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ScienceDirect

Catalysis Today 119 (2007) 301–304

CATALYSIS TODAY

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Destruction of trichloroethylene (TCE) and trichloromethane (TCM) in the presence of selected VOCs over Pt-Pd-based catalyst

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Abstract

Catalytic oxidation of trichloroethylene (TCE) and trichloromethane (TCM) oxidized alone and in two-component mixtures with selected volatile organic compounds (VOCs) such as toluene, *n*-hexane, ethanol or acetone was investigated over a Pt-Pd-based catalyst on a monolithic, metallic, γ-Al_2O_3-washcoated support. TCE and TCM were more difficult to oxidize than VOCs and temperatures of their 50% conversion ($T_{50\%}$) amouted to 420 and 330 °C, respectively. All the VOCs added were found to enhance the conversion of the two chlorinated compounds, drecreasing $T_{50\%}$ by 20 °C, at the most, for TCM in the presence of toluene and by 50 °C for TCE in the presence of acetone. Both the chlorinated compounds lowered the conversion of the VOCs added (except that of toluene), and this lowering was particularly distinct with *n*-heptane; they also raised the concentration of acetaldehyde formed during the oxidation of oxyderivative compounds.

Keywords: Air pollution control; Catalytic oxidation; Chloroorganic compounds

1. Introduction

Chlorinated chydrocarbons (CVOCs) are classified as hazardous to the environment and public health. They are emitted to the atmosphere from a wide range of industrial processes, often in mixtures with other VOCs or carbon monoxide. In this context, catalytic incineration seems to be an efficient and economical method for the abatement of such emissions. Platinum group metals are well-known highly active catalysts for the oxidation of hydrocarbons in general, and this includes chlorinated hydrocarbons [1–3]. Recently, metal oxide catalysts, particularly of perovskite structures [4,5] and zeolites [6] have been extensively tested in the oxidation of CVOCs.

When mixtures of chlororganic compounds and VOCs are oxidized, the rate of complete oxidation of each component may increase or decrease, as compared to the reaction rates of particular compounds oxidized alone. This effect depends both on the chemical structure of the compound to be oxidized and on the catalyst used. Generally, over noble metal catalysts, the presence of hydrogen-rich donor, such as water or non-halogenated VOCs, exerts a beneficial effect not only on the conversion of chlorinated hydrocarbons but also on the production of HCl, the desired reaction product [1,7–10]. In some studies it has been concluded that enhanced conversion of chlorinated compounds depends on the destructibility of the VOCs. Windawi et al. [1] have come to the concludsion that unsaturated and aromatic VOCs strongly enhance the oxidation of unsaturated chlorocarbons, while saturated VOCs only slightly raise the conversion of CVOCs. The enhancement of TCE destruction over alumina-supported Pt or Pd in the presence of hydrogen-rich compounds, i.e. water, hexane and toluene, has been reported by Gonzalez-Velasco et al. [7]. Reports are also available on the enhanced rate of chlorobenzene combustion over Pt-based catalysts in binary mixtures with various hydrocarbons [8,9]. The beneficial effect of acetone and methanol on the conversion of methylene chloride oxidized in two-component mixtures over a Pt-Pd-based catalyst has been detected by Sharma et al. [10]. Enhanced conversion of CVOCs in the presence of water or hydrocarbons has also been observed over perovskite-based [4,5], as well as Cu-Cr and Mn-based catalysts [11]. Only with zeolite catalysts water played an inhibiting role in chlorinated hydrocarbons oxidation, and the addition of water accounted for the rise in the $T_{50\%}$ value [6]. On the other hand, CVOCs

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doi:10.1016/j.cattod.2006.08.059

usually inhibit a complete oxidation of the non-chlorinated VOCs added, and this inhibiting effect depends on the total chlorine content in the chlorinated hydrocarbon molecule rather than on the chemical structure of the chlorinated compound.

