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Catalytic oxidation of chlorinated hydrocarbons in two-component mixtures with selected VOCs

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Abstract

The catalytic oxidation of chlorobenzene (ChB) and 1,2-dichloroethane (DCE) oxidized alone and in two-component mixtures with selected non-chlorinated volatile organic compounds (VOCs) such as toluene, *n*-hexane, acetone ethanol, ethyl acetate, was investigated. The tests were carried out over Pt-based catalyst on a monolithic metallic support. Only both hydrocarbons and ethanol enhanced ChB oxidation. DCE conversion was inhibited in the presence of each non-chlorinated admixture. Both chlorinated compounds lowered the catalytic reactivity of non-chlorinated VOCs and increased the concentration of incomplete oxidation products, first of all acetaldehyde.

Keywords: Air pollution control; Chlorobenzene; 1,2-Dichloroethane

1. Introduction

Chlorinated volatile organic compounds (CVOCs) are emitted to the atmosphere in waste gases from a wide range of industrial processes. They are often used in degreasing and dry-cleaning processes, as well as solvents and chemical intermediates in the production of plastics, synthetic resins or pharmaceuticals. Such compounds are known to be hazardous to the environment and human health; they are also active in stratospheric ozone depletion.

CVOCs are often emitted in a mixture with other non-chlorinated volatile organic compounds or carbon monoxide. For this reason, a catalytic oxidation seems to be an efficient and economic method of such emission control. Catalytic oxidation can be efficiently performed at temperatures between 250 and 550 °C, much lower as those required for direct thermal incineration, exceeding 850–1000 °C.

Generally, two kinds of catalysts are used for destructive oxidation of CVOCs—noble metals (mostly platinum and palladium) and metal oxides, such as chromium oxide, copper-chromite or manganese oxides [1–6]. Noble metal catalysts can be reversible deactivated by chlorine atoms adsorbed on active sites. Metal oxides-based catalysts can be deactivated by active phase lose via production of volatile metal chlorides. Perovskite-based catalysts seem to be the most promising for the total oxidation of volatile organic compounds, including CVOCs [7,8].

The desired reaction products of the oxidation of chlorinated hydrocarbons are CO_2, H_2O and HCl, as only chlorinated product. CVOCs containing more chlorine atoms than hydrogen atoms in the molecule cannot be efficiently converted to HCl. It was found that such reaction product can be formed when hydrogen-reach compounds or water vapor were added to the feedstream. Those additives can be found in original industrial effluents, but it is impossible to predict a mutual effect of the presence of chlorinated and non-chlorinated VOCs on their reactivity in the mixtures from their catalytic reactivity when they were oxidized individually. Trichloroethylene (TCE) was usually chosen as a suitable hydrogen-lean model compound present often in waste gases. It was reported that TCE oxidation was enhanced in the presence of hydrogen-containing organic compounds as well as water vapor [1,4,9]. The presence of hydrocarbons such as 2-butene, heptane, toluene and benzene had a beneficial effect on the rate of chlorobenzene destruction [2,3]. Our earlier study showed that over M-1 monolithic platinum catalyst each selected VOCs added (toluene, *n*-heptane, ethanol, acetone methyl ethyl ketone,

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ethyl acetate) strongly enhanced TCE conversion, in the same time TCE inhibited the oxidation of each VOCs. This effect depended on the catalyst used; over palladium, only toluene and ethanol had promoting effect on TCE conversion. Over perovskite, inhibiting effect on TCE conversion was observed for each compound added [10,11].

This work is a continuation of an earlier study [11], in which the mutual influence of TCE and selected VOCs oxidized in two-component mixtures was investigated. The objective of present study is an evaluation of the influence of selected VOCs on chlorobenzene (ChB) and 1,2-dichloroethane (DCE) on their catalytic reactivity and product distribution, when they were oxidized in two-component mixtures over the same platinum catalyst (M-1) on monolithic metallic support.

