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Modelling of *n*-hexadecane hydroisomerization and hydrocracking reactions on a Mo/Hβ-alumina Bi-functional catalyst, using the single event concept

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Abstract

Hydrocracking of a long chain paraffin, hexadecane, was carried out on a Mo/Hβ-alumina bi-functional catalyst with a weak dehydrogenating function. It was found through an isomerization selectivity analysis that the behavior of the system is away from ideal hydrocracking conditions. To implement for this system the single event concept, until now applied only to systems for which the ideal hydrocracking assumption was valid, a hybrid model that includes the more general case in which reactions on the acid sites are not rate determining was developed. This model was called the single-event-lumped-parameter hybrid (SELPH) model, for it considers fundamental rate constants for the reactions that take place on the acid sites using the single event concept, and lumped rate constants for the reactions on the metal sites. The kinetic coefficients at 533 K were estimated and the agreement between the calculated and experimental data was satisfactory.

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1. Introduction

Hydrocracking is a very important process through which relatively heavy oil feedstocks are converted into lighter more valuable transportation fuel products under high hydrogen pressure. Hydrocracking reactions are usually carried out over dual function catalysts which combine both acidic and metal functions. Commonly used catalysts are Ni, Mo, Co or Pt supported on zeolite.

Mechanistically, the first step in the hydrocracking process of paraffins is the dehydrogenation of alkanes to produce olefin intermediates, which in turn can form carbenium ions which are adsorbed on the acid sites. These carbenium ions can undergo the usual acid-catalyzed reactions, namely types A and B isomerizations and subsequent cracking in the β position with respect to the

* Corresponding author. E-mail address: jrs@servidor.unam.mx (J. Ramírez). carbon atom bearing the positive charge [1–4]. The isomerized and cracked species can then be desorbed from the acid sites and hydrogenated on the metal sites to form the corresponding paraffins. The cracked products species can undergo further cracking reactions (secondary cracking). As a result of this process, paraffins with a smaller number or carbon atoms and higher degree of branching are produced.

Development of mathematical models to predict the behavior of hydrocracking reactions is of great importance in the oil refinery industry, since they are useful for reactor design and catalyst development. A comprehensive and reliable model could also be used to guide the operation of the plant and serve as a basis for its control.

Nevertheless, given the complexity of the hydrocracking reaction systems, modelling of such processes has been particularly difficult and, traditionally, it has been necessary to make a drastic lumping of the feed, intermediate and end product species. A typical example is the 10-lump model for catalytic cracking of Jacob et al. [5].

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Nomenclature			
C	surface concentration		
C	concentration of acid sites		
$C_{\mathrm{H^+}}$	concentration of actu sites		
$C_{\rm s}$	total appartmetion of paid sites		
C_t	hudrogen		
Π_2	nydrogen		
$\kappa_{\rm Cr}(m, u)$	rate coefficient for cracking of a carbonium ion of type m into a carbonium ion of type u with the formation of an olefin		
$k_{\mathrm{De}}(m;\mathbf{O}_{i,j})$	rate coefficient for deprotonation of a car- benium ion of type m, with formation of olefin O		
$k_{\mathrm{DH},i}$	lumped rate coefficient for dehydrogena- tion of lump of paraffins ' i '		
$k_{\mathrm{DH,P}_j}$	rate constant for the dehydrogenation reac- tion of lump of paraffins with 'j' number of carbon atoms		
$k_{\rm iso}(m, u)$	rate coefficient for isomerization between carbenium ions of types m and u		
$K_{\mathrm{DH},i}$	dehydrogenation equilibrium constant for lump of paraffins ' <i>i</i> '		
$K_{\mathrm{DH},\mathrm{P}_{j}}$	dehydrogenation equilibrium constant for the lump of paraffins whit 'j' number of carbon atoms		
K_{L_i}	Langmuir physisorption equilibrium con-		
K _{Pr/De,i}	equilibrium constant for protonation/ deprotonation with reference to related olefin <i>'i'</i>		
$k_{\rm Pr}(m)$	rate coefficient for protonation of an olefin to a carbenium ion of type m		
n _{es}	number of single events for reaction s		
O _{ref}	reference olefin		
p_i	partial pressure for hydrocarbon 'i'		
$r_{\rm Cr(L1)}$	rate of formation of carbenium ions of lump L1 through cracking reactions		
$r_{\mathrm{DH},i}$	net rate of dehydrogenation for paraffin lump ' <i>i</i> '		
$r_{isom(L1 \rightarrow L2)}$	net rate of isomerization of lump L1 to lump L2		
\mathbf{R}_{i}^{+}	carbenium ion with reference to related olefin ' <i>i</i> '		
r_{L1}	net rate of formation for lump L1 of ions		
r_{LO_i}	net rate of formation for lump 'i' of olefins		
$k_{\text{PCP}}(m, u)$	rate coefficient for PCP isomerization between carbenium ions of types m and u		
r_{P_i}	net rate of formation of lump of paraffins 'i'		
S	secondary type carbenium ion		
SELPH	single event-lumped parameter hybrid model		
t	tertiary type carbenium ion		
Subscripts			
H^+	acid site		
i	lump or species ' <i>i</i> '		

