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CATALYTIC OXIDATION OF TRICHLOROETHYLENE (TCE) IN TWO-COMPONENT MIXTURES

The efficiency of TCE oxidation over monolithic Pt-Rh catalyst on metallic support with γ -Al₂O₃ washcoat was investigated when TCE was oxidized alone or in two-component mixtures with nonhalogenated organic compounds (two hydrocarbons and three oxyderivatives) in air. The presence of TCE inhibited the catalyst activity in each nonhalogenated compound conversion, and the oxidation of ethyl acetate or methyl ethyl ketone (MEK) yielded acetaldehyde, typical product of incomplete oxyderivatives oxidation not detected in flue gases when these compounds were oxidized in the absence of TCE. The presence of nonhalogenated organic compound in reaction mixtures generally enhanced TCE oxidation; only ethanol had no effect on TCE conversion. After 70 h of catalyst exposure to chlorine compounds, test reaction of toluene oxidation showed a slight loss of catalyst activity, recovered almost completely after its regeneration in air flow at 450 °C for 5 h.

1. INTRODUCTION

Halogenated hydrocarbons present environmental hazards in a number of different ways. They are widely used in dry cleaning processes or degreasing operations, they are components of refrigerants, transformer fluids and solvents. Halogenated hydrocarbons have found wide application in pharmaceutical industry and in the manufacture of plastics, synthetic resins or pesticides. These compounds are emitted with a mixture of other organic or inorganic combustible components; e.g., in the process of vinyl chloride manufacturing, not only organic chlorine compounds (methyl, ethyl and vinyl chlorides, dichloroethane) are emitted, but also other components (ethane, ethylene, carbon monoxide) [1]. Recently, an ever-increasing popularity of solid waste incineration (comprising both municipal and hazardous industrial wastes) has brought about an emission of hazardous gases, particularly when chlorine-containing wastes are incinerated; the flue gases released to the atmosphere carry various very toxic chlorine compounds such as polychlorinated

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biphenyles (PCBs), polychlorinated dibenzofuranes (PCDFs) or polychlorinated dibenzo-*p*-dioxines (PCDDs) [2].

Catalytic incineration is an energy-efficient method allowing us to destroy halogenated hydrocarbons emitted in industrial exhaust gases. The process involves lower temperatures as thermal combustion and yields such harmless or less toxic products as CO₂ and H₂O, and HCl as chlorine-containing product, while in the course of thermal combustion process some dangerous or toxic intermediate products (e.g. phosgene), acid gases such as NO_x, or even PCDDs and PCDFs can be yielded [3]. Various catalysts have been tested for their activities in catalytic oxidation of halogen derivatives in the air. These catalysts are divided into two major groups: catalysts either with noble metals or with transition metal oxides as active phase. It is generally assumed that only catalysts with a very high platinum content (1–3 wt.%) can be used for this purpose. However, our earlier study showed that even catalysts with a decreased platinum content (0.15–0.1 mass %) can be applied to the oxidation of halogenated hydrocarbons [4]–[6]. The catalyst used must be resistant to deactivation or poisoning by chlorine and its compounds. Halogenated hydrocarbons have been usually a reversible poison for noble metal catalysts. When chlorocarbon is removed from the reaction mixture, catalyst activity usually returns to the initial value.

There are some reports on the catalytic destruction of the mixtures of volatile organic compounds (VOCs), but there is relatively sparse data relating to catalytic combustion of halogenated VOCs, particularly in the mixtures with nonhalogenated compounds [1], [7]–[9]. Our earlier investigations showed that the presence of hydrocarbons (xylene, toluene, *n*-heptane) in multicomponent mixtures enhanced conversion of halogenated hydrocarbons [5], [6], [10]. The "mixture effect" can influence not only the catalyst activity, but also selectivity of the reaction.

Recently we developed a new technology of the preparation of monolithic catalysts on metallic supports. Platinum content reduced to 0.02–0.05 mass % depended strongly on the thickness of the γ -Al₂O₃ washcoat. These catalysts were tested for the oxidation of various organic compounds, first of all for the post-combustion of motor exhaust gases. It was interesting to test their activity, stability and resistance to deactivation also in the oxidation of halogenated hydrocarbons. For the purpose of the study a Pt-Rh catalyst on metallic monolithic support was prepared and tested for the oxidation of selected VOCs, including chlorinated hydrocarbons. The activity of the catalyst in TCE oxidation (the less catalytically reactive chloroorganic compound) was tested when TCE was oxidized alone or in two-component mixtures with selected hydrocarbons and oxyderivatives. On the other hand, it was interesting to find out how the presence of TCE influences the activity and selectivity of the catalyst in the oxidation of nonchlorine compound. In order to determine the catalyst resistance to deactivation by chlorine compounds, the test reaction of toluene oxidation was run prior to, and after all the experimental series.