The investigations into the influence of selected non-chlorinated VOCs on the conversion of selected CVOCs in two-component mixtures, carried out at our laboratory, have shown that this influence differed from one chlorinated compound to another, and depended on the catalyst used. We have found that TCE conversion over Pt/γ-Al_2O_3 distinctly increased in the presence of selected hydrocarbons and oxyderivatives. Over Pd/γ-Al_2O_3, this enhanced effect was very poor, but over the perovskite the addition of each non-chlorinated compound brought about a decrease in the extent of TCE conversion [12]. Chlorobenzene conversion over Pt/γ-Al_2O_3 was only slightly enhanced by the addition of VOCs, but the conversion of 1,2-dichloroethane over the same catalyst was remarkably inhibited in the presence of each of the VOCs added [13].

Our earlier study has shown that of the bimetallic catalysts tested (Pt-Pd, Pt-Rh and Pt-Ce), the Pt-Pd-based one was the most active in the oxidation of selected CVOCs differing in the chemical structure and was also resistant to chlorine compounds [14].

The aim of the present study was to determine the mutual effect of the presence of chlorinated hydrocarbons with the same chlorine atoms in the molecule – TCE and TCM – and selected non-chlorinated compounds: hydrocarbons (toluene and *n*-hexane) and oxyderivatives (acetone and ethanol) on the conversion of each component of a binary mixture, without analyzing the mechanism of the reaction in more detail.

2. Experimental

For the purpose of the study a Pt-Pd-based catalyst was prepared on a monolithic metallic support from heat-resisting alumel steel, with a γ-Al_2O_3 washcoat. After etching in an acid solution, the support was coated with γ-Al_2O_3; rare earth elements (lanthanum and cerium) were added to upgrade its chemical and thermal stability. After drying and calcination at 550 °C, the washcoat content amounted to 2.5 wt.%. The catalyst was prepared by impregnation in the solutions of chloroplatinic acid and palladium chloride, successively, being dried and calcined after each operation. Noble metal content amounted to 0.2 and 0.1 wt.% for Pt and Pd, respectively. The BET specific surface area measured for the whole monolith totalled 1.64 m^2/g. A more detailed description of the catalyst used has been published elsewhere [14].

Tests were carried out in a typical cross-flow glass reactor of ‘‘tube in tube’’ type. Reaction temperature measured inside the catalyst block ranged from 200 to 450 °C; gas hourly space velocity was 10,000 h^{-1}. The reaction mixtures were produced by evaporation and mixed with air to the desired concentration of 1 and 0.5 g/m^3 for non-chlorinated and chlorinated compounds, respectively, which is equivalent to the concentration of 243 ppm of toluene, 260 ppm of *n*-hexane, 386 ppm of acetone and 487 ppm of ethanol. The concentration of TCE and TCM was lower, amounting to 85 and 95 ppm, respectively. Such concentration of reagents in binary mixtures of TCE or TCM with toluene, *n*-hexane, ethanol and acetone corresponded to the ratio of H:Cl atoms of 1:0.125, 0.068, 0.08 and 0.1, respectively. Catalytic activity tests included oxidation of each non-chlorinated VOC alone, oxidation of TCE and TCM alone and in binary mixtures with each VOC, and oxidation of toluene after all tests with chlorinated compounds to determine potential deactivation of the catalyst.

Qualitative and quantitative analysis of the reagents and the potentially yielded organic intermediates was carried out by gas-chromatography, using a Mera-Elwro Poland GC with flame ionisation detector (FID) and a 2.2 m glass column packed with commercial 10% Carbowax 20.4-TPA (terephthalic acid). The parameters of chromatographic analysis enable the separation of each compound and organic intermediate. The temperature of the column, injector and detector amounted to 130, 200 and 300 °C, respectively. The concentrations of such reaction products as HCl, chlorine or CO were not measured.

3. Results and discussion

The results are plotted in Figs. 1 and 2.

The catalytic reactivity of the compounds studied (expressed as the $T_{50\%}$ and $T_{90\%}$ conversion of each component oxidized alone) is presented below:

	Toluene	*n*-Hexane	Acetone	Ethanol	TCE	TCM
$T_{50\%}$	220	280	250	<220	420	330
$T_{90\%}$	270	400	350	220	>450	>450

and was found to decrease in the folloeing order: ethanol > toluene > acetone > *n*-hexane > TCM > TCE, which is in agreement with the reactivity pattern of the VOCs of choice, oxidized over noble metal-based catalysts [15,16].