LO_i	lump 'i' of olefins
LP_i	lump 'i' of paraffins
O_i	olefin 'i'
P_i	paraffin ' <i>i</i> '
R_i^+	carbenium ion with reference to related olefin ' i '

More recently, in the decade of the 80s, Baltanas et al. [6] developed the now well-known single events methodology, which is based upon the carbenium ion underlying chemistry. Under this approach, the reaction rates of every elementary step involving carbenium ion intermediates can be taken into account on a molecular level. Since the olefins and ions intermediates are non measurable and in very small quantities compared to the saturated species, a classical assumption is made: hydrogenation/dehydrogenation and protonation/deprotonation are taken at thermodynamical equilibrium; in consequence the rate determining steps are the acid surface reactions [7].

According to the single event theory, if ideal hydrocracking is assumed, the concentration of every intermediate carbenium ion can be expressed in terms of the partial pressures of either the individual feed and product paraffins or lumps of paraffins [8–10]. Calculating the carbenium ion concentrations and substituting them in expressions for the formation of olefins, the concentrations of paraffins can be found by direct extrapolation, since quasi equilibrium for the (de)hydrogenation reactions is implied under ideal hydrocracking assumption.

Ideal hydrocracking behavior implies that hydrogenation is fast compared to the reactions on the acid sites whereby consecutive reactions, like secondary cracking play a subordinate role. Under these conditions, the product distribution is a unique function of conversion. Ideal hydrocracking conditions are enhanced when both hydrogenating and acid functions are in close proximity, which can be achieved by using adequate loadings of well dispersed noble metals [11].

A weak metal function used in the catalyst results in a hydrocracking far from the ideal behavior. In such case, the rate of hydrogenation is comparable or less than that of cracking, whereby the rate of desorption of alkenes will be low relative to β scission, thus resulting in multiple cracking events. As a result, higher iso:normal ratios will be observed in the products compared to the ideal case, since secondary isomerization is now possible [12].

Besides the composition of the catalyst, operating conditions could also be important in the hydrocracking behavior. As temperature increases and pressure decreases hydrocracking moves away from the ideal case, and the product distribution is no longer a unique function of conversion; the hydrocracking is no longer ideal. Furthermore, it has been found that this phenomenon becomes more important as the chain length grows longer [13].

Until now, the single event concept has been applied to the hydrocracking of model compounds as well as catalytic cracking of complex feedstocks, but in all these cases the approximation of an ideal behavior has been made [6,9,10,14–19]. In the present work, n-hexadecane hydroisomerization and hydrocracking was carried out over a dual function Mo/H\beta-alumina catalyst, which has a (de)hydrogenating function weaker than Pt metal. This condition moves the system away from ideal behavior as will be shown below. Hence, the assumption that the rate determining steps are those taking place on the acid sites is no longer valid, making necessary the introduction of kinetic equations for the (de)hydrogenation reactions. However, there is not currently an available model for the reactions on metal sites based on a fundamental approach, analogous to the single event concept applied for the acid catalyzed reactions, so traditional lumped rate constants were introduced for the reactions on the metal sites.

Thus, the resulting hybrid mathematical model called here SELPH model, includes fundamental rate coefficients for carbenium ion reactions and lumped rate constants for (de)hydrogenation reactions.

