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Catalytic oxidation of trichloroethylene in two-component mixtures with selected volatile organic compounds

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Abstract

The activity of two noble metal catalysts (Pt and Pd) on metallic monolithic support and one perovskite ($La_{0.5}Ag_{0.5}MnO_3$) on cordierite monolith was tested in the oxidation of selected volatile organic compounds (VOCs) and trichloroethylene (TCE), oxidized alone and in two-component mixtures of TCE with a non-halogenated compound. Only over the Pt catalyst each compound in the reaction mixtures strongly enhanced TCE oxidation. Over Pd, promoting effect on TCE oxidation was observed for toluene and ethanol only. Over perovskite, each non-chlorinated compound was found to inhibit TCE oxidation. The presence of TCE was found to inhibit the oxidation of each compound added over both noble metal catalysts, but it had no influence on the oxy-derivatives oxidation over the perovskite catalyst.

Keywords: Trichloroethylene; Two-component mixtures; Volatile organic compounds; $La_{0.5}Ag_{0.5}MnO_3$

1. Introduction

Chlorinated hydrocarbons are widely used in industry not only as solvents, dry cleaners or degreasing media, but also as chemical intermediates in the production of plastics, synthetic resins or pharmaceuticals. In general, they are toxic to the environment, and some of them have been recognized as muta- and cancerogenic species, and so their emission to the atmosphere should be blamed for serious contamination of air, soil and water. Halogenated hydrocarbons are active in depletion of stratospheric ozone. Recently, the incineration of municipal or medical waste has become the preferential method for their treatment in large residential areas. The flue gases of such process contain chlorinated organic compounds, and these include traces of polychlorinated dibenzodioxins (PCDDs) or dibenzofurans (PCDFs). Catalytic oxidation can be a preferred method of their destruction, especially over the same modified catalysts that are used for selective catalytic reduction of nitrogen oxides, namely those based on V–Ti or V–W–Ti oxides [1,2].

Chlorinated volatile organic compounds (CVOCs) are often emitted in a mixture with other organic or inorganic combustible compounds, e.g. carbon monoxide. Such mixtures are normally destroyed by thermal incineration at high temperatures exceeding 1200 °C. This temperature is recognized to ensure complete combustion, without yielding harmful by-products like phosgene, PCDDs or PCDFs. Catalytic oxidation seems to be an effective and economic alternative to the thermal process for CVOCs destruction. Catalytic oxidation effectively performed at lower temperatures (300–600 °C) is more economic than thermal combustion in terms of fuel consumption. It is also friendlier to the environment owing to the evidently lower emission of NO_x and products of incomplete oxidation. The desired chlorinated reaction product is

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HCl, easy to eliminate in the next step of gas cleaning, e.g. by scrubbing.

Supported noble metals (platinum or palladium) and mixed metal oxides (oxides of vanadium, chromium, manganese, cobalt, cuprum) in bulk pellet form or on supports are usually tested in the total oxidation of chlorinated hydrocarbons. Pt on Al_2O_3, as well as Pt or Pd on various supports, with a minimum noble metal content of 0.3 wt.% has been extensively studied and has been found to be more active then metal oxides [3–7]. The catalyst for such processes should be not only of high activity, but also of high resistance to deactivation. Our earlier investigations showed that even catalysts with platinum content reduced to 0.1–0.15 wt.% could be effectively used for the destruction of chlorinated hydrocarbons [8,9].

Of the metal oxide catalysts, the perovskite-type catalyst seems to be the most active in the total oxidation of organic air pollutants, including chloro-organic compounds. Catalysts prepared on the basis of $LaMnO_3$, $LaCoO_3$ or $(La_{0.84}Sr_{0.16})(Mn_{0.67}Co_{0.33})O_3$ on a cordierite monolith were found to be mechanically stable and active in the total oxidation of different hydrocarbons, including chlorinated methanes, saturated and unsaturated C_2 hydrocarbons and chlorobenzene. $LaMnO_{3+\delta}$ showed the best catalytic performance in the oxidation of chlorinated hydrocarbons to CO_2 and HCl at 500–550 °C. Other catalysts, such as $Cu/KCl/SiO_2$ or uranium oxides, were also found to be of high activity in the process of chloro-organic compounds oxidation [10–15].

