

ToF-SIMS studies of the surface of Pd/ZrO₂-TiO₂ catalyst used in the hydrodechlorination process

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Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used in order to obtain the information about the surface composition of Pd/ZrO₂-TiO₂ catalyst and to estimate the changes in the concentration of particular components on its surface during the hydrodechlorination of CCl₄. The results demonstrated that the hydrodechlorination process led to the increase in the concentration of chlorine and the drop in the amount of surface accessible palladium, while the quantity of Pd-Cl bounds did not change considerably. It suggested that the presence of ZrO₂ protected the surface of the studied catalyst against the formation of PdCl₂.

Keywords: ToF-SIMS, palladium, catalysis, hydrodechlorination, ZrO₂, TiO₂.

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INTRODUCTION

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a very useful technique for the investigation of supported catalysts¹. Owing to the utilization of ToF-SIMS additional information about the surface of the studied catalysts can be obtained². One of the most important ToF-SIMS capabilities is the possibility of observing the deactivation process of catalysts. In this case the above mentioned technique makes it possible to trace the changes in the surface composition of investigated catalysts during a catalytic reaction. Owing to that the reasons for catalyst deactivation can be determined.

In this work time-of-flight secondary ion mass spectrometry was used to observe the surface composition of Pd/ZrO₂-TiO₂ catalysts during the hydrodechlorination reaction. The earlier studies³⁻⁴ showed that the deactivation process of palladium catalysts utilized in the hydrodechlorination reaction may be caused by chlorine adsorption on the catalyst surface, the formation of Pd-Cl bounds, a considerable drop in the surface area, deterioration of Pd dispersion, a decrease in the amount of palladium and arising of carbon deposit. The ToF-SIMS measurements confirmed that the hydrodechlorination process led to the increase in the amount of chlorine on the surface of investigated catalysts. Moreover, a decrease in the content of surface accessible palladium and a rise in the quantity of Pd-Cl bounds were observed. It was clearly visible that the intensity of the formation of Pd-Cl bounds on the surface of the studied catalyst depended on the kind of the support used. It appeared that the catalyst composed of Pd and ZrO₂ manifested small susceptibility to the formation of PdCl₂ during the studied reaction. However, its working time was relatively short. Therefore, it was decided to investigate a new system containing not only palladium and zirconium oxide but also titanium oxide.

EXPERIMENTAL

The support was prepared by the impregnation of TiO₂ (Degussa, 50 m²/g, anatase/rutile – 30/70) by aqueous

solution of ZrO(NO₃)₂ (Fluka). The obtained material was aging for 48 h at room temperature. After the evaporation of water, the support was submitted to drying under atmospheric pressure at 110°C for 2 h and calcination in air at 500°C for 4h. In the next step, the support was impregnated with aqueous solution of PdCl₂ (POCH Gliwice). Then, drying and calcination procedures were repeated. This way 2%Pd/20%ZrO₂-TiO₂ (47 m²/g) and 2%Pd/5%ZrO₂-TiO₂ (51 m²/g) catalysts were obtained. They were deactivated in the hydrodechlorination of CCl₄, which was carried out at 100°C using CCl₄/H₂ (1:10) as a reactant mixture. Before the reaction the above mentioned catalysts were reduced in the flow of hydrogen at 500°C for 4h.

ToF-SIMS measurements were performed using an ION-TOF GmbH instrument (TOF-SIMS IV) equipped with 25 kV pulsed ⁶⁹Ga⁺ primary ion gun in the static mode (primary ion dose did not exceed 3.0 x10¹¹ ions/cm²). The powder catalysts were tableted before the measurements. The secondary ion mass spectra were collected from the area corresponding to a square of 500 μm x 500 μm. A pulsed electron flood gun was used for the compensation of the charge accumulated on the analyzed surfaces during the ToF-SIMS experiments.

RESULTS AND DISCUSSION

ToF-SIMS measurements of Pd/ZrO₂-TiO₂ catalysts were divided into two parts. The first one concerned surface characterization of the „fresh” samples, whereas the other was devoted to the studies of the changes in the surface composition of the catalysts submitted to the hydrodechlorination reaction.

