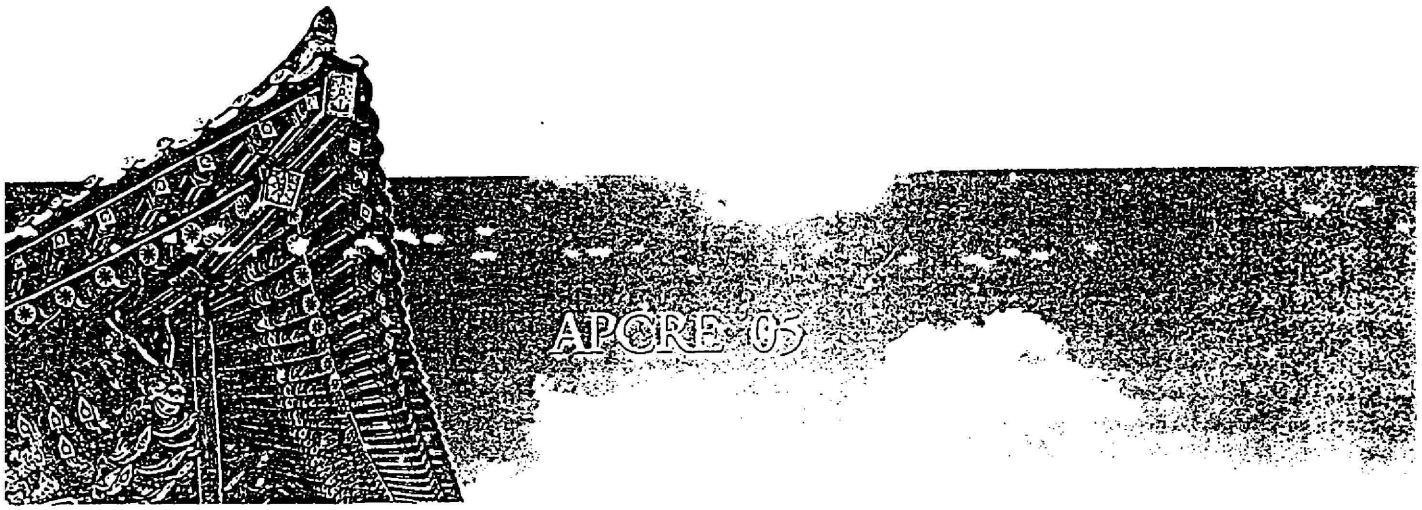
Book of Abstracts

The 4th ASIA-PACIFIC CHEMICAL REACTION ENGINEERING SYMPOSIUM



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$SiCl_4$-modified H-ZSM-5 as support in bimetallic chromium-copper catalyst for the combustion of VOCs in air stream

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Abstract

The performance of silicon tetrachloride ($SiCl_4$) modified H-ZSM-5 (Si/Al=240) as support to bimetallic chromium-copper catalyst for the combustion of non-chlorinated and chlorinated volatile organic compounds (VOCs) is reported. H-ZSM-5 was modified by exposing to $SiCl_4$ vapor in nitrogen at 500°C for 3 h followed by co-impregnation with 1.0 wt. % of chromium and 0.5 wt. % of copper. Activity study was performed in a reactor operated at between 100° and 500°C at a gas hourly space velocity (GHSV) of 32,000 h^{-1} and fed with either 2,000 ppm of ethyl acetate and benzene or 2,500 ppm of trichloromethane (TCM) and trichloroethylene (TCE). Deactivation was studied by ageing the catalysts with 32,000 ppm to 55,000 ppm of VOC at 400°C for up to 12 h. Changes in the activity of Cr-Cu/$SiCl_4$-Z were ascribed to extraframework deposits, changes in acid site distribution and mesopores created after $SiCl_4$ treatment. $SiCl_4$ treatment significantly improved the stability of H-ZSM-5 support against hydrothermal and HCl ageing tests also showed lower tendency to coking. The catalyst also produced more softer coke fractions in the combustion of ethyl acetate. Upon ageing with TCM and TCE for 12 h at 400°C, Cr-Cu/$SiCl_4$ managed to retain an average of about 89 % of its original activity compared to about 84 % with unmodified ZSM-5 catalyst. Hydroxyl groups in Cr-Cu/$SiCl_4$-Z were generally not chemically altered during ageing test with TCE. The deactivation was more contributed by the chlorination of its metal species rather than changes in the characteristics of the support.
Keywords: $SiCl_4$, H-ZSM-5, VOC, combustion, stability, coking.

Tables and Figures

Table 1. Characteristics of H-ZSM-5(240) and bimetallic $Cr_{1.0}Cu_{0.5}$/modified ZSM-5 catalysts used.

Properties	[a]Material		
	H-Z	Cr-Cu/Z	Cr-Cu/$SiCl_4$-Z
S_{BET} (m^2/g)	386	360	324
Micropore area (m^2/g)	315	278	198
Mesopore area (m^2/g)	71	82	126
Metal loading (wt.%)	-	1 % Cr and 0.5 % Cu	
[b]Crystallinity (%)	100	95	66
Acidity (mmol NH_3/g)	0.22	0.17	0.09

[a]Z=ZSM-5(240)
[b]Relative to H-ZSM-5(240)

Table 2. Summary of changes occurred after exposure to 32,000 ppm of ethyl acetate at 400°C for 12 h.