2. Experimental

The studies were carried out over Pt-based catalyst on metallic monolithic support. The metallic support from heat-resisting alumel steel, thermally pretreated and etched in acids solution, was coated with γ-Al_2O_3 with addition of rare earth elements, first of all lanthanum and cerium, which are known to improve the thermal stability of catalysts. After drying and calcinations the content of washcoat amounted to 2.5 wt.%. Such prepared support was impregnated with chloroplatinic acid. The content of the active ingredient after calcinations reached 0.15 wt.%. The short description of catalyst is presented below:

- shape of cells: triangle,
- cell density: 240/cm^2,
- cell dimension: 0.9 mm,
- wall thickness: 0.05 mm,
- catalyst block dimension: $h = 70$ mm, $\phi = 21$ mm,
- open area: 80%.

The activity of the catalyst was tested in the oxidation of two hydrocarbons—toluene and *n*-hexane, three oxy-derivatives—acetone, ethyl acetate and ethanol, and two chlorinated hydrocarbons—chlorobenzene and 1,2-dichloroethane.

Tests were carried out in a typical cross-flow glass reactor, of “tube-in-tube” type, electrically heated. The reaction temperature measured with a thermocouple inside the catalyst block, ranged from 200 to 450 °C. Each oxidized compound was dosed by evaporation and mixed with air to desire concentration of 1 g/m^3. The gas hourly space velocity (GHSV), 10 000 h^{-1} at room temperature, was the same for all tests. Catalyst activity was estimated as conversion efficiency of oxidized compound, measured from its inlet and outlet concentration. The concentrations of oxidized compounds and intermediates yielded were calculated as the average value of minimum three measurements.

The qualitative and quantitative analysis of oxidized compounds as well as potentially yielded intermediates was carried out by gas-chromatography, on Perkin-Elmer GC with integrator, FID and column of 1.8 m/2.7 mm, packed with 10% PEG 2000 on Chromosorb W. The parameters of analysis were selected so as to separate pick of every oxidized compound and potentially intermediates, both non-halogenated (first of all aldehydes and light hydrocarbons C_1–C_4) and chlorinated organic compounds. Temperature of column reached 73 °C, while that of injector and detector was set at 100 °C. Other chlorinated reaction products—HCl and Cl_2—were analyzed by titration and colorimetrically, respectively. Separated stream of effluent was bubbled through distillated water. Then, HCl concentration was determined by titration with 0.0125 N NaOH solution using phenolphthalein, and Cl_2 was detected by reaction with *o*-tolidine in acidified solution.

Tests of catalyst activity were carried out in the following order:

- oxidation of each compound alone—toluene, *n*-hexane, acetone, ethyl acetate, ethanol, chlorobenzene, 1,2-dichloroethane;
- oxidation of chlorobenzene in two-component mixtures with each non-halogenated compound;
- oxidation of 1,2-dichloroethane in two-component mixtures.

3. Results and discussion

3.1. Tests of catalyst activity

The results of conversion of each compound oxidized individually are plotted in Fig. 1. The catalytic reactivity of oxidized compounds decreased in the following order:

$$\text{toluene} = \text{ethanol} > n\text{-hexane} = \text{ethyl acetate} \geq \text{acetone} > \text{ChB} > \text{DCE}$$

Similar order of compounds reactivity over platinum has been reported earlier [11–13]. The catalyst showed distinctly higher activity in non-chlorinated compounds oxidation. At 200 °C, conversion of ethanol, the most reactive compound, reached 80%. Toluene conversion with 50% efficiency required 220 °C, while for the other volatile organic compounds (VOCs) temperatures of their 50% conversion

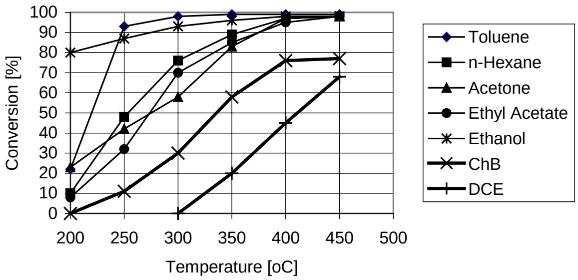

Fig. 1. Catalyst activity in the oxidation of selected compounds.

