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Catalytic destruction of halogenated air toxins and the effect of admixture with VOCs

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Abstract

Supported platinum group metal catalysts have been successfully commercialized for complete destruction of environmentally harmful halogenated volatile organic pollutants. Catalyst properties and oxidative destruction mechanisms were further investigated by evaluating the effects of admixture with nonhalogenated organic compounds. Catalyst composition and organic species were found to control the light-off characteristics.

Destruction mechanisms for saturated chlorocarbons were found to depend on catalyst support. Surface Brønsted acidity appears to play an important role on alumina-based catalysts; the light-off curves are not dependent on the Cl/C ratio. Radical initiation is suggested on titania supported catalyst; light-off temperature is directly related to the energy required for a radical dissociation of a chlorocarbon.

Unsaturated chlorocarbons are more stable than saturated ones. As a result, their oxidation generally requires high temperatures. The light-off characteristics of unsaturated chlorocarbons were also found to be determined by the mechanism of the destruction. The light-off temperatures were 200°C lower on a titania-based catalyst than on an alumina-based catalyst.

Oxidation temperature of volatile organic compounds (VOC) is also a function of the chemical nature of the compound. In contrast to chlorinated hydrocarbons, temperatures of activation for oxidation of unsaturated hydrocarbons are lower than saturated ones. Therefore, admixing unsaturated hydrocarbons with chlorinated hydrocarbons significantly decreased the light-off temperatures of the latter. The effect of saturated hydrocarbons such as ethane had little effect on the light-off characteristics of the chlorinated hydrocarbons.

The destruction of brominated compounds was also evaluated to determine the tolerance of catalyst supports to bromide poisoning at low temperature. Bromide was strongly adsorbed on an alumina-based catalyst and became a catalyst poison. As a result, toluene light-off in the admixture was shifted to a much higher temperature. The oxidation of toluene can be restored by removing Br from the catalyst by heating. On the titania-based catalyst, however, the light-off temperature of methyl bromide was shifted to a higher temperature in the presence of toluene. Toluene may either compete for the same adsorption site or suppress the formation of radicals from methyl bromide.

Keywords: Light-off temperatures; Alumina-based catalysts; Titania-based catalysts; Volatile organic compounds

1. Introduction

Halogenated organic compounds are considered potent environmental pollutants. Examples include chlorinated and brominated halocarbons

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that are environmentally hazardous chemicals which threaten human health and other biological systems, and chlorofluorocarbons (CFCs) that are known to destroy ozone in the stratosphere. These halogenated hydrocarbons are, therefore, receiving wide attention for phase out from industrial sources for which emissions are being regulated [1,2]. Catalytic incineration of halogenated volatile organic compounds (HVOC) is currently receiving increased attention for the potential technological and economic advantages it provides compared to thermal combustion systems [3,4]. A properly designed catalytic process can achieve complete destruction of all halocarbons, including the toxic by-products that can result from incomplete combustion of parent halocarbon. Additionally, catalytic incineration occurs at relatively low temperatures. Since the heats of combustion of HVOCs are low when compared with those of VOCs [5], low temperature operation is desired to minimize external energy consumption [6]. The catalytic incineration process can, therefore, offer significant cost savings over a thermal process.

Catalysts reported for destructive oxidation of HVOCs mostly consist of transition or noble metals on acidic supports [7–9]. Platinum group metals are well known active oxidation catalysts. They also resist halogen poisoning. For chlorocarbons of high Cl/C ratio, the Brønsted acidity alone provided by an acidic metal oxide support can also dissociate the C–Cl bond [10] and the catalyst can be effective for complete destruction.

Complete oxidative destruction of halocarbons is achieved through the following general reaction stoichiometry:

$$C_xH_yX_z + O_2 + nH_2O \rightarrow HX + CO_2 + mH_2O$$

where X represents a halogen. Typically water is added to generate HX which is controlled by the Deacon reaction and is readily scrubbed downstream of the catalytic oxidizer and before exiting the stack.

