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# Oxidation of chlorinated hydrocarbons over Pt–Pd-based catalyst Part 1. Chlorinated methanes

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**Abstract**

The activity of Pt–Pd-based catalyst manufactured on a monolithic metallic support was tested in the oxidation of selected chlorinated hydrocarbons. Chlorinated methanes were found to be the most catalytically reactive compounds. To find out the parameter conclusively influencing the ability of catalytic destruction of oxidized compounds, the atomic excitation energy, as well as the dissociation energies of C–Cl and C–H bonds in oxidized molecules, was calculated. The catalytic reactivity of chlorinated methanes increased with the decreasing energy for the C–Cl bond, and the decreasing number of C–H bonds in the molecule. $CO_2$ and HCl were detected in the flue gases as the main reaction products. Some amounts of CO and $Cl_2$ were found in the reaction gas, but the reaction selectivity to those products generally did not exceed 2%.


*Keywords:* Air pollution control; Oxidation; Catalytic reactivity

## 1. Introduction

Chlorinated volatile organic compounds (CVOCs) are widely used in industry as solvents, dry-cleaning agents, degreasing agents, and intermediates in the production of plastics, synthetic resins or pharmaceuticals. Emitted to the atmosphere, they constitute a very important environmental problem. According to EPA Report "Clean Air Act" (1990), 19 chlorinated hydrocarbons have been classified as dangerous and toxic compounds.

Catalytic oxidation seems to be an economical and efficient way of CVOCs destruction. The catalyst applied in such process should be not only of high activity, but also of high resistance to deactivation by chlorine and its compounds. The desired reaction products are $CO_2$, water and HCl, easy to remove from the effluents e.g. by scrubbing with water or caustic.

The catalytic reactivity of chlorinated hydrocarbons, as well as the distribution of the reaction products, depends strongly on the catalyst used and the chemical structure of the oxidized compounds. The differences in the catalytic reactivity of chlorinated methanes can be explained by the different dissociation energies in the C–Cl bonds [1]. Chintawar and Greene have found the correlation between the catalytic reactivity of chlorinated ethylenes and their adsorption capacities. They have concluded that the adsorption capacity was lower for compounds containing a larger number of chlorine atoms in the molecule [2]. Studies performed by Windawi and Wyatt showed that the oxidation reaction rate was influenced not only by the number of chlorine atoms in the molecule, the C–Cl ratio and the strength of the C–Cl bond, but first of all by the strength of the C–H bonds in the molecule [3].

Two main groups of catalysts are intensively tested in CVOCs oxidation—supported noble metal catalysts, based on Pt or Pd, with a minimum noble metal content of 0.3 wt.%, and metal oxides such as chromium, vanadium, manganese or cobalt oxides [4–8]. Among the metal oxides, perovskite-based catalysts seem to be the most interesting, in terms of their high activity as well as their high thermal and chemical resistance, in the process of total oxidation of organic air pollutants, including chlorinated hydrocarbons [9,10]. Monolithic catalysts, because of their evident technical advantage over granular catalysts (e.g. low drop pressure, uniform cross-flow of gases, easier contact of reagents with active sites) have been readily applied to the control of industrial waste gases. Normally, a thin-wall cordierite or metallic foil is used as a support for those cat-

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alysts. At the Wroclaw University of Technology, a method for the manufacture of catalysts on monolithic metallic supports from foiled heat-resisting steel with additives has been developed. Metallic monolithic catalysts with a low platinum content (0.05–0.15 wt.%) show a high activity in the oxidation of typical VOCs. They were tested also in the oxidation of chlorinated compounds [11,12].

