

Combustion of chlorinated volatile organic compounds (VOCs) using bimetallic chromium-copper supported on modified H-ZSM-5 catalyst

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Abstract

The paper reports on the performance of chromium or/and copper supported on H-ZSM-5 (Si/Al = 240) modified with silicon tetrachloride ($\text{Cr}_{1.5}/\text{SiCl}_4\text{-Z}$, $\text{Cu}_{1.5}/\text{SiCl}_4\text{-Z}$ and $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$) as catalysts in the combustion of chlorinated VOCs (Cl-VOCs). A reactor operated at a gas hourly space velocity (GHSV) of $32,000\text{ h}^{-1}$, a temperature between 100 and $500\text{ }^\circ\text{C}$ with 2500 ppm of dichloromethane (DCM), trichloromethane (TCM) and trichloroethylene (TCE) is used for activity studies. The deactivation study is conducted at a GHSV of 3800 h^{-1} , at $400\text{ }^\circ\text{C}$ for up to 12 h with a feed concentration of 35,000 ppm. Treatment with silicon tetrachloride improves the chemical resistance of H-ZSM-5 against hydrogen chloride. TCM is more reactive compared to DCM but it produces more by-products due to its high chlorine content. The stabilization of TCE is attributed to resonance effects. Water vapor increases the carbon dioxide yield through its role as hydrolysis agent forming reactive carbocations and acting as hydrogen-supplying agent to suppress chlorine-transfer reactions. The deactivation of $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$ is mainly due to the chlorination of its metal species, especially with higher Cl/H feed. Coking is limited, particularly with DCM and TCM. In accordance with the Mars–van Krevelen model, the weakening of overall metal reducibility due to chlorination leads to a loss of catalytic activity.

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1. Introduction

Chlorinated volatile organic compounds (Cl-VOCs) are important environmental pollutants due to their high toxicity, inertness and widespread application in industries [1–3]. Catalytic combustion is a viable technology for the abatement of VOC in an air stream and a packed bed reactor is the most commonly used type of reactor. However, it should be noted that there has been an introduction of innovative reactors, such as a fleece reactor by Everaert et al. [4,5] to serve the same purpose. Despite being relatively more reactive compared to non-chlorinated homologues, catalytic combustion of Cl-VOC still faces several drawbacks [1]. Depending on reaction conditions, chlorine-transfer reactions could significantly occur with unsuitable type of catalyst to produce high molecular weight chlorinated by-products [2,6,7]. Oxidation of Cl-VOC also produces hydrogen chloride (HCl), and sometimes, molecular chlorine (Cl_2), which

can attack and deactivate the catalyst. Hydrogen-lean Cl-VOCs are often less reactive and tend to cause the occurrence of highly chlorinated substances in the product stream [8].

The reactivity of Cl-VOCs is governed by several factors. Chlorine is an electron-pulling atom due to its high electronegativity and can induce electron clouds in the chemical bonds leading to changes in the reactivity of the molecule. It also has a lone pair of electrons to interact, and can sometimes, be involved in the formation of chemical bonds with adjacent atoms [9]. The presence of double bonds in a Cl-VOC molecule might induce resonance that can also affect the stabilization of the molecule [10]. In addition, an increasing number of chlorine atoms in an organic molecule also affects its reactivity and this finding should be explained based on the understanding of the intra-molecular electronic flow during the combustion process [6].

Larger molecules will generally have to undergo more oxidation steps to completely break their molecules and ultimately produce carbon dioxide and water. In this longer process, and under specific conditions, there will be more opportunity for chlorine-transfer reactions to take place. In fact, the low carbon

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Nomenclature

a	activity
$F_{v,in}, F_{v,out}$	molar flow rates of VOC (mol/s)
$-r'_t$	rate of reaction (mol/(s g _{cat}))
t	time on stream (h)
W_{cat}	weight of catalyst (g)

dioxide yield in the combustion of higher molecular weight Cl-VOC is reported by most researchers investigating this matter [1,6,8]. An incomplete combustion will also lead to the formation of higher molecular weight by-products, often, chlorinated ones [1,5]. These undesirable by-products always occur with most of the catalyst, especially at low conversion, low oxygen concentration, high feed concentration and high Cl/H ratio Cl-VOCs [6,11,12].

Water vapor is known to inhibit the combustion of Cl-VOCs [7], decrease the by-product formation [6] and improve the selectivity towards HCl, while suppressing the formation of molecular chlorine [13]. However, the role of water vapor in the combustion mechanism and the reactivity of Cl-VOCs leading to changes in the products distribution is rarely reported. Gervasini et al. [8] reported that hydrogen-lean substances, such as carbon tetrachloride could be partially destroyed in the absence of oxygen in a gas of high humidity. It was suggested that the water molecule could hydrolyze Cl-VOC in the presence and absence of oxygen. The rate and extent of this reaction were determined by the chemical nature of the feed, but might be influenced by the reaction temperature. Water vapor also can play a role as a polar solvent that increases the mobility of the chloride anion, the effect of which is expected to suppress chlorine-transfer reactions and minimize catalyst deactivation [7].

Catalyst deactivation in Cl-VOC combustion is mainly ascribed to physical and chemical changes occurred on the catalyst support and active metal species. The deactivation of a zeolite-supported catalyst can originate from interactions between chlorine atoms with certain sites in the support, to consequently cause the formation of defects in the framework [14]. Generally, chlorinated molecules can selectively attack the Al–O bonds in the zeolite framework to form aluminum chloride [15]. Changes in the active metal species are primarily due to the formation of metal chlorides that are less efficient in catalyzing the combustion reaction [6]. The occasional formation of highly volatile oxychloride species, leading to the loss of active metal from the catalyst, has been reported by Padilla et al. [1]. However, the type and contribution of each mechanism of catalyst deactivation vary with the catalyst system employed in the combustion process [5,12,16].

The Mars–van Krevelen model is the most reliable model describing the VOC combustion reaction [12,17,18]. It is a model consisting of a set of model equations that originates from a mechanistic representation of the combustion reaction. According to this model, the combustion reaction occurs according to two separate redox schemes:

- oxidation of the metal species by oxygen from the gas phase;
- reduction of the oxidized metal species by the VOC or its intermediates.

This model assumes the reaction to occur when an organic molecule interacts with an oxygen-rich portion of the catalyst [17,19]. The form of the oxygen in the catalyst could be the chemisorbed oxygen on metal sites, especially those showing multiple oxidation states [18,20]. The particular portion of the catalyst will be alternately reduced by the organic reactant and reoxidized by the oxygen in the feed. A more detail discussion on the application of this model in VOC combustion reaction is available in our previous reports [21,22]. An investigation on the reducibility of the metal species upon reaction with Cl-VOC, hence, will create a better understanding of the catalyst deactivation phenomena in the combustion process.

