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BEHAVIOUR OF COKING PROCESS IN CATALYTIC COMBUSTION OF ETHYL ACETATE AND BENZENE IN AIR OVER Cr-ZSM-5 CATALYST

Ahmad Zuhairi Abdullah*, Mohamad Zailani Abu Bakar and Subhash Bhatia

School of Chemical Engineering, Engineering Campus
Universiti Sains Malaysia, Seri Ampangan
Nibong Tebal, 14300 Pulau Pinang, Malaysia.
***(chzuhairi@eng.usm.my)**

ABSTRAK: *Kajian kelakuan dan kinetik pengkokan mangkin Cr-ZSM-5 (Si/Al=240) semasa proses pembakaran etil asetat (EAc) dan benzena (Bz) dilaporkan. Model kinetik pengkokan yang melihat proses pengkokan sebagai gabungan pengumpulan kok jenis monolapisan dan 'whisker' telah diuji. Pengkokan Cr-ZSM-5 dilakukan dengan cara mendedahkan mangkin itu terhadap kepekatan suapan VOC yang berbeza-beza antara 2,000 ppm dan 32,000 ppm bagi setiap bahan organik tersebut pada GHSV 3,800 jam*$^{-1}$ *di antara 200°C dan 600°C sehingga 12 jam. Pembentukan kok didapati bergantung kepada kepekatan suapan dan mencapai tahap maksimum pada suhu sekitar 300°C dan 400°C masing-masing bagi etil asetat dan benzena. Pada suhu yang lebih tinggi, data ujikaji boleh diramalkan dengan tepat oleh model pengkokan. Berbanding pemalar kadar bagi pengkokan jenis 'whisker'* (k_w)*, pemalar kadar bagi pengkokan jenis monolapisan* (k_m) *untuk etil asetat didapati lebih peka terhadap perubahan suhu. Namun, ia adalah sebaliknya bagi benzena. Model kinetik pengkokan ini mencadangkan yang pengkokan dan pembakaran bahan organik berlaku pada tapak aktif yang berlainan.*

ABSTRACT: The coking behaviour and kinetic study of Cr-ZSM-5 (Si/Al=240) catalyst during ethyl acetate (EAc) and benzene (Bz) combustion are reported. Coking kinetic model seeing the process as a combination of monolayer-type and whisker-type coke accumulations was tested. Coked Cr-ZSM-5 was prepared by exposing the catalyst to different feed concentrations from 2,000 ppm to 32,000 ppm of each organic at a GHSV of 3,800 h^{-1} between 200°C to 600°C for up to 12 h. Coke formation was feed concentration-dependent and was at its maximum at around 300°C and 400°C for ethyl acetate and benzene, respectively. Above these temperatures, the experimental data fitted the coking model. Compared to the whisker-type coking rate constant (k_w), the monolayer-type coking rate constant (k_m) for ethyl acetate was found to be more sensitive to temperature change while it was vice versa for benzene. The kinetic model also suggested that coking and organic combustion occurred at different active sites.

KEYWORDS: VOC, ethyl acetate, benzene, Cr-ZSM-5, coking, kinetics.

MATERIALS AND METHODS

Preparation of Cr-ZSM-5

Na-ZSM-5 (Si/Al=240) sample was obtained from Sud-Chemie and was used as received. Chromium exchanged ZSM-5 was prepared in two steps. In the first step, NH_4^+ exchange of Na-ZSM-5 was performed in 2.25 M NH_4Cl solution for 6 h. The chromium exchange step was done in acidified (to pH 4) aqueous solution of 0.086 M $Cr(NO_3)_3$ for 6 h followed by filtration, drying and calcination at 500°C for 6 h. Before use in the reactor, the catalysts were palletised, crushed and sieved between 0.25-0.30 mm.

Experimental set up

The preparation of coked Cr-ZSM-5 and activity study was performed using an 11 mm i.d. glass reactor (Figure 1). VOC-laden air stream as feed to the reactor was generated by bubbling nitrogen gas through the VOC saturators. Another flow of high purity air was used to make up the total flow rate to give the desired gas hourly space velocity (GHSV). The accurate control of flow rate was achieved by means of Aalborg (AFC 2600) mass flow controllers. The reactor was operated at atmospheric pressure and the reaction temperature of the catalyst bed was monitored using K-type thermocouple temperature probe. The feed and product gases were analysed using an off-line Shimadzu GC-8A gas chromatograph. A 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. All the experiments were conducted under oxygen-rich condition.

