

Modeling of the deactivation kinetics for the combustion of ethyl acetate and benzene present in the air stream over ZSM-5 catalyst loaded with chromium

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Accepted 31 October 2003

Abstract

Deactivation kinetics of chromium exchanged ZSM-5 (Cr-ZSM-5, Si/Al = 240) catalyst by coking during the combustion of ethyl acetate (EAc) and benzene (Bz) present in the air stream is reported. Lumped coking deactivation model (LCDM), monolayer–multilayer coking deactivation model (MMDM) and heterogeneous surface coking deactivation model (HSDM) are used for the analysis of deactivation process. Coked Cr-ZSM-5 was prepared by exposing the catalyst to 32,000 ppm of each organic at gas hourly space velocity (GHSV) of 3800 h⁻¹ and temperature 400 °C for a period of 12 h. The activity data were obtained with 2000 ppm of each organic at 400 °C and GHSV of 78,900 h⁻¹. HSDM accurately predicted progressive coke content, activity with time-on-stream and profiles of activity–coke content for both organics. In line with experimental observations, the model predicted faster activity drop with lower residual activity during the combustion of ethyl acetate. The combustion reaction of ethyl acetate and benzene could take place over both coking sites (S_c) and metal sites (S_m) but, the role of S_m was more dominant especially in benzene combustion.

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Keywords: VOC combustion; Coking; Deactivation; Ethyl acetate; Benzene; Cr-ZSM-5

1. Introduction

Catalytic combustion is the most plausible solution to volatile organic compound (VOC) removal due to its efficiency and low operating costs [1,2]. Unfortunately, combustion catalyst deactivates, more or less, primarily due to the accumulation coke that tends to physically cover the catalytic active surface and/or blocking pores. The chemical nature of these carbonaceous deposits depends upon reaction conditions and types of feed, and may amount to 15–20% (w/w) of the catalyst [3]. The modeling of catalyst deactivation process by coking can provide valuable information on the performance of the catalytic system after extensive hours on stream when significant amount of coke has deposited.

One of the main problems in the estimation and interpretation of deactivation by coking phenomena lies in the choice of the most suitable model [4,5]. A wrong choice of model can result in misleading conclusions about the reaction mechanism. A good model for coking should consider

sufficient number of parameters while maintaining simplicity to ensure good fit of the experimental data. The parameter estimation must be based on either coke content or activity data [6].

Progressive formation of coke with time-on-stream is normally associated with corresponding decrease in the activity. Thus, the modeling of deactivation by coking should incorporate two main aspects, i.e. coke formation rate and deactivation kinetics. The adequacy of the separability concept has been reported for various reaction systems by Rodríguez et al. [4], Klemm et al. [7] and Gascón et al. [8]. Generally, the main challenge which often results in divergence between models proposed lies in relating the progressive coke content with the activity function.

Reports on deactivation by coking in VOC catalytic combustion, in which, support and metal sites play significant role is quite scanty. In this application, coking can be seen as lumped accumulation of this carbonaceous deposit so that deactivation is a direct function of its quantity [3]. This approach provides simplicity and practicality in many applications especially in the case when only one type of active site present on the catalyst. Further improvement to this ap-

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Nomenclature

a	dimensionless activity function
a_r	residual activity
C	coke content (g/g _{cat})
C_m	actual amount of coke in the monolayer (g/g _{cat})
C_{max}	maximum coke content independent of monolayer or multilayer (g/g _{cat})
$C_{m,max}$	maximum amount of coke in monolayer (g/g _{cat})
C_M	actual amount of coke in multilayer (g/g _{cat})
dC/dt	rate of coke formation (g/g _{cat} h)
f	number of coking sites involved in coking reaction
$F_{voc,in}$ $F_{voc,out}$	VOC molar flow rates at the inlet and outlet of the reactor, respectively (mol/s)
h	number of active sites involved in the controlling steps of coke formation
j	number of experimental point
k_c	coking reaction rate constant (g/g _{cat} h atm ^{m})
k_d	deactivation constant
k_m	rate constant of monolayer coke formation (g _{cat} /g h)
k_M	rate constant of multilayer coke formation (g/g _{cat} h)
p	number of parameters
P_c	partial pressure of VOC (atm)
q	number of chemisorbed molecules that react to form coke
r_v, r_{v0}	reaction rates of VOC combustion at time t and 0 h, respectively (mol/h g _{cat})
S_t, S_c	two types of active sites on Cr-ZSM-5
t	time-on-stream (h)
W_{cat}	weight of the catalyst (g)
x_{t0}, x_{c0}	initial fractions of sites S_t and S_c present on fresh Cr-ZSM-5
\hat{Y}_{obs}	weighted mean of the experimental observation
z	number of active sites involved in controlling step in the main reaction mechanism