Despite being reported to be the most active transition metal for VOC combustion, the high toxicity of chromium is its main disadvantage [5,8,10,18]. Therefore, research on finding a combustion catalyst with lower chromium content through a combination with relatively non-toxic metals is a worthwhile effort. Several metal combinations have been tested for the combustion of non-chlorinated and chlorinated VOCs and a review by Everaert et al. [5] provides good information on important findings. In the present study, a combination of chromium and copper was used. Our previous result showed that with this combination, the carbon dioxide yield in the combustion of non-chlorinated VOCs was improved, while the coking activity was suppressed [22]. The present paper, therefore, is extended to Cl-VOC. Also, compared to mordenite and beta, ZSM-5 was found to be the most promising zeolite support for VOC combustion due to its characteristic pore system, high hydrothermal stability and low coking tendency [23].

A silicon tetrachloride treatment on H-ZSM-5 was also found to improve the hydrothermal stability of the zeolite with further suppression on the coking tendency of the catalyst [22]. In the activity study, dichloromethane (DCM), trichloromethane (TCM) and trichloroethylene (TCE) were used as Cl-VOC model compounds due to differences in their chemical nature. Emphasis is paid to characterizing changes either of the active metal species or of the zeolite support, and the consequent effects on the activity and deactivation behavior of the bimetallic catalyst. The role of water vapor in the combustion of Cl-VOC is also elucidated.

2. Experimental methods

2.1. Preparation of the catalyst support

The ZSM-5 (Si/Al = 240) zeolite sample was supplied by Süd-Chemie AG in its sodium form. H-ZSM-5 (coded H-Z) was prepared through exchanging the Na⁺ cation by NH₄⁺ in a 2.25 M NH₄Cl for 12 h followed by filtration, drying and calcination at 500 °C for 3 h. The chemical modification of H-ZSM-5 was performed by reacting the H-ZSM-5 sample with silicon tetrachloride vapor in nitrogen at 50 ml/min and 500 °C for 3 h. The modified ZSM-5 sample was then subjected to acid

leaching to remove extra framework species using a 2 M HCl solution at 60 °C for 2 h, followed by filtration, washing with deionized water and drying. Hereafter, the silicon tetrachloride-modified zeolite support is coded as SiCl₄-Z. In our study, the extent of dealumination after the silicon tetrachloride treatment was found to be dependent on the procedure and conditions of the chemical treatment used. However, the discussion of this process is beyond the scope of the present paper. A more detail discussion on the dealumination of H-ZSM-5 is, however, available in our recent papers [22,24].

2.2. Resistance of ZSM-5 support against gaseous HCl

In order to study their suitability to act as the catalyst support in the combustion of chlorinated VOC, the chemical resistance of the modified and unmodified ZSM-5 support against hydrogen chloride was demonstrated using the method proposed by Kulażyński et al. [25]. First, the support material was heated in the reactor at 400 °C, while an air flow at 50 ml/min was passed through the reactor for 4 h. This air stream was previously passed through a saturator containing concentrated HCl.

2.3. Preparation of impregnated catalysts

The single and bimetallic impregnated catalysts were prepared via the impregnation method of Zhang et al. [26], Paulis et al. [27] and Kim [28]. In this procedure, 5 g of the modified ZSM-5 support was slurried into 100 ml of nitrate solutions of Cr or/and Cu that were previously acidified to pH 4. The concentrations of these solutions were chosen to give the desired final metal loading of 1.5 wt.% of chromium or copper for single metal catalysts and 1.0 and 0.5 wt.% of chromium and copper, respectively, for the bimetallic catalyst. The solution was then evaporated to dryness and the impregnated catalyst was then calcined at 550 °C for 6 h, pressed and sieved to particle sizes between 250 and 300 μm. These catalysts were coded as Cr_{1.5}/SiCl₄-Z, Cu_{1.5}/SiCl₄-Z and Cr_{1.0}Cu_{0.5}/SiCl₄-Z.

2.4. Experimental setup and conditions

The schematic diagram of the experimental setup is shown in Fig. 1. It consisted of nitrogen (99.999%) and air (20.8% O₂ and 79.2% N₂) streams, the flow rates of which were controlled using Aalborg (AFC 2600) mass flow controllers. VOC-laden air stream at a fixed concentration as feed to the reactor was generated by bubbling the nitrogen gas at suitable flow rate through the VOC saturators. The flow of air was used to make up the total flow rate to give the desired gas hourly space velocity (GHSV) in the catalyst bed. The catalytic activity test and the preparation of aged catalyst samples were performed in an 11 mm i.d. and 450 mm long cylindrical borosilicate glass reactor heated with a Lindberg/Blue tubular furnace.

The feed and product gases were analyzed using an off-line Shimadzu GC-8A gas chromatograph equipped with a Shimadzu C-R8A Chromatopac integrator. A Porapak Q column was used for separation of carbon dioxide and organic components, while

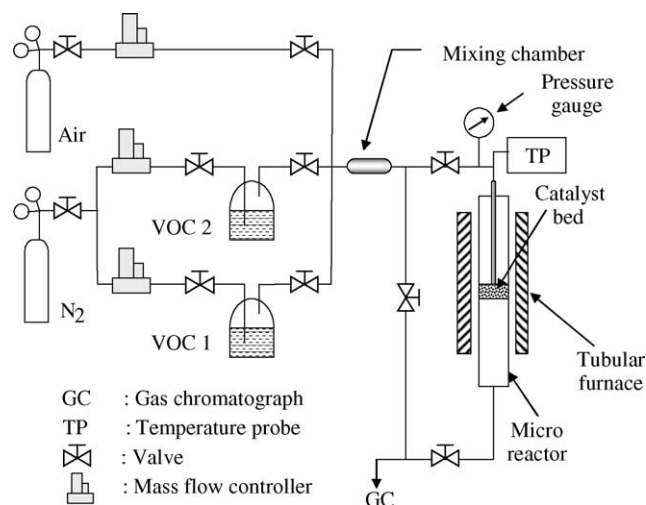


Fig. 1. Schematic diagram of the experimental setup.

the separation of carbon monoxide was achieved by means of a molecular sieve 5 A column.

The performance of the catalyst was assessed on the basis of the conversion and carbon dioxide yield determined at a total feed flow rate of 250 ml/min with a corresponding GHSV of 32,000 h⁻¹. The feed Cl-VOC concentration was kept constant at 2500 ppm of DCM, TCM or TCE. All the experiments were carried out at reaction temperatures between 100 and 500 °C with feeds containing 18.3% of oxygen (excess oxygen). In this study, all operating variables of the reactor were purposely selected in order to avoid the complete conversion or 100% carbon dioxide yield below 500 °C. The main objective was indeed to compare the performance of the catalyst on the basis of these two parameters. Generally, higher conversion and carbon dioxide yield could be easily achieved if the GHSV were reduced, if the feed Cl-VOC concentration were increased or if the reactor was operated at higher temperature.

