would be taken in a continuous run from the same reactor. Of course that requires quite huge number of runs and exhausts a lot of time and resources. The above mentioned reasons make time on stream theory an attractive and a more efficient way to study catalyst deactivation.

On the other hand empirical correlations have been widely used for a quantitative description of the deactivation process as a function of time on stream. The Voorhies correlation for coking in the catalytic cracking of hydrocarbons has been widely adopted:

$$a = A \times t^{-n} \tag{1}$$

a being the activity, A a constant and n the Voorhies coefficient. Many other models were proposed with the aim to relate the catalytic activity decay to time on stream employing both exponential and power law. In these equations the amount of coke formed on the catalyst is assumed to be independent on the reactants concentration, and the mechanism of carbon formation is not considered. Among these, a more satisfactory model employing a power law, is due to Wojciechowski [23]. Present work takes advantage of Wojciechowski model to describe the catalyst deactivation because of some peculiar feature provided by this depiction. The model allows us to relate the activity with the time on stream maintaining an explicit relation with the active site concentration which is, in our opinion, an outstanding aspects of this model that joins the advantages of models based on coke deposition theory to the straightforwardness of empirical model on which time on stream theory is usually established. Model supplies not a mere quantitative law, valid in the range where data were collected but it is also useful to predict the deactivation rate at any process time and to compare the rate of deactivation among quite a few reaction condition or catalyst, but it accomplishes this goal having some additional helpful knowledge about the deactivation mechanism at least regarding the order of site deactivation.

Catalyst deactivation studies in Beckmann rearrangement were performed both in a plug flow reactor and in a fluidized bed reactor. The Beckmann kinetic reaction is well known as a monomolecular reaction [24] hence the rate expression of the conversion in a tubular reactor is the following:

$$X = 1 - e^{-k(t)\tau} \tag{2}$$

where X is the conversion at time t, $k(t)$ is the kinetic rate constant at time t and we must consider it as function of time because, in our occurrence, it is affected by decay. In order to describe $k(t)$ as function of the time we can use the general expression from time on stream theory catalyst decay [25]

$$k(t) = k^{o}[1 + (m - 1)k_d t]^{-(n/(m-1))} \tag{3}$$

where k^{o} is the kinetic reaction constant for a fresh catalyst, k_d is the constant of catalyst site deactivation, m is the deactivation reaction order and n is the order of the main reaction (in the case of Beckmann rearrangement $n = 1$). Introducing Eq. (3) into Eq. (2) we obtain a general expression (4) of the conversion as function of time.

$$X = 1 - e^{-\left(k^{o}[1+(m-1)k_d t]^{-(n/(m-1))}\right)\tau} \tag{4}$$

Through best fitting of experimental data set the three equation parameters k^{o}, k_d and m are determined. The mth deactivation order highlights what kinetic mechanism most suitably describes the site deactivation. If m is equal to 0 the decay is a linear function of time and is not depending on active site concentration, this occurs for example in catalyst sintering; a first order decay implies that one site at a time is blocked by each deactivation event, while a second order suggests that two sites are inhibited at the same time. The case in which $m > 2$ puts forward the hypothesis that pores blocking yields to catalyst deactivation.

In order to deal with data obtained from fluidized bed tests we can start from the same equation of plug flow reactor introducing the pertinent corrections. We can therefore consider an efficiency factor f due to mass transfer rate from bubbles phase to slurry phase and a rectified time $\langle\tau\rangle$ which is the average residence time of the bubble in the bed. Therefore we obtain from Eq. (2) the following Eq. (5):

$$X = 1 - e^{-fk(t)\langle\tau\rangle} \tag{5}$$

where $0 < f < 1$. We can now introduce some variables according to the description of a fluidized bed by Carberry [26]

$$\langle\tau\rangle = \frac{H \times (1 - \varepsilon)}{\left\langle V_{br} \right\rangle} \tag{6}$$

$$\left\langle V_{br} \right\rangle = 0.711 \times \left(g \times \left\langle D_e \right\rangle\right)^{1/2} \tag{7}$$

