

Influence of microwave activation on the catalytic behavior of Pd-Au/C catalysts employed in the hydrodechlorination of tetrachloromethane

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Abstract This work investigates the influence of activation by microwave irradiation on the catalytic properties of Pd-Au/C_{Sibunit} catalysts in the hydrodechlorination of CCl₄. Pd and Pd-Au samples were thoroughly characterized by CO chemisorption, X-ray diffraction, TPHD and STEM, and used in gas phase hydrodechlorination of tetrachloromethane. The studies showed that homogenous Pd-Au alloys are formed more efficiently if short-time microwave activation is applied instead of conventional activation by H₂ reduction at 380 °C. These catalysts show higher activity, stability and higher selectivity towards the desired products (C1–C5 hydrocarbons) than the catalysts activated by conventional reduction in 10%H₂/Ar flow.

Keywords Microwave activation · Tetrachloromethane · Hydrodechlorination · Pd-Au alloys

Introduction

Volatile chlorinated compounds pose serious health implications, which led to the development of stringent environmental protection regulations, aiming to regulate and curbe emissions of these chemicals to the atmosphere. Nonetheless, the chemicals remain important bulk substrates for the manufacturing of polymers, pesticides and insulators, and as solvents. Hydrodechlorination (HDC) is one of the most promising, cheap and source-saving method to convert wanted chloroorganic

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compounds to desirable products. The HDC running costs relates to hydrogen consumption plus the initial investment associated with the catalyst [1]. However, the running costs are partially offset by the generation of products with commercial value and recirculation of unreacted hydrogen [1].

Catalytic HDC is commonly considered a structurally sensitive process [2, 3], where the size and electronic structure of the supported metal particles can determine HDC efficiency [4, 5]. An efficient way to modify the electronic structure is to add dopant [6–8]. Alloy formation usually affects selectivity, activity and stability of catalysts used in HDC. In the previous studies of our group, gas phase CCl_4 HDC on Pd-Au catalysts was investigated [9, 10]. The catalysts show very good activity and selectivity towards the desired products (mainly hydrocarbons) but the catalytic performance was influenced by synthesis method employed. Characterization studies revealed that the catalytic behavior of Pd-Au catalysts strongly depends on the quality of Pd-Au alloying, namely well mixed Pd-Au particles uphold very good catalytic performance, while increasing presence of small unalloyed Pd particles leads to rapid catalyst deactivation [10].

Since early works demonstrated that microwave (MW) irradiation improves bimetallic catalysts homogeneity [11], we decided to investigate the effect of MW activation treatment in CCl_4 HDC [11–13]. Thorough analysis of the published literature shows that this has not been tried before, making the investigations timely and justifiable.

Experimental part

Synthesis of the catalysts

The support was *Sibunit* carbon [14] in the form of powder (grain size between 10 and 30 μm), washed with boiling concentrated HCl, rinsed with large amounts of redistilled water and dried at 90 $^\circ\text{C}$ in an air oven for 12 h. Its nitrogen BET surface area measured with ASAP 2020 Micromeritics instrument was 271 m^2/g , BJH pore volume (from desorption branch) was 0.31 cm^3/g , and average pore diameter was 57 \AA . The cumulative micropore volume (Horvath–Kawazoe) was 0.13 cm^3/g , as estimated at relative pressure of 0.304, and the median micropore diameter was 13 \AA .

The *Sibunit*-supported Pd, Au and Pd-Au catalysts were prepared by impregnation method (or direct redox method in a case of one Pd-Au catalyst) using the required amounts of metal solutions by fixing constant loading of 2.64 wt% of active component in each catalyst. In the PdAu/ $\text{C}_{\text{Sibunit}}$ catalysts, the molar ratio of Pd:Au was 85:15.

Aqueous solutions (with volume corresponding to the total pore volume of carbon) of palladium(II) acetate (spectral purity, from *Ventron*, Karlsruhe, Germany) and/or ammonium chloroaurate (specpure, from *Johnson Matthey*, England) were used to prepare the catalysts. The details of the preparation using incipient wetness (co-) impregnation procedures have been described previously [15]. During the impregnation and preliminary drying with infrared lamp, the rotary motion of a

beaker containing the catalyst precursor ensured good mixing. Then, the solid was further dried overnight in an oven at 100 °C.

One PdAu/C_{Sibunit} catalyst was prepared from monometallic 2.0 wt% Pd/C_{Sibunit}-Gold (from an aqueous solution of ammonium chloroaurate) was deposited onto the Pd/C using the direct redox method [16]. The 2.0 wt% Pd/C_{Sibunit} catalyst was pre-reduced at 300 °C for 3 h in a special reactor in flowing 50% H₂-Ar (200 cm³/min), then purged in argon flow at 300 °C for 1 h, cooled to room temperature in Ar, and, finally, immersed in water. The solution was continuously stirred by bubbling argon, at 100 cm³/min. Then the aqueous solution of ammonium chloroaurate was slowly introduced into the reactor. The solution was stirred with bubbling argon for the next 10 min. The resulting solid was separated by filtration, washed with water, and dried in flowing argon at 120 °C for 1 h. The total added amounts of the used metals (Pd and Au) were found in the catalysts.

