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Application of a three-dimensional network model to the coke formation in FAU, MFI and BEA zeolites

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Abstract

Three-dimensional site-bond-site network modeling was applied to simulate the deactivation process of three types of zeolites: BEA, FAU and MFI. A simple process rate model was used to describe the deactivation in terms of relative activity while a detailed Monte-Carlo reaction model was used to study the coke formation, including adsorption, desorption, reaction and diffusion effects. The simulation results were compared with experimental data for coke formation. The study shows the importance of catalyst morphology and topology described in the present model by measurable parameters like: connectivity of network and size distribution of cavities and channels. The present model correlates effectively the available experimental deactivation data for the cases studied, both for short or long times of reaction, showing the importance of taking the pore structure into account when modeling catalyst deactivation.

Keywords: Network model; Monte-Carlo; Pore structure; Zeolite; Coke; Deactivation

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1. Introduction

The lifetime of catalyst is a key factor in the economics of many industrial processes. In the petroleum refining process such as fluid catalytic cracking, carbon deposition is the main cause of temporary catalyst deactivation. Mathematical modeling of catalyst deactivation is of great importance for the design, operation, control and optimization of these processes and also for catalyst design [1].

During the industrial transformations of organic substances, hydrocarbons of high molecular weight (coke) are formed by both thermal and catalytic mechanisms. In both cases, secondary products of high molecular weight are formed and retained in the catalyst pores prior to the formation of carbonaceous deposits [2]. The carbonaceous deposits thus formed can deactivate the catalysts either by poisoning the active sites or by blocking the pore entrances.

Flow conditions, mass and heat transfer play a significant role in the formation of coke [1]. The formation and composition of carbonaceous compounds and thus the deactivation effect are determined by the network structure of pores. The role played by the size and shape of zeolite pores can be even more important than chemical properties such as strength and density of active sites [3]. Network models have been recently proposed for catalyst pore structures. The main advantage of this approach is that pore size distribution and connectivity can be incorporated to the derived kinetic models. Several authors have studied the mass transfer and reaction kinetics in such models, relating coke laydown and pore structure with the application of stochastic network models [4,5]. Muhammad and Kann [6] applied a similar stochastic network model and compared it with experimental kinetics of cumene disproportioning. The simulations considered a two-dimensional site or bond networks. Mann [5] emphasized that full realism could only be achieved with three-dimensional pore network models.

More recently, Zgrablich and co-workers [7,8] applied the site-bond-site model of Mayagoitia adopted by

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Kornhauser [9] for studying deactivation of catalysts. A percolative Bethe network model was used for the calculation of catalytic activity. They compared the predicted activity with the experimental data previously obtained by Marin et al. [10] and activities estimated by an earlier statistical model [11]. Their correlated network model predicted the experimental behavior, with superior quality when compared to previous contributions, especially for long times. Their methodology is limited to homogenous Bethe networks (Cayley trees) with a coordination number of three. The authors proposed an approximate analytical solution for the calculation of the relative activity. Recently, Guo et al. [12] have simulated the formation of coke in zeolites using a two-dimensional lattice model with two types of network sites, but the simulations were not compared with experimental data.

Many authors have discussed the effect of pore structure on zeolite deactivation [3,13–15]. Early simulation studies of internal coke formation in zeolites indicate that the coke would (at least initially) form in the channel intersections or cavities rather than in the channels themselves [16].

The simulation of catalyst deactivation by coke formation using a three-dimensional site-bond-site network model (see Fig. 1) is of particular interest in the case of zeolites, as the processes occurring in the cavities (intersections in the network) and in the channels (connections between intersections in the network) can be readily distinguished. Such model is flexible and the connectivity of pores as well as the local homogeneity of the catalyst can be easily altered.

In the present paper, a three-dimensional site-bond-site cubic network is employed to describe zeolite deactivation due to poisoning and blockage of pores. The lattice of the zeolite is modeled as a three-dimensional cubic structure with a dimension of 10 × 10 × 10 (representing 1000 network sites). The connectivity (the average number of channels connected per intersection) can be varied in the range of 0–6, which is higher than the low range of 0–4 in a two-dimensional square lattice. Therefore, there is a higher possibility for the formation of internal clusters in this kind of structure. Two different applications of the three-dimensional network model are studied. In the first application, a simple relative activity model is incorporated into the structured model to describe the deactivation of three different types of zeolites (FAU, MFI and BEA). In the second application, the deposition of coke is simulated considering a consecutive reaction mechanism of coke formation by Monte-Carlo method. The detailed reaction model is adopted and takes into account diffusion, adsorption, desorption and reaction mechanisms. The structures of the zeolites studied are well known and can be well represented by the present three-dimensional model.