Figure 1 showed fragments of the positive ion mass spectrum obtained from the surface of the 2%Pd/20%ZrO₂-TiO₂ catalyst before its utilization in the hydrodechlorination process. The ToF-SIMS experiment demonstrated the presence of signals corresponding to contaminants (not marked on the spectrum), such as sodium, potassium, calcium or compounds containing carbon and peaks originating from palladium, titanium oxide

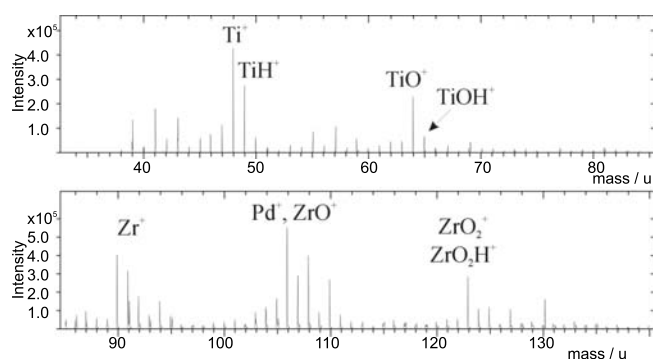


Figure 1. Fragments of the positive ion mass spectrum obtained from the surface of the „fresh” 2%Pd/20%ZrO₂-TiO₂ catalyst

