# CATALYTIC DECOMPOSITION OF VOLATILE ORGANIC COMPOUND (VOC) POLLUTANTS IN AIR STREAM OVER CHROMIUM EXCHANGED ZEOLITES

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## ABSTRACT

The catalytic activity and stability studies of chromium exchanged beta (Cr-BEA), mordenite (Cr-MOR) and ZSM-5 (Cr-ZSM-5) zeolites of different Si/Al ratios for VOCs decomposition are reported. A continuous flow fixed-bed catalytic reactor operated between reaction temperatures of 100° to 500°C and at GHSV of 32,000 hour$^{-1}$ was used in this study. Methanol (MeOH), ethyl acetate (EAc), methyl ethyl ketone (MEK), benzene (Bz), hexane (Hex), toluene (Tol) and xylene (Xyl), all at the concentration of 2,000 ppm, were selected as VOC model compounds. The activity of these catalysts was found to be associated with their metal loading and types and shapes of pore system. Oxygen-containing VOCs were found to be both more reactive and producing good carbon dioxide yield upon decomposition on Cr-BEA (Si/Al=25) due to the presence of highly reactive sites for catalytic action. Aromatics, on the other hand, were generally more stable but the stability decreased when its electronic structure was perturbed with the attachment of electron donor group like methyl to the aromatic ring. Cr-ZSM-5 (Si/Al=240) showed highest hydrothermal stability due to its high Si/Al ratio. Deactivation study using 25,600 ppm of ethyl acetate and conducted at 400°C and GHSV of 3,800 hour$^{-1}$ revealed that Cr-ZSM-5 (Si/Al=240) can sustain its activity due to its stability and low affinity towards accumulation of coke. Cr-BEA(Si/Al=25), despite giving the highest initial activity due to high metal loading, was less stable especially after 30 hours time on stream but it showed the best carbon dioxide yield in the long run. Cr-ZSM-5 (Si/Al=240) accumulated more carbonaceous coke as confirmed by the TGA test.

*Keywords*: VOC, decomposition, zeolites, deactivation, coke.

## 1.0 INTRODUCTION

Catalytic decomposition is considered to be an effective way for reducing the emissions of volatile organic compounds (VOCs) from stationary sources. Its operating costs are lower with respect to thermal combustion and more flexible than other means of VOCs removal from air streams such as adsorption, absorption or condensation.

The reactivity of VOCs to be catalytically decomposed is expected to be very much depending on their chemical nature (Isaacs, 1995). A model VOC for decomposition study should be selected on 'worst player' basis that is the most difficult compounds to be decomposed. As the reaction parameters such as conversion and carbon dioxide yield are strongly influenced by feed concentration, it need to be maintained constant for meaningful result.

Beside conventional catalyst supports being used in VOC catalytic decomposition such as alumina, silica, titania and mixed metal oxides, zeolites are also one of the potential support reported (Becker and Forster, 1998 ; Niu *et al.*, 1999). Some prelimirary works have been reported using zeolite Y (Karmakar and Greene, 1992 ; Dégé *et al.*, 2000) and ZSM-5 (Chintawar and Greene, 1997) to host active metal species. The stability of ZSM-5 is reported to be much higher compared to zeolite Y for high temperature and often high humidity application (Atwood et al., 1998 ; Chintawar and Greene, 1997). Limited review is reported on other zeolites such as beta (BEA) and mordenite (MOR) despite having found application in many industrial processes.

Zeolite pore structure plays major role in hosting metal catalysts, diffusion and adsorption of reactants as well as coke formation in the reaction catalyzed by zeolite (Chen *et al.*, 1994). Coke formation is another aspect of catalytic activity that is strongly associated with zeolitic pore structure as what have been concluded by Dégé *et al.* (2000) in their study on coke formation during *o*-xylene decomposition on Pd-HFAU.