After preparation, catalyst precursors were divided into two parts. The first part of each material was reduced in 20% H₂-Ar flow at 380 °C for 3 h to prepare the catalyst using the conventional method (marked in the text with suffix -red). The second portions of dried catalyst precursors were subjected to MW heating at 1050 W for 10 s in a MW oven (Sharp R-941 INW, 2.45 GHz). Thus, these catalysts are termed as catalysts prepared by MW irradiation and marked with suffix-MW. All catalysts selected for investigation are listed in Table 1.

Catalysts characterization

CO chemisorption was measured at 35 °C in a static system, using a double isotherm method (ASAP 2020C instrument from Micromeritics).

Temperature-programmed hydride decomposition (TPHD) experiments were performed in a flow system, equipped with a Gow-Mac thermal conductivity detector. After reduction in 10% H₂/Ar at 380 °C for 3 h (for catalysts prepared by conventional method) or after MW treatment in 10% H₂/Ar at 130 °C for 1 h (for catalysts prepared by MW irradiation), the catalyst sample (0.20 g) was cooled to 0 °C and subjected to subsequent temperature-programmed study in 10% H₂/Ar flow, with temperature

Table 1 PdAu/C_{Sibunit} catalysts used in this work

Catalyst composition and preparation method	Treatment after preparation	Catalyst designation
Pd-Imp (2.64 wt%Pd) prepared by impregnation	Reduction in H ₂ /380 °C/3 h	Pd-Imp-red
	MW/1050 W/10 s	Pd-Imp-MW
PdAu-Imp (2.64 wt%Pd ₈₅ Au ₁₅) prepared by co-impregnation ^a	Reduction in H ₂ /380 °C/3 h	PdAu-Imp- red
	MW/1050 W/10 s	PdAu-Imp-MW
PdAu-Rdx (2.64 wt%Pd ₈₅ Au ₁₅) prepared by direct redox method	Reduction in H ₂ /380 °C/3 h	PdAu-Rdx- red
	MW/1050 W/10 s	PdAu-Rdx-MW
Au-Imp (2.64 wt%Au) prepared by impregnation	Reduction in H ₂ /380 °C/3 h	Au-Imp-red
	MW/1050 W/10 s	Au-Imp-MW

^aIn Pd_xAu_{100-x} x stands for atom % of palladium in the metal phase

ramping from 0 to 130 °C, at 8 °C/min. The aim of such experiments was to monitor hydrogen evolution in the process of β -hydride decomposition [17].

X-ray diffraction (XRD) was used to investigate the crystalline characteristics of the catalysts. Powder diffraction patterns were collected on a D5000 powder diffractometer (Bruker AXS) equipped with a LynxEye strip detector consisting of 192 diode strips, providing good resolution and fast data collection. Cu K_{α} , Ni filtered (1:20) radiation was employed, with an X-ray tube operating at 40 kV and 40 mA, and stability better than 0.01% for 8 h. The patterns were measured in continuous mode with scan rate of 0.02°/s. The diffractometer was operating in low resolution, set in Bragg–Brentano geometry with beam divergence of 1° in the scattering plane and 5° divergence perpendicularly (Soller slits). The goniometer radius was 220 mm.

Monometallic Pd, PdAu-Rdx-red and PdAu-Rdx-MW catalysts for transmission electron microscopy (TEM) measurements were prepared by dispersing the material in ethanol, placing it in an ultrasonic bath and then putting droplets of the dispersed material onto copper grids coated with a film of amorphous carbon and dried in air at room temperature. TEM observations were performed on a probe Cs-corrected S/TEM Titan 80-300 FEI microscope with EDAX EDS detector. The images were recorded in STEM-mode, using the high-angle annular dark field (HAADF) detector and an electron beam with convergence semi-angle of 24 mrad at 300 keV. HAADF is a ring-shaped detector used to collect electrons scattered at a large angle. In this situation, contrast is proportional to the square of the electric charge of the nucleus [$I(\chi) \propto Z^2$]. HAADF detector can distinguish crystallites containing elements with different Z value thanks to the difference in contrast.