Greek symbols

α_1, α_2	constants
γ	deactivation kinetic order
φ_a	intrinsic activity functions
φ_c	intrinsic coking functions (h ⁻¹)
ξ	ratio of initial rate of the main reaction over S_t sites ($-r_{S_t}$) to the initial rate of the main reaction over S_c sites ($-r_{S_c}$)

proach has been proposed by Romeo et al. [9] and Gascón et al. [8] treating coking as a combination of monolayer and multilayer-type coke deposition. Depending on the reaction system, each type of coke has different influences on the activity of the catalyst and should be modeled separately. Another approach is by assuming heterogeneous catalytic surface on which selective accumulation of coke on certain sites occurred while the other type of site is unaffected. In reaction systems where more than one type of active sites is involved in the main reaction, this approach is more appropriate [4].

In the present study, three models of deactivation by coking adopting different mechanistic approaches of coke formation, viz. lumped coking deactivation model (LCDM), monolayer–multilayer coking deactivation model (MMDM) and heterogeneous surface deactivation model (HSDM) are studied. These models are used to simulate the data related to the coke content and activity variation with the coke content. The parameters are estimated using experimental coke content and catalyst activity data. The experimental data were fitted to the best model on the consideration of three factors: (a) profile of coke formation with time, (b) profile of activity with time and (c) profile of activity with coke content. The best model was selected on the basis of good fit of the experimental data and the physical meaning of the kinetic parameters.

Chromium is reported to be the most active metal among the transition metals for VOC combustion due to its ability to present at multiple oxidation states [10,11]. Chromium exchanged of ZSM-5 (Cr-ZSM-5) produced a catalyst of high activity and stability, and therefore, was used in the present study. As for VOC model compounds, ethyl acetate and benzene were used for the purpose of comparison because of differences in their chemical natures.

2. Experimental procedure

2.1. Preparation of Cr-ZSM-5

Chromium exchanged ZSM-5 (Si/Al = 240) was prepared in two steps. In the first step, NH_4^+ exchange of Na-ZSM-5 (Si/Al = 240) was performed in 2.25 M of NH_4Cl solution for 6 h. The metal exchange step was carried out in acidified (to pH 4) aqueous $Cr(NO_3)_3$ solution at 0.086 mol/l, for 6 h followed by filtration, drying and calcination at 500 °C for 6 h. Before used in the reactor, the catalysts were palletized, crushed and sieved to particle sizes of between 0.25 and 0.30 mm.

2.2. Experimental setup

The preparation of coked Cr-ZSM-5 samples was performed in an 11 mm i.d. glass reactor charged with 0.2 g of zeolite catalysts (Fig. 1). VOC-laden air stream as feed to the reactor was generated by bubbling nitrogen gas through

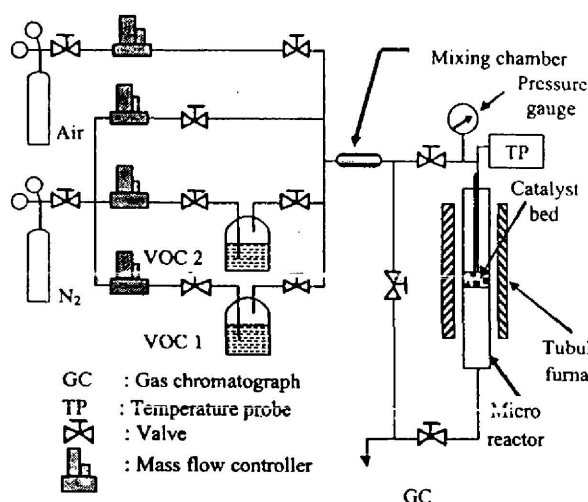


Fig. 1. Schematic diagram of the reactor system used.

the VOC saturators. Another flow of air was used to make up the total flow rate to give the desired GHSV. The accurate control of flow rate was achieved by means of Aalborg (AFC 2600) mass flow controllers. In order to prepare coked Cr-ZSM-5 samples, feeds containing 32,000 ppm of either ethyl acetate or benzene were passed through the reactor at reaction temperature of 400 °C and GHSV of 3800 h⁻¹ for different times on stream of up to 12 h. Before collecting the coked samples, nitrogen was passed through the catalyst bed at the reaction temperature for 10 min to remove any non-coke species from the samples. The feed and product gases were analyzed using an off-line Shimadzu GC-8A gas chromatograph. Porapak Q column was used for separation of carbon dioxide and organic components while the separation of carbon monoxide was achieved by means of a molecular sieve 5A column.