This study addresses the reactivity study of VOC model compounds and comparative study on the deactivation behaviour of chromium exchanged beta (Cr-BEA), mordenite (Cr-MOR) and ZSM-5 (Cr-ZSM-5) zeolites of different Si/Al ratios. Emphasis has been given on the catalytic activity, hydrothermal stability and coke formation of the zeolite catalysts. Chromium has been used in this study as it has been identified as the most active metal among the transition metals for VOC decomposition

## 2.0 EXPERIMENTAL

Chromium exchanged zeolites were prepared in two steps. In the first step, $NH_4^+$ exchange of the zeolite was performed in 2.25 M of $NH_4Cl$ solution for 6 hours. The metal exchange step was done using acidified (pH 4) 28.85 mmol/l of aqueous $Cr(NO_3)_3$ solution (3 % metal loading), for 6 hours followed by filtration, drying and calcination at 500°C for 6 hours. All zeolite samples were characterized for surface area using Quantachrome Autosorb-1 and final metal loading using Shimadzu AA-6650 atomic absorption spectroscopy (AAS).

The catalytic activity test was performed in an 11 mm i.d. glass reactor charged with 0.2 gram of zeolite catalysts (Figure 1). A VOC-laden stream was obtained by bubbling $N_2$ through the required organic liquid and another air flow was used to make up the total flow rate. The total flow rate was fixed at 250 ml/min to give corresponding GHSV of 32,000 hour$^{-1}$ while the concentration of organics in the reactor feed stream was targeted to be at 2,000 ppm. The inlet and outlet gases were analyzed using an off-line Shimadzu GC-8A gas chromatograph equipped with Porapak-Q and Molecular Sieve 5A columns. Methanol (MeOH), ethyl acetate (EAc), methyl ethyl ketone (MEK), benzene (Bz), hexane (Hex), toluene (Tol) and xylene mixed isomers (Xyl) were taken as VOC model compounds.

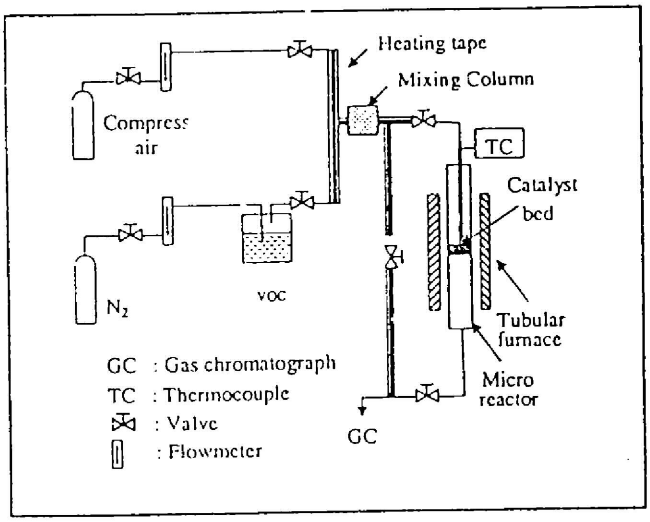

Figure 1 : Experimental set up for catalyst activity testing.

In the hydrothermal deactivation study, the catalyst samples were subject to steam treatment while heated at 500°C for 6 hours. These hydrothermally treated samples were then characterized for loss in BET surface area, and structure stability. The deactivation study on time on stream was performed by operating the catalytic reactor at GHSV of 3,800 hour$^{-1}$ and reaction temperature of 400°C. The conversion of ethyl acetate at feed concentration of 25,600 ppm and corresponding carbon dioxide yield was taken to represent the catalytic activity on time on stream of up to 48 hours. The high feed concentration was used to accelerate the rate of coke formation at the reaction temperature which allowed sufficiently high activity but not too high to decompose any coke formed. At the end of 48 hours, the used zeolite catalysts were characterized for BET total surface area and pore size distribution to determine the extent of deactivation occurred. Thermal gravimetric analyses (TGA) in 20 ml/min of oxygen and at increasing temperature of 10°C/min were also conducted to characterize the extent of catalyst coking and their oxidizability.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Catalysts Characteristics

Table 1 summarizes the characteristics of zeolite catalysts prepared and used in the present study. In general, the BET surface area for beta is the highest followed by mordenite and ZSM-5. Metal exchange procedures are found to cause less than 10 % drop in BET surface area. Corresponding reductions in micropore area are also detected while mesopore area is adversely affected. This could be due to the introduction of bigger $Cr^{3+}$ cation in place of smaller $H^+$ cation into zeolites structure and partial structural changes due to heat treatment during metal exchange process. The extent of metal exchange is found to decrease as the Si/Al ratio of the zeolite increased.