2. MATERIALS AND METHODS

The catalyst (M-9) on a metallic support from heat-resisting steel with additives was prepared for the purpose of these investigations. The metallic support of very small specific surface demands deposition of a washcoat. After earlier thermal pre-treatment of support, the γ - Al_2O_3 washcoat (in gel form) with rare earth elements as additives was smeared on the metal surface. After drying at 85 °C and calcination at 760 °C the washcoat content accounted for 1.5 mass % of the support. The monolith was impregnated with active ingredients (platinum and rhodium in the same proportion of 0.04 mass %) by immersion in the solution of chloroplatinic acid and rhodium chloride for 12 h. Similar catalysts prepared for our earlier investigations showed high activity in the oxidation of typical organic solvents [10]. The parameters of the catalyst are presented below:

- cell geometry – triangle,
- cell density – 430/cm²,
- cell dimension – 0.7 mm,
- wall thickness – 0.05 mm,
- catalyst dimension – $\phi = 23$ mm, $h = 70$ mm.

The test reactions were carried out in an electrically heated laboratory-scale glass “tube-in-tube” reactor. Every component was dosed individually by evaporation. The inlet concentration of each compound approached 1g/m³. Space velocity amounted to 10000 h⁻¹ and reaction temperature ranged between 200 and 500 °C. The concentrations of the reagents in the reaction mixtures were detected by gas-chromatography (Perkin-Elmer GC with integrator, FID and column of 1.8 m, packed with 10% PEG 2000 on Chromosorb W). The conditions of analysis were selected so as to detect every investigated compound as well as potentially yielded intermediate products – first of all aldehydes or light hydrocarbons (C₁–C₄) (temperature of column – 72 °C, temperature of injector and detector – 100 °C). Concentration of hydrochloric acid was measured by titration, and chlorine concentration – colorimetrically.

The tests involved the following steps:

- toluene oxidation,
- oxidation of every nonhalogenated compound alone: toluene, *n*-heptane, ethanol, methyl ethyl ketone (MEK), ethyl acetate,
- oxidation of halogenated hydrocarbons alone: chlorobenzene, dichloroethylene (DCE), TCE,
- oxidation of two-component mixtures (TCE with nonhalogenated compound),
- toluene oxidation.

3. RESULTS AND DISCUSSION

3.1. CATALYTIC OXIDATION OF SELECTED VOCs

The results of catalytic oxidation of selected compounds are presented in figure 1.

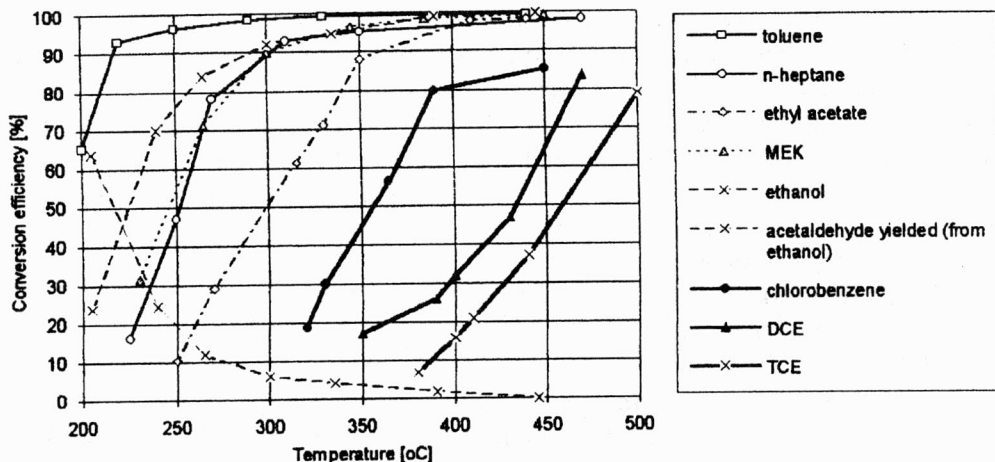


Fig. 1. Conversion efficiency of selected VOCs, including chlorinated hydrocarbons, with selectivity of ethanol oxidation with respect to acetaldehyde (dotted line)