As most industrial exhaust sources of HVOCs also contain VOCs, determination of the mutual effects on catalytic activity is necessary for the optimization and selection of effective catalysts. Typically, the effects are characterized by monitoring the combustion efficiency as a function of temperature (light-off) for the various species at given test conditions.

The purpose of this paper is to summarize work carried out to characterize the impact of catalyst support material on the performance of platinum catalysts for streams containing HVOCs and VOCs.

2. Experimental

Catalysts were prepared by supporting Pt group metals on a honeycomb matrix washcoated with alumina-based (hereafter referred as catalyst A) or titania-based (hereafter referred as catalyst B) material.

Catalysts were tested in a fixed bed reactor interfaced with a Hewlett Packard 5890A gas chromatography for component analysis and quantification. The light-off curves were determined over a wide temperature range until complete destruction of the halocarbons. For clarification, T_x in the text is used to describe temperature at which $x\%$ conversion is achieved. At a specific conversion level ($x\%$), a lower T_x indicates a more active catalyst.

The flow-rates of gases in the feeds were individually controlled by mass flow controllers. Hydrogen halides were scrubbed with a 5% NaOH bath. The water concentration in the feed was controlled at 1.5%.

3. Results and discussion

Fig. 1 summarizes the light-off characteristics for C_1 chlorocarbons as a function of the Cl/C ratio and the types of catalyst support. As Cl/C ratio decreases, T_{50} and T_{90} increase on catalyst B, indicating an increased activation barrier for chlorocarbons of low Cl/C ratio. On catalyst A,

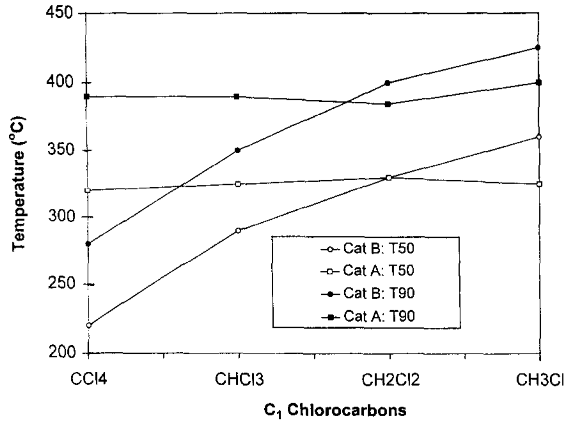

Fig. 1. Light-off temperatures of C_1 chlorocarbons. Cat A: alumina-based catalyst; Cat B: titania-based catalyst; T_{90}: temperature at which 90% conversion was reached; T_{50}: temperature at which 50% conversion was reached.

Table 1
Free energy of combustion for C_1 chlorocarbons

T (°C)	ΔG (kcal/mol)			
	CCl_4	$CHCl_3$	CH_2Cl_2	CH_3Cl
100	−67	−95	−125	−158
200	−74	−99	−128	−159
300	−80	−103	−131	−160
400	−87	−108	−133	−162

however, light-off curves are independent of Cl/C ratio. Similar behavior is also found for saturated C_2 chlorocarbons (not shown). For unsaturated C_2 chlorocarbons, higher temperatures are generally required for the oxidation when compared with the saturated counterparts, though light-offs are lower for catalyst B than for catalyst A.

Even though large differences exist in the free energy of combustion among the C_1 chlorocarbons (Table 1), they are not reflected in the light-off curves on catalyst A. On catalyst B, the variation of light-off temperature was, in fact, the opposite of what would be predicted on the basis of thermodynamic consideration.