Properties	[a]Condition	Catalyst	
		Cr-Cu/Z	Cr-Cu/$SiCl_4$-Z
[b]Activity, a	Dry	0.91	0.95
	Humid	0.85	0.89
Coke content (wt.%)	Dry	8.8	7.2
	Humid	6.4	5.2
[c]Crystallinity (%)	Dry	80.8	93.6
	Humid	71.2	88.6

[a]Humid condition contains 9,000 ppm H_2O.
[b]$a = -r'_A/-r'_{A,i}$ (measured with 2,000 ppm ethyl acetate at 400°C).
[c]Relative to respective fresh catalysts.

Table 3. Changes in characteristics of Z and $SiCl_4$-Z after treatment with gaseous hydrogen chloride at 400°C for 4 h.

Characteristics	[a]Support	[d]Treated Z		
	Fresh Z		Fresh $SiCl_4$-Z	[d]Treated $SiCl_4$-Z
S_{BET} ($m^2 \cdot g$)	386	368	346	340
Micropore area (m^2/g)	315	290	211	204
Mesopore area (m^2/g)	71	78	134	136
[b]Strong acidity (mmol NH_3 /g)	0.121	0.112	0.045	0.042
Weak acidity (mmol NH_3 /g)	0.099	0.042	0.063	0.030
[c]Crystallinity (%)	100	91	100	96

[a] Z=H-ZSM-5(240)
[b] Sites retaining ammonia at temperatures higher than 250°C
[c] Relative to respective fresh support
[d] After reaction with gaseous HCl at 400°C for 4 h

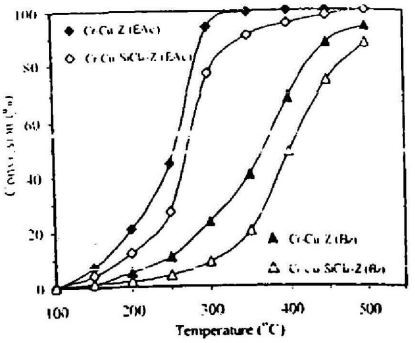

Figure 1. Combustion of ethyl acetate (EAc) and benzene (Bz) over Cr-Cu/Z and Cr-Cu/$SiCl_4$-Z. (C_{voc}=2,000 ppm, GHSV=32,000 h^{-1}).

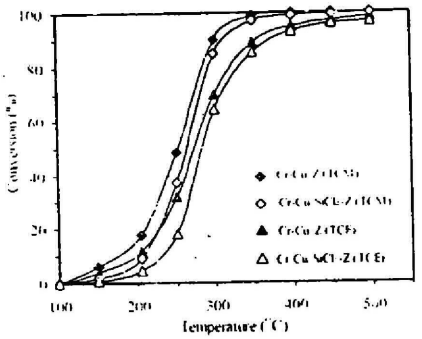

Figure 2. Combustion of trichloromethane (TCM) and trichloroethylene (TCE) over Cr-Cu/Z and Cr-Cu $SiCl_4$-Z (C_{voc}=2,500 ppm, GHSV=32,000 h^{-1}).

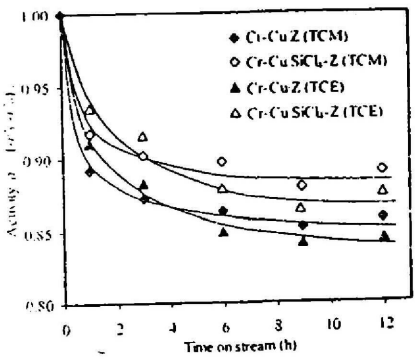

Figure 3. Deactivation of Cr-Cu/Z and Cr-Cu/$SiCl_4$-Z catalysts in the combustion of trichloromethane (TCM) and trichloroethylene (TCE). (C_{voc}=35,000 ppm, GHSV=32,000 h^{-1}, T=400°C).

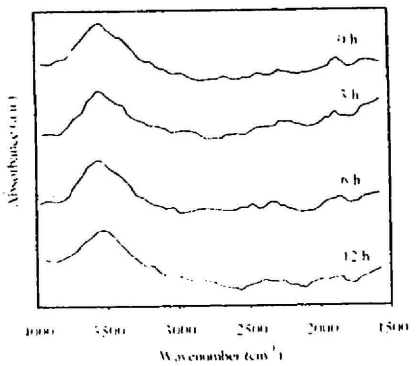

Figure 4. Infrared absorbance of Cr-Cu/$SiCl_4$-Z after ageing with 35,000 ppm of TCE at 400°C for four different times on stream.

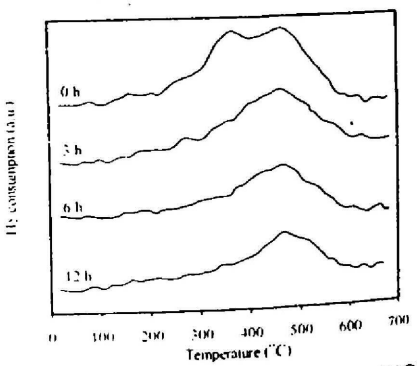

Figure 5. TPR profiles of Cr-Cu/$SiCl_4$-Z catalyst after ageing with 35,000 ppm of TCE at 400°C for four different times on stream.