$$\varepsilon = 1 - [(1 - \varepsilon_{mf}) \times (1 - \delta)] \tag{8}$$

$$\delta = \frac{\nu - \nu_{mf}}{\nu - \nu_{mf} + 0.711 \times (g \times D_e)^{1/2}} \tag{9}$$

where H is the bed height, V_{br} is the bubble relative linear velocity with respect to the slurry linear velocity, D_e is bubbles average diameter along the bed, ε is the bed void grade, ε_{mf} is the minimum fluidization void grade, δ is the bed fraction containing bubbles, ν is the linear velocity and ν_{mf} is the minimum fluidization linear velocity. Again we achieve an explicit expression of conversion versus time.

Activity curves were thus fitted by means of Eqs. (2) and (5), a non-linear least squares regression analysis was used and the

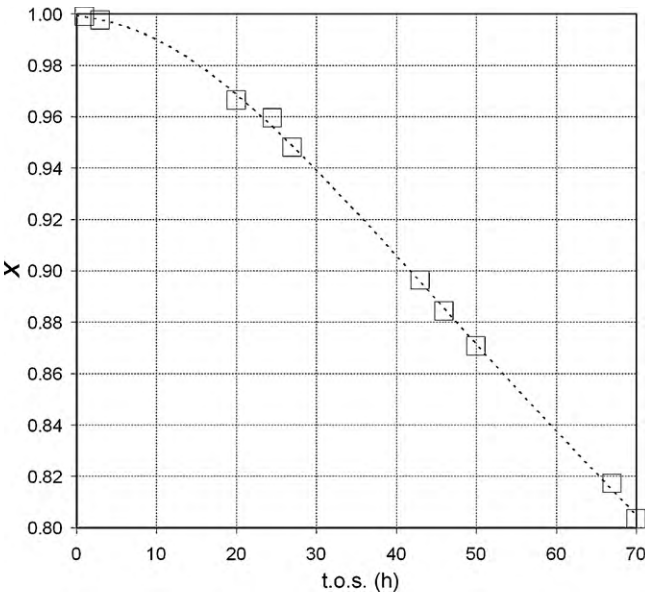

Fig. 1. Selection of m, deactivation reaction order, for catalyst aging in Beckmann rearrangement, experiments carried out in fixed bed reactor on catalyst belonging to batch 1 ($T = 623$ K; WHSV = 2.15 $g_{CEOX}\,g_{cat.}^{-1}\,h^{-1}$; $p_{CEOX} = 1.72$ kPa; $p_{MeOH} = 38.3$ kPa; $p_{Toluene} = 38.3$ kPa; $p_{N_2} = 21.6$ kPa; $\tau = 0.11$ s).

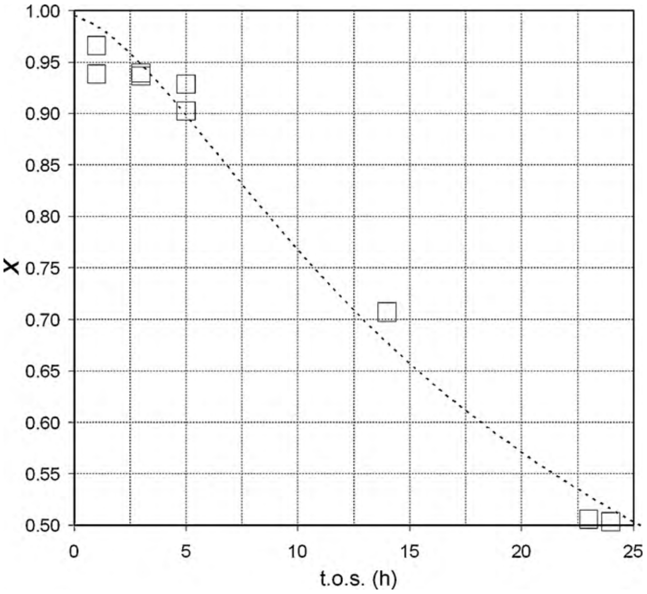

Fig. 2. Evaluation of k^o, initial rate constant of fresh catalyst, in plug flow reactor of batch 2 catalyst employed in runs I–VI ($T = 631$ K; WHSV = 2.15 $g_{CEOX}\,g_{cat.}^{-1}\,h^{-1}$: $p_{CEOX} = 1.72$ kPa; $p_{MeOH} = 40.0$ kPa; $p_{Toluene} = 40.0$ kPa; $p_{N_2} = 18.2$ kPa; $\tau = 0.11$ s).