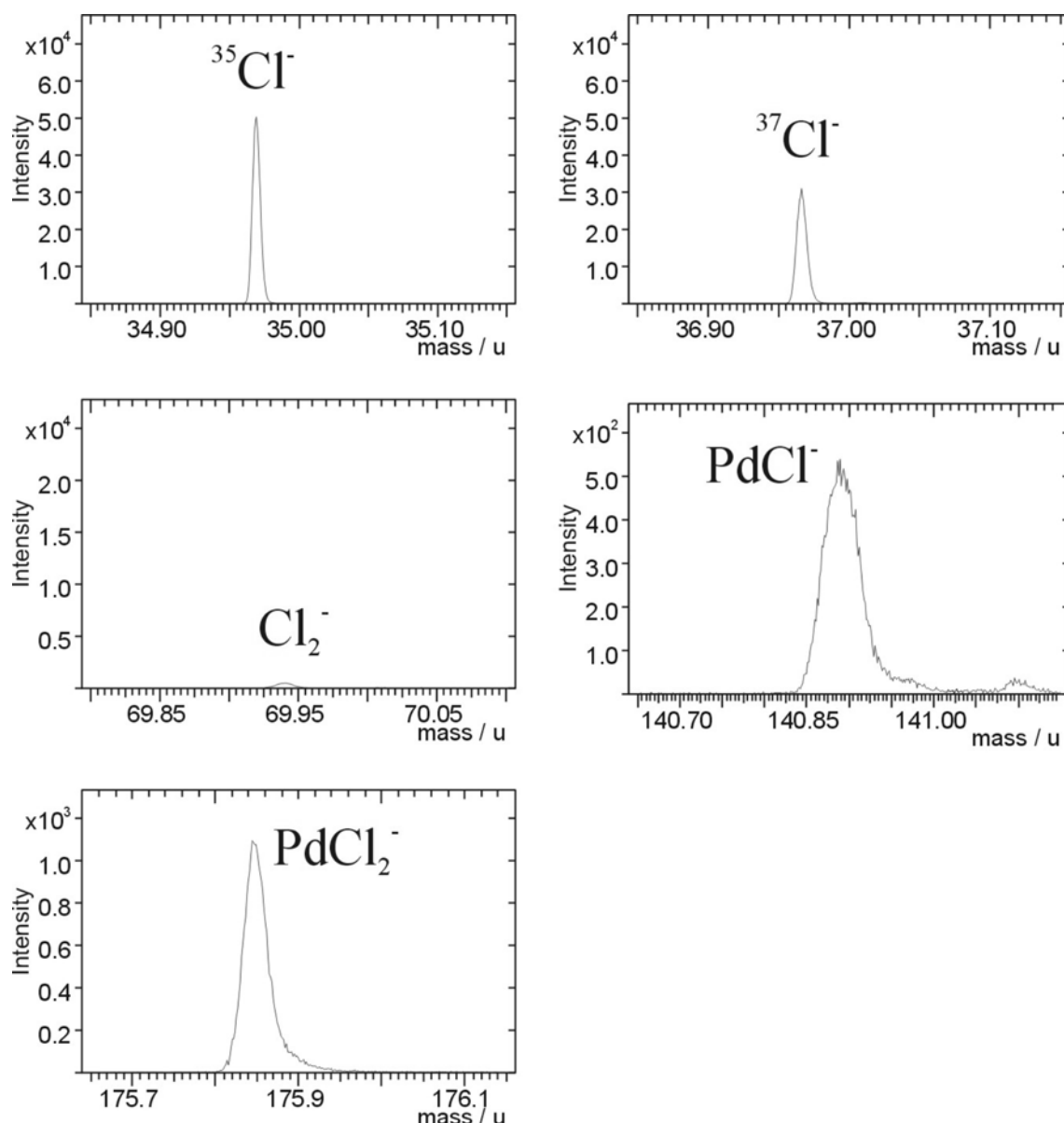


Figure 2. Fragments of the negative ion mass spectrum obtained from the surface of the „fresh” 2%Pd/20%ZrO₂-TiO₂ catalyst

and zirconium oxide. The most intensive signals coming from catalyst components were ascribed to Ti⁺, TiH⁺, TiO⁺, TiOH⁺, Zr⁺, Pd⁺, ZrO⁺, ZrO₂⁺ and ZrO₂H⁺ ions. It appeared that an interpretation of the above mentioned spectrum was hindered because of overlapping of some part of peaks. For example the mass of ¹⁰⁶Pd⁺, ¹⁰⁸Pd⁺ and ¹¹⁰Pd⁺ isotopes is very close to the mass of ⁹⁰ZrO⁺, ⁹²ZrO⁺ or ⁹⁴ZrO⁺ ions. The same phenomenon was ob-

served for the signals corresponding to PdO⁺ and ZrO₂⁺ ions containing the above mentioned Pd and Zr isotopes. Therefore, to make sure that the obtained results were interpreted correctly only the selected ions (i.e. ¹⁰⁴Pd⁺, ¹⁰⁵Pd⁺) were chosen for further calculations.

The negative ion mass spectrum obtained from the surface of the „fresh” 2%Pd/20%ZrO₂-TiO₂ catalyst (not shown in this publication) revealed the presence of chlorine (³⁵Cl⁻ and ³⁷Cl⁻ ions), which was not totally removed from the sample surface during calcination and reduction steps. Apart from chlorine a certain amount of PdCl⁻ and PdCl₂⁻ ions was also observed on the spectrum. All these ions came from PdCl₂, which was used as a catalyst pre-

cursor during the sample preparation process and did not undergo decomposition under treatment conditions mentioned in the experimental part.

The investigation of the activity of Pd/ZrO₂-TiO₂ catalyst showed that in the beginning the conversion of CCl₄ during hydrodechlorination reaction was near 100% and subsequently dropped below 20%. It was observed that the system containing 2% of Pd supported on binary sup-

