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ToF-SIMS studies of the regeneration of Pd/TiO_2 catalyst used in hydrodechlorination process

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ABSTRACT

This paper is devoted to the surface studies of deactivation-regeneration process of Pd/TiO_2 catalyst used in the hydrodechlorination of CCl_4. The samples were prepared by the incipient wetness impregnation method. The time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used as a main analytical tool in these investigations. The advantages of this technique result from high sensitivity of secondary ion mass spectrometers, possibility of detection of not only elemental but also molecular ions and the fact that ToF-SIMS can give information from the upper layer of the investigated material. The results of ToF-SIMS measurements of as prepared, deactivated and regenerated specimens showed that the regeneration of the deactivated sample in the O_2 atmosphere among other causes an increase in the ability of the catalyst to the formation of palladium chloride in the next working cycles. A growth in the amount of $PdCl_2$ was accompanied by a decrease in the quantity of surface accessible palladium atoms. It resulted in a more violent drop in the conversion of CCl_4 and faster deactivation of the regenerated catalyst. The observations described above indicate that not only carbon deposition and deterioration of the surface area of the catalyst are serious problems in the hydrodechlorination process. The bigger attention should also be focused on the prevention of the formation of palladium chloride in the next working cycles of the catalyst after its regeneration.

1. Introduction

It is generally known that the presence of chlorinated organic compounds in the atmosphere exerts an undesirable influence on the environment (i.e., stratospheric ozone depletion, global warming, and human health effects). Therefore, it is important to find effective technologies leading to the reduction of their emission in different industrial processes [1,2]. One of the most promising methods of the elimination of the above mentioned substances is catalytic hydrodechlorination [3–5], which makes it possible to convert toxic chlorides into the corresponding hydrocarbon molecules without producing other undesirable chemical compounds such as dioxins [6,7]. The literature data indicates that palladium catalyst is the most active in this reaction [8]. However, it undergoes relatively fast deactivation. The earlier studies demonstrate that the main reasons for catalyst deactivation in hydrodechlorination process are the formation of carbon deposit, sintering of palladium and a considerable drop in the surface area among others [9–11]. Nevertheless, the processes of chlorine adsorption and formation of Pd–Cl bonds on the catalyst surface also influence an efficiency of the reaction and should be taken into consideration [12]. Therefore, it was decided to apply time-of-flight secondary ion mass spectrometry (ToF-SIMS), which creates new potentialities in this kind of measurements in comparison with the convectional methods of catalyst investigation (i.e., X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR) or temperature-programmed measurements) [13–17]. ToF-SIMS can be helpful in gaining a deeper knowledge about the modification of the surface of the catalyst during the studied reaction and undertaking an attempt to work out an effective method of its regeneration. In spite of the fact that ToF-SIMS is generally applied in the study of biological samples, polymers and materials used in electronic industry, it can also be very useful in the characterization of heterogeneous catalysts [18–24]. The main advantages of this technique result from high sensitivity of secondary ion mass spectrometers, possibility of detection of not only elemental but also molecular ions and the fact that ToF-SIMS can give information from the upper layer of the investigated material [25,26]. Owing to that, data concerning the formation of new compounds and changes in the amount of various contaminants and poisons on the catalyst surface during the catalytic processes can be obtained.

ToF-SIMS experiments consist in the bombardment of the surface of the sample fixed to the sample holder by short pulses of

