Catalyst activity decay due to pore blockage during catalytic cracking of hydrocarbons

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HIGHLIGHTS

▶ We set an activity decay model based on catalyst structural properties.
▶ We develop catalytic runs with a model compound in a CREC Riser Simulator.
▶ We measure cumulative pore volume and pore size distribution.
▶ We correlated changes in catalyst structural properties with coke formed.
▶ We establish catalyst activity decay as a function of micropore volume changes.

GRAPHICAL ABSTRACT

Coke deposits on catalyst's surfaces, provoking loss of accessibility of reactants to active sites inside the catalytic particle; this is function of coke deposited.
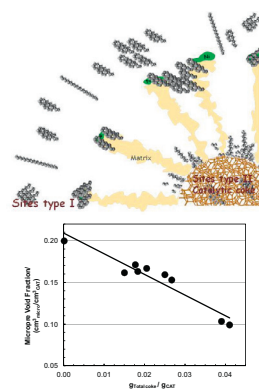
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ABSTRACT

Catalytic cracking reactions exhibit complex pathways because of the simultaneous reactions and transport phenomena taking place. In Fluidized-bed Catalytic Cracking (FCC), fast reactions take place concurrently with mass transport at the gas–solid interphases and inside the catalyst particles. In addition, the phenomenon known as "deactivation" is involved, with this leading to a selective decrease of reaction rates. Deactivation is associated to coke formation on the catalyst's external and internal surfaces. Since coke deposition blocks chemical species accessibility to catalyst active sites, located inside micropores, both fast primary reactions and slow secondary reactions are affected. This behaviour can be evaluated using the Thiele's modulus for each reaction involved. The Thiele's modulus is a function of the chemical species effective diffusivity and intrinsic kinetic parameters. This work reports the experimental evaluation of specific surface area and cumulative pore volume distribution of a commercial equilibrium catalyst, prior and after catalytic cracking of 1,3,5-tri-iso-prophyl benzene (TIPB). Observed changes in TIPB conversion and cracked product distribution are correlated with coke deposition. It is found that catalyst activity decay is strongly related to the accessibility of hydrocarbon species to the catalyst inner micropore network; therefore an activity decay model is postulated based on micropore volume fraction changes, this approach allows explaining the reduction of cracking reaction rates. The methodology described can be extended to the cracking of other hydrocarbon molecules on FCC catalysts.

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Nomenclature

a	catalyst activity, dimensionless
a_0	initial catalyst activity, dimensionless
A_{Arom}	area corresponding to products with aromatic ring, arbitrary
$A_{GasProd}^{Total}$	total chromatography area of products, arbitrary
Bi_m^i	number of Biot-modified of the i-th reactant, dimensionless
C	concentration of the i-th reactant, k mole/m³
C/O	catalyst to oil ratio, dimensionless
D	molecular diffusivity coefficient, m²/s
D_{eff}	effective diffusivity coefficient, m²/s
d_p	pore diameter, Å
k	first order reaction rate constant, s⁻¹
k_g	mass transfer coefficient, m/s
M	molecular weigth, Daltons
N_{Arom}	amount of products with aromatic ring, mole
N	amount of product, mole
r_{obs}	observable reaction, m³/mol∗s
T_k	temperature of the j-th reaction experiment,°C
$W_{coke}^{E-Cat-ini}$	weight of coke on the catalyst before reaction, g

W_{coke}^{Rxn}	weight of coke formed by reaction, g
W_{coke}^{Total}	total weight of coke on the catalyst after reaction, g
$W_{GasProd}$	weight of gas products, g
W_{TIPB}^{ini}	weight of injected feedstock, g

Greek letters

T	tortuosity factor, dimensionless
ε	volumetric void fraction of the catalyst, $m_{pore}^3/m_{particle}^3$
η_G	global effectiveness factor for spherical particles, dimensionless
ϕ	thiele modulus of the j-th reaction, dimensionless
χ_{TIPB}	conversion of TIPB, wt.%

Subscripts and superscripts

E-Cat	equilibrium catalyst conditions
i	related to the i-th reactant
j	related to the j-th reaction
p	relative to the catalyst micropores