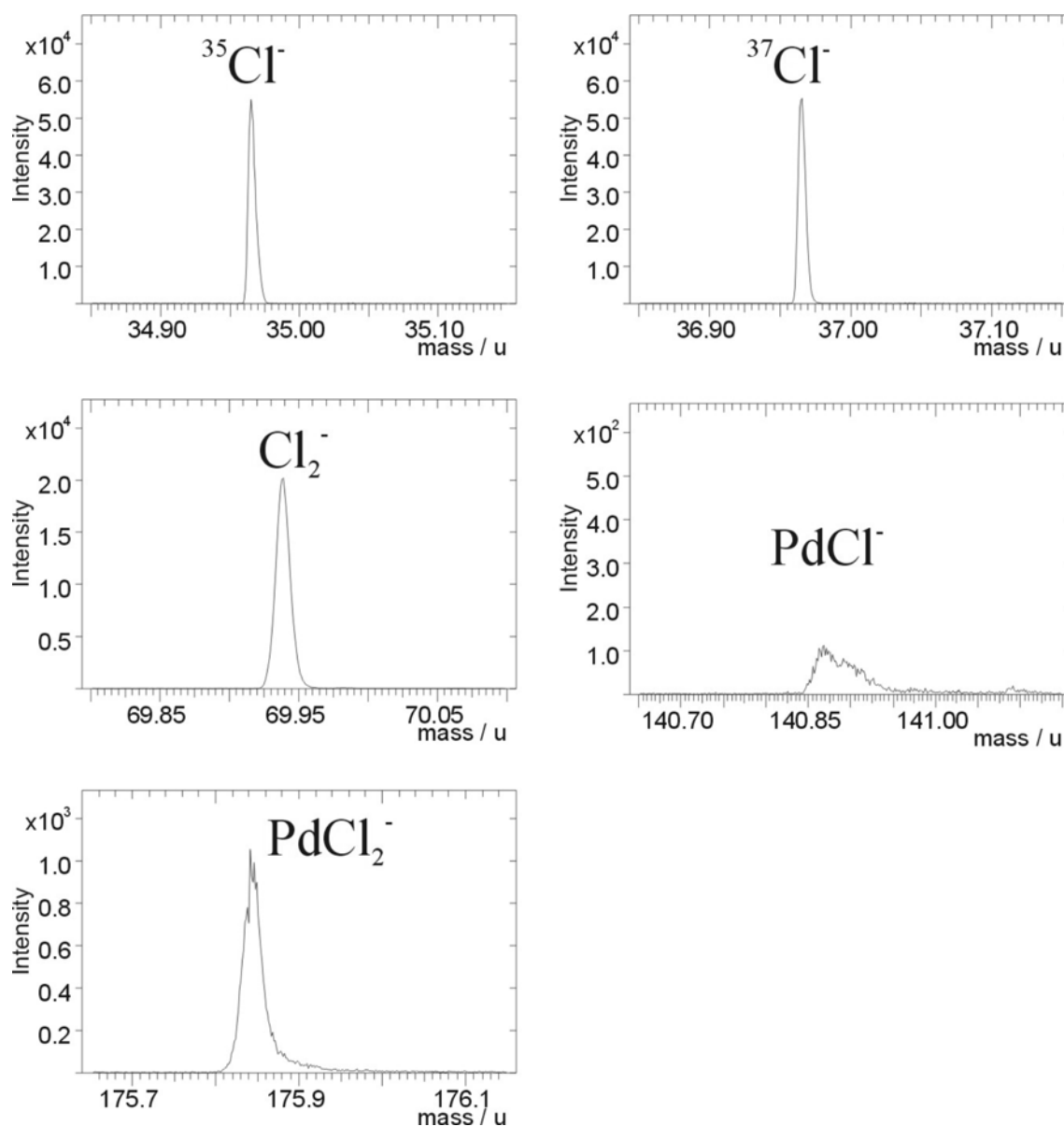


Figure 3. Fragments of the negative ion mass spectrum obtained from the surface of the „used” 2%Pd/20%ZrO₂-TiO₂ catalyst

Table 1. Normalized intensity of the ions selected from the mass spectrum of the 2%Pd/5%ZrO₂-TiO₂ catalyst

2%Pd/ 5%ZrO ₂ -TiO ₂	„fresh”	„used”
Cl ⁻	0,11	0,34
Cl ₂ ⁻	8,1·10 ⁻⁴	0,06
PdCl ⁻	2,2·10 ⁻³	8,6·10 ⁻⁴
PdCl ₂ ⁻	3,0·10 ⁻³	3,5·10 ⁻³
¹⁰⁴ Pd ⁺	2,3·10 ⁻³	8,3·10 ⁻⁴
¹⁰⁵ Pd ⁺	3,7·10 ⁻³	1,0·10 ⁻³

port composed of 5%ZrO₂ and 95%TiO₂ maintained the conversion of CCl₄ above 20% for about 20 h, while 2%Pd/20%ZrO₂-TiO₂ catalyst kept the above mentioned level of CCl₄ conversion for not less than 24 h.

The ToF-SIMS measurements of both deactivated samples revealed noticeable modifications in the composition of the surface of the studied material comparing to „fresh” catalysts (figures 2 – 4). One of the changes was an increase in the concentration of chlorine. A more precise comparison of the amount of chlorine (and other substances) on the surface of the catalyst before and after hydrodechlorination was possible owing to the normalization of the intensity of secondary ion emission during the

Table 2. Normalized intensity of the ions selected from the mass spectrum of the 2%Pd/20%ZrO₂-TiO₂ catalyst

2%Pd/ 20%ZrO ₂ -TiO ₂	„fresh”	„used”
Cl ⁻	0,11	0,36
Cl ₂ ⁻	1,3·10 ⁻³	0,07
PdCl ⁻	3,4·10 ⁻³	7,7·10 ⁻⁴
PdCl ₂ ⁻	4,3·10 ⁻³	3,9·10 ⁻³
¹⁰⁴ Pd ⁺	3,0·10 ⁻³	1,2·10 ⁻³
¹⁰⁵ Pd ⁺	4,1·10 ⁻³	1,2·10 ⁻³