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primary ions (i.e., Ga^+, $O_2{}^+$, Ar^+, Cs^+, $Bi_x{}^+$, $Au_x{}^+$, $C_{60}{}^+$). These ions interact with the investigated material. They penetrate the surface of the analyzed sample and transfer kinetic energy to the atoms of the measured solid in a succession of individual collisions. It results in the disruption of the chemical bonds and the emission of the surface particles from the studied material. These particles originate almost entirely from the uppermost layer of the molecules or atoms of the analyzed sample. Only the ionized species are used in the further part of the measurements. The arising secondary ions are directed to the mass analyzer, where they are accelerated to a given kinetic energy and mass-analyzed on the basis of the measurement of flight-time needed by the investigated ions to reach the detector. The quality of the obtained results depends on the kind of the primary ion gun, energy of the primary ions, time of the measurement (ion dose) and composition of the sample among others. It is generally known that this method causes the destruction of the analyzed material. Therefore, in order to obtain molecular information from the investigated surface, the measurements in the "static" mode are usually performed. It means that not more than 1% of the surface atoms are removed in the single ToF-SIMS experiment by primary ion beam. More details concerning ToF-SIMS principles can be found in Refs. [27–29]. It appears that this kind of analysis also causes several difficulties in the interpretation of the obtained results connected with the matrix effect, fragmentation reactions and quantification problems. It should be mentioned that the mass resolution of collected secondary ion mass spectra depends also on the topography of the sample surface. These phenomena hinder obtaining valuable information from the surface of the investigated catalysts and make it necessary to normalize the spectra after ToF-SIMS experiment and use special standards in order to achieve quantitative data from the analyzed samples. However, in spite of that in many cases it is impossible to compare the results obtained for the materials which differ considerably in the chemical composition.

The aim of this work is to determine changes of the surface properties of Pd/TiO_2 catalyst during the regeneration process after its deactivation in hydrodechlorination of CCl_4. In order to do that the investigations of as prepared, deactivated and regenerated samples were performed. The TiO_2 carrier was chosen for palladium catalyst on the basis of earlier studies [30,31] demonstrating that such a system possesses the best stability among the investigated materials (Al_2O_3, ZrO_2, SiO_2, CeO_2, MgO and their combinations) and works the longest time maintaining high activity. As it was mentioned earlier this paper is focused on the study of the process of chlorine adsorption and formation of palladium chloride on the catalyst surface, which is considered to be one of the reasons for the deactivation of the catalyst in the hydrodechlorination reaction. The time-of-flight secondary ion mass spectrometry was used as a main analytical tool in these investigations.

2. Experimental

2.1. Samples preparation

2%, 3% and 5%Pd/TiO_2 catalysts were prepared by the incipient wetness impregnation method. $PdCl_2$ (POCh Gliwice) was introduced onto TiO_2 (P-25, Degussa). Samples were aging for 48 h at room temperature. After evaporation of water, the support was dried under atmospheric pressure at 110 °C for 2 h. Then, the sample was calcined in the flow of O_2 at 500 °C for 4 h and reduced in the flow of H_2 under the same conditions. The metal content was confirmed by an inductively coupled plasma emission spectroscopy (ICP-AES)—obtained data showed that in all cases the amount of introduced palladium did not differ more than 15% from the theoretical value. The surface areas of the catalysts were established by a nitrogen adsorption method.

2.2. Instrumental

The amount of carbon deposited on the surface of the investigated catalysts was measured by an automatic carbon analyzer TOC 5000 (Shimadzu) equipped with a solid sample module (mass of the samples varied in the range of 10–100 mg).

The ToF-SIMS measurements were performed using an ION-TOF GmbH instrument (TOF-SIMS IV) equipped with 25 kV pulsed Bi^+ primary ion gun in the static mode (primary ion dose about 10^{11} ion/cm^2). The analyzed area corresponds to a square of $500\,\mu m \times 500\,\mu m$. For each sample three spectra from different surface areas were made. The samples were pressed into the pellets and attached to the sample holder using a double-sided tape. A pulsed electron flood gun was used for charge compensation. In order to compare the quantity of chlorine and palladium present on the surface of investigated catalysts, the number of counts of selected ions obtained from the collected mass spectra was normalized on the basis of the value of total counts.

The thermal gravimetric experiments connected with mass spectrometry analysis (TG–MS) were carried out applying a sample of 5–50 mg with a linear growth of temperature 1–10 °C and temperature range from 25 °C to 800 °C (flow rate of 5%O_2–95%Ar gas mixture–40 cm^3/min). The analysis was conducted using mass spectrometer – Thermostar (Balzers) connected on-line with thermal analyzer – SETSYS-16/18 (Setaram).