ranged from 250 °C for *n*-hexane to 275 °C for ethyl acetate and acetone. Above 250–260 °C, the conversion of ethanol and toluene exceeded 90%. For such conversion of *n*-hexane, acetone and acetate temperatures of 350–370 °C were needed. Oxidation of both hydrocarbons ran to CO_2 and water, no other reaction product was found in the effluent. The process of oxy-derivatives oxidation was more complicated and ran via series of parallel and consecutive reactions, yielding intermediates detected in the flue gas. The oxidation of ethanol and acetone went via acetaldehyde (AA) production, typical product of incomplete oxidation. When ethyl acetate was oxidized, ethanol and acetaldehyde were detected as by-products. As it was explained earlier [11], in the first reaction step acetate hydrolyzed to acetic acid and ethanol which in the next reaction step was oxidized, partially via acetaldehyde, to the total oxidation products, according to the following scheme:

$$CH_3COOCH_2CH_3 + H_2O \longrightarrow CH_3COOH + CH_3CH_2OH$$

$$\begin{tikzcd}
 & \text{acetaldehyde} \arrow[dr] & \\
\text{ethanol} \arrow[ur] \arrow[rr] & & CO_2 + H_2O
\end{tikzcd}$$

The process of acetone oxidation yielded only traces of acetaldehyde, detected only at the lowest reaction temperature. The concentration and distribution of reaction by-products in process of ethanol and ethyl acetate oxidation will be analyzed in details later.

Chlorinated hydrocarbons destruction was much more difficult and required higher temperatures. Fifty percentage conversion of ChB, more reactive compound, was achieved at 330 °C; for such conversion of DCE, temperature of 410 °C was necessary. At the highest temperature tested of 450 °C, ChB and DCE were oxidized with 78 and 68% efficiencies, respectively. In process of both chloroorganic compounds oxidation no other chlorinated organic compounds as well as chlorine were found in the effluents. HCl was detected as the only chlorinated reaction product, and its concentration generally was in the balance with that calculated theoretically from the conversion of chlorinated compound.

Higher reactivity of ChB than DCE over platinum, despite higher energies both of C–Cl and C–H bonds in ChB, accounting for 235 and 213 kJ/mol as well as 370 and 248 kJ/mol for ChB and DCE, respectively, can be attributed to higher H/Cl atoms ratio in ChB and its easier reactivity from gas phase with oxygen adsorbed on Pt active sites, analogously to the high reactivity of non-chlorinated light aromatics over platinum [2,3].

3.2. *Oxidation of chlorinated compounds in two-component mixtures*

The results of non-chlorinated compounds influence on the catalytic reactivity of ChB and DCE are plotted in Fig. 2. The conversion of ChB and DCE oxidized alone and in the mixtures with selected VOCs, at 300 and 450 °C for ChB, and 350 and 450 °C for DCE, are presented in Table 1.

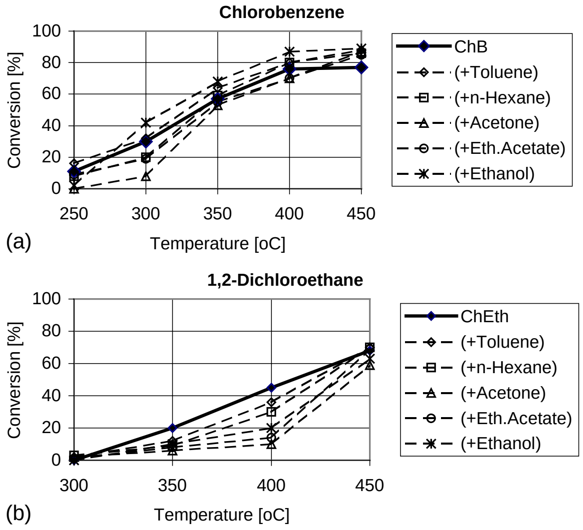

Fig. 2. Conversion of chlorobenzene (a) and 1,2-dichloroethane (b) oxidized alone (full lines) and in two-component mixtures (dotted lines).