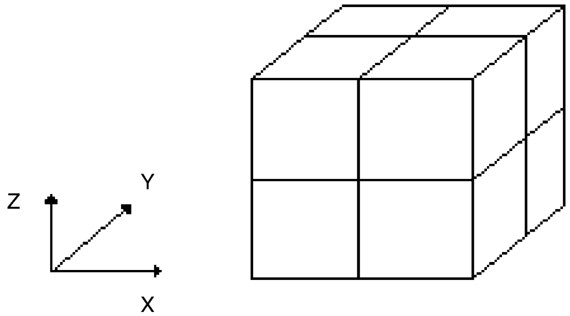

Fig. 1. The three-dimensional site-bond-site network applied (the structural model). The network sites (the intersections) are considered the cavities and the bonds (the connections between network sites) the channels of the catalyst.

2. Materials and methods

2.1. Experimental

Previously published experimental data for methylcyclohexane conversion over different zeolites at 450 °C was used for modeling [17]. Details of the zeolite samples can be found elsewhere [18].

2.2. Relative activity model

In the simulations, the construction of cavities (the network sites) and channels (network bonds) followed the methodology of Kornhauser [9]. The site and bond sizes were represented by the frequency distribution functions with an overlap between the functions (Fig. 2). In the Fig. 2d, F_s and F_b represent the frequency distribution functions of site and bond, respectively. The advantage of this methodology is that only three parameters are sufficient to generate the site and bond size distributions and to vary the local homogeneity of the network. The size range of bond ($B2$–$B1$) and the size range of site ($S2$–$S1$) control the domain of the distributions, being the local homogeneity characterized by an overlap parameter (Ω). The higher the Ω value (represented by the shaded areas), the more homogeneous are the structures generated. It may be noted that in Fig. 2a for the case $\Omega = 0$, the size distributions of network sites (cavities) and bonds (channels) are not correlated. This case corresponds to porous structures formed by cavities and channels of distinct size ranges, as in a random packing of spheres of different sizes. On the other hand, for $\Omega = 1$, we have a network of different but locally homogeneous regions. For intermediate values of Ω, the structure is more complex because the cavities can be of a completely different size from the size of the interconnecting channels. For the case of a uniform distribution of cavities and of channels the overlap parameter is presented in Fig. 2d. The characteristic parameters are $B1$, $S2$ and Ω. The overlap parameter Ω is given by $(B2–S1)/(B2–B1)$ where the channel size range from $B1$ to $B2$ while the cavity size vary from $S1$ to $S2$.

The following additional assumptions are made about the pore space:

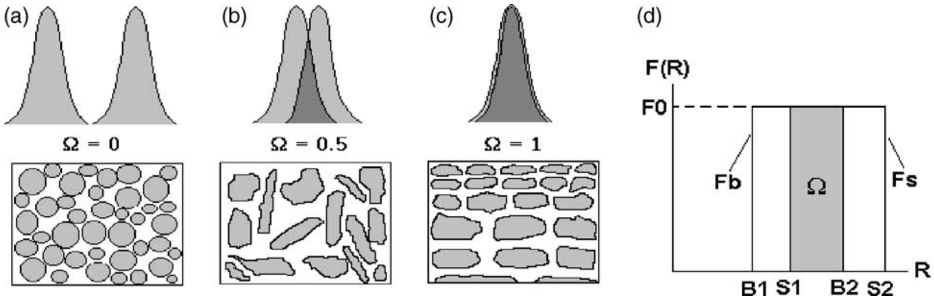

Fig. 2. Porous structures for different overlap parameters. (a) Pores structure not correlated ($\Omega = 0$), generated by the distribution functions of cavities and channels. (b) Structure with intermediary correlation ($\Omega = 0.5$) between the distribution functions of cavities and channels. (c) Structure with high correlation ($\Omega = 1$) between the distribution functions of cavities and channels.