2. Kinetic modelling

2.1. Reaction network generation

Using a computer program the complete reaction network for the hidroconversion of *n*-hexadecane was generated. The reaction network comprises every single step generally accepted to occur in the reaction scheme for the hydroisomerization and hydrocracking of paraffins. According to the bi-functional mechanism proposed by Weisz [20], paraffins are dehydrogenated on the metal function to form alkenes, which after adsorption on the acid sites are transformed through a series of types A and B isomerization reactions. Smaller carbon atom chain lengths are obtained as a result of β scission reactions. The ions produced are deprotonated to form new olefins, which in turn are hydrogenated on the metal sites to form new paraffins. The program was coded following the algorithm developed by Baltanas et al. [6] in which, every single species is represented through a Boolean relation matrix, while reaction transformations are performed through a series of matrix operations.

The generated reaction network for the case of *n*-hexadecane as a single feed paraffin comprises the formation of 8170 species, from which 3711 are carbenium ions, 3984 are olefins and 475 are paraffins. The number of generated species was limited by allowing the computer program to form only those species with a maximum of three branches and not more than one atom per branching (only methyl groups were allowed to generate), in accordance with the product distribution observed experimentally.

Every single reaction step implies an associated rate constant which in turn must be estimated for simulation purposes. In view of the overwhelming number of rate constants comprised in the complete reaction network, it was necessary to implement a series of simplifying assumptions in order to obtain a tractable number of independent rate constants to be estimated.

2.2. Kinetics on the acid sites

Kinetics on the acid sites was modelled according to the single event concept, which has been described elsewhere [8]. According to this model, making a series of assumptions based on the current knowledge on the carbenium ion chemistry and introducing the transition state concept, it is possible to express the kinetic rate coefficient of each elementary step as a multiple of the single event rate coefficient and a factor called number of single events (n_e). This last being related to the global symmetry numbers of reactant and transition state of the elementary step. The single event rate coefficients thus obtained are dependent only on the types of carbenium ions (secondary or tertiary) involved in the reaction step.

However, the previous simplification still leaves an overwhelming number of independent rate constants to be estimated. In order to further reduce this number of rate constants, Baltanas et al. [6] implemented a series of thermodynamic constraints that allow reducing the number of independent fundamental rate constants to only 14 for the reaction steps taking place on the acid sites.

2.3. Relumping

After reaction network generation, a lumped reaction scheme was constructed starting from single events. Lumps were constructed according to the types of species (olefins or ions), number of carbon atoms and degree of branching. As relumping was made a posteriori, carbenium ion reaction rate constants maintain their fundamental character and independence of the species from which they were derived. The way the species were lumped is better visualized in a lumped reaction scheme, Scheme 1, in which (de)hydrogenation reactions have been included. In the scheme, n-, MB-, DB- and TB-denotes normal, mono-, di-, and tribranched species, respectively, while P, O and R⁺ stands for paraffin, olefin and ion species.

Cracking species are lumped in the same way; according to their number of carbon atoms and degree of branching, although this is not shown in the scheme. Contrary to previous publications [8,9], in which lumped rate coefficients are constructed for the reactions involving carbenium ions after relumping is made, in the present work independent expressions were kept for the concentration of each carbenium ion, written in terms of the concentration of the olefins and protonation and deprotonation fundamental rate coefficients, as it will be seen below.



Scheme 1. Lumped reaction scheme for paraffin hydrocracking.

2.4. Kinetics on the metal sites

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Rate equations for the (de)hydrogenation reactions were written in terms of lumps of olefins and paraffins. For these reactions, lumps were treated as pseudo compounds and traditional lumped rate constants were estimated. Integration of the lumps was done according to the number of carbon atoms and degree of branching.

2.5. Kinetic equations

The physisorption in the zeolite was described using a Langmuir isotherm, which is a simple enough model that has probed to fit satisfactorily to experimental data [21] having the advantage of introducing only a few parameters if compared to other models [22], matching the compromise between accuracy and simplicity.

$$C_{\mathbf{P}_i} = \frac{C_s K L_i p_i}{1 + \sum_i K L_i p_i} \tag{1}$$

Rates of (de)hydrogenation on the metal sites are described by Eq. (2). In which p_{LO_i} and p_{LP_i} refer to lumps of olefins and paraffins respectively while $k_{DH,i}$ is a lumped dehydrogenation rate constant.

$$r_{\mathrm{DH},i} = k_{\mathrm{DH},i} \left(p_{\mathrm{LP}_i} - \frac{p_{\mathrm{LO}_i} p_{\mathrm{H}_2}}{K_{\mathrm{DH},i}} \right)$$
(2)

Since reaction rates for protonation and deprotonation are so fast, these processes can be assumed to reach pseudo equilibrium [15].

