

Combustion of Volatile Organic Compound (VOC) Pollutants In Air Stream Over ZSM-5 Supported Bimetallic Catalysts

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ABSTRACT

The performance of ZSM-5 supported bimetallic catalysts with chromium as the base metal in the combustion of ethyl acetate (EAc) and benzene (Bz) is reported. A catalytic reactor operated between 100° and 500°C and at gas hourly space velocity (GHSV) 32,000 h⁻¹ was used for activity measurement. Combination of 1.0 wt % chromium and 0.5 wt % copper was found to slightly improve the organic conversion while showing marked improvement in carbon dioxide yield especially with ethyl acetate. Higher metal loading, lower activity was associated with the blockage of ZSM-5 micropores due to the growth of bigger metal crystallites. The combustion of ethyl acetate produced acetaldehyde, acetic acid, formaldehyde, formic acid and carbon monoxide as the intermediate products while benzene produced only carbon monoxide. The incorporation of 0.5 wt % of copper in Cr_{0.1}Cu_{0.5}/Z shifted the product distribution towards lower temperatures.

Keywords: Bimetallic, catalyst, Combustion Products, VOC, ZSM-5

1.0 INTRODUCTION

There are numerous metals that are commonly used as active component of the catalysts for volatile organic compound (VOC) combustion. Despite showing high activity, noble metals (Pt and Pd) are not favoured due to their high cost and rapid deactivation (Brink *et al.*, 2000, Paulis *et al.*, 2000). Transition metals are potential replacements to noble metals with chromium being reported as the most active metal (Chintanar and Greene, 1997, Atwood *et al.*, 1998). However, single metal catalyst subjects to several drawbacks. An increase in metal loading always associated with an increase in the organic conversion but the yield towards carbon dioxide weakens (Degé *et al.*, 2000). The reactivity of different VOC over certain metal catalyst may also be catalyst specific. For example contradictory conclusions were reached on the reactivity of benzene and toluene over Pt/Al₂O₃ and Rh/Al₂O₃ reported respectively by Ordóñez *et al.* (2002) and Patterson *et al.* (1999).

In VOC combustion reaction, the organic reactants could be the feed or the intermediates. If the reactivity of any of these substances is low over the active metal component, the reaction will pose as the rate-limiting step (Minicò *et al.*, 2000). Since it is desirable to achieve high carbon dioxide yield at high conversion to suppress the occurrence of products of incomplete combustion, this rate-limiting step should be accelerated as much as possible. Thus, with the right combination of metals, bimetallic catalysts can improve the overall performance of the catalyst for a wider range of organic compounds (Alexandru and Gates, 2003).

The current study focuses on finding the right metal combination and its optimum composition to achieve complete combustion of VOC. Chromium was used as the base metal component as it was the most active transition metal for this application and the support used was H-ZSM-5. The performance of bimetallic catalysts was scrutinized on the basis of organic conversion, carbon dioxide yield and product distribution in the outlet stream. Ethyl acetate and benzene were selected as VOC model compounds because of differences in their chemical nature.

The ZSM-5 (Si/Al=240) zeolite sample was supplied by Sud-Chemie AG in the form of Na-ZSM-5. H-ZSM-5 was prepared by exchanging Na^+ cation with NH_4^+ in 2.25 M NH_4Cl for 12 h followed by filtration, drying and calcinations at 500°C for 3 h. The ZSM-5 supported bimetallic catalysts were prepared via impregnation method using respective nitrate solutions that were previously acidified to pH 4. The concentrations of these solutions were chosen such to give the desired final metal loadings. The solution was then evaporated to dryness, calcined at 500°C for 6 h, pressed and sieved to particle sizes of between 250-300 μm . All the catalyst samples were characterized for surface area using Quantachrome Autosorb-1.

