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VOC removal by synergic effect of combustion catalyst and ozone

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Abstract

The synergic effects of the combustion catalyst Ba–CuO–Cr_2O_3/Al_2O_3 and ozone, used as strong oxidant species in the combustion of various VOCs, were studied. The experiments were performed with five different methods by feeding the organics with air (1000 ppmV) before (methods 2 and 4) and after the ozone generator (methods 1, 3 and 5), they entered into the catalytic reactor (methods 1, 2 and 3) or were directly analyzed (methods 4 and 5). The concentration profiles of the organics were compared as a function of the reaction temperature (from 100 to 500°C) for the methods 1, 2 and 3 and as a function of the peak voltage of the ozone generator (2–10 kV), that is the ozone concentration (up to 2000 ppm) for methods 4 and 5. Ozone strongly reacted in the gas phase with aromatic molecules and organics having functional groups. Moreover, a positive ionizing effect produced by the corona discharge in the ozone generator on the destruction of the organics was found too.

Keywords: VOC combustion; BaO–CuO–Cr_2O_3/Al_2O_3

1. Introduction

Catalytic combustion [1–3] is a promising way to control the emissions of the volatile organic compounds (VOC) whose concentrations in air have to be minimized according to regulations of federal, state and local government agencies due to their harmful effects. The use of oxidation catalysts permits to decrease the temperatures to obtain complete decomposition of the organics (< 600°C) with respect to those utilized in thermal incinerators (> 1000°C). The lowering of reaction temperatures leads to several advantages in terms of environmental impact as well as energy saving: very low production of secondary pollutants (i.e., NO_x and micropollutants) and reduction of fuel costs [1,4]. The coupling of a low-temperature oxidation catalyst with an improved combustion technology can lead to further decrease of reaction temperatures at which the complete destruction of VOCs is obtained [5].

We have recently presented a catalytic technology in which ozone, used as strong oxidant (oxidation potential of ozone: 2.07 eV), coupled with electric discharge improves the air-catalytic combustion of hydrocarbons and chlorocarbons [6–8]. The improvement is reflected by the decrease of temperatures required to obtain the VOC destruction as well as the decrease of byproducts formed during combustion [9]. In

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order to better govern this technology, the action of ozone on the improvement of the catalytic process requires an intimate knowledge.

In this study, the different steps occurring during the combustion process have been investigated, including the action of ozone in the gas-phase, the ionizing effect of the corona discharge in the ozone generator, the catalyst activity with and without ozone. For the study, VOCs belonging to different chemical classes have been considered: acrylonitrile, methanol, styrene, toluene and 1,2-dichloroethane.

2. Experimental

The VOCs used for this study were all commercial products of guaranteed degree of purity (Fluka, > 99.0%). Their principal characteristics and a toxicity index, TLV [10], have been collected in Table 1. The average value of the standard enthalpy of combustion ($\Delta_c H^0$) of each compound was calculated in the temperature range from 300 to 1000°C according to the stoichiometry of complete combustion to CO_2 and H_2O; HCl and NO_2 were taken into account for 1,2-dichloroethane and acrylonitrile, respectively.

The catalyst used was a supported mixed oxide, i.e., barium promoted copper–chromite on alumina (Ba = 5.4%, Cu = 23.2%, Cr = 21.9%), supplied from Engelhard Industries Italy (code Cu-1230E). The BET surface area was 110 m^2/g.