 $O_i + H^+ \Leftrightarrow R_i^+$

Equilibrium constants for such processes can be expressed in terms of carbenium ion, olefin and acid sites concentrations but also in terms of protonation an deprotonation fundamental rate constants derived from the single event concept, as shown in Eq. (3).

$$K_{\text{Pr/De},i} = \frac{C_{\text{R}_{i}^{+}}}{C_{\text{O}_{i}}C_{\text{H}^{+}}} = \frac{k_{\text{Pr}}(m)}{k_{\text{De}}(m, \text{O}_{i,j})}$$
(3)

where m denotes the type (secundary or tertiary) of carbenium ion ivolved in the process. Since the active sites are either free or occupied by carbenium ions, the concentration of free active sites in Eq. (3) is accounted for through the following total balance for the acid sites:

$$C_{\rm t} = C_{\rm H^+} + \sum_i C_{\rm R_i^+} \tag{4}$$

where C_t is the total concentration of active acid sites. Isolating the carbenium ion concentration for the second equality in Eq. (3) and substituting the resulting expression in Eq. (4), the total acid sites balance can be written in terms of olefin an hydrogen concentrations and protonation and deprotonation fundamental rate coefficients as shown in Eq. (5).

$$C_{\rm t} = C_{\rm H^+} \left(1 + \sum_{j} \frac{k_{\rm Pr}(m)}{k_{\rm De}(m, {\rm O}_{i,j})} C_{{\rm O}_j} \right)$$
(5)

Now, substituting the free active sites from Eq. (5) in Eq. (3) and solving for the carbenium ion concentration, it is obtained an expression in terms of the olefin concentrations in which the unknown free acid sites concentration does not appear:

$$C_{\rm R_{i}} = \sum_{j} \frac{k_{\rm Pr}(m) C_{\rm O_{j}}(C_{\rm t}/1 + \sum_{k} (k_{\rm Pr}(m)/k_{\rm De}(m, {\rm O}_{k,j})) \cdot C_{\rm O_{k}})}{k_{\rm De}(m, {\rm O}_{i,j})}$$
(6)

the external sum comes from the fact that each carbenium ion can be formed starting from protonation of up to three different olefins. Once the equations for the individual carbenium ion concentrations were developed, we were able to write down expressions for the net rate of formation of lumps of ions.

If L1 and L2 would represent, for example, two lumps of carbenium ions with the same number of carbon atoms and one and two branches, respectively, then the rate equation for the isomerization of lump L1 to produce lump L2 would be the sum of all the elementary reaction rates of the carbenium ions belonging to lump L1 which through fundamental isomerization reactions produce carbenium ions belonging to lump L2. This can be expressed in terms of fundamental rate constants as follows:

$$r_{\text{isom}(\text{L1}\to\text{L2})} = \sum_{s} n_{\text{e}_{s}} k_{\text{iso}}(m, u) C_{\text{R}_{i}}$$
(7)

where n_{e_s} represents the number of single events in the elementary step *s*, while *m* and *u* correspond to the types of reactive and produced carbenium ions.

Eq. (8) on the other hand accounts for the formation and disappearance of carbenium ions of lump L1 through only cracking reactions. This expression is given as the algebraic

sum of all the fundamental cracking steps through which carbenium ions belonging to lump L1 are formed or consumed:

$$r_{\rm Cr(L1)} = \sum_{s} n_{\rm e_{s}} k_{\rm Cr}(m, u) C_{\rm R_{j}} - \sum_{l} n_{\rm e_{l}}' k_{\rm Cr}'(u, m) C_{\rm R_{i}}$$
(8)

to account for all reactions in which carbenium ions belonging to lump L1 are involved, Eqs. (7) and (8) combined in the following expression, said, the net rate of formation of carbenium ions of lump L1, in terms of the fundamental isomerization and cracking reaction steps.

$$r_{L1} = r_{Cr(L1)} - \sum_{i} (r_{isom(L1 \to Li)} - r_{isom(Li \to L1)})$$
 (9)

Since lumps of ions are interconnected by means of isomerization reactions (see Scheme 1), the contribution of the isomerization reactions is indicated by a sum in the second term of the right hand side of Eq. (9).

