

Characteristic of physicochemical properties of Pd/MgO catalysts used in the hydrodechlorination process with CCl_4

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The aim of this paper was to investigate the physicochemical properties of palladium catalyst containing basic support MgO which was used in hydrodechlorination reaction with carbon tetrachloride. In order to characterize the investigated sample the catalyst was put to tests of XRD, TOF – SIMS, TG-DTA-MS and TPR_{H_2} measurements, activity tests were also performed. The XRD and TPR results demonstrated the presence of PdO_xCl_y species whose decomposition takes place above 700°C. The calcination of the Pd/MgO catalyst at 700°C resulted in the transformation of PdO_xCl_y to PdO.

Keywords: palladium catalyst, basic properties of MgO, hydrodechlorination, CCl_4 .

Presented at VII Conference Wasteless Technologies and Waste Management in Chemical Industry and Agriculture, Międzyzdroje, 12 – 15 June, 2007.

INTRODUCTION

Carbon tetrachloride together with other chlorinated compounds like CFCs and PCBs has noxious effects on environment, particularly high ozone potential depletion.

It was in fact classified among chlorofluorocarbons in group IV and so its use was banned in developed countries from 1996¹. Among more diffuse CFCs disposal methods such as thermal combustion and catalytic combustion, catalytic hydrogenation is one of the most promising one due to the low reaction temperature and the production of useful compounds, without pollutant by-products like dioxins, CO, Cl_2 and COCl_2 ^{2,3,4}. Palladium is identified as the best metal for hydrodechlorination reaction of organic compounds. The problem with catalysts used in the HDC process is their high susceptibility to poisoning effect. The systems containing palladium are commonly used showing high activity, but the main disadvantage is the fact that they are quickly deactivated.

Besides adequately chosen reaction conditions to prevent catalyst deactivation one of the most important factors is the selection of property supports. Even not a significant change of the acidity can considerably change the coke rate, which is one of the reasons for palladium catalysts deactivation. Hydrogen chloride which is one of the HDC reaction products^{5,6} has a substantial influence on the mechanism of carbon deposition and coke rate. Adsorption of HCl causes the formation of strong acid sites, which facilitates carbon deposition.

Advantages of MgO as appropriate support of the catalyst for hydrodechlorination reaction are presented by a lot of authors^{4,7}. The high activity of the Pt/MgO catalyst was ascribed to the basic properties of MgO. The basicity of this oxide seems to be responsible for retarding the coke formation and suppression of C_2 oligomers (C_2Cl_4 and C_2Cl_6 mainly) which are the principal reasons for the catalyst deactivation.

The aim of this paper was to determine the physicochemical properties of the Pd/MgO catalyst and examine the influence of the type support on the activity of the catalyst in the investigated reaction.

EXPERIMENTAL

The catalyst was prepared by the incipient wetness impregnation methods. Palladium was introduced from PdCl_2 (POCH Gliwice) on commercial support MgO (POCH Gliwice). The total loading of metallic phase was 2 wt %. Then the obtained material was aging for 48 h at room temperature. After the evaporation of water, the catalyst was submitted to drying under atmospheric pressure at 110°C for several hours. After such synthesis one sample was calcined in the flow of O_2 at 500°C for 4 h and reduced before reaction in the flow on H_2 under the same conditions. The second sample was used in the hydrodechlorination reaction without any pretreatment, after drying only.

The activity tests were carried out under atmospheric pressure at 120, 150, 200 and 250°C, the reactant mixture CCl_4/H_2 (1:10) was passed through the reactor at a flow rate of 40 cm^3/min . The load of the catalyst bed was 0.20g. The samples were analyzed using a gas chromatography (Chrom 5 with FID) equipped with 15%OV-17/1,95%OV 210/ CWHF 80/100 column.

An AMI1 system from Altamira Instruments (USA) equipped with a thermal conductivity detector (TCD) was used for the TPR_{H_2} and TPO experiments. In these measurements mixtures of 5 vol.% H_2 and 95 vol.% Ar or 2 vol.% O_2 and 98 vol.% Ar, respectively, were used at space velocity $W/F = 1.11 \cdot 10^{-5} \text{ g} \cdot \text{h} \cdot \text{cm}^{-3}$ and the linear growth of temperature 20°C/min. Prior to the TPR/TPO measurements the samples were oxidated before the measurements for 30 min at 500, 700, 800, 900°C after all the procedures were taken in situ.

The X-ray diffraction (XRD) patterns were obtained at room temperature using a PANalytical X'pert Pro MPD diffractometer, operating at 40 KV and 30 mA (CuK α radiation) data were collected in the range of 10 – 90 2 θ with step size of 0.0167° and step time of 30 s.

