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Alkylcarbenium ion concentrations in zeolite pores during octane hydrocracking on Pt/H-USY zeolite

Joris W. Thybaut[a], C.S. Laxmi Narasimhan[a], Guy B. Marin[a,]*, Joeri F.M. Denayer[b],
Gino V. Baron[b], Pierre A. Jacobs[c], and Johan A. Martens[c]

[a]*Laboratorium voor Petrochemische Techniek, Universiteit Gent, Krijgslaan 281 S-5, B-9000 Gent, Belgium*
[b]*Dienst Chemie Ingenieurstechniek, Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussel, Belgium*
[c]*Centrum voor Oppervlakchemie en Katalyse, Katholieke Universiteit Leuven, Kasteelpark Arenberg 23, B-3001 Heverlee, Belgium*

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Hydroconversion of octane over platinum loaded acid zeolites was simulated using a single-event microkinetic model. Significantly different values for the alkene standard protonation enthalpies, i.e., −59.2 and –94 kJ mol^{-1} for the charging of secondary and tertiary carbon atoms respectively, were obtained. This difference is in favor of a carbocationic nature of the reactive intermediates on the acid sites rather than surface alkoxides. The concentration of alkylcarbenium ions on a Pt/H-USY catalyst resulting from protonation of alkenes in *n*-octane hydrocracking was calculated. It was strongly dependent on pressure and temperature. At a reaction temperature of 506 K, a total pressure of 0.45 MPa and H_2/HC molar ratio of 13.13, the concentration of alkylcarbenium ions corresponds to 15% of the total acid site concentration. At higher total pressures this percentage is lower and can be assumed to be negligible. The presence of a finite alkylcarbenium ion concentration in the zeolite pores results in a reduction of the free space available for physisorption of alkanes. Refined kinetic models are obtained when including this effect. Depending on the nature of the zeolite, alkylcarbenium ion concentrations can be significantly different owing to differences in alkane physisorption and alkene protonation. Literature data were rationalized using the refined kinetic model.

KEY WORDS: hydrocracking; alkylcarbenium ion concentrations; alkylcarbenium ions; protonation enthalpy; single-event microkinetics; ultrastable Y zeolite.

Symbols

A	statistical parameter for model discrimination
AS	Alkyl-Shift
B	statistical parameter for model discrimination
b	model parameter vector containing the estimated parameter values
C	concentration [mol kg_{cat}^{-1}]
C_t	total concentration of acid sites [mol kg_{cat}^{-1}]
F	molar flow rate [mol s^{-1}]
H	Henry coefficient
ΔH^0	standard reaction enthalpy [J mol^{-1}]
HS	Hydride-Shift
j	Index
K_{deh}	equilibrium coefficient for dehydrogenation [MPa]
K_{isom} $(O_{i,j};O_r)$	equilibrium coefficient for isomerization between alkene j and the reference alkene
K_L	Langmuir physisorption coefficient [MPa^{-1}]
K_{prot} $(O_{i,j};\ m)$	equilibrium coefficient for protonation of alkene j with formation of a alkylcarbenium ion of type m [kg_{cat} mol^{-1}]
$K(m;\ n)$	rate coefficient of a reaction converting a alkylcarbenium ion of type m into another alkylcarbenium ion of type n [s^{-1}]
K	Index
m	alkylcarbenium ion type (secondary or tertiary)
n	alkylcarbenium ion type (secondary or tertiary)
ncar	number of alkylcarbenium ions
nob	number of observations
nole	number of alkenes
npar	number of parameters
nresp	number of responses
$O_{i,j}$	alkene j stemming from alkane i
P_i	alkane i
PCP	protonated cyclopropane
p	partial pressure [MPa]
$R_{i,k}^{+}$	alkylcarbenium ion k stemming from alkane i
$r(m;n)$	rate of a reaction converting a alkylcarbenium ion of type m into another alkylcarbenium ion of type n [mol (kg s)$^{-1}$]
SSQ	sum of squares
w	response weighing factor
X	Conversion

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* To whom correspondence should be addressed.
E-mail: Guy.Marin@UGent.be

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Greek symbols

α	probability of accepting a wrong model
β	β-scission
β	probability of accepting a wrong model
β	model parameter vector containing the real parameter values
σ	symmetry number

Superscript

$\hat{}$	model calculated value
$\sim$	single event
comp	composite

Subscript

$\neq$	transition state
0	inlet
act	activation
calc	calculated
cat	catalyst
cr	cracking
deh	dehydrogenation
i	component number
Iso	isomerization
P_i	corresponding to alkane i
phys	physisorption, physical
prot	protonation
sat	saturation
tot	total

1. Introduction

Hydrocracking is an important refinery conversion process [1,2]. It typically yields high quality fuels and lubricants with very low sulfur level and aromatics content. A bifunctional catalytic conversion scheme of hydrocarbons comprises metal and acid catalyzed elementary steps [3]. Saturated hydrocarbon reactants are dehydrogenated on the metal function. The unsaturated intermediates are then protonated on the acid function where they can undergo skeletal rearrangements such as isomerization and cracking. After deprotonation the unsaturated isomers and cracked product are hydrogenated on the metal sites yielding the observable saturated reaction products. These elementary chemical reaction steps occur on molecules that are physisorbed within the zeolite pores.

