Hydrodechlorination of tetrachloromethane over silica-supported palladium-gold alloys

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This article is dedicated to Professor Walerian Arabczyk on the occasion of his 70th birthday.

Compared with the monometallic palladium, bimetallic Pd-Au/SiO$_2$ catalysts show much higher activity and better stability in the reaction of hydrodechlorination of tetrachloromethane, also providing higher selectivity to longer than methane hydrocarbon products. Reasonably mixed Pd-Au particles show better catalytic performance during ~60 h operation, whereas the monometallic palladium and very rich in palladium catalysts suffer rapid deactivation. Smaller amounts of carbon- and chlorine-containing deposits found after reaction on Pd-Au catalysts correspond to their superior catalytic behavior.

Keywords: Pd-Au/SiO$_2$, CCl$_4$ hydrodechlorination, synergy, selectivity for hydrocarbons, catalyst deactivation.

INTRODUCTION

Catalytic hydrodechlorination (HdCl) is regarded as one of the most prospective methods of destruction of harmful chlorine-containing compounds[1, 2]. Compared to incineration and catalytic burning, which destroy the carbon skeleton material and would result in the formation of even more harmful compounds (dioxins, phosgene, etc.), HdCl offers the transformation to more benign and still valuable chemicals. Until recently, HdCl of tetrachloromethane to chloroform carried out in the presence of Pt-based catalysts was regarded as a suitable method[3–5], but now the high toxic and carcinogenic character of CHCl$_3$ placed this substance in the U.S. EPA's Toxic Release Inventory (TRI). Therefore, conversion of CCl$_4$ to hydrocarbons appears now a more reasonable solution. In contrast to platinum, palladium catalysts were found useful in such transformation, however they quickly deactivate on stream[6–10]. Interestingly enough, Pd-Au bimetallic nano-particles were recently discovered to exhibit superior catalyst activity and improved deactivation resistance in HdCl of chlorinated ethenes[11–13]. In this report we present new data on the catalytic behavior of Pd-Au/C and Pd-Au/SiO$_2$ catalysts in HdCl of CCl$_4$.

EXPERIMENTAL

The support was Davison 62 silica gel, 75–120 mesh, precalcined in air at 450ºC for 3 h. The 2 wt% Pd/SiO$_2$ catalyst was prepared by impregnation of silica with an aqueous solution of palladium dichloride (analytical reagent from POCh Gliwice, Poland), using an incipient wetness technique. After impregnation, the solid was dried in an air at 120ºC for 6 h. After drying, the material was precalcined in a fluidized bed in an air flow from room temperature to 450ºC at a 2 deg./min ramp and maintained at 450ºC for 3 h. After cooling down, the precursor was flushed out with argon and reduced in a 50% H$_2$/Ar stream from room temperature to 400ºC (a 4 deg./min ramp) and kept at 400ºC for 3 h. After reduction and passivation in air (at room temperature) the catalyst was kept in a desiccator.

The bimetallic silica-supported palladium-gold catalysts were prepared by sequential reduction impregnation[14].

The monometallic Pd/SiO$_2$ catalyst was prereduced at 300ºC for 3 h in a special reactor in flowing H$_2$-Ar (300 cm^3/min), then purged in an argon flow at 300ºC for 1 h, cooled to room temperature in Ar, and, finally, immersed in de-aerated doubly distilled water. The solution was continuously stirred by bubbling argon, at 200 cm^3/min. Then, a de-aerated aqueous solution of ammonium chloroaurate (Johnson Matthey, specpure) was slowly introduced into the reactor. The solution was stirred with bubbling argon for the next 20 min. The resulting solid was separated by filtration, washed with redistilled water, and dried in flowing argon at 60ºC for overnight, and finally stored in a desiccator. Three bimetallic Pd-Au/SiO$_2$ catalysts were prepared in this manner. Their basic characteristics, after reduction in hydrogen at 400ºC for 3 h, along with designation are in Table 1. Metal dispersion was assessed by CO and H$_2$ chemisorption (details in Table 1). After H$_2$ chemisorption, the samples were cooled to ~0ºC in H$_2$/Ar flow (to be transformed into respective Pd(Au)H phases). Next, they were heated to ~150ºC, at the temperature ramp of 8 deg./min. Such runs, called temperature-programmed hydride decomposition (TPHD), carried out in 10% H$_2$/Ar mixture[15] are supposed to reveal the stability and composition of the β-hydride phase as a function of gold content in palladium.