For each combustion run, dosed amount of VOC as pure compound was mixed with air (gas-chromatographic dry air, from SIAD Italy) before being introduced in the reaction line. All the runs were carried out feeding 1000 ppmV of the organics. The gaseous mixture flowed at 20 Nl/h corresponding to space velocity of 10000 h^{-1} with 2 cm^3 of catalyst introduced in the reactor (700 mm long, 15 mm id) in extrudate physical form. An analytical apparatus for the analysis of the total organic carbon (TOC, from N.I.R.A. Italy) equipped with a FID detector, was employed. The analytical data corresponded to an average of 30 values, collected at intervals of 2 min during 1 h. The concentration of the VOCs was determined from the signal given by the TOC apparatus corrected for each organic by a suitable factor. The following factors were used: 0.467, 0.623, 0.750, 0.795 and 0.844 for methanol, acrylonitrile, styrene, toluene and 1,2-dichloroethane, respectively. Calibration measurements were carried out with known concentrations of CH_4 in air (512 ppmV), taking 1 the factor for CH_4.

The ozone generator (HRS Engineering, Italy) produced ozone from the air by electric discharge, i.e., corona effect, working at fixed frequency (1000 Hz) and variable peak voltage (0–12 kV). Typical runs were performed at 6.5 or 8.5 kV. The amount of ozone produced was

Table 1
Characteristics of the VOCs studied

Name	Formula	Molecular Weight (g/mol)	Vapor Pressure [a] (Torr)	$\Delta_c H^0$		Toxicity [b] (ppm)
				kcal/mol	kcal/g	
Acrylonitrile	C_2H_3CN	53	106.7	−397.6	−7.49	2
Methanol	CH_4O	32	113.9	−160.9	−5.02	200
Styrene	C_8H_8	104	7.2	−1020.4	−9.80	50
Toluene	C_7H_8	92	26.8	−901.6	−9.79	100
1,2-Dichloroethane	$C_2H_4Cl_2$	99	75.6	−258.9	−2.62	100

[a] Vapor pressure at 25°C.

[b] Threshold limit values (TLV's): highest level of exposure to toxic chemicals at which no deleterious effect is noted for human exposure in industry. The TLV's refer to air concentrations of a given chemical to which an individual can be repeatedly exposed for 8 hours per day, 5 days per week.

Table 2
Production of ozone

Voltage (kV)	Air stream (Nl/h)	Ozone		
		mg	g/h	ppm
5.0	20	5.44	0.0218	842
6.5	10	5.36	0.0214	1659
	20	6.40	0.0251	972
	38	8.32	0.0333	678
8.5	20	12.24	0.0490	1894

measured by iodometric titration as a function of the peak voltage in the ozone generator and of the air stream flowing in the apparatus (Table 2). From reactions (1) and (2), it was possible to quantitatively determine the ozone produced from the amount of $S_2O_3^{2-}$ utilized for the iodine titration.

$$2KI + O_3 \rightarrow K_2O + I_2 + O_2 \quad (1)$$

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \quad (2)$$

A system of valves permitted to perform the experiments with five different methods corresponding to different plant configurations. The combustion runs were performed according to the methods 1, 2 and 3 as a function of reaction temperature (Fig. 1). The action of the electric discharge (ionizing effect) and of ozone in the gas-phase on the destruction of the compounds were separately investigated operating at room temperature according to the methods 4 and 5 (Fig. 1).

3. Results and discussion

The residue concentrations of VOCs obtained from the catalytic combustion with methods 1, 2 and 3 (Fig. 2) have been compared as a function of the reaction temperature up to complete combustion. Complete combustions were considered to be reached when the analytical apparatus (TOC) revealed a signal corresponding to 2 ppm or less of total organic carbon in the exhaust gas-stream. The air-catalytic combustion on Ba–CuO–Cr_2O_3/Al_2O_3 permitted to completely destroy the various VOCs at temperatures not greater than 500°C, Fig. 2 (M.1). The good activity of the copper–chromite as combustion catalyst was tested for the toluene and styrene combustions in comparison to the various catalysts (supported noble metal and oxide catalysts) [8]. Fig. 2 (M.1) shows that deep decrease of the residue concentrations of the organics was observed starting from temperatures around 180°C for methanol and styrene, 220°C for acrylonitrile, 250°C for toluene and 370°C for 1,2-dichloroethane.