The difficulty in exchanging a multivalent cation such as $Cr^{3+}$ in ZSM-5s as compared to beta and mordenite stems from the weak anionic field, hydrophobicity and low density of $AlO_4$ tetrahedra particular to those zeolites. An increase in Si/Al ratio further decreased the density of $AlO_4$ tetrahedra and so the cation-exchange capacity dropped.

The possibility of precipitation of $[Cr(OH)_n^{(3-n)+}]$ type species in the zeolites was insignificant as the cation exchanges were carried out under acidic conditions. Also, the zeolites were washed thoroughly after every cation exchange. Therefore, it can be hypothesized that the chromium cations present were in the exchange positions.

Table 1
Characteristic of Cr-exchanged zeolites samples as compared to their original H-form.

| Catalyst* | BET surface area ($m^2/g$) | Metal loading (%) | Pore area | | |
|---|---|---|---|---|---|
| | | | Micro ($m^2/g$) | Meso ($m^2/g$) | Average pore size (Å) |
| H-BEA(25) | 500 | - | 365 | 135 | 22.8 |
| H-BEA(50) | 557 | - | 430 | 127 | 22.6 |
| H-MOR(40) | 429 | - | 364 | 65 | 22.2 |
| H-MOR(90) | 413 | - | 319 | 94 | 22.2 |
| H-ZSM-5(90) | 374 | - | 291 | 83 | 22.4 |
| H-ZSM-5(240) | 393 | - | 321 | 72 | 22.5 |
| Cr-BEA(25) | 488 | 0.99 | 341 | 147 | 23.5 |
| Cr-BEA(50) | 415 | 0.74 | 334 | 111 | 23.6 |
| Cr-MOR(40) | 419 | 0.88 | 359 | 70 | 23.8 |
| Cr-MOR(90) | 374 | 0.72 | 283 | 91 | 23.3 |
| Cr-ZSM-5(90) | 364 | 0.78 | 278 | 86 | 23.3 |
| Cr-ZSM-5(240) | 353 | 0.66 | 282 | 71 | 22.8 |

* Values in bracket denote Si/Al ratio of the zeolites.

### 3.2 Catalyst Activity Studies

Catalytic decomposition of several selected VOCs is depicted in Figures 2 (a) and (b). Figure 2 (a) shows the reactivity in terms of conversion at 300°C and 400°C of various VOC tested. Figure 2 (b) shows carbon dioxide yield from different VOC. The conversion, and hence, the reactivity of oxygenated compound was relatively higher compared to that of linear paraffin like *n*-hexane. Aromatic compounds, on the other hand show some degree of stability. The attachment of methyl group to benzene ring; one in toluene and two in xylene, is found to markedly improve the reactivity of the compounds.

Methanol, ethyl acetate and methyl ethyl ketone are reactive as they had oxygen-containing groups; well known electron-withdrawing groups. The oxygen atom had unpaired electron that can easily interacted with vacant $p$-orbital of chromium ion in zeolite. In methanol, destabilization effect was brought about by methyl group as an electron-donating group. The destabilization of ethyl acetate compound by ethyl group attached to electron-rich acetate group. In methyl ethyl ketone, electron deficiency experienced by carbonyl carbon atom is lessened by the attachment of methyl and ethyl groups as electron-donating groups. As such, this compound is quite stable as compared to ethyl acetate.