Such a dramatic difference between catalysts A and B for chlorocarbon oxidation can only be attributed to different reaction mechanisms. On catalyst A, the alumina surface acidity may play an important role. The adsorption of chlorocarbons on catalyst A possibly occurs at acid sites via hydrogen bonding between Cl of the chlorocarbon and surface proton. While a detailed reaction mechanism on catalyst A remains to be investigated with spectroscopic techniques, the cleavage of C–Cl bond as a rate determining step can be ruled out as the four C_1 chlorocarbons of different Cl/C ratio are not discriminated on the acidic support (see Table 2), resulting in light-off curves of little difference. The function of surface acidity for chlorocarbon destruction found in present study is consistent with previous reports by others on alumina and zeolites supported catalysts [11,12]. The chlorination of surface alumina was considered to be the initial step of the reaction for CH_3Cl, followed by hydrolysis of chlorinated alumina. The oxidation of CH_3OH was proposed to proceed on the metal sites [12].

On the other hand, surface acidity is consid-

Table 2
Free energy and equilibrium constant of bond dissociation for C_1 chlorocarbons

T (°C)	$CCl_4 \rightarrow CCl_3 + Cl$		$CHCl_3 \rightarrow CHCl_2 + Cl$		$CH_2Cl_2 \rightarrow CH_2Cl + Cl$		$CH_3Cl \rightarrow CH_3 + Cl$	
	ΔG	K	ΔG	K	ΔG	K	ΔG	K
0	62.1	2.1E − 50	61.7	4.3E − 50	70.7	2.5E − 57	75.6	3.0E − 61
100	58.5	5.8E − 35	58.2	8.6E − 35	67.4	3.3E − 40	72.6	2.9E − 43
200	54.8	4.8E − 26	54.6	6.2E − 26	64.0	2.7E − 30	69.5	8.0E − 33
250	53.0	7.3E − 23	52.8	9.1E − 23	62.3	9.7E − 27	67.9	4.3E − 29
300	51.2	3.1E − 20	50.9	3.8E − 20	60.5	8.3E − 24	66.3	5.3E − 26
350	49.4	4.9E − 18	49.1	5.9E − 18	58.8	2.4E − 21	64.6	2.1E − 23
400	47.5	3.7E − 16	47.3	4.4E − 16	57.0	3.1E − 19	63.0	3.5E − 21
500	43.9	3.8E − 13	43.6	4.7E − 13	53.5	7.6E − 16	59.7	1.3E − 17
600	40.3	8.2E − 11	40.0	1.0E − 10	50.0	3.2E − 13	56.4	7.5E − 15

erably weaker on catalyst B. A different reaction mechanism prevails. In Table 2, the free energy for C–Cl bond cleavage is shown to increase with decreasing Cl/C ratio. The increase in light-off temperature in accordance with such a trend suggests that C–Cl bond cleavage is a rate determining step on titania surface. During the bond cleavage process, radicals are formed, possibly suggesting a radical mechanism may be involved prior to the oxidation of intermediate chlorocarbon radicals. In fact, titania in anatase structure has been extensively studied for photo-initiated destruction by radical mechanism [13]. Formation of thermal radicals may be assisted by anatase titania at temperatures compatible with the C–Cl bond dissociation energy. It is also important to note that the T_{50}s fell in the somewhat constant range of $K = 10^{-22}$ to 10^{-25} as highlighted in Table 2. At decreasing Cl/C ratio, K values at such a constant range can be reached only at increasing temperature. Higher temperatures corresponding to a higher value of K are required to reach a higher conversion.

For unsaturated chlorocarbons, the C–Cl bond energy is further increased, which may account for the increased light-off temperature on titania support. Unsaturated C_2 chlorocarbons are stabilized by the p–π conjugation. The stabilized structure may account for the higher oxidation temperature on both catalysts A and B. However, an observed 200°C higher on catalyst A than on catalyst B for complete destruction could also be attributed to inhibition of the reaction by chlorinated alumina surface [5]. With acidic zeolite catalyst, larger amount of coke was reported for trichloroethylene than methylene chloride and carbon tetrachloride [11].