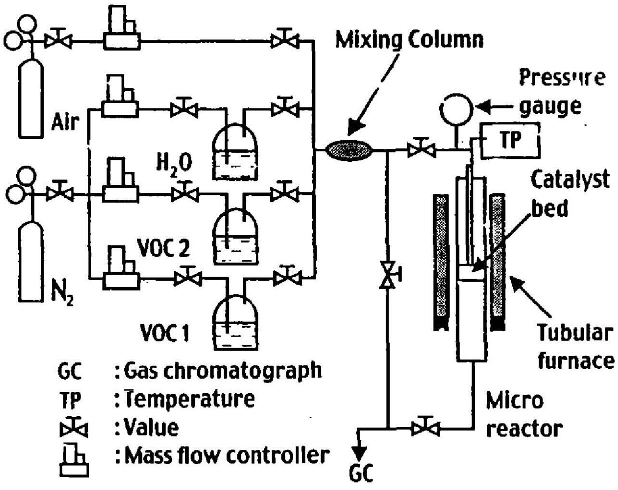

Figure 1. Schematic diagram of reactor system

MODELLING OF COKING PROCESS

Coking process can be modelled with some insight into the mechanism involved. In zeolites, coking initiates on the Brønsted acid sites to form the primary or monolayer coke (Sahoo *et. al.,* 2001). Subsequent coking can either form on the new (different) acid sites or on the primary layer to form the secondary, normally in the form of whisker-like coke (Romeo *et. al.,* 1999). These two types of coke play different roles in the activity and selectivity, and their relative concentrations depend on the reactions leading to their formation. At an early stage of the reaction, while the organic conversion is still high, coke forms rapidly on acidic sites (monolayer-type coke) while high amounts of coke precursors are formed. These sites will gradually self-deactivate and lead to a decrease in the rate of its formation. Simultaneously, the whisker-type coke grows in weak interaction with and anchored on monolayer coke. Thus, total coke content and the overall rate of coke formation can be written as;

$$C = C_m + C_w \qquad (2)$$

$$r_c = \frac{dC}{dt} = \frac{dC_m}{dt} + \frac{dC_w}{dt} \qquad (3)$$

The rate of monolayer coke formation is considered to be a function of available coking sites on the primary catalytic surface and is calculated as;

$$\frac{dC_m}{dt} = k_m(C_{m,max} - C_m)^h \qquad (4)$$

where k_m stands for the constant rate of monolayer-type coke formation, $C_{m,max}$ is the maximum amount of coke in monolayer, C_m is 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 whiskers is assumed to be constant (k_w) at a given temperature;

$$\frac{dC_w}{dt} = k_w \qquad (5)$$

Several values for h were tested on trial-and-error basis and it was found that the best results were obtained with h=2. Thus, integrating Equations 4 and 5 yields;

$$C = C_m + C_w = \frac{C_{m,max}k'_m t}{1 + k'_m t} + k_w t \text{ where } k'_m = k_m C_{m,max} \qquad (6)$$

Parameters $C_{m,max}$, k_m and k_w can be estimated by non-linear regression of the experimental data obtained in the TGA analysis.

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

Characteristics	**Catalyst**			
	Na-ZSM-5	**Cr-ZSM-5**	**[b]Cr-ZSM-5(EAc)**	**[c]Cr-ZSM-5(Bz)**
S_{BET} (m^2/g)	393	366	326	338
Micropore area (m^2/g)	321	272	183	213
Mesopore area (m^2/g)	72	94	143	125
Chromium loading (%)	-	0.98	0.98	0.98
[a]Crystallinity (%)	100	96	78	85
Acidity (mmol NH_3/g_{cat})	0.28	0.25	0.10	0.16
Coke content (wt. %)	-	-	7.6	6.4

[a] Relative to parent Na-ZSM-5

[b] Exposed to 32,000 ppm of ethyl acetate for 12 h at 400°C.

[c] Exposed to 32,000 ppm of benzene for 12 h at 400°C.