In order to prepare aged Cr_{1.0}Cu_{0.5}/SiCl₄-Z catalyst samples, feeds containing 35,000 ppm of DCM, TCM or TCE were passed through the reactor at a reaction temperature of 400 °C and a GHSV of 3800 h⁻¹ for different reaction times of up to 12 h. After the desired reaction time was reached, the aged catalyst samples were taken out for activity determination and characterization. The reaction rate over the catalyst was determined by operating the reactor in a differential mode at a GHSV of 78,900 h⁻¹ at 400 °C using respective Cl-VOC at 2500 ppm as feed. The reaction rate was defined as,

$$\text{reaction rate, } -r' = \frac{F_{v,\text{in}} - F_{v,\text{out}}}{W_{\text{cat}}} \text{ mol}/(\text{s g}_{\text{cat}}) \quad (1)$$

where $F_{v,\text{in}}$, $F_{v,\text{out}}$ is the molar flow rate of Cl-VOC in the feed and product gases and W_{cat} is the weight of catalyst used.

The activity (a) of the catalyst was taken as the ratio between reaction rate at time t to that of fresh Cr_{1.0}Cu_{0.5}/SiCl₄-Z catalyst ($t = 0$) and or:

$$\text{activity, } a = \frac{-r'_t}{-r'_0} \quad (2)$$

where $-r'_t$ and $-r'_0$ were reaction rates at time t and $t=0$ h, respectively.

2.5. Catalyst characterization

The catalyst samples were analyzed for surface characteristics using the Quantachrome Autosorb-1, while crystallinity was determined using a Siemens D2000 X-ray diffractometer. The acidity determination was made using the Chembet 3000 system, in which, the ammonia adsorption process was performed at 150 and 250 °C for total and strong acidity, respectively. The weak acidity was obtained by taking the difference between these two acidity values [14]. Meanwhile, the coke content of aged catalyst, taken as weight loss of an oven dried sample upon heating to 700 °C in oxygen, was determined using a Perkin-Elmer TGA7. Infrared spectroscopy characterization of the catalyst sample was carried out using a Perkin-Elmer 2000 FT-IR system, while the profile of a temperature programmed reduction of the catalyst was obtained with the Chembet 3000 system.

3. Results and discussion

3.1. Characteristics of support materials and catalysts

Table 1 summarizes important characteristics of the support and metal impregnated catalysts used in the present study. Changes in the micropore area give a qualitative indication of the degree of modification experienced by the zeolite framework as they constitute about 80% of total surface area of the unmodified H-Z support. When treated with silicon tetrachloride, the zeolite experiences significant drops in BET and micropore areas, while mesopore area is adversely affected. These drops signify the presence of defects that contribute to mesoporosity of the material that resulted from partial atomic extraction from the zeolite framework. Impregnation of chromium or/and copper on SiCl₄-Z results in a further decrease of the BET surface area and of the micropore area, but with corresponding drop in mesopore area.

In this study, the actual Si/Al ratio after the silicon tetrachloride treatment is not measured as the treatment process is also expected to produce extra framework species that can interfere with the Si/Al ratio measurement process (either using XRF or

XPS). This will lead to erroneous results and eventually result in misleading conclusions. It is expected that some of these extra framework species will remain in the SiCl₄-Z as they cannot be totally removed during the acid leaching process due to limited solubility of certain species in the acid solution.

It is generally accepted that the type and strength of acid sites in a catalyst play important roles in catalyst coking during a VOC combustion process, leading consequently to the deactivation of the catalyst [13,14,22]. For this reason, the acidity study of the catalyst is also conducted. The acidity of the support materials used in the present study is characterized by weak and strong acid sites, based on the temperature at which the ammonia adsorption process is carried out. Weak acid sites are associated with the framework Lewis acid sites and aluminum-rich extra framework species due to its amphotericity [29], while amorphous Si-Al oligomers formed during silicon tetrachloride treatment have little contribution to the acidity [30]. This is supported by the lower value of weak acidity of SiCl₄-Z compared to H-Z as some of the acid-soluble extra framework species in SiCl₄-Z have been removed during the acid leaching process in the preparation step. Strong acid sites are mainly attributed to Brønsted acid sites in the framework of the zeolite [14]. The impregnation of chromium and copper on SiCl₄-Z appears to further weaken the overall acidity, mainly due to the masking of acid sites by metal deposits as indicated by a lower BET surface area, and a reduced micropore and mesopore areas in Cr_{1.0}Cu_{0.5}/SiCl₄-Z.

New mesopores in SiCl₄-Z are formed through two different ways. Upon treatment with silicon tetrachloride, amorphous Si-Al oligomers and SiO₂ species are created and remain after acid leaching due to their low solubility in acid solution [30]. These species form secondary pores that are different from the primary internal pores and normally of meso size range. Extracted aluminum atoms from the framework also lead to the formation of aluminium-rich extra framework phases, normally in the form of Al³⁺, Al(OH)₂⁺ or Al(OH)₂²⁺ [26]. These species are readily extractable in an acid solution leaving new mesopores behind. A more detail discussion on the extent of the dealumination and the formation of extra framework species at different dealumination conditions are available in our previous reports [22,24] and these matters are not discussed any further here.

It should be noted in this study that as the Si/Al ratio of the parent zeolite is quite high (240), the aluminum content

Table 1
Characteristics of support materials and catalysts used

Characteristics	Material ^a				
	H-Z	SiCl ₄ -Z	Cr _{1.5} /SiCl ₄ -Z	Cu _{1.5} /SiCl ₄ -Z	Cr _{1.0} Cu _{0.5} /SiCl ₄ -Z
S _{BET} (m ² /g)	386	346	320	318	324
Micropore area (m ² /g)	315	211	214	207	198
Mesopore area (m ² /g)	71	134	106	111	126
Strong acidity ^b (mmol NH ₃ /g)	0.121	0.045	0.042	0.045	0.044
Weak acidity ^c (mmol NH ₃ /g)	0.099	0.063	0.054	0.058	0.056
Metal content (wt.%)	–	–	1.5 (Cr)	1.5 (Cu)	1.0 (Cr), 0.5 (Cu)

^a Z = H-ZSM-5 (Si/Al = 240).

^b Sites retaining ammonia at temperatures exceeding 250 °C.

^c Difference between total acidity and strong acidity.

cannot be, therefore, high. However, overall changes in the characteristics of the catalyst support after the silicon tetrachloride treatment process are not merely due to the dealumination of the zeolite. Other mechanisms, such as the masking of certain sites and the formation of extra framework species could also contribute in characterizing the resultant material after the treatment. However, dealumination does occur and reported by most researchers investigating the dealumination under almost similar reaction conditions [14,22,31,32]. In the present study, discussions are more focused to the overall changes of the zeolite after the silicon tetrachloride treatment, as this will certainly affect the performance of the material as support in the combustion of Cl-VOC.