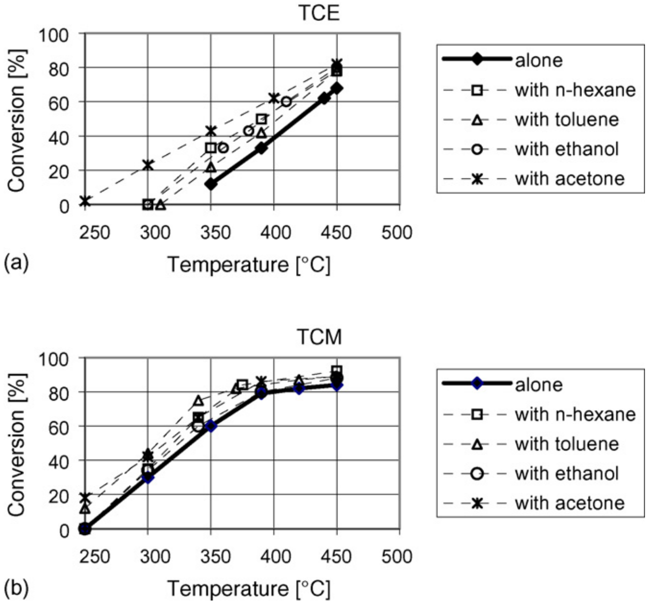


Fig. 1. Conversion of TCE (a) and TCM (b) oxidized separately (full lines) and in two-component mixtures (dotted lines) with selected VOCs.

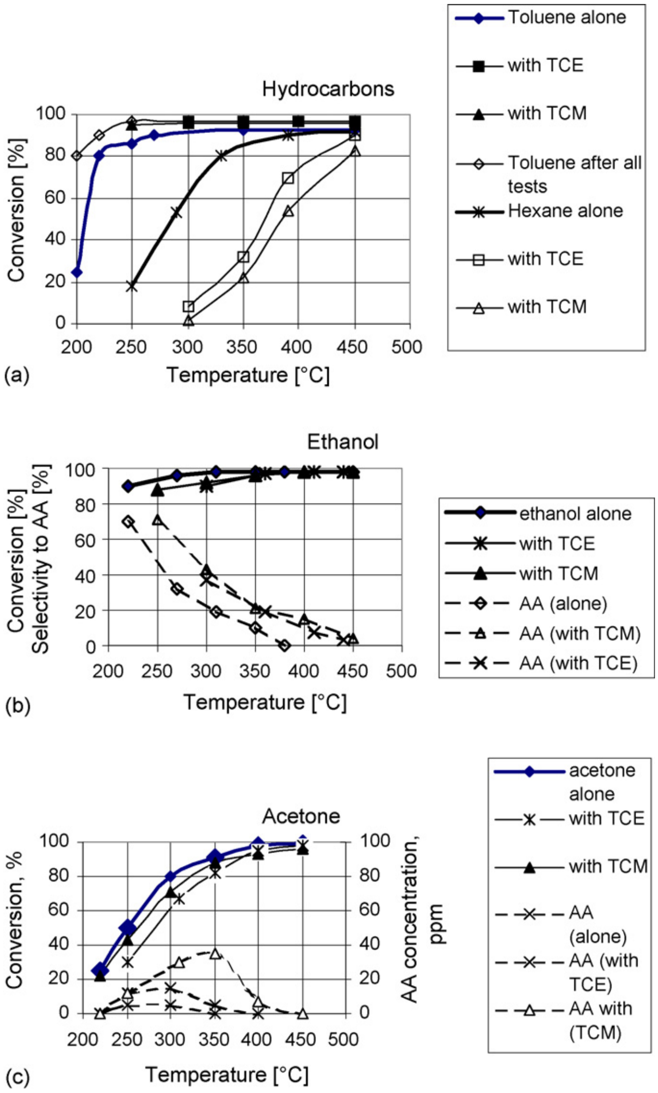
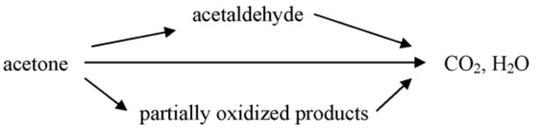


Fig. 2. Influence of TCE and TCM on the conversion of selected VOCs: (a) hydrocarbons, (b) ethanol conversion with reaction selectivity to acetaldehyde (AA) and (c) acetone conversion and AA concentration in ppm.

