

# DEVELOPMENT OF ZEOLITE-BASED CATALYSTS FOR THE COMBUSTION OF VOCs IN AIR STREAM

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Chromium was found to be the most active transition metal for Volatile Organic Compound (VOC) combustion. Oxygenated VOCs were found to be relatively more reactive while aromatics were relatively stable. Chromium exchanged ZSM-5 (Si/Al=240) zeolite (Cr-ZSM-5(240)) showed high hydrothermal stability due to its high Si/Al ratio. The low coking tendency of this catalyst was attributed to lower acidity and the smaller interconnected pore system of uniform sizes. Coke forming on Cr-ZSM-5(240) was also found to be more carbonaceous and oxidatively decomposed at higher temperatures.



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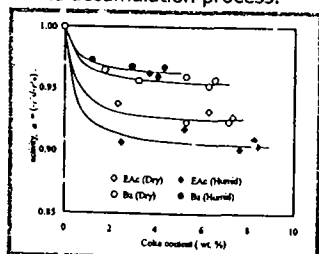
growth of larger metal crystallites. The incorporation of copper in Cr<sub>0.1</sub>Cu<sub>0.5</sub>Z shifted the product distribution towards lower temperatures i.e., to favour deep oxidation products.



Cr-ZSM-5(240) catalyst as seen under SEM (72.5 X).

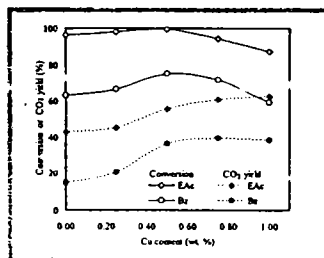
When the catalytic reactor was operated under oxygen-rich conditions, the variation in oxygen concentration had little effect on the conversion of ethyl acetate and benzene. Water vapour negatively affected the conversion of both organics, especially at lower temperatures. The inhibition was attributed to competitive adsorption between water and organic molecules for adsorption on the catalyst active sites. The presence of benzene as co-feed could promote the combustion of ethyl acetate while its conversion was adversely affected.

The combustion of ethyl acetate over Cr-ZSM-5(240) produced more coke and correspondingly, the catalyst experienced more deactivation compared to that of benzene combustion. Coke from ethyl acetate reactions, especially under humid conditions, made up oxygenated aromatics which were softer but caused more activity decay with time on stream. Reaction temperatures of 300°C and 400°C for ethyl acetate and benzene respectively resulted in the most active coke accumulation process.



Profile of activity with coke content for dry and humid ethyl acetate (EAc) and benzene (Bz).

A combination of 1.0 wt. % chromium and 0.5 wt. % copper in H-ZSM-5(240) supported a bimetallic catalyst (Cr<sub>1.0</sub>Cu<sub>0.5</sub>/Z) of slightly improved ethyl acetate and benzene conversions and gave marked improvements in carbon dioxide yields. At a higher metal loading, lower activity was associated with the blockage of ZSM-5 micro pores due to the

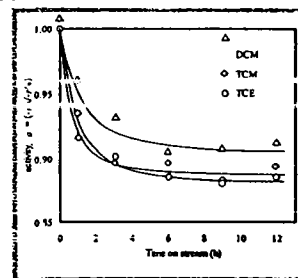


Effect of copper content in the Cr<sub>1.0</sub>Cu<sub>x</sub>/Z catalyst on the conversion and carbon dioxide yield

Changes in the characteristics of bimetallic chromium-copper supported over H-ZSM-5 modified with SiCl<sub>4</sub> and steam (Cr<sub>1.0</sub>Cu<sub>0.5</sub>/SiCl<sub>4</sub>-Z and Cr<sub>1.0</sub>Cu<sub>0.5</sub>/H<sub>2</sub>O-Z, respectively) were ascribed to extra framework deposits, changes in acid site distribution and mesopores created by extracted acid soluble extra framework species. Cr<sub>1.0</sub>Cu<sub>0.5</sub>/SiCl<sub>4</sub>-Z and Cr<sub>1.0</sub>Cu<sub>0.5</sub>/H<sub>2</sub>O-Z gave slightly lower conversion and carbon dioxide yield but were significantly more stable compared to Cr<sub>1.0</sub>Cu<sub>0.5</sub>/Z. Cr<sub>1.0</sub>Cu<sub>0.5</sub>/SiCl<sub>4</sub>-Z and Cr<sub>1.0</sub>Cu<sub>0.5</sub>/H<sub>2</sub>O-Z. These two catalysts also possessed less acid sites making them less susceptible to deactivation by coking. The coke formed was also relatively softer and easier to be decomposed in oxygen for activity regeneration.