2.3. Activity study

The reaction rates over the coked Cr-ZSM-5 samples were measured by operating the reactor in differential mode at GHSV of 78,900 h⁻¹. The feed concentration for respective organic was kept at 2000 ppm. The rate of reaction for coked Cr-ZSM-5 was calculated as

$$-r_v = \frac{F_{\text{voc.in}} - F_{\text{voc.out}}}{(1 - C)W_{\text{cat}}} \quad (1)$$

where $-r_v$ is the reaction rate (mol/s g_{cat}), $F_{\text{voc.in}}$, $F_{\text{voc.out}}$ the VOC molar flow rates at the inlet and outlet of the reactor (mol/s), C the coke content of the catalyst (g/g_{cat}), and W_{cat} is the weight of the catalyst (g).

2.4. Characterization of Cr-ZSM-5

The catalyst samples were characterized for surface area and pore size measurements using Quantachrome Autosorb-1, metal loading using Shimadzu AA-6650 atomic

absorption spectroscopy, acidity via temperature programmed desorption of ammonia (NH₃-TPD) using Quantachrome Chembet 3000 and crystallinity using Siemens D2000 X-ray diffractometer. The amount of coke accumulated on the catalyst was determined using Perkin-Elmer TGA7 thermogravimetry analyzer, in which the previously dried sample (at 105 °C for 2 h) was heated under pure oxygen flow at 20 ml/min to 700 °C and the weight loss was determined. The kinetic parameters were estimated using non-linear regression with Polymath software.

3. Modeling

3.1. Lumped coking deactivation model (LCDM)

This model lumps coke formed during VOC catalytic combustion into single type. VOC catalytic combustion is normally operated in an oxygen-rich environment and the rate of coke formation is reported to be organic concentration dependent but independent of oxygen partial pressure [1,2]. Generally, coking rate progressively decreases with the decrease in the number of the available coking site [3,7]. The rate of coking is given as

$$\frac{dC}{dt} = k_c P_v^m \left[\frac{C_{\text{max}} - C}{C_{\text{max}}} \right]^f \quad (2)$$

where k_c is the coking rate constant (unit varies with m), P_v the VOC partial pressure, m a temperature-independent parameter. C and C_{max} the progressive and maximum coke content, respectively, and f is the number of coking sites involved in coking reaction. Since f should be a positive integer, experimental data fitting by Eq. (2) was performed on trial-and-error basis using f values between 1 and 4. The best fit was obtained with the value of $f = 2$ for the combustion of ethyl acetate and benzene.

The catalyst activity is defined as

$$a = \frac{r_v}{r_{v0}} \quad (3)$$

where r_v and r_{v0} are the reaction rates of VOC combustion at time t and 0 h, respectively. Assuming the total coke deposited on the catalyst is responsible for the loss of activity and relation between a and C is represented as an exponential function:

$$a = \exp \left[-k_d \frac{C}{C_{\text{max}}} \right] \quad (4)$$

where k_d is the deactivation constant.

3.2. Monolayer-multilayer coking deactivation model (MMDM)

This model considers coking to initiate on the acid site to form the primary or monolayer coke [12]. Subsequent coking can either form on the new (different) acid site or on the

primary layer to form the secondary coke, normally in the form of multilayer coke [8,9]. Both types of coke will cause the masking of active metal sites for VOC combustion leading to deactivation and their relative concentrations depend on the reactions leading to their formation. At high conversion during early hours on stream, coke forms rapidly on acidic sites (monolayer coke) while high amounts of coke precursors are formed [13]. Simultaneously, the multilayer coke grows in weak interaction with, and anchored on monolayer coke. Thus, total coke content is

$$C = C_m + C_M \quad (5)$$

and the overall rate of formation is

$$\frac{dC}{dt} = \frac{dC_m}{dt} + \frac{dC_M}{dt} \quad (6)$$

where C_m and C_M are the amount of monolayer and multilayer coke, respectively.