(i) The pore space is a lattice of spherical cavities interconnected by cylindrical channels.
(ii) Active sites are uniformly distributed over the pore space.
(iii) During the course of the catalytic reaction, active sites are covered by deposition of contaminant materials and simultaneously cavities and channels may be blocked by the growth of contaminant deposits in the pore structure.

2.3. Process model

Similar to Faccio et al. [7], the deactivation process is simulated with a simple rate process model, in which a relative activity A is defined by:

$$A = w^{ac}\, exp(-kt) \tag{1}$$

w^{ac} represents the fraction of porous surface belonging to open pores, which is calculated by simulation. The pores are blocked at time t if their radii fall below the critical values S^* and B^*, respectively, given by the equations:

$$S^* = S1 + 3\alpha(1 - exp(-kt)),\quad B^* = B1 + 2\alpha(1 - exp(-kt)) \tag{2}$$

where $S1$ and $B1$ are the lower limits of the respective size distribution, and α is a blockage parameter that is proportional to the concentration of coke. It represents the growth rate of coke in the system. This amount can be estimated [7,8] by the following relation.

$$\alpha = \frac{C_t M_c}{s\rho_c} \tag{3}$$

where C_t (kmol of sites/kg of catalyst), M_c (kg/kgmol), s (m^2/kg) and ρ_c (kg/m^3), represent the total concentration of active sites, the molecular mass of coke, the specific BET surface area, and the coke density, respectively.

We consider the parameter (α) proportional to the minimum diameter of the zeolite structure, since the formation of coke precursor depends on the zeolite pore size. This assumption reduces the number of parameters without interfering with the correlation between the experimental data and the simulated results.

2.4. Coke formation by Monte-Carlo simulation

In this application, the two y–z planes in the x-directions of the three-dimensional lattice are subjected to constant pressure of the reagents (see Fig. 1). Periodic boundary conditions are applied to the planes located in the other directions, i.e. for each molecule leaving the lattice plane in the y and z directions, another molecule is assumed to enter in the opposite plane. The periodic boundary conditions are introduced to consider the zeolite lattice infinite in the y and z directions. Each intersection is assumed to contain only one active site on the average, and only one molecule is permitted to occupy a channel or a cavity in the structure. The reaction occurs only inside the cavities.

The reaction model is the same as the one adopted by Guo et al. [12]. Coke formation is considered to follow sequential steps such as growing, cyclization, aromatization and condensation. The following sequence of reactions is assumed:

$$\mathrm{A} + \mathrm{As} \rightarrow \mathrm{Bs}$$

$$\mathrm{A} + \mathrm{Bs} \rightarrow \mathrm{Cs}$$

$$\mathrm{A} + \mathrm{Cs} \rightarrow \mathrm{Ds}$$

where A, B, C and D, respectively represent the reagent, product, coke precursor and coke deposited; s represents the active site where the reaction occurs.

Simulation studies for coke formation in zeolites require good experimental data. For the cases studied, the coke molecules soluble in CH_2Cl_2 after acid treatment were considered as coke precursors. The coke deposition simulations were carried out in a sequence of Monte-Carlo steps (MCS) using a method similar to that of Guo et al. [12]. Each step is subdivided into adsorption, diffusion/reaction and desorption. Adsorption is represented by the introduction of molecules in the lattice.

In the adsorption step, every external cavity is checked one by one. The molecule enters into the lattice if the chosen element is empty and the random number generated by a uniform distribution is less than the predetermined adsorption probability. Because of an earlier evidence of the relationship between the contact time and the adsorption probability [19], this last parameter was set equal to 0.2 for all zeolites. In the diffusion step, each molecule in the system is associated with a velocity vector. Molecular diffusion is determined by jumps between elements in the network. In the simulations, each kind of molecule has a probability to diffuse in the pore structure, with fixed value of 1.0 for reactant ($p_{\mathrm{reag}} = 1$). The diffusion of products and coke precursors are defined by the probability of product diffusion ($p_{\mathrm{pro}} = 1$) and probability of precursor diffusion ($p_{\mathrm{pre}} = 1$). Molecules can pass through an occupied cavity with a probability of 0.2. The direction of the molecule in the lattice is chosen randomly.