The relative potential reaction rates of the metal and acid catalyzed elementary steps significantly determine the observed product distributions in hydrocracking [4,5]. When the metal catalyzed elementary steps are potentially much faster than the acid catalyzed elementary steps and, hence, can be assumed to be quasi-equilibrated, so-called *ideal* hydrocracking occurs. The term *ideal* hydrocracking is used because a maximum of information can be obtained on the acid catalyzed elementary steps when the metal catalyzed elementary steps are quasi-equilibrated [4]. Also, maximum feed isomer yields are observed under *ideal* hydrocracking conditions. *Non-ideal* hydrocracking conditions, i.e., when the metal catalyzed steps are no longer quasi-equilibrated, are characterized by higher cracked product yields [5].

The nature and concentration of reactive intermediates on acid sites in zeolite catalyzed hydrocarbon conversions are matters of debate, particularly in hydrocracking. Traditionally, on the analogy from alkylcarbenium and alkylcarbonium ions in superacid solutions, reactive intermediates on the acid sites were assumed to be carbocations [6,7]. Tertiary alkylcarbenium ions are present in higher concentrations than secondary alkylcarbenium ions for reasons of stability. Though activation energies of reactions of tertiary alkylcarbenium are higher than for reactions departing from secondary alkylcarbenium ions [8] conversions of tertiary alkylcarbenium ions proceed at the highest rates because of differences in relative concentrations of the two types of ions [9,10]. Quantumchemical calculations on cluster models of zeolite fragments suggest that proton transfer to alkenes leads to surface alkoxides having a covalent bond between a carbon atom and an oxygen atom of the zeolite framework [11,12]. The involvement of alkoxides was postulated from kinetic studies as well [13–15]. Secondary and tertiary alkoxides have similar stabilities [11]. The activation energies calculated for reactions starting from tertiary alkoxides are lower than those for reactions starting from secondary alkoxides. Given the absence of a concentration difference between the two types of alkoxides, differences in activation energies results in higher reaction rates for reaction pathways *via* tertiary alkoxides. As a result the two views on reactive intermediates on the acid sites, i.e., alkylcarbenium ions versus alkoxides, lead to the same general conclusion that reaction pathways *via* activation of tertiary carbon atoms proceed at higher rates than reaction pathways *via* activation on secondary carbon atoms. In the most advanced theoretical studies, involving long-range and environmental effects inside zeolite crystals, chemisorbed alkoxy species appear to become as unstable as protonated hydrocarbons because of steric constraints which are neglected in cluster calculations [16,17]. Kinetic models of *n*-octane hydrocracking on Pt/H-USY indicated or assumed that the concentration of the reactive intermediates on the acid sites were either negligible [18–22], or not [23–27]. In this paper, we show that this apparent contradiction is due to differences in reaction conditions, differences in catalysts as well as differences in kinetic model conception. A key issue is the reduced capacity of the zeoliote micropores for alkane adsorption in situations with high concentration of reaction intermediates on the acid sites.

2. Procedures and model equations

2.1. Experiments

Pt/CBV-760, a H-USY zeolite (PQ-corporation) with an atomic framework Si to Al ratio of 60 [28,29] loaded with 0.5 wt% platinum by cation exchange with $Pt(NH_3)_4Cl_2$, followed by oxidation and reduction was used.

N-octane hydrocracking experiments were performed in a tubular flow reactor packed with catalyst pellets with a diameter between 0.25 and 0.5 mm in a temperature range from 506 to 563 K, a total pressure range of 0.45–1.5 MPa and a molar H_2 to hydrocarbon ratio range of 4.2–250. Under these conditions *ideal* hydrocracking occurs [4,5]. The space time was varied between 4 and 1400 $\mathrm{kg_{cat}\ s\ mol^{-1}}$. Conversions in the range from 1% to 95% were observed. No catalyst deactivation was observed. Reaction products were analyzed on-line using capillary GC.

In zeolite Y catalyst pellets, the most important mass transport resistance is located in the macropores [30]. It was assumed that the same holds true for the CBV-760 zeolite used in this work, given the similarity of pellet size and porosity [31]. The Weisz modulus for macropore diffusion for the Y-zeolite pellet is of the order of 10^{-3} [32].

The total conversion was calculated as

$$X_{\text{tot}} = \frac{F_{P_i,0} - F_{P_i}}{F_{P_i,0}}. \tag{1}$$

Under the experimental conditions used, cracking can be considered as an irreversible reaction [22] and, hence, the total conversion X_{tot} can amount to 100%.

2.2. Parameter estimation and reactor model

Parameter estimations were performed using a combination of a Rosenbrock [33] and a Marquardt [34-35] algorithm. The weighed sum of the squared differences between the observed and the calculated outlet flow rates of the isomerized and cracked alkanes was minimized by adjusting the model parameter vector $\boldsymbol{b}$, which is expected to approach the real parameter vector $\boldsymbol{\beta}$ when the optimum is reached,

$$SSQ = \sum_{k=1}^{\text{nob}} \sum_{j=1}^{\text{nresp}} w_{P_j} \left(F_{P_j,k} - \hat{F}_{P_j,k}\right)^2 \xrightarrow{b} \text{Min}. \tag{2}$$

The number of observations, nob, amounted to 52, the number of independent responses, nresp, to 21. The weighing factors w_{P_j} are the diagonal elements of the inverse of the covariance matrix of the experimental errors of the responses.

