



Assessment of thermogravimetric methods for calculating coke combustion-regeneration kinetics of deactivated catalyst



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HIGHLIGHTS

- Guidelines for calculating combustion kinetics of coke combustion.
- Data obtained in a thermobalance using a spent FCC catalyst.
- Kinetic model-based, isoconversional and modulated methods.
- Best practices for each method and its pros-cons.

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ABSTRACT

This work compares different methodologies for calculating the kinetic parameters of coke combustion, employed for catalyst regeneration, using thermogravimetric methods. A reference fluid catalytic cracking (FCC) spent catalyst was used as a representative example of the deactivated catalyst for the combustion runs, pre-used in the cracking of a vacuum gas oil at 773 K and 3 s. Three different types of approaches have been performed in order to obtain kinetic combustion parameters: (i) kinetic model-based, (ii) isoconversional and (iii) modulated methods. Additionally, a series of empirical modifications have been proposed to predict the kinetic behavior at different heating rates for the model-based approach. Using the best conditions and methods, the combustion activation energy of coke, deposited after the reaction mentioned, is in the order of ~ 114 , ~ 156 , and ~ 162 kJ mol⁻¹ for the kinetic model-based, isoconversional and modulated methods, respectively. The recommendations for measuring kinetic parameters are reported together with the benefits/disadvantages using the three mentioned approaches.

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1. Introduction

Coke fouling is an inevitable and unwanted problem in many heterogeneous catalytic processes involving hydrocarbons (Bartholomew and Farrauto, 2006). Indeed, coke fouling causes millions of dollars of worldwide investment for a variety of catalytic processes such as hydrogenation, hydrotreating, reforming and cracking, among many others (Argyle and Bartholomew, 2015; Guisnet and Ribeiro, 2011). In fluid catalytic cracking (FCC), coke fouling has a critical role in the overall process design and throughput, as a typical unit ca. 35,000 bpd (219 t h⁻¹) fed with gas oil yields 13 t h⁻¹ of coke (Gary et al., 2007). Thus, coke is eliminated in this process by combustion in the regeneration stage, continuously withdrawing coked catalyst from the FCC

stripper and continuously delivering regenerated catalyst to the cracking inlet (Borio et al., 1992; Čejka et al., 2007). The regenerator consists in a fluidized bed at ca. 973 K with continuous feeding of air or oxygen-enriched air (Upson and Lomas, 2000).

The coked FCC catalysts, as well as many other catalysts deactivated by coke, have been routinely analyzed by temperature programmed oxidation (TPO) techniques with three different aims related with coke properties (Aguayo et al., 1999; Guisnet and Ribeiro, 2011; Opfermann et al., 2002): (1) quantitative yet fast analysis of the amount (and yield) of coke, (2) qualitative analysis of the nature and location of coke deposits and (3) evaluation of the kinetic parameters of coke combustion. In this sense, TPO allows to discretize coke into fractions with differentiated composition or location on the catalytic surface, and additional insights can be performed analyzing the exhausts with mass spectrometry (Aguayo et al., 2011) or the solid by FTIR spectroscopy (Ibáñez et al., 2014). The general criterion is that one type of coke burns

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Nomenclature

Symbols

A	pre-exponential factor ($\text{atm}^{-1} \text{s}^{-1}$)
A'	constant of the calorimeter in which DSC analysis is performed (m)
b	total number of chosen temperatures in the 17 isoconversional method, in Eq. (40) (–)
C_{coke}	coke content of the catalyst ($\mu\text{g g}_{\text{catalyst}}^{-1}$ or $\text{mg g}_{\text{catalyst}}^{-1}$)
D_{eff}	effective diffusivity ($\text{m}^2 \text{s}^{-1}$)
DTG	derivative weight loss ($\mu\text{g s}^{-1}$ or $\mu\text{g s}^{-1} \text{g}_{\text{catalyst}}^{-1}$)
E	activation energy (kJ mol^{-1})
E_1, E_2	activation energies obtained in the modulated method from the lower and higher value of the modulation, respectively (kJ mol^{-1})
F	function defined in Eqs. (SI-17) and (SI-18) (–)
$f(\alpha)$	kinetic model (–), mathematical expression describing coke combustion as a function of conversion
$g(\alpha)$	integral form of the kinetic model in Eq. (SI-4) (–)
$G(\alpha)$	kinetic parameter defined in Eq. (SI-8) (–)
H	modulation amplitude (K)
J	function defined in Eq. (35) (I4 method) and Eq. (36) (I5 method)
k	kinetic parameter (s^{-1})
m	mass (g)
M_c	heat capacity (J K^{-1})
n	reaction order (–)
N_{WP}	Weisz-Prater modulus (–)
$p(x)$	temperature integral in Eq. (SI-5) (–)
P_o	oxygen partial pressure (atm)
R	gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
$-r_x$	combustion rate (s^{-1})
r_p	particle diameter (m)
SSE	sum of square errors (K^{-2})
T	temperature (K)
t	time (s)
T^\dagger	reference temperature (K)
T_1, T_2	unmodulated temperature at which T_m-T_u is minimum or maximum, respectively (K)
T_r	real temperature on the combustion zone, estimated in Eqs. (47)–(50) (K)