Fifty percent conversion was attained below 280 °C for all the non-chlorinated VOCs being oxidized. The highest reactivity was that of ethanol, with 90% conversion obtained at 220 °C. The catalyst also displayed a high activity in the combustion of toluene, with the $T_{90\%}$ value of 270 °C. The lowest activity of the catalyst was that in the reaction of *n*-hexane oxidation ($T_{90\%} = 400$ °C).

In the case of ethanol oxidation, acetaldehyde (AA), a typical product of incomlete oxidation of alcohols, was detected in the reaction gas. Over noble metals, ethanol oxidation may follow two parallel reaction paths—direct oxidation to CO_2, and partial oxidation to ethanal, next oxidized to CO_2 [17]. The highest selectivity of the ethanol oxidation reaction towards AA, which amounted to 70%, was detected at 220 °C, i.e. at the temperature of 90% conversion. With the rise in the reaction temperature, AA concentration decreased continually. At 370 °C, no ethanal was detected in the reaction gas.

AA was also detected during oxidation of acetone, but its concentration was noticeably lower and practically did not exceed 5 ppm. The mechanism of acetone combustion is more complicated than that of alcohols. Lintz and Wittstock [18] have proposed the following path:



The catalyst under test was found to be less active in the oxidation of TCM and TCE; their 50% conversion was attained at 330 and 420 °C, respectively. At the highest reaction temperature (450 °C), the extent of conversion for TCM was 84% and only 68% for TCE.

Generally, saturated chlorinated hydrocarbons are oxidized more readily than unsaturated ones [1]. Chlorinated methanes are classified as a group of CVOCs with the highest readiness for oxidation. Their reactivity increases with the increasing number of chlorine atoms in the molecule, because the bond dissociation energy is lower for the C–Cl bond (338.5 ± 4.2 kJ/mol) than for the C–H bond (392.5 ± 2.5 kJ/mol). It is generally assumed that the first reaction step in CVOCs oxidation is the abstraction of the chlorine atom from the molecule. TCE is more difficult oxidized because of the higher activation energy that is needed for the rupture of the double C=C bond.

In mixtures with non-chlorinated VOCs, both TCE and TCM showed an enhanced conversion, which was similar in the two chlorinated hydrocarbons. The value of $T_{50\%}$ conversion in binary mixtures is listed below:

	Alone	With toluene	With hexane	With acetone	With ethanol
TCE ($T_{50\%}$)	420	405	385	370	390
TCM ($T_{50\%}$)	330	310	315	320	325

The promoting effect the VOCs is slightly greater for TCE than for TCM. During oxidation of TCE in the presence of toluene, the $T_{50\%}$ value decreased by only 15 °C; in the presence of acetone, the drop in $T_{50\%}$ reached 50 °C (Fig. 1a). In the oxidation of TCM, the greatest decrease of the $T_{50\%}$ value amounted to 20 °C and was achieved in the presence of toluene (Fig. 1b). TCE and TCM contain the same number of both chlorine and hydrogen atoms in the molecule. This finding, as well as the large excess of hydrogen atoms (as compared to chlorine atoms) in all the mixtures tested, suggests that it is the number of chlorine atoms in the molecule, not the chemical structure of CVOCs, that accounts for the ehanced conversion of both CVOCs.