Table 1. Catalyst characterization – designation, palladium dispersion by chemisorption and temperature-programmed hydride decomposition (TPHD) data

Catalyst[a]	Pd dispersion		Temperature programmed hydride decomposition	
	CO/Pd[b]	H/Pd[c]	H/Pd[d]	T$_{max}$, ºC[e]
2.0% Pd$_{100}$	0.268	0.21	0.233	59.9 and 80.5
2.2% Pd$_{95}$Au$_5$	0.075	0.07	0.201	61.0 and 81.0
2.2% Pd$_{80}$Au$_{20}$	0.071	0.025	0.198	67.6 and 82.7
2.7% Pd$_{60}$Au$_{40}$	0.039	0.012	0.156	72.8 and 86.0

[a] X% denotes total metal (Pd + Au) loading in wt.% (assesed by atomic absorption), whereas in Pd$_Y$Au$_{100-Y}$, Y stands for atom % of palladium in the metal phase,
[b] from CO chemisorption measured in a static system at 35ºC,
[c] from H$_2$ chemisorption measured in a pulse-flow system at 70ºC,
[d] H/Pd ratio from the amount of hydrogen released in palladium hydride decomposition,
[e] Positions of temperature maxima of TPHD profiles.

Reduced catalyst samples were investigated by X-ray diffractometry (Rigaku Denki, Ni-filtered CuK$_\alpha$ radiation). One selected, the most promising Pd-Au catalyst was also investigated by high resolution transmission electron microscopy studies, using a FEI Titan Cubed at 300 kV accelerating voltage.

The reaction of hydrodechlorination of tetrachloromethane (analytical reagent from POCh, Gliwice, Poland, purity > 99.6%) at 90°C and the H_2:CCl_4 ratio ~14:1 was carried out in a glass flow system, previously described[16, 17]. The flows of H_2 and diluting Ar (all 99.999% pure, further purified by passing through MnO/SiO_2 traps), were preset by using mass flow controllers (Bronkhorst Hi-Tec). Prior to reaction, the catalyst samples were reduced at 400°C for 3 h. A typical run lasted 60–70 hours. 2 wt.% Au/SiO_2 catalyst was not active in this reaction and it is not included into description of results and discussion.

Post-reaction catalyst samples were also investigated by temperature programmed hydrogenation (TPH-MS). TPH-MS runs were carried out in a flowing 10%H_2/He mixture (25 cm^3/min) at a 10 deg./min ramp and followed by mass spectrometry (MA200, Dycor-Ametek, Pittsburgh, USA). Principal attention was paid to m/z 15 and 16 (methane evolution), and m/z 36 and 38, which are suggestive of HCl liberation from catalysts used.

RESULTS AND DISCUSSION

The results of catalysts' characterization are shown in Table 1 and Figures 1, 2 and 3. It is seen that the prepared catalysts are characterized by medium metal dispersion. The monometallic Pd/SiO_2 catalyst showed the crystallite size of ~5 nm (by XRD, Fig. 1), in agreement with a predicted metal particle size assessed from chemisorption (d_{nm} = 1.12/dispersion[18]). Lower, in comparison with the monometallic Pd/SiO_2, palladium dispersions in Pd-Au/SiO_2 catalysts, judged from lower gas uptakes, most probably result from a surface segregation of gold. In such a case surface composition of palladium is lower than its bulk content, which served for determination of H/Pd and CO/Pd ratios for the bimetallics[19].