The rate of monolayer coke formation is considered to be a function of available coking sites on the primary catalytic surface and is calculated from Eq. (7):

$$\frac{dC_m}{dt} = k_m(C_{m,\max} - C_m)^h \quad (7)$$

where k_m is the rate constant of monolayer-type coke formation ($\text{g}_{\text{cat}}/\text{g h}$), $C_{m,\max}$ the maximum amount of coke in monolayer, C_m the actual concentration of coke in the monolayer, and h is the number of active sites involved in the controlling step of coke formation. The rate of formation of multilayer coke is normally a constant at a given temperature [9] and given by

$$\frac{dC_M}{dt} = k_M \quad (8)$$

where k_M is the rate constant of multilayer coke formation. By definition, h should be a positive integer and values for h from 1 to 4 were tested one by one. It was found that when $h = 2$, the best fit of Eq. (9) as the product of integration of Eqs. (7) and (8) to the experimental data was obtained:

$$C = C_m + C_M = \frac{k'_m t C_{m,\max}}{1 + k'_m t} + k_M t, \quad k'_m = k_m C_{m,\max} \quad (9)$$

According to the mechanistic model, only monolayer coke will promote deactivation [7,8]. However, experimental activity–time results proved that activity decreases with time, even after complete monolayer has been formed. This suggests that multilayer coke also deactivates. Thus, the activity is represented as

$$a = \exp(-\alpha_1 C_m - \alpha_2 C_M) \quad (10)$$

where α_1 and α_2 are the two constants independent of temperature.

3.3. Heterogeneous surface coking deactivation model (HSDM)

This model considers two types of active sites (S_1 and S_c) present on the surface of the catalyst. The main reaction

occurs simultaneously on both sites, but only one of them (S_c) deactivated by coke [4]. Significant activity of organics combustion over H-form zeolites (Y, ZSM-5 and mordenite) has been reported by Fonseca et al. [14,15]. Generally, the oxidation reactions were attributed to Brønsted acid sites on the zeolites. These acid sites are also identified as the coking sites during reactions involving organics over zeolite catalysts [12,16,17]. However, by incorporation of active metal species in zeolites such as Pd [1,2], Cu [18,19] and Cr [10,11] was reported to significantly improve the conversion of organics. As such, it can be considered that the roles of S_1 and S_c sites in Cr-ZSM-5 are played by chromium sites and Brønsted acid sites, respectively.

At certain time, these sites deactivate, but the catalyst will maintain a constant residual activity due to the main reaction continuing to occur on the S_1 sites. Simultaneously, the rate of coke formation over S_c sites will decrease as the reaction progresses. The rate of coke formation is defined as

$$\frac{dC}{dt} = q C_{\max} \varphi_c \left[1 - \frac{C}{C_{\max}} \right]^q \quad (11)$$

where q is the number of chemisorbed molecules that react to form coke and C_{\max} is the maximum coke content independent of monolayer or multilayer coke. The value of q should be a positive integer and the best fit of Eq. (11) with the experimental data was obtained when $q = 2$. φ_c is defined as the intrinsic coking function, therefore in Eq. (11) it multiplies the driving force for coking $(1 - C/C_{\max})$.

The rate of deactivation is defined by

$$-\frac{da}{dt} = \varphi_a (a - a_r)^\gamma \quad (12)$$

where φ_a is the deactivation function, a_r the residual activity, and γ is the deactivation kinetic order.

The activity, a is given as

$$a = \left[x_{10} + \left(\frac{C_{\max} - C}{C_{\max}} \right) x_{c0} \right]^z \quad (13)$$

where x_{10} and x_{c0} are the fractions of sites S_1 and S_c , respectively, in the fresh catalyst and z is number of active sites involved in controlling step in the main reaction mechanism. It was found that the best fit of Eq. (13) to the experimental data was obtained when $z = 2$. In Eq. (12), φ_a is actually a function of φ_c according to

$$\varphi_a = z q x_{10}^{q-1} (\xi + 1)^{(q-1)/z} \varphi_c \quad (14)$$

where the value of γ is given by

$$\gamma = \left(\frac{z + q - 1}{z} \right) \quad (15)$$

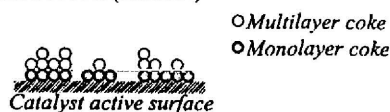
and ξ is the ratio of initial rate of the main reaction over S_1 sites ($-r_{S_1}$) to the initial rate of the main reaction over S_c sites ($-r_{S_c}$) or

$$\xi = \frac{(-r_{S_1})_0}{(-r_{S_c})_0} \quad (16)$$

i) Lump Coking Deactivation Model (LCDM)



ii) Monolayer-Multilayer Coking Deactivation Model (MMDM)



iii) Heterogeneous Surface Coking Deactivation Model (HSDM)

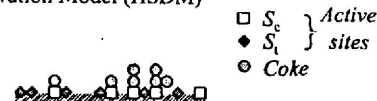


Fig. 2. Schematic diagram of coking mechanism by the three models proposed.