The tubular flow reactor with packed catalyst bed was modeled based on a pseudo homogeneous one-dimensional model. The reactor was assumed to be fully isothermal and without any pressure drop. The integration of the set of ordinary differential equations (ODE's) was performed with the LSODA-subroutine available at Netlib [35,37].

2.3. Kinetic equations and parameters

2.3.1. Rate equations derived assuming negligible alkylcarbenium ion concentrations on the acid sites

In the previous kinetic modeling of hydrocracking [21,22,38] the following rate equation has been used for alkyl shifts (AS), protonated cyclopropane branching reactions (PCP) and β-scissions (β):

$$r^{\text{AS/PCP/}\beta}\left(m_{i,k}; n_{q,r}\right) = \frac{\sigma_{R^+_{i,k}}}{\sigma_{\neq_{ikqr}}} \tilde{k}^{\text{AS/PCP/}\beta} C_{R^+_{i,k}} \tag{3}$$

with

$$C_{R^+_{i,k}} = \frac{C_t \frac{\sigma_{O_{i,j}}}{\sigma_{R^+_{i,k}}} \tilde{K}_{\text{prot}}(O_{\text{ref}}; m) \tilde{K}_{\text{iso}}\left(O_{i,j}; O_{\text{ref}}\right) K_{\text{deh}}\left(P_i; O_{i,j}\right) C_{\text{sat},P_i} K_{L,P_i} \frac{p_{P_i}}{p_{H_2}}}{1 + \sum_{j=1}^{\text{npar}} K_{L,P_j} p_{P_j}}. \tag{4}$$

A key assumption leading to this equation is the neglect of the alkylcarbenium ion concentrations on the acid sites, i.e., in the Langmuir expression for alkene protonation:

$$C_{R^+_{i,k}} = \frac{C_t K_{prot}(O_{i,j}; m) C_{O_{i,j}}}{1 + \sum_{i=1}^{\text{npar}} \sum_{j=1}^{\text{nole}_{P_i}} K_{\text{prot}}(O_{i,j}; m) C_{O_{i,j}}}. \tag{5}$$

the summation in the denominator, $\sum_{i=1}^{\text{npar}} \sum_{j=1}^{\text{nole}_{P_i}} K_{\text{prot}}(O_{i,j}; m) C_{O_{i,j}}$, is assumed to be negligible compared to unity. Alkene concentrations are even lower than alkylcarbenium ion concentrations and, hence, are neglected a fortiori [22]. A detailed derivation of this equation is given elsewhere [22,39]. The sole occurrence of alkanes in non-negligible amounts within the zeolite pores is reflected in the denominator of equation (4), where only a summation relating to alkanes is present.

Ten adjustable parameters are to be estimated, i.e., the composite activation energies for the ten different types of elementary steps involving skeletal rearrangement between secondary and tertiary intermediates [21,22,38]:

$$E_{\text{act}}^{\text{comp}} = E_{\text{act}} + \Delta H_{\text{prot}}. \tag{6}$$

The composite pre-exponential factors have been calculated following an earlier developed methodology [38]. Note that based on equation (4) the real activation energies and the standard protonation enthalpies cannot be estimated separately by regression of the experimental data.

2.3.2. *Rate equations accounting for alkylcarbenium ion concentrations on the acid sites*

When the alkylcarbenium ion concentrations are not neglected, the denominator of equation (4) expands with a summation over the alkylcarbenium ions and becomes:

$$1 + \sum_{j=1}^{\mathrm{npar}} K_{L,P_j} p_{P_j} + \sum_{i=1}^{\mathrm{npar}} \sum_{j=1}^{\mathrm{nole}_{P_i}} C_{\mathrm{sat}} K_{\mathrm{prot}}(O_{i,j}; m) K_{\mathrm{deh}}(P_i; O_{i,j}) K_{L,P_i} \frac{p_{P_i}}{p_{H_2}}. \quad (7)$$

Rate equation (4) with the denominator replaced by equation (7) corresponds to the original rate equations constructed by Steijns and Froment [18], Baltanas *et al.* [19,20] and Svoboda *et al.* [21]. The partial pressure dependence of equation (4) with the denominator replaced by equation (7) corresponds to that of the rate equations used by de Gauw *et al.* [24,25]. With the replacement of the denominator of equation (4) by equation (7) the protonation coefficient is introduced in the rate equation separately from the rate coefficient. Hence, using this rate equation the protonation enthalpies of alkenes leading to formation of secondary and tertiary alkylcarbenium ions can be estimated separately from the activation energies for the elementary steps. This leads to a number of 12 adjustable parameters, i.e., 10 real activation energies corresponding to the rate-determining skeletal rearrangements and two protonation enthalpies.