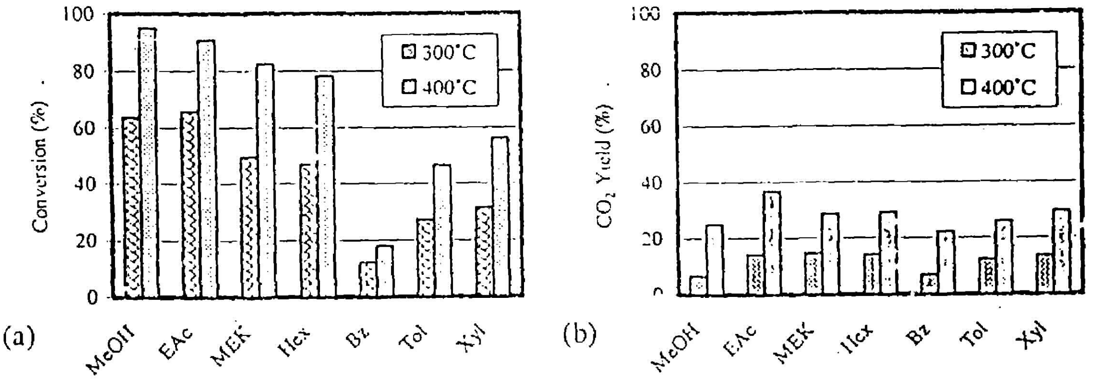

Figure 2 : Conversion (a) and carbon dioxide yield (b) in the conversion of different organics at 300°C and 400°C. (Cr-BEA(25), GHSV=32,000 hour$^{-1}$, $C_{VOC}$=2,000 ppm).

Benzene was the least reactive substance due to the occurrence of resonance effect in its ring. Methyl group in toluene did not possess a $p$- or $\pi$-orbital to conjugate with the $\pi$-molecular orbital of the aromatic system. Since methyl was an electron-donating group, the stability of the substance was lowered as benzene ring itself was an electron-rich group. In a similar way, the reactivity of xylene was higher than that of toluene and benzene. The stability of these substances could also be seen from their ionization potential i.e. 9.24 eV (benzene), 8.82 eV (toluene), 8.56 eV ($o$-xylene) and 8.45 eV ($p$-xylene).

Carbon dioxide, as the ultimate VOC oxidation product was readily formed when oxygenated compounds were decomposed (Figure 2(b)). The highest carbon dioxide yield was achieved with ethyl acetate while benzene demonstrated the lowest carbon dioxide yield. Still, as in reactivity, the carbon dioxide yield increased from benzene to xylene.

### 3.3 Catalytic activity of Cr exchanged zeolites

Catalytic decomposition of benzene as the most stable compounds studied was used to demonstrate the activity of various chromium exchanged zeolites. The result is shown in Figure 3. Cr-BEA(25) was found to be the most active followed by Cr-ZSM-5(240). Cr-MOR at both Si/Al ratios were the least active ones. In terms of carbon dioxide yield, Cr-BEA(50) and Cr-ZSM-5(240) produced high and almost similar selectivity while those of mordenite supported catalysts did not even reach 50% below 500°C.

Cr-BEA(25) was the most active catalyst in the present study. With comparatively bigger pore system and low Si/Al ratio, the exchange of chromium ion was favoured and consequently resulted in high metal loading. An increase in Si/Al ratio from 25 to 50 weakened the chromium intake by the zeolite and the activity dropped as shown in Figure 3(a). Cr-ZSM-5 at both Si/Al ratios were moderately active as they possess uniform channels system to allow easy diffusion of reactant and products. Despite having higher chromium loading, Cr-ZSM-5(90) was less active compared to Cr-ZSM-5(240). This could be due to hydrophobicity which increased with an increase in Si/Al ratio (Chintawar and Greene, 1997).

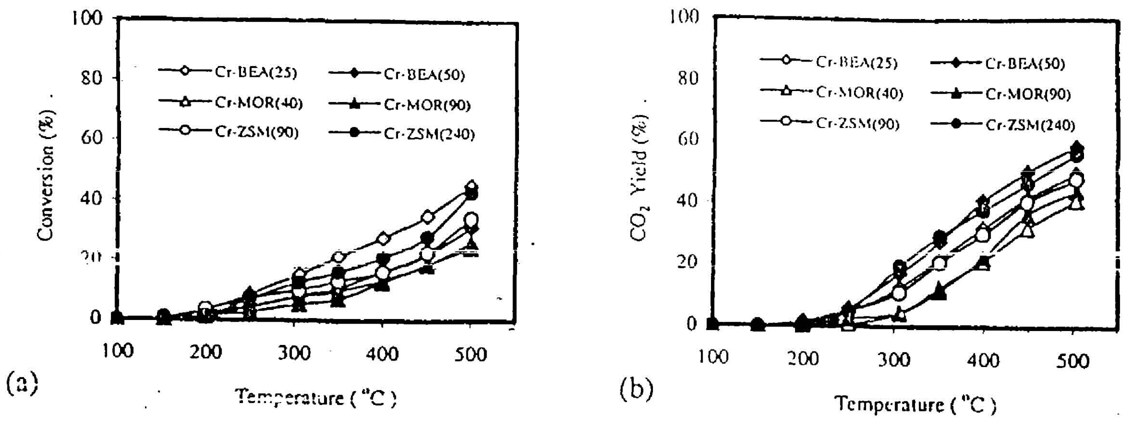

Figure 3 : Conversion (a) and carbon dioxide yield (b) in the conversion of benzene (Bz) for different chromium exchanged zeolites. (GHSV=32,000 hour$^{-1}$, $C_{Bz}$=2,000 ppm).