The effect of chlorinated hydrocarbons on VOCs combustion differed from one species to another (Fig. 2a). Practically, neither TCE nor TCM contributed to the combustion of toluene, which oxidized even slightly better in binary mixtures than alone over the fresh catalyst, probably owing to the redispersion of the noble metals in the presence of chlorine and its compounds. Both TCE and TCM exerted a strongly inhibiting effect on the conversion of *n*-hexane, whose $T_{50\%}$ value decreased by 90 and 100 °C, respectively. The remarkable difference in behaviour between toluene and *n*-hexane in mixtures may be attributed to the mechanism governing their oxidation over Pt-Pd. The reaction of TCE and TCM oxidation is likely to run via dissociative chemisorption and their reaction with oxygen atoms chemisorbed at the active centres of Pt and Pd. Dissociation of oxygen onto the active centres resulted in the full coverage of the active sites with atomic oxygen. The first reaction step in the oxidation of CVOCs is abstraction of chlorine atom from the molecule. The excess of hydrogen atoms in the binary mixtures facilitates the reaction with hydrogen atoms yielding HCl, easily desorbed from catalyst surface. In contrast to toluene, which may react directly from the gas phase, the reaction of *n*-hexane oxidation runs preferentially by dissociative chemisorption on the catalyst surface [19]. It is probably the competition of oxygen, CVOCs and *n*-hexane for the same active sites that produces such inhibition of *n*-hexane oxidation.

The presence of TCE and TCM also exerted an inhibiting effect upon the conversion of oxyderivatives. Ninety percent conversion of ethanol was achieved at temperatures with practically no oxidation of TCE or TCM, i.e. at 250 and 300 °C, respectively, in binary mixtures (Fig. 2b). Over a fresh catalyst, $T_{90\%}$ equalled 220 °C. During combustion of acetone, $T_{50\%}$ increased by 10 and 25 °C in the mixture with TCM and TCE, respectively, while $T_{90\%}$ increased by 70 °C in both mixtures. Our previous studies [12,13] have shown that CVOCs had a noticeable effect on the selectivity of the reaction of oxyderivatives oxidation. With ethanol, the selectivity of the reaction to AA was similar to that of ethanol combusted both in binary mixtures and alone, but there was a shift to higher reaction temperatures by ca. 35 °C. In the mixtures, it was only at 450 °C that no aldehyde was detected in the reaction gas (Fig. 2b). During combustion of acetone in binary mixtures, the AA concentrations detected were higher than when acetone was combusted alone, and amounted to a maximum of 35 ppm at 350 °C and 15 ppm at 300 °C with TCM and TCE, respectively (Fig. 2c). With higher reaction temperatures, the concentration of AA systematically decreased and at 400 and 450 °C in the mixture with TCM and TCE, respectively, aldehyde was not detected in the reaction gas.

The test of toluene oxidation after ca. 100 h of exposure to TCE and TCM showed no deactivation of the catalyst, and toluene conversion was similar to that observed in binary mixtures, i.e. slightly higher than over a fresh catalyst. The high chemical resistance of the noble metal catalyst to chlorine compounds has been reported by Corella et al. [20]. The deactivation of some Pt-based catalysts should be sttributed in their opinion, to the alumina support.

4. Conclusions

The Pt-Pd-based catalyst on a monolithic, metallic, γ-Al_2O_3-washcoated support shows high activity in the oxidation of selected hydrocarbons and oxyderivatives. The chlorinated compounds used in this study (TCE and TCM) required higher oxidation temperatures than did VOCs. At the highest reaction temperature, 450 °C, the conversion of TCM and TCE amounted to 84 and 68%, respectively.

In binary mixtures, each of the non-chlorinated VOCs added enhances the conversion of chlororganic compounds, lowering the temperature of 50% conversion maximally by 20 °C in the presence of *n*-hexane for TCM and as much as by 50 °C in the presence of acetone for TCE.

The presence of TCE and TCM has no significant effect on the combustion of toluene, though it evidently inhibits the oxidation of *n*-hexane and, to a smaller extent, of the oxyderivatives. In binary mixtures with CVOCs, there is a rise of the concentration of acetaldehyde, an intermediate of their oxidation.

The test of toluene oxidation carried out after all tests with TCE and TCM has revealed no deactivation of the catalyst and has confirmed its high chemical resistance.

The study reported on in this paper, as well as some of our previous investigations into the oxidation of mixtures, has substantiated the need for a careful choice of the catalyst to be used. It is therefore of cruciual importance, as well as highly recommended that the choice should include the specific mixture effect depending on the composition of the industrial waste gas.

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