A serious problem in the catalytic oxidation of CVOCs is the formation of different by-products. Addition of water or some organics to the reaction mixture plays an important role in the catalytic destruction of chlorinated hydrocarbons. Over platinum catalysts, water had a positive effect on the conversion and the selectivity of the reaction to HCl. The formation of HCl is favoured at high temperatures. According to the Deacon reaction, in the presence of water, phosgene—a toxic by-product of TCE oxidation—hydrolysed to HCl and CO_2. On the other hand, the concentration of the other by-products (e.g. dichloroethylene, by-product of the oxidation of 1,1,1-trichloroethane) was suppressed by the increasing concentration of water. It was found that, in the presence of a perovskite catalyst, the addition of water to the feed did not affect the efficiency of chlorinated hydrocarbons destruction, whereas methane or propane leads to a decrease of chlorinated VOCs destruction [10]. Our earlier research on TCE oxidation in two-component mixtures with selected hydrocarbons or oxy-derivatives over Pt–Rh on a metallic monolithic support showed that every compound added enhanced TCE oxidation. On the other hand, the presence of TCE not only decreased the conversion of each non-halogenated compound, but also influenced the selectivity of oxy-derivatives oxidation to acetaldehyde, a product of incomplete oxidation [9].

The objective of this study was to test the activity of platinum, palladium and perovskite catalysts on monolithic supports in the reaction of TCE oxidation, alone and in two-component mixtures with selected hydrocarbons and oxy-derivatives. It seemed interesting to find out if the component of the reaction mixture had a noticeable effect on their conversion and on the distribution of potential products of incomplete oxidation.

2. Catalysts

Three laboratory-scale monolithic catalysts were prepared for the purpose of the study. Two of them—platinum (M-1) and palladium (M-2)—were manufactured on metallic monolithic supports made from heat-resisting steel with additives. Because of the very small specific surface area of such supports, it was necessary to place a washcoat, which was the proper support for the active phase. After thermal pre-treatment of the metallic support, the washcoat was deposited by spreading of γ-Al_2O_3 in gel form, followed by drying and calcination. Active phase was incorporated by impregnation of the support with chloroplatinic acid or palladium chloride. After drying and calcination, the content of the active ingredient amounted to 0.15 wt.%. The perovskite catalyst was developed and manufactured on a cordierite monolithic support at Dresden University of Applied Technology. It was prepared by wet impregnation with the slurry of $LaMnO_3$–perovskite and aluminium oxy-hydrate in 2:1 mass proportion. Fifty percent of La^{3+} ions were substituted by Ag^+ ions. X-ray diffraction analysis showed the pattern of $LaMnO_{3+x}$ phase, silver (both in Ag–Mn–O and metallic form)

Table 1
Description of manufactured and tested catalysts

Parameter	M-1	M-2	PER-1
Shape of cells	Triangle	Triangle	Square
Cell density (cm^{-2})	240	240	32
Cell dimension (mm)	0.9	0.9	1.45
Wall thickness (mm)	0.05	0.05	0.3
Block dimension (mm)	$h = 70$, $\phi = 21$	$h = 70$, $\phi = 21$	$h = 76$, $\phi = 21$
Washcoat	γ-Al_2O_3; 2.5 wt.%	γ-Al_2O_3; 2.7 wt.%	–
Active phase	Pt; 0.15 wt.%	Pd; 0.15 wt.%	$La_{0.5}Ag_{0.5}MnO_3$; 12 wt.%

and some traces of unidentified oxide phases [16]. After 2-fold impregnation, drying and calcination, the content of the active phase amounted to 12% of support mass. The catalysts under study are described in Table 1.

3. Experimental

Catalytic activity was tested in the oxidation of two hydrocarbons (toluene and *n*-heptane), four oxy-derivatives of different chemical structure (ethanol, ethylacetate, acetone and methylethylketone (MEK)), and trichloroethylene (TCE). TCE was chosen as a model for an unsaturated chlorinated C_2 hydrocarbon, difficult to destroy catalytically. Tests were carried out in an electrically heated typical cross-flow glass reactor of "tube-in-tube" type. Reaction temperature ranged from 200 to 500 °C and was measured inside the block of the catalyst. Every oxidized compound was dosed individually by evaporation, and mixed with air to the desired concentration of 1 g/m^3. Space velocity of the reaction mixture was the same for all tests and amounted to 10 000 h^{-1}. Catalytic activity was estimated in terms of the conversion of the oxidized compound, calculated from the inlet and outlet concentrations. The concentration of each product of incomplete oxidation was related to the inlet concentration of the oxidized compound amounting to 1 g/m^3. Reaction selectivity to the product of incomplete oxidation was calculated from the concentration of the detected by-product related to the converted substrate. Catalyst deactivation by chlorinated compounds was estimated in the test reaction of toluene oxidation carried out after all tests. The quantitative and qualitative analysis of the reagents, as well as the potentially yielded intermediates, was carried out by gas chromatography on Perkin-Elmer GC with integrator, FID and a 1.8 m/2.7 mm column packed with 10% PEG 2000 on Chromosorb W. The parameters of chromatographic analysis were selected so as to separate peak of every oxidized compound and yielded by-products, first of all aldehydes and light hydrocarbons C_1–C_4. The temperature of the column reached 72 °C, while that of the injector and detector was set to 100 °C. Tests were carried out in the following order:

- toluene oxidation,
- oxidation of each non-chlorinated compound—*n*-heptane, MEK, acetone, ethyl acetate, ethanol, and
- oxidation of TCE alone and in two-component mixtures with each non-chlorinated VOC.