Nonhalogenated compounds were oxidized with higher efficiency than chloroorganic compounds. The reactivity of these compounds and the temperatures of their 90% conversion efficiency can be arranged according to the following descending order:

$$\text{toluene} = \text{ethanol} > \text{MEK} = n\text{-heptane} > \text{ethyl acetate.}$$

220 °C 300 °C 360 °C

Chlorinated hydrocarbons were less reactive, their reactivity decreased in the following order:

$$\text{chlorobenzene} > \text{DCE} > \text{TCE.}$$

When selected compounds were oxidized individually, only ethanol was found to yield acetaldehyde, a typical product of incomplete oxidation, detected in the flue gases. Selectivity of oxidation to acetaldehyde, very high at low reaction temperatures (reached even 50% at 220 °C), decreased to 3% at 350 °C. The other VOCs were oxidized to CO_2 and H_2O . Irrespective of the reaction conditions, catalytic oxidation of chloroorganic compounds yielded HCl as only chlorinated organic product, neither chlorine nor other chlorinated organic compounds were detected in the flue gases. The concentration of hydrochloric acid in the flue gases changed irregularly from 65 to 130% of stoichiometric value.

It have been found also in our earlier experiments, and it should be attributed to the HCl periodical adsorption on and desorption from the active sites of catalyst and washcoat.

3.2. CATALYTIC OXIDATION OF TCE IN TWO-COMPONENT MIXTURES

The efficiencies of TCE oxidation in two-component mixtures with selected VOCs are presented in figure 2.

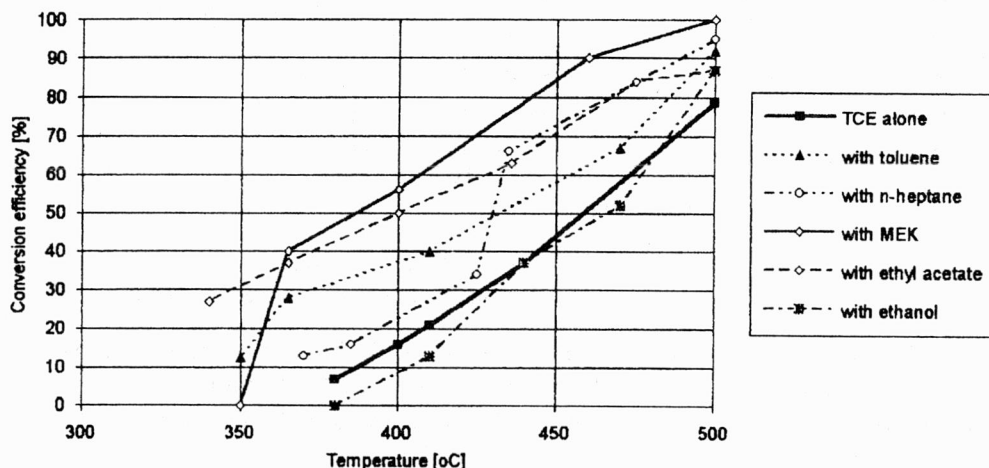


Fig. 2. Efficiency of TCE oxidation in two-component mixtures

Generally, the presence of nonhalogenated organic compounds in the reaction mixture enhanced the conversion of TCE. Only ethanol was found to have no effect on the catalytic activity during TCE oxidation. In the presence of ethyl acetate, the efficiency of TCE oxidation was significantly higher, particularly at temperatures lower than 450 °C. Toluene and *n*-heptane had no noticeable influence on the process of TCE oxidation at lower temperatures, but at 500 °C TCE was oxidized with more than 90% efficiency. MEK improved the efficiency of TCE oxidation in the whole range of the temperatures investigated; at 350 °C oxidation of TCE practically did not occur, but at 365 °C its efficiency reached 40%. At the highest temperature under investigation (500 °C), in the presence of MEK, TCE was completely oxidized.

TCE oxidation ran to CO₂ and HCl which is the only chlorination-containing product, irrespective of the reaction conditions; no other intermediate or incomplete oxidation products were detected in the flue gases. Only when TCE was oxidized in the presence of oxyderivatives, some amounts of acetaldehyde (a typical product of incomplete oxidation of the oxyderivatives) were detected in the flue gases. This finding is explained in point 3.3.