3.2. The resistance of ZSM-5 support against gaseous HCl

In the combustion of Cl-VOC, the occurrence of hydrogen chloride as the desired chlorine-containing product in the outlet stream gas can pose significant problems to some combustion catalysts [13,25]. In the present study, the chemical resistance of the SiCl_4 -Z support and H-Z as the reference (control) against hydrogen chloride is tested using gaseous hydrogen chloride at 400°C for 4 h. Changes in the surface characteristics, acidity and crystallinity of these support materials could provide useful information on their nature and degree of deactivation in the combustion of Cl-VOC.

Table 2 summarizes changes in characteristics of H-Z and SiCl_4 -Z after the reaction with gaseous hydrogen chloride. The treatment is found to cause a minimal reduction in BET and micropore surface areas, particularly with SiCl_4 -Z. The result suggests that only minor changes occur in the zeolite framework of both materials upon treatment with hydrogen chloride. This fact is supported by a high crystallinity retention of over 90% by both of these materials. Treatment of H-Z with silicon tetrachloride slightly improves the integrity of the framework against hydrogen chloride as indicated by a higher crystallinity retention of SiCl_4 -Z. Table 2 evidences that hydrogen chloride mainly affects weak acid sites with reductions of between 52 and 58%, while the effect on strong acid sites are limited to below 8%.

Table 2
Changes in characteristics of H-Z and SiCl_4 -Z after reaction with gaseous hydrogen chloride at 400°C for 4 h

Properties	H-Z		SiCl_4 -Z	
	Value	% Difference ^a	Value	% Difference ^a
S_{BET} (m^2/g)	368	-4.7	346	-1.7
Micropore area (m^2/g)	290	-7.9	211	-3.3
Mesopore area (m^2/g)	78	+9.9	134	+1.5
Strong acidity ($\text{mmol NH}_3/\text{g}$)	0.112	-7.4	0.045	-6.7
Weak acidity ($\text{mmol NH}_3/\text{g}$)	0.042	-57.6	0.063	-52.4
Crystallinity ^b (%)	91	-	96	-

^a Relative to values of fresh support materials shown in Table 1.

^b Relative to respective fresh materials.

The high resistance of H-Z against hydrogen chloride at 400°C is mainly ascribed to its high Si/Al ratio, involving more Si–O bonds than Al–O bonds in its framework. This conclusion is based on the fact that Si–O bonds are stronger and more resistant to hydrolytic and acid attacks than the Al–O bonds [32]. The higher bond strength is attributed to the smaller atomic size and higher electronegativity of Si atoms compared to Al, thus resisting electron polarity in the chemical bond. The introduction of more silicon atoms into the framework of the zeolite through dealumination with silicon tetrachloride causes the partial replacement of framework aluminum atoms. The overall strength of the bonds in the framework is then increased. The effect manifests itself in a further improvement of the resistance against hydrogen chloride as showed by SiCl_4 -Z.

Stronger acid sites are relatively less affected by hydrogen chloride. This is translated by a lower ability of hydrogen chloride to break the bridging $\text{Si}(\text{OH})\text{Al}$ bonds in the framework of the zeolite that form strong acid sites in both H-Z and SiCl_4 -Z. In contrast, aluminum-containing extra framework species, forming weak acid sites, easily interact with hydrogen chloride leading to the loss of a significant portion of its acid property. This could be due to the amphotericity of the extra framework aluminum species that makes it more reactive for interaction with an acid.

As SiCl_4 -Z is found to be sufficiently resistant to hydrogen chloride attack at high temperatures, it is selected as the support in the bimetallic catalyst for the combustion of Cl-VOC. The justification is based on the fact that catalysts deactivation associated with the support during the combustion of Cl-VOC is primarily due to their intolerance to hydrogen chloride [7,11,25]. Thus, the deactivation of the SiCl_4 -Z-supported bimetallic catalyst in the process should be mostly ascribed to chemical and physical changes occurring in the metal species, rather than those of the catalyst support. In addition, the framework dealumination, assisted by the formation of siliceous extra framework species makes the SiCl_4 -Z support more hydrophobic to resist deactivation by humidity in the feed. The modified materials also have lower tendency to coking as significant portion of its acid sites, that are responsible for coking activity, have been eliminated through dealumination process or through the masking by siliceous species. All these phenomena have been discussed thoroughly in our previous papers and are not repeated here [22,24].

3.3. Effects of copper in $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4$ -Z

Active metal species in the catalyst have been known to have different abilities to promote the combustion activity of VOC in a catalytic reactor. It is generally accepted that these metals act by improving the redox activity of the catalysts [8,21,33]. Each metal will catalyze the combustion reaction through different reaction mechanisms, rendering differences in the distribution of the combustion products and the overall behavior of the process [3,5,7]. Single metal catalysts might subject to several drawbacks, such as low carbon dioxide yield at high conversion [24] or sometimes, the high reactivity of VOC over a certain metal could be catalyst-specific [17,24,34]. Thus, efforts towards

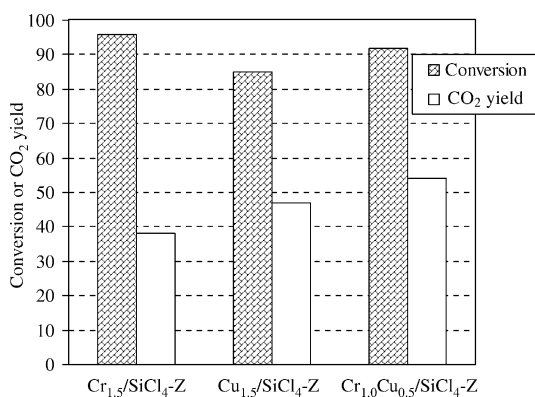


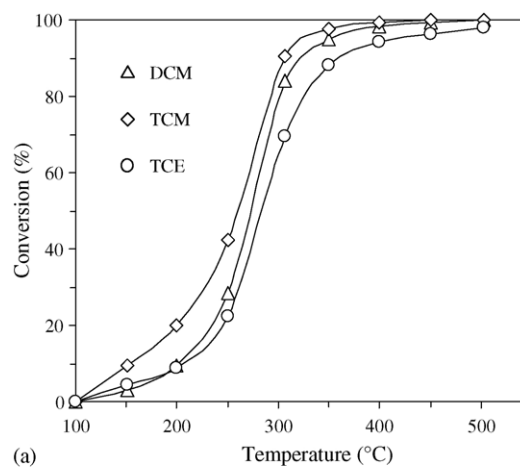
Fig. 2. Role of copper in a bimetallic Cr_{1.0}Cu_{0.5}/SiCl₄-Z catalyst in the combustion of 2500 ppm of TCE at GHSV 32,000 h⁻¹ and 400 °C.

finding multimetallic catalyst that show more flexibility in the combustion process are deemed worthwhile.