The value of residual activity in Eq. (12) is determined as

$$a_r = \frac{\xi}{\xi + 1} \quad (17)$$

The mechanism of coke formation considered in each model is schematically shown in Fig. 2.

4. Results and discussion

4.1. Characteristics of the catalysts

The characteristics of Cr-ZSM-5 catalyst prepared are shown in Table 1. Chemical and thermal treatment during chromium exchange process resulted in some degree of ZSM-5 framework defects as indicated by lower crystallinity and reduced total surface and micropore areas. Total acidity of zeolite is mostly contributed by Lewis and Brønsted acid sites [20]. In chromium exchange process, the masking of some of these acidic sites by extraframework species [21,22] and unexchanged chromium deposit coupled by the dehydroxylation of Brønsted acid sites [23] led to a decreased total acidity. The defects created during chromium exchange process increased the concentration of silanols group terminating the framework, and together with extraframework phase

or silica-alumina debris, Lewis acid sites that were relatively weaker than Brønsted acid sites were created [22].

4.2. Deactivation parameters estimation

The kinetic parameters for each model were determined by minimizing the following objective functions:

$$f = \sum_{i=1}^n (C_{\text{experimental}} - C_{\text{predicted}})^2 \quad (18)$$

or

$$f = \sum_{i=1}^n (a_{\text{experimental}} - a_{\text{predicted}})^2 \quad (19)$$

The estimated values of kinetic parameters for all three deactivating models under consideration are summarized in Table 2.

LCDM predicted more coke accumulation in ethyl acetate combustion as indicated by higher value of C_{max} . With almost similar values of m , it can be concluded that both organics had almost similar dependence of coke accumulation on feed concentration. Meanwhile, significantly higher value of k_d with ethyl acetate suggested that coke formed in the combustion of this organic had more deactivating effect on the activity of Cr-ZSM-5 compared to benzene.

In agreement with experimental data, MMDM predicted faster accumulation of coke with ethyl acetate as suggested by higher value of k_m . Based on the values of k_m , it can be concluded that the specific rates of formation of multilayer coke were lower compared to that of monolayer coke with about four and three orders of magnitude for ethyl acetate and benzene, respectively. Both organics gave higher value of α_1 compared to α_2 . This result indicated that monolayer coke had more deactivating effect on the activity of Cr-ZSM-5. This is in line with the theory as monolayer coke covers catalytic active sites renders them unavailable for the main reaction. The deactivating effect of multilayer coke could be as a consequence of diffusion limitation of the reactants to certain active sites.

HSDM predicted that the initial site fractions (x_{l0} and x_{c0}) are independent of the type of organic feed. In addition, the S_c sites predicted to be outnumbered by S_l sites with a ratio of about 2.4–1. This model also predicted more coke accumulation in ethyl acetate combustion as indicated by higher value of C_{max} for this organic. In terms of residual activity (a_r), lower activity is expected in the combustion of ethyl acetate compared to benzene. Based on the values of ξ , it can be concluded that the combustion of both types of organic can take place on both sites. However, the role of S_l was more dominant especially with benzene where higher value of ξ was obtained.

The discrimination of various models has been carried out using the statistical criteria (S.D. and coefficient of determination, R^2) backed with physical interpretation of the estimated parameters. In the case where similar values of R^2 are obtained, the model selection criteria (MSC) was used

Table 1
Characteristics of Cr-ZSM-5 catalyst as compared to its parent Na-form

Characteristics	Na-ZSM-5	Cr-ZSM-5
S_{BET} (m^2/g)	393	366
Micropore area (m^2/g)	321	272
Mesopore area (m^2/g)	72	94
Chromium loading (%)	–	0.98
Crystallinity ^a (%)	100	96
Acidity (mmol $\text{NH}_3/\text{g}_{\text{cat}}$)	0.18	0.14

^a Relative to parent Na-ZSM-5.