ToF-SIMS experiments by the use of a number of total counts from an adequate mass spectrum. The results of such normalization are presented in Tables 1 and 2. It appeared that the normalized intensity of ³⁷Cl⁻ ion increased from 0.11 to 0.34 and 0.36 in the case of 2%Pd/5%ZrO₂-TiO₂ and 2%Pd/20%ZrO₂-TiO₂, respectively. Apart from a rise in the emission intensity of chlorine ions also a considerable growth in the intensity of Cl₂⁻ ions was noticed. It confirmed that chlorine atoms adsorbed on the catalyst surface during the hydrodechlorination process.

The opposite phenomenon was observed in the case of PdCl⁻ and PdCl₂⁻ ions. The emission intensity of such ions

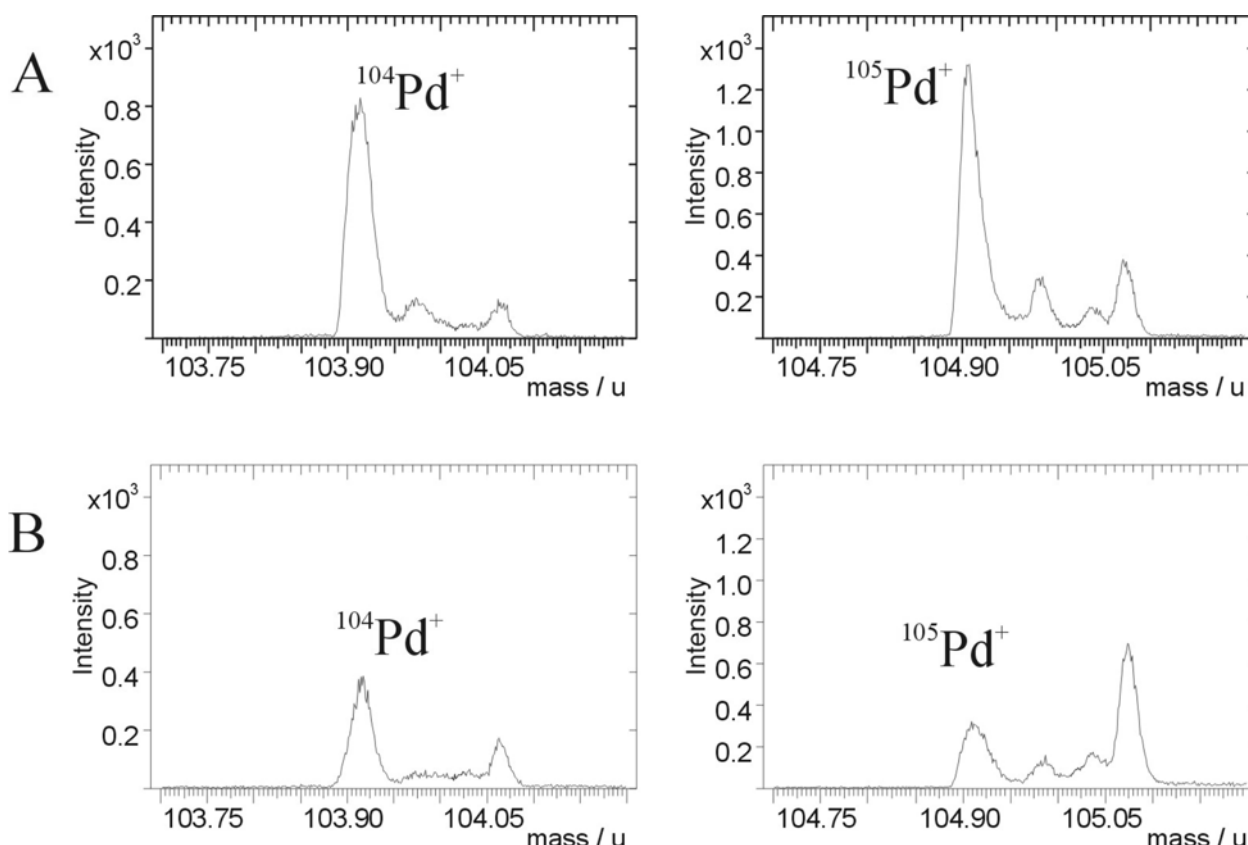


Figure 4. Fragments of the positive ion mass spectrum ($m/z = 103.70\text{--}104.10$ and $104.70\text{--}105.10$) obtained from the surface of A – „fresh” and B – „used” 2%Pd/20%ZrO₂-TiO₂ catalyst