The influence of non-chlorinated VOCs on ChB and DCE conversion differed from one compound to another. It had been reported that the enhancement of chlorinated compounds conversion depended on the chemical structure of the non-chlorinated compound added, and decreased, accordingly to their catalytic reactivity, in the following order [4]:

oxygenates > alkenes > aromatics > alkanes.

The results of our investigations showed that at the whole range of temperatures tested, ChB conversion was enhanced by 10% in the presence of ethanol, the most reactive compound when oxidized alone. This positive effect was slightly lower for both hydrocarbons. Easier conversion of ChB with toluene than with *n*-hexane can be explained by greater reactivity of toluene because of lower strength of C–H bond in the molecule of toluene (370 kJ/mol) than in saturated hydrocarbons (ca. 400 kJ/mol). Gervasini already observed similar effect, in the reaction of CCl_4 oxidation in the mixtures

Table 1
Conversion of ChB and DCE oxidized individually and in two-component mixtures, at 300 °C (for ChB), 350 °C (for DCE) and 450 °C

Additive	Conversion (%)			
	ChB		DCE	
	300 °C	450 °C	350 °C	450 °C
Alone	30	78	20	68
With toluene	32	86	12	70
With hexane	20	85	10	70
With acetone	8	85	6	58
With ethyl acetate	20	86	10	68
With ethanol	43	88	10	63

with toluene or *n*-hexane [6]. On the other hand, toluene may react directly from the gas phase with chemisorbed oxygen, while *n*-hexane oxidation runs preferentially by dissociative chemisorption on the catalyst surface [14,15]. The presence of the other compounds—acetone and ethyl acetate—inhibited the oxidation of ChB. Temperature of 50% ChB conversion ranged from 315 and 325 °C, when ChB was oxidized with ethanol and toluene, respectively, to 340 °C—in the mixture with acetone and ethyl acetate. At the highest tested temperature of 450 °C, conversion of ChB in mixtures independently of the compound added was by 8–10% higher as conversion of ChB oxidized alone.

In opposite, DCE conversion was inhibited in the presence of each non-chlorinated VOCs added. The most distinctly diversities of DCE conversion were observed at 400 °C, and in this temperature DCE conversion decreased from 45%, when DCE was oxidized alone, to 36% in the mixture with toluene, but even to 8%—with acetone. At 450 °C, DCE conversion varied from 58%, with acetone added, up to 70%—when DCE was oxidized with toluene or *n*-hexane. Because of distinctly higher catalytic reactivity of selected VOCs than that of DCE, the oxidation of DCE in mixtures probably underwent in two steps: in the first step non-chlorinated compounds were oxidized with preferential adsorption on the active sites of the catalyst, and in the next step DCE was destructed.

Such different behavior of ChB and DCE oxidized in mixtures is difficult to explain. The results of the mixtures oxidation showed that probably the competition among all oxidized compounds for the same adsorption sites played the major role in the reaction pathway. It is possible that the great differences in dissociation energy of C–H bonds in non-chlorinated compounds and DCE, and only slight—in non-chlorinated aromatics and ChB, influenced the different reactivity of CVOCs oxidized in the mixtures. Some electronic and steric factors in DCE and ChB structure seem to play an important role in their catalytic destruction. Chlorine in the benzene ring increases the molecule polarity resulting in easier interaction between the ChB molecule and the catalyst surface [14]. A dipole moment for ChB reaches 1.56, while the alternately situated chlorine atoms in DCE molecule results in no polar character of the compound. Moreover, tetrahedral structure of DCE makes difficult its accessibility to the active sites of the catalyst. Our earlier investigations carried out over the same catalyst on the oxidation of TCE in two-component mixtures with similar selected non-chlorinated VOCs showed that every compound added enhanced TCE conversion [10,11]. In this case, very low H/Cl ratio in TCE molecule seems to be the most important factor. TCE oxidized alone cannot be efficiently converted to desired HCl. Yielded chlorine strongly adsorbed on the catalyst surface, blocking the active sites of the catalyst, necessary for the competitive adsorption of both reagents—TCE and oxygen. Addition of hydrogen-rich compound allowed for HCl production, easily desorbed from the catalyst to the gas phase [3,4,16].