Operating the combustion according to method 2, Fig. 2 (M.2), the residue concentrations of the various VOCs at any temperature were much lower than those obtained operating with method 1. This behaviour could be ascribed to the pre-catalytic effects, that is, the

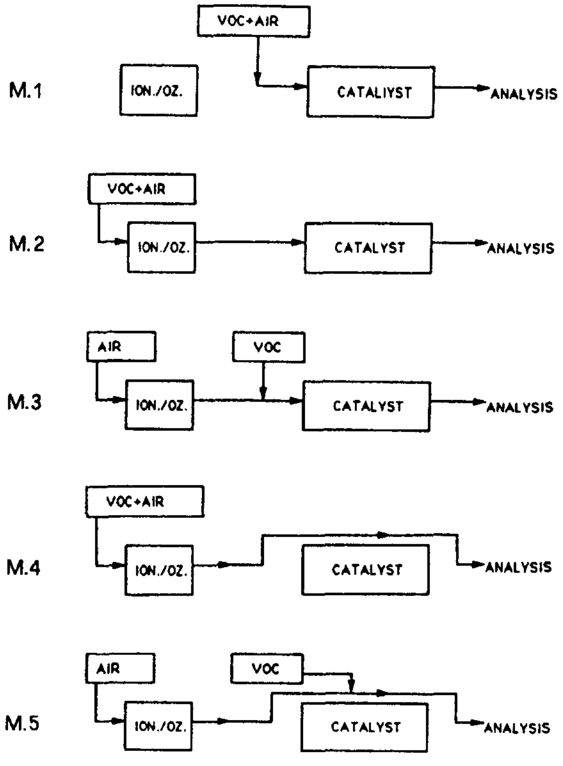

Fig. 1. Operative methods used for the experiments. Method 1 (M.1): air-catalytic combustion; method 2 (M.2): catalytic combustion with ozone and with ionization of VOC; method 3 (M.3): catalytic combustion with ozone; method 4 (M.4): ionization and oxidation with ozone of VOC; method 5 (M.5): oxidation of VOC with ozone.

