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Perfromance of Chromium-Exchanged Zeolite Catalysts in the Combustion of Volatile Organic Compound Pollutants

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The activity and stability of chromium-exchanged beta (Cr-BEA), mordenite (Cr-MOR), and ZSM–5 (Cr-ZSM–5) zeolites of different Si/Al ratios for volatile organic compounds (VOCs) combustion were reported. A fixed-bed catalytic reactor operated between 100 and 500 °C and at a gas hourly space velocity (GHSV) of 32,000 h^{-1} was used for the study. Methanol, ethyl acetate, methyl ethyl ketone, benzene, hexane, toluene, and xylene, all at 2,000 ppm, were selected as the VOC model compounds. Oxygenated VOCs were more reactive while showing good carbon dioxide yield. Aromatics were more stable due to their resonance effect but the reactivity increased with the attachment of an electron donor group such as the methyl group. Cr-ZSM–5(240) demonstrated the highest hydrothermal stability due to its high Si/Al ratio. Despite giving a high initial activity due to its high metal loading, Cr-BEA(25) was susceptible to coking in the long run. The high coke formation in mordenite and beta zeolites was attributed to their high acidity, interconnecting channels of different sizes, and relatively larger pore sizes. The coke that formed on Cr-ZSM–5(240) was more carbonaceous and oxidized at higher temperatures.

Keywords: Coke, chromium-exchanged zeolites, combustion, deactivation, stability, *and* volatile organic compounds (VOC).

INTRODUCTION

Volatile organic compounds (VOCs), which are emitted in dilute concentrations by many industrial processes, can be most effectively abated by catalytic combustion. This process is similar to thermal combustion in that the gaseous organic impurities to be destroyed are reacted with oxygen at elevated temperatures to form primarily carbon dioxide and water (Zhang, Zhao, and Chuang 1997). However, it differs from thermal combustion since the reaction occurs at relatively lower temperatures of 150–480 °C using solid catalysts (Kohl and Nielsen 1997). This lower operating temperature translates as lower energy requirement to run the catalytic unit.

The reactivity of VOCs to be catalytically decomposed is influenced by their chemical nature (Isaacs 1999). A model VOC for combustion study is generally selected on a "worst player" basis, depending on the compounds that are most difficult to decompose. There are cases, however, where the reactivity of a VOC is catalyst-specific. Ordóñez et al. (2002) found that benzene was more reactive than toluene over Pt/Al_2O_3 while Petterson et al. (1999) reported higher reactivity for toluene over Rh/Al_2O_3.

Aside from the conventional catalyst supports being used for VOC-catalytic combustion such as alumina, silica, and titania, zeolites are among the potential supports that are actively being investigated for their role in this process (Becker and Forster 1998, Niu et al. 1999). Some promising results 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 that of zeolite Y at high temperatures and also more suitable for application under high humidity (Chintawar and Greene 1997, Atwood et al. 1998).

Limited information is available on other zeolites such as beta (BEA) and mordenite (MOR) despite having found application in many industrial processes. These zeolites possess higher surface area and organic sorption than ZSM–5 (Chen, Degnan, and Smith 1994). Together with their characteristic pore structures, the differences in the behavior of their supported catalysts in VOC-combustion application is expected.

Catalyst coking in zeolite-catalyzed reaction is a function of acidity and pore structure (Blauwhoff 1999). Coke formation results from undesirable side-reactions occurring on strong acid sites that are responsible for hydrogen transfer reactions (Sahoo et al. 2001). Pore structure plays a significant role in the coke-accumulation process as it affects the condensation of coke and/or coke precursors which are normally made up of polyaromatic rings (Antunes et al. 2001). Generally, zeolites with narrow pore mouths, or windows, while having a sinusoidal channel system are more susceptible to coking (Chen, Degnan, and Smith 1994). In most reactions, a 3D interconnected pore system will minimize coke accumulation by allowing coke precursors to exit from any of its pore mouths (Blauwhoff 1999). In this type of pore system, the tendencies of coke accumulation on the channel intersections have been reported by several authors (Guisnet, Dégé, and Magnoux 1999; Bartholomew 2001).

