Chemical Engineering Journal 326 (2017) 528–539

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Kinetics of coke formation in the dimethyl ether-to-olefins process over SAPO-34 catalyst

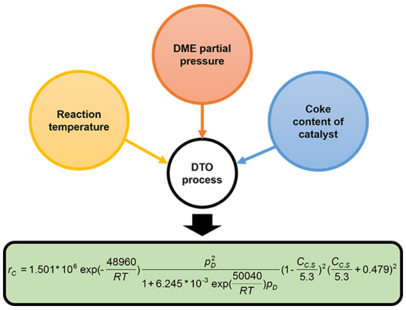
Yuli Gao, Sheng-Li Chen *, Yaqian Wei, Ya Wang, Wei Sun, Yingqian Cao, Penghui Zeng

State Key Laboratory of Heavy Oil Processing, Chemical Engineering Department, China University of Petroleum-Beijing, Beijing 102249, PR China

HIGHLIGHTS

- A kinetic model of coke formation was built for DME conversion to coke over SAPO-34 catalyst.
- The activation energy of coke formation in DTO reaction is 99 kJ/mol.
- The activation energy of adsorption of DME onto the active sites of SAPO-34 catalyst is 49 kJ/mol.

GRAPHICAL ABSTRACT



$$r_C = 1.501*10^6 \exp(-\frac{48960}{RT}) \frac{p_D^2}{1+6.245*10^{-3}\exp(\frac{50040}{RT})p_D} (1-\frac{C_{C.S}}{5.3})^2 (\frac{C_{C.S}}{5.3}+0.479)^2$$

ARTICLE INFO

Article history:
Received 25 February 2017
Received in revised form 24 May 2017
Accepted 25 May 2017
Available online 27 May 2017

Keywords:
Dimethyl ether to olefins
Methanol to olefins
SAPO-34
Coking kinetics

ABSTRACT

A kinetic of coke formation during dimethyl ether (DME) conversion to light olefins over SAPO-34 was studied by the use of a thermogravimetry (TG) reactor. Coke formation experiments were conducted at the heating rate from 4 K/min to 10 K/min and DME partial pressure between 40.53 kPa and 101.325 kPa. The effects of reaction temperature, DME partial pressure and coke content of catalyst on coking rate were investigated. The results showed that high reaction temperature and DME partial pressure led to high coking rate. The coking rate increased with coke content during the early stage of the DME to olefins (DTO) reaction, indicating that the coking reaction was autocatalytic reaction. A mechanism was proposed for the coke formation and a kinetic equation was established to correlate the rate of coke formation with DME partial pressure, reaction temperature and coke content of catalyst. The activation energies of coke formation and adsorption of DME onto the active sites of catalyst surface in DTO reaction were found to be 99 kJ/mol and 49 kJ/mol, respectively.

1. Introduction

Light olefins (ethylene and propylene), which present in most of chemical intermediates in the chemical industry, are produced from petroleum [1]. Due to the increasing demands of light olefins, alternative process—methanol/dimethyl ether (DME) to olefins (MTO/DTO) process has attracted researchers' intense attention. The MTO/DTO process becomes a promising way for production of ethylene and propylene, due to its high selectivity for ethylene and propylene [2,3]. Methanol and DME can be obtained via syngas from non-petroleum sources such as coal, natural gas or biomass [4–7]. Hence, the exploration of MTO/DTO process can relieve the shortage in petroleum in China[8].

Among molecular sieve catalysts applied in MTO/DTO process, the SAPO-34 molecular sieve with a well-defined framework with chabazite cages of 1.27 nm × 0.94 nm connected via 8-ring windows of 0.38 nm is widely considered as the best MTO/DTO catalyst [9,10]. The SAPO-34 molecular sieve's small pore opening and mild acid strength contribute to the highest selectivity to light

---

* Corresponding author.
E-mail address: slchen@cup.edu.cn (S.-L. Chen).

http://dx.doi.org/10.1016/j.cej.2017.05.158
1385-8947/© 2017 Elsevier B.V. All rights reserved.

Nomenclature

A	preexponential factor, $kPa^{-2} \cdot s^{-1}$
A'	constant, kPa^{-1}, defined by Eq. (15)
A_1	preexponential factor in the step of DME adsorption
A_2	preexponential factor in the step of coke formation
a	power of the portion of residual active sites
b	power of the portion of coke deposited on active sites
B_1	parameter to be estimated in Eq. (2)
B_2	parameter to be estimated in Eq. (2)
C_a	adsorption of hydrocarbon pool on the active sites
$C_{C.S}$	coke content, Wt%, $C_{C.S} = \frac{g_{coke}}{g_{catalyst}} \times 100\%$
$C_{(CH_2)_n \cdot S}$	concentration of hydrocarbon pool adsorbed on the active sites, mol/g_{cat}
$C_{i.exp}$	experimental coke content for i^{th}
$C_{i.cal}$	calculated coke content for i^{th}
C_t	total active sites, mol/g_{cat}
C_v	vacant active sites, mol/g_{cat}
d	parameter to be estimated in Eq. (2)
Ea_1	activation energy of DME adsorption, kJ/mol
Ea_2	activation energy of coke formation, kJ/mol
H	heating rate, $(\frac{dT}{dt})$
k	rate constant, $kPa^{-2} \cdot s^{-1}$, defined by Eq. (11)
k_1	rate constant in the step of DME adsorption [Eq. (4)], $kPa^{-2} \cdot s^{-1}$
k_2	rate constant in the step of coke formation [Eq. (5)], $kPa^{-1} \cdot s^{-1}$
k_3	rate constant in the step of gas products formation [Eq. (6)]
K_P	constant, kPa^{-1}, defined by Eq. (11)
m	constant, defined by Eq. (11)
OF	objective function
p_D	DME partial pressure, kPa
R	gas constant, 8.314 J/(mol·K)
r_C	coking rate, $r_C = \frac{dC_{C.S}}{dt}$, Wt%/h
$r_{(CH_2)_n \cdot S}$	rate of hydrocarbon pool formation, mol/(g_{cat}·h)
r_3	rate of gas product formation, mol/(g_{cat}·h)
S	active site
T	temperature, K
T_0	parameter to be estimated in Eq. (2)
x	reaction order with respect to DME in the step of DME adsorption [Eq. (4)]
y	reaction order with respect to DME in the step of coke formation [Eq. (5)]
z	reaction order with respect to DME in the step of gas products formation [Eq. (6)]
λ	the difference of the activation energy of coke formation and DME adsorption, kJ/mol, defined by Eq. (15)
ρ^2	correlation coefficient
φ_C	deactivation function, representing for a fraction of active sites remaining active

