

PERFORMANCE OF CHROMIUM-COPPER ON MODIFIED H-ZSM-5 CATALYSTS IN THE COMBUSTION OF VOC POLLUTANTS IN AIR

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

School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus,
Seri Ampangan, 14300 Nibong Tebal, Penang, Malaysia.

Tel: +604 594 1012 ; Fax: +604-594 1013 ;

Email: chzuhairi@eng.usm.my

KEYWORDS: H-ZSM-5, SiCl_4 , VOC, activity, deactivation, stability, chlorination.

ABSTRACT

The characteristics, activity, stability of chromium and copper on silicon tetrachloride modified H-ZSM-5 catalyst (Cr-Cu/ SiCl_4 -Z) for VOC combustion is reported. H-ZSM-5, modified with SiCl_4 at 500°C for 3 h was impregnated with 1.0 wt. % of Cr and 0.5 wt. % of Cu. Performance studies were performed at GHSV of 3,800 to 32,000 h^{-1} with 2,000 to 35,000 ppm of VOCs. Changes in the activity of Cr-Cu/ SiCl_4 -Z were ascribed to extra framework deposits, surface acidity and pore characteristics. Cr-Cu/ SiCl_4 -Z showed improved stability to coking, hydrothermal treatment and coking tendency.

INTRODUCTION

Volatile organic compounds (VOCs) are important environmental pollutants and catalytic combustion is a viable technology their removal from air [1,2]. An catalyst should show high activity, high carbon dioxide yield, high hydrothermal stability, low coking activity and cheap [3]. The overall performance of chromium (Cr) and copper (Cu) on silicon tetrachloride modified H-ZSM-5 (SiCl_4 -Z) catalyst, developed to meet all these requirements is reported.

EXPERIMENTAL DETAILS

H-ZSM-5, modified with SiCl_4 at 500°C for 3 h was impregnated with 1.0 wt. % of Cr and 0.5 wt. % of Cu. Activity was measured at GHSV of 3,800 to 32,000 h^{-1} with 2,000 to 35,000 ppm of VOCs. Ethyl acetate and benzene were used as non-chlorinated VOC model compounds while trichloromethane and trichloroethylene were used to represent chlorinated VOCs. The hydrothermal stability, coking behavior and hydrogen chloride resistance of the catalyst were also characterized.

RESULTS & DISCUSSION

Cr-Cu/ SiCl_4 -Z showed higher activity, higher carbon dioxide yield and reduced coking tendency. Benzene was more stable than ethyl acetate with a $T_{50\%}$ of 270°C (Figure 1). Changes in the activity of Cr-Cu/ SiCl_4 -Z were ascribed to changes in extra framework deposits, surface acidity and pore characteristics [1]. Cr-Cu/ SiCl_4 -Z was also more stable to coking, humidity and hydrogen chloride.

The catalyst also produced softer and less aromatic coke in the combustion of ethyl acetate [4].

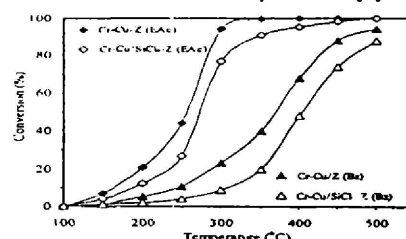


Figure 1. Activity of Cr-Cu/ SiCl_4 -Z.

For chlorinated VOC, coking was minimal and the chlorination of metal deactivated the catalyst [2]. After 12 h, the catalyst managed to retain about 85 % of its activity (Figure 2). More activity loss with trichloroethylene feed was ascribed to higher chlorine content of the substance, coupled with significant coking [4]. The deactivation profile of the catalyst was governed by the ability of Cr and Cu to present at multiple oxidation states, coupled by the ability of chlorine to act as a strong oxidizing agent [1].

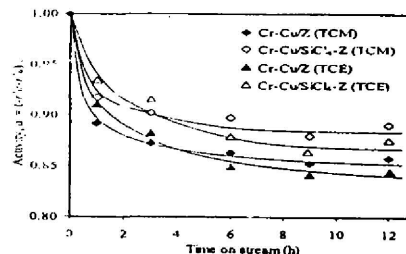


Figure 2. Deactivation profiles of Cr-Cu/ SiCl_4 -Z.

CONCLUSIONS

Cr-Cu/ SiCl_4 -Z showed superior qualities in terms of activity, stability and coking tendency.

References

- [1] Zuhairi, A.A., Zailani, M.A.B., and Bhatia, S. (2004). *J. Chem. Technol. Biotechnol.* 79, pp. 761-768.
- [2] Zuhairi, A.A., Zailani, M.A.B. and Bhatia, S. (2003). *Chem. Eng. J.*, 99, pp. 161-168.
- [3] Zuhairi, A.A., Zailani, M.A.B. and Bhatia, S. (2003). *Ind. Eng. Chem. Res.* 42, pp. 6059-6067.
- [4] Zuhairi, A.A., Zailani, M.A.B. and Bhatia, S. (2003). *Ind. Eng. Chem. Res.* 42, pp. 5737-5744.