The low activities of Cr-MOR(40) and Cr-MOR(90) were attributed partly to their low metal loading. The mordenite 12-membered ring channels were crossed by 8-membered ring channels with aperture size of 2.8 x 5.7 Å. These apertures are actually windows rather than channels and are not readily accessible to chromium ions during metal exchange (Chen *et al.*, 1994. In addition, such narrow apertures make it difficult for benzene molecule to diffuse.

### 3.4 Hydrothermal stability

Hydrothermal stability is an important factor and must be tested after exposure to severe hydrothermal treatment. Unfortunately, as for any other catalysts, zeolite based catalysts may also undergo some physical and chemical changes to consequently resulted in changes in their surface characteristics. Table 2 summarizes several changes on surface characteristics as a result of hydrothermal deactivation test.

Table 2
Effect of hydrothermal treatment on catalysts' surface characteristics.

| Catalyst | Percent effect on* | | | |
|---|---|---|---|---|
| | BET surface area | Micropore area | Mesopore area | Average pore size |
| Cr-BEA(25) | -16.4 | -14.0 | +31.5 | +9.8 |
| Cr-BEA(50) | -9.6 | -11.7 | +17.2 | +8.7 |
| Cr-MOR(40) | -51.3 | -70.7 | +41.0 | +7.3 |
| Cr-MOR(90) | -21.7 | -31.4 | +8.6 | +8.4 |
| Cr-ZSM-5(90) | -11.3 | -17.0 | +1.6 | +4.3 |
| Cr-ZSM-5(240) | -6.2 | -8.1 | +1.2 | +3.6 |

*Relative to fresh catalysts.

Table 2 shows that the hydrothermal treatment eliminated some of the micropore of the zeolites and new mesopores were formed. The reduction in micropore area varied from more than 70 % for Cr-MOR(90) to less than 10 % for Cr-ZSM-5(240) reflecting the stability of the letter. Cr-ZSM-5(240) was the most stable one with minimal changes in surface characteristics with the stability adversely affected by an increase in alumina component in its lattice structure. The stability of the material was contributed by its hydrophobic nature to withstand the effect of water.

The changes in zeolite surface characteristics by water at high temperatures were mainly attributed to the occurrence of dealumination. During dealumination, aluminium atoms are extracted from zeolites framework often with partial structural collapse among the consequences. This can be directly translated into loss of surface area and crystallinity.

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## 3.5 Effect of coking on catalytic activity

The profile of catalytic activity during ethyl acetate conversion with time on stream is depicted in Figure 4. Cr-ZSM-5(240) showed the most stable conversion with only about 5 % drop in conversion after 48 hours time on stream. Cr-BEA(25), despite quite stable for the first 18 hours, experienced relatively sharper deactivation after this period. There was no clear trend observed for carbon dioxide yield except Cr-BEA(25) gives best yield in the long run.