4. Catalyst activity and reaction selectivity in the oxidation of single selected compounds

The results of VOCs oxidation over M-1, M-2 and PER-1 are plotted in Fig. 1.

All catalysts under investigation showed high activity in the oxidation of non-chlorinated VOCs. The catalytic reactivity of the oxidized compounds decreased in the following order:

over M-1: toluene = ethanol > *n*-heptane > MEK > acetone = ethylacetate
over M-2: toluene = ethanol > MEK > ethylacetate > acetone > *n*-heptane
over PER-1: ethanol > MEK = toluene = acetone = ethylacetate > *n*-heptane

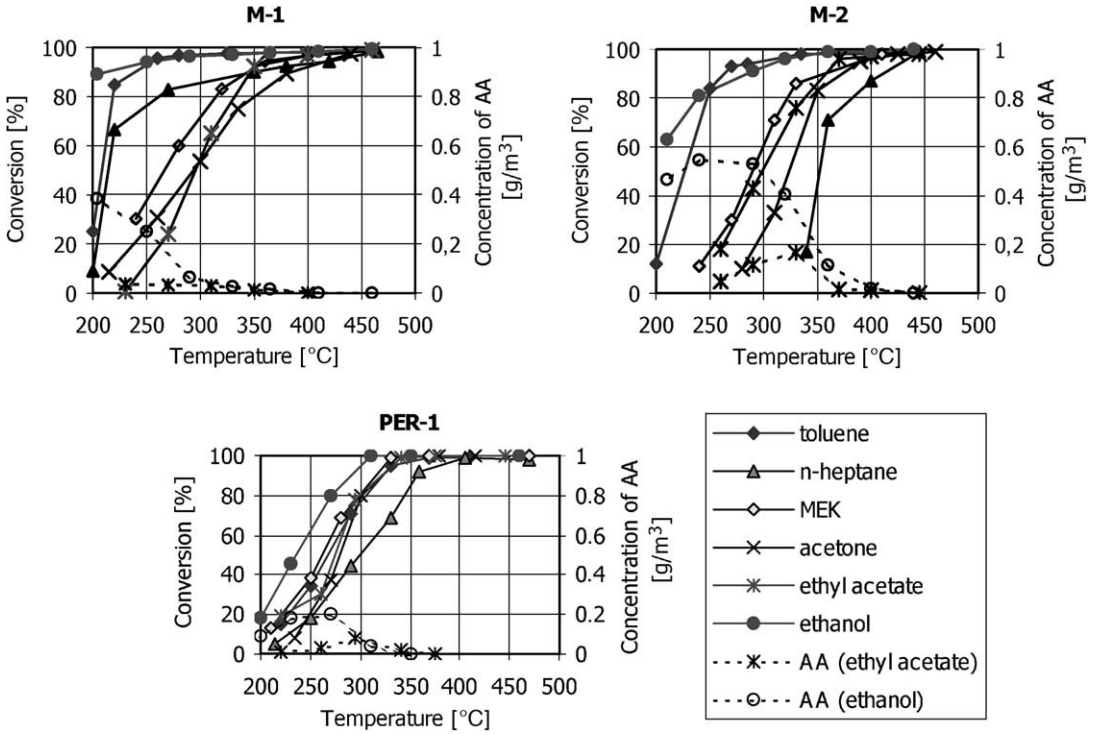


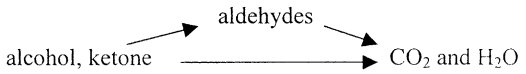
Fig. 1. Conversion of selected VOCs oxidized separately over M-1, M-2 and PER-1, with concentration of yielded acetaldehyde (AA).