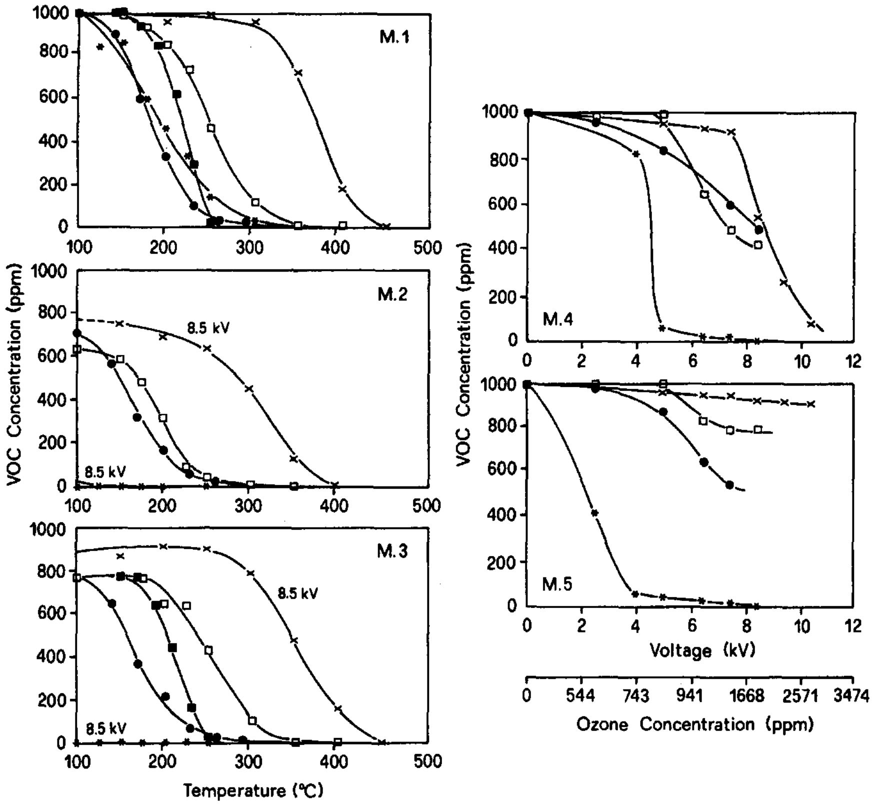

Fig. 2. VOC residue concentrations from the experiments performed according with the methods 1 (M.1), 2 (M.2), 3 (M.3), 4 (M.4) and 5 (M.5). (■) Acrylonitrile; (●) methanol; (∗) styrene; (□) toluene; (×) 1,2-dichloroethane. (When not specified, a peak voltage of 6.5 kV was used). Experiments according to methods 4 and 5 were performed at room temperature.

ionization of the VOC by the electric discharge in the ozone generator and the gas-phase action of ozone on the VOC, which decreased the total concentrations of VOC arriving on the catalyst. Moreover, the organic molecules could be shattered by the ionization/ozonization, predisposing them to the catalytic destruction. Therefore, the catalyst action was facilitated by the pre-catalytic effects. Styrene was completely destroyed at temperature as low as 125°C, temperature at which the catalyst could be hardly active. In this case, the styrene destruction was principally affected by the pre-catalytic effects. [1]

It was not possible to operate the combustion according to method 2 for acrylonitrile, the ionization gave rise to decomposition of the organic compound leading to by-products such as cycloheptatriene, 2-methoxyfuran and hydroxymethylpentanone, as revealed by mass spectrometric analysis, which deposited on the ozone generator and reactor walls.

The experiments performed according to method 3, Fig. 2 (M.3), allowed us to observe an improved combustion by the combination of ozone and catalyst. The improvement was noticed by the decrease of the VOC residue concentrations at any reaction temperature with respect to those observed with method 1. The difference in the VOC concentrations between methods 1 and 3 was higher at lower temperatures (< 200°C). The combination O_3/catalyst could display both in the gas-phase and on the

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[1] However, some heavy condensed products of polymerization or decomposition of styrene were formed in the ozone generator following the combustion with method 2. Work is in progress to qualitatively evaluate these products.

catalyst; this last point is a topic which will be further examined. As shown in Fig. 2 (M.3), styrene was very sensitive to the ozone. In fact, as observed also for method 2, styrene was almost totally decomposed at so low a temperature that the catalyst is not active, yet. The combustion of 1,2-dichloroethane at a lower temperature than that obtained with method 1, air-catalytic combustion, was particularly difficult to achieve even with the combination O_3/catalyst, as expected.

To get insight in the role of ozone and/or the ionization on the destruction of the organics and to quantify the pre-catalytic effects, experiments without catalyst were performed, too (methods 4 and 5). The experiments were carried out at room temperature as a function of the voltage applied in the ozone generator, that is the ozone concentration (see Table 2).

Fig. 2 (M.4) shows the destructive effect of the ionization plus ozone on the various VOCs. The effect increases with raising the voltage applied in the ozone generator. Each VOC underwent the destructive effect in a different way depending on which functional groups it possessed. From Fig. 2 (M.4), it is possible to evaluate the destructive effects of the pre-catalytic actions for each VOC at the same voltage used in the M.2 and M.3 combustions. At 8.5 kV (i.e., 1894 ppm of ozone, Table 2), the residue concentrations of 1,2-dichloroethane and styrene were 542 and 16 ppm, respectively. Methanol and toluene residue concentrations at 6.5 kV (i.e., 972 ppm of ozone, Table 2) were 697 and 647 ppm, respectively.