The aim of the present study was to find out which property of the oxidized compound—the number of chlorine atoms in a molecule, the molecular mass, the dissociation energy of the C–H and C–Cl bonds, the excitation energy of a molecule—conclusively influenced the reactivity of the oxidized compound over the selected catalyst. In a preliminary study, a number of catalysts based on platinum alone and on a bimetallic system (Pt–Pd, Pt–Rh, Pt–Ce) with a granular $\gamma$-$Al_2O_3$ support have been manufactured and tested in the oxidation of selected chlorinated hydrocarbons—chlorobenzene, dichloroethane and trichlorethylene. The Pt–Pd-based catalyst showed the highest activity in the destruction of each compound under investigation; moreover, no deactivation of this catalyst was found in the tests of toluene oxidation over a fresh and used catalyst [13]. Making use of those results, a Pt–Pd catalyst on a monolithic metallic support was manufactured and tested in the oxidation of selected groups of CVOCs differing in chemical structure. The distribution of the reaction products was intensively studied as well. The tests of catalytic oxidation were performed for the following groups of CVOCs:

- C1 chlorinated hydrocarbons (dichloromethane, trichloromethane, and tetrachloromethane);
- C2 chlorinated hydrocarbons (1,2-dichloroethane, 1,1,2,2-tetrachloroethane, trichloroethene, tetrachloroethene); and
- chlorobenzenes (chlorobenzene, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene).

This paper presents the first part of the study—catalytic oxidation of chlorinated methanes.

## 2. Experimental

To prepare the Pt–Pd-based catalyst, a monolithic metallic support made from heat-resisting alumel steel with additives, was thermally pretreated, etched in an acids solution, and thereafter coated with $\gamma$-$Al_2O_3$ with the admixture of rare earth elements, first of all lanthanum and cerium, which are known to improve the thermal properties of a catalyst. After drying and calcination, the washcoat content amounted to 2.5 wt.%. The support was impregnated in the solution of chloroplatinic acid and palladium chloride, successively. After drying and calcination, the noble metal content reached 0.2 and 0.1 wt.% for platinum and palladium, respectively. A short description of the catalyst is presented below:

| | |
|---|---|
| Shape of cells | Triangle |
| Cell density | 240/cm$^2$ |
| Cell dimension | 0.9 mm |
| Wall thickness | 0.05 mm |
| Open surface area | 80% |
| Dimension of catalyst block | $h = 70$ mm, $\phi = 21$ mm |

The tests were carried out in a typical, electrically heated cross-flow glass reactor of “tube-in-tube” type. The reaction temperature, measured with a thermocouple inside the catalyst block, ranged from 250 to 500 °C. The vapors of the oxidized compound were generated in a glass doser by evaporation and mixed with air to the desired concentration of 1 g/m$^3$ (equivalent to 267 ppm of $CH_2Cl_2$, 188 ppm of $CHCl_3$ and 145 ppm of $CCl_4$). Gas hourly space velocity amounted to 10 000 h$^{-1}$. Catalyst activity was estimated in terms of conversion of oxidized compound measured on the basis of inlet and outlet concentrations.

The desired reaction products of chlorinated hydrocarbons oxidation are $CO_2$ and $H_2O$, as well as HCl as the only chlorinated product. In some cases, the reaction may yield other chlorinated organic species, chlorine or carbon monoxide, a typical product of incomplete oxidation. The concentrations of oxidized compounds and potential organic intermediates were analyzed using a GCHF 18.3 gas-chromatograph with FID and 1.8 m/2.7 mm column packed with 10% Carbowax 20,4-TPA. The temperature of the column was 100 °C, that of the injector and detector amounting to 250 °C. HCl concentration was measured by ion-chromatography, using a Shimadzu HIC-6 equipped with an anion-exchange column. Chlorine concentration was determined with a colorimetric method by absorption of $Cl_2$ from the separate stream of the effluent in 0.0125N NaOH solution; analyses were carried out using *o*-toluidine. Both carbon oxides were analyzed by the non-dispersive infrared method (NDIR) with a Horiba PG 250 Analyzer, the typical apparatus for the analysis of industrial and automotive waste gases.

## 3. Results and discussion

The results of oxidation of the selected chloromethanes dichloromethane (DCM), trichloromethane (TCM) and tetrachloromethane (carbon tetrachloride, CTC), as well as the results of toluene oxidation over a fresh catalyst, are shown in Fig. 1.