T_c	temperature calculated for the 17 isoconversional method, in Eq. (40) (–)
ν_1, ν_2	DTG _u value at the same time as ν_{min} and ν_{max} , respectively ($\mu\text{g s}^{-1}$)
$\nu_{\text{max}}, \nu_{\text{min}}$	maximum and minimum local value in DTG _m , respectively ($\mu\text{g s}^{-1}$)
V_p	total pore volume ($\text{cm}^3 \text{ g}^{-1}$)
x	apparent activation energy at T temperature (–)
y	total number of heating programs (–)
z	total number of reaction steps (–)

Greek letters

α	combustion conversion (–)
β	heating rate (K min^{-1})
λ_g	thermal conductivity of the crucible ($\text{W m}^{-1} \text{ K}^{-1}$)
τ_{HFM}	characteristic response time value of the heat flowmeter (s)
$\phi_{N-\text{REC}}$	net recorded heat flow during a DSC analysis (W)
$\gamma_1, \gamma_2, \gamma_3$	empirical parameters used in Eqs. (47)–(49), respectively (min K^{-1})
φ	sum of the logarithmic expressions in the right side of Eq. (SI-13) (–)
κ	intrinsic kinetic parameter ($\text{atm}^{-1} \text{ s}^{-1}$)
λ_1, λ_2	empirical parameters used in Eq. (45) (min K^{-1})
θ_1, θ_2	constants defined in Eqs. (51) and (52), respectively (K)
ω	modulation frequency (Hz)

Subscripts and superscripts

0	initial value of the combustion run (–)
calc	calculated data (–)
exp	experimental data (–)
f	final value of the combustion run (–)
h	number of the chosen temperature in the 17 isoconversional method, in Eq. (40) (–)
i	number of a reaction step or the fraction of coke (–)
j, k	number of a heating program (–)
max, min	maximum and minimum value, respectively (–)
m, u	modulated and unmodulated signal, respectively (–)

at lower temperature when its composition is more hydrogenated (higher proportion of aliphatics respect to aromatics) (Ibáñez et al., 2012) and/or it is more accessible (Epelde et al., 2015), e.g. in the case of FCC catalyst, when it is located in the catalyst matrix instead of within the micropores.

The coke combustion mechanism involves many different reaction steps in parallel and in series, and the overall mechanism is not fully understood (Le Minh et al., 1997). Coke also suffers “aging” in the process of heating or stripping (made in specific sections of the FCC unit), leading to compositional and location changes of coke (Aguayo et al., 2003; Magnoux et al., 2002; Marcilla et al., 2008; Royo et al., 1996). Moreover, FCC catalyst comprises zeolites having shape selective microporosity and acidity, among other materials like metal oxides for promoting coke combustion. Thus, the kinetics of coke combustion depends on many factors including the complex composition of the catalyst and a wide spectrum of operational conditions (Moljord et al., 1995; Royo et al., 1996). Having a reliable coke combustion kinetic model and its corresponding parameters may have two different targets: (i) the design of the FCC regenerator or more in general, choosing the right operational conditions for the regeneration

stage of coked catalysts, and (ii) in order to obtain representative and intrinsic values of coked catalysts, useful for a systematic comparison of the nature or location of coke within the catalytic surface. Besides, for the first target, the model should incorporate heat and mass transfer rates as well as the proper fluid dynamic equations. On the other hand, if a mechanistic understanding is sought, then the chemical events associated with high-temperature oxidation of hydrocarbons should be considered, using a modeling software like ReaxFF (Chen et al., 2013).

The standard experimental procedure of the temperature programmed oxidation (TPO) of coke by thermogravimetric analysis (TGA or TG) involves a linear heating program:

$$T = T_0 + \beta t \quad (1)$$

Then, assuming a combustion kinetic model, we can obtain its parameters with a single experiment and performing a non-linear fitting of the experimental results. Due to the complex nature of coke deposited on the spent catalyst, it is commonly assumed that the combustion profile is the sum of independent combustion steps of each fraction of coke, each having one kinetic

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