did not change considerably after hydrodechlorination of CCl₄. The results demonstrated that the amount of PdCl₂⁺ and PdCl₂⁺ ions present on the investigated surface slightly decreased during the analyzed reaction. It suggested that in the case of Pd/ZrO₂-TiO₂ the hydrodechlorination process did not lead to the formation of Pd-Cl bounds on the catalyst surface. These findings are in agreement with the results obtained for Pd/ZrO₂-Al₂O₃ system³. In order to determine the influence of zirconium oxide on the ability to form Pd-Cl bounds on the catalyst surface during the hydrodechlorination reaction the investigations of the systems containing monoxide supports (without ZrO₂) were performed^{5,6}. It appeared that in the case of 2%Pd/TiO₂ catalyst the emission intensity of PdCl₂⁺ ion increased from $2.2 \cdot 10^{-3}$ to $8.5 \cdot 10^{-3}$ for the „fresh” and the „used” samples, respectively⁶. A similar tendency was observed for the 2%Pd/Al₂O₃ system. In this case the emission intensity of PdCl₂⁺ ion changed from $1.5 \cdot 10^{-4}$ before the reaction to $6.1 \cdot 10^{-4}$ after the hydrodechlorination process⁵. It corresponds to a quadruple increase in the concentration of PdCl₂⁺ ions on the surface of both the 2%Pd/TiO₂ and the 2%Pd/Al₂O₃ catalysts during the reaction. The behavior of the 2%Pd/ZrO₂ sample differed from the trend manifested by the two above mentioned systems. In the case of the 2%Pd/ZrO₂ catalyst the hydrodechlorination process did not cause any increase in the amount of Pd-Cl bounds on the analyzed surface. All these observations indicated that systems containing ZrO₂ are more resistant to the formation of PdCl₂ on their surface during hydrodechlorination of CCl₄.

One of the possible reasons for the deactivation of the above mentioned catalysts during the hydrodechlorination process may be a decrease in the amount of surface acces-

sible palladium. Secondary ion mass spectra of different catalysts containing palladium (presented in Refs.^{5,6}) demonstrated that the emission intensity of Pd⁺ ion decreased during hydrodechlorination of CCl₄. The results of the ToF-SIMS measurements of the 2%Pd/5%ZrO₂-TiO₂ and the 2%Pd/20%ZrO₂-TiO₂ samples were in agreement with the tendency observed earlier. The emission intensity of ¹⁰⁵Pd⁺ ion dropped from $3.7 \cdot 10^{-3}$ and $4.1 \cdot 10^{-3}$ to $1.0 \cdot 10^{-3}$ and $1.2 \cdot 10^{-3}$ in the case of the „fresh” and the „used” 2%Pd/5%ZrO₂-TiO₂ and the 2%Pd/20%ZrO₂-TiO₂ catalysts, respectively. It indicated that palladium may be removed from the catalyst surface during the hydrodechlorination reaction or metal atoms are covered by chlorine or carbon deposit. The determination of the exact reason for decrease in the amount of surface accessible palladium will be possible after performing additional experiments.

SUMMARY

Time-of-flight secondary ion mass spectrometry gave a possibility to obtain information about surface composition of Pd/ZrO₂-TiO₂ catalyst. Moreover, the estimation of the changes in the concentration of the particular surface components during the hydrodechlorination process was possible. It was demonstrated that hydrodechlorination of CCl₄ led to the increase in the concentration of chlorine and the drop in the amount of surface accessible palladium, while the quantity of Pd-Cl bounds did not change considerably. The comparison of the obtained results with the studies described earlier confirmed that the application of ZrO₂ decreases susceptibility of the catalyst to the formation of PdCl₂ during the hydrodechlorination reaction. However, it cannot be for-

gotten that besides the adsorption of chlorine and formation of Pd-Cl bounds also a drop in the surface area and arising of carbon deposit play an important role in the catalyst deactivation process.

ACKNOWLEDGEMENTS

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