The catalyst was very active in toluene oxidation, accounting for a conversion over 90% even at 250 °C. Chlorinated methanes were more difficult to oxidize and their catalytic reactivity decreased in the following order: CTC > TCM > DCM.

CTC was found to be the most reactive compound; its 50 and 90% conversion was obtained at 275 and 410 °C, respectively. The temperature of TCM oxidation with 50% efficiency was by 40° higher than that for CTC. At the re-

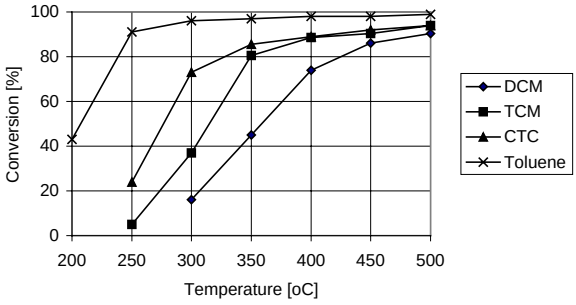



Fig. 1. Activity of Pt–Pd-based monolithic catalyst in the oxidation of toluene and selected chloromethanes: gas space velocity, 10 000 $h^{-1}$; concentration of reagents, 1 $g/m^3$ (243 ppm of toluene, 267 ppm of $CH_2Cl_2$, 188 ppm of $CHCl_3$ and 145 ppm of $CCl_4$).

action temperatures between 400 and 500 °C, conversion of TCM and CTC was nearly the same and reached 89 and 94% at 400 and 500 °C, respectively. DCM, the least reactive C1 compound, required temperatures of 360 and 500 °C for 50 and 90% conversion, respectively. A similar order of the catalytic reactivity of chloromethanes, not only in the process of oxidation, but also in the catalytic hydrodechlorination, has already been reported [1,14].

The catalytic reactivity of the oxidized chloromethanes increased with the increasing number of chlorine atoms in the molecule, as well as with the increase of the molar mass, boiling temperature and density of the oxidized compounds. It may suggested, that the catalytic reactivity depends probably on the C–Cl bonds. For this reason, the energy of atomic excitation, and the dissociation energies for the C–Cl and C–H bonds in the molecule of chlorinated methanes were compared. The energies of atomic excitation have been calculated with the configuration interaction with single substitution (CIS) method [15]. The values of the most probable excitation energy $\Delta E_{max}$, the lowest energy of excitation $\Delta E_{min}$ (i.e. the maximum value of oscillation), and the dissociation energy of the C–Cl and C–H bonds are listed in Table 1.

Generally, the minimum excitation energy values are similar for each investigated compound. The minimum values of both excitation energies were found for CTC, the most catalytically reactive compound. For TCM and DCM, no consistency was found between the values of the excitation energies and the reactivity of the compounds. The results show that these energies are not the determining step in the overall reaction rate.

Greater differences were found in the values of dissociation energy between the C–Cl and C–H bonds. Generally, the dissociation energies for the C–Cl bonds are lower than those for the C–H bonds, and probably they influence the total oxidation rate of chloromethanes. The values of C–Cl bond energy decreased with increasing number of chlorine atoms in the molecule, and with the increase in catalytic reactivity. With the most reactive CTC, the dissociation energy for the C–Cl bond was by 32.6 and 44.3 kJ/mol lower than that for TCM and DCM, respectively. Lower dissociation energies for the C–Cl than the C–H bonds, as well as the consistency between the dissociation energies for the C–Cl bonds and the ability to catalytic destruction suggest that the first reaction step, which is also the rate determining step, includes the dissociative chemisorption of the oxidized compound on the active sites of the catalyst, followed by the rupture of the C–Cl bond and the abstraction of chlorine atoms.