parameter estimation was performed by minimizing the sum of squares of residuals (10) of the differences between the experimental and the calculated conversion.

$$\mathrm{SSR} = \sum_i (X_{\mathrm{exp}} - X_{\mathrm{calc}})^2 \qquad (10)$$

The best parameters m, k^o, k_d and f were obtained when the minimum sum of square residuals were reached.

3.3. Deactivation reaction order

Early kinetic data were acquired by plug flow reactor and are shown in Fig. 1. The parameters of the model obtained from the SSR are reported in Table 1 as catalyst belonging to batch 1. This first regression allowed to establish the reaction order with respect to the active site. Since in our case m is very close to 2 a second order deactivation should be assumed and we tune the other parameters setting $m = 2$ (see again Table 1, second column).

A proposed mechanism of Beckman rearrangement on silicalite-1 implies the support of more than an isolated silanol to carry out the reaction [10]. CEOX interacts through both N and O atoms with SiOH nests enlarging the energy gain from this plurality of bonds with the OH despite the strain forces deriving by the structural constraints. The synergy between different silanols allows the H-bond with oxygen atom after initial interaction of nitrogen with SiOH, maintains the cycle-configuration during the alkyl group migration, stabilizes the intermediate. This behaviour is also attributed to probe molecules as ammonia [27,28]. Hence, more than a single site is necessary to complete the reaction. The evidence that more active sites is blocked by a single deactivation event supports the fact that the active site would be a silanol nest leaved by a silicon atom vacancy whose have a multiple interaction with reagent rather than an isolated silanol.

Table 1
Model estimated parameter m, k^o and k_d resulting for the fixed bed runs showed in Figs. 1 and 2.

Catalyst	Batch 1		Batch 2
m	2.18	2	2
k^o (s^{-1})	64.39	56.02	48.04
k_d (h^{-1})	0.0562	0.0398	0.2622

3.4. Influence of residence time

In the same apparatus data were collected concerning a different batch of catalyst whose results and regression are shown in Fig. 2 and Table 1 as batch 2 catalyst. Whole experiments carried out to estimate the impact of reaction parameter on the catalyst decay were performed on samples of catalyst belonging to the latter batch. As abovementioned, the parameter m was maintained from now on equal to 2 and the initial constant rate for the fresh catalyst k^o at the experiment temperature was derived.

Successive data set were collect by means of the fluidized bed reactor and data were analyzed maintaining the parameter m and k^o derived from previous experiments as describe above.

In this way it was possible to measure the dependence of k_d by means of residence time τ in some trials carried out at the same linear velocity and at same ε. The experiment diagram is showed in Fig. 3, fitted parameters and test condition is reported in Table 2, columns I and II. What we found was that the k_d was not affected by τ alteration. Since residence time does not have any influence on the deactivation rate, we can argue that the decay reaction should be a parallel reaction of the main one. This remark is in disagree

Table 2
Summary of experimental conditions and estimated parameters f, k^o and k_d obtained via experimental data regression for the catalyst aging in Beckmann rearrangement experiments carried out in fluidized bed.