The catalytic activity test was performed in an 11 mm id glass reactor charged with 0.2 g of zeolite catalysts and heated in a tubular furnace. VOC-laden air stream as feed to the reactor was generated by bubbling nitrogen gas through the VOC saturators. The flow of air was used to make up the total flow rate of 250 ml/min with corresponding gas hourly space velocity (GHSV) $32,000 \text{ h}^{-1}$ and feed concentration 2,000 ppm. The flow rate was controlled using Aalborg (AFC 2600) mass flow controllers. The feed and product gases were analyzed using an off line Shimadzu GC-8A gas chromatograph equipped with a Porapak Q column for the separation of carbon dioxide and organic components, and a Molecular Sieve 5A column for the separation of carbon monoxide.

RESULTS

The Catalyst Characteristics

The characteristics of all catalysts prepared in this study are given in Table 1. Depending on catalyst, metal impregnation resulted in a drop of up to 13.5% in BET surface area. Generally, this drop was correspondingly followed by a drop in micropore area while mesopore area slightly increased. With increasing copper content in $\text{Cr}_{1.0}\text{Cu}_x/\text{Z}$, BET surface area gradually decreased until the copper content reached 0.5 wt %, exceeding which, steeper slump was detected. An increase in mesopore area upon metal impregnation was ascribed to secondary pores formed by metal deposits especially at the external surface of the catalyst.

Table 1
Characteristics of the ZSM-5 Based Catalysts Prepared

Catalyst*	S_{BET} (m^2/g)	Metal loading (wt %)	Pore Area (m^2/g)	
			Micro	Meso
Z	386	-	315	71
$\text{Cr}_{1.0}/\text{Z}$	372	Cr (1.0)	297	75
$\text{Cr}_{0.5}\text{Fe}_{0.5}/\text{Z}$	360	Cr (0.5) & Fe (0.5)	279	81
$\text{Cr}_{0.5}\text{Co}_{0.5}/\text{Z}$	373	Cr (0.5) & Co (0.5)	284	89
$\text{Cr}_{0.5}\text{Cu}_{0.5}/\text{Z}$	368	Cr (0.5) & Cu (0.5)	286	82
$\text{Cr}_{0.5}\text{Mo}_{0.5}/\text{Z}$	356	Cr (0.5) & Mo (0.5)	276	80
$\text{Cr}_{0.5}\text{La}_{0.5}/\text{Z}$	359	Cr (0.5) & La (0.5)	288	71
$\text{Cr}_{1.0}\text{Cu}_{0.75}/\text{Z}$	366	Cr (1.0) & Cu (0.25)	286	80
$\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{Z}$	360	Cr (1.0) & Cu (0.5)	278	82
$\text{Cr}_{1.0}\text{Cu}_{0.75}/\text{Z}$	346	Cr (1.0) & Cu (0.75)	259	87
$\text{Cr}_{1.0}\text{Cu}_{1.0}/\text{Z}$	334	Cr (1.0) & Cu (1.0)	237	97

*Z=H-ZSM-5

Metal crystallites on H-ZSM-5 might have blocked some pores leading to reduction in surface area. Due to geometrical constraint by small sized pores of H-ZSM-5, the crystallites growth was mainly localized around pore intersections and external surfaces. However, minimal effect on total surface area was detected as H-ZSM-5 consisted of interconnecting pores with access was possible from parallel and lateral pores. At higher metal loading, bigger crystallites resulted which were only allowed to form on the external surface of the zeolites. Complete pore mouth blockage rendered surface area that lined the pore

is accessible leading to sudden reduction in the surface area is observed when more than 0.5 wt % of Cu were impregnated in $Cr_{1.0}Cu_x/Z$.

3.2 Catalytic Activity of Various Bimetallic Catalysts

Despite containing the same total metal content bimetallic catalysts showed slightly lower conversion of both ethyl acetate and benzene compared to $Cr_{1.0}/Z$ (control) as shown in Fig. 1(a). Increasing conversion was observed from Fe, Co and Cu i.e. moving from the left to the right of the first row of transition metals in the periodical table. Marked drop was observed with Mo (the element right below Cr (second row) in the transition metal series) while La produced comparable activity with that of Co. Fig. 1(a) shows that the best conversion was obtained with Cu as the second element in the bimetallic catalyst, slightly lower ethyl acetate conversion but almost similar benzene conversion with that of $Cr_{1.0}/Z$.