This paper investigates the reactivity of various VOC-model compounds as well as the combustion behavior of the most stable organic compounds. A comparative study of the hydrothermal stability and activity of chromium exchanged beta (Cr-BEA), mordenite (Cr-MOR), and ZSM-5 (Cr-ZSM–5) zeolites of different Si/Al ratios were conducted. The amount and characteristics of coke accumulated on these catalysts were correlated with their acidity and types of pore system. Chromium was used as the active metal species in this study since it was identified as the most active metal among the transition metals for VOC combustion (Zuhairi, Zailani, and Bhatia 2003a, 2003b).

EXPERIMENTAL

Zeolite beta (BEA, Si/Al=25 and 50), mordenite (MOR, Si/Al=40 and 90), and ZSM–5 (ZSM–5, Si/Al=90 and 240) were obtained from Süd-Chemie AG in their sodium form and were used as received. Chromium-exchanged zeolites were prepared in two steps. In the first step, the NH_4^+ exchange of the zeolite was performed in 2.25 M of NH_4Cl solution for 6 h. The metal exchange step was carried out in acidified (pH 4) 28.85 mmol/l of aqueous $Cr(NO_3)_3$ solution for 6 h, followed by filtration, drying, and calcination at 550°C for 6 h. The chromium-exchanged zeolites were pressed, crushed, and sieved between 250 to 300 μm before being used in the activity studies. All zeolite samples were characterized for surface area using a Quantachrome Autosorb–1, final metal loading using a Shimadzu AA–6650 atomic absorption spectroscopy (AAS), and acidity via thermal desorption of ammonia (NH_3–TPD) using a Quantachrome Chembet 3000 system.

The catalytic activity test was performed in an 11-mm I.D. glass reactor charged with 0.2 g of zeolite catalysts (see Figure 1). The accurate control of the flow rates was achieved by means of Aalborg AFC–2600 mass flow controllers. A VOC-laden stream was obtained by bubbling N_2 gas through a VOC saturator containing the required organic and another air flow was used to make up the total flow rate. The total flow rate

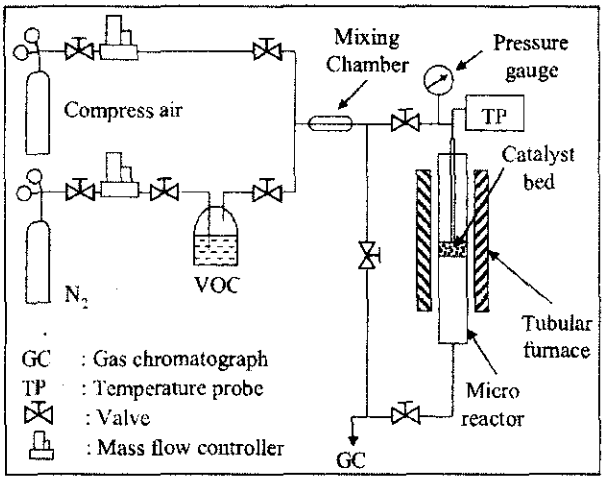

Figure 1. Experimental Setup for Catalyst-Activity Testing

was fixed at 250 ml/min to give the corresponding gas hourly space velocity (GHSV) of 32,000 h^{-1} while the concentration of organics in the reactor feed stream was fixed 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 for the separation of gas components. The components were detected by means of a thermal conductivity detector (TCD). 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.

In the hydrothermal stability study, the catalyst samples were subjected to steam treatment at 500°C for 6 h. These hydrothermally treated samples were then characterized for changes in surface characteristics. The deactivation behavior of the catalysts with time on stream was demonstrated by operating the catalytic reactor at a GHSV of 3,800 h^{-1} and at a reaction temperature of 400°C for up to 48 h. The conversion of ethyl acetate at a feed concentration of 25,600 ppm and corresponding CO_2 yield were taken to represent the catalytic activity. At the end of 48 h, the aged zeolite catalysts were taken out and characterized for surface characteristics to determine the extent of deactivation. Thermal gravimetric analyses (TGA) in 20 ml/min of oxygen and at a temperature ramping rate of 10 °C/min were also conducted to characterize the extent of coking and to study the oxidizability of the coke. The molar H/C ratios of the coke formed on the catalysts were determined using a Perkin–Elmer Elemental Analyzer.