Now, the equation for the net rate of formation of lump '*i*' of olefins (LO_i) can be written in terms of Eq. (2) and the equation for the net rate of formation of lump '*i*' of carbenium ions (r_{L_i}) with the same skeletal structure as the olefins for which the expressions are to be developed, since pseudo equilibrium has been assumed for the protonation/ deprotonation reactions.

$$r_{\mathrm{LO}_i} = r_{\mathrm{DH},i} + r_{\mathrm{L}i} \tag{10}$$

The pseudo-steady state approximation, applied to the olefin intermediates, sets the net rate of formation of the olefins equal to zero:

$$r_{\mathrm{LO}_i} = 0 \tag{11}$$

substituting Eqs. (2) and (9) into Eq. (10) and setting it to zero, according to equality (11) gives the following equation.

$$0 = k_{\text{DH},i} \left(p_{\text{LP}_i} - \frac{p_{\text{LO}_i} p_{\text{H}_2}}{K_{\text{DH},i}} \right) + r_{\text{Cr}(\text{L1})} - \sum_i (r_{\text{isom}(\text{L1} \to \text{L}i)} - r_{\text{isom}(\text{L}i \to \text{L1})})$$
(12)

Expression (12) is a set of non linear equations, the solution of which are the concentrations of the different lumps of olefins. Once these concentrations are found, they are substituted into the expressions for the net rate or formation of the lumps of paraffins, which are calculated according to Eq. (2) as:

$$r_{\mathrm{P}_{i}} = -k_{\mathrm{DH},i} \left(p_{\mathrm{LP}_{i}} - \frac{p_{\mathrm{LO}_{i}} p_{\mathrm{H}_{2}}}{K_{\mathrm{DH},i}} \right)$$
(13)

3. Experimental

A bi-functional Mo/H β (20%)-alumina catalyst was prepared, using the protonated form of a commercial H β zeolite with a molar ratio SiO₂/Al₂O₃ of 75, then it was impregnated with Mo (6%) and P (1.5%) by pore volume impregnation using aqueous solutions of ammonium heptamolybdate and a HPO₃, respectively.

The reaction experiments were performed in a tubular reactor (30 cm length, 1 cm inner diameter), equipped with a thermocouple placed in the center. The catalyst particles were sized to 40–150 mesh (0.104–0.42 mm diameter) in order to eliminate diffusive effects. A feed consisting of H₂/n-hexadecane mixture with a molar ratio of 5 was used. The catalyst was sulfided in situ using a liquid feed of CS₂ (10,800 ppm S) in cyclohexane and under a hydrogen pressure of 700 lb/in.², at 573 K during 4 h. The reaction experiments were performed at a 700 lb/in² pressure and at a temperature interval ranging from 533 to 598 K. CS₂ was incorporated in the feed, to give a 150 ppm S. Liquid and gas reaction products were analyzed by chromatography. The identification of the products was achieved by GC–MS.

4. Results

Table 2

From the available experimental data, rate constants were estimated for only one temperature (533 K) and their units are given in 10^{-3} kmol/kg-h. Estimates for the fundamental rate constants, belonging to the reactions on the acid sites are listed in Table 1. Lumped rate constants, belonging to the reactions on the metal sites are shown in Table 2, in

 Table 1

 Estimates for the fundamental rate constants

Fundamental rate constant	Value at 533 K ^a		
$\overline{k_{\rm Pr}({\rm s})/k_{\rm De}({\rm s, O_{\rm ref}})}$	6.83245E9		
$k_{\rm Pr}(t)/k_{\rm De}(t, {\rm O}_{\rm ref})$	4.69254E10		
$k_{\rm PCP}(s, s)$	1.964554E6		
$k_{\rm PCP}({\rm s, t})$	1.49654E5		
$k_{\rm PCP}(t, t)$	2.014501E2		
$k_{\rm Cr}({\rm s, \ s})$	1.0243541E10		
$k_{\rm Cr}({\rm s, t})$	8.249635E9		
$k_{\rm Cr}(t, s)$	7.6201023E7		
$k_{\rm Cr}({\rm t},{\rm t})$	1.296546E7		

^a These values correspond to the single rate constant times $C_{\rm t}$.

raoie 2				
Lumped rate	e constants	for the	dehydrogenation	reactions

Lumped rate constant	Value at 533 K ^a	
k _{DH,P16}	1.265465E16	
k _{DH,P13}	5.16351E15	
k _{DH,P12}	5.53431E14	
k _{DH,P11}	3.151201E12	
$k_{\mathrm{DH,P_{10}}}$	6.131213E12	
k _{DH,P9}	1.206506E10	
k _{DH,P8}	2.01515E8	
k _{DH,P7}	1.064506E6	
$k_{\rm DH,P_6}$	6.13151E4	

^a Values divided by the corresponding dehydrogenation equilibrium constant $K_{\text{DH},P_{f}}$.