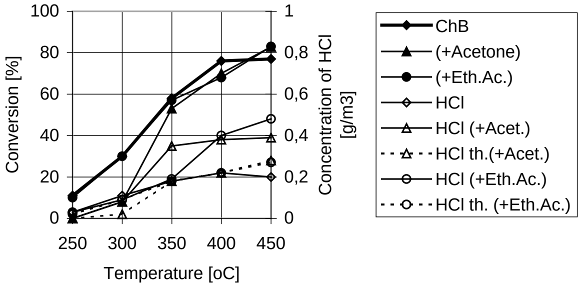

Fig. 3. Conversion of chlorobenzene oxidized alone and in the mixture with ethyl acetate and acetone, and HCl concentration in flue gas (open symbols), measured (full lines) and theoretically calculated (dotted lines).

HCl detected in the effluent was found to be the only chlorinated reaction product. Generally, its concentration was in balance with theoretically calculated from the conversion of chlorinated compound, except ChB oxidation with ethyl acetate and acetone (Fig. 3). Beginning from 350 °C, both VOCs did not influence ChB conversion, but their catalytic destruction was lowered and simultaneously increased the concentration of reaction by-products. In the same time, the measured concentration of HCl was evidently higher than that calculated from ChB conversion. Probably, the total oxidation of both oxy-derivatives was inhibited by ChB, underwent by carboxylic acids yielding, and the results of titration included both HCl and organic acids concentrations.

3.3. *Influence of chlorinated compounds on the oxidation of non-chlorinated VOCs*

The conversion of each non-chlorinated compounds at 300 and 400 °C, oxidized individually and in two-component mixtures with ChB or DCE, are presented in Table 2.

Both chlorinated hydrocarbons inhibited VOCs oxidation. The lowest inhibiting effect was observed for toluene; at 300 °C toluene conversion decreased by 18% in the mixture with ChB, but only by 13% with DCE. This effect was the most distinct for *n*-hexane, its conversion lowered by 67 and 65%, when it was oxidized with ChB and DCE, respectively. Among investigated oxy-derivative compounds, acetone oxidation was the most markedly inhibited in the

Table 2

Conversion of non-chlorinated compounds at 300 and 400 °C, oxidized individually and in two-component mixtures with ChB and DCE

Compound	Conversion (%)					
	300 °C			400 °C		
	Alone	With ChB	With DCE	Alone	With ChB	With DCE
Toluene	98	80	85	99	86	91
n-Hexane	76	9	11	96	55	56
Acetone	58	10	16	96	43	59
Ethyl acetate	70	40	57	95	93	97
Ethanol	93	59	68	97	92	92

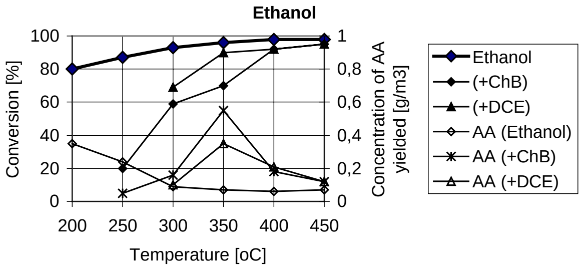

Fig. 4. Conversion of ethanol oxidized alone and in the mixture with ChB and DCE, with concentration of acetaldehyde (AA) yielded (open symbols).