The oxidation of saturated C_2 chlorocarbons on catalyst A is usually accompanied by the formation of unsaturated intermediates that require relatively higher temperature for complete destruction [5]. For example, dichloroethylene is a byproduct in the oxidation of 1,1,1-trichloroethane at low temperatures. The T_{90} for 1,1,1-trichloroethane is at 275°C, but T_{90} for the oxidation of dichloroethylene intermediate is near 400°C, with a maximum formation occurring below 350°C.

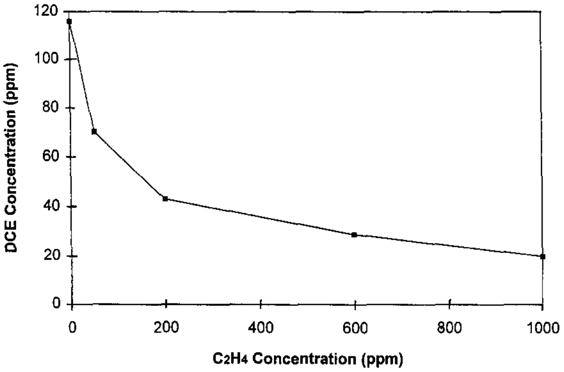

Fig. 2. Concentration of dichloroethylene (DCE), formed at 350°C during trichloroethane oxidation, as a function of C_2H_4 concentration in feed.

Generally, VOCs such as hydrocarbons are also present in effluent streams containing halocarbons. The presence of such VOCs in most cases affects the light-off characteristics of HVOCs. The effect of ethylene on the destruction of trichloroethane was studied at various ethylene concentrations and the results are shown in Fig. 2. While increasing ethylene concentration only slightly improved trichloroethane conversion, the formation of dichloroethylene byproduct was significantly suppressed. Thus the presence of ethylene effectively suppresses the formation of dichloroethylene and reduces the temperature for the total destruction of trichloroethane including the dichloroethylene byproduct.

The effect of other VOCs on the destruction efficiency for trichloroethlyene was also investigated and the results are shown in Fig. 3A. The light-off temperature of trichloroethylene was significantly lowered by the presence of ethylene. The effectiveness of saturated hydrocarbons (e.g. ethane) and aromatics (e.g. toluene) for trichloroethylene light-off are shown in Fig. 4. The effectiveness of the hydrocarbons for the enhanced destruction of trichloroethylene follows the order:

ethylene > toluene > ethane

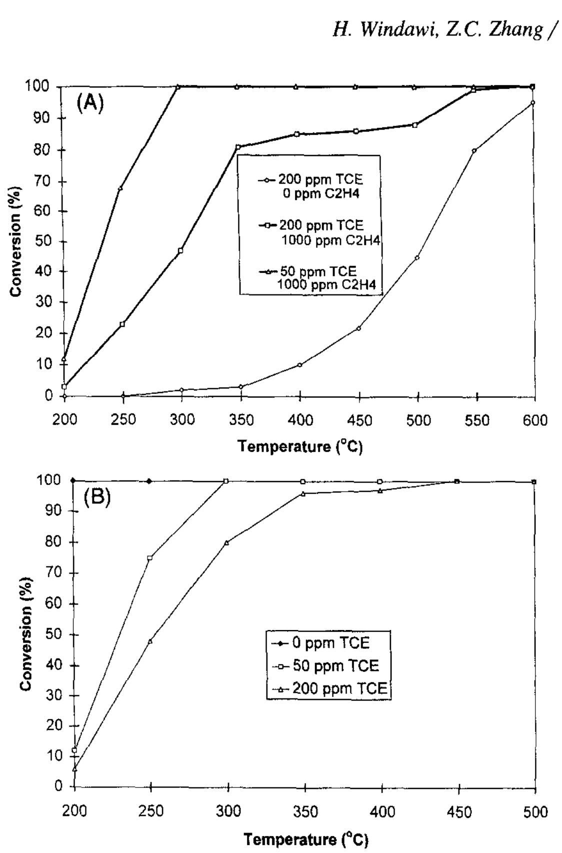

Fig. 3. The light-off curves of trichloroethylene (TCE) at different TCE/C_2H_4 concentration ratios.