The modification of H-ZSM-5(240) with silicon tetrachloride was found to further improve its chemical resistance against hydrogen chloride. Trichloromethane (TCM) was more reactive compared to dichloromethane (DCM) but produced more by-products due to its high chlorine content. Water vapour increased the carbon dioxide yield through its role as hydrolysis and hydrogen-supplying agents. The effect was more noticeable in trichloroethylene (TCE) combustion as it involved the formation of relatively unstable vinyl carbocation compared to DCM and TCM that gave rise to alkyl carbocations. Cr<sub>1.0</sub>Cu<sub>0.5</sub>/SiCl<sub>4</sub>-Z demonstrated high stability in its activity with time on stream and more deactivation was detected with higher Cl/H ratio feed substance. Chlorination of metal species in Cr<sub>1.0</sub>Cu<sub>0.5</sub>/SiCl<sub>4</sub>-Z was responsible for loss of activity due to the weakening of their overall reducibility which

was in agreement with the Mars-van Krevelen model.



Deactivation of the Cr<sub>1.0</sub>Cu<sub>0.5</sub>/SiCl<sub>4</sub>-Z catalyst in the combustion of DCM, TCM and TCE.

Several kinetic models proposing different reaction mechanisms such as the Power Law Model, the Eley-Rideal Model, the Langmuir-Hinshelwood-Hougen-Watson (LHHW) Model and the Mars-van Krevelen Model were studied for their accuracy and applicability in the modelling of the VOC combustion process. The Mars-van Krevelen model satisfactorily fitted the experimental data for the combustion of a single VOC component over Cr-ZSM-5(240). The effect of water on the reaction rate was satisfactorily modelling by a competitive adsorption mechanism based on this Mars-van Krevelen model. The competitive mechanism also satisfactorily predicted reaction rates in a binary mixture of ethyl acetate and benzene. In this process, oxidation and reoxidation of the catalysts active sites were identified as the rate limiting steps.

$$(-r) = \frac{k_0 x_s P_s P_v}{k_0 P_0 + x k_s P_v}$$

$$(-r'_{w/w}) = \frac{k_0 k_1 P_s P_v}{k_0 P_0 [1 + (k_w P_w / k_s P_s)] + x k_s P_v}$$

$$(-r'_{1/2}) = \frac{k_0 k_1 P_s P_v}{[k_0 P_0 (1 + (b_2 P_2 / b_1 A)) + x k_1 A + 1/2 k_2 (b_2 P_2^2 / b_1 A)]}$$

Mars-van krevelen model equations

Several deactivation models i.e.; the Lumped Coking Deactivation Model (LCDM), Monolayer-multilayer Coking Deactivation Model (MMDM) and the Heterogeneous Surface Deactivation Model (HSDM) were also developed and tested for the VOC combustion process. HSDM satisfactorily fitted the experimental data for Cr-ZSM-5(240) catalyst deactivation. This model also predicted that the initial site fractions (x<sub>0</sub> and x<sub>c0</sub>) were independent of the type of organic feed. In addition, the coking sites (S<sub>c</sub>) were predicted to be outnumbered by metal sites (S<sub>t</sub>) with a ratio of about 2.4 to 1. HSDM also accurately predicted more coke accumulation in ethyl acetate combustion as indicated by a higher value of the maximum coke amount (C<sub>max</sub>) for this organic. In terms of residual activity (a<sub>r</sub>), lower activity was expected in the combustion of ethyl acetate compared to benzene. The VOC combustion could take place on S<sub>t</sub> and S<sub>c</sub> with a dominant role played by S<sub>t</sub>, especially in the combustion of benzene.

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$$\frac{dC}{dt} = qC_{in}\phi_a \left[ 1 - \frac{C}{C_{sat}} \right]^n \quad a = \left[ x_w + \left( \frac{C_{sat} - C}{C_{sat}} \right) x_o \right] \quad a_f = \frac{\xi}{(\xi + 1)}$$

$$\frac{da}{dt} = \phi_a (a - a_f)^{\gamma} \quad \xi = \frac{(-r'_{St})_0}{(-r'_{Sc})_0} \quad \phi_a = 2\phi_{T0}^{q-1} (\xi + 1)^{(q-1)/\gamma} \phi_c$$

HSDM model equations

#### Research Significance

This research study has generated a better understanding of the characteristics, activity and deactivation of a zeolite-based catalyst in the combustion of VOCs as well as the behaviour of the process under various operating conditions. This allows for an affordable system to be built, installed and used by most of the small- and medium-sized industries (SMIs); the costs of the air treatment system are the main constraints for their failure or reluctance to treat air emission. Lower emission levels of VOCs could directly result in lower risks the industrial employees, in particular, and the public, in general. They may be affected by immediate and delayed effects associated with the presence of these organic substances in the environment.