Table 2
Estimated values of kinetic parameters for each model

Model	Ethyl acetate		Benzene	
	Parameter value	S.D.	Parameter value	S.D.
LCDM ^a	$k_c = 2.93 \text{ g/g}_{\text{cat}} \text{ h atm}^{0.12}$	0.22	$k_c = 2.25 \text{ g/g}_{\text{cat}} \text{ h atm}^{0.14}$	0.32
	$m = 0.12$	0.008	$m = 0.14$	0.03
	$C_{\text{max}} = 8.89 \times 10^{-2} \text{ g/g}_{\text{cat}}$	0.92×10^{-2}	$C_{\text{max}} = 7.95 \times 10^{-2} \text{ g/g}_{\text{cat}}$	1.10×10^{-2}
	$k_d = 0.12$	0.01	$k_d = 0.06$	0.02
MMDM ^b	$k_m = 5.70 \text{ g}_{\text{cat}}/\text{g h}$	0.85	$k_m = 2.52 \text{ g}_{\text{cat}}/\text{g h}$	0.38
	$k_M = 3.61 \times 10^{-4} \text{ g/g}_{\text{cat}} \text{ h}$	0.58×10^{-4}	$k_M = 1.10 \times 10^{-3} \text{ g/g}_{\text{cat}} \text{ h}$	0.22×10^{-3}
	$C_{m,\text{max}} = 9.07 \times 10^{-2} \text{ g/g}_{\text{cat}}$	1.67×10^{-2}	$C_{m,\text{max}} = 9.71 \times 10^{-2} \text{ g/g}_{\text{cat}}$	0.86×10^{-2}
	$\alpha_1 = 2.30 \text{ g}_{\text{cat}}/\text{g}$	0.21	$\alpha_1 = 1.02 \text{ g}_{\text{cat}}/\text{g}$	0.14
	$\alpha_2 = 0.81 \text{ g}_{\text{cat}}/\text{g}$	0.11	$\alpha_2 = 0.33 \text{ g}_{\text{cat}}/\text{g}$	0.05
HSDM ^c	$x_{\text{H}} = 0.68$	0.08	$x_{\text{H}} = 0.74$	0.09
	$x_{\text{C}} = 0.32$	0.03	$x_{\text{C}} = 0.26$	0.02
	$C_{\text{max}} = 9.82 \times 10^{-2} \text{ g/g}_{\text{cat}}$	1.02×10^{-2}	$C_{\text{max}} = 8.84 \times 10^{-2} \text{ g/g}_{\text{cat}}$	0.92×10^{-2}
	$a_r = 0.61$	0.07	$a_r = 0.71$	0.08
	$\xi = 1.55$	0.22	$\xi = 2.40$	0.25

^a Parameters estimated using $f = 2$.

^b Parameters estimated using $h = 2$.

^c Parameters estimated using $q = 2$ and $z = 2$.

[8]. The MSC is computed as

$$\text{MSC} = \ln \left[\frac{\sum_{j=1}^j (Y_{\text{obs}_j} - \hat{Y}_{\text{obs}})^2}{\sum_{j=1}^j (Y_{\text{obs}_j} - Y_{\text{calc}_j})^2} \right] - \frac{2p}{j} \quad (20)$$

where j is the number of experimental points, p the number of parameters and \hat{Y}_{obs} is the weighted mean of the experimental observations. The MSC is useful as it takes into account the number of parameters of a given model and therefore allows a comparison of different models [8].

4.3. Comparison between experimental and simulated values

4.3.1. Coke formation profiles

The changes in the coke content with time-on-stream for the combustion of ethyl acetate was accurately predicted by

HSDM model as shown in Fig. 3(a). With this model, 5.2% of the variance was observed. LCDM, on the other hand, demonstrated negative deviation at lower time-on-stream but were on positive sign at longer time-on-stream. Despite accurately predicting the coke content at longer time-on-stream, MMDM failed to predict the evolution of coke during early hours on stream. LCDM and MMDM predicted higher coke content at longer time-on-stream than experimental values during the combustion of benzene (Fig. 3(b)). HSDM predicted values comparable with experimental values of coke content with high values of R^2 among the three models proposed.