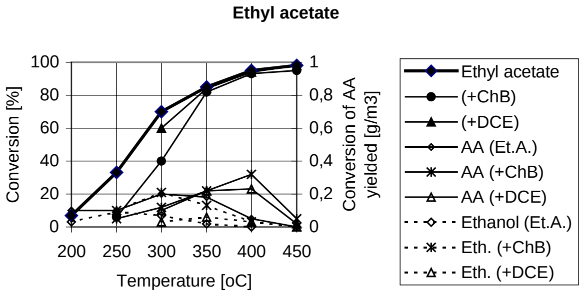

Fig. 5. Conversion of ethyl acetate oxidized alone and in the mixture with ChB and DCE, with concentration of by-products yielded: acetaldehyde (AA)—full lines, and ethanol—dotted lines.

presence of both chlorinated compounds. The efficiency of acetone oxidation dropped by 48 and 42% when it was oxidized in the mixtures with ChB and DCE, respectively. At higher reaction temperatures the influence of chlorinated compounds on VOCs reactivity was poorer. Generally, ChB inhibited stronger than DCE the conversion of selected non-chlorinated VOCs, which may be explained by greater differences in the reactivity and the ignition temperatures of non-chlorinated compounds and DCE.

The presence of chlorinated hydrocarbons influenced not only lower VOCs conversion. In the process of oxy-derivative compounds oxidation, both investigated CVOCs inhibited the reaction selectivity to the total oxidation products. The conversion of ethanol and ethyl acetate, and the concentration of incomplete reaction products, when they were oxidized alone and in mixtures with ChB and DCE are plotted in Figs. 4 and 5. The reaction selectivity to yielded by-products, calculated from the converted substrate, is presented in Tables 3 and 4 for ethanol and ethyl acetate, respectively.

As it was shown earlier, ethanol oxidized alone was the most reactive compound over M-1 catalyst (Fig. 1), but its oxidation ran via acetaldehyde (AA) production (Fig. 4). When alcohol was oxidized alone, the maximum concentration of AA (0.35 g/m^3) was detected at the lowest reaction temperature of 200 °C, with reaction selectivity of 46%, and the concentration of AA and the reaction selectivity systematically decreased with the raising reaction temperature. The presence of chlorinated additives in reaction mixtures resulted not only in lower ethanol conversion, but also increased the concentration of AA yielded and simultaneously the reaction selectivity to such product. In the presence of both CVOCs, the maximum concentration of aldehyde was observed at 350 °C, and reached 0.35 and 0.55 g/m^3, what corresponded with the selectivity of 40% and even 82%, when ethanol was oxidized with DCE and ChB, respectively. At this temperature, ethanol conversion decreased from 96% when ethanol was oxidized alone, to 90 and 70% in the mixture with DCE and ChB, respectively. Even at 450 °C, aldehyde concentration in the flue gas amounted to 0.12 g/m^3 (with the reaction selectivity of 13%), in the presence of both chlorinated compounds added.

Similar behavior was observed in the process of ethyl acetate oxidation (Fig. 5). As it was explained earlier, the

Table 3
Conversion of ethanol (η) and the reaction selectivity to acetaldehyde (S)

Temperature (°C)	Ethanol alone		Ethanol with ChB		Ethanol with DCE	
	η (%)	S (AA) (%)	η (%)	S (AA) (%)	η (%)	S (AA) (%)
450	98	7.5	95	13.2	95	13.2
400	98	6.4	92	20.4	92	30.1
350	96	7.6	70	82.2	90	40.7
300	93	10.1	59	28.3	69	11
250	87	29	20	16.4	–	–
200	80	45.7	–	–	–	–

Table 4
Conversion of ethyl acetate (η) and the reaction selectivity to ethanol and acetaldehyde (S)