The activity tests were performed under atmospheric pressure at 100 °C. The reactant mixture CCl_4/H_2 (1:10) was passed through a flow reactor with a rate of 40 cm^3/min. The load of the catalyst bed was 0.2 g. The analysis of the reaction products was conducted using a gas chromatograph – Chrom 5 – equipped with 15%OV-17/1, 95%OV-210/CWHP 80/100 column and flame ionization detector (FID) (column temperature 50 °C, detector temperature 160 °C). The regeneration of the totally deactivated catalysts was carried out in a flow reactor at 500 °C for 1 h using 5%O_2–95%Ar gas mixture (flow rate—40 cm^3/min). After that the analyzed samples were reduced in the flow of H_2 at 500 °C for 4 h.

3. Results and discussion

It is generally known that palladium catalysts used in the hydrodechlorination process undergo relatively fast deactivation. The earlier studies [30,31] of the activity of such systems revealed that Pd/TiO_2 prepared with using $PdCl_2$ as a precursor was the most stable catalyst in the hydrodechlorination of carbon tetrachloride among the investigated materials. Nevertheless, in spite of the optimization of the treatment and working conditions of Pd/TiO_2 catalyst its activity decreased during the reaction. Within the first 24 h the conversion of CCl_4 on 2%Pd/TiO_2 dropped from almost 100% to about 85%. In the next 4 days a mild fall in the conversion of CCl_4 was observed after which its drop became more evident. The reaction was stopped after 240 h when the conversion of CCl_4 decreased to about 20%. The main product of this reaction was methane. The formation of CH_4 was facilitated by the presence of a bigger amount of H_2, a relatively low reaction temperature and the presence of metallic phase of palladium. The investigation of the samples containing higher content of palladium did not exhibit any substantial differences in the activity and working time of the studied catalysts, which is in agreement with the results obtained by Golubina et al. [32].

The studies of as prepared and deactivated specimens reveal that some of the reasons for the deactivation of 2%Pd/TiO_2 are a decrease in the surface area of the catalyst and the formation of carbon deposit. The results presented in Table 1 show that in this case the surface area of the catalyst deactivated in the hydrodechlorination of CCl_4 dropped more than 30% in comparison with as prepared