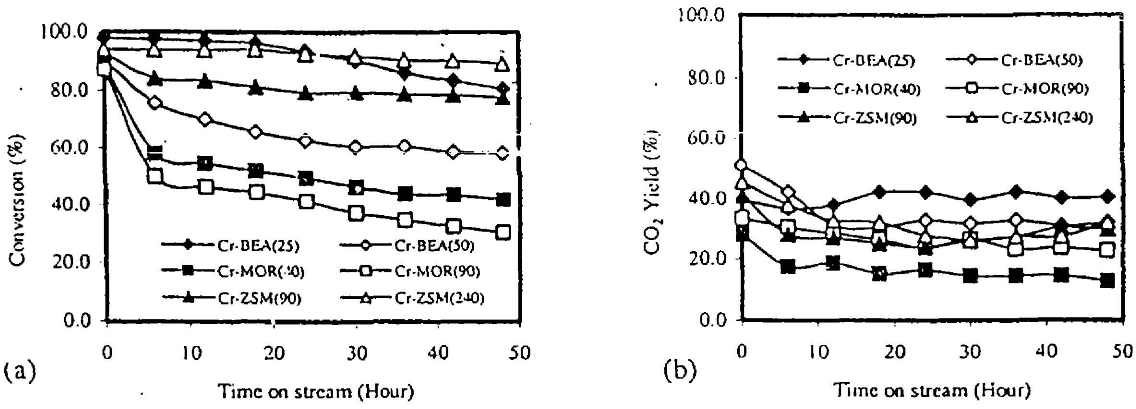

Figure 4 : Profile of ethyl acetate (EAc) conversion (a) and carbon dioxide selectivity (b) with time on stream. (Reaction temperature=400°C, GHSV=3,800 hour$^{-1}$, $C_{EAc}$ =25,600 ppm).

The much lower coke production and thus much lower rate of deactivation of ZSM-5 can be related to its three dimensional channel structure. The uniform channels and the absence of bottlenecks in its pore system easily permit the entrance of feed molecules as well as the leaving of the product molecules (Chen *et al.*, 1994). Other contributing factors include their high Si/Al ratio and the geometrical constrain imposed by the 10-membered oxygen ring sized pores. The former factor means lower acidity, thus lower coke forming tendency (Dégé *et al.*, 2000) while latter factor make it sterically difficult to form the large polynuclear hydrocarbons responsible for coking and irreversible deactivation (Chen *et al.*, 1994).

Mordenite as well as beta exhibited high tendencies to coking as they possessed intersecting channels of two different sizes. It was also evident that the pore structure exerts a very large effect on the rate of coking as bulky molecules might trapped within and end up as coke deposits (Chen *et al.*, 1994). Zeolites with large 12-membered oxygen ring openings which include MOR and BEA or those possessing supercages such as zeolite Y deactivate much more rapidly than zeolites with medium or small pores.

The accumulation of coke caused the zeolite catalysts to loose significant portion of their surface area as summarized in Table 3. The extent of area loss was different depending on the type of zeolite support with the worst can be observed with both Cr-MOR catalysts. Cr-ZSM-5 catalysts on the other hand, experienced the least loss in the BET surface area. More coke was formed with higher Si/Al ratio catalysts. This could be explained from the fact that more chromium was exchanged with these zeolites and thus, the resultant catalysts were more acidic due to more lewis acid sites. High acidity, was always associated with high tendency to coke formation (Dégé *et al.*, 2000).

Figure 5 depicts the profile of weight loss with temperature while the coked samples were heated in 100 ml/min of pure oxygen. For the purpose of clarity only curves for Cr-BEA(50), Cr-MOR(90) and Cr-ZSM-5(240) were plotted as the effect of different Si/Al ratio on the characteristic weight loss was not clearly noted. Oxidation of coke was found to start from as early as 150°C with steady decrease in weight until a sudden drop detected in the 350°C to 550°C region depending on the type of samples. The temperature at which this drop occurs reflects the ease or difficulty for coke to be oxidized and was in the following order;

Cr-ZSM-5(240) > Cr-MOR(90) > Cr-BEA(50)

Table 3
Effect of catalyst deactivation on their surface characteristics.

| Catalyst | Percent effect on* | | | |
|---|---|---|---|---|
| | BET surface area | Micropore area | Mesopore area | Average pore size |
| Cr-BEA(25) | -79.9 | -92.8 | -50.6 | +105.8 |
| Cr-BEA(50) | -20.0 | -19.7 | -41.4 | +12.9 |
| Cr-MOR(40) | -90.0 | -97.2 | -54.3 | +23.8 |
| Cr-MOR(90) | -21.9 | -19.4 | -47.6 | +19.4 |
| Cr-ZSM-5(90) | -80.8 | -80.6 | -38.0 | +8.6 |
| Cr-ZSM-5(240) | -18.9 | -12.2 | -26.7 | +7.4 |

* Relative to fresh catalysts.