The XRD profiles (Fig. 1) of reduced Pd-Au/SiO_2 catalysts showed a reasonable, although not full, degree of Pd-Au alloying. The dominant part of the material contributes to the occurrence of single, relatively narrow XRD reflections.

But some inhomogeneity of the prepared material was manifested in the profiles of the temperature programmed hydride decomposition (TPHD) experiments, Figure 2. Two maxima found for TPHD of the monometallic Pd/SiO_2 show that this catalyst contains two metallic fractions characterized by smaller and larger metal particles[20]. Introduction of gold to Pd/SiO_2 smoothly shifts these maxima towards higher temperatures, suggesting similar modification for both palladium fractions. It has to be remarked that such shifts are consistent with an earlier observation of Ziemecki et al.[21] who found that a commercial Pd–Au powder (of 20 wt.% Pd) showed a TPHD peak at the temperature ~35°C, higher than that exhibited for a physical mixture of Pd and Au powders.
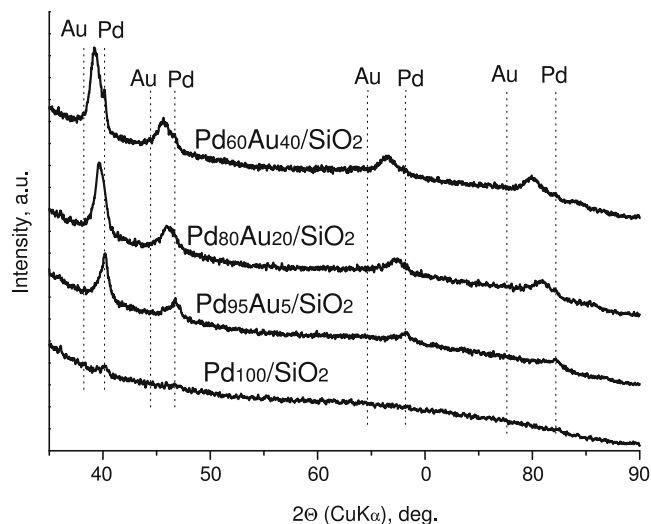

Figure 1. XRD profiles of reduced silica-supported Pd-Au catalysts. Basic XRD reflections from palladium and gold are marked. For catalyst designation see Table 1
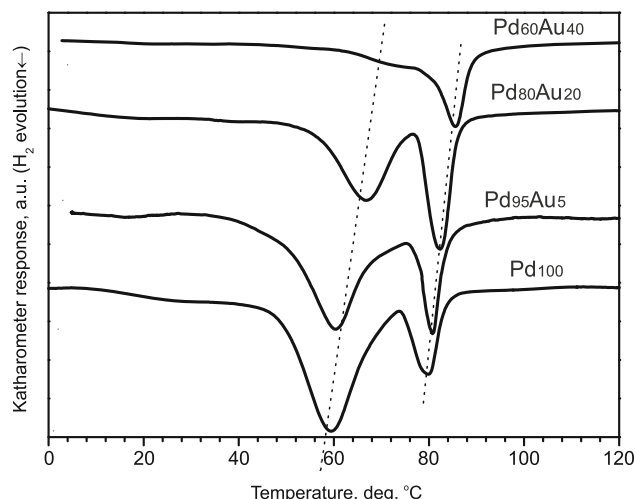

Figure 2. Temperature programmed (palladium) hydride decomposition (TPHD) profiles from silica-supported Pd-Au catalysts. For catalyst designation see Table 1

Our TEM studies show that, apart from smaller metal particles (~5–10 nm), larger alloy particles are also present in $Pd_{60}Au_{40}/SiO_2$ (15–20 nm), Figure 3. This confirms conclusions drawn from the TPHD studies about the size heterogeneity of our metal particles.