Coking activity is concentrated around acid sites and these sites will be masked upon deposition of coke (Antunes *et. al.,* 2001). The blockage of pore mouth by coke also rendered some unmasked acid sites inaccessible tor ammonia adsorption in acidity determination. The effect was observed as reduced acidity of coked Cr-ZSM-5. Coking with ethyl acetate caused more loss in the acidity of the catalyst as compared to that of benzene reaction. This was attributed to higher amount of coke accumulated with ethyl acetate reaction that caused the masking of more acid site.

Effect of feed concentration on coking

The total amount of coke accumulated with time on stream was found to be strongly dependent on ethyl acetate and benzene feeds concentration as shown in Figure 2(a) and 2(b), respectively. More coke accumulation with higher feed concentration was ascribed to the presence of higher concentration of reactant as starting material toward the formation of coke. The effect was also observed as higher coking rate (or steeper slope in Figure 2) at lower time on stream with higher concentration of feed organics.

More compounds in the product stream provide more reaction pathways toward the formation of coke. In ethyl acetate combustion, products of incomplete combustion detected in the outlet stream were acetic acid, acetaldehyde, formic acid, formaldehyde and carbon monoxide The concentration of these intermediates was higher with higher feed concentration as the oxidation process was less complete. In contrast, benzene produced only carbon monoxide as the carbon-containing compound in the product stream. Therefore, the starting material to form coke should be the benzene molecule itself, as short-lived intermediates could not participate in slow coke formation reactions.

higher reaction temperature resulted in higher mobility and faster diffusion of coke precursors to avoid condensation and subsequent coke growth. Again, the presence of coke precursors at high temperature was short-lived and could not participate in rate-limiting steps to further weaken the rate of coke formation on the catalyst.

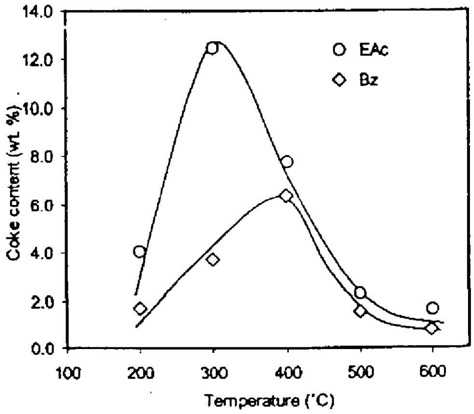

***Figure 3.** Profiles of coke content at the end of 12 h time on stream with reaction temperature for ethyl acetate (EAc) and benzene (Bz) combustion. (Reaction temperature=400°C, GHSV=3,800 h^{-1}).*

Coking kinetic modelling

i) Dependence of k_m and k_w on feed concentration

The estimated k_m and k_w values were found to increase with an increase in organic feed concentration as shown in Figure 4(a) and Figure 4(b), respectively. The increase was attributed to higher concentration of feed reactants and/or intermediates in the reaction system. For both organics, an increase in feed concentration had more significant effect on k_m than on k_w. As the feed concentration was increased from 2,000 ppm to 32,000 ppm, the values of k_m quadrupled while that of k_w only doubled. Values of these two parameters for benzene were found to be lower than that of ethyl acetate.

The values of k_m were generally about two orders of magnitude larger than their corresponding k_w values. This result suggested that the formation of monolayer-type coke on acid sites proceeded at higher rate to be the main contributor to overall coking while whisker-type coke grew at lower and constant rate on the primary coke until all the coking sites on the monolayer were exhausted. Then the overall coking activity prevailed at a much lower rate which was equal to k_w.