Thermal analysis TG – DTA – MS was performed in the Setaram thermobalance unit (Setsys 16/18) connected to the Balzers quadrupole mass spectrometer (Thermostar) using oxidizing atmosphere (2% O_2 and 98% Ar). Typically, ca. 5 – 15 mg of used the catalyst was linearly heated at 10°C·min⁻¹ from room temperature to 1000°C.

The TOF-SIMS measurements were described in detail in⁸.

RESULTS AND DISCUSSION

The TPR run of the investigated samples is presented in Figure 1. Calcination of the Pd/MgO catalyst at the 500 °C (curve 1) did not cause an appearance of PdO whose reduction takes place at room temperature⁵. We did not observe the desorption of H₂ from the bulk of palladium which is confirmed by the reduction of PdO. It is supposed that after the calcination at 500°C the broad peak (200 ÷ 400 °C) can be attributed to the reduction of connections of PdO_xCl_y with the MgO surface^{9, 10}. A distinct peak with the maximum at 620°C probably corresponds to the decomposition of magnesium hydroxycarbonates. Calcination at 700°C (curve 2) caused a partial decomposition of oxychloride species and appearance of the negative peak (at 80°C) assigned to the reduction of a metallic phase (a very small desorption peak of H₂). The residual indecomposed PdO_xCl_y interacting with the support undergoes the reduction process in the range of temperature 200 ÷ 400°C. From the comparison of the TPR profiles after the calcination at 500 and 700°C we can see that the higher temperature brings about a rise in palladium oxychlorides interacting with the MgO surface.

An increase in the calcination temperature to 800°C (curve 3) results in an enlargement of the PdO amount reduced at room temperature and in the decrease in the PdO_xCl_y – MgO connections. Further increase in the calcination temperature leads to deepening of these effects.

In the case of high-temperature calcinations (900°C) the reduction peak with the maximum at 320°C can be represented by the PdO_xCl_y-MgO or/and PdO-MgO species.

The phases present in all catalysts were determined by XRD. Crystalline phases were identified by a comparison with the JCPDS file. The XRD patterns of the samples after calcination at 500°C (Figures 2) show the peaks coming from PdO_xCl_y. Lack of the PdO patterns confirms that the temperature of 500°C is too low for the decomposition of palladium oxychlorides which are on the strong basic MgO support. On the other hand, the presence of palladium oxide in an amorphous form on MgO surface was not excluded. An increase in the calcination temperature to 700°C (curve 2 in Figure 2) causes removal of crystalline PdO_xCl_y forms and appearance of PdO. After the calcination at 900°C the peaks assigned to PdO disappear due to the decomposition to metallic palladium. For the catalysts calcinated at 500 and 900°C, respectively and reduced at 900°C (Figure 3) we observed the peaks corresponding to metallic palladium and magnesium oxide only. A higher reduction of the temperature produces the sintering of palladium crystallites (curve 2).

TG-DTA-MS method was used for the studies of the decomposition of the PdCl₂ precursor supported on MgO. Investigations were carried out for the samples after calcination at 500, 900°C and drying only. An analysis of the PdCl₂ products distributions did not reveal any formation of Cl₂ or ClO_x which means that chlorine formed during decomposition reacts with MgO surface producing MgCl₂¹. CO₂ was the only product observed during measurements

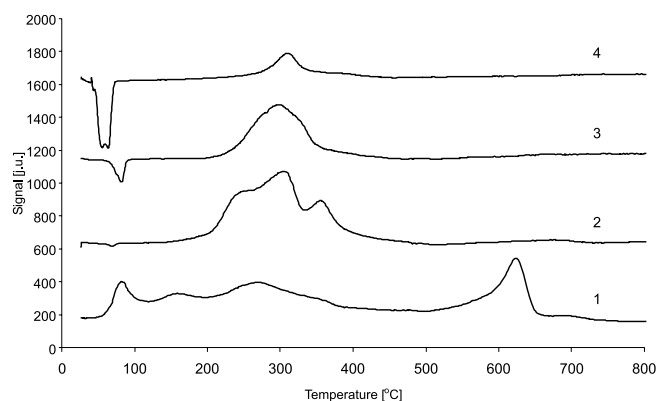


Figure 1. The TPRH2 profiles for the catalyst 2%Pd/MgO after calcination at different temperatures for 30 min.: 1 – 500°C, 2 – 700°C, 3 – 800°C, 4 – 900°C

