Unsteady-state kinetic simulation of naphtha reforming and coke combustion processes in the fixed and moving catalyst beds

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ABSTRACT

The work is dedicated to the construction of kinetics models for the naphtha reforming process and the adjacent process of catalyst regeneration by coke combustion. The proposed kinetic model for the reforming process is based on the use of common rate equations for the groups of similar reactions with account of difference in reaction rates for individual homologs within these groups by simple correlations with thermodynamic properties (first of all – with the values of Gibbs free energy) of individual reactions and by other simplification methods. Such approach gives the way to construct the kinetics models optimal from the point of view of compromise between accuracy and simplicity. The proposed naphtha reforming model is characterized with the high level of kinetic scheme detailization (62 individual and group reactants and 146 individual reactions), at the same it is rather simple and provides the accurate description of the experimental data using only 22 kinetic parameters. This model is thermodynamically consistent and provides accurate description of experimental data in a wide range of process parameters. Account of catalyst deactivation by coke deposition in the model gives the way to simulate transient reforming process performance both in fixed and moving catalyst beds. Kinetics of coke combustion for catalysts with moderate coke content (up to 3% mass) may described by simple kinetic equation with apparent reaction rate orders closed to unit for relative coke content and to 1/2 for oxygen. Demonstration simulations of naphtha reforming and coke combustion processes are presented.

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1. Introduction

The process of naphtha reforming under controlled coking of the catalyst in the moving catalyst bed is an efficient technology for production of high-octane gasoline. The process of the coked catalyst regeneration is an important part of this technology.

Both these processes are complicated from the chemical and engineering point of view and the efficient procedure of their development and optimization must actively involve the mathematical simulation tools. In general, the mathematical models for both processes are rather evident, so the key feature, defining the success of such development is a proper kinetic model, which must be accurate enough to provide adequate description of reaction rates and, at the same time, simple enough to be applicable in engineering purposes.

A lot of research was done earlier in the area of kinetics of reforming reactions as well as kinetics of coke combustion. Nevertheless, the existing kinetic models are still far from ideal, especially in terms of optimal combination of efficiency and simplicity,

therefore, the development of new models is quite an important task from both scientific and practical point of view.

This work was dedicated to construction of the transient kinetic models for naphtha reforming and coke combustion reactions applicable for further mathematical simulation of the steady-state and transient operation regimes of naphtha reforming and catalyst regeneration processes in the moving and fixed beds of catalyst. The methodology included the performance of kinetic experiments in a wide range of process parameters, construction of the reasonable kinetic models, determination of kinetic parameters and test simulation of the naphtha reforming and coke combustion processes.

2. Experiments

2.1. Investigation of the reforming reaction

Kinetic experiments for naphtha reforming reactions were performed at the laboratory plug flow reactor loaded with the Pt-containing domestic catalyst PR-71 [1].

The scheme of the laboratory setup is presented in Fig. 1. This installation included the system of the preparation of the inlet reaction mixture, reactor with temperature control, separation block and control system. Analysis of reactants was performed by means of chromatography.

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Nomenclature

C_{cat}, C_{coke} heat capacity of the catalyst and coke respectively (kJ/kg/K)

C_p heat capacity of the reaction mixture (kJ/st.m^3/K)

c_i molar concentration of i-th component in the reaction mixture (dimensionless = molar fraction)

E_a activation energy (kJ/mol)

F total standard volume flux of the reaction mixture (st.m^3 of the reaction mixture per m^3 of the catalyst bed per second)

f_i standard volume flux of the i-th substance (st.m^3 of the i-th substance per m^3 of the catalyst bed per second)

ΔG_j changing of the Gibbs free energy for j-th reaction (kJ/mol)

H catalyst bed height (m)

h coordinate along the catalyst bed height (m), $h = 0$ corresponds to the upper bed level

k_0 pre-exponent of the reaction rate constant (s^{-1})

K_{Pj} equilibrium constant for j-th reaction (bar^n)

ΔM_i и ΔM_{max} current and maximum loss of the catalyst sample after incineration (in % from initial catalyst sample mass)

N_C the number of individual substances and group components considered in the kinetic model