Both noble metal catalysts were highly active in toluene oxidation. Fifty and ninety percent conversion was observed at 210 and 240 °C over the platinum catalyst (M-1), and 225 and 270 °C in the presence of the palladium catalyst (M-2). Heptane was more difficult to oxidize than toluene, and 90% conversion was achieved at 350 and 420 °C over M-1 and M-2, respectively. Typically for metal oxide catalysts, the activity of the perovskite catalyst in the process of hydrocarbons oxidation was lower than that observed for Pt- and Pd-type catalysts. Fifty and ninety percent conversion of toluene was achieved at 270 and 320 °C, respectively. Such conversion of *n*-heptane required a temperature of 300 and 360 °C, respectively. Over all the catalysts under investigation, irrespective of the reaction temperature, oxidation of both hydrocarbons ran to CO_2 and water, no products of incomplete oxidation being found in the flue gases.

Of the oxy-derivative compounds, ethanol was the most reactive one over all catalysts tested. Over M-1 and M-2, even at the lowest reaction temperature of 200 °C, the conversion of ethanol exceeded 50%, amounting to 90% at 210 and 290 °C for M-1 and M-2, respectively. Perovskite catalysts needed temperature of 230 and 285 °C for 50 and 90% conversion of ethanol, respectively. Typically for metal oxide catalysts, the perovskite catalyst showed a very high activity in the oxidation of each of the other oxy-derivative compounds, and its activity was even higher than that of the noble metal catalysts: above the temperature of 330–340 °C, the conversion of oxy-derivatives exceeded 90%. In the presence of M-1 and M-2, temperatures of 370–380 °C were needed to achieve a 90% conversion of acetone, which was the most difficult compound to oxidize.

Oxidation of oxy-derivative compounds was much more complicated and ran via a series of parallel and consecutive reactions, yielding intermediates detected in the flue gas. The oxidation of alcohols and ketones

may run according to the following scheme:



In the process of ethanol, acetone and MEK oxidation, acetaldehyde, a typical product of incomplete oxidation, was detected in the reaction gas. When ethylacetate was oxidized, ethanol and acetaldehyde were found in the flue gas. It is likely that in the first step ethylacetate partially hydrolysed to ethanol, whereas in the next reaction step, it was oxidized according to the above scheme:

$$CH_3COOCH_2CH_3 + H_2O \xrightarrow{\text{hydrolysis}} CH_3COOH + CH_3CH_2OH$$

$$CH_3CH_2OH + 0.5O_2 \rightarrow CH_3CHO + H_2O$$

The harmful character of aldehydes is commonly known, and the emission limits are usually more strictly for these compounds than for the solvents themselves. In Poland, for example, the admissible maximum concentration of acetaldehyde in air amounts to 20 $\mu g/m^3$, whereas that for acetone and ethylacetate is 350 and 100 $\mu g/m^3$, respectively.

Over M-1 and M-2, only ethanol and ethylacetate oxidation resulted in the formation of acetaldehyde, a product of incomplete oxidation. In the presence of M-1, maximum concentration of acetaldehyde reached 0.38 g/m^3 at 205 °C to decrease to 0.06 g/m^3 at 290 °C. Reaction selectivity to aldehyde decreased from 45% at 205 °C to 7 and 1.5% at 290 and 360 °C, respectively. Above 360 °C acetaldehyde was not present in the flue gas. Over M-2, maximum concentration of acetaldehyde (0.55 g/m^3) was detected at 240 °C, when ethanol conversion reached 82%. At that temperature, reaction selectivity to aldehyde reached 70%. At 400 °C, acetaldehyde concentration reached 0.018 g/m^3 (which is equivalent to a selectivity of 2%). Only at reaction temperatures higher than 400 °C, acetaldehyde was not found in the reaction gas. The concentration of acetaldehyde produced in the course of ethylacetate oxidation was evidently lower, amounting to 0.03 and 0.18 g/m^3 (reaction selectivity to aldehyde being 13 and 22%) over M-1 and M-2, respectively. Above 370 °C, ethylacetate was oxidized to CO_2 and water.

In the presence of PER-1, each oxy-derivative oxidation yielded acetaldehyde detected in the flue gas. When ethanol was oxidized, the highest concentration of acetaldehyde (0.2 g/m^3) was detected at reaction temperatures below 270 °C; selectivity to aldehyde increased from 25% at 270 °C up to 50% at 200 °C. In the course of ethylacetate and MEK oxidation, the maximum acetaldehyde concentrations of 0.084 and 0.063 g/m^3 were detected at 295 and 280 °C, respectively. In the oxidation of acetone, aldehyde concentration was as low as 0.03 g/m^3. Reaction selectivity to acetaldehyde did not exceed 15% when MEK, ethylacetate and acetone were oxidized. Above 340 °C, no intermediates were found in the reaction gas.

5. Oxidation of two-component mixtures

5.1. Oxidation of TCE in two-component mixtures

The results of TCE oxidation over the investigated catalysts, alone and in two-component mixtures are plotted in Figs. 2–4.