The dissociation energies for the C–H bonds of DCM and TCM are nearly twice as high as those for the C–Cl bonds. This suggests that the catalytic reactivity is greater for the compounds with a lower number of C–H bonds. The results obtained confirmed this assumption; the most reactive compound, CTC, has no C–H bond in the molecule; on the other hand the most resistant compound to oxidation is DCM with two C–H bonds. Considering the process of catalytic destruction of chloromethane, Hung et al. have found, that over manganese oxides, chloromethane was oxidized easier than methane, in spite of a similar strength energy of the C–H bonds in both compounds. They have concluded that the first reaction step was the abstraction of chlorine atom, because of the lower strength energy of the C–Cl bond (351 kJ/mol), compared with the strength of the C–H bond in the $CH_3Cl$ molecule (422 kJ/mol), which is very close to the C–H bond dissociation energy (434 kJ/mol) of the first hydrogen removed from methane [16]. Ordonez et al. have concluded that after chlorine abstraction, the behavior of the resulting radicals is different. $CCl_3^{\bullet}$ and $CCl_2H^{\bullet}$ formed by chlorine atom abstraction from $CCl_4$ and $CH_2Cl_2$ molecules, respectively, are very stable with free enthalpy $\Delta G^{\circ} = -9$ kJ/mol, whereas the $CH_2Cl^{\bullet}$ radical formed from DCM is unstable ($\Delta G^{\circ} = 44$ kJ/mol). Such different thermodynamical properties influenced the reaction pathway of the oxidized compounds [1].

A different mechanism of the catalytic oxidation of selected chlorinated methanes can be concluded from the anal-

Table 1
Values of atomic excitation energies, bond dissociation energies for C–Cl and C–H bonds and ignition temperatures (50% conversion) for oxidized compounds

| Compound | $T_{50\%}$ (°C) | $\Delta E_{max}$ (kJ/mol) | $\Delta E_{min}$ (kJ/mol) | $\Delta E_{C-Cl}$ (kJ/mol) | $\Delta E_{C-H}$ (kJ/mol) |
|---|---|---|---|---|---|
| $CCl_4$ | 275 | 774.19 | 774.19 | 305.9 ± 7.5[a] (305)[b] | – |
| $CHCl_3$ | 315 | 923.92 | 774.18 | 338.5 ± 4.2[a] (325)[b] | 392.5 ± 2.5 |
| $CH_2Cl_2$ | 360 | 875.52 | 778.43 | 350.2 ± 0.8[a] (339)[b] | 402.5 ± 2.7 |

[a] Ref. [22].
[b] Ref. [1].

Table 2
Concentration ($C_{Cl_2}$) of $Cl_2$ in the reaction gas and reaction selectivity ($S_{Cl_2}$) to $Cl_2$

| Temperature (°C) | $CH_2Cl_2$ | | $CHCl_3$ | | $CCl_4$ | |
|---|---|---|---|---|---|---|
| | $C_{Cl_2}$ (ppm) | $S_{Cl_2}$ (%) | $C_{Cl_2}$ (ppm) | $S_{Cl_2}$ (%) | $C_{Cl_2}$ (ppm) | $S_{Cl_2}$ (%) |
| 500 | 1.1 | 0.5 | 2.3 | 0.9 | 4.95 | 1.8 |
| 450 | 1.0 | 0.4 | 1.67 | 0.7 | 4.3 | 1.6 |
| 400 | 0.66 | 0.3 | 1.42 | 0.6 | 3.47 | 1.3 |
| 350 | 0 | 0 | 0.35 | 0.2 | 1.23 | 0.5 |
| 300 | 0 | 0 | 0 | 0 | 0.16 | 0.1 |
| 250 | – | – | 0 | 0 | 0 | 0 |

Table 3
Concentration ($C_{CO}$) of CO in the reaction gas and reaction selectivity ($S_{CO}$) to CO

| Temperature (°C) | $CH_2Cl_2$ | | $CHCl_3$ | | $CCl_4$ | |
|---|---|---|---|---|---|---|
| | $C_{CO}$ (ppm) | $S_{CO}$ (%) | $C_{CO}$ (ppm) | $S_{CO}$ (%) | $C_{CO}$ (ppm) | $S_{CO}$ (%) |
| 500 | 0.655 | 0.1 | 0.9 | 0.5 | 0 | 0 |
| 450 | 1.64 | 0.4 | 1.39 | 0.8 | 0.24 | 0.2 |
| 400 | 1.03 | 0.3 | 2.215 | 1.3 | 0.3 | 0.2 |
| 350 | 1.2 | 0.6 | 3.74 | 2.4 | 0.6 | 0.5 |
| 300 | 1.4 | 2 | 19.66 | 28.1 | 0.58 | 0.5 |
| 250 | – | – | 4.6 | 51.5 | 0.56 | 1.6 |