In the derivation of equation (7) for the denominator of the rate equation alkane physisorption and alkene protonation are assumed to occur independently. In reality it can be expected that the volume within the zeolite micropores occupied by the alkylcarbenium ions reduces the micropore volume available for alkane physisorption. Accounting for this effect leads to the following expression for the denominator of the rate equation:

$$1 + \sum_{i=1}^{\mathrm{npar}} K_{L,P_i} p_{P_i} + \sum_{i=1}^{\mathrm{npar}} \sum_{k=1}^{\mathrm{ncar}_{P_i}} \frac{C_t K_{\mathrm{prot}}(O_{i,j}; m_k) K_{\mathrm{deh}}(P_i; O_{i,j}) K_{L,P_i} \frac{p_{P_i}}{p_{H_2}}}{1 + \sum_{i=1}^{\mathrm{npar}} \sum_{k=1}^{\mathrm{ncar}_{P_i}} K_{\mathrm{prot}}(O_{i,j}; m_k) K_{\mathrm{deh}}(P_i; O_{i,j}) K_{L,P_i} \frac{p_{P_i}}{p_{H_2}} C_{\mathrm{empty}}}. \quad (8)$$

In this expression for the denominator the complexity of the term corresponding to the alkylcarbenium ion concentration has increased. It contains the concentration of the empty physisorption sites, C_{empty}, which can be calculated from a quadratic expression resulting from a balance over the species in the micropores. Using equation (4) with the denominator replaced by equation (8) in the parameter estimation based on *n*-octane hydrocracking data on Pt/CBV-760 leads to the same 12 adjustable parameters as when the denominator is replaced by equation (7).

3. Results and discussion

3.1. *Model assuming negligible alkylcarbenium ion concentrations on the acid sites*

The regression of the *n*-octane hydrocracking data on CBV-760 to the model in which the alkylcarbenium ion concentrations were neglected resulted in the values for the composite activation energies mentioned in table 1 [22]. The composite activation energies for reactions starting from tertiary alkylcarbenium ions are lower than for reactions starting from secondary alkylcarbenium ions. As a result, higher reaction rates for tertiary alkylcarbenium ion conversions compared to secondary ones are obtained. A comparison of model and experimental data (figure 1), illustrates the adequacy of this model.

Table 1

Composite activation energies ($\Delta H_{\mathrm{prot}} + E_{\mathrm{act}}$) estimated using the model neglecting the alkylcarbenium ion concentrations (equation 4)

	Alkylshift	PCP-branching (kJ mol^{-1})	β-scission
(s;s)	16.7 (±0.1)[a]	45.6 (±0.1)	79.2 (±0.6)
(s;t)	13.7 (±2.4)	38.8 (±5.5)	63.7 (±4.5)
(t;s)			55.1 (±0.6)
(t;t)	7.7 (±2.9)	31.5 (±2.3)	33.9 (±1.7)

[a] 95% confidence region.

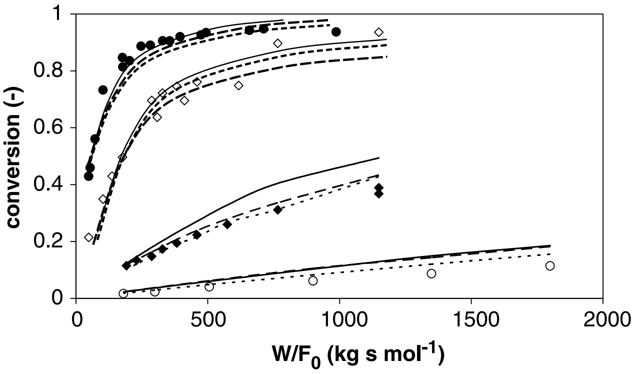

Figure 1. Experimental (symbols) and calculated (lines) *n*-octane conversion on Pt/CBV-760 as a function of space time (◆: 506 K – 0.45 MPa – H$_2$/HC = 13.13, ◇: 539 K – 0.45 MPa – H$_2$/HC = 13.13, ●: 563 K – 0.45 MPa – H$_2$/HC = 13.13, ○: 506 K – 0.7 MPa – H$_2$/HC = 250; full line: model neglecting alkylcarbenium ion concentrations; long dashed line: model accounting for alkylcarbenium ion concentrations without effect on alkane physisorption; short dashed line: model accounting for alkylcarbenium ion concentrations with effect on alkane physisorption).