Experiment	I	II	III	IV	V	VI
T (K)	631	631	637	631	631	631
$W_{cat.}$ (g)	2.7	6	4	4	4	4
WHSV ($g_{CEOX}\,g_{cat.}^{-1}\,h^{-1}$)	2.15	0.9	4.3	4.3	6.45	8.6
p_{CEOX} (kPa)	1.72	1.72	3.45	3.45	5.17	6.89
τ (s)	0.11	0.25	0.11	0.11	0.11	0.11
V_{lin} (cm/s)	6.7	6.7	10.7	10.7	10.7	10.7
$\langle\tau\rangle$ (s)	0.07	0.13	0.07	0.07	0.07	0.07
ε	0.54	0.52	0.62	0.62	0.62	0.62
f	0.80	0.65	0.68	0.68	0.68	0.68
k^o (s^{-1})	48.04	48.04	59.25	48.04	38	48.04
k_d (h^{-1})	0.026	0.026	0.014	0.016	0.035	0.062

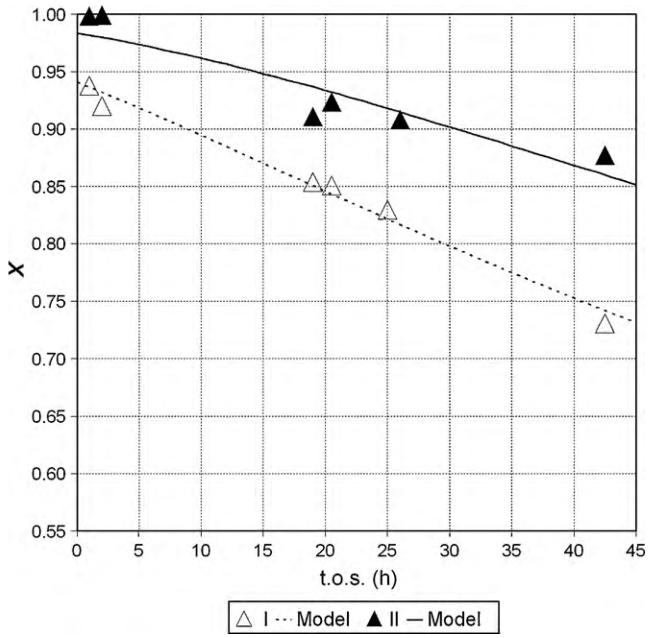

Fig. 3. Influence of residence time. Plot of the experimental results versus model results. Experiments carried out in fluidized bed reactor. Exp. I: $\tau = 0.11$ s; Exp. II: $\tau = 0.25$ s ($T = 631$ K; $p_{\mathrm{CEOX}} = 1.72$ kPa; $p_{\mathrm{MeOH}} = 40.2$ kPa; $p_{\mathrm{Toluene}} = 40.2$ kPa; $p_{\mathrm{N_2}} = 17.7$).

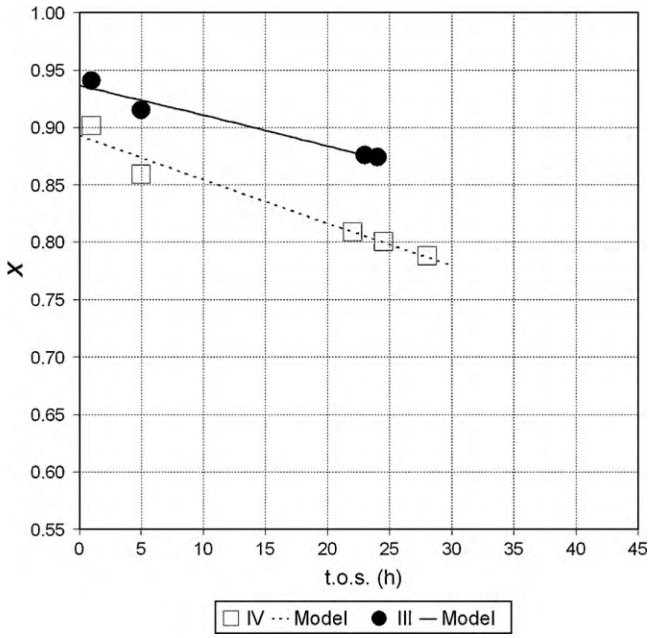

Fig. 4. Effect of temperature. Plot of the experimental results versus model results. Experiments carried out in fluidized bed reactor. Exp. IV: $T = 631$ K; Exp. III: $T = 637$ K (WHSV = 4.3 $g_{\mathrm{CEOX}}\,g_{\mathrm{cat.}}{}^{-1}\,h^{-1}$; $p_{\mathrm{CEOX}} = 3.45$ kPa; $p_{\mathrm{MeOH}} = 39.0$ kPa; $p_{\mathrm{Toluene}} = 39.0$ kPa; $p_{\mathrm{N_2}} = 18.3$; $\tau = 0.11$ s).