ysis of the reaction products distribution. Generally, HCl was found to be the only chlorinated reaction product. No organic non-chlorinated compounds or other organic chlorocarbons were determined in the effluents. Such a high reaction selectivity to HCl was possible to achieve owing to the presence of water vapor in the reaction gas; the reaction mixture was prepared by the addition of oxidized compound vapors to the ambient air. It was particularly important, when compounds with a H/Cl ratio lower than 1, such as TCM or CTC, were oxidized. For those compounds, $Cl_2$ formation may be preferred. The concentrations of the detected chlorine and carbon monoxide, as well as the reaction selectivity to those products, are presented in Tables 2 and 3, respectively. The distribution of all reaction products detected in the process of chlorinated methanes oxidation is shown in Figs. 2–4.

The concentration of both chlorinated products, HCl and $Cl_2$, increased with the raise in reaction temperature. The increasing concentration of HCl resulted from a higher conversion of the oxidized compound. $Cl_2$ was detected

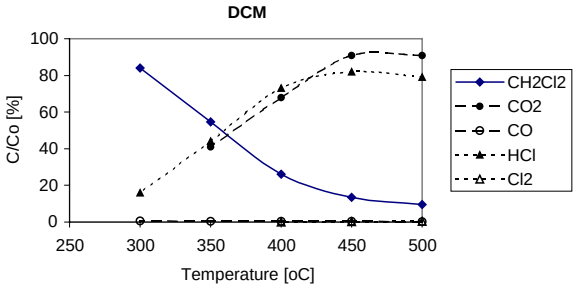



Fig. 2. Distribution of reaction products from the oxidation of DCM.

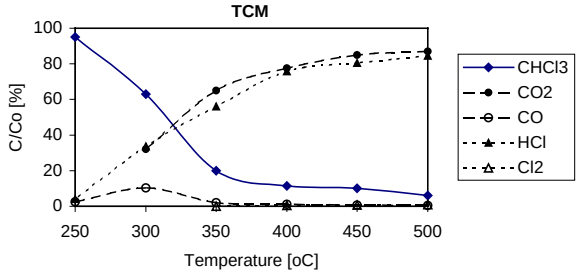



Fig. 3. Distribution of reaction products from the oxidation of TCM.

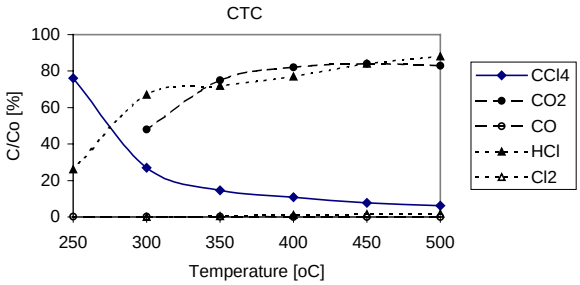



Fig. 4. Distribution of reaction products from the oxidation of CTC.

in the reaction gas for each of the investigated chlorinated methanes. $Cl_2$ concentration and the reaction selectivity to chlorine increased both with the number of chlorine atoms in the molecule (simultaneously, the H/Cl ration decreased in the same order) and with the reaction temperature. This latter may be explained by the greater probability of HCl oxidation, resulting from its higher concentration, when compounds with higher number of chlorine atoms in the molecule were oxidized. During CTC oxidation, traces of $Cl_2$ were determined even at 300 °C, but at the highest reaction temperatures the reaction selectivity to $Cl_2$ did not exceed 2%. When TCM and DCM were oxidized, the maximum reaction selectivity to $Cl_2$ occurred at 500 °C and reached 0.9 and 0.5%, respectively. The increasing concentration of chlorine with the raise in reaction temperatures can be explained by the greater probability of HCl oxidation to chlorine according to the Deacon reaction:

$$2HCl + 0.5O_2 \rightleftarrows Cl_2 + H_2O$$

The thermodynamic parameters of this reaction are presented in Table 4 [17]. The increase of chlorine concentra-