Temperature (°C)	Ethyl acetate alone			Ethyl acetate with ChB			Ethyl acetate with DCE		
	η (%)	S (eth.) (%)	S (AA) (%)	η (%)	S (eth.) (%)	S (AA) (%)	η (%)	S (eth.) (%)	S (AA) (%)
450	98	0	0	95	0	10.2	98	0	4.5
400	95	0	10.2	93	6	62.7	94	6.1	48.6
350	85	4.5	42.3	82	30.4	57.6	84	13.7	52.6
300	70	19	57.2	40	>100	60.6	60	9.6	33.8

first reaction step—hydrolysis—yielded acetic acid, ethanol and acetaldehyde. Acetic acid was not found in the reaction gases; probably, in such conditions acid was easy oxidized to CO_2 and water. At the whole range of reaction temperatures, ethanol concentration was lower than that of AA. When ethyl acetate was oxidized alone, maximum concentration of ethanol (0.09 g/m^3) was detected at 250 °C, while that of AA (0.2 g/m^3) was found at 300 °C. Like in the process of ethanol oxidation, ChB more readily than DCE influenced both conversion efficiency of acetate and the distribution of incomplete oxidation products. When acetate was oxidized with ChB, the maximum concentrations of ethanol (0.2 g/m^3) and AA (0.32 g/m^3) yielded were detected at 300 and 400 °C, respectively. At the reaction temperature ranging from 300 to 400 °C, the reaction selectivity to acetaldehyde reached 57–60%; with rising temperature this selectivity markedly decreased, to 10% at 450 °C. The reaction selectivity to ethanol at 300 °C (the temperature of its maximum concentration) exceeded 100%. Also at temperatures below 300 °C, the concentration of ethanol detected in the flue gas varied considerably, and in some cases the selectivity exceeded 100%. Probably, alcohol was periodically adsorbed on and desorbed from the catalyst or γ-alumina washcoat surface. At the higher reaction temperatures, the selectivity to alcohol distinctly decreased (Fig. 5).

Summing up, both the concentration of yielded by-products and the reaction selectivity to those products increased when selected oxy-derivative compounds were oxidized in mixtures with chlorinated hydrocarbons. It was already reported by Feijen-Jeurissen et al. that the oxidation of chlorinated compounds could run via acetaldehyde production [5]. Probably, some amounts of aldehyde detected in the flue gas could be yielded in the course of chloroorganic compounds oxidation also.

When acetone was oxidized with both chlorinated compounds, only the traces of AA were found in the reaction gas, but only in these reactions the concentrations of HCl yielded measured in the flue gas by titration exceeded the stoichiometric values, calculated theoretically from the conversion efficiency of CVOCs. Probably, acetone destruction yielded acetic acid, detected by titration together with HCl (Fig. 3).

4. Conclusions

The Pt-based catalyst on metallic monolithic support, with an γ-Al_2O_3 washcoat, showed high activity in the oxidation of selected hydrocarbons and oxy-derivatives. The destruction of ethanol and ethyl acetate went by intermediates detected in the flue gas: acetaldehyde in ethanol oxidation and acetaldehyde and ethanol, when ethyl acetate was oxidized. Chlorinated compounds were much more difficult to oxidation; at the highest investigated temperature of 450 °C, the conversion reached 78 and 68% for ChB and DCE, respectively. HCl was found to be the only chlorinated reaction product; no chlorine or other chloroorganic intermediate compounds were detected in the flue gas.

The influence of non-chlorinated compounds on ChB oxidation differed from one compound to another. At the whole range of reaction temperatures, ethanol enhanced by 10% the conversion of ChB. The addition of both hydrocarbons also slightly improved ChB destruction. DCE conversion was inhibited in the presence of each non-chlorinated compound added. Both chlorinated hydrocarbons not only inhibited catalytic destruction of each non-chlorinated compound added, but increased the reaction selectivity and concentration of intermediates yielded, first of all acetaldehyde.

The mechanism of the mutual influence of non-chlorinated VOCs and CVOCs oxidized in the mixtures seems to be complicated and has not been particularly considered in this study. Probably, the competition between all oxidized compounds in the mixture to the same active sites seems to play the most important role in the reaction pathway. The enhancement of ChB oxidation and the inhibition of DCE conversion can be explained by the differences in their electronic and steric structures.

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