RESULTS AND DISCUSSION

Characteristics of catalysts

Table 1 summarizes the characteristics of zeolite catalysts prepared for and used in the present study. In general, the Brunauer-Emmet-Teller (BET) surface area measurement for beta was the highest followed by mordenite and ZSM–5. The chromium-exchange procedure was found to cause less than 10% drop in the BET surface area. Corresponding reduction in micropore area was also detected while mesopore area was adversely affected. This could be due to the introduction of bigger Cr^{3+} cation in place of smaller Na^+ cation into the zeolites' structure and partial structural changes due to heat treatment during the chromium-exchange process. The extent of chromium exchange was found to decrease as the Si/Al ratio of the zeolite

Table 1. Characteristics of Cr-Exchanged Zeolite Samples vs. Their Original Na Form

Catalyst^a	S_{BET} (m^2/g)	Cr loading (%)	Pore Area Micro (m^2/g)	Pore Area Meso (m^2/g)	Acidity mmol NH_3/g
Na-BEA(25)	500	-	365	135	nd
Na-BEA(50)	557	-	430	127	nd
Na-MOR(40)	429	-	364	65	nd
Na-MOR(90)	413	-	319	94	nd
Na-ZSM–5(90)	374	-	291	83	nd
Na-ZSM–5(240)	393	-	321	72	nd
Cr-BEA(25)	488	0.99	341	147	0.83
Cr-BEA(50)	415	0.74	334	111	0.58
Cr-MOR(40)	419	0.88	359	70	0.78
Cr-MOR(90)	374	0.72	283	91	0.56
Cr-ZSM–5(90)	364	0.78	278	86	0.43
Cr-ZSM–5(240)	353	0.66	282	71	0.18

^{a} Values in parentheses denote the Si/Al ratio of the zeolites.
nd = not determined

increased, a pattern that was attributed to the lower capacity of framework charge compensation in higher Si/Al zeolites.

The lower Si/Al zeolites possessed higher acidity since aluminum atoms were associated with acid sites that could take the form of Brønsted or Lewis acid sites. The relation, however, was not straightforward to be generalized for different types of zeolites because acidity was likewise determined by atomic arrangement in the framework structure and by the extra framework species present (Blauwhoff et al. 1999).

It was noted in this study that Cr-ZSM–5(90) was less acidic compared to Cr-MOR(90) which had the same Si/Al value. Similarly, Cr-BEA(50) showed almost similar acidity compared to that of Cr-MOR(90) despite having a relatively lower aluminum content in its framework.

VOC reactivity study

The catalytic combustion of several selected VOCs measured based on the conversion and CO_2 yield are as depicted in Figure 2a and Figure 2b, respectively. The conversion and, hence, the reactivity of oxygenated compounds, such as methanol, ethyl acetate, and methyl ethyl ketone, was relatively higher compared to that of a linear paraffin such as *n*-hexane. The aromatic compounds, however, showed some degree of stability. The attachment of a methyl group to the benzene ring, one in toluene and two in xylene, was found to markedly improve the reactivity of these compounds.

Methanol, ethyl acetate, and methyl ethyl ketone were more reactive as they had oxygen-containing groups which are well-known electron-withdrawing groups, making the adjacent C–O and C–H bonds more susceptible to breakage. The oxygen atom also had unpaired electrons that can easily interact with a vacant *p*-orbital of chromium ion in zeolite to form active intermediates. However, there was also the stabilizing effect that was brought about by the attachment of alkyl groups which were electron-donating groups. The stabilization of methanol was attributed to the presence of a methyl group, while that in ethyl acetate, the ethyl and methyl groups presented the stablizing effects on the carboxyl group. In methyl ethyl ketone, the electron- deficiency experienced by the carbonyl–carbon atom was lessened by the attachment of the methyl and ethyl groups. Consequently, this compound became relatively more stable compared to both ethyl acetate and methanol.