3.2. *Model accounting for the alkylcarbenium ion concentrations on the acid sites*

3.2.1. *Independent occurrence of alkane physisorption and alkene protonation*

In the development of the rate equation discussed in this section, i.e., equation (4) with the denominator replaced by equation (7) it is assumed that the alkylcarbenium ions do not occupy micropore volume for alkane physisorption, which corresponds to previously developed rate equations [18–21]. A regression of the experimental *n*-octane hydrocracking data to this rate equation leads to the values for the activation energies

Table 2
Activation energies (E_{act}) and standard protonation enthalpies (ΔH_{prot}) estimated using the model accounting for the alkylcarbenium ion concentration with independent occurrence of alkane physisorption and alkene protonation (equation (4) with the denominator replaced by equation (7))

	Alkylshift (kJ mol^{-1})	PCP-branching	β-scission	Protonation
(s;s)	77.5 (±0.2)[a]	108.7 (±0.7)	142.7 (±1.0)	-64.9[b] (±0.5)
(s;t)	74.4[b] (±0.1)	98.6[c] (±1.9)	127.9 (±4.9)	
(t;s)			148.6 (±1.0)	-95.6[d] (±1.2)
(t;t)	104.5 (±1.2)	127.9 (±3.3)	125.1 (±3.8)	

[a] 95% confidence region, [b] protonation to secondary ions, [c] $E_{act}(t;s) = \Delta H_{prot}(s) + E_{act}(s;t) - \Delta H_{prot}(t)$, [d] protonation to tertiary ions.

and standard protonation enthalpies reported in table 2. The activation energies for reactions converting tertiary alkylcarbenium ions are significantly higher than the activation energies for the reactions departing from secondary alkylcarbenium ions. A similar situation was observed in liquid superacids by Brouwer for hydride-shifts [8,9]. The only exception is the activation for (t;t)-β-scission which has been reported to be a very fast reaction [10,21]. The standard protonation enthalpy for tertiary alkylcarbenium ion formation is more negative than that for secondary alkylcarbenium ion formation. This difference leads to lower composite activation energies and, hence, higher reaction rates for reactions departing from tertiary alkylcarbenium ions than for reactions of secondary alkylcarbenium ions. The difference in standard protonation enthalpies for secondary and tertiary alkylcarbenium ion formation amounts to 30.7 kJ mol^{-1} which is a little lower than the range of 40–50 kJ mol^{-1} reported by Brouwer [8,9]. The significant difference between the standard protonation enthalpies for secondary and tertiary alkylcarbenium ion formation can be considered as a confirmation of the cationic character of the reactive intermediates. If the reactive intermediates on the acid sites were alkoxides rather than alkylcarbenium ions, an identical value for the standard protonation enthalpies would be expected, independent of the secondary or tertiary nature of the intermediate [11,12].

From the comparison of model calculated and experimentally observed conversions (figure 1), it can be observed that the correspondence of the calculations using the model accounting for the alkylcarbenium ion concentration on the acid sites with the experimental data are somewhat better than the calculations using the model neglecting this concentration. In general somewhat lower conversions are obtained, which can be related to the presence of an extra term in the denominator of the rate expression. The superior behavior of the model accounting for the alkylcarbenium ion concentrations is somehow remarkable because more than once values for the protonation parameters not significantly different from zero have been obtained [18–21]. The total pressure effect on the alkylcarbenium ion concentrations is such that under the higher total pressures used in those works [18–21] the alkylcarbenium ion concentrations are clearly lower than under the total pressures applied in this work, cfr. infra. In addition, the reduction in the number of adjustable parameters by the calculation of the pre-exponential factors for the rate coefficients and the protonation equilibrium coefficients [38] contributes to the fact that the protonation enthalpies in the rate equation accounting for the alkylcarbenium ion concentrations on the acid sites can be estimated significantly in the present work.

3.2.2. *Interference of alkylcarbenium ions with alkane physisorption*

The difference of the model accounting for a reduced micropore volume availability for alkane physisorption with the previously discussed model is in the expression for the alkane physisorption. It can reasonably be assumed that the alkylcarbenium ions present in the zeolite micropores reduce the free micropore volume available for alkane physisorption. In the previously discussed model it was tacitly assumed that the presence of alkylcarbenium ions on the acid sites does not reduce the free micropore volume available for alkane physisorption. The reduced micropore volume by the presence of alkylcarbenium ions can be accounted for by substituting the denominator of rate equation equation (4) with equation (8). A regression of the experimental *n*-octane hydrocracking data on CBV-760 with this rate equation leads to the values for the activation energies and standard protonation enthalpies reported in table 3. These parameter values are very close to the values reported in table 2 not accounting for the reduced micropore volume by the physical presence of alkylcarbenium ions. The behavior of the two models, accounting for the reduce micropore volume by the physical presence of alkylcarbenium ions or not, is very similar (figure 1), although the model accounting for a reduced micropore volume availability for alkane physisorption presents a slight improvement. Note that in

Table 3
Activation energies (E_{act}) and standard protonation enthalpies (ΔH_{prot}) estimated using the model accounting for the alkylcarbenium ion concentration and the effect of a reduced micropore availability for alkane physisorption (equation (4) with the denominator replaced by equation (8))

	Alkylshift (kJ mol^{-1})	PCP-branching	β-scission	protonation
(s;s)	76.4 (±0.7)[a]	104.7 (±0.3)	139.8 (±0.7)	-59.2[b] (±0.3)
(s;t)	72.2[b] (±0.3)	95.6[c] (±0.3)	127.3 (±1.1)	
(t;s)			148.6 (±0.5)	-94.0[d] (±0.5)
(t;t)	101.5 (±0.3)	127.3 (±0.9)	128.6 (±0.9)	

[a] 95% confidence region, [b] protonation to secondary ions, [c] $E_{act}(t;s) = \Delta H_{prot}(s) + E_{act}(s;t) - \Delta H_{prot}(t)$, [d] protonation to tertiary ions.

this latter model the difference between the standard protonation enthalpies for secondary and tertiary carbenium ion formation amounts to 34.8 kJ mol^{-1}, which is closer to the range reported by Brouwer [8,9] than the difference obtained with the former model, i.e., the one not accounting for the reduced micropore volume.