Generally, the catalytic reactivity of TCE was distinctly lower than that of non-chlorinated VOCs. Perovskite and palladium catalysts showed similar activities in the oxidation of TCE alone (50 and 90% conversion being observed at 400 and 500 °C, respectively). The activity of Pt catalyst was distinctly lower than that of Pd and perovskite, and at the highest temperature tested (500 °C), TCE conversion reached only 55%.

The influence of the components of the reaction mixture on TCE conversion depended strongly on the type of the catalyst used. In the presence of Pt catalyst (M-1), each of the components added enhanced TCE conversion (Fig. 2). The influence of particular compounds on TCE conversion at 500 °C (TCE conversion being listed below) can be arranged as follows:

$$\underset{78\%}{\text{toluene}} > \underset{75\%}{\text{ethanol}} > \underset{70\%}{\text{MEK} = n\text{-heptane}} > \underset{58\%}{\text{acetone} = \text{ethylacetate}} > \underset{55\%}{\text{TCE alone}}$$

The temperature of 50% TCE oxidation increased in the following sequence, according to the compound

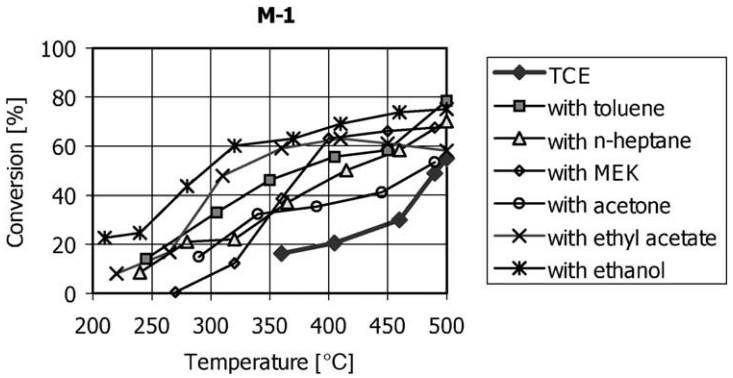


Fig. 2. Efficiency of TCE oxidation alone and in two-component mixtures over M-1.

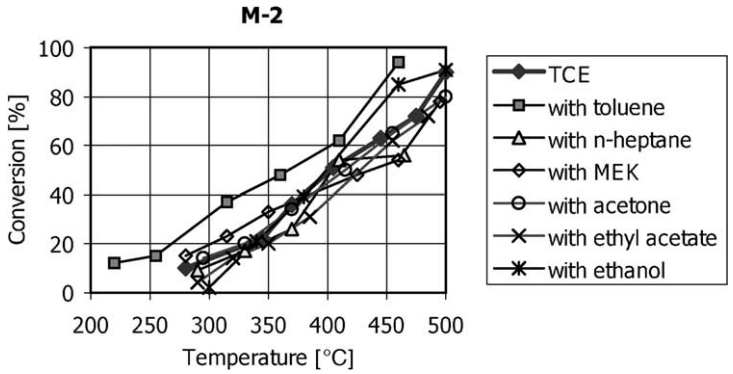


Fig. 3. Efficiency of TCE oxidation alone and in two-component mixtures over M-2.

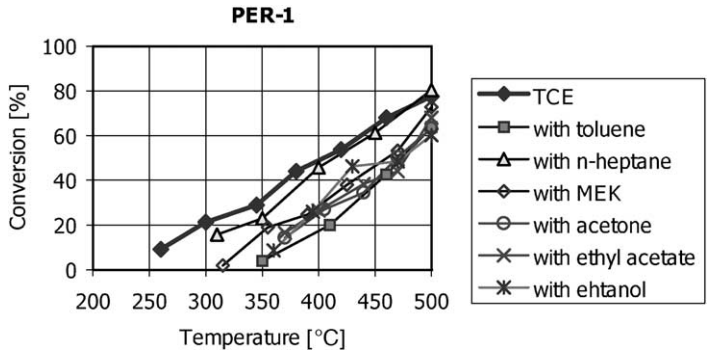


Fig. 4. Efficiency of TCE oxidation alone and in two-component mixtures over PER-1.

added:

$$300\,^{\circ}\mathrm{C}\ (\text{ethanol}) \rightarrow 320\,^{\circ}\mathrm{C}\ (\text{ethylacetate}) \rightarrow 370\,^{\circ}\mathrm{C}\ (\text{toluene}) \rightarrow 380\,^{\circ}\mathrm{C}\ (\text{MEK}) \rightarrow 415\,^{\circ}\mathrm{C}\ (n\text{-heptane}) \rightarrow 480\,^{\circ}\mathrm{C}\ (\text{acetone})$$

TCE alone was oxidized with 50% efficiency at 490 °C.