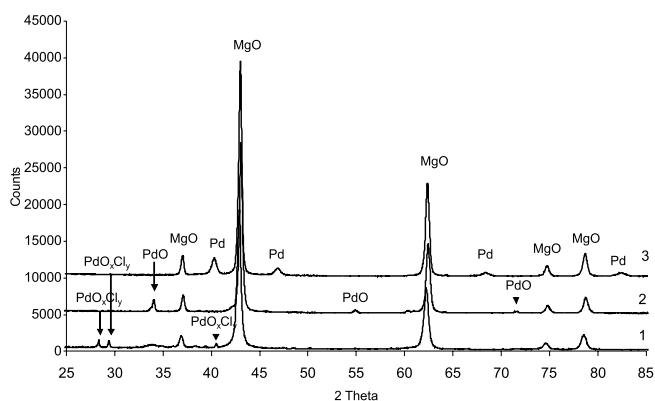


Figure 2. The XRD patterns of 2%Pd/MgO catalyst after calcination at different temperatures for 30 min.: 1 – 500°C, 2 – 700°C, 3 – 900°C

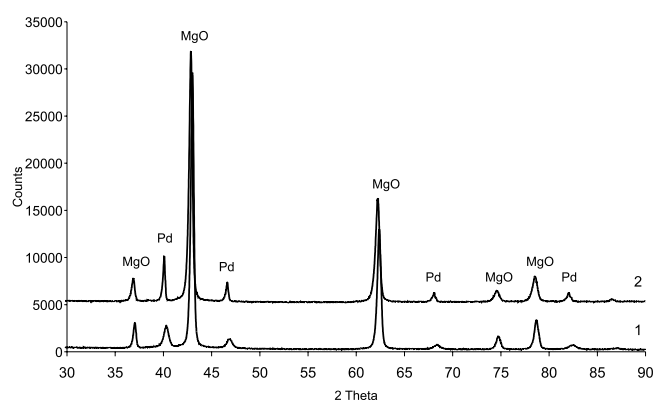


Figure 3. The XRD patterns of the 2%Pd/MgO catalyst: 1 – after calcination at 500°C for 30 min and reduction at 900°C for 30 min, 2 – after calcination at 900°C for 30 min and reduction at 900°C for 30 min

which came from the decomposition of magnesium hydroxycarbonate.

The results of time-of flight secondary ion mass spectrometry (TOF-SIMS) were given for the catalysts 2%Pd/MgO after calcinations at 500, 700 and 900°C. The obtained results (Figure 4 and Table 1) indicate a drop in the amount of chlorine and Pd-Cl bounds on the catalyst surface after the calcination at 900°C. In the case of the 500 and 700°C calcination temperature the amounts are similar. It is supposed that the temperature of 700°C did not cause the removal of chlorine ions from the surface of strong support like MgO.