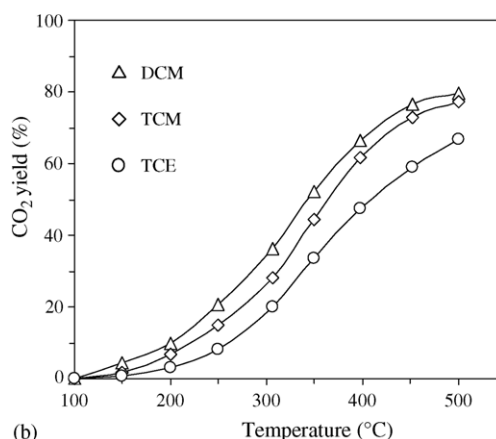
An attempt is made to compare the performance in the TCE combustion of the single metal chromium and copper catalysts with the bimetallic chromium and copper catalyst, with the same total metal content. Fig. 2 shows that Cr_{1.5}/SiCl₄-Z is more active than Cu_{1.5}/SiCl₄-Z with about 12% difference in the conversion at 400 °C. However, the higher activity of Cr_{1.5}/SiCl₄-Z is also accompanied by the occurrence of higher amounts of products of incomplete combustion in the outlet stream as indicated by the lower carbon dioxide yield. At this operating condition, Cu_{1.5}/SiCl₄-Z shows approximately, a 9% better carbon dioxide yield than Cr_{1.5}/SiCl₄-Z. A replacement of 0.5 wt.% of chromium by 0.5 wt.% of copper in Cr_{1.0}Cu_{0.5}/SiCl₄-Z results in a minimal reduction of 3% in the conversion but with a corresponding increase of about 16% in the yield towards carbon dioxide with Cr_{1.0}/SiCl₄-Z. This yield is also significantly higher than that of Cu_{1.5}/SiCl₄-Z.

Copper is an element located on the left of chromium in the first row of transition metals of the periodical table. In a VOC combustion environment, both metals could be oxidized to higher valencies by attachment to extra-lattice oxygen atoms [10]. Due to the larger atomic radius, electrons in the outermost shell (3d) of chromium were relatively easier to remove to present at higher oxidation states. With an increase in oxidation state, the electron accepting ability of chromium was expected to increase, thereby making it highly susceptible to reduction by Cl-VOC. The higher activity of chromium in the combustion of Cl-VOC was hence, in agreement with the mechanisms considered by the Mars–van Krevelen model.

A minimum drop in the conversion with lower chromium content in Cr_{1.0}Cu_{0.5}/SiCl₄-Z compared to Cr_{1.5}/SiCl₄-Z is an expected consequence of copper being relatively less active for Cl-VOC combustion. However, a marked increase in the carbon dioxide yield is considered as too high to only consider the activity of the bimetallic catalyst as the sole summation of the activity of their individual metal components. This observation leads to the conclusion that some kind of synergism might have taken place between the metal components in Cr_{1.0}Cu_{0.5}/SiCl₄-Z, thus promoting the high oxidation yields.



(a)



(b)

Fig. 3. (a) Conversion and (b) carbon dioxide yield in the combustion of 2500 ppm of chlorinated VOCs over Cr_{1.0}Cu_{0.5}/SiCl₄-Z at a GHSV of 32,000 h⁻¹.

3.4. The activity study of Cr_{1.0}Cu_{0.5}/SiCl₄-Z

Fig. 3(a and b) shows the conversion and corresponding carbon dioxide yield, respectively, in the combustion of DCM, TCM and TCE. The data reported in figure are average values out of three readings. In the present study, the % errors are usually within ±3% and it is more meaningful to observe trends obtained for the conversion and the carbon dioxide yield rather than the accuracy of the specific points.

An increasing chlorine content in a VOC molecule is found to positively affect the reactivity of the molecule as suggested by higher conversions of TCM compared to DCM as shown in Fig. 3(a). The difference in the reactivity of these two chlorinated organics is more evident at lower temperatures but the gap gradually narrows down as the temperature increases until total conversion is reached above 450 °C. Meanwhile, TCE with three chlorine atoms and one double bond in its molecule is clearly less reactive compared to DCM and TCM and cannot be totally destroyed below 500 °C.

It has been noted that the use of metallic catalysts could lead to the formation of highly chlorinated by-products [7,11,12]. However, the active metal species is indispensable for a VOC combustion catalyst as it significantly improves VOC conversion

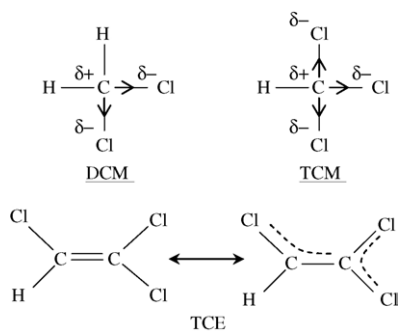


Fig. 4. Electron shift in the C–Cl bonds.

to consequently achieve high removal efficiency at lower temperatures. In the present study, the completion of the combustion process, and indirectly, the occurrence of high molecular weight by-products (including chlorinated ones) is measured based on the carbon dioxide yield of the process. It is evident in Fig. 3(b) that despite an increasing conversion, the higher chlorine content in TCM also promotes the formation of higher by-products as suggested by the lower carbon dioxide yield with this compound compared to that of DCM (Fig. 3(b)). With a TCE feed, the low conversion is also accompanied by low carbon dioxide yield.

The chlorine atom is well-known for its high electronegativity and can induce an electron shift in the chemical bond [10]. In DCM and TCM molecules, chlorine affects the electron distribution of the covalent bond with carbon (Fig. 4). As a consequence, a partial positive charge center, stronger in TCM, forms on the carbon atom and can act as electrophilic site in the combustion reactions. Due to the polarity of the C–Cl bonds, a carbon center bearing three chlorine atoms in TCM becomes more reactive than that bearing two chlorine atoms in DCM [7]. The effect manifested itself by a higher reactivity and higher conversion of TCM compared to that of DCM.

The stabilization of TCE molecules is attributed to the occurrence of a resonance effect in the molecule from interactions between lone pair electron in chlorine atoms and the π electron in the C=C double bond. First, the more electronegative chlorine atoms pull electrons from the π system of the C=C double bond. Conversely, lone pairs of electrons from the chlorine are extended to the new π -bonding in the C=Cl bond by donating some electrons back to the π system [10]. This interaction is possible as the electronic configuration of an atom of chlorine is $1s^2 2s^2 2p^6 3s^2 3p^5$ and the σ -bond formation with the carbon atom leave one diagonal lone pair ($3s^2$) and two p-orbital lone pairs ($3p_{xy}^2$ and $3p_{yz}^2$) (in the valence shell). One of these lone pairs is free to overlap with the π -bond (of the C=C entity) to give an extended π -electron system [4].