N_R the number of reaction considered in the model

N_{exp} number of experiments in the reforming kinetics studies

n_c number of carbon atoms in the hydrocarbon molecule

P total pressure (bar)

P_i partial pressure of i-th component (bar)

q reaction heat effect (kJ/mol)

R catalyst bed radius (m)

r coordinate along the catalyst bed radius (m)

R_g universal gas constant (kJ/mol/K)

T temperature (K)

t time (s),

Δt time interval between experimental points in the coke combustion experiments (s)

u linear velocity of the reaction mixture in the reactor (m/s)

W_i reaction rate for i-th component (s^{-1})

w_j rate of j-the reaction ($j = 1 \div N_R$)

x,y coke combustion reaction orders in respect to oxygen and coke

β kinetic correlation factor

χ function, describing the dependence of the reaction rate upon the relative coke content

γ heat capacity of the catalyst (kJ/m^3/K)

ϑ velocity of the vertical catalyst movement in the bed (m/s)

ν_{ij} stoichiometric coefficient for i-th substance in j-th reaction

θ relative coke loading of the catalyst (dimensionless)

τ residence time in the lab kinetic experiments (s)

ρ solid phase density (kg/m^3)

ρ_{st} gas phase density at standard conditions (kg/st.m^3)

Indexes

AR   aromatic hydrocarbons

calc   calculated values

exp   experimental values

i index of the reaction mixture component ($i = 1 \div N_C$)

IP i-paraffins

in   reactor inlet

n index of experimental points in coke combustion experiments

NA5   alkylcyclopentanes

NA6   alkylcyclohexanes

NP n-paraffins

out   reactor outlet

ox   coke oxidation reaction

z index of experimental point number in reforming kinetics studies

Experiments were performed in the isothermal stainless steel reactor. Before the charging into the reactor the catalyst pellets were milled and the fraction 0.63–1.25 mm was separated by sieving. Such size of the catalyst particles provides absence of the diffusion limitations in the reforming reactions. The catalyst in the reactor was diluted with quartz particles (1.5–2.5 mm), preliminary calcined at 500 °C. It was necessary to achieve the reaction zone isothermicity along the reactor length, as well as to provide clear attribution of the reactor to the plug flow type.

Experiments included variation of the feedstock composition and flowrate (1.5–2.5 h^{-1}), reaction temperature (450–490 °C) and pressure (3.5–10 bars), HCG recirculation ratio (500–2000 m^3 per 1 m^3 of liquid feed per hour). Special experiment was made to study the dynamic catalyst coking.

2.2. Coke combustion studies

Coke combustion experiments were performed at the thermogravimetric lab setup, where coke oxidation velocity was measured under programmed temperature rise. Experiments were performed at differential scanning calorimeter Netzsch STA-449C. Experimental program included variation of heating rate (2.5/20 °C/min) and oxygen concentration (from 1 to 20 vol.%).

The catalyst samples were prepared by direct coke deposition in the conditions of reforming reaction under different operation pressures (0.35, 0.7 and 1.0 MPa) with variation initial coke content from 2.3% mass (at 0.35 MPa) up to 3.1% mass (at 1.0 MPa).

It was found, that active coke combustion starts at temperatures of ∼300 °C, with maximum oxidation rates, according to peaks at the DTG curves, in the region of 500–550 °C. Further temperature rise results in a much slower velocity of the sample mass loss, in our opinion, due to completion of coke combustion. The loss of samples mass in the temperature range above 600 °C may be explained by dehydroxylation and other transformations of the catalyst alumina support. This thesis is confirmed by the fact, that overall loss of the catalyst mass after such thermal treatment is significantly (at least, twice) higher than the initial coke content of this catalyst.

Therefore, the temperature range from ∼300 to ∼600 °C was further considered as the most informative region for investigation of the coke combustion kinetics.

3. Kinetic models

3.1. Kinetics of the reforming process

3.1.1. Methodology

The reactor with the long catalyst bed and relatively high fluid velocities was applied in the experiments, thus enabling the use of the plug flow reactor approximation:

$$W_i = \frac{\partial f_i}{\partial \tau} \tag{1}$$