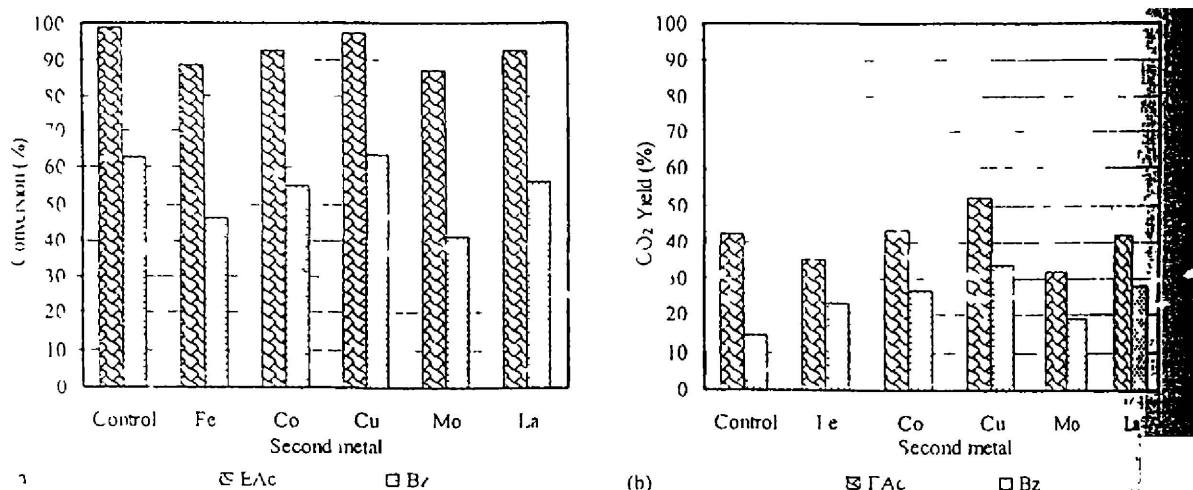


FIG. 1 Conversion (a) and Carbon Dioxide Yield (b) in the Combustion of 2,000 ppm of Ethyl Acetate (EAc) and Benzene (Bz) at 400°C Over $Cr_{0.5}/Z$ With Various Second Metals at 0.5 wt % as the Active Component (Control: $Cr_{1.0}/Z$).

Carbon dioxide yield also shows increasing trend when Fe, Co and Cu were used as the second component (Fig. 1 (b)). It should be noted that with bimetallic catalysts, an improvement in carbon dioxide yield was obtained with slight decrease in the conversion as compared to $Cr_{1.0}/Z$. The best carbon dioxide yield was demonstrated by Cu with narrower difference between carbon dioxide yield in ethyl acetate and benzene conversion compared to that of $Cr_{1.0}/Z$.

Chromium could present in multiple oxidation states by attachment to extra-lattice oxygen (Chintawar and Greene, 1997). Due to its high atomic radius, the electron in its outermost shell (3d) is relatively easier to be removed to present at higher oxidation states, thus, producing high redox potential. The high activity of chromium in VOC combustion was in agreement with the mechanisms proposed by Mars-van Krevelen model. When half of the metal content was replaced by other metal, lower activity resulted for both organics.

Among the second metals used, copper was the smallest in atomic radius. Thus, it showed lower tendency towards oxidation but probably higher tendency than chromium for reduction by VOC or intermediates during VOC combustion. Since intermediates especially carbon monoxide were better reducing agents, the oxidation of these species by oxidized copper species on H-ZSM-5 was more efficient and consequently produce higher carbon dioxide yield.

3.3 Effect of Copper Content on the Activity of $Cr_{1.0}Cu_x/Z$

Fig. 2 shows that below 0.5 wt %, increasing copper content in $Cr_{1.0}Cu_x/Z$ resulted in an increase in conversion and carbon dioxide yield. Further increase in copper content weakened the conversion but the same was not observed in carbon dioxide yield. These trends were shared by ethyl acetate and benzene indicating changes in conversion or carbon dioxide yield were explained by copper content.