Fig. 1. Conversion toward isomerization versus total hexadecane conversion. Ideal (- -) and experimental (\diamondsuit) hydrocracking.

which $k_{\text{DH,P}_6}$, $k_{\text{DH,P}_7}$, etc., are rate constants for the dehydrogenation reactions of lumps of paraffins with 6, 7, etc. number of carbon atoms. The parameter given in Table 2 is the lumped rate constant divided by the dehydrogenation equilibrium constant for the same reaction step $(k_{\text{DH,P}_i}/K_{\text{DH,P}_i})$.

Fig. 1 shows the conversion toward isomerization against total conversion. The dotted curve was determined from experimental data taken from literature and corresponds to ideal hydrocracking behavior. From 0 to 30% total



Fig. 2. Calculated vs. experimental mono-branched -C₆ yield.



Fig. 3. Calculated vs. experimental mono-branched -C7 yield.

conversion, this curve is in close proximity to the straight line, indicating that most products are feed isomers. The lower curve corresponds to the experimental data of the present work. Similar curves have been reported by Debrabandere and Froment [13] and other authors to describe the influence of temperature, pressure, chain length and Pt % on the isomerization selectivity.

A comparison between experimental and calculated yields for some of the paraffin lumped products are shown in the parity plots of Figs. 2–6.



Fig. 4. Calculated vs. experimental mono-branched -C₈ yield.



Fig. 5. Calculated vs. experimental mono-branched -C₁₆ yield.



Fig. 6. Calculated vs. experimental di-branched -C₁₆ yield.

5. Discussion

As can be seen in Fig. 1, the data of the present work is considerably far from ideal hydrocracking behavior. This means that carbenium ion reaction rates are not rate determining, i.e. hydrocracking is non ideal. This behavior can be understood in terms of the weak (de)hydrogenating component used in the catalyst, as predicted by Debrabandere and Froment [13]. The chain length and the relatively high temperatures are also factors that could enhance such behavior.

Under these conditions, quasi-equilibrium for the (de)hydrogenation reactions cannot be assumed, and the general equations for the application of the single event method, derived in previous reported works cannot be used. To model the reactions on the metal sites a traditional lumped scheme was employed, since there is not currently an available single event approach for these reactions. Coupling both approaches results in the novel single event-lumped parameter hybrid (SELPH) model, which predicts the behavior of the system with high accuracy.

The use of lumped parameters in the model was necessary to allow the application of the single event concept to a system far from ideal hydrocracking conditions. However, since the lumped parameters are in nature strongly dependent on the feed composition, they could have introduced some bias into the fundamental single event fitted parameters, which are by definition independent of the species from which they were estimated. Analysis of the importance of this possible problem is out of the scope of the present work and will be the object of future work.

The mathematical SELPH model gives a good fit of the experimental data as demonstrated by the very good correspondence between observed and calculated yields, shown in the parity plots presented above.

6. Conclusions

Non-ideal hydrocracking behavior is not an exception in the processes encountered in the oil refining industry. Among the variables that enhance such non ideal behavior are low content of noble metal in the catalyst, high temperatures, low pressures, the presence of long chain paraffins and, as illustrated in this work, a weak (de)hydrogenating function.

The SELPH model presented here incorporates the single event concept for the reactions on the acid sites and lumped rate constants for the reactions on the metal sites. The combination of both approaches made possible the modeling of *n*-hexadecane hydroisomerization and hydrocracking over a catalyst with a weak dehydrogenating component, i.e. allowed the extrapolation of the single event concept to a system away from ideal hydrocracking behavior. Rate constants were estimated only for the isothermal case, where a surprisingly good fit of the model to the experimental data was obtained.

The SELPH model can thus be applied to systems with a weak hydrogenating function and presumably to systems with a low content on hydrogenating material, or those systems which, due to operating conditions, behave in a way different from ideal hydrocracking. In addition, the SELPH model could be applicable to study the influence of the catalyst acid/metal balance on the isomerization selectivity in the hydrocracking of paraffins.

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