Table 4
Thermodynamic parameters of Deacon reaction: enthalpy ($-\Delta H^\circ_R$), free enthalpy ($\Delta G^\circ_R$), reaction rate constant ($K_{eq}$), and HCl production ($\eta_{HCl}$) at selected temperatures

| Temperature (°C) | $-\Delta H^\circ_R$ (kJ/mol) | $\Delta G^\circ_R$ (kJ/mol) | $\log K_{eq}$ | $\eta_{HCl}$ (%) |
|---|---|---|---|---|
| 25 | 57.8 | −38.7 | 6.77 | 99.9 |
| 327 | 56.9 | −18.7 | 1.63 | 85 |
| 627 | 59.5 | 1.5 | −0.08 | 51 |
| 927 | 60.1 | 21.9 | −0.95 | 29 |
| 1227 | 60.6 | 42.4 | −1.48 | 19 |

tion depends also on thermodynamically data, and with the increase of temperature the reaction equilibrium shifted to $Cl_2$ production.

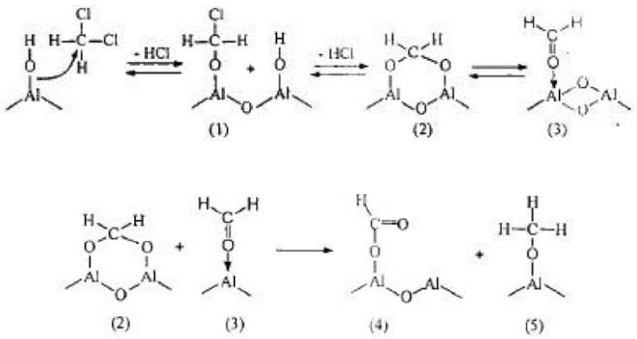
Besides chlorinated reaction products, the concentration of carbon oxides—carbon monoxide and carbon dioxide—was measured in reaction gases. $CO_2$ was found to be the main non-chlorinated reaction product. Carbon monoxide was detected in the effluent gas during oxidation of each compound, particularly at lower reaction temperatures. With the raise in the reaction temperature its concentration decreased, according to the increasing catalyst activity. As the ingredient of the active phase, palladium probably promoted CO yield. Hicks et al. have found that when methane was oxidized over palladium, $CO_2$ as the reaction product dissociated over the catalyst surface, and this dissociation was followed by the dehydrogenation of $CO_2$ according to the following reaction scheme:

$$CO_2 + H_2 \rightleftarrows CO + H_2O$$

At 300 °C, the constant of the reaction rate amounted to 0.026, and according to these authors was sufficient to produce some amounts of CO [18]. Gonzalez-Velasco et al. have found that CO produced as the reaction intermediate during 1,2-dichloroethane oxidation, was easily oxidized in the next reaction step over platinum, and only traces of CO were detected in the off-gas, whereas palladium produced a relatively high amount of CO [19].

The lowest concentrations of CO were detected when CTC was oxidized. Its maximum concentration was measured at 350 °C, and reached 0.6 ppm only. Under these conditions, the reaction selectivity to CO accounted for 0.5%. The highest reaction selectivity to CO (1.6%) was found at 250 °C. Carbon monoxide was detected in the flue gases in experiment reported by Sinquin et al. [14] and Ramachandran et al. [20]. They proposed the reaction pathway via phosgene production, which was consequently oxidized to $CO_2$ and HCl.