TGA results concluded that although Cr-ZSM-5(240) collected less coke, the coke formed on this catalyst would be more stable to oxidation. In other words, it is more carbonaceous than that forming on Cr-BEA(50) than Cr-MOR(90). This type of coke normally derived from molecules that are too large to enter the pores of the zeolite (5.5Å). Through hydrogen transfer and dealkylation reactions, these molecules continued to become more carbonaceous (higher in atomic H/C ratio). Softer and less carbonaceous cokes that were forming on Cr-BEA(50) and Cr-MOR(90) normally formed by oligomerization or alkylation reactions within the zeolites (Chen *et al.*, 1994).

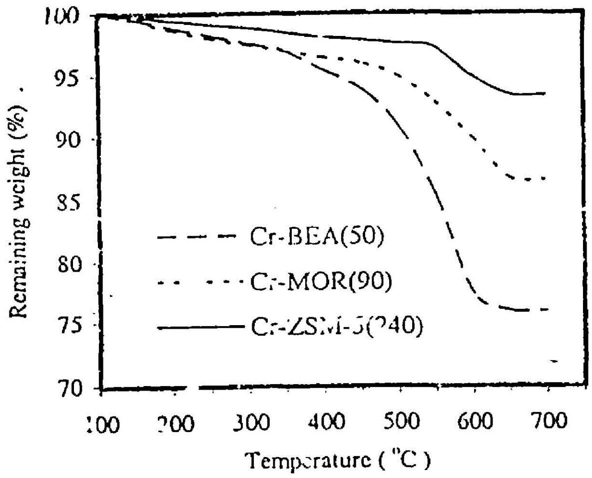

Figure 5 : Profile of weight loss during thermal gravimetric analysis for three different chromium exchanged zeolites. (Conditions : 10°C/min, 20 ml/min oxygen).

Chen *et al.* (1994) from their review on wide variety of organic molecules came to the conclusion that a lattice model with randomly placed coke molecules successfully simulated the empirical results of following expression;

$$\frac{D_c}{D} = \frac{1}{(1+0.23C_c)} \tag{1}$$

Here, $D_c$ is the diffusivity of coked zeolite, $D$ is diffusivity of uncoked zeolite and $C_c$ is the weight percent coke in the zeolite. Table 4 summarizes coke content obtained from TGA result and calculated diffusivity ratio using equation 1. Cr-BEA catalysts were found to collect more coke compared to Cr-MOR and Cr-ZSM-5 with the diffusivity stood at 15% of the original value. However, clear correlation between diffusivity and ethyl acetate conversion (in Figure 4) could not be established as the activity of the catalyst may not solely proportional to the diffusion of reactants. The location of coke deposition either at the pore mouth or inside the pore can also affect the catalyst activity.

Table 4
Coke content and diffusivity ratio of zeolite catalysts after 48 hours exposure to 26,500 ppm of ethyl acetate at 400°C, GHSV=3,800 $hour^{-1}$.

| Catalyst | Coke content (%) | $D_c/D$ |
|---|---|---|
| Cr-BEA(25) | 24.2 | 0.15 |
| Cr-BEA(50) | 24.0 | 0.15 |
| Cr-MOR(40) | 14.2 | 0.23 |
| Cr-MOR(90) | 13.4 | 0.25 |
| Cr-ZSM-5(90) | 7.0 | 0.38 |
| Cr-ZSM-5(240) | 6.5 | 0.40 |

## 4.0 CONCLUSION

Oxygenated VOCs with carbonyl (C=O) group were found to be both very reactive and showing good carbon dioxide yield. Aromatics were stable but the reactivity increased when the electron cloud in a benzene ring was perturbed by an electron donor group such as methyl group. Deactivation study revealed that Cr-ZSM-5 (240) was the most stable catalyst. Despite giving the highest initial activity due to high metal loading, Cr-BEA(Si/Al=25) was less stable and deactivated especially after 30 hours time on stream but it showed the best carbon dioxide yield in the long run. The high coke formation in MOR and BEA zeolites was associated with the presence of interconnecting channels of different sizes and the relatively bigger pore sizes compared to ZSM-5. The high stability of Cr-ZSM-5(240) was attributed to its high Si/Al to resist structural collapse during thermal treatment and smaller pore system to avoid pore clogging due to the accumulation of coke. Coke forming on Cr-ZSM-5(240) was more carbonaceous and more resistant to oxidation as confirmed by TGA test.

## 5.0 ACKNOWLEDGEMENT

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