Benzene was the least reactive substance due to the occurrence of a resonance effect in its ring. Consequently, higher energy was required to cause the extraction of protons which would initiate its combustion. In toluene, the methyl group did not possess a *p*- or π-orbital to conjugate with the π-molecular orbital of the aromatic system. Thus, the resonance effects were only limited within the benzene ring. Since methyl was

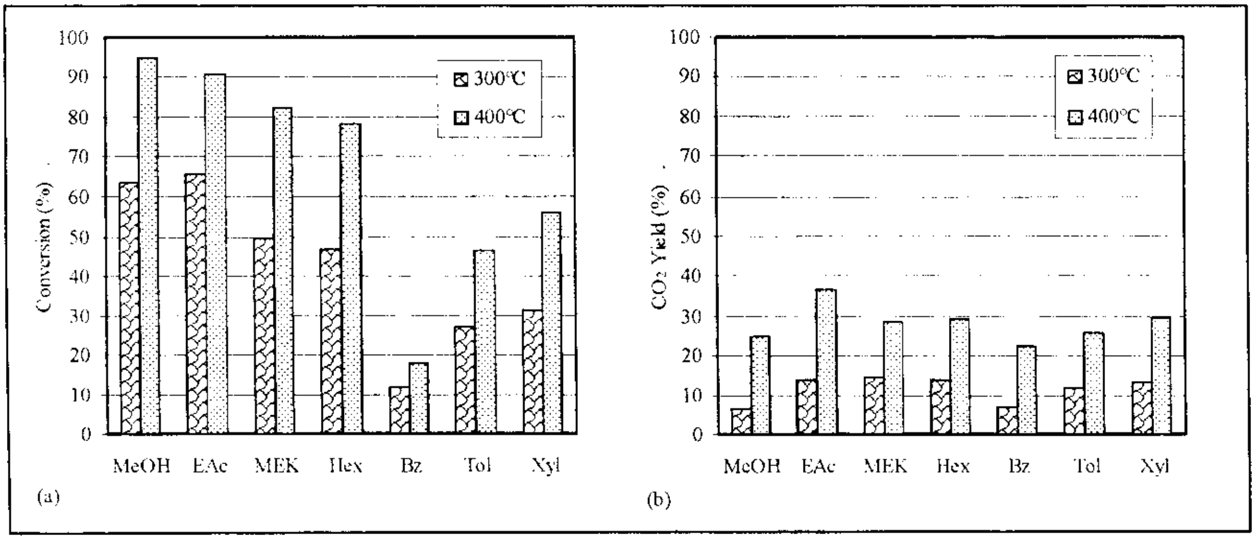

Figure 2. Conversion (a) and CO_2 yield (b) in the Conversion of Different Organics at 300°C and 400°C [Cr-BEA(25), GHSV=32,000 h^{-1}, and C_{voc}=2,000 ppm].

an electron-donating group, the stability of the substance was lowered since the benzene ring itself was an electron-rich group. The effect manifested as a marked increase in the conversion (*reactivity*) from benzene to toluene. Similarly, the reactivity of xylene with the two methyl groups was higher than that of toluene and benzene. The stability of these substances could also be seen from their ionization potential, namely: 9.24 eV (benzene), 8.82 eV (toluene), 8.56 eV (*o*-xylene) and 8.45 eV (*p*-xylene).

Despite their being readily decomposed, methanol, ethyl acetate, and methyl ethyl ketone did not produce a high CO_2 yield as suggested by Figure 2b. This was due to the occurrence of significant amounts of products of incomplete combustion in the outlet stream with these organics. Generally, these organics were in the form of aldehydes and carboxylic acids. However, as in the reactivity, the CO_2 yield increased from benzene to xylene. With these aromatic compounds, the only product of incomplete combustion detected in the outlet stream was carbon monoxide

Effects of zeolite supports on catalytic activity

The catalytic combustion of benzene as the most stable compound used in the present study was selected for demonstrating the activity of various chromium-exchanged zeolites. Figure 3 shows that Cr-BEA(25) was the most active catalyst, followed by Cr-ZSM-5(240). Cr-MOR at both Si/Al ratios was relatively less active with conversions falling below 30% in the temperature range studied. In terms of CO_2 yield, Cr-BEA(50) and Cr-ZSM-5(240) produced high and almost similar yields, while those of mordenite-supported catalysts did not even reach 50% below 500°C. As a general trend, higher chromium loading in lower Si/Al BEA, MOR, and ZSM-5 often resulted in higher conversion but at the expense of the CO_2 yield.