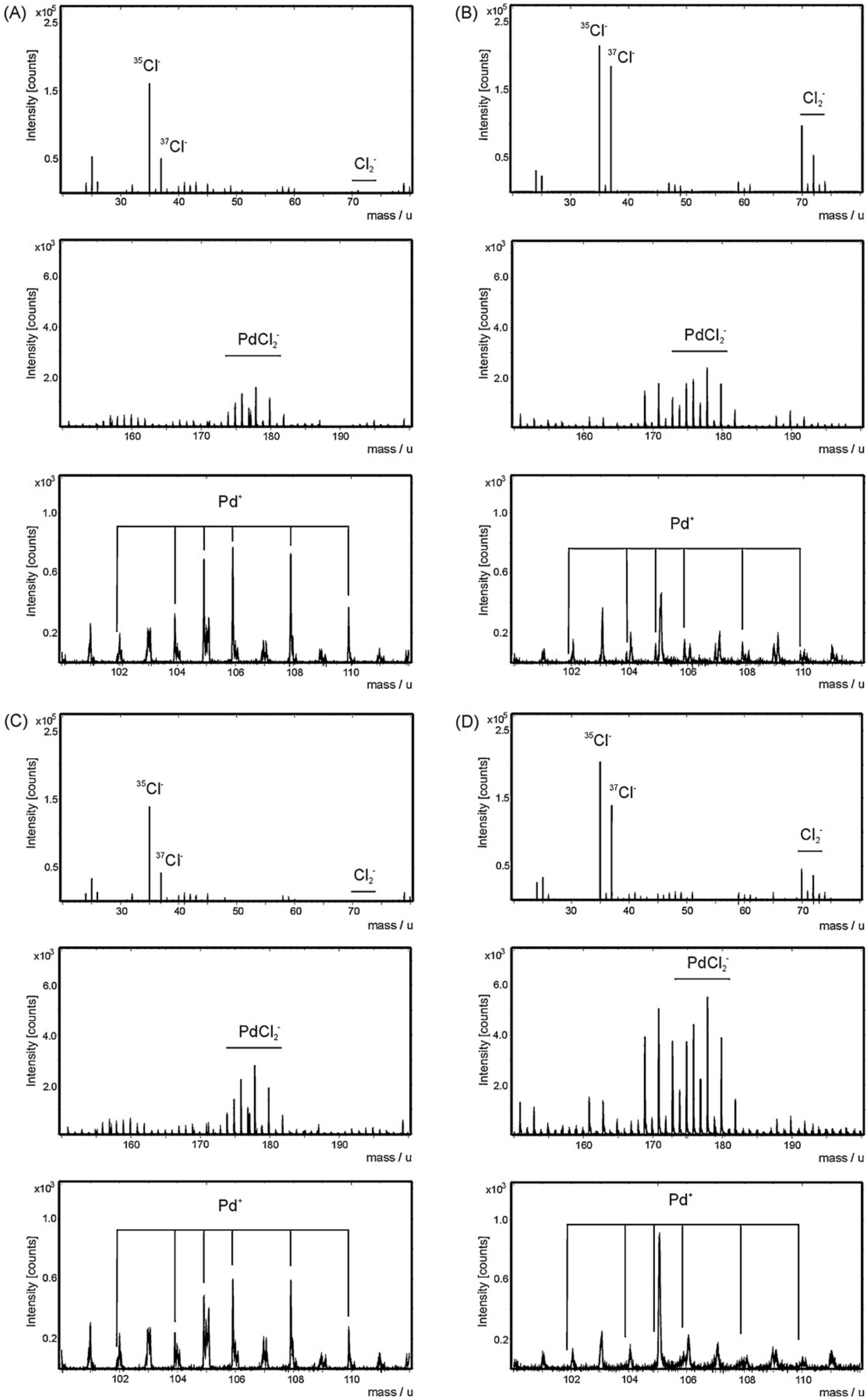

Fig. 1. Secondary ion mass spectra of—A: as prepared, B: deactivated, C: regenerated and D: deactivated again 2%Pd/TiO$_2$ catalyst.

Table 1
Surface area and amount of carbon—2%Pd/TiO_2 catalyst.

2%Pd/TiO_2	As prepared	Deactivated	After regeneration	Deactivated again
Surface area [m^2/g]	43	29	36	26
Carbon amount [%]	0	5.1	0.1	5.0

sample. Simultaneously, the hydrodechlorination process caused deposition of carbon on the catalyst surface (the final amount of C was about 5% of the total mass of the sample). Moreover, ToF-SIMS measurements exhibited an increase in the intensity of signals corresponding to the presence of chlorine species on the surface of the deactivated sample. It confirms an adsorption of chlorine on the catalyst surface during the reaction. ToF-SIMS spectra of the analyzed specimens (Fig. 1) show the presence of not only $^{35}Cl^-$ and $^{37}Cl^-$ but also a series of peaks coming from Cl_2^-, $PdCl_2^-$ and Pd^+ ions. The Cl_2^- ions probably do not exist on the measured surface. They are rather formed in the recombination reaction after excitation of the sample by the beam of primary ions. A probability of the occurrence of such a phenomenon is considerably higher for a deactivated catalyst (with a noticeably bigger amount of adsorbed chlorine), therefore an appreciable increase in the intensity of signals at m/z = 70, 72 and 74 is observed in this case. The presence of signals originating from Cl^- and $PdCl_2^-$ ions on the mass spectrum collected from as prepared sample indicates that the treatment of the catalyst before the hydrodechlorination reaction did not cause a removal of the total amount of palladium precursor from the analyzed surface. It should be remembered that not only adsorbed chlorine but also the fragmentation process of the excited molecules of palladium chloride may be the source of Cl^- ions. The changes in the intensity of signals corresponding to different palladium isotopes also seem to be very interesting. It appears that the hydrodechlorination process causes a considerable decrease in the number of counts of ions originating from palladium. It suggests a drop in the quantity of surface accessible palladium atoms in the case of the deactivated sample caused by the formation of carbon deposit and adsorption of chlorine on the analyzed surface.