with what usually reported in literature [29,30] that asserts catalyst deactivation is due to CPL polymerization inside the zeolitic channel when desorption from active site is hindered, especially at low reaction temperature because of high activation energy required to remove protonated lactam from active site. Since the coke formation is due to a reaction product, the deactivation is a consecutive reaction and as a consequence should be influenced by residence time alteration. Anyhow Sumitomo recently supposed that catalyst decay depends on CEOX polymerization [31] as a consequence our observation would be confirmed.

3.5. *Influence of temperature*

Tests performed at different temperatures displayed an inverse proportionality between temperature and deactivation rate. A 6 °C increase in reaction temperature gave a k_d decrease from 0.016 to 0.014 h^{-1} (see Fig. 4 and Table 2, columns III, IV). The outcome of temperature effect is quite plain even for a variability of only 6 K and it makes clear that a higher temperature allows to stabilize the catalyst performance flattening the conversion curve against time on stream. Catalyst at high temperature is able to reach longer reaction time since minor conversion loss. Moreover catalyst activity is strongly improved at higher temperature, as it is possible to infer by means of the increasing of the k^0 initial rate constant. The upper limit of temperature increase is only due to selectivity decline. So it is essential tuning the trade-off between catalyst activity-stability and catalyst selectivity to reach optimal catalyst performances. Since it was ascertained the catalyst decay is a parallel reaction of the main one, the dependence from the temperature is driven by the activation energies of the two parallel reactions. As the influence of temperature on deactivation rate is inversely proportional hence the activation energy of main reaction is higher than that of deactivation and, as consequence, Beckmann rearrangement is promoted by a temperature increase while the decay is favoured on decreasing temperature.

Since rate expression (3) for the conversion includes the k^0 rate constant which is the term due to the reaction rate when there is no influence produced by catalyst deactivation, thus tests at different temperature allow us to determine the kinetic constant for the Beckmann rearrangement as well. Besides the quite little difference between the two temperature levels, setting the Arrhenius law for the two kinetic constants allowed to estimate Beckmann reaction activation energy of 116.7 kJ mol^{-1}.

The activation energy for the Beckmann rearrangement in gas phase has been predicted with the aid of computational methods as well. Fois et al. [32] studied oxide catalysts represented by cluster models and had found that the homogeneous Beckmann promoted by strong acid carries on with a multi-step mechanism in which internal proton transfer from N to O in the oxime is the rate determining step while weaker acids proceed through a single-step mechanism. Moreover the activation energy is correlated with acid strength: the weaker the acid the higher the activation energy. It was estimated that a silanol-catalyzed rearrangement requires activation energy of about 280 kJ mol^{-1} while an HCl-catalyzed rearrangement requires only 185 kJ mol^{-1}. Using the same computational method, Yamaguchi et al. [33] calculated rather different reaction barriers of 214 kJ mol^{-1}. More recently Bucko et al. [34] studied the Beckmann rearrangement of cyclohexanone oxime to CPL over mordenite using periodic ab initio DFT calculations. The reaction at the Brønsted acid site has been found to be most favourable for the Beckmann rearrangement with activation energy of 142 kJ mol^{-1}. The reaction at silanols nest site has also been estimated and a value of about 184 kJ mol^{-1} has been found.

The energy activation calculated by models is spread over a quite wide range nevertheless the value obtained from our experimentation is lower with respect to what calculated. This could be due to lack of the experimentation that has been established simply on two, very close levels of temperature. Despite this restriction the value is fairly in according with the latter data.