Cr-BEA(25) was the most active catalyst used in the present study. With a comparatively larger pore system and low Si/Al ratio, the exchange of chromium ion was favored and, consequently, resulted in high chromium loading. An increase in Si/Al ratio from 25 to 50 weakened the chromium intake by the zeolite and the activity dropped accordingly as shown in Figure 3a. Cr-ZSM-5 at both Si/Al ratios were moderately active as they possessed a relatively lower surface area and a uniformly sized interconnecting channel system to allow the easy diffusion of reactants and product molecules. Despite having higher chromium loading, Cr-ZSM-5(90) was less active compared to Cr-ZSM-5(240). This could be due to a higher hydrophobicity that generally increased with each increase in Si/Al ratio (Chintawar and Greene 1997). In this case, higher hydrophobicity translated as better organic sorption for this catalyst.

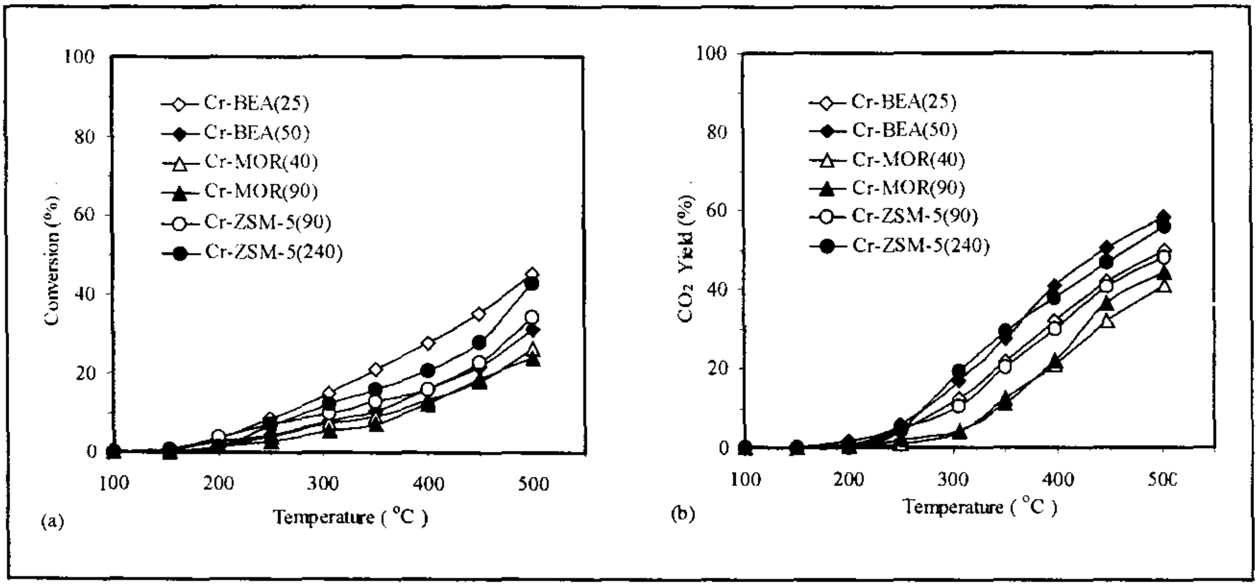

Figure 3. Conversion (a) and CO_2 Yield (b) in the Conversion of Benzene (Bz) for Different Cr-Exchanged Zeolites [GHSV=32,000 h^{-1} and C_{Bz}= 2,000 ppm].