In the reaction section, each molecule that enters a cavity can react with an adsorbed molecule in the active site with a reaction probability. The reaction probabilities for the formation of products, coke precursors and coke are represented by the formation constants $k1$, $k2$ and $k3$, respectively. The reaction occurs when one molecule jumps to a chosen cavity in which another molecule is adsorbed. Similarly, in the desorption step every external cavity was checked one by one, throwing to the gas phase reactants, products and precursors with probabilities of 0.8, 0.6 and 0.4, respectively.

3. Simulation results

The connectivity ratio of zeolite in the simulations was calculated as the ratio between the total acidity and the theoretical micromoles number of hydrogen in the unit cell for each type of zeolite. The total acidity is defined as the sum of Brönsted and Lewis sites measured by pyridine adsorption at 150 °C (Table 1). The basic assumption is that all hydrogen atoms can be potential acid sites. The calculated connectivity ratios of FAU, BEA and MFI were 0.447, 0.734 and 0.771, resulting in connectivity values of 2.7, 4.4 and 4.6, respectively for a 3D cubic network compared to a maximum value of 6 for a fully connected network representing six possible directions (Table 2).

Initially, we considered the connectivity ratio as the ratio of the number of moles of Brönsted sites alone to the total number of moles of hydrogen atoms in the zeolite unit cell. The correlation between simulation results and the experimental data were not satisfactory directing us to consider in the calculations the sum of moles number of Lewis and Brönsted sites.

Table 2
Connectivity values for three types of zeolite

	Accessible acid sites/total acid sites[a]	Connectivity
FAU	0.447	2.7
BEA	0.734	4.4
MFI	0.771	4.6

[a] Connectivity ratio = the sum of Lewis and Brönsted sites in micromoles divided by the theoretical micromoles number of hydrogen in the unit cell.

The simulation results of the relative activity model for the three different zeolite structures are presented in Figs. 3–5. The channel length was taken to be 20 Å for all zeolites. Earlier results [19] indicate that the deactivation rate can be significantly lower for higher values of Ω, when the α parameter is different from zero, i.e. when the blockage depends on the concentration of coke. Moreover, the deactivation rate is lower in the case of a positively biased distribution of pores (distribution of pores that generate more pores with small sizes or more pores with large sizes), as compared to a network with uniform pores. In Figs. 4 and 5, the simulations considered the presence of macropores in the zeolite structure. In Fig. 3 the presence of macropores was not considered and the cavity and channel distribution were obtained considering the maximum and minimum diameters values for each zeolite structure (7.4 Å < D < 13 Å, 5.5 Å < D < 7.6 Å and 5.1 Å < D < 5.6 Å for FAU, BEA and MFI, respectively). In the Figs. 3 and 4 the relative activity is plotted against the dimensionless time (kt), assuming α and Ω equal to 0.3 Å and 0.5, respectively. The results in Fig. 3 shows the deactivation rate of the FAU zeolite lower than that of other zeolites, in spite of the fact that this zeolite has the lowest connectivity value. This observation agrees with the experimental result in which the FAU has the highest resistance to deactivation. On the other hand, the MFI presented the lowest resistance of deactivation, in spite of its highest connectivity value. This evidence can be attributed to the low range of cavity and channel size in its structure. We can observe that although MFI has the highest number of acid sites, its low resistance to deactivation is related to a mode of deactivation by pore blockage [17].

The presence of macropores was further considered in the simulations, with results presented in the Fig. 4, by the

Table 1
Characterization of zeolite samples[a]

	Unit cell formula	Si/Al	Crystallite size (μm)	Pore volume (cm^3/g)		Acidity (μmol/g)	
				Microporous	Mesoporous	Brönsted	Lewis
FAU	$Na_{0.30}H_{11.00}Al_{11.3}Si_{180.7}O_{384.0}$, 7.3 EFAL[b]	16	0.5	0.344	0.163	327	74
BEA	$H_{3.88}Al_{3.88}Si_{60.12}O_{128.0}$, 1.5 EFAL	15	0.02	0.282	0.505	345	372
MFI	$H_{6.40}Al_{6.40}Si_{89.60}O_{192.0}$	14	1.0	0.151	0.016	732	126

[a] Data [18].

[b] EFAL: extra-framework aluminum species.