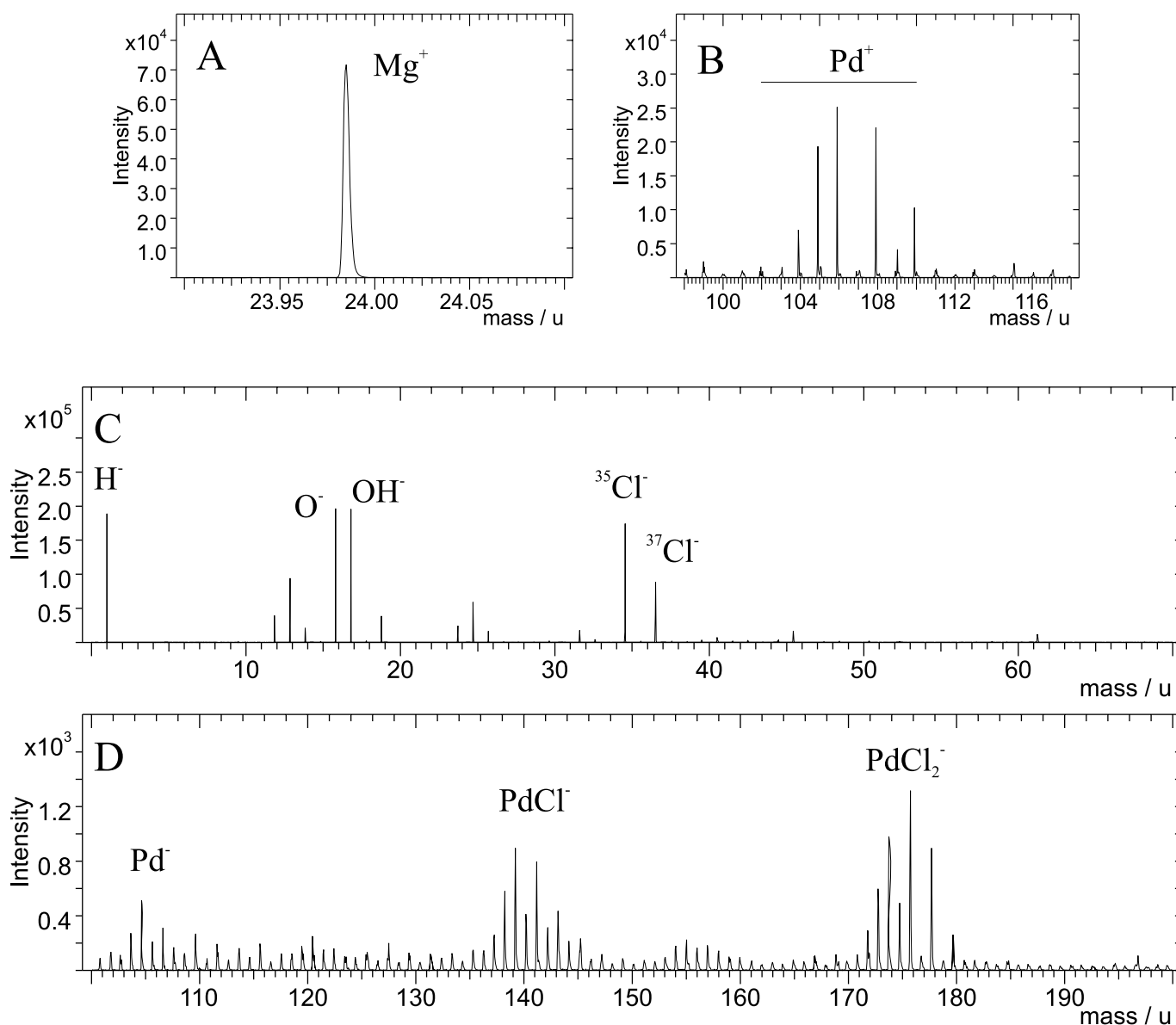


Figure 4. Fragments of the ion mass spectrum obtained from the surface of the 2%Pd/MgO catalyst after calcination at 700°C: A,B – positive ions; C,D – negative ions

Table 1. Normalized intensity of the ions selected from the mass spectrum of the 2%Pd/MgO catalyst after calcinations at 500°C, 700°C and 900°C

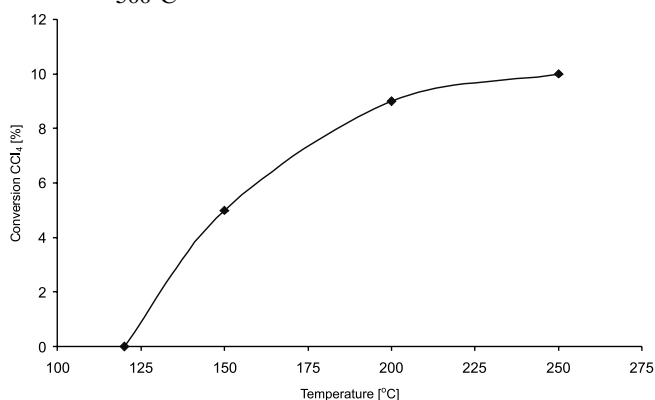
Intensity of ions	calcination at 500°C	calcination at 700°C	calcination at 900°C
$\text{Cl}^-/\text{total counts}$	0,097	0,115	0,043
$\text{PdCl}^-/\text{Pd}^-$	2,2	2,0	1,2
$\text{PdCl}_2^-/\text{Pd}^-$	2,3	2,0	0,8

Conversion of carbon tetrachloride versus temperature reaction for 2%Pd/MgO was presented in Figure 5. We observed that the conversion of CCl_4 grows with the increase in temperature. The main product was methane and trace amount of ethane was formed.

SUMMARY

The investigations revealed a presence of some palladium in the form of oxychlorides species strongly connected with the basic MgO support. It was observed that the surface of MgO was covered by chloride ions coming from the decomposition of PdCl_2 . This process results in the increase in the acidity of the support and promotes

Figure 5. Conversion of CCl_4 versus the temperature hydrodechlorination reaction for the 2%Pd/MgO catalyst after calcination and reduction for 4h at 500°C



carbon deposition on the catalyst surface. Both the TPR and XRD measurements demonstrate the existence of PdO_xCl_y species in the crystalline form which are weakly connected with the support. An increase in the calcination temperature resulted in the decomposition of PdO_xCl_y to PdO. If the calcinations temperature does not exceed

500°C, magnesium hydroxycarbonates are present on the surface of MgO.

The TOF-SIMS measurements revealed that calcination of the catalyst at 700°C did not cause a removal of the Pd-Cl bounds. Only a treatment at 900°C leads to their decomposition.

ACKNOWLEDGEMENTS

The financial support of this work by the Polish Scientific Research Council (KBN) Grant No. 3 T09B 085 27 is gratefully acknowledged.

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