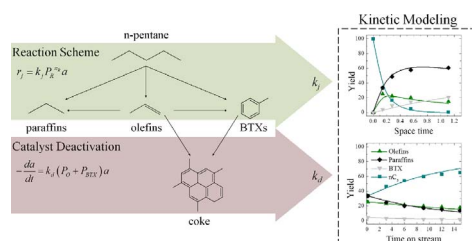# Simultaneous modeling of the kinetics for n-pentane cracking and the deactivation of a HZSM-5 based catalyst

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GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

A kinetic model for the catalytic cracking of n-pentane over a HZSM-5 zeolite (Si/Al = 15) based catalyst has been proposed. In this model, the kinetic scheme of reactions is based on the paraffin cracking mechanisms and uses lumps (light olefins, light paraffins, C_{5+} paraffins, aromatics and methane). The reaction steps of the scheme are related with the catalytic cracking routes: protolytic cracking, β-scission, oligomerization-cracking, hydride transfer, olefin condensation and methane formation. In addition, a kinetic deactivation equation has been used for modeling the catalyst deactivation, depending on the coke precursors (light olefins and aromatics) concentration. The catalyst has been prepared by agglomerating the HZSM-5 zeolite with a mesoporous matrix of weak acidity, using pseudoboehmite as a binder. The kinetic runs have been carried out in a fixed bed reactor using the following conditions: 350–550 °C, 1.4 bar, space time up to 1.1 g_{cat} h^{-1} mol$_C$$^{-1}$ and time on stream up to 15 h. The formation of olefins and aromatics, as well as the catalyst deactivation, are favored at high temperatures. A mathematical methodology based on the Levenberg-Marquardt algorithm has been used for the kinetic parameters estimation. The method has allowed for the simultaneous computing of the kinetic parameters of each step of the reaction scheme and the deactivation kinetics, from the experimental results of evolution with the time on stream of each lump concentration.

1. Introduction

The industrial processes involving acid catalytic conversion aim to obtain fuels (gasoline or diesel) or petrochemical raw materials (light olefins or benzene, toluene and xylene aromatics) from less interesting, heavy or waste feeds. Examples of those processes are the fluid catalytic cracking (FCC) unit or the conversion of methanol to olefins (MTO) unit. In these processes, low added value normal paraffins with 5–11

carbons are also obtained as by-products, normally through hydrogen transfer reactions catalyzed by the acid sites. Paraffins have a relatively low octane number [1] and low commercial interests, so they need to be separated, upgraded or recirculated to the acid catalytic conversion units [2,3]. Thus, the valorization of this paraffin fraction is an encouraging challenge in order to enhance the efficiency of these processes and intensify the oil and organic waste valorization [4,5].

Catalytic cracking is one of the most studied alternatives for low

Nomenclature

Abbreviations

$\mathbf{A}$	C balance coefficient matrix
a	activity parameter
$\mathbf{a_k}$	vector of each k activity
d	deactivation order
D_e	effective dispersion coefficient, $m^2\,h^{-1}$
E	activation energy, $kJ\,mol^{-1}$
$\mathbf{E}$	activation energy vector, $kJ\,mol^{-1}$
$\mathbf{E_j}, \mathbf{E_d}$	activation energy vectors of each j step of the reaction scheme and of deactivation equation, respectively, $kJ\,mol^{-1}$
F	Fisher distribution
F_C	carbon molar flow rate in the reactor, $mol_C\,h^{-1}$
F_i	carbon molar flow rate of each i lump at the outlet of the reactor, $mol_C\,h^{-1}$
F_{nC_5}	carbon molar flow rate of n-pentane at the outlet of the reactor, $mol_C\,h^{-1}$
$\mathbf{J}$	Jacobian matrix of the objective function
$\mathbf{J_o}, \mathbf{J_d}$	Jacobian matrices of zero time on stream and deactivation terms of the objective function, respectively
k	number of activities of the kinetic model
$\mathbf{k}, \mathbf{k}^*$	kinetic constants vector (includes the kinetic constant of each j reaction step and deactivation kinetic constants) and the corresponding vector at the reference temperature, respectively
k_d, k_d^*	deactivation kinetic constant and the corresponding value at the reference temperature, respectively, $atm^{-1}\,h^{-1}$
$\mathbf{k_d}, \mathbf{k_d}^*$	deactivation kinetic constants vector and the corresponding vector at the reference temperature, respectively, $atm^{-1}\,h^{-1}$
k_j, k_j^*	kinetic constant of each j reaction step and the corresponding value at the reference temperature, respectively
$\mathbf{k_j}, \mathbf{k_j}^*$	kinetic constants vector of the steps of the reaction scheme and the corresponding vector at the reference temperature, respectively
l	reactor bed length, m
LM	Levenberg-Marquardt
N_C	(carbon molar flow rate)/(total molar flow rate) ratio, $mol_C\,mol^{-1}$
$n_{e,o}, n_{e,d}$	number of experiments at zero and at t time on stream, respectively
n_l, n_p	number of lumps and parameters of the model, respectively
n_R	reaction order
$\mathbf{OF}$	objective function vector
P	total pressure, atm