Unsaturated hydrocarbons such as ethylene and toluene are completely oxidized below 200°C on these catalysts in the absence of HVOCs. Oxidation of ethane and other saturated hydrocarbons occurs at higher temperatures. It was observed that the light-off temperature for ethylene was increased with increasing trichloroethylene concentration (Fig. 3B). The hydrocarbon light-off temperature was instantaneously restored to lower temperature by turning off the trichloroethylene feed. The increased light-off temperature for hydrocarbons suggests that unsaturated chlorocarbons strongly compete for adsorption sites. This results in the attenuation of catalytic oxidation of hydrocarbons.

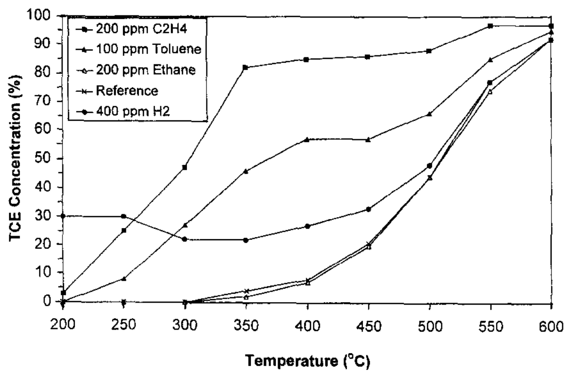

Fig. 4. Light-off curves of ethylene (2000 ppm) at different trichloroethylene (TCE) concentrations (as indicated in the figure).

Close inspection of Fig. 4 shows that the light-off curve of trichloroethylene is composed of two distinct components: enhanced light-off at temperature below 400°C and complete destruction at higher temperature. The partial conversion at the plateau is a function of the effectiveness of a particular hydrocarbon for trichloroethylene oxidation. Comparison of trichloroethylene light-off (Fig. 3A) and ethylene light-off (Fig. 3B) reveals that the plateau for trichloroethylene conversion is reached at complete consumption of ethylene. For 50 ppm trichloroethylene, the appearance of the plateau coincides with full oxidation of ethylene, both appearing at 300°C. Increasing the concentration of trichloroethylene to 200 ppm shifts this temperature to 350°C. Thus the enhanced destruction of trichloroethylene is dependent on the concentration ratio of ethylene/trichloroethylene. The coupled effect of ethylene and trichloroethylene light-offs suggests the involve-

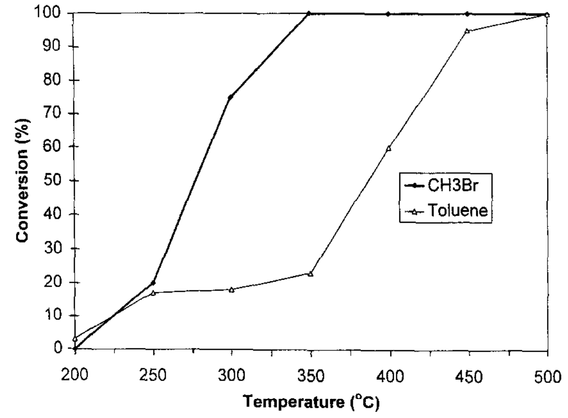

Fig. 5. The light-off curves of trichloroethylene (TCE, in 200 ppm) in admixtures with various VOCs (species and corresponding concentrations are indicated in the figure).