The oxidant power of ozone in the gas-phase was revealed by performing experiments as shown in Fig. 1 (M.5). The oxidation of VOCs increased with the ozone concentration, that means with increasing voltage applied in the ozone generator (Table 2). When working at 6.5 kV in the ozone generator, the ozone produced was 972 ppm and at 8.5 kV it was 1894 ppm. This means, in terms of the molar ratio between O_3/organic molecule, a value of about 1 for O_3/methanol and O_3/toluene and a value of 1.9 for O_3/styrene and O_3/1,2-dichloroethane. The oxidation was observed for styrene and methanol to a great extent. The residue concentrations for styrene and methanol were 35 and 653 ppm, evaluated at 8.5 and 6.5 kV, respectively, when air flowed through the ozone generator only, according to method 5. Toluene and 1,2-dichloroethane were affected by the oxidant power of ozone in a minor extent (residue concentrations 834 and 924 ppm at 6.5 and 8.5 kV for toluene and 1,2-dichloroethane, respectively).

The residue concentration profiles of VOCs on Fig. 2 (M.2) and (M.3) are shifted at lower temperatures compared to those on Fig. 2 (M.1), especially at low reaction temperatures (< 300°C). This behaviour seems mainly due to the pre-catalytic destructive action of the ionization/ozonization on VOCs, when working according to method 2, and to the ozone oxidant power, when working with method 3. At low reaction temperatures (< 300°C), if the contribution of VOCs destroyed by the pre-catalytic actions were summed up to the residue concentration profiles of VOCs obtained with methods 2 and 3, it would be possible to find about the same concentration profiles obtained with the air-catalytic combustion, according to method 1. However, when the reaction temperatures are high enough to activate the catalyst, the catalytic action prevails the pre-catalytic effects. As a consequence, at high reaction temperatures the residue concentration profiles for the various VOCs obtained with the three methods (M.1, M.2 and M.3), tend towards coalescence.

Fig. 3 shows the comparison between the temperatures required to obtain 50% and 95% conversion ($T_{50\%}$ and $T_{95\%}$) by combustion with methods 1, 2 and 3 for the various VOCs. For clarity, $T_{50\%}$ and $T_{95\%}$ have been reported in Table 3, too. The decrease of $T_{50\%}$, obtained when performing the combustion with the combination of ionization and/or ozone (M.2 and M.3) with respect to those obtained with method 1, was dependent on the nature of VOC. As pointed out above, aromatic compounds (i.e.,

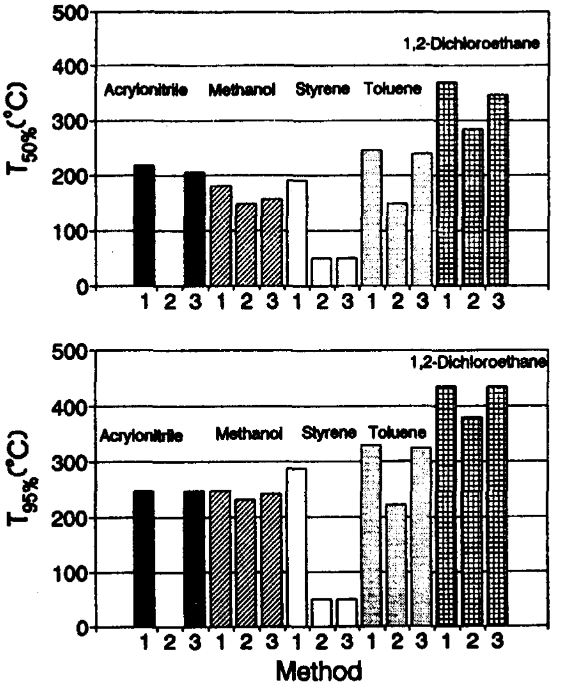

Fig. 3. Temperatures to achieve 50% and 95% conversion of VOC by combustion performed according to methods 1, 2 and 3.