By lumping coking as a single process, LCDM failed to fit the experimental data probably due to insufficient sets of parameter put into consideration. The breaking down of coking process into monolayer and multilayer coke formation by MMDM seemed to improve the data fitting

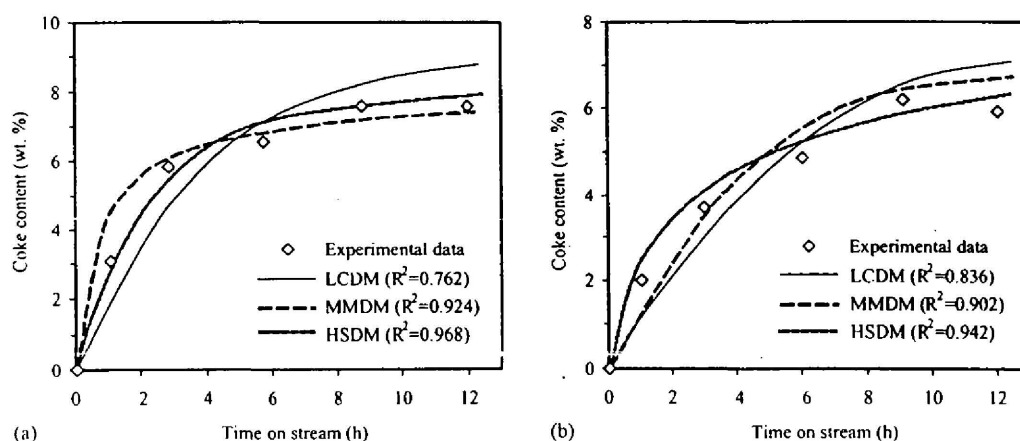


Fig. 3. Evolution of coke with time as predicted by the models and experimental data during the combustion: (a) ethyl acetate; (b) benzene at 400 °C.

with both ethyl acetate and benzene especially at longer time-on-stream. Next, the combination of the driving force for coking (i.e. $1 - C/C_{\max}$) and coking function (φ_c) in HSDM improved the fitting particularly with ethyl acetate at earlier time-on-stream where rapid coke formation occurred.

The rate of coke formation during early hours on stream was associated with high concentration of S_c (or acid sites) in a fresh catalyst. As time passed, some of these sites were coked and coke formation gradually slowed down. The accumulation of coke on these sites was more active when ethyl acetate was used as feed and this was successfully predicted by HSDM for both organics. The model also predicted higher C_{\max} for coking by ethyl acetate reaction; the situation which was closely related with the types, density and coverage of coke formed.

4.3.2. Activity profiles

The simulated activity data of Cr-ZSM-5 with time-on-stream for the combustion of ethyl acetate using three models are shown in Fig. 4(a). Significant deviation at early

time-on-stream for all three models was noted but in general, HSDM predicted the experimental data well. At longer time-on-stream, the activity was under predicted by LCDM but over predicted by MMDM. In the case of benzene combustion, LCDM and MMDM failed to satisfactorily predict the activity of Cr-ZSM-5 especially at longer hours of time-on-stream (Fig. 4(b)).

Cr-ZSM-5 demonstrated faster activity drop during the combustion of ethyl acetate during early hours on stream compared to benzene. This phenomenon was ascribed to the masking of S_c sites by coke compounds. Since the activity of ethyl acetate combustion was relatively higher than that of benzene on S_c sites (based on values of ξ in HSDM), the disappearance of these sites had deactivating effect of higher magnitude on the combustion of ethyl acetate. The lower value of ξ in the combustion of ethyl acetate also explained relatively lower residual activity achieved in the process compared to that of benzene. Near complete deactivation was not achieved in this study due to high initial concentration of S_t (or x_{t0}) which constituted about 70% of total active sites for organic combustion.