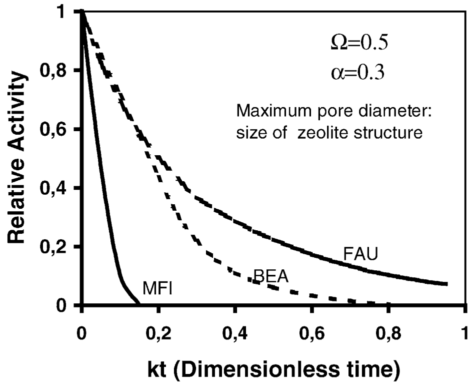

Fig. 3. Relative activity vs. dimensionless time for different zeolite structures with α and Ω equal to 0.3 Å and 0.5, respectively. The dimensions of pores correspond to the dimension of the microstructure of each zeolite.

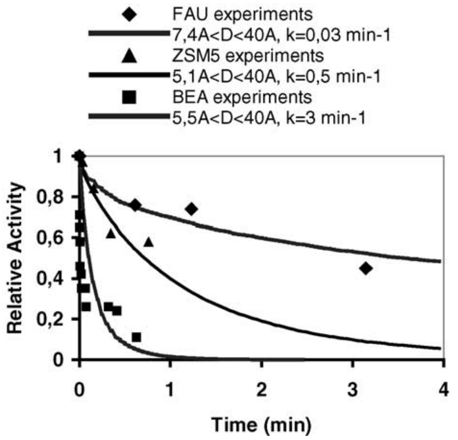

Fig. 5. Relative activity vs. time for different zeolite structures. The points are the experimental data and solid lines the model results.

assumption of the presence of pores with the highest size in the zeolite (assumed to be 40 Å diameter). In this manner all zeolites have a pore size distribution that range from the minimum size of the zeolite structure to the maximum size of the macropore. The deactivation decreases with the increase in the connectivity for an equivalent range of pore sizes. The results show an increase in the resistance of deactivation compared with the results obtained without considering the macropores. As a consequence, the connectivity seems to play an important role on the rate of deactivation. A high resistance to the deactivation was found for the high connectivity zeolites (MFI and BEA). The increase in the range of pore distribution increased the resistance of deactivation by a factor of 3 as can be observed comparing Figs. 3 and 4.

In the correlation between the simulations and the experimental results, Fig. 5, was assumed the presence of macropore in the structure of each zeolite, with maximum diameter of 40 Å (pore size distribution from the minimum size of the zeolite structure to the maximum size of the macropore). The Fig. 5 compares experimental values [17] and the present model results for the deactivation of three kinds of zeolites. All the simulations were carried out using the same value of overlap parameter (Ω = 0.50). The distribution functions of cavities and channels were considered with a negative bias of 2% so that there is an increased presence of channels and cavities with small sizes. The α parameter was considered as 0.3, 0.5 and 0.5 Å for MFI, BEA and FAU, respectively. These values suggest that the initial coke molecules of FAU and BEA zeolites have the same initial size that are higher than the coke size of MFI zeolite. The simulations reproduced the experimental data very well for both short and long reaction times. The kinetic deactivation constants reflect the high resistance to deactivation presented by zeolite FAU (k = 0.03 min^{-1}). The relative deactivation kinetic constant is higher for BEA than to MFI: $k_{\mathrm{MFI}}/k_{\mathrm{FAU}}$ = 16.7, $k_{\mathrm{BEA}}/k_{\mathrm{FAU}}$ = 100. The high proportionality between zeolites FAU and BEA is related to the low resistance to the deactivation.

The Monte-Carlo simulations of the three-dimensional network model are shown in Figs. 6–8. In the Fig. 6, the number of coke molecules is plotted against the total amount of coke formed (sum of coke precursor and coke) following the same ratio between the constants of formation. The black line and gray line, in the Fig. 6, correspond to coke precursors and insoluble coke, respectively. Coke formation

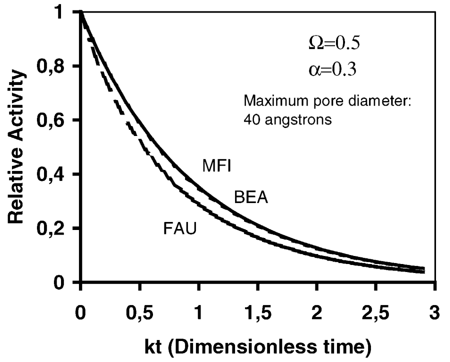

Fig. 4. Relative activity vs. dimensionless time for different zeolite structures with α and Ω equal to 0.3 Å and 0.5, respectively. It was considered the presence of macropores represented by a maximum pore size of 40 Å.