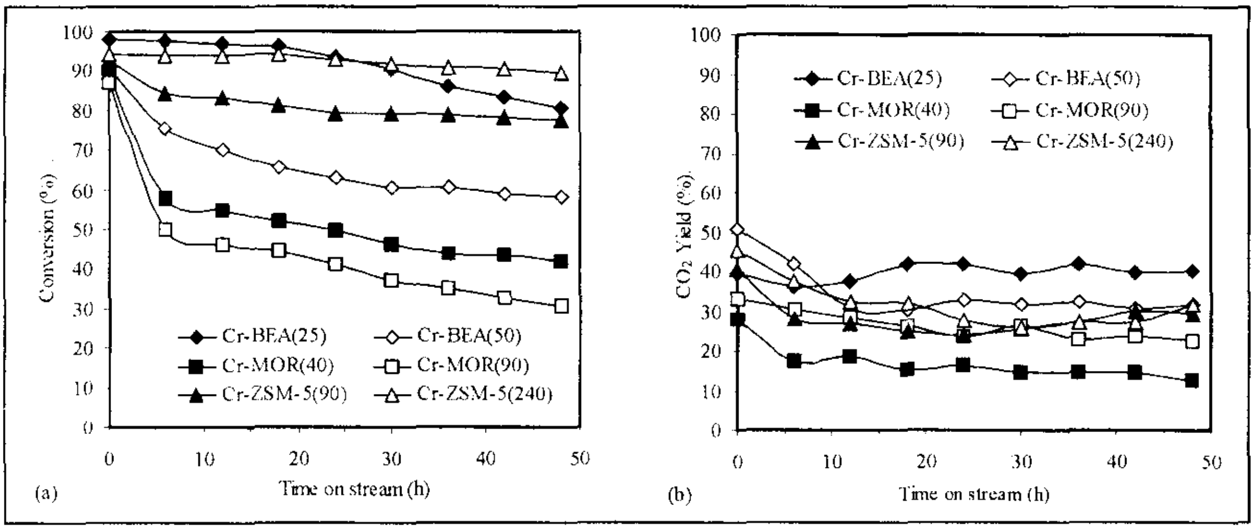

Figure 4. Profile of Ethyl Acetate (EAc) Conversion (a) and CO_2 Selectivity (b) with Time on Stream [Reaction Temperature=400°C, GHSV=3,800 h^{-1}, and C_{EAc}= 25,600 ppm].

The low activities of Cr-MOR(40) and Cr-MOR(90) were partly attributed to their pore system. Note that the mordenite pore structure consists of 12-membered ring channels that are crossed by 8-membered ring channels with aperture size of 2.8 x 5.7 Å. These apertures are actually windows rather than channels which are not readily accessible to benzene molecules due to steric effect (Chen, Degnan, and Smith 1999). Therefore, the reaction was only limited to the external surface of the zeolite crystal. Shorter diffusion path of the reactant and/or intermediates also constrained the repeated oxidation of these substances to ultimately produce CO_2. As a consequence, these two catalysts produced low CO_2 yield as shown in Figure 3b.

Hydrothermal stability test

Table 2 summarizes the changes in surface characteristics as a result of the hydrothermal stability test. The treatment was found to eliminate some micropores while new mesopores were created. 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 latter. All three types of zeolites, however, demonstrated higher stability with higher Si/Al ratio of the framework. In general, the most stable zeolite was ZSM–5, followed by BEA and MOR.

Table 2. Effects of Hydrothermal Treatment on Surface Characteristics

Catalyst	Percent effect on*		
	S_{BET}	Micropore Area	Mesopore Area
Cr-BEA(25)	-16.4	-14.0	+31.5
Cr-BEA(50)	- 9.6	-11.7	+17.2
Cr-MOR(40)	-51.3	-70.7	+41.0
Cr-MOR(90)	-21.7	-31.4	+ 8.6
Cr-ZSM–5(90)	-11.3	-17.0	+ 1.6
Cr-ZSM–5(240)	- 6.2	- 8.0	+ 1.2

* Relative to the fresh catalyst

Changes in the surface characteristics of the catalyst upon hydrothermal treatment were attributed to the hydrolysis of Si–O–Si and Si–O–Al bonds in the framework of the zeolite support (Kuhl 1999). Owing to the higher affinity of Si atom towards electron, O–Al bonds were relatively amenable to hydrolytic cleavage than O–Si to subsequently result in a partial framework collapse. The effect manifested itself as a decrease in micropore area but with an increase in mesopore area.

Thus, the higher hydrothermal stability demonstrated by higher Si/Al ratio zeolites was associated with the lesser number of aluminum atoms in their framework. In addition, higher Si/Al ratio also translated as higher hydrophobicity of the catalyst to resist hydrolytic effect by water molecules at high temperature.

Effects of coking on activity

In the study of coking process, ethyl acetate was used as the test substance having been found to cause the greatest coke accumulation compared to other substances. The profile of conversion and corresponding CO_2 yield during ethyl acetate combustion with time on stream are shown in Figure 4 a and Figure 4b, respectively. Cr-ZSM-5(240) showed the most stable conversion with only about 5% drop in the conversion after 48 h time on stream.