The relatively fast deactivation process and the facts described above indicate the necessity of undertaking an attempt to work out the regeneration method of the investigated catalyst. In order to improve the parameters of the regeneration process preliminary studies concerning an optimization of treatment conditions of the deactivated samples were performed. The results of TG–MS measurements revealed that heating of the catalysts in the flow of the gas mixture 5%O_2/95%Ar first of all causes a release of chlorine from the investigated surface and the formation of carbon dioxide as a product of carbon oxidation. This process is accompanied by the removal of water from the analyzed sample. The removal of chlorine (see MS profiles—Fig. 2) proceeds in the range of temperatures between 100 and 200 °C, while the formation of carbon dioxide begins at about 200 °C and finishes at the temperature above 500 °C. However, the maximal rate of the removal of carbon deposit was observed at 410 °C. Therefore, it was decided to carry out a regeneration process at 500 °C maintaining the catalyst at this temperature for 1 h. TG–MS analysis may suggest that the total amount of chlorine and carbon deposits can be removed from the studied surface under the conditions mentioned above. Nevertheless, ToF-SIMS results (Fig. 1, Table 2) indicate that some amount of chlorine and palladium chloride remains on the measured surface. An analysis of the presence of carbon (Table 1) confirmed that it was totally removed from the catalyst in the regeneration process. The regeneration of the catalyst caused an increase in the surface area of deactivated sample, but its size was not as large as in the case of the as prepared material.

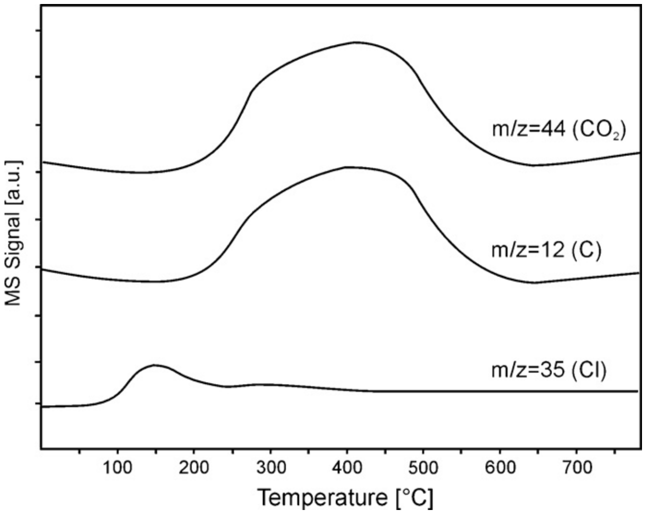

Fig. 2. MS profiles of the gas products emitted in the regeneration process of 2%Pd/TiO_2 catalyst deactivated in the hydrodechlorination of CCl_4.

The subsequent use of the regenerated catalyst in the hydrodechlorination of CCl_4 revealed that owing to the regeneration process it is possible to restore an activity of the catalyst to the same level (the conversion of CCl_4 almost 100%) as in the case of “fresh” material. Unfortunately, the stability of the regenerated catalyst is much worse in comparison with as prepared sample and the conversion of CCl_4 begins to drop a few minutes after the start of the reaction and reaches only a few per cent after about 10 h of the process. Moreover, it appears that the rate of coking of the regenerated material is significantly higher (more than 20 times) than for “fresh” catalyst. In fact, the final mass of deposited carbon is similar in both cases (Table 1), but it should be considered that time of the reaction for the samples mentioned above is substantially different. What are the reasons for such behaviour of the regenerated catalysts? They may be connected with not only widely described deterioration of the surface area of the studied samples, but also with the changes in the surface properties of an active phase connected with its different ability to the adsorption of chlorine or formation of Pd–Cl bounds. The evaluation of this phenomenon can be possible owing to the application of time-of-flight secondary ion mass spectrometry. The results of ToF-SIMS experiments show that chlorine is present on the surface of all analyzed samples (Table 2). The biggest intensity of signals corresponding to Cl^- and Cl_2^- ions was observed in the case of the catalyst after the first deactivation cycle. As it was mentioned earlier the regeneration process of the deactivated sample does not cause a removal of all the amount of the adsorbed chlorine from the studied surface. The investigation of the catalyst deactivated again after the regeneration process demonstrated that during the second deactivation cycle an adsorption of a smaller quantity of chlorine was observed. In spite of that ToF-SIMS results showed in this case the highest

Table 2
Normalized intensity of selected ions (containing the most abundant isotopes—^{35}Cl and ^{106}Pd) calculated on the basis of ToF-SIMS spectra of 2%Pd/TiO_2 catalyst.