When the Pd catalyst was used (Fig. 3), only toluene and ethanol enhanced oxidation of TCE above 400 °C. At 450 °C, TCE conversion rose from 62%, when TCE was oxidized alone, up to 80 and 88%, when ethanol and toluene were present in the reaction mixture, respectively. The other non-halogenated compounds added had no evident influence on TCE conversion.

Over the perovskite catalyst (Fig. 4), each non-chlorinated VOC added to the reaction mixture inhibited TCE conversion. Only for *n*-heptane, this effect was negligible nearly in the whole range of the reaction temperatures applied.

Analysis of the reaction products confirmed that TCE oxidation ran to HCl, as the only chlorinated reaction product, irrespective of the process temperature. No other chlorinated organic compounds or Cl_2 were detected in the reaction flue gas. Chlorine balance (relating the concentration of detected HCl to stoichiometric proportion) varied from 95 to 105%. This can be attributed to the periodical HCl adsorption on, and HCl desorption from, the active phase and washcoat, as it was suggested earlier [8]. When oxy-derivative compounds were oxidized in mixtures with TCE, acetaldehyde (or ethanol and acetaldehyde in the oxidation of ethylacetate) was detected in the flue gas, but this should be attributed to the incomplete oxidation of the oxy-derivatives. In all these tests, only the concentration of organic compounds was measured. Thus, when no information about the concentration of carbon oxides is available, the mass balance for carbon cannot be performed.

5.2. Influence of TCE on the catalytic oxidation of non-chlorinated VOCs

The temperatures of 50 and 90% conversion of selected hydrocarbons and oxy-derivatives oxidized alone and in mixtures with TCE over platinum and palladium catalysts, as well as hydrocarbons oxidation over perovskite, are presented in Table 2.

The presence of TCE in the reaction mixture inhibited oxidation of each VOC over both noble metal catalysts. This effect was more distinct for the

Table 2
Comparison of 50 and 90% conversion temperatures (°C) of non-halogenated VOCs, oxidized individually and in two-component mixtures with TCE

Compound	50% Conversion			90% Conversion		
	Alone	With TCE	ΔT	Alone	With TCE	ΔT
M-1						
Toluene	210	250	40	240	290	50
n-Heptane	220	370	150	350	470	120
MEK	270	335	65	340	395	55
Acetone	290	365	75	380	425	45
Ethylacetate	290	300	10	340	355	15
Ethanol	<200	<200	0	210	340	130
M-2						
Toluene	225	245	20	270	280	10
n-Heptane	350	410	60	420	>500	>80
MEK	285	315	30	350	415	65
Acetone	320	375	50	370	440	70
Ethylacetate	300	315	15	360	380	20
Ethanol	200	270	70	290	345	55
PER-1						
Toluene	270	350	80	320	425	105
n-Heptane	300	335	35	360	400	40

platinum catalyst. Over both the catalysts, the inhibiting effect was very poor for ethylacetate. Temperatures necessary for 50 and 90% conversion were higher by 10–15 °C for M-1, and by 15–20 °C higher for M-2, as compare to those observed for acetate oxidized alone. Similar relationship was found in our earlier study of TCE oxidation with ethylacetate over a Pt–Rh catalyst [9]. Over M-2, the poor effect of TCE was observed also for toluene conversion. Temperatures for 50 and 90% oxidation of toluene in the mixture were only by 10–20 °C higher than when toluene was oxidized alone. In the presence of M-1, these temperatures were higher by 40–50 °C. The most evident inhibiting effect of TCE was found for *n*-heptane. The temperature of 50 and 90% conversion of *n*-heptane for M-1 was by 150 and 120 °C higher, and for M-2 by 60 and over 80 °C higher, respectively. For the perovskite catalyst, the temperature of 50 and 90% conversion was by 80 and 105 °C higher when toluene was oxidized with TCE, and only by 35–40 °C higher, when *n*-heptane was oxidized with TCE.

The presence of TCE in the reaction mixtures influenced not only the conversion of non-chlorinated VOCs, but also the quality and quantity of the by-products. The conversion and product distribution of ethanol and ethylacetate oxidation over M-1 and M-2 are plotted in Figs. 5 and 6.