Although quite stable for the first 18 h, Cr-BEA(25) experienced relatively sharper deactivation after this period. With Cr-MOR at both Si/Al ratios, sharper drop in the conversion was observed during the first 6 h, after which relatively stable activity was achieved. There was no clear trend observed for CO_2 yield except that Cr-BEA(25) produced the best yield in the long run and that Cr-MOR(40) demonstrated the lowest yield.

The much lower coke production and, thus, the much lower rate of deactivation of ZSM-5 catalysts were both attributed to its 3D channel structure. The uniform channels and the absence of bottlenecks in its pore system easily permitted feed molecules to enter and product molecules to leave (Chen, Degnan, and Smith 1999). The two other contributing factors were low acidity and the geometrical constrain imposed by the 10-membered oxygen ring-sized pores. The former factor translated as lower coke formation activity (Dégé et al. 2000), while latter factor made it sterically difficult to form large polynuclear hydrocarbons responsible for coking and irreversible deactivation (Chen, Degnan, and Smith 1999).

Mordenite as well as beta exhibited high tendencies to coking for being of higher acidity and for having intersecting channels of two different sizes. Due to high acidity, the acid catalyzed dehydrogenation reaction was more active and led to fast coke formation, especially during early hours on stream. The effect was more noticeable in the smaller pored mordenite than in the bigger pored beta zeolite. The channel intersection generally acted as a window to trap coke precursors and end up as coke deposits in the large 12-membered oxygen ring openings (Chen, Degnan, and Smith 1999, Batholomew 2001). More activity reduction was observed with both Cr-MOR catalysts since most of the available active sites for VOC combustion were the ones that lined the bigger channels.

The accumulation of coke caused the zeolite catalysts to lose a significant portion of their surface area (see summary form in Table 3). The extent of area loss varied depending on the type of zeolite support. The worst effect was observed for both Cr-MOR catalysts which explains the greater deactivation evident in Figure 4a. In contrast, the Cr-ZSM-5 catalysts were the least affected by coking, even showing improved stability with their higher Si/Al ratio support.

Table 3. Effects of Catalyst Deactivation on Surface Characteristics

Catalyst	Percent effect on*		
	S_{BET}	Micropore Area	Mesopore Area
Cr-BEA(25)	-79.9	-92.8	-50.6
Cr-BEA(50)	-20.0	-19.7	-41.4
Cr-MOR(40)	-90.0	-97.2	-54.3
Cr-MOR(90)	-21.9	-19.4	-47.6
Cr-ZSM-5(90)	-60.8	-80.6	-38.0
Cr-ZSM-5(240)	-18.9	-12.2	-26.7

* Relative to fresh catalyst

Data in Table 3 show that upon treatment with ethyl acetate at 400°C for 48 h, Cr-MOR(40) experienced a greater drop in S_{BET} compared to Cr-MOR(90). However, it was Cr-MOR(90) that suffered more reduction in activity as suggested by Figure 4a. This contradiction could be explained based on several reasons. It was expected that at lower Si/Al ratio, Cr-MOR(40) was less hydrothermally stable and might have experienced significant framework loss after 48 h and the effect was observed as heavy S_{BET} loss. However, the chromium atoms in this catalyst, which were higher in amount compared to Cr-MOR(90), might still be available for ethyl acetate combustion. It was also possible that the main combustion reaction and coke formation occurred at different sites. In this circumstance, the loss of surface area due to coke accumulation did not necessarily lead to a corresponding loss of activity as the active sites (*metal sites*) on the catalyst were still available and accessible for reaction.

Coke analysis

Figure 5 depicts the profile of weight loss with temperature while the coke catalysts were heated in 20 ml/min of pure oxygen. For the purpose of clarity, only the curves for Cr-BEA(50), Cr-MOR(90), and Cr-ZSM–5(240) were plotted since the effects of the different Si/Al ratios on characteristic weight loss were not clearly observed.