2%Pd/TiO_2	As prepared	Deactivated	After regeneration	Deactivated again
Cl^-	3.3×10^{-2}	6.1×10^{-1}	5.6×10^{-2}	1.7×10^{-1}
Cl_2^-	5.0×10^{-4}	1.1×10^{-1}	6.5×10^{-4}	3.1×10^{-2}
$PdCl_2^-$	2.6×10^{-3}	4.3×10^{-3}	2.8×10^{-3}	5.6×10^{-3}
Pd^+	2.4×10^{-3}	9.0×10^{-4}	2.4×10^{-3}	4.9×10^{-4}

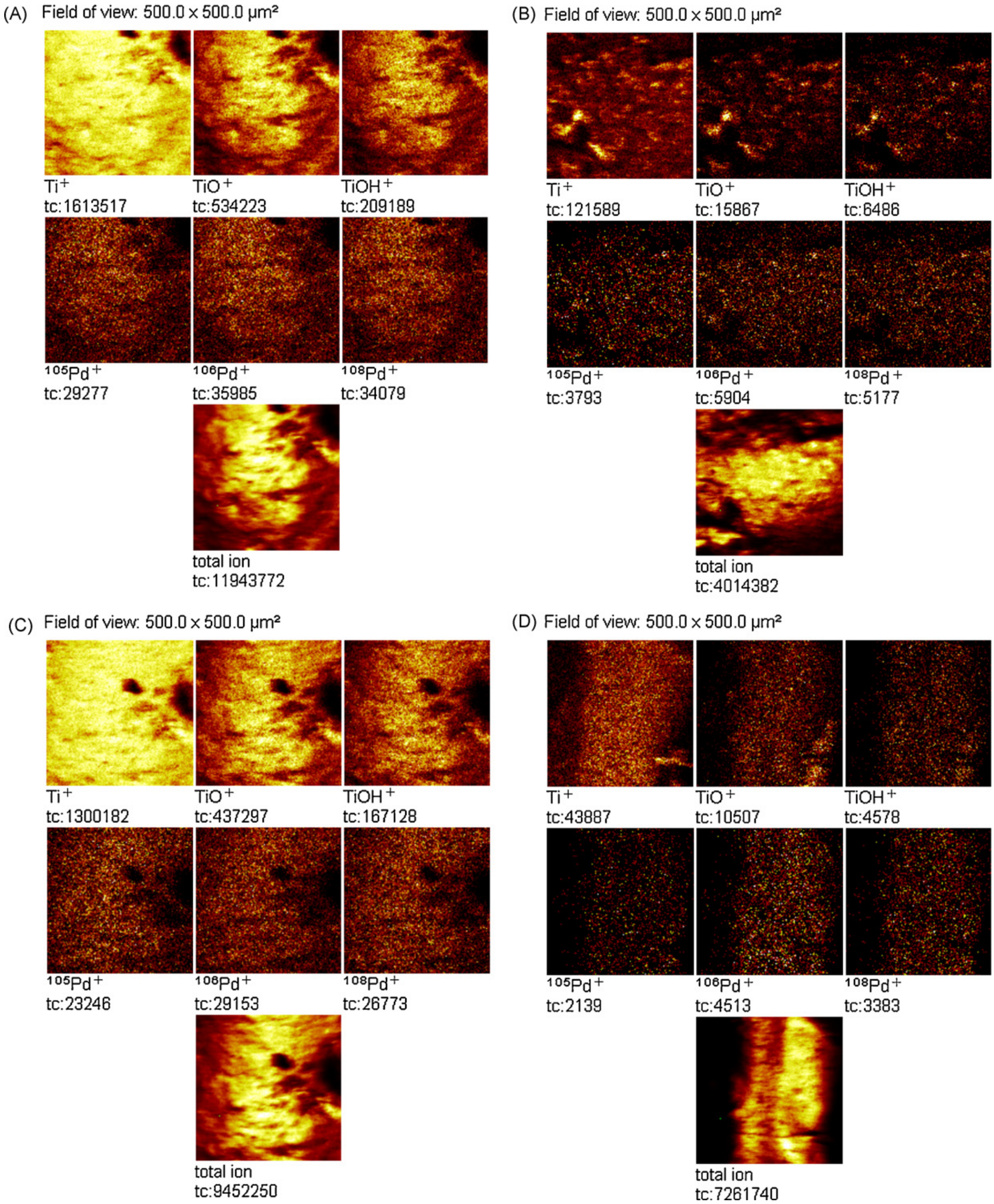

Fig. 3. ToF-SIMS images of—A: as prepared, B: deactivated, C: regenerated and D: deactivated again 2%Pd/TiO_2 catalyst.

increase in the intensity of the signal originating from $PdCl_2^-$ ion among the studied specimens. It means that the regeneration process increases an ability of the active phase to the formation of Pd–Cl bonds. An appearance of a bigger amount of palladium chloride may cause a more violent decrease in the conversion of CCl_4 in the hydrodechlorination process. The same trends were observed for the catalysts with all Pd concentrations.

The results of ToF-SIMS measurements exhibit also changes in the intensity of signals corresponding to the presence of palladium (Table 2). A considerable decrease in the intensity of Pd^+ signal observed on the mass spectrum of deactivated sample in comparison with as prepared catalyst is connected with the drop in the amount of surface accessible palladium atoms caused by the formation of carbon deposit or adsorption of chlorine. An analysis of the mass spectra of the deactivated and regenerated specimens revealed that owing to the regeneration process it is possible to uncover palladium crystallites. This fact is confirmed by the increase in the intensity of Pd^+ signal in the case of the regenerated material to the same level as for the “fresh” sample. However, as it was earlier mentioned, the behaviour of the catalyst in the second reaction cycle is different. The ToF-SIMS results show that the amount of surface accessible palladium atoms decreases considerably faster than in the case of as prepared sample. Moreover, in spite of the substantially shorter time of the deactivation of the catalyst, a decrease in the intensity of Pd^+ signal was twice bigger than for the first working cycle. The reasons for the faster drop in the amount of surface accessible palladium atoms are complex and apart from arising of carbon deposit they may also be connected with higher ability of the catalyst to form palladium chloride and bigger deterioration of surface area. On the other hand ToF-SIMS results prove that palladium is not removed from the catalyst surface in the regeneration step. The intensity of the signal corresponding to the presence of palladium is exactly the same for the as prepared and regenerated samples.