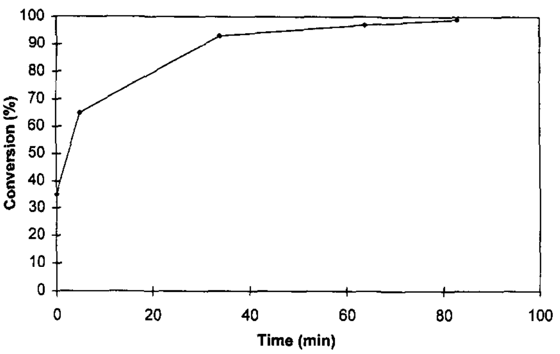

Fig. 6. The light-off curves of toluene and methyl bromide in their admixture. In the absence of methyl bromide, toluene oxidation is complete below 200°C.

ment of intermediate(s) from ethylene partial oxidation.

Similarly, brominated hydrocarbons were found to impact the light-off characteristics of aromatics. In a mixed feed of methyl bromide and toluene, the light-off temperature for CH_3Br on catalyst A was unaffected by the presence of toluene. However, the toluene light-off was shifted to a significantly higher temperature (Fig. 5), while complete toluene oxidation was reached at below 200°C in the absence of CH_3Br. In this case, Br^- poisoning was found to be the major cause of attenuation for toluene. Fig. 6 shows that the catalyst activity for toluene oxidation was gradually restored after shutting off the CH_3Br feed. It took about 1.5 h to reach near 99% conversion at 350°C. On catalyst B, however, the toluene light-off was not affected by the presence of CH_3Br. As oxidation takes place on noble metal catalyst, the data suggest that Br^- anions are largely stored on alumina support. The Br^- anions attenuate the catalytic activity for toluene oxidation. On titania support, on the other hand, Br^- poisoning is minimal and toluene light-off occurs at a lower temperature.

4. Conclusions

The destruction of halogenated compounds strongly depends on catalyst support material. On an alumina-based catalyst, adsorption of molecular halogenated hydrocarbons on acid sites may be a prevailing step and the light-off curves of saturated chlorocarbons are independent of the Cl/C ratio. On a titania-based catalyst, however, C–Cl dissociation energy is directly correlated to the light-off temperature at different Cl/C ratios, suggesting that a radical mechanism may be involved.

Another striking difference between the two types of catalysts is that titania-based catalyst is capable of completely destroying unsaturated chlorocarbons at much lower temperatures than alumina-based catalysts. A higher destruction temperature for unsaturated chlorocarbons with respect to saturated ones on a titania-based catalyst is again consistent with a radical cleavage mechanism. A largely increased temperature for unsaturated chlorocarbons on an alumina-based catalyst with respect to the saturated ones may be attributed to the immobilized adsorption of the unsaturated chlorocarbons on acid sites and/or inhibition by the chlorinated surface.

The presence of volatile organic compounds (VOCs) was found to enhance the destruction of unsaturated chlorocarbons on alumina-based catalysts; chlorocarbon light-off temperatures were lowered. The magnitude of the shift was dependent on the VOC species and on the relative concentration of VOCs with respect to unsaturated chlorocarbons. Simultaneously, VOC light-offs were shifted to moderately higher temperatures. Unsaturated and aromatic VOCs produce a strong effect toward the enhancement of halocarbon oxidation, while saturated VOCs show little enhancement. For example, the effectiveness of VOCs for enhanced destruction of trichloroethylene (TCE) was found to follow the order: ethane < toluene < ethylene.

The complete destruction of brominated compounds was also evaluated to determine the tolerance of catalyst supports to bromide poisoning at low temperatures. In a mixture of methyl bromide and toluene, it was found that bromide was strongly adsorbed onto the surface of catalyst A and became a strong catalyst poison. As a result, toluene light-off was shifted to a much higher temperature. The oxidation activity of catalyst A for toluene can be restored by removing Br from the catalyst such as by heating to moderately higher temperatures. On catalyst B, however, toluene light-off was not significantly affected by bromide, while the light-off temperature of methyl bromide was shifted to a higher temperature.

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