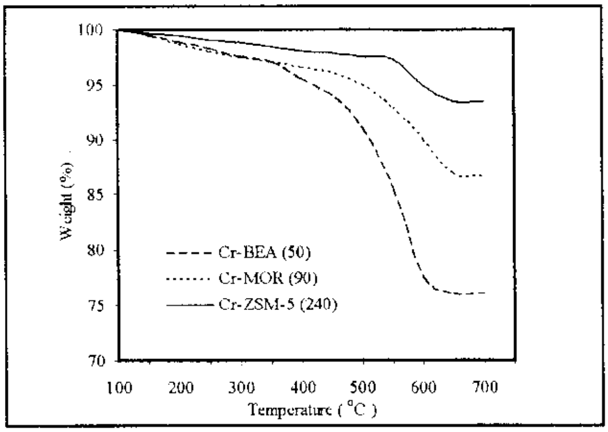

Figure 5. Profile of Weight Loss During TGA for Three Different Cr-Exchanged Zeolites [10*C/min and 20 ml/min oxygen]

The oxidation of coke was initiated from 150°C with a steady decrease in weight until a sudden drop was detected within the 350–550°C region depending on the type of sample. The temperature at which this drop occurred reflected the ease or difficulty for coke to be oxidized. In the present study, the oxidizability of coke followed this following order:

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

The TGA results concluded that although Cr-ZSM–5(240) accumulated less coke, the cokes that formed on this catalyst were more stable to oxidation. In other words, they were more carbonaceous than those which formed on Cr-BEA(50) and Cr-MOR(90) as confirmed by the data in Table 4. This type of coke normally derives from molecules that are too large to enter the pores of these zeolites that they accumulated at the pore intersections. Through hydrogen transfer and dealkylation reactions, these molecules continued to become more carbonaceous and the effect was observed as lower overall H/C ratio. Softer and less carbonaceous cokes that accumulated on Cr-BEA(50) and Cr-MOR(90) normally formed by oligomerization or alkylation reactions within the zeolites (Thomas, Degnan, and Smith 1999).

Table 4. Coke Content of the Catalysts Used and Their Corresponding H/C Ratio

Catalyst	Coke content (wt. %)	Coke H/C ratio
Cr-BEA(25)	25.7	1.72
Cr-BEA(50)	23.6	1.56
Cr-MOR(40)	16.4	1.43
Cr-MOR(90)	13.2	1.28
Cr-ZSM–5(90)	8.6	0.88
Cr-ZSM–5(240)	6.4	0.72

Table 4 shows that although zeolite beta-based catalysts are more prone to coking than mordenite-based catalysts, they experience less deactivation (as suggested by Figure 4a). For example, Cr-BEA(50) accumulated 23.6 wt.% coke after 48 h, but ethyl acetate conversion dropped only to about 61% while Cr-MOR(90) showed about 32% conversion upon accumulation of 13.2 wt.% coke.

This contradiction was due to several reasons. Despite experiencing an almost similar percentage drop in S_{BET} after treatment with ethyl acetate for 48 h, the actual S_{BET} of coked Cr-BEA(50) was still higher at 332 m^2/g compared to 292 m^2/g for Cr-MOR(90). Also, the pore system of beta zeolite was larger than that of mordenite to lessen the effects of diffusion limitation posted by coke deposition. This was especially true if the coke formed on the larger straight 12-membered ring channels of a beta zeolite. The contradiction also led to the possibility that coke deposition could occur on the different sites that were actively involved in the combustion reactions.

CONCLUSIONS

Oxygenated VOCs were found to be both very reactive and produced high CO_2 yield. Aromatics were more stable due to the resonance effect, but the reactivity increased when the electron cloud in the benzene ring was perturbed by an electron-donor group such as the methyl group.

Cr-ZSM–5(240) demonstrated the highest hydrothermal stability due to its high Si/Al ratio. Despite giving higher initial activity due to high metal loading, Cr-BEA(25) was less stable and deactivated rapidly, especially after 30 h on stream. Nevertheless, Cr-BEA(25) showed the best CO_2 yield in the long run.

High coke formation in mordenite and beta zeolites was attributed to their (a) high acidity, (b) interconnecting channels of different sizes, and (c) relatively larger pore sizes compared to ZSM–5. In contrast, the low coking tendency of Cr-ZSM–5 catalysts was attributed to their (a) lower acidity and (b) smaller interconnected pore system of uniform sizes. Likewise, coke-formation on Cr-ZSM–5(240) was more carbonaceous and oxidized at higher temperatures.

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