3.6. *Influence of reactant concentration*

Further step was to investigate how CEOX concentration influences decay rate. A few tests were performed at different CEOX

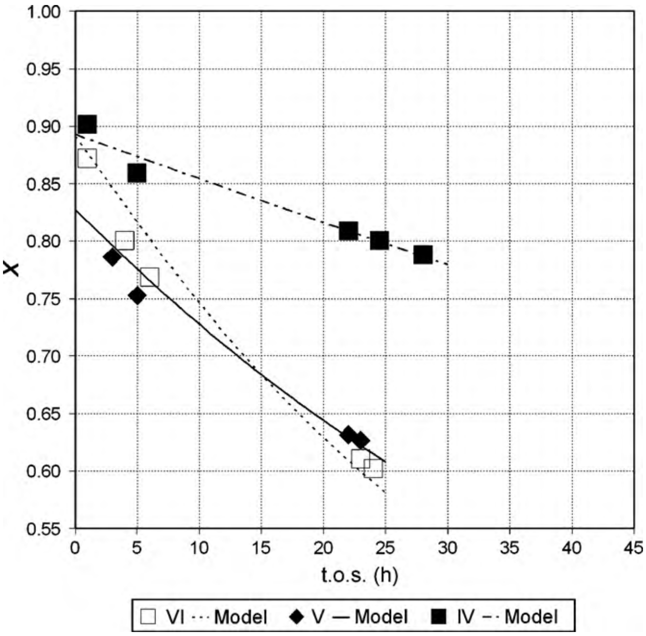

Fig. 5. Influence of cyclohexanone oxime concentration. Plot of the experimental results versus model results. Experiments carried out in fluidized bed reactor. Exp. IV: $p_{\mathrm{CEOX}} = 3.45\,\mathrm{kPa}$; $p_{\mathrm{MeOH}} = 39.0\,\mathrm{kPa}$; $p_{\mathrm{Toluene}} = 39.0\,\mathrm{kPa}$; $p_{\mathrm{N_2}} = 18.3$; Exp. V: $p_{\mathrm{CEOX}} = 5.17\,\mathrm{kPa}$; $p_{\mathrm{MeOH}} = 38.5\,\mathrm{kPa}$; $p_{\mathrm{Toluene}} = 38.5\,\mathrm{kPa}$; $p_{\mathrm{N_2}} = 17.7$; Exp. VI: $p_{\mathrm{CEOX}} = 6.89\,\mathrm{kPa}$; $p_{\mathrm{MeOH}} = 37.6\,\mathrm{kPa}$; $p_{\mathrm{Toluene}} = 37.6\,\mathrm{kPa}$; $p_{\mathrm{N_2}} = 17.7$ ($T = 631\,\mathrm{K}$; $W_{\mathrm{cat.}} = 4\,\mathrm{g}$; $\tau = 0.11\,\mathrm{s}$).

partial pressure (p_{CEOX}) at the same linear velocity and, as a consequence, at same ε and τ (see Fig. 5 and Table 2, columns IV, V, VI). As it is possible to ascertain initial activity of test V is lower than other ones. All the tests were done consecutively regenerating the catalyst after each run. If regeneration had been completed successfully initial reaction rate of the catalyst would have been the same. The lower initial rate for run V was probably due to a non-complete regeneration between the tests. As the reactor fluid dynamics did not change among considered three tests it is permissible to suppose that the efficiency of the reactor is the same and set the parameter *f* equal in the three attempts and perform SSR allowing the program to adjust k^{o} as well in the V run. As consequence a lower k^{o} in this run was established. That seems not to influence the deactivation rate constant whose values is well correlated with the other ones and only the initial rate is affected by bland regeneration. Thus it was found that the k_d increases along with p_{CEOX}. Because the previous tests showed that decay is independent from τ and it relates to a parallel pathway we can postulate that it depends from the partial pressure of the reactant in the n'th order; therefore, according to Levenspiel [35], the following equation can be used to describe the kinetic rate constant

$$k_d = K_d^{\mathrm{o}} \times p_{\mathrm{CEOX}}^{n'} \tag{11}$$

In order to find out the deactivation reaction order n' Eq. (11) should be solved for two different p_{CEOX}.

$$\frac{k_{d1}}{k_{d2}} = \left(\frac{p_{\mathrm{CEOX1}}}{p_{\mathrm{CEOX2}}}\right)^{n'} \tag{12}$$