olefins [11]. However, the SAPO-34 catalyst easily suffers from a rapid deactivation, which is caused by coke deposition inside pores [12,13].

Coke not only can deactivate the SAPO-34 catalyst during MTO/DTO process, but also can influence the selectivity of MTO/DTO process [5,14,15]. Kinetic models can accurately quantify coke formation, contribute to optimize reaction conditions and improve the availability of the catalyst. Therefore, it is of significance to study kinetics of coke formation in MTO/DTO process.

According to literature, kinetic models for coke deposition on catalysts can be divided into two types, including the empirical models and the semi-theoretical models, which are deduced from the mechanism of coke formation. The empirical models are further divided into the power function model [16,17] and exponential function model [18,19]. The Voorhies equation ($C = \alpha t^{\beta}$, where C is coke content on catalyst, t is residence time, and α and β are parameters to be estimated and are dependent on catalyst, feed stock, and temperature), a kind of power function model, is a well known model proposed by Voorhies through relating coke formation to residence time in the catalytic cracking of gasoil[16]. Chen et al.[14] made a modification of the Voorhies equation for its application in the MTO reaction, and studied the effects of the space velocity, temperature and partial pressure of methanol on coke content of catalyst, and concluded that cumulative amount of hydrocarbon formed *(CAHF)* was a more precise parameter than time on stream to relate the coke content. The modified Voorhies equation is $C = \alpha CAHF^{\beta}$, where C is coke content of catalyst, α and β are parameters depended on reaction temperature. Qi et al. [17] found that the amount of coke formed on catalyst was dependent on the cumulative amount of methanol fed *(CAMF)* into the catalysts during the MTO reaction in an isothermal fixed-bed integral reactor and proposed a modified Voorhies equation relating *CAMF* to coke content ($C = \alpha CAMF^{\beta}$, where C is the coke content of catalyst, α and β are parameters depending on reaction temperature). The equation of $C = \alpha CAHF^{\beta}$ can be applicable for the case of conversion less than 100% while the equation of $C = \alpha CAMF^{\beta}$ is applicable only when the conversion is 100%.

Some exponential equations were proposed for calculation of coke content of catalyst in MTO/DTO process [14,18,19]. Chen et al. [18] proposed an exponential equation ($C = 1/\alpha_C \ln[1 + \alpha_C k_C^0 AF_{DME}(1 - \exp(-k^0 C_{A0} W/(\rho_C F_{A0})))]$, where α_C is the deactivation constant, k_C^0 is the initial coking rate constant, AF_{DME} is the cumulative amount of DME fed per catalyst mass, k^0 is the initial intrinsic rate constant of DTO reaction, C_{A0} is the initial reactant concentration, W is the catalyst weight, ρ_C is the catalyst density, F_{A0} is the molar flow rate of the reactant) to predict the coke content on catalyst in DTO reaction. Chen et al. [14] studied coke deposition behavior during the MTO process by the use of a tapered element oscillating microbalance (TEOM) reactor. They made several assumptions as follows**:** firstly, since the initial oxygenates (methanol and DME) conversion was approaching to 100%, the reactor was treated as an integral plug-flow reactor rather than a differential reactor. The integral plug-flow reactor further was assumed to be a series continuous-stirred tank reactor (CSTR), and in each CSTR reactor, the coke deposition was assumed to be uniform. Secondly, the conversion of oxygenates was treated as a first-order reaction. Based on the assumptions above, they obtained an exponential equation to calculate the coke content in each CSTR reactor ($C_i = 1/\alpha_C(1 - \exp(-\alpha_C k_C^0 (t/\tau_i) \Delta x_i))$, where C_i is the coke content in the ith CSTR, α_C the empirical deactivation constant, k_C^0 the initial rate constant for coke formation, t the time on stream, τ_i the space time in the ith CSTR, Δx_i the conversion of oxygenates in the ith CSTR.), and found the apparent coking activation energy at temperature between 673 K and 698 K being 30 kJ/mol. Hu et al. [19] also proposed an exponential equation ($C = C_0(1 - \exp(((a + b(T/1000) + c(T/1000)^2 + d(T/1000)^3) + f \cdot p \cdot WHSV)t))$, where C_0 is the maximum coke content; a, b, c, d, f are parameters to be estimated, they are dependent on methanol concentration and temperature; p is the methanol partial pressure, $WHSV$ the weight hourly space velocity, t the time on stream, T