3.5. Roles of water vapor in the combustion of Cl-VOC

Table 3 shows that in the presence of 9000 ppm of water vapor in the feed, the conversions of DCM and TCM drop by about 18% compared to about 6% for TCE. This drop is expected as water vapor is known to inhibit a combustion reaction by competing with an organic molecule for adsorption on active

Table 3

Conversion and corresponding carbon dioxide yield in the combustion of DCM, TCM and TCE (at $C_{voc} = 2500$ ppm, $T = 400$ °C, GHSV = 32,000 h⁻¹)

Feed	Conversion (%)		Carbon dioxide yield (%)	
	Dry	Humid ^a	Dry	Humid ^a
DCM	98.3	85.2	66.4	70.8
TCM	99.3	86.6	61.7	74.5
TCE	94.2	88.5	47.5	68.4

^a In the presence of 9000 ppm of water vapor as co-feed.

sites [6,14,35]. Similar observation with zeolite-based catalyst has also been reported by many researchers [2,10], while the effect was not so obvious with fleece reactors as reported by Everaert et al. [4,5]. Adsorption of water molecules, especially at the pore mouth of the zeolite, may also create a diffusion limitation for organic reactants, resulting in a lower catalytic activity [14]. The TCE conversion is the least affected by water vapor in the feed, probably due to more favorable adsorption of this substance on the metal sites. This is due to relatively stronger interactions between π electrons in a C=C double bond with an unoccupied p orbital in the metal species of the combustion catalyst [6,11].

Despite lower conversions in a feed containing moisture, the reactivity of Cl-VOCs and their combustion intermediates over $Cr_{1.0}Cu_{0.5}/SiCl_4$ -Z catalyst are enhanced by the presence of water vapor as suggested by the higher carbon dioxide yield, regardless of the model substance being oxidized. This is reflected by a lower selectivity of higher carbon-containing products, particularly undesirable chlorinated ones in the reactor outlet stream. This positive effect is more noticeable in the TCE combustion with an increment of about 21% compared to that of DCM and DCM that stand at 7–9%.

Higher carbon dioxide yields with a humid feed proves that despite inhibiting the conversion of the organic feed, water molecules are also directly involve in the combustion reactions. Siquin et al. [7] reported that carbon tetrachloride in a humid feed could be destroyed in the absence of oxygen at high temperature. This experimental observation is theoretically in agreement with this hypothesis. The most probable mechanism involves the hydrolytic attack by a water molecule on the polar C–Cl bonding in the Cl-VOC [6]. This reaction would create mineral acid and chlorinated species that could participate in any subsequent chlorine-transfer reactions.

Water molecules can initiate the hydrolysis mechanism by hydroxylating the metal species in the combustion catalyst [13]. These hydroxylated species, with a more localized charge than in the initial state, are then involved in the reaction with Cl-VOC to form carbocations through the S_N^2 substitution reaction [9]. Since the S_N^2 substitution reaction is generally enhanced in the presence of a polar solvent like water [6], the formation of the carbocations is enhanced in the presence of excess water. The highly reactive carbocation species will subsequently undergo further oxidation reactions over the active metal species at an accelerated rate due to their high reactivity yielding more carbon dioxide as the complete oxidation product.

Hydrolytic attack by a water molecule on TCE produces a vinyl carbocation, while the corresponding reaction of DCM and TCM produces alkyl carbocations. Despite being more difficult to form since the cation is on a more electronegative sp hybridized carbon, the vinyl carbocation is relatively unstable and reactive [9]. Therefore, it can undergo subsequent oxidation over the catalyst at an accelerated rate to ultimately produce more carbon dioxide. In contrast, alkyl carbocations from DCM and TCM are relatively stable as they are sp² at the cationic center. Thus, the combustion reaction demonstrates a further improvement in the carbon dioxide yield with humid TCE compared to that of DCM and TCM.

The positive role of the water molecule on the carbon dioxide production can also be explained by its hydrogen-supplying role to the reacting system. Water has been reported to suppress the formation of chlorinated by-products in the combustion of hydrogen-deficient VOCs [14,36]. Thus, it is suggested that chloride surface species ($-\text{Cl}_s^-$) reacts with water to form hydrochloric acid and lattice oxygen species (O_s^{2-}) or surface hydroxide groups ($-\text{OH}_s^-$). The reaction equilibria are presented as:



In the presence of water vapor, the equilibria are shifted to the right hand side. The decrease in the by-product formation in the presence of water is explained by the fact that the chloride transfers in adsorbed Cl-VOCs and/or intermediates are suppressed [6].

3.6. The deactivation study

It is more accurate to measure the deactivation based on the reaction rate as it is measured in a differential mode rather than the conversion that is measured in an integral reactor mode. As such, in the present study, the activity loss is demonstrated based on the activity (a), calculated based on the rate of reaction at t h to that of $t=0$. Profiles of $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$ deactivation with time after ageing with different feed Cl-VOCs are shown in Fig. 5. The profiles are characterized by an initial sharp drop followed by a gradual decrease in the activity until a relatively stable activity is reached at a longer operation time. The $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$ catalyst appears to be resistant to deactivation with less than 15% activity drop detected for all three types of chlorinated organics. The activity is least affected when DCM is used as the feed with more than 90% activity retention after 12 h on stream. Compared to TCM, TCE shows an initial slower deactivation but as the time progresses, a larger activity drop is experienced by the catalyst.

Upon completion of the ageing test, the coke deposition on the catalyst is found to be very minimal with less than 1 wt.% for DCM and TCM feeds, and 1.8 wt.% for TCE. Thus, it can be concluded that the catalyst deactivation is mainly attributed to interactions between the catalyst and chlorine bearing in mind that the $\text{SiCl}_4\text{-Z}$ support is highly resistant to hydrogen chloride. Low coking activity with DCM and TCM is ascribed to their

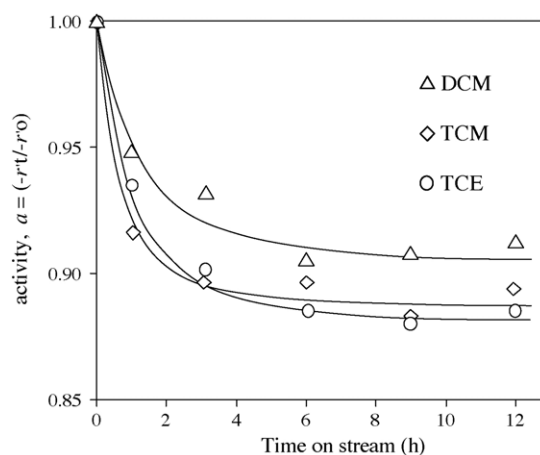


Fig. 5. Deactivation of $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$ catalyst with time on stream in the combustion of 35,000 ppm of chlorinated VOCs at GHSV $32,000\text{ h}^{-1}$ and 400°C .

small molecules and highly reactive intermediates to give high selectivity to gaseous products [1,37]. With increasing molecular size in TCE, the coking activity increases but is still low compared to that of non-chlorinated VOCs as reported by Dégé et al. [38] and Antunes et al. [39].