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Tel: +604-599 6411 ; Fax: +604-594 1013

***Email: chzuhairi@eng.usm.my**

ABSTRACT

The performance of chromium (Cr) and copper (Cu) on silicon tetrachloride modified H-ZSM-5 ($\text{SiCl}_4\text{-Z}$) catalyst in VOC combustion is reported. H-ZSM-5, modified with SiCl_4 at 500°C for 3 h was impregnated with 1.0 wt. % of Cr and 0.5 wt. % of Cu. Performance studies were carried out at GHSV of 3,800 to 32,000 h^{-1} with 2,000 to 35,000 ppm of VOC. Changes in the activity of Cr-Cu/ $\text{SiCl}_4\text{-Z}$ was limited to low temperatures and were ascribed to extra framework deposits, surface acidity and pore characteristics. Cr-Cu/ $\text{SiCl}_4\text{-Z}$ catalyst was more stable to coking, humidity and HCl than Cr-Cu/Z. In the combustion of chlorinated VOC, the chlorination of metal species deactivated the catalyst by rendering lower redox ability.

Keywords: H-ZSM-5 ; SiCl_4 ; VOC ; activity ; deactivation ; stability

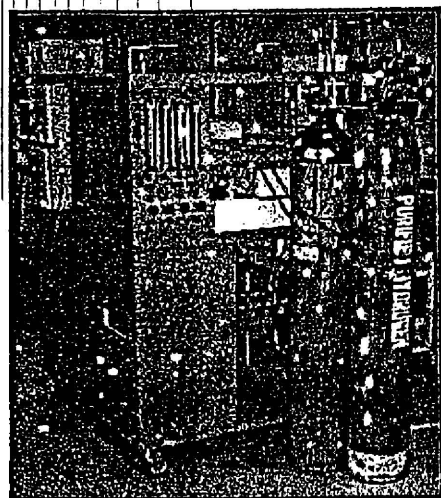
INTRODUCTION

Volatile organic compounds (VOCs) are environmental pollutants and catalytic combustion is a viable technology for their removal from air [1-6]. An ideal catalyst should have high activity, high carbon dioxide yield, high hydrothermal stability, low coking activity and most importantly, produced at low cost [2,3,7]. In the combustion of chlorinated VOC (Cl-VOC), HCl, Cl₂ that are produced and can cause rapid deactivation of the catalyst [8].

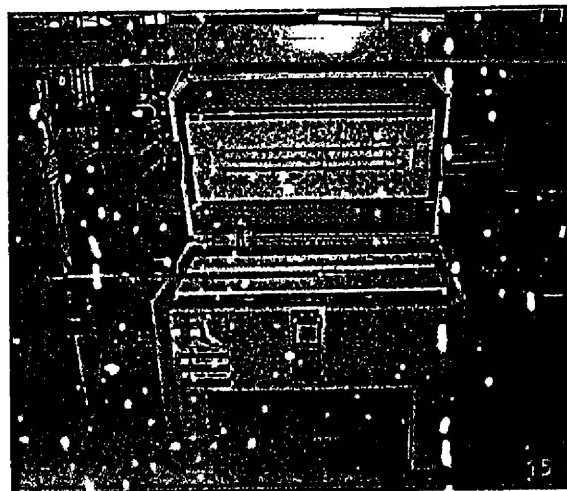
A combination of Cr and Cu produced a catalyst with high activity and high CO₂ yield while, showing lower coking tendency [9]. SiCl₄ treatment increased the hydrophobicity of H-ZSM-5 while suppressing coking activity [7]. Therefore, it is of interest to study the activity of Cr-Cu/SiCl₄-Z catalyst in the combustion of VOC. Ethyl acetate (EAc), benzene (Bz), trichloromethane (TCM) and trichloroethylene (TCE) were used as model compounds. The deactivation of the catalyst was scrutinized on the basis of the physicochemical changes occurred on the active metal species and the catalyst support to identify the more dominant deactivation mechanism.