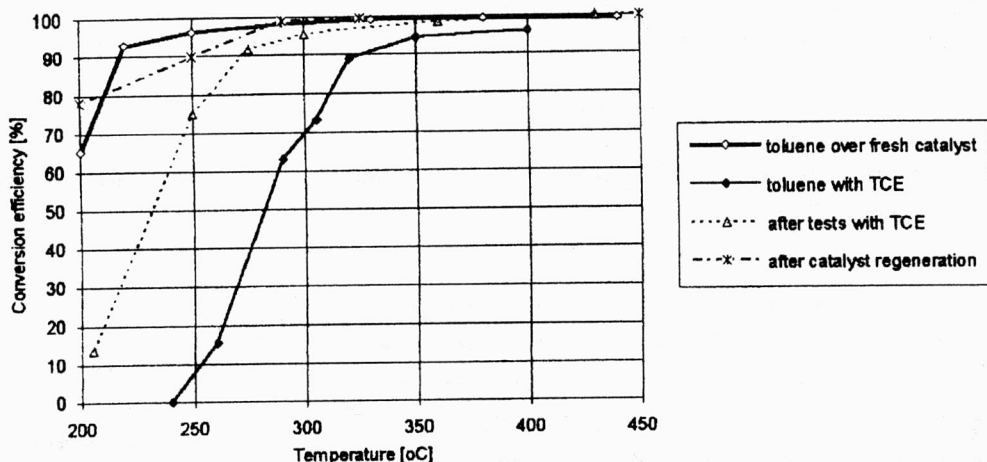


Fig. 3. Test reaction of toluene oxidation over fresh catalyst in the mixture with TCE and after 70 hours exposition to chlorine compounds

The test reaction of toluene oxidation after ca. 70 hours of catalyst exposure to chlorine compounds showed a slight, but reversible, deactivation of the contact. After regeneration in hot (450 °C) air flow for 5 h, catalyst activity was recovered almost completely (figure 3).

3.3. ACTIVITY AND SELECTIVITY OF VOCs OXIDATION IN TWO-COMPONENT MIXTURES WITH TCE

The temperatures of 50% and 90% conversion efficiencies of the oxidized hydrocarbons and their oxyderivatives, with and without TCE in the reaction mixtures, are compared in the table. The results of conversion efficiency and reaction selectivity with respect to acetaldehyde oxidation of oxyderivatives are presented in figure 4.

Table

Temperatures of 50% and 90% deep oxidation efficiencies of selected hydrocarbons and oxyderivatives when oxidized alone and in two-component mixtures with TCE

Compound	Temperature (°C)			
	50% oxidation		90% oxidation	
	alone	with TCE	alone	with TCE
Toluene	< 200	280	220	325
<i>n</i> -heptane	255	430	300	490
Ethanol	< 200	360	220	440
Ethyl acetate	300	350	360	325
MEK	245	370	300	445

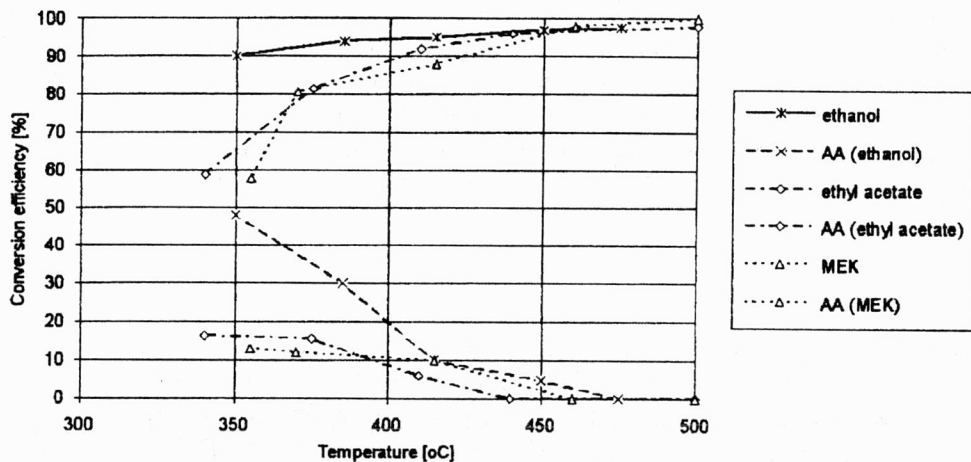


Fig. 4. Oxidation efficiency and reaction selectivity with respect to acetaldehyde of oxyderivatives in two-component mixtures with TCE