Initial interactions between metallic species and chlorine atoms to form metal chloride cause rapid deactivation of the catalyst as indicated by a steeper drop in the activity. As the reaction time progresses, a more stable activity is obtained suggesting a limited capacity of the metallic species to receive chlorine. By theory, highly stable Cr^{3+} can only receive three chlorine atoms to form chloride, while it is two atoms with Cu^{2+} . However, with the ability of chromium and copper to present multiple oxidation states, coupled with the ability of molecular chlorine to act as strong oxidizing agent, these interactions become more complicated. This is, probably, the governing factor characterizing the deactivation profile of the catalyst with operating time.

TCM with a higher chlorine content in its molecule causes more deactivation compared to DCM, as it is more reactive and consequently causes more chlorination of the active metal species in $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$. In fact, the H/C ratio of the Cl-VOC is the key factor that determined the life of a combustion catalyst [25]. In a similar way, the initial slower activity decay with TCE compared to that caused by TCM can be attributed to the lower reactivity of the former substance. However, at longer operating times, TCE causes more deactivation as the effect of coke accumulation gains significance.

3.7. Effects of ageing on surface hydroxyl groups

In zeolites, surface hydroxyl groups fall under two major groups viz. bridging hydroxyl belonging to Brønsted acid sites and silanols associated with a wide infrared absorption band centered at 3595 and 3735 cm^{-1} , respectively. Since the infrared absorption spectra for these two types of hydroxyl groups do not show well separated peaks (Fig. 6), qualitative comparison between samples is based on the shape of the peaks between 3300 and 3800 cm^{-1} .

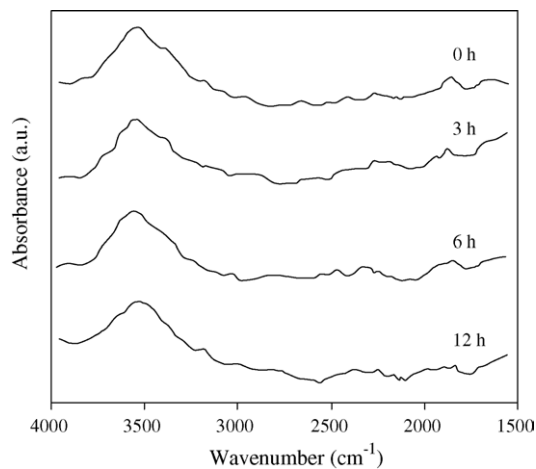


Fig. 6. Infrared absorbance of $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$ after ageing with 35,000 ppm of TCE at 400 °C for four different operating times.

Fig. 6 shows that the hydroxyls absorption region is characterized by an almost symmetrical peak between 3300 and 3800 cm^{-1} . When the $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$ catalyst is deactivated with time, a minimum reduction in the intensity of the peak is detected but the basic shape of the peak remains unchanged. Changes in the shape of the absorption profile upon ageing with TCE suggest that a non-selective elimination of both bridging hydroxyl and silanol with time.

If there were chemical interactions between Si or Al atom with chlorine, it should be in favor of Al and lead to the disappearance of bridging hydroxyl groups. This is based on the fact that the Al atom with an outer electron configuration of $3s^23p^1$ can more readily donate its electron to form aluminum chloride. The corresponding loss of strong acid sites should be the other consequence. However, this loss is not observed through the acidity study on $\text{SiCl}_4\text{-Z}$ upon ageing with hydrogen chloride. This result thus leads to the general conclusion that hydroxyl groups on the surface of $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$ are not chemically altered during the combustion of Cl-VOCs. The disappearance of hydroxyls upon ageing with TCE might be due to physical means, such as coking rather than chemical interactions.

3.8. XRD analysis of aged $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$

In order to investigate the type and extent of changes occurred in $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$ upon ageing with TCE, an XRD analysis is performed for the catalyst, before and after the ageing process. Ageing at 400 °C for 12 h results in the emergence of new diffraction peaks marked with vertical lines in Fig. 7. However, the characteristic diffraction peaks belonging to oxides of chromium and copper in the catalyst (marked with blank and filled circle, respectively, in Fig. 7) are still present, but with lower intensity. The catalyst, however, maintains the basic diffraction pattern with a crystallinity calculated to be 97% relative to fresh $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$. This result suggests a high integrity of the framework of the zeolite, which is in agreement with its resistance to hydrogen chloride at high temperature.

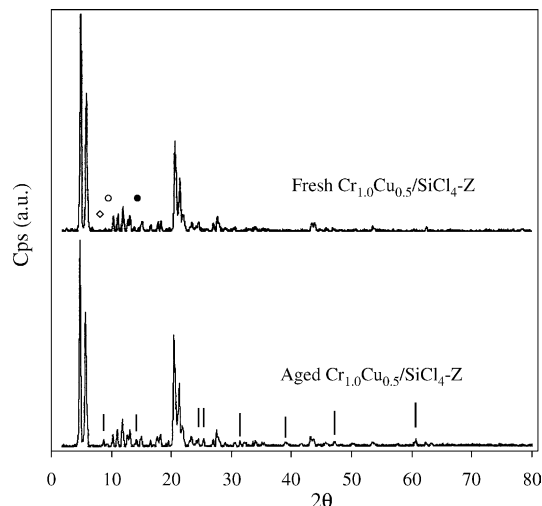


Fig. 7. XRD of fresh and aged $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$ with TCE at 400 °C for 12 h with new emerged peaks marked with vertical lines.

The emergence of additional sharp and well-defined diffraction peaks in aged $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$ suggests the presence of materials of high crystallinity. Since those peaks are not present in the diffractogram of the $\text{SiCl}_4\text{-Z}$ support treated with hydrogen chloride, these materials should be ascribed to those created from interactions between chlorine atoms, and chromium and copper in the catalyst. These crystalline materials were predominantly in the form of metal chlorides [1,8]. Despite not detected in the aged catalyst (diamond marker in Fig. 7), the formation of oxychlorides, especially at low concentration, cannot be totally ruled out [7].