The acetaldehyde concentration and reaction selectivity to aldehyde in the course of oxidation of ethanol alone and with TCE over M-2 were similar (Fig. 5). The lower concentration of aldehyde at temperatures below 300 °C in the presence of TCE can be attributed to the lower overall conversion of ethanol. Over M-1, the reaction efficiency dropped not as low as over M-2, but the concentration of acetaldehyde rose distinctly up to 0.46 g/m^3 at 240–280 °C. For both noble metal catalysts, in the presence of TCE, traces of aldehyde were found in the reaction gas also at 450 °C. Reaction selectivity to aldehyde exceeded 50% below 320 °C and still amounted to 5% even at 410 °C.

Over both noble metal catalysts, only acetaldehyde was formed when ethylacetate was oxidized

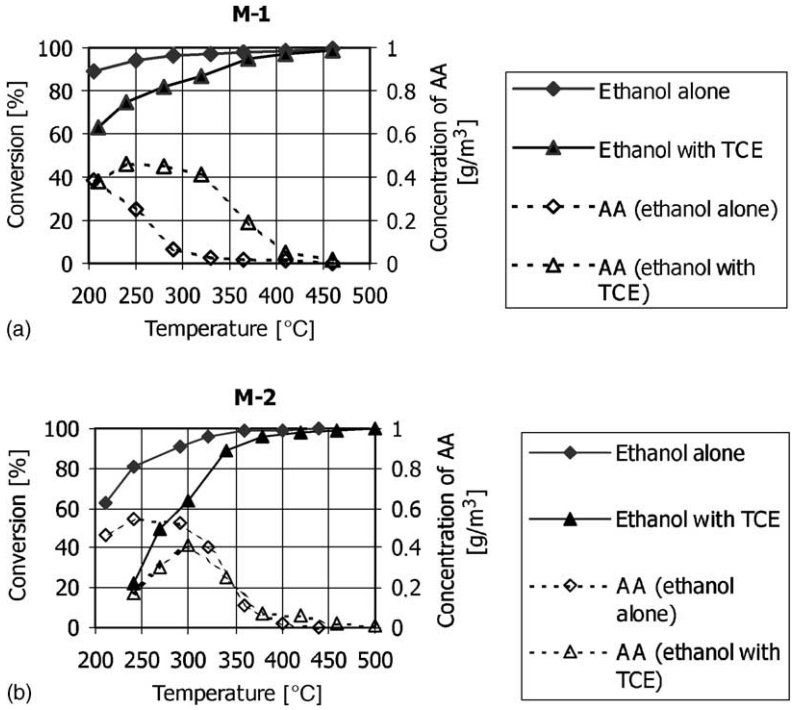


Fig. 5. Conversion of ethanol and concentration of yielded acetaldehyde (AA) for ethanol oxidized alone and with TCE over M-1 (a) and M-2 (b).

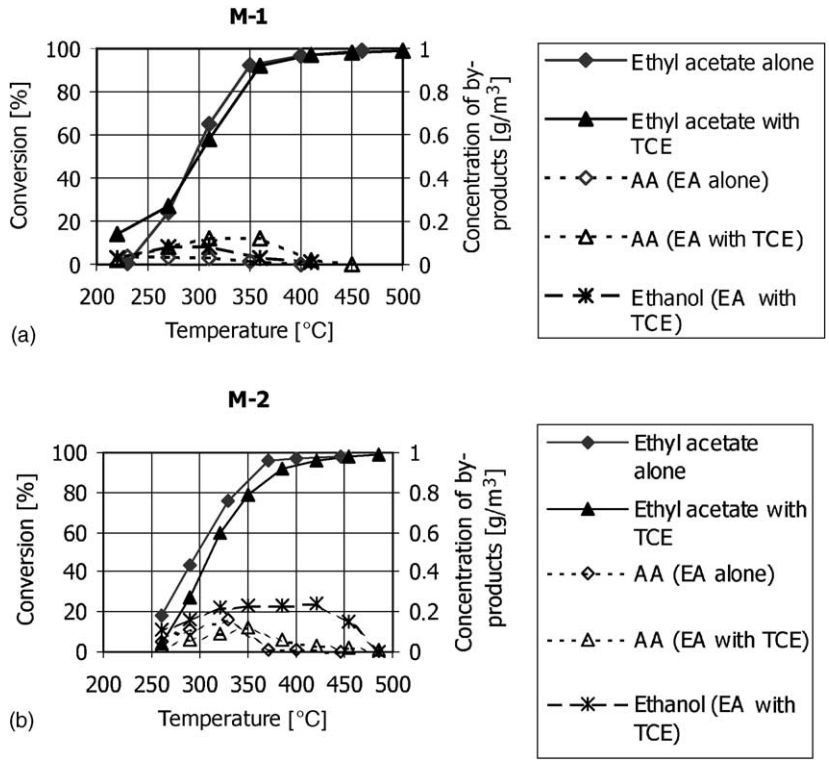


Fig. 6. Conversion of ethylacetate (EA) and concentration of yielded by-products over M-1 (a) and M-2 (b) (AA: acetaldehyde).