In three different CEOX partial pressure experiments almost the same value for n' arose with an average value 1.96. Therefore we may assume that the deactivation constant k_d is the second order with respect to p_{CEOX} and we set $n' = 2$; according to this hypothesis a $K_d^{\mathrm{o}} = 1.32 \times 10^{-3}\,\mathrm{h^{-1}\,kPa^{-2}}$ was found. It is remarkable that k_d, is a function of CEOX concentration and there is a second order kinetics: this means that two molecules should bind on active site to bring about blocking of site or, better, that site loss is due to an intermediate species which is formed in a bimolecular reaction, probably a dimer of oxime or cyclohexanone.

In all the experiments data were collected within the early hundred hours of each test. A strong increase in decay rate was noticed at longer times. Therefore to describe a more aged catalyst a more complex law should be settled with additional parameters: a term regarding the possible autocatalytic behaviour of coke itself or an increase in the order of deactivation ($m > 2$) originated from an incipient pore plugging. We did not judge the matter worth to be refined any more because such kind of deactivated catalyst would not have enough activity to be interesting and it is not worth to push aging of catalyst so deeply. Moreover a too aged catalyst becomes refractory to regeneration and demands severe regeneration conditions. In our experience harsh regeneration is harmful to catalyst life and brings to enhanced irreversible decay. As a matter of fact, focusing onto the industrial exploitation of silicalite-1 in vapour phase Beckmann catalytic rearrangement of CEOX to CPL, our investigation showed the best way of carrying out the process was through short reaction/regeneration cycles in a fixed bed reactor or through continuous catalyst regeneration in a fluidized bed reactor. The strategy of carrying out the reaction with short reaction/regeneration cycles allows maximizing both affordable WHSV and catalyst productivity and makes catalyst consumption bearable by an industrial process.

4. Conclusions

Silicalite-1, a high silica MFI type zeolite, was utilized as catalyst in the vapour phase Beckmann rearrangement of CEOX. Although the initial reaction rate is very high catalyst is subjected to a significant deactivation during time and conversion declines quickly. Such considerable catalyst deactivation is mainly due to coke build up. The kinetic of deactivation was investigated in a fixed bed and a fluidized bed reactor with the aid of time on stream theory. The silicalite-1 deactivation rate has been found to be a second order reaction both in active site concentration and in CEOX concentration. The evidence that the deactivation kinetic proceeds through a two site mechanism confirms that reaction takes place over silanol nests instead of isolated silanols.

In view of the fact that deactivation rate has not been found related to residence time, deactivation of active site should be a parallel reaction of the main. As a consequence, because the deactivation rate constant has been found to be inversely proportional to temperature, the activation energy of the Beckmann rearrangement is supposed to be greater than deactivation one. By means of the constant rate evaluated at different temperatures the activation energy for the Beckmann rearrangement was found to be $116.7\,\mathrm{kJ\,mol^{-1}}$.

Thorough study of decay data in Beckmann rearrangement contributed to improve knowledge about catalyst aging behaviour. The achieved awareness allowed us to define the best mode of industrial exploitation; in order to reduce catalyst aging Beckmann rearrangement requires low cyclohexanone oxime concentration in the feed and high reaction temperature, in the range between 623 and 653 K.

References

[1] P. Roffia, G. Leofanti, A. Cesana, M. Mantegazza, M. Padovan, G. Petrini, S. Tonti, P. Gervasutti, Stud. Surf. Sci. Catal. 55 (1990) 43.
[2] G. Petrini, G. Leofanti, M.A. Mantegazza, F. Pignataro, American Chemical Society Symp. Ser., vol. 626, American Chemical Society, Washington, 1996, pp. 33–44.
[3] H. Ichihashi, M. Kitamura, Catal. Today 73 (2002) 23–28.
[4] B.M. Trost, Science 254 (1991) 1471.
[5] B.M. Trost, Angew. Chem. Int. Ed. Engl. 34 (1995) 259.
[6] R.A. Sheldon, Consider the environmental quotient, Chemtech (March) (1994) 38–47.