P_R, P_{cp}	partial pressures of reactant and coke precursors, respectively, atm
$\mathbf{r}$	vector containing the reaction rates of each j reaction step and the deactivation rates
$\mathbf{r_d}$	deactivation rates vector, h^{-1}
$\mathbf{r_i}$,	formation rates vector of each i lump, $mol_C\,g_{cat}^{-1}\,h^{-1}$
$\mathbf{r_j}, \mathbf{r_{j,0}}$	reaction rates vectors of each j reaction step at t and zero time on stream, respectively, $mol_C\,g_{cat}^{-1}\,h^{-1}$
$\mathbf{r_L}$	vector containing the reaction rates of each i lump and the deactivation rates
R	universal gas constant
R_n	number of repetitions of each n experimental condition
s^2	variance of the lack of fit
S	reactor section, m^2
$S_{BET}, S_{mesopore}$	BET and external specific surface area, respectively, $m^2\,g^{-1}$
SSE	sum of the square errors
t	time, h
T, T^*	temperature and reference temperature, respectively, $^\circ C$
$\mathbf{u}$	dependent variables vector
$V_{mesopore}, V_{micropore}$	mesopore and micropore volume, respectively, $cm^3\,g^{-1}$
X	conversion expressed in C units
Y_i	yield of each i lump expressed in C units
y_i	molar fraction of each i lump expressed in C units
$\mathbf{y_i}$	molar fractions vector of each i lump expressed in C units
$y_{i,n}{}^{o}, y_{i,n}{}^{t}$	calculated molar fraction of i lump at n experimental condition at zero and at t time on stream, respectively, expressed in C units
$y_{i,n}{}^{o*}, y_{i,n}{}^{t*}$	experimental molar fraction of i lump at n experimental condition at zero and at t time on stream, respectively, expressed in C units
$\mathbf{y_{i,0}}, \mathbf{y_{i,in}}$	molar fractions vectors of each i lump at zero time on stream and at the inlet of the reactor, respectively, expressed in C units
W	catalyst weight

Greek symbols

α	confidence level
ε_b	effective bed-particle porosity
ν	degrees of freedom of the model
ρ_b	reactor bed density, $g_{cat}\,m^{-3}$
ω_i	weight factor for each i lump

Abbreviations of lumps and compounds

BTX, C_{5+}, O and P	aromatics (Benzene, Toluene, Xylenes), long chain paraffins, C_{2-4} olefins and C_{2-4} paraffins, respectively

quality naphtha (blend of C_{5-11} paraffins) upgrading, and it is frequently studied using normal alkanes as model molecules with the main goal of olefin production [5–11]. An advantage of the catalytic cracking regarding alternative routes for producing olefins (such as the production of ethylene through steam cracking) is the possibility of avoiding the energy requirement (and the CO_2 emissions) by co-feeding methanol. The coupled methanol and hydrocarbon cracking (CMHC) is a proposed route for obtaining olefins in which a thermoneutral reaction is reached [12–14]. Higher olefin yields and an attenuation of the catalyst deactivation are also reported as advantages of co-feeding, and are attributed to synergies in the cracking mechanism of hydrocarbons and oxygenated compounds [15–17].

Both n-paraffins cracking and CMHC require a catalyst with high Brønsted acid sites density [9–11] and high temperatures [7,8] for

protonating and cracking the alkanes. The catalytic cracking mechanism is well-established in the literature and three main routes are widely accepted [18]: (i) classical or bimolecular cracking, in which a carbenium ion abstracts a hydride from an alkane, forming other carbenium ion. An olefin and a smaller carbenium ion are yielded through β-scission; (ii) protolytic or monomolecular cracking, in which paraffin is protonated, forming a pentacoordinated carbonium that decomposes into a lighter paraffin and a carbenium ion. Olefins are yielded through the desorption of this ion, which gives back protons to the catalyst; (iii) oligomerization-cracking mechanism, which explains the formation of long chain paraffins by the carbenium chain growth.

HZSM-5 zeolite is an appropriate catalyst in order to activate the monomolecular pathway of paraffin cracking and selectively produce olefins [6]. This zeolite presents high capability of adsorbing and