Figure 4 shows changes in the overall catalytic activity for silica supported Pd-Au catalysts with time on stream. It is evident that a gradual increase of Au content contributes to a more stable behavior. Both Pd_{100} and $Pd_{95}Au_5$ catalysts show rapid deactivation, accompanied by an increase of formation of dimeric $C_2H_xCl_y$ products. At the end of catalytic run, when these catalysts are nearly inactive because their surfaces are largely blocked by deposits, methane formation dominates over other products. The performance of $Pd_{80}Au_{20}$ and $Pd_{60}Au_{40}$ differ much from that exhibited by Pd_{100}. Now the deactivation is found much less serious. This situation must follow from a higher content of gold on the surface of palladium containing catalysts. It must be noticed that even the initial (not only final) activities of $Pd_{80}Au_{20}$ and $Pd_{60}Au_{40}$ are much higher than that of Pd_{100}, especially after considering much lower palladium dispersions in bimetallic catalysts. The fact that a relatively fresh (not
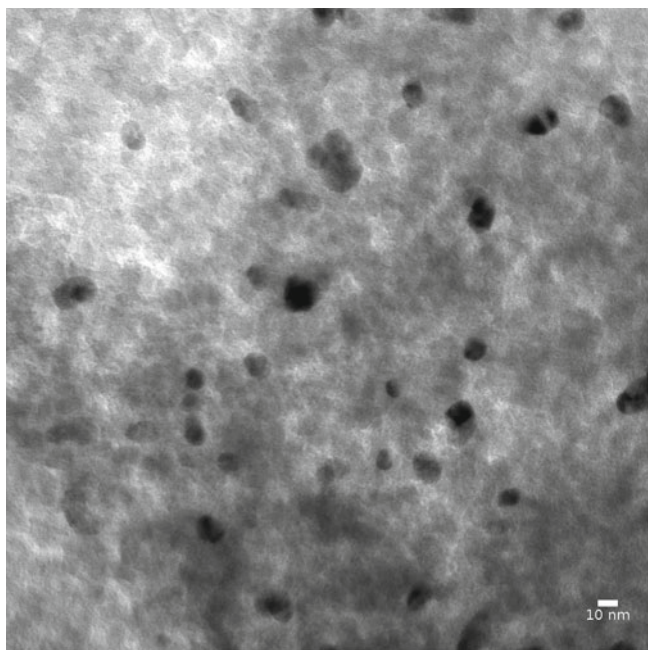
Figure 3. TEM micrograph of reduced $Pd_{60}Au_{40}/SiO_2$ catalyst

carbon-containing species (*vide infra*) suggests operation of the ensemble effect, when the contiguity of active palladium sites is interrupted by diluting gold[22].

Table 2 collects the overall activity and selectivity data for all tested catalysts. It is seen that although gold itself is inactive in HdCl of CCl_4, its addition to Pd vastly increases the selectivity to hydrocarbons, which are desired reaction products. Remarkably, $Pd_{80}Au_{20}$ and $Pd_{60}Au_{40}$ also produce much larger amounts of C_{2+} hydrocarbons, which are the most desired products.

Figure 5 shows that the post-reaction deposits have mainly chlorine-containing species. Their amount seems to be inversely correlated with the gold content. So, the degree of catalyst deactivation must be linked to the gold content. Figure 5 also shows that although carbonaceous deposits are much less plentiful than surface chloride species, their removal needs much higher temperatures, ~600°C. Therefore, their influence on catalyst deactivation would also be significant.