Oxidation of DCM yielded higher CO concentration than that of CTC. The maximum concentration was measured at 300 °C and reached 1.4 ppm, which is equivalent to the reaction selectivity of 2%. Van den Brink et al. have proposed the following reaction pathway of DCM oxidation over $\gamma$-$Al_2O_3$, in which carbon monoxide can be produced [21]:



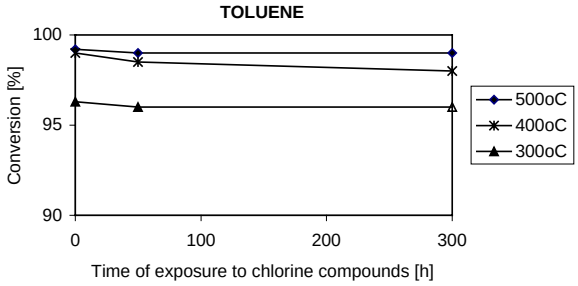




Fig. 5. Toluene conversion at 300, 400 and 500 °C over fresh catalyst and after tests with chlorinated hydrocarbons.

Over the investigated Pt–Pd-based catalyst with a $\gamma$-$Al_2O_3$ washcoat, such reaction mechanism should be taken into account.

The highest amounts of CO were found when TCM was oxidized. At 250 and 300 °C, the concentration of CO reached nearly 5 and 20 ppm, respectively, which is equivalent to 51 and 28% of the reaction selectivity. Such great amounts of CO can be attributed to the reaction pathway proposed by Sinquin et al. [14]:

$$CHCl_3 \rightarrow CHCl_2^+ + Cl^-$$

$$CHCl_2^+ + OH^- \rightarrow HO\text{–}CHCl_2 \rightarrow ClHC{=}O + HCl$$

$$ClHC{=}O \rightarrow CO + HCl$$

The Pt–Pd catalyst manufactured for the purpose of this study had comparatively small quantities of the active metals, 0.2 wt.% of platinum and 0.1 wt.% of palladium, deposited on the $\gamma$-$Al_2O_3$ washcoat. Probably, some part of the catalyst surface remained uncovered with the active ingredients and thus made available to the reactants. That is why the most probable way of CO yielding was the incomplete oxidation of chloromethanes over $\gamma$-$Al_2O_3$. On the other hand, carbon monoxide production could have been promoted by palladium. It is also possible that the reaction of chloromethanes oxidation could have run via a series of consecutive reactions, yielding different intermediates not detected in the flue gas, particularly at lower reaction temperatures.

To determine potential catalyst deactivation, the test of toluene oxidation was performed after each test of chlorinated compound oxidation. The results of toluene oxidation at 300, 400 and 500 °C over a fresh catalyst, after chloromethanes destruction (ca. 50 h of exposure to chlorine compounds) and after all tests with chlorinated hydrocarbons are presented in Fig. 5. After ca. 300 h of exposure to chlorinated compounds, the conversion of toluene did not change, and no deactivation of the catalyst was observed.

## 4. Conclusions

The Pt–Pd-based catalyst on the metallic monolithic support showed a high activity in the oxidation of chlorinated

methanes. Their catalytic reactivity increased with the increasing number of the chlorine atoms and the decreasing number of the C–H bonds in the molecule. There was no agreement between the catalytic reactivity of each oxidized compound and the calculated values of atomic excitation energies.

The bond dissociation energies have lower values for C–Cl than for C–H bonds in each compound under investigation. The dissociation energy of the C–Cl bonds decreased with the number of the Cl atoms in the molecule of chlorinated methane. The results suggest that the first reaction step is the rupture of the C–Cl bond and the abstraction of the chlorine atom from the molecule, and this means that the catalytic reactivity should be greater for the compounds with a lower number of C–H bonds.

$CO_2$ and HCl were found to be the main reaction products. No other chlorinated organic compounds were detected in the effluents. Some amounts of $Cl_2$ and CO were found in the reaction gas, but the reaction selectivity to such products did not exceed 2%. During TCM oxidation only, the selectivity to CO at lower reaction temperatures, 300 and 250 °C, reached 28 and 51.5%, respectively. The concentration of $Cl_2$ increased with the decrease in the H:Cl ratio in the oxidized molecule and was the highest for $CCl_4$. Probably, $Cl_2$ yielding can be inhibited in the presence of additional hydrogen donors, such as water or non-chlorinated VOCs, in the reaction feed.

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