When hydrocracking is performed under conditions leading to higher alkylcarbenium ion concentrations than observed in this kinetic modeling, i.e., low total pressures and intermediate temperatures, the alkylcarbenium ion concentrations are expected to have significant effects on the observed hydrocracking behavior and, hence, have to be accounted for in the model. Under such conditions, the model selection should be more critical.

4. Alkylcarbenium ion concentrations on acid sites

In figure 2 the actual alkylcarbenium ion concentrations relative to the total acid site concentration are shown. These relative concentrations were calculated using the model accounting for the reduced availability of micropore volume for alkane physisorption owing to alkylcarbenium ions, i.e., using equation (4) with the denominator replaced by equation (8). The relative alkylcarbenium ion concentration in *n*-octane hydrocracking at 0.45 MPa pressure and a temperature of 506 K, and H_2/octane ratio of 13.13 amounts to 15%. The relative alkylcarbenium ion concentration decreases rapidly with increasing total pressure to below 5% at 1 MPa. This is explained by the shifting of the (de)hydrogenation equilibrium disfavoring alkenes with increasing total pressure. The influence of temperature on relative alkylcarbenium ion concentrations arises from the involvement of exo- and endothermic steps in alkylcarbenium ion formation. Alkane physisorption and alkene protonation are exothermic steps, alkane dehydrogenation to yield the corresponding alkene and hydrogen is endothermic. At high total pressures and low temperatures, i.e., regions where adsorption saturation effects occur, the endothermic hydrogenation effect is the most important, resulting in an increase of the relative alkylcarbenium ion concentration with temperature. At low total pressures and high temperatures, i.e., regions where adsorption occurs in the Henry regime, the exothermic effects dominate. Under such conditions, increasing the temperature results in a decrease of the relative alkylcarbenium ion concentration. The high relative alkylcarbenium ion concentrations inferred by other groups [23–25] thus can be explained by differences in operating conditions, and especially total pressure, vide table 4. In addition, differences in physisorption and protonation behavior due to the different nature of the zeolite used also contribute to the differences in relative alkylcarbenium ion concentrations (figure 3). Parameter values needed in the calculations of these relative concentrations, i.e., physisorption and protonation parameters were taken from de Gauw *et al.* [24]. The highest relative alkylcarbenium ion concentrations are observed in zeolites exhibiting the strongest physisorption, i.e., mordenite and ZSM-5. Despite the small pores of ZSM-22, resulting in very exothermic physisorption, no extremely high alkylcarbenium ion concentrations are observed owing to significant entropy losses upon adsorption in such narrow zeolite channels. Alkylcarbenium ion concentrations on zeolite β are a little higher than on USY.

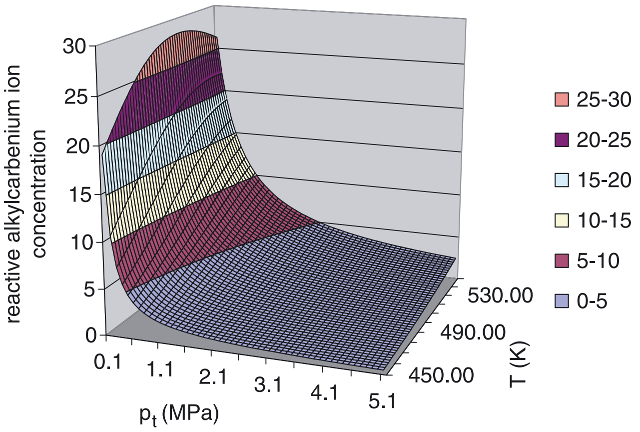

Figure 2. Alkylcarbenium ion concentration relative to the total acid site concentration calculated as a function of the total pressure and the temperature on Pt/USY using the model accounting for a reduced micropore volume available for alkane physisorption, i.e., equation (4) with the denominator replaced by equation (8).

Table 4
Zeolites, feed components, operating conditions and resulting carbenium ion concentrations in hydrocracking experiments

	Zeolite	Feed	T (K)	p_t (MPa)	H_2/HC	Carbenium ion concentration
This work	CBV-760 (USY)	C_8	506	0.45	13.13	Low
	Mordenite					High
de Gauw *et al.* [24]	Beta					Low – intermediate
	ZSM-5	C_6	513	0.1	14	High – intermediate
	ZSM-22					Intermediate