Initial increase in VOC conversion and carbon dioxide yield at low copper content was due to higher total metal content on H-ZSM-5. Copper content reached its optimum at 0.5%. A decrease in conversion with increase in copper content after that was attributed to excessive metal agglomeration to form bigger crystallites at high loading. This resulted in low metal distribution and partial blockage of some pore area as suggested by low BET surface area of $Cr_{1.0}Cu_{0.5}/Z$ and $Cr_{1.0}Cu_{1.0}/Z$.

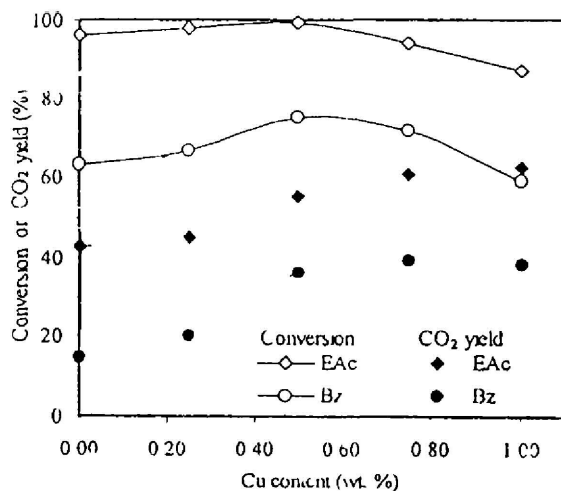


Fig. 2 Effect of Copper Content in the $Cr_{1.0}Cu_x/Z$ Catalyst on the Conversion and Carbon Dioxide Yield in the Combustion of 2,000 ppm of Ethyl Acetate (EAc) and Benzene (Bz) at 400°C

4.1 Effect of Copper on Products Distribution

The combustion of ethyl acetate produced acetaldehyde, acetic acid, formaldehyde, formic acid, carbon monoxide and carbon dioxide as the carbon containing products is shown in Fig. 3. Data below 200°C were not plotted as at low conversion, the calculation of yield was subject to large error. At lower temperature, higher products especially acetaldehyde and acetic acid predominated. Intermediate products like formaldehyde and formic acid gradually increased with increasing temperature, peaking at between 300°C and 400°C, and disappeared with further increase in temperature. At 500°C, the products were primarily in the form of carbon dioxide but significant amount of carbon monoxide was also detected in the product stream.

The incorporation of 0.5 wt % of copper in $Cr_{1.0}Cu_{0.5}/Z$ shifted the products distribution towards lower temperatures as shown by Fig. 3 (b). At lower temperature, lower yield of acetaldehyde but in favor of acetic acid, formaldehyde and formic acid was demonstrated by this catalyst compared to that of $Cr_{1.0}/Z$. Above 450°C, higher products started to disappear and carbon monoxide and carbon dioxide were almost the only carbon containing products.