EXPERIMENTAL

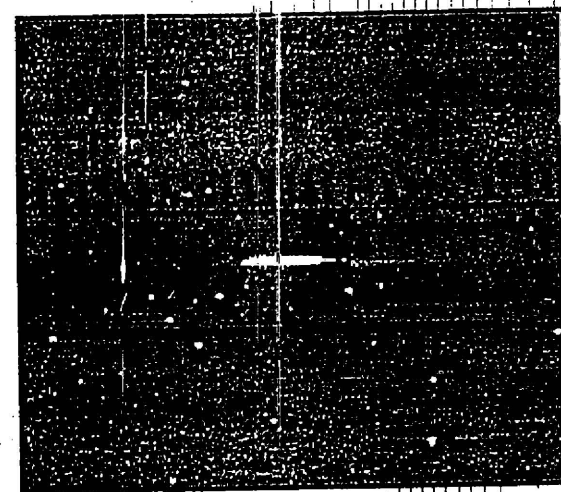
H-ZSM-5, modified with SiCl_4 at 500°C for 3 h was impregnated with 1.0 wt. % of Cr and 0.5 wt. % of Cu. Details are available in [3,4]. Activity was measured at GHSV of 3,800 to 32,000 h^{-1} with 2,000 to 35,000 ppm of VOCs. Ethyl acetate and benzene were used as non-chlorinated VOC model compounds while trichloromethane and trichloroethylene were used to represent chlorinated VOCs. The hydrothermal stability, coking behavior and hydrogen chloride resistance of the catalyst were also characterized.



Test rig



Micro reactor



Catalyst bed

RESULTS & DISCUSSION

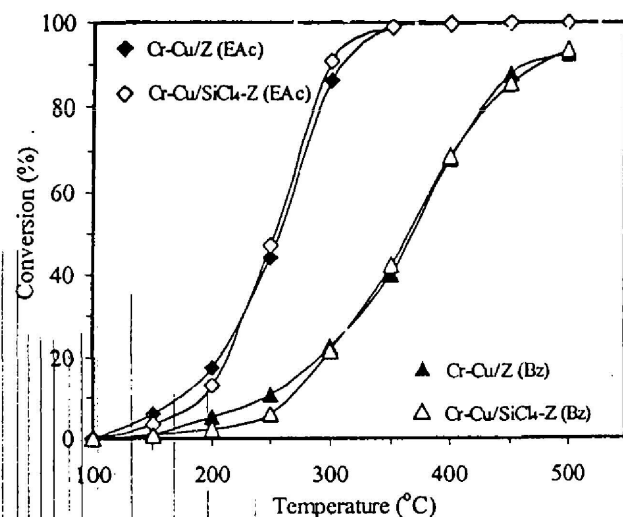


Fig. 1. Combustion of EAc and Bz.

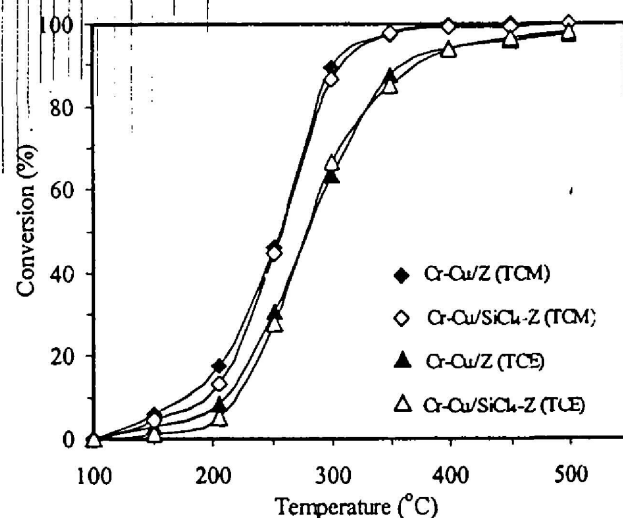


Fig. 2. Combustion of TCM and TCE.

At low temperatures, the activity of the two catalysts was mainly governed by their pore characteristics and the length of diffusion pathways. However, at high temperatures, there was no clear difference between the activity of Cr-Cu/Z and Cr-Cu/SiCl₄-Z as the rate of the oxidative reaction.

TCM and TCE were more reactive compared to benzene with conversions exceeding 90 % above 400°C. TCE was also more stable than TCM, attributed to the occurrence of a resonance effects in the molecule from interactions between lone pair electron in chlorine atoms and the π electron in the C=C double bond.

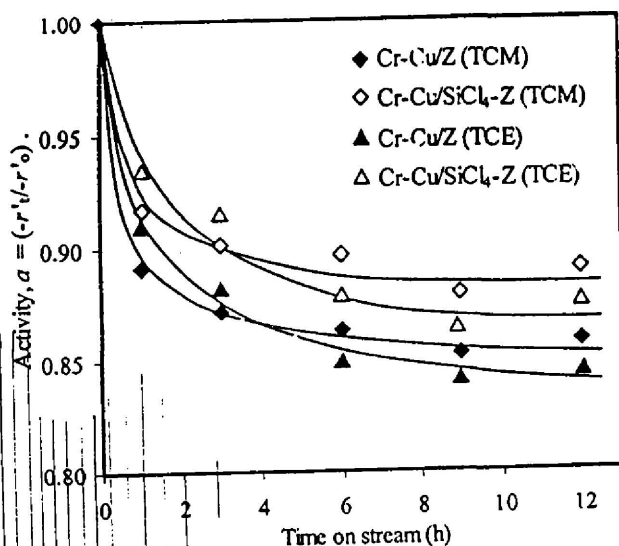


Fig. 3. Deactivation in TCM and TCE.