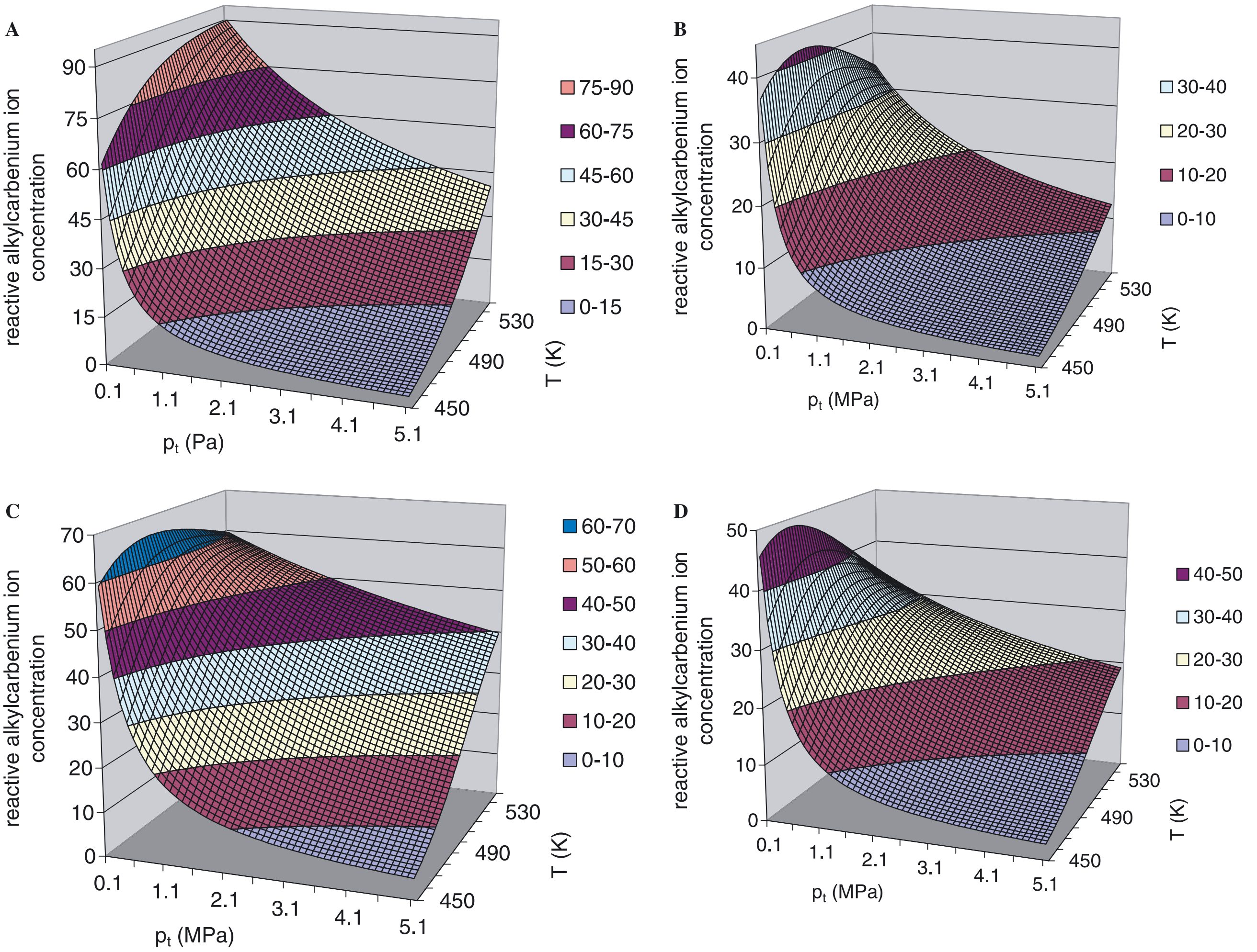

Figure 3. Alkylcarbenium ion concentrations relative to the total acid site concentration calculated as a function of the total pressure and the temperature on (a) Pt/Mordenite, (b) Pt/Beta, (c) Pt/ZSM-5 and (d) Pt/ZSM-22 using the model accounting for a reduced micropore volume available for alkane physisorption, i.e., equation (4) with the denominator replaced by equation (8).

5. Conclusions

The parameter values of microkinetic models for octane hydrocracking are consistent with an ionic character of the reactive intermediates on the acid sites. Reactions starting from tertiary alkylcarbenium ions have higher activation energies than reactions starting from secondary alkylcarbenium ions. Due to concentration effects the reactions starting from tertiary alkylcarbenium ions occur at higher rates than reactions starting from secondary alkylcarbenium ions. The alkylcarbenium ions present in the zeolite channels, reduce the micropore volume available for alkane physisorption.

Differences in alkylcarbenium ion concentrations on the acid sites relative to the total acid site concentration reported by various authors are a combined effect of differences in operating conditions and of the nature of the zeolite under investigation. The zeolite effect on the relative alkylcarbenium ion concentration is not only due to the zeolite protonation properties but also due to physisorption properties. Under laboratory conditions with pressures below 1 MPa, alkylcarbenium ion concentrations need to be accounted for in physisorption expressions. At high total pressures typical of industrial processes, alkylcarbenium ion concentrations on the acid sites become so low that these concentrations can be neglected in kinetic models.

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References

[1] J. Scherzer and A.J. Gruia, *Hydrocracking Science and Technology* (Marcel Dekker Inc., New York, 1996).