1. Introduction

1.1. Industrial process

Catalytic cracking in fluidized beds (FCC) is one of the most important processes in petroleum refining. The manufacturing of gasoline range fuels is based on the breaking of carbon–carbon bonds using *Y-type* zeolite crystallites (micropores with diameters ranging from 0.3 nm to 1.4 nm). These 0.5–1 µm zeolite crystallites are supported on γ-alumina mesopores with diameters ranging from 1.4 nm to 234 nm. The average size of these microspherical FCC catalytic particles is in the range of 55 µm to 70 µm. Together with cracking reactions, there is coke deposition on external and internal catalyst surfaces leading to the decay of reactions rates, called "deactivation" [e.g. 1].

At the industrial scale [2,3], catalytic cracking of hydrocarbons (C_{30}s–C_{60}s, with a boiling point ranging from 280 °C to 545 °C, coming from blends of gas oils and residua, called feedstock), is performed in riser reactors. In FCC units, these VGOs (vacuum gasoil) are injected at the lower section of the riser reactor. A liquid feedstock at about 200 °C is mixed with a hot catalyst, called the "equilibrium catalyst" or "E-Cat", coming from the regenerator at about 700 °C.

After contacting the hot catalyst, the feedstock evaporates instantaneously, and the hydrocarbons–solid blend reaches about 580 °C. Following this, vapour molecules transport the catalyst upwards in the riser; and simultaneously the cracking of hydrocarbons takes place. The blend of catalyst and reactants/products continues upwards until it reaches the riser exit, where catalyst particles and hydrocarbon vapours are separated in a cyclone followed by stripping with steam (Fig. 1). The average residence time of the catalyst inside the riser is between 3 s and 5 s. Catalyst and hydrocarbon products leave the riser cracker at about 520–545 °C; this final riser temperature is a function of the kind of VGO being processed and the desired FCC products.

Typical FCC products include: (a) light cycle oil which is hydrotreated downstream the FCC unit to produce diesel and jet oil; b.p. > 221 °C, (b) gasoline (C_5s–C_{12}s; 38.5 °C < b.p. < 221 °C) and (c) liquefied petroleum gas (C_3s–C_4s).

In addition, some by-products are produced, such as: (a) dry gas (H_2 + CH_4 + C_2s) which is burned to generate thermal energy in the refinery, (b) sour gas containing H_2S which is sent to the Claus–sulphur recovery processes, (c) heavy cycle oil which contributes to the unconverted feedstock and (d) coke which remains adsorbed on the catalyst with this being true even after the catalyst is stripped with mid-pressure steam to desorb products. Since a decrease of reaction rates is observed after this coke deposition, it has been established that it "deactivates" the catalyst [e.g. 1].

Coke is burned in the presence of air in the regenerator reactor. In this manner, coke is used as a fuel to heat the catalyst particles coming from the riser unit; catalyst particles are heated in this manner up to 680–700 °C. Hot catalyst particles are sent back to the riser inlet, preserving the energy self sufficiency of the FCC unit [e.g. 3].
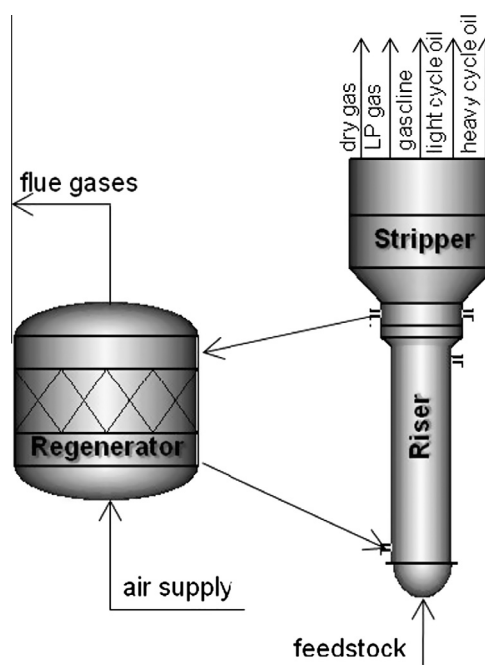

Fig. 1. Schematics of an industrial Fluidized-bed Catalytic Cracking (FCC) converter with single feed [2].