[7] G. Bellussi, A. Carati, M.G. Clerici, G. Maddinelli, R. Millini, J. Catal. 133 (1992) 220.
[8] H. Sato, K. Hirosa, N. Ishii, Y. Umada, EP 0234088 (1986).
[9] H. Sato, K. Hirose, N. Ishii, Y. Umada, U.S. Patent 4,709,024 (1987).
[10] C. Flego, L. Dalloro, Micropor. Mesopor. Mater. 60 (2003) 263.
[11] M. Kitamura, H. Ichihashi, Stud. Surf. Sci. Catal. 90 (1994) 67.
[12] M. Kitamura, M. Shimazu, JP 2000-229939 (1999).
[13] M. Taramasso, G. Perego, B. Notari, U.S. Patent 4,410,501 (1983).
[14] T. Komatsu, T. Maeda, T. Yashima, Micropor. Mesopor. Mater. 35–36 (2000) 173–180.
[15] L. Balducci, R. Buzzoni, L. Dalloro, G. De Alberti, EP 1002577 (2003).
[16] G. Artioli, C. Lamberti, G.L. Marra, Acta Cryst. B56 (2000) 2–10.
[17] A. Zecchina, S. Bordiga, G. Spoto, L. Marchese, G. Petrini, G. Leofanti, M. Padovan, J. Phys. Chem. 96 (12) (1992) 4985–4990.
[18] R. Buzzoni, S. Bordiga, G. Ricchiardi, C. Lamberti, A. Zecchina, G. Bellussi, Langmuir 12 (1996) 930–940.
[19] R.W. Groose, E.M. Flaningen, U.S. Patent 4,061,724 (1977).
[20] G.F. Froment, K.B. Bishoff, Chem. Eng. Sci. 16 (1961) 189.
[21] G.F. Froment, K.B. Bishoff, Chem. Eng. Sci. 17 (1962) 105.
[22] S. Szepe, O. Levenspiel, Proceedings of the 4th European Symposium on Chemical Reaction Engineering, 1971.
[23] B.W. Wojciechowski, Can. J. Chem. Eng. 46 (1968) 48.
[24] T. Takahashi, K. Ueno, T. Kai, Can. J. Chem. Eng. 69 (1991) 1096.
[25] B.W. Wojciechowski, Cat. Rev.-Sci. Eng. 9 (1) (1974) 79–113.
[26] Carberry, Chemical and Catalytic Reaction Engineering, McGraw-Hill, 1976, pp. 567–571.
[27] S. Bordiga, I. Roggero, P. Ugliengo, A. Zecchina, V. Bolis, G. Artioli, R. Buzzoni, G. Marra, F. Rivetti, G. Spanò, C. Lamberti, J. Chem. Soc., Dalton Trans. (2000) 3921.
[28] S. Bordiga, P. Ugliengo, A. Damin, C. Lamberti, G. Spoto, A. Zecchina, G. Spanò, R. Buzzoni, L. Dalloro, F. Rivetti, Top. Catal. 15 (2001) 43.
[29] T. Takahashi, M.N.A. Nasution, T. Kai, Appl. Catal. A: Gen. 210 (2001) 339–344.
[30] D. Mao, G. Lu, Qingling Chen J. Mol. Catal. A: Chem. 240 (2005) 164–171.
[31] Y. Izumi, H. Ichihashi, Y. Shimazu, M. Kitamura, H. Sato, Bull. Chem. Soc. Jpn. 80 (7) (2007) 1280–1287.
[32] G.A. Fois, G. Ricchiardi, S. Bordiga, C. Busco, L. Dalloro, G. Spanò, A. Zecchina, Proceedings of the 13th International Zeolite Conference, 2001, p. 149.
[33] Y. Yamaguchi, N. Yasutake, M. Nagaoka, J. Mol. Struct. 639 (2003) 137.
[34] T. Bucko, J. Hafner, L. Benco, J. Phys. Chem. A 108 (2004) 11388–11397.
[35] Levenspiel, Chemical Reaction Engineering, John Wiley & Sons Inc., 1972.