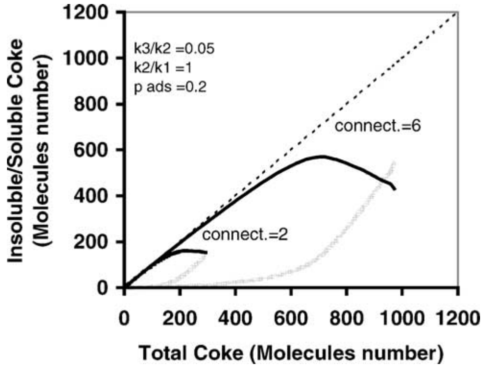

Fig. 6. Content of soluble and insoluble coke in CH_2Cl_2 after HF treatment vs. total coke content. Monte-Carlo simulation results varying the connectivity value.

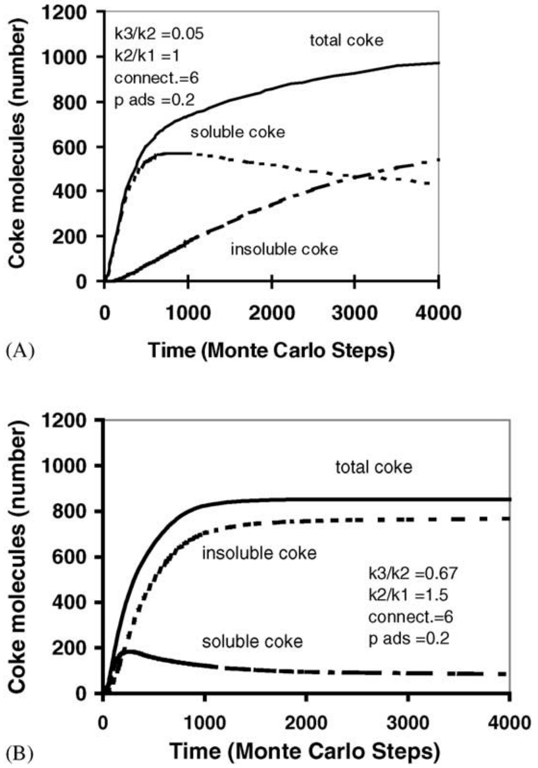

Fig. 7. Number of soluble and insoluble coke molecules vs. number of Monte-Carlo steps considering adsorption probabilities of 0.2 and connectivity of 6. (A and B) *k*1, *k*2 and *k*3 represent the formation constants of product, soluble coke and insoluble coke, respectively. These quantities are associated to the reaction probabilities of each type of molecule in the zeolite. (A) *k*2/*k*1 = 1 and *k*3/*k*2 = 0.05. (B) *k*2/*k*1 = 1.5 and *k*3/*k*2 = 0.67.

was considered to be proportional to the reaction probability, which varies in each step of the reaction mechanism. From the Fig. 6, can be observed, initially, that first there is the formation of coke precursor (superior line), following the formation of insoluble coke (inferior line). Each value of connectivity corresponds to a pair of insoluble and soluble curves of coke. As observed in a previous work [19], the final amount of coke is determined by the accessibility or network connectivity of the system. Thus, the higher the accessibility the higher the amount of coke formed in the material, having different profiles of formation. Small ratios between the constants lead to profiles in which the coke precursors are formed followed by the formation of insoluble coke.

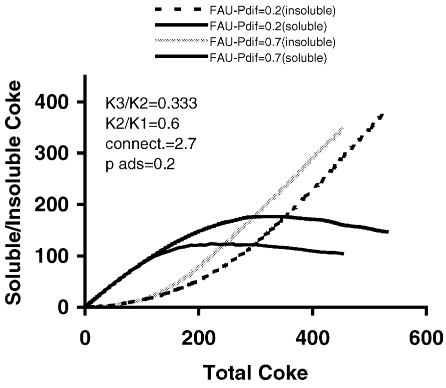

Fig. 8. Number of soluble and insoluble coke molecules vs. total number of coke molecules. Monte-Carlo simulation results varying the diffusion of coke precursor.