[2] I.E. Maxwell, J.K. Minderhoud, W.H.J. Stork and J.A.R. van Veen, in: *Handbook of Heterogeneous Catalysis*, eds. Knözinger, Ertl, and Weitkamp (Wiley – VCH 1997) ch. 3.13.
[3] P.B. Weisz, Adv. Catal. 13 (1962) 137.
[4] J. Weitkamp, Erdol Kohle Erdgas P. 31 (1978) 13.
[5] B. Debrabandere and G.F. Froment, Stud. Surf. Sci. Cat. 106 (1997) 379.
[6] H. Pines, *The Chemistry of Catalytic Hydrocarbon Conversions* (Academic Press, New York, 1981).
[7] B.W. Wojciechowski and A. Corma, *Catalytic Cracking, Catalysts, Chemistry and Kinetics* (Marcel Dekker, New York, Basel, 1986).
[8] D.M. Brouwer, Rec. Trav. Chim. 87 (1968) 210.
[9] D.M. Brouwer, in: *Chemistry and Chemical Engineering of Catalytic Processes*, NATO ASI Ser. E 39, eds. R. Prins and G.C.A. Schuit (Sijthoff and Noordhoff, Rockville, MD, 1980).
[10] J.A. Martens, P.A. Jacobs and J. Weitkamp, Appl. Catal. 20 (1986) 283.
[11] V.B. Kazansky, M.V. Frash and R.A. van Santen, Appl. Catal. A: Gen. 146 (1996) 225.
[12] A.M. Rigby, G.J. Kramer and R.A. van Santen, J. Catal. 170 (1997) 1.
[13] G.B. McVicker, G.M. Kramer and J.J. Ziemak, J. Catal. 83 (1983) 292.
[14] G.M. Kramer, G.B. McVicker and J.J. Ziemiak, J. Catal. 92 (1985) 355.
[15] M.A. Natal-Santiago, M. Alcala and J.A. Dumesic, J. Catal. 181 (1999) 124.
[16] X. Rozanska, R.A. van Santen, T. Demuth, F. Hutschka and J. Hafner, J. Phys. Chem. B 107 (2003) 1309.
[17] L.A. Clark, M. Sierka and J. Sauer, J. Am. Chem. Soc. 125 (2003) 2136.
[18] M. Steijns and G.F. Froment, Ind. Eng. Chem. Prod. Res. Dev. 20 (1981) 660.
[19] M.A. Baltanas, H. Vansina and G.F. Froment, Ind. Eng. Chem. Prod. Res. Dev. 22 (1983) 531.
[20] M.A. Baltanas, K.K. Van Raemdonck, G.F. Froment and S.R. Mohedas, Ind. Eng. Chem. Res. 28 (1989) 899.
[21] G.D. Svoboda, E. Vynckier, B. Debrabandere and G.F. Froment, Ind. Eng. Chem. Res. 34 (1995) 3793.
[22] J.W. Thybaut, G.B. Marin, G.V. Baron, P.A. Jacobs and J.A. Martens, J. Catal. 202 (2001) 324.
[23] A. van de Runstraat, J. van Grondelle and R.A. van Santen, Ind. Eng. Chem. Res. 36 (1997) 3116.
[24] F.J.M.M. de Gauw, J. van Grondelle and R.A. van Santen, J. Catal. 204 (2001) 53.
[25] F.J.M.M. de Gauw, J. van Grondelle and R.A. van Santen, J. Catal. 206 (2002) 295.
[26] J.A.Z. Pieterse, K. Seshan and J.A. Lercher, J. Catal. 195 (2000) 326.
[27] G.S. Nivarthy, A. Feller, K. Seshan and J.A. Lercher, Micropor. Mesopor. Mater. 35 (2000) 75.
[28] M.J. Remy, D. Stanica, G. Poncelet, E.J.P. Feijen, P.J. Grobet, J.A. Martens and P.A. Jacobs, J. Phys. Chem. 100 (1996) 12440.
[29] F. Collignon, M. Mariani, S. Moreno, M. Remy and G. Poncelet, J. Catal. 166 (1997) 53.
[30] J.F.M. Denayer and G.V. Baron, Adsorption 3 (1997) 1.
[31] J.F. Denayer, G.V. Baron, G. Vanbutsele, P.A. Jacobs and J.A. Martens, J. Catal. 190 (2000) 469.
[32] J.F. Denayer, G.V. Baron, W. Souverijns, J.A. Martens and P.A. Jacobs, Ind. Eng. Chem. Res. 36 (1997) 3242.
[33] H.H. Rosenbrock, Comput. J. 3 (1960) 175.
[34] D.W. Marquardt, Ind. Appl. Math. 11 (1963) 431.
[35] Netlib, http://www.netlib.org.
[36] P.T. Boggs, R.H. Byrd, J.E. Rogers and R.B. Schnabel, NISTIR 92 (1992) 4834.
[37] L.R. Petzold, Siam. J. Sci. Stat. Comput. 4 (1983) 136.
[38] G.G. Martens, G.B. Marin, J.A. Martens, P.A. Jacobs and G.V. Baron, J. Catal. 195 (2000) 253.
[39] J.W. Thybaut and G.B. Marin, Chem. Eng. Technol. 26 (2003) 509.