The presence of TCE in the reaction mixtures inhibited oxidation of each nonhalogenated component. The inhibiting effect was poor for ethyl acetate as the temperature necessary for 50% and 90% efficiencies of its oxidation had to be higher by 30 deg than when acetate was combusted alone. But in the presence of TCE, acetaldehyde, the product of incomplete acetate oxidation, was identified in the flue gases. At the reaction temperature of 370 °C the per cent share of acetaldehyde in the flue gases reached 16%, and decreased to zero at temperatures higher than 440 °C. No such product was found when ethyl acetate was oxidized alone. The inhibiting effect of TCE was more pronounced in the case of toluene and MEK oxidation, particularly at lower reaction temperatures; a 90% conversion efficiency was obtained at the reaction temperature higher by 100 deg, reaching 325 °C and 410 °C for toluene and ketone, respectively. Like the reaction of ethyl acetate oxidation, the process of MEK oxidation with TCE in the reaction mixture yielded acetaldehyde detected in the flue gases. The per cent share of aldehyde amounted to 8% at 410 °C (the temperature of 90% conversion efficiency of MEK). The inhibiting effect of TCE in the mixture was the most distinct in *n*-heptane oxidation; the temperature for its 90% conversion had to be raised by 190 deg (from 300 to 490 °C). Oxidation of ethanol in the presence of TCE yielded the higher concentration of acetaldehyde; even at the comparatively high temperature of 380 °C, when ethanol conversion efficiency reached 93%, reaction selectivity with respect to acetaldehyde was very high, amounting to 30%. At the same temperature, when ethanol was oxidized separately, its conversion efficiency reached 98%, but simultaneously the per cent share of acetaldehyde in flue gases did not exceed 2%.

The mechanism yielding such a high concentration of acetaldehyde from ethanol as well as the generation of aldehyde from the two other oxyderivatives (ethyl acetate and MEK) when combusted in two-component mixtures with TCE can be explained by partially blocked active sites on the catalyst surface by HCl, the chlorine-containing product of TCE oxidation. In this case, the activity of partially blocked catalyst is insufficient to ensure a deep oxidation of the compounds selected.

4. CONCLUSIONS

When the compounds under investigation were oxidized in one-component mixtures with air, only ethanol conversion yielded acetaldehyde, the product of incomplete alcohol oxidation, detected in the flue gases. Irrespective of the reaction conditions, catalytic oxidation of halogenated hydrocarbons, including TCE, produced CO₂ and HCl which was the only chlorine-containing reaction product; no chlorinated organic compounds were detected in the flue gases.

The presence of nonhalogenated organic compounds (hydrocarbons or oxyderivatives) in the reaction mixture generally enhanced TCE oxidation; only ethanol was found to be an exception and had no influence on the conversion of TCE.

The presence of TCE in the reaction mixtures not only inhibited the oxidation of each nonhalogenated compounds added, but also influenced the reaction selectivity with respect to acetaldehyde when oxyderivatives were oxidized. The inhibiting effect became the most remarkable in the oxidation of *n*-heptane, but poor in the case of ethyl acetate.

The tests of toluene oxidation at the beginning of the experiments and after 70 hours of catalyst exposure to chlorine compounds showed no significant loss of catalyst activity, only its slight deactivation of a reversible character. After regeneration in air flow at a temperature of 450 °C for 5 h the catalyst activity was recovered almost completely.

The results of investigations showed that even the catalyst with the reduced contents of active phase can be used in the halogenated hydrocarbons' oxidation, particularly when halogen derivatives are emitted in the mixtures with specific nonhalogenated organic compounds (e.g. acetates or ketones), at the optimum process parameters exactly selected.

ACKNOWLEDGEMENT

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KATALITYCZNE UTLENIANIE TRÓJCHLOROETYLENU (TRI) W MIESZANINACH DWUSKŁADNIKOWYCH

Przebadano skuteczność spalania TRI samego i w mieszaninach dwuskładnikowych z dwoma węglowodorami i trzema połączeniami tlenopochodnymi w obecności katalizatora na bazie Pt-Rh na monolitycznym nośniku metalicznym. Obecność węglowodorów lub ich tlenopochodnych wpływała na wzrost skuteczności przereagowania TRI. Jedynie etanol nie miał istotnego wpływu na przebieg reakcji spalania TRI. Z kolei obecność TRI hamowała przereagowanie wszystkich związków nie zawierających chloru, a w przypadku octanu etylu i metylo-etylo ketonu w gazach poreakcyjnych wykryto aldehyd octowy – typowy produkt niepełnego ich spalania. Testy spalania toluenu na katalizatorze świeżym i po około 70 godzinach jego pracy ze związkami chloru wykazały pewien spadek aktywności kontaktu, jednak gdy wygrzano go w przepływającym powietrzu w temperaturze 450 °C przez 5 h, aktywność katalizatora niemal całkowicie powróciła do początkowej.