alone, and both potential intermediates—ethanol and acetaldehyde—when ethylacetate was oxidized in mixture with TCE (Fig. 6). The concentrations of intermediates were distinctly higher for M-2 than for M-1. The higher concentration of ethanol than that of acetaldehyde yielded in the presence of M-2 proved that the presence of TCE promoted reaction of ethylacetate hydrolysis and inhibited catalytic oxidation of the yielded ethanol. The presence of TCE did not change reaction selectivity to acetaldehyde over M-2, as compared to that when acetate was oxidized alone. The ethanol yielded accounted for 14.5% of converted acetate even at 455 °C, and this selectivity to ethanol increased up to 56% below 290 °C. Over M-1, the concentration of ethanol did not exceed 0.08 g/m^3, whereas that of the detected acetaldehyde was higher and rose up to 0.14 g/m^3 at 310–360 °C. Thus, the presence of TCE promoted hydrolysis to ethanol and did not inhibit the oxidation of ethanol to acetaldehyde. Over M-1, reaction selectivity to acetaldehyde increased up to 30% at 270–310 °C, whereas that to ethanol reached 34% at 220 °C, and decreased systematically down to 15 and 1% at 310 and 410 °C, respectively. When ketones were oxidized with TCE, traces of acetaldehyde were detected in the flue gas, but they did not exceed 0.01 g/m^3. The mechanism yielding such a high concentration of acetaldehyde from ethanol, as well as ethanol and acetaldehyde, when ethylacetate was oxidized, can be explained by partial blocking of the active sites on the catalyst surface with strongly adsorbed chlorine compounds.

Because of the noticeable decrease of TCE conversion in mixtures in the presence of the perovskite catalyst, the minimum reaction temperatures were as high as 320–350 °C. Unlike in the presence of noble metal catalysts, TCE did not influence the conversion of oxy-derivative compounds or the product distribution. At reaction temperatures higher than 320 °C, no products of incomplete oxidation were detected in the flue gas. The temperature of 50 and 90% conversion

of toluene in the mixture reached 350 and 425 °C and was by 80 and 105 °C higher as compared to the conversion of toluene oxidized individually. The influence of TCE was much poorer in the case of *n*-heptane oxidation, and the temperatures of 50 and 90% conversion were only by 30 and 40 °C higher than those of *n*-heptane oxidized individually (Table 2).

6. Conclusions

The platinum catalyst showed very high activity in the oxidation of non-chlorinated VOCs, particularly of toluene and ethanol. The perovskite catalyst was even more active than the Pt catalyst in the oxidation of ketones and ethylacetate. The oxidation of TCE was the most difficult over all the catalysts under the investigated conditions. In this process, palladium and perovskite catalysts were more active than platinum.

Each VOCs added to the reaction mixture strongly enhanced TCE oxidation over platinum. Over palladium, only toluene and ethanol had a promoting effect on TCE oxidation. Over the perovskite catalyst, *n*-heptane did not influence TCE oxidation, whereas the other added compounds strongly inhibited TCE conversion.

Over both noble metal catalysts, the presence of TCE decreased the oxidation rate for each non-halogenated compound and increased the concentration of acetaldehyde and acetaldehyde and ethanol, when ethanol and ethylacetate were destroyed, respectively. Over Pt, the presence of TCE induced an increase in reaction selectivity to aldehyde, when ethanol and ethylacetate were oxidized. Despite the still low conversion of TCE over the perovskite catalyst, there was no inhibiting effect on the conversion of oxy-derivative and on the distribution of products at reaction temperatures above 320 °C.

After all the tests carried out with TCE, the conversion of toluene experienced only a slight decrease. No physical changes in catalyst surface—attrition or crushing of the active phase or of the washcoat—were observed as a result.

The mechanism governing these findings has not been considered in this study. It may be anticipated that such distinct differences in the activities of the investigated catalysts should be attributed to the differences in the bond energies of oxygen and oxidized compounds for platinum, palladium and metal oxide catalysts. It seems likely that if the reaction of TCE and VOCs oxidation is a competitive one and runs on the same active sites, there will be either no effect of the VOCs on TCE conversion (over Pd) or the conversion of TCE will be inhibited (over perovskite). These findings are interesting enough to deserve furtherance of extensive studies.

The results of this study have shown that it is necessary to select very carefully not only the catalyst to be used but also the reaction conditions when treating industrial flue gases containing different organic compounds, including chlorinated hydrocarbons.

Acknowledgements

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