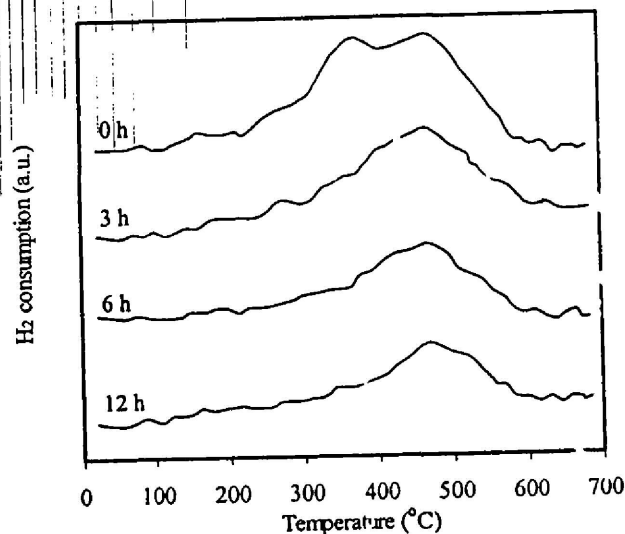


Fig. 4. TPR profiles of aged Cr-Cu/SiCl₄-Z.

The deactivation profiles were characterized by an initial sharp drop followed by a gradual decrease in the activity. Residual activity was achieved at longer time. The Cr-Cu/SiCl₄-Z catalyst appeared to be more resistant to deactivation with less than 15 % activity drop detected for both types of chlorinated organics.

The peak at 380°C was due combined reduction of Cr⁶⁺ and Cu²⁺ while, that occurring at 480°C was due to Cr³⁺ and Cu⁺ [4]. The chlorination weakened the reducibility of the metals. Changes in the activity could be explained by the Mars-van Krevelen model. As chlorides species were more resistance to reduction, a reduction in redox activity is the likely consequence.

CONCLUSIONS

Changes in the activity of Cr-Cu/SiCl₄-Z occurred especially at low temperatures and were ascribed to extra framework deposits, surface acidity and pore characteristics. At above 250°C, there was no clear difference between the activity of Cr-Cu/Z and Cr-Cu/SiCl₄-Z. SiCl₄-Z showed improved hydrothermal and hydrogen chloride stabilities with a suppressed coking tendency. Cr-Cu/SiCl₄-Z catalyst also produced less aromatic coke. This catalyst was less deactivated by chlorinated VOCs. The deactivation was primarily attributed to the chlorination of active metal species rather than chemical changes on the catalyst support. The chlorination of metal species deactivated the catalyst by rendering lower redox ability. The result was in agreement with the Mars-van Krevelen model.

Acknowledgement : IRPA research grant (08-02-05-139 EA 001) from the Ministry of Science, Technology and Innovation of Malaysia (MOSTI) and zeolite samples from Süd-Chemie AG, Munich Germany are gratefully acknowledged

REFERENCES

- [1] Zuhairi, A.A., Zailani, M.A.B. and Bhatia, S. (2003). *Chem. Eng. J.*, 99, pp. 161-168.
- [2] Zuhairi, A.A., Zailani, M.A.B. and Bhatia S. (2003). *Ind. Eng. Chem. Res.* 42, pp. 6059-6067.
- [3] Zuhairi, A.A., Zailani, M.A.B. and Bhatia, S. (2003). *Ind. Eng. Chem. Res.* 42, pp. 5737-5744.
- [4] Zuhairi, A.A., Zailani, M.A.B. and Bhatia, S. (2004). *AJChE.* 4 (2), pp. 66-75.
- [5] Zuhairi, A.A., Zailani, M.A.B. and Bhatia, S. (2003). *React. Kinet. Catal. Lett.*, 79 (1), pp. 143-148.
- [6] Zuhairi, A.A., Zailani, M.A.B. and Bhatia, S. (2003). *Catalysis Communications*, 4, pp. 555-560.
- [7] Zuhairi, A.A., Zailani, M.A.B., and Bhatia, S. (2004). *J. Chem. Technol. Biotechnol.* 79, pp. 761-768.
- [8] Zuhairi, A.A., Zailani, M.A.B. and Bhatia, S. (2005). *Journal of Hazardous Materials Part B. (to appear).*
- [9] Zuhairi, A.A., Zailani, M.A.B. and Bhatia, S. (2005). *J. Chemical Technol. Biotechnol.*, 80 (9), pp. 1016-1025.