Despite the high concentration of TCE and the long reaction time used in the ageing process, the complete chlorination of chromium and copper in $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$ is not achieved. This conclusion is based on the presence of diffraction peaks corresponding to oxides of these metals in aged catalyst. It is highly probable that only the external portion of metal oxide clusters on $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$ are susceptible to chlorination, while the internal portion remains unchanged. Similar results have been reported by Sinquin et al. [7] with LaCoO_3 perovskite catalyst for the combustion of carbon tetrachloride. The limited 12% activity loss after aged for 12 h ageing is also contributed by coke accumulation. It can be concluded that the outer metal chloride layer of the metal cluster present in a $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$ catalyst is also capable of catalyzing the combustion reaction.

If the chlorination of non-porous metal oxides nanocrystals (consisting of Cr and Cu oxides) that are distributed on the $\text{SiCl}_4\text{-Z}$ support is assumed to follow the Shrinking-Core Model which normally approximates real fluid-particle reactions in a wide variety of situations [40], the presence of remaining metal oxides can be explained. Upon chlorination, the outer metal chloride layer acts as a protective layer for further chlorination of the oxides in the core of the clusters. A progressive growth in the size of the metal cluster is the expected consequence, as this reaction involves the substitution of oxygen with large chlorine atoms. Since the charge of the chlorine ion (-1) is lower than the oxygen ion (-2), the loss of one oxygen ion is replaced by

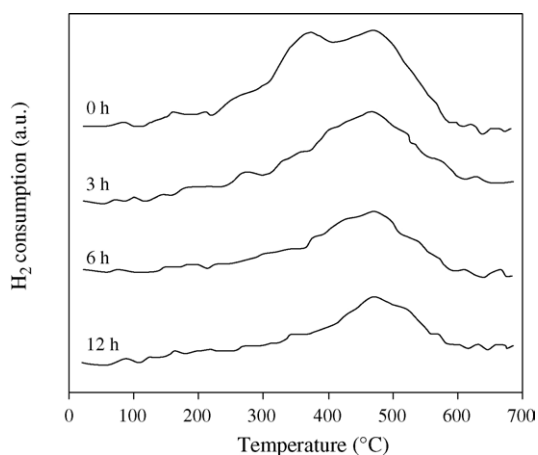


Fig. 8. TPR profiles of $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$ after ageing with 35,000 ppm of trichloroethylene at 400 °C for four different times on stream.

two chlorine atoms. With the formation of a non-flaking chloride layer at the boundary of the mixed oxide clusters, the integrity of the final clusters is kept intact.

3.9. TPR profiles of aged $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$

The TPR profile of fresh $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$ is characterized by two major peaks occurring at different temperature regions (Fig. 8). The peak at around 380 °C is assigned to the combined reduction of Cr^{6+} and Cu^{2+} , while the second peak occurring at about 480 °C is attributed to the reduction of Cr^{3+} and Cu^+ . Upon ageing with TCE, the first peak appears to be eliminated with time, while the overall reducibility of the metal species on the catalyst is found to be on a decreasing trend.

The TPR result suggests that with the chlorination of the metal species in the catalyst, the overall reducibility of the metals weakens. This can be due to a higher electronegativity of chlorine atom compared to the oxygen atom that originally formed oxides with the metal species in fresh $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$. As a result, the ionic bond in metal chloride should be stronger than that in metal oxide to pose more resistance to reduction during TPR analysis. However, the chlorination and oxidation of the metal species in the combustion reactions are reversible processes that are dictated by reaction temperature and prevalent chloride concentration [8]. This reversibility explains why the catalyst does not show complete deactivation but only achieves its relatively stable activity at longer operating time for all three types of Cl-VOCs.

When present in association with chromium or copper in $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$, chlorine atoms could affect the electron acceptance properties of these metals by strongly forming ionic bonds with them [2]. In the TPR analysis, hydrogen has a lower ability to reduce these metal chlorides as the first step involved the extraction of a chlorine atom to form metal hydrides. The hydrogen consumption in the TPR profile of the aged catalyst should thus be attributed to the reduction of remaining oxides of chromium or copper in the catalyst, explaining the decreasing trend in the reducibility of the metals with time.

The shape of the peak in the TPR profile upon ageing with TCE suggests that the first peak is selectively eliminated. More favorable redox reactions between Cr^{6+} and Cu^{2+} with chlorine producing oxychlorides or molecular chlorine (Cl_2) leading to the reduction of these metal species is deemed as the main factor behind this result. Of these two metal species, Cr^{6+} is relatively less stable and more susceptible to reduction. The formation of oxychlorides in the combustion of Cl-VOCs has been reported by several authors [1,8,41]. The formation of molecular chlorine is always associated with the chromium-containing catalyst as reported by Padilla et al. [1] and Karmakar and Greene [41]. Therefore, the main peak in the TPR profile of aged catalyst must be mainly attributed to the combined reduction of Cr^{3+} and Cu^+ .

Changes in the activity due to changes in the reducibility of the metal species in the catalyst can be explained with Mars–van Krevelen model that is regarded as the most reliable model to represent VOC combustion process [12,17]. Since the chlorination of the metal species in $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$ reduces some of its metal species, while metals in chloride form are generally more resistance to reduction, an overall reduction in redox activity of the catalyst is expected as suggested by results in Fig. 8. In other words, upon the chlorination of its metal species, the catalyst loses a certain degree of its ability to undergo oxidation through the reaction with the chemisorbed oxygen and subsequently has weakened ability to undergo reduction during the reaction with the Cl-VOC molecule. According to the Mars–van Krevelen model, a decrease in the overall activity of the catalyst is the likely consequence.

4. Conclusions

H-ZSM-5 (Si/Al=240) showed high chemical resistance against hydrogen chloride and this desired property was further improved by modifying the zeolite with silicon tetrachloride. TCM was more reactive compared to DCM but it produced more incomplete combustion products due to its high chlorine content. The stabilization of TCE was attributed to the resonance effect in the molecule. Despite inhibiting the conversion of Cl-VOC, water vapor increased the carbon dioxide yield by being directly involved in the combustion reaction through its role as hydrolysis agent. The effect was more noticeable in the TCE combustion, as it involved the formation of the relatively unstable vinyl carbocation compared to DCM and TCM that gave rise to alkyl carbocation. In addition, the role of water as hydrogen-supplying agent decreased the by-product formation by suppressing chlorine-transfer reactions. $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$ demonstrated high stability in its activity with time and more deactivation was detected with increasing Cl/H ratio feed substances. Coking was very low, especially with DCM and TCM due to their small molecules while producing highly reactive intermediates to give high selectivity towards gaseous products. The chlorination of metal species in $\text{Cr}_{1.0}\text{Cu}_{0.5}/\text{SiCl}_4\text{-Z}$ was responsible for loss of activity due to the weakening of their overall reducibility. This result was in agreement with the Mars–van Krevelen model explaining VOC combustion reactions.

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