styrene and toluene) were more affected by either the ionizing and the ozone oxidant actions than aliphatic compounds (i.e., 1,2-dichloroethane), therefore a good detectable improvement could be obtained by performing the combustion of styrene and toluene with methods 2 and 3 in comparison with method 1. The temperature to achieve 50% conversion for toluene combustion, performed with the combination of catalyst plus ionization/ozonization, was 50% lower than that obtained with method 1. A reduction of about 20%–25% for $T_{50\%}$ was observed for the combustion of methanol and 1,2-dichloroethane, performing the combustion with method 2. As a general trend, a lighter decrease of the temperatures corresponding to 50% conversion was observed when working according to method 3 in comparison with the decrease in $T_{50\%}$ observed with method 2.

When considering the temperatures corresponding to 95% conversion, the differences observed comparing $T_{95\%}$ for methods 1, 2 and 3 were in any case lower than those observed in case of $T_{50\%}$ (Table 3). The positive pre-catalytic effects are more clearly visible at low temperatures, where the catalyst is not yet or hardly active. For the total removal of the organics, it is necessary to perform the catalysis at high temperatures (> 300°C). Under these conditions of temperature, the decrease in the organic concentration arriving on the catalyst, obtained with the pre-catalytic effects, can not be sufficient to facilitate its action. In fact, there were not very important decreases of the temperatures corresponding to complete combustion, when comparing the methods. In the present case for toluene and 1,2-dichloroethane, the combustion performed with the method 2 gave rise to effective advantages with respect to the air-catalytic combustion (Table 3). Regarding the oxidant power of ozone, it could be expressed in the gas-phase and probably on the catalyst surface, too. In fact as known, the half-life of ozone is a function of temperature and of the oxygen concentration [11]. Ozone decomposes thermally to oxygen ($2\ O_3 \rightarrow 3\ O_2$) with an activation energy value of 134

Table 3
Temperatures required to obtain 50% and 95% of total degradation with the three combustion methods used

Name	$T_{50\%}$ (°C)			$T_{95\%}$ (°C)		
	M.1	M.2	M.3	M.1	M.2	M.3
Acrylonitrile	217	–	–	247	–	246
Methanol	180	148	156	247	231	242
Styrene	191	< 150	< 150	286	< 150	< 150
Toluene	246	148	239	329	221	323
1,2-Dichloroethane	369	284	346	435	397	434

kJ/mol calculated in air (i.e., 22 wt.-% of oxygen). The ozone decay at temperatures higher than 200°C is very fast, in the order of a few seconds. At low temperatures, ozone could reach the catalyst on which it could decompose giving rise to the formation of active oxygen radicals that improve the activity of catalyst. In contrast, at higher temperatures ozone decomposes before reaching the catalyst.

4. Concluding remarks

In conclusion, the decrease of reaction temperatures observed in the combustion assisted by ozone, derives from several factors: the pre-catalytic actions of ozone in gas-phase and the ionizing effect of the electric discharge in the ozone generator, in addition an improved catalytic action by ozone. At sufficiently low temperatures ($\leq$ 200°C), the ozone decomposition on the catalyst surface could give oxygen radicals active during the reaction. The pre-catalytic actions could decompose or shatter the organics arranging the molecules to be more easily destroyed by the catalyst. Then, the process could occur at lower temperatures by synergic effects among the catalyst, ozone and the ionization. It is difficult to recognize a general trend for VOCs belonging to different chemical classes with reference to the action of ionization plus ozonization. Each organic molecule, depending on the functional group possessed, is sensitive in a unique way to the ionizing effect and to the oxidant power of ozone. The catalytic combustion assisted by ozone can be more or less effective depending on the VOC characteristics. It was recently observed that the improvement of the catalytic combustion performed with ionization/ozonization is also revealed from the absence of by-products and micropollutants formed during the combustion of organics, also halogenated, as pointed out in Ref. [9]. This important aspect will be further developed in future works.

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