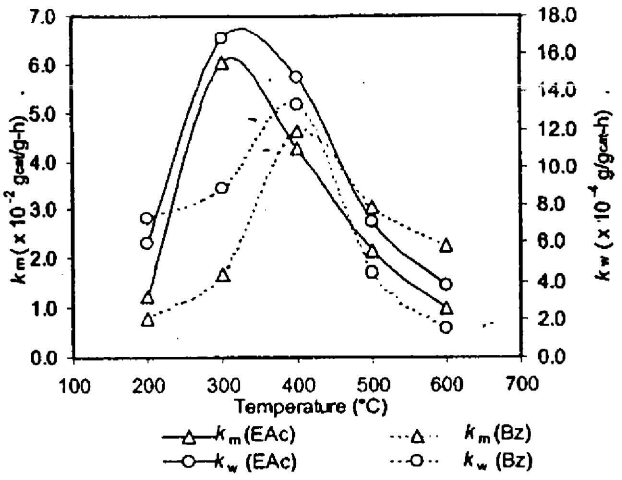

Figure 5. k_m and k_w values as a function of reaction temperature for ethyl acetate (EAc) and benzene (Bz) combustion (C_{voc}=32,000 ppm)

unreacted. It could also be due to the limitations of the kinetic model or the existence of many simultaneous processes involved in the coke formation and growth, which were not considered in the model. In zones best represented by the model, negative values of activation energies obtained clearly suggested the negative dependence of coking with reaction temperature. Again, the k_m value for ethyl acetate was found to be more sensitive to temperature change as it had larger value of activation energy. As for benzene, it was the reverse.

Table 2. Summary of kinetic parameters with 32,000 ppm of feed organics

Ethyl acetate		**Benzene**	
Parameters	r^2	**Parameters**	r^2
<300°C		**<400°C**	
$C_{m,max}$ =7.87 x 10^{-2} g/g_{cat}		$C_{m,max}$ =8.75 x 10^{-2} g/g_{cat}	
k_m =1.43 exp (-950/T) g_{cat}/g-h	0.780	k_m =2.04x10^{-1} exp (-666/T) g_{cat}/g-h	0.825
k_w =1.33x10^{-2}exp(-622/T)g/$g_{cat\cdot h}$		k_w =2.12x10^{-3} exp (-222/T) g/$_{gcat}$-h	
p=0.12		p=0.16	
>300°C		**>400°C**	
$C_{m,max}$ =7.87 x 10^{-2} g/g_{cat}		$C_{m,max}$ =8.75 x 10^{-2} g/g_{cat}	
k_m =2.40x10^{-3}exp(1024/T)g_{cat}/g-h	0.968	k_m =5.54x10^{-3} exp (850/T) g_{cat}/g-h	0.980
k_w =1.16x10^{-4} exp (866/T) g/g_{cat}-h		k_w =2.32x10^{-6} exp (2561/T) g/g_{cat}-h	
p= 0.05		p=0.04	

CONCLUSION

Chromium exchange process of Na-ZSM-5 was found to cause the material to lose about 15% of its micropore area, 4% drop in crystallinity but the effect on its acidity was negligible Catalyst coking was found to reduce all the above characteristics especially when ethyl acetate was used as the organic feed. Higher concentration of feed resulted in more coke accumulation. Coke formation process was found to be at its maximum at around 300°C for ethyl acetate and 400°C for benzene. Above these temperatures, kinetic model that assumed the coking process to be a combination of monolayer-type and whisker-type cokes accumulation satisfactorily fitted the experimental data. Compared to the whisker-type coking rate constant (k_w), the monolayer-type coking rate constant (k_m) for ethyl acetate was found to be more sensitive to temperature change with a higher apparent activation energy but it was vice versa for benzene. The higher values of $C_{m,max.}$ averaged at 8.75×10^{-2} g/g$_{cat}$ for benzene, compared to 7.87×10^{-2} g/g$_{cat}$ for ethyl acetate, reflected the higher density of coke resulting from the combustion of the former substance. This kinetic model also suggested that coking and catalytic combustion of VOC molecules occurred at two different active sites.

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NOTATION

a	activity
C	coke content (g/g$_{cat}$)
C_m	actual amount of coke in the monolayer (g/g$_{cat}$)
$C_{m,max}$	maximum amount of coke in monolayer (g/g$_{cat}$)
C_{voc}	concentration of ethyl acetate or benzene in the feed (ppm)
E_c	activation energy of coking reaction (kJ/mole)
$F_{voc,in}$, $F_{voc,out}$	molar flow rate at the inlet and outlet of the reactor, respectively (mol/h)
h	number of active sites involved in the controlling steps of coke formation
k_m	rate constant of monolayer-type coke formation (g$_{cat}$/g-h)
k_w	rate constant of whisker-type coke formation (g/g$_{cat}$-h)

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