The experimental data confirmed the relationship between the maximum amount of coke formed and the connectivity of the zeolite, when the kinetic factors of coke formation were considered [17]. Although MFI has the highest value of connectivity it showed an intermediate formation of coke.

Fig. 7A and B presents the concentration profiles for coke precursor, coke and total coke molecules with time. Each Monte-Carlo step was considered as a unit of time. The results presented consider the same conditions of connectivity, probabilities of adsorption, diffusion of product and diffusion of precursor that were 6.0, 0.2, 0.7 and 0.5, respectively. The low coke formation constants in the Fig. 7A produced a profile corresponding to a high formation of coke precursor. The time for the complete saturation is increased in this condition.

Increasing the constants for coke formation causes a reduction in the total amount of coke precursor (Fig. 7B). This was expected since these compounds are quickly transformed into coke, which causes the material to be saturated earlier, causing stagnation in the total coke concentration.

An important parameter in the simulation of the zeolites is the precursor diffusion in the pore media, which is expressed by the diffusion probability of precursor (p_{dif}). Fig. 8 shows the influence of precursor diffusion in the coke formation assuming the structure of FAU zeolite (connectivity equals to 2.7). It can be observed that the total formation of coke in the structure is inversely proportional to the diffusion of coke precursor. The explanation for this observation can be attributed to the increase in the residence time of precursor in the active sites with the decrease in the diffusion probability that increase the reaction chance to coke formation leading to a high saturation profile in the network.

Correlation between the experimental data and the applied model are shown in the Fig. 9, in which the good agreement can be seen. The markers, circles, triangles and squares, represent the experimental coke formation of precursor (coke soluble) for BEA, MFI and FAU, respectively. The correspondent shaded markers represent the experimental insoluble coke formation for BEA, MFI and FAU, respectively. The simulation results are represented by the black lines and the gray lines, in which correspond to soluble and insoluble coke, respectively. The molecule numbers of coke were converted to total amount of coke [17]. The maximum numbers of coke molecules are 1.5×10^{20}, 1.1×10^{20} and 2.4×10^{19} (molecules/gram of zeolite) to BEA, MFI and FAU, respectively. Assuming a linear relation between the number of molecules and the amount of coke and considering the zeolite densities, the amount of coke precursor was estimated as well as the total

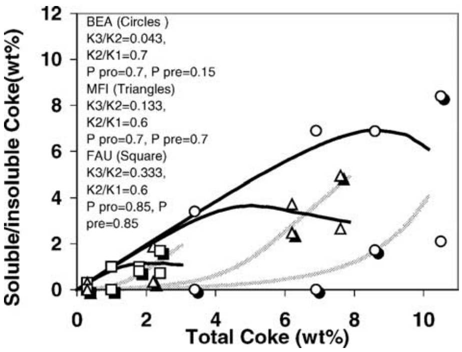

Fig. 9. Content of soluble and insoluble coke in CH_2Cl_2 after HF treatment vs. total coke content. Monte-Carlo simulation and experimental data for FAU, MFI and BEA zeolites.

amount of coke formed in each case. The simulations show the lowest ratio between the constants of coke formation for BEA (k_3/k_2 = 0.043) indicating a small rate of coke formation with time for this zeolite. The zeolite FAU had the highest diffusion of precursor in the structure followed by MFI and BEA.

4. Conclusions

The application of a three-dimensional network model to represent the well-defined structures of different zeolites (FAU, MFI and BEA) illustrates the importance of the pore structure in the deactivation process. In the case of a large range of pore sizes, complete blockage of the structure would be more difficult to occur because the coke molecules would have to grow to the equivalent size of the largest pores of the zeolite.

The proposed correlated site-bond-site cubic network model can easily represent the shapes, structures and sizes of cavities and channels of zeolites. This model can be used in Monte-Carlo simulations of deactivation kinetics and in empirical pore level deactivation models. The connectivity of the zeolites can be considered as the accessible hydrogen atoms in the structure. The results show that the model is effective in describing the deactivation of zeolites. Unlike earlier models, the experimental deactivation data are successfully correlated for both long and short times.

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