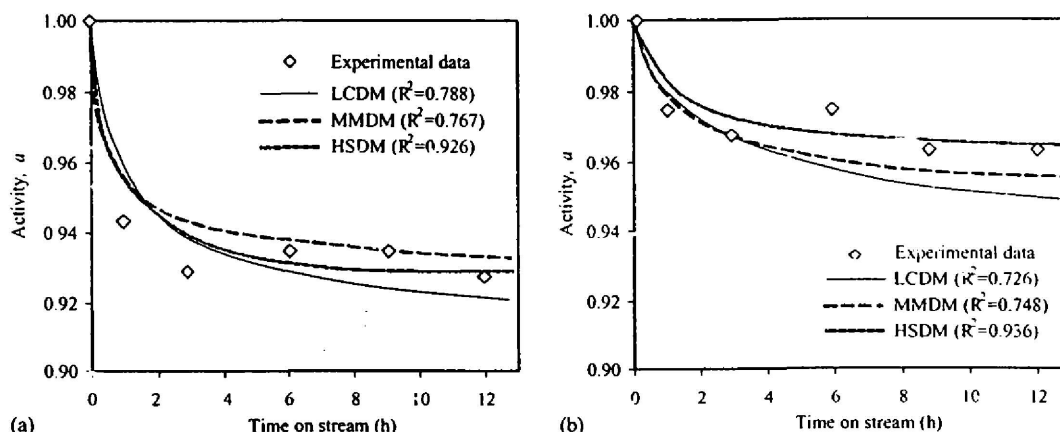


Fig. 4. Activity of Cr-ZSM-5 as predicted by the models and experimental data during the combustion: (a) ethyl acetate; (b) benzene at 400 °C.

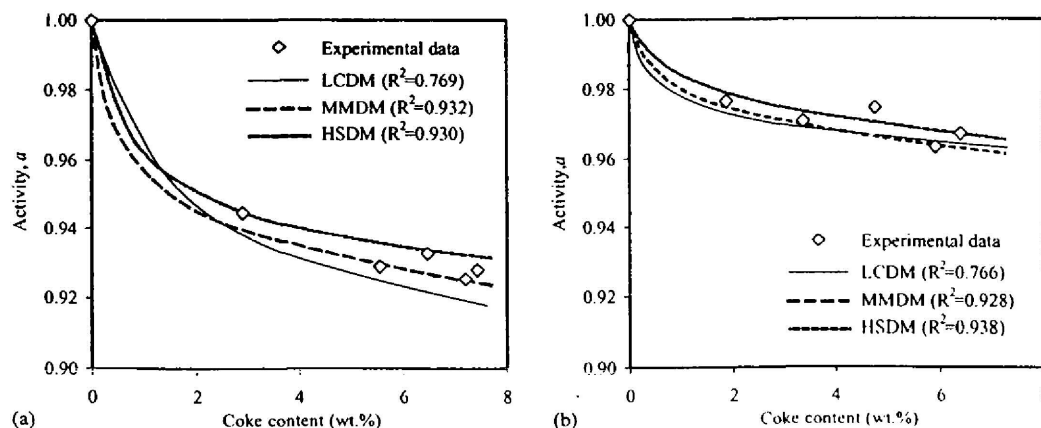


Fig. 5. Profiles of activity with coke content of Cr-ZSM-5 as predicted by the models and experimental data during the combustion: (a) ethyl acetate; (b) benzene at 400 °C.

Table 3
Model selection criteria (MSC) values of MMDM and HSDM

Model	Model selection criteria	
	Ethyl acetate	Benzene
MMDM	0.72	0.46
HSDM	0.88	0.59

4.3.3. Activity-coke profiles

The profiles of activity against coke content for ethyl acetate and benzene are as shown in Fig. 5(a) and (b), respectively. The three models proposed were used to predict activity against total coke content data. LCDM showed clear negative deviation at higher coke content while MMDM and HSDM both gave better predictions for ethyl acetate. With benzene, HSDM showed slightly better fit compared to MMDM. Since both MMDM and HSDM gave predictions comparable to the experimental data, model selection criteria (MSC) was performed on the two models. Table 3 shows the comparison of the two models using model selection criteria for both ethyl acetate and benzene. It is clear from the table that HSDM was slightly better than MMDM in describing the relation between activity and coke content with higher values of model selection criteria for both ethyl acetate and benzene.

5. Conclusions

Deactivation by coking of Cr-ZSM-5 during the combustion of VOC can be modeled by separating the inter-related coke formation function and the deactivation function. Heterogeneous surface deactivation model (HSDM) was found to satisfactorily fit the experimental data with meaningful physical interpretation of the kinetic parameters. The model predicted progressive coke content and activity with time-on-stream and demonstrated best fit of activity-coke content profile for both ethyl acetate and benzene. In line with experimental observations, this model predicted faster activity drop with lower residual activity during the combustion of ethyl acetate. Combustion reaction of ethyl acetate and benzene could take place over both coking sites (S_c) and metal sites (S_t) but, the role of S_t was more dominant especially in benzene combustion.

Acknowledgements

IRPA research grant (08-02-05-1039 EA 001) from The Ministry of Science, Technology and Environment of Malaysia (MOSTE) and zeolite samples from Süd Chemie AG are gratefully acknowledged.

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