The ToF-SIMS images made for as prepared, deactivated, regenerated and again deactivated samples (Fig. 3) show the differences in the intensity of the signals corresponding to the presence of Pd^+ and ions containing titanium. A lower intensity of the signals mentioned above was observed for both deactivated catalysts, while the same samples were distinguished by the highest emission intensity of ions containing chlorine or carbon (not presented in this work). It confirms covering of the investigated surface by the carbon and chlorine deposited in the hydrodechlorination process.

4. Conclusions

Time-of-flight secondary ion mass spectrometry appears to be a very useful tool in the study of the surface properties of palladium catalyst used in the hydrodechlorination process. Owing to the use of ToF-SIMS the changes in the composition of the surface of Pd/TiO_2 during deactivation and regeneration steps were determined. The results showed that the regeneration of the sample in the O_2 atmosphere makes it possible to remove carbon deposit from the investigated surface but also causes an increase in the ability of the catalyst to form palladium chloride in the next working cycle. A growth in the amount of $PdCl_2$ is accompanied by a decrease in the quantity of surface accessible palladium atoms. It results in a more violent drop in the conversion of CCl_4 and faster deactivation of the regenerated catalyst. The facts mentioned above indicate that not only carbon deposition and deterioration of the surface area of the catalyst are serious problems in the hydrodechlorination process. Therefore, the attention should also be focused on the prevention of the formation of palladium chloride in the next working cycles of the catalyst after its regeneration. Difficulties of the choice of the conditions of the regeneration (i.e., temperature, atmosphere) consist in the necessity of removal of different substances from the catalyst with simultaneous maintaining of other parameters of the studied sample such as the surface area. That is why additional investigations are necessary in order to develop an optimal method of the regeneration of this type of catalysts.

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