It seems that main role of gold is understood in an improved deactivation resistance in HdCl of CCl_4. Also, larger amounts of stripped surface chlorine from the surface of Pd-Au catalysts during reaction would explain their better selectivity to hydrocarbons. It should be mentioned that palladium modification with another Group IB metal, copper, brings about positive changes in product selectivity, i.e. yielding more hydrocarbons than on pure Pd[23]. However, the presence of copper, although beneficial for the selectivity, does not improve the poor stability of palladium catalysts. Massive retention
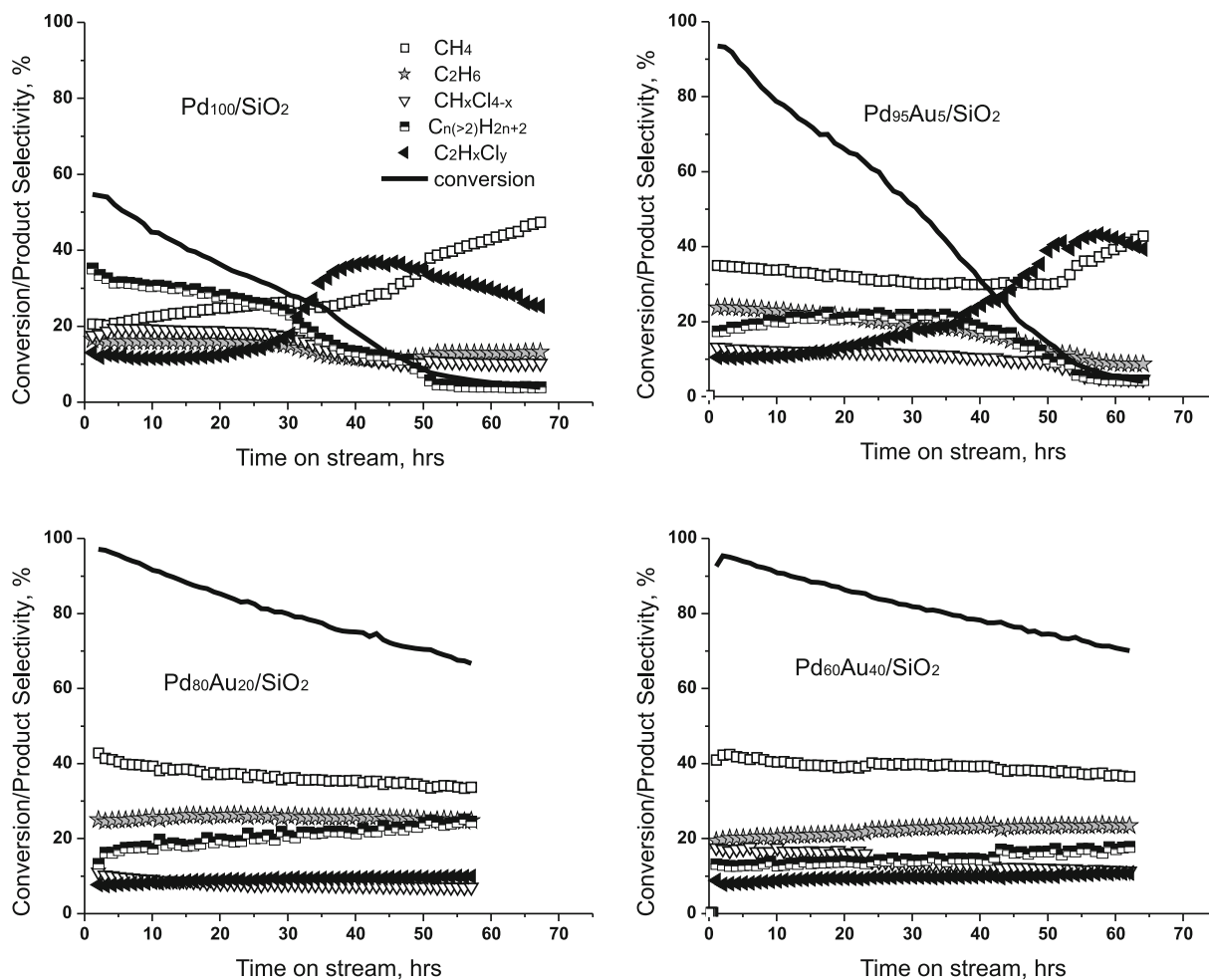
blocked by deposits) surface of Pd-Au catalysts is more active than that of pure palladium suggests the occurrence of ligand effect, understood as an electronic modification of "too active" surface Pd atoms by neighboring gold species[22]. Changing the d character of Pd would cause weaker interaction between surface palladium and reactant/product molecules. On the other hand, much better resistance to deactivation by deposited chlorine- and