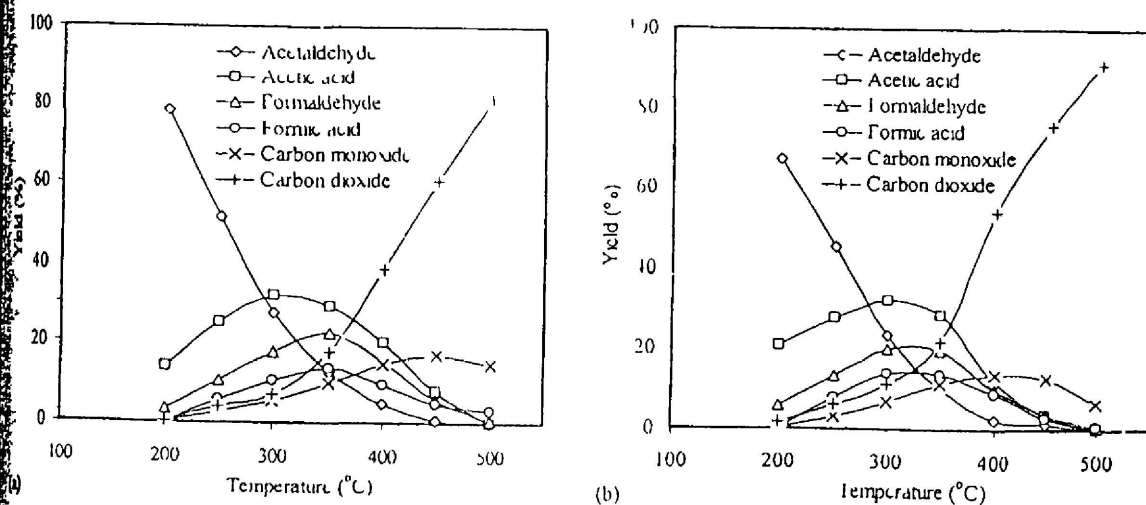


Fig. 3 Products Distribution in the Combustion of Ethyl Acetate Over (a) $Cr_{1.0}/Z$ and (b) $Cr_{1.0}Cu_{0.5}/Z$

40 CONCLUSIONS

Combination of 1.0 wt % chromium and 0.5 wt % copper was found to slightly improve the organic conversion while showing marked improvement in carbon dioxide yield. The improvement was more noticeable in ethyl acetate combustion. At higher metal loading, lower activity was associated with the blockage of ZSM-5 micropores due to the growth of bigger metal crystallites. The combustion of ethyl acetate produced acetaldehyde, acetic acid, formaldehyde, formic acid and carbon monoxide as the intermediate products while benzene produced only carbon monoxide. The incorporation of 0.5 wt % of copper in $\text{Cr}_{0.1}\text{Cu}_{0.5}/\text{Z}$ shifted the products distribution towards lower temperatures.

5.0 ACKNOWLEDGMENT

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6.0 REFERENCES

- 1 Alexeev, O S and Gates, B C, Supported Bimetallic Cluster Catalysts *Ind. Eng. Chem. Res.* 42, 1571-1587 (2003)
- 2 Atwood, G A., Greenc, H. L., Chintawar, P, Rachapudi, R, Ramachandran, B. and Vogel, C. Trichloroethylene Sorption and Oxidation Using a Dual Function Sorbent/catalyst in a Falling Furnace Reactor *Appl Catal B* 18, 51-61 (1998)
- 3 Brink, R W V D, Mulder, P and Louw, R, Increased Combustion Rate of Chlorobenzene on $\text{Pt}/\text{Al}_2\text{O}_3$ in Binary Mixtures With Hydrocarbons and With Carbon Dioxide *Appl Catal. B.* 25, 229-237 (2000)
- 4 Chintawar, P S and Greene, H L, Combustion Characteristics of Chlorinated Ethylenes on Metal loaded Zeolite Y and $\gamma\text{-Al}_2\text{O}_3$ *Appl Catal B* 13, 81-92 (1997)
- 5 Dége, P, Pinard, L, Magnoux, P and Guisnet, M, Catalytic Oxidation of Volatile Organic Compounds II Influence of the Physicochemical Characteristics of Pd/HFAU Catalysts on the Oxidation of *o*-xylene *Appl Catal B* 27, 17-26 (2000)
- 6 Minicò, S, Scire S, Crisafulli, C, Maggiore, R and Galvagno, S, Catalytic Combustion of Volatile Organic Compounds on Gold/Iron Oxide Catalysts *Appl Catal B* 28, 245-251 (2000).
- 7 Ordoñez, S, Bello, L, Sastre, H, Rosal, R and Diez, F V, Kinetics of the Deep Oxidation of Benzene, Toluene, n-hexane and Their Binary Mixtures Over a Platinum on γ -alumina Catalyst *Appl Catal B* 38, 139-149 (2002)
- 8 Patterson, M J, Angove, D E, Cant, N W and Nelson, P F, The Formation of Benzene and Chlorobenzene During the Oxidation of Toluene Over Rhodium-based Catalysts. *Appl Catal. B.* 20, 123-131 (1999)
- 9 Paulis, M, Gandia, L M, Gil, A, Sambeth, J, Odriozola, J A and Montes, M., Influence of the Surface Adsorption-Desorption Process on the Ignition Curves of Volatile Organic Compounds (VOCs) Complete Oxidation Over Supported Catalyst *Appl Catal B* 26 (1), 37-46 (2000).