Figure 4. Time on stream behavior of silica-supported Pd-Au catalysts in the hydrodechlorination of CCl_4. Reaction temperature 90°C, $H_2/CCl_4 = 14$, catalyst weight 0.24 g. For catalyst designation see Table 1

Table 2. Catalytic performance of Pd-Au/SiO$_2$ catalysts in the reaction of CCl$_4$ hydrodechlorination (after 60–70 hours of reaction at 90°C).

Catalyst[a]	Conversion, [%]	Product selectivity, [%]					
		CH$_4$	C$_2$H$_6$	CH$_3$Cl	CHCl$_3$	C$_{n(>2)}$H$_{2n+2}$	C$_2$H$_x$Cl$_y$
2.0% Pd$_{100}$	4	47	13	6	4	4	25
2.2% Pd$_{95}$Au$_5$	4	43	9	5	–	4	39
2.2% Pd$_{80}$Au$_{20}$	67	34	25	5	2	24	10
2.7% Pd$_{60}$Au$_{40}$	70	36	23	9	2	18	11

[a] as in Table 1.
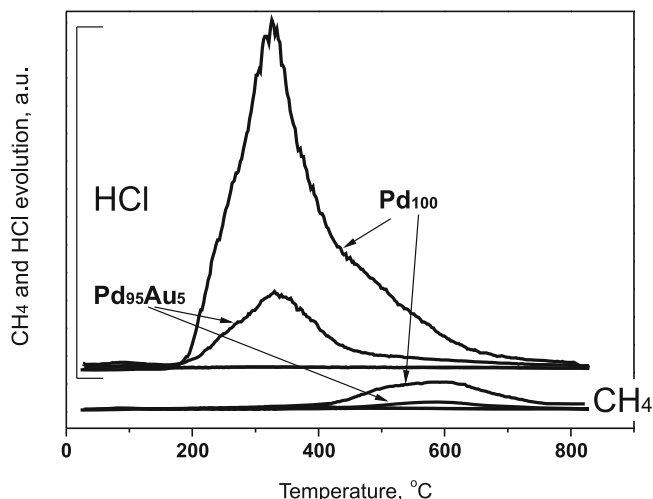
Figure 5. Temperature programmed hydrogenation profiles of postreaction deposits from silica-supported Pd and Pd-Au catalysts: upper profiles- HCl (m/z 36) and lower profiles – methane (m/z 16) evolution. Featureless horizontal lines were obtained for Pd$_{80}$Au$_{20}$ and Pd$_{60}$Au$_{40}$ indicating negligible deposition of chlorine and carbon containing species

of C$_2$H$_x$Cl$_y$ species found after HdCl of 1,2-dichloroethane on Pd-Cu/Sibunit carbon catalysts[24] would also be responsible for deactivation of Pd-Cu catalysts in the reaction of CCl$_4$.

CONCLUSIONS

Sequential impregnation of silica-supported palladium with the gold salt followed by reduction in hydrogen at 400°C results in a reasonable, although not full degree of Pd-Au alloying. Although gold itself is not active in tetrachloromethane hydrodechlorination at 90°C, its introduction to palladium generates beneficial changes both in the overall activity and product selectivity, giving large amounts of longer hydrocarbons and relatively little amounts of heavier chlorine-containing compounds. Bimetallic Pd-Au/SiO$_2$ catalysts are also much less susceptible to deactivation during long term operation (60–70 h). Post-reaction deposits contain both chloride as well as carbon species. However, their amounts are much less abundant on the surface of Pd-Au alloys than on pure palladium.

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