Catalytic activity

The reaction of HDC of tetrachloromethane (analytical reagent from POCh, Gliwice, Poland, purity 99.9%), provided from a saturator maintained at 0 °C (± 0.1 °C) and bubbled in a flow of H₂/Ar mixture (29 cm³/min), was carried out at 90 °C and the H₂: CCl₄ ratio 14:1, in a glass flow system, as previously described [4]. The flows of H₂ and Ar (both 99.999% pure, further purified by passing through MnO/SiO₂ traps) were fixed by using mass flow controllers. The partial pressures of the reaction mixture were: CCl₄—4.3 kPa, H₂—60.5 kPa, Ar—36.5 kPa. Prior to reaction, catalyst samples were dried at 120 °C for 0.5 h in an argon flow and then reduced in 10% H₂/Ar at 380 °C for 3 h (for catalysts prepared using the conventional method) or at 100 °C for 0.5 h (for catalysts prepared using MW irradiation). The reaction was followed by gas chromatography (HP 5890 series II with FID, 5% Fluorcol/Carbopack B column (10 ft) from Supelco). In all cases, the catalyst weight of 0.2 g was used. A typical run lasted 24 h. The time on stream behavior showed the stability of the catalytic properties all of the investigated catalysts after 16–17 h of the experiment. Very small catalyst grains (10–30 μ m) allow us to neglect potential internal diffusion limitations. Blank kinetic experiments with carbon support showed very low conversions, < 0.1%.

Results and discussion

The CO chemisorption in static conditions is an effective way to determine metal dispersion in monometallic palladium and Pd-Au catalysts. All samples are characterized by a rather low level of palladium dispersion both in monometallic Pd and bimetallic samples, Table 2. Comparison of the results obtained for all catalysts clearly shows that application of MW irradiation leads to decreased metal dispersion both in monometallic and bimetallic samples. Additionally, the results are in line with XRD results (Table 2).

Temperature-programmed hydride decomposition (TPHD) was investigated to estimate the degree of Pd-Au alloy formation. Based on the literature data and our earlier experience concerning the formation and decomposition of β -PdH phase [15, 18–24], the position, shape (width, distortion), and intensity of a TPHD peak depend on different variables, among which Pd dispersion, type of support, and modifying additives play a dominant role. The introduction of gold to the palladium lattice brings about a more-or-less serious decrease in hydrogen dissolution (i.e., a lower H/Pd ratio in respective hydride phase). Simultaneously, the addition of gold to palladium increases the stability of the hydride phase, so the decomposition of this phase occurs at higher temperature. On the other hand, the stability of the hydride phase formed by small crystallites is much lower than the stability of this phase formed by large crystallites which results in shifting of the maximum TPHD profile towards lower temperatures [18, 23].

Table 2 Characterization of PdAu/C_{Sibunit} catalysts

Catalyst	From XRD	From CO chem.		TPHD results	
	d (nm)	D (%)	d (nm)	H/Pd	T _{max} (°C)
Pd-Imp-red	4.2	20	5.6	0.31	77.7
Pd-Imp-MW	9.1	12	9.2	0.35	79.0
PdAu-Imp-red	Pd 4.5 Pd ₃₀ Au ₇₀ * 2.0 Au 35.0	22	5.1	0.19	66.7
PdAu-Imp-MW	Pd ₉₀ Au ₁₀ 9.0 Au 29.0	11	9.4	0.38	86.2
PdAu-Rdx-red	Pd ₂₈ Au ₇₂ 6.4 Pd ₈₃ Au ₁₇ 3.0 Pd ₉₄ Au ₆ 13.7	13	8.8	0.25	81.4
PdAu-Rdx-MW	Pd ₃₇ Au ₆₃ 7.3 Pd ₇₅ Au ₂₅ 3.4 Pd 11.0	12	9.7	0.31	82.9
Au-Imp-red	30.0	nm		nm	
Au-Imp-MW	24.7	nm		nm	

*In Pd_XAu_Y X and Y stand for atom % of palladium and gold in the metal phase, respectively

Fig. 1 shows the TPHD profiles for all catalysts. Pd-Imp-red and Pd-Imp-MW catalysts showed a TPHD maximum at 77.7 or 79 °C, respectively. The differences between the position, shape (width, distortion), and intensity of a TPHD peak for two palladium catalysts could be explained by different Pd dispersion in both samples. Based on the literature data concerning the distinct relationship between the palladium dispersion and the stability of a hydride phase [8, 15], it seems possible that the TPHD maximum shift toward higher temperatures for the Pd-Imp-MW catalyst results from presence of > 1.6 times bigger palladium nanoparticles in Pd-Imp-MW than in the case of the palladium catalyst reduced by conventional method (Table 2).

The addition of Au to palladium catalyst shifted the maximum of TPHD profile towards higher temperatures in the case of almost all bimetallic samples. This phenomenon is in agreement with literature data [25] and could be assigned to the presence of PdAu alloys with Pd-rich hydride phase in these catalysts. Additionally, this shift in the hydride decomposition peak is accompanied by a decrease in the amount of released hydrogen (manifested as the H/Pd ratio in Table 2, Fig. 1). This phenomenon indicates that a considerable amount of gold interacts with palladium in these catalysts. Only in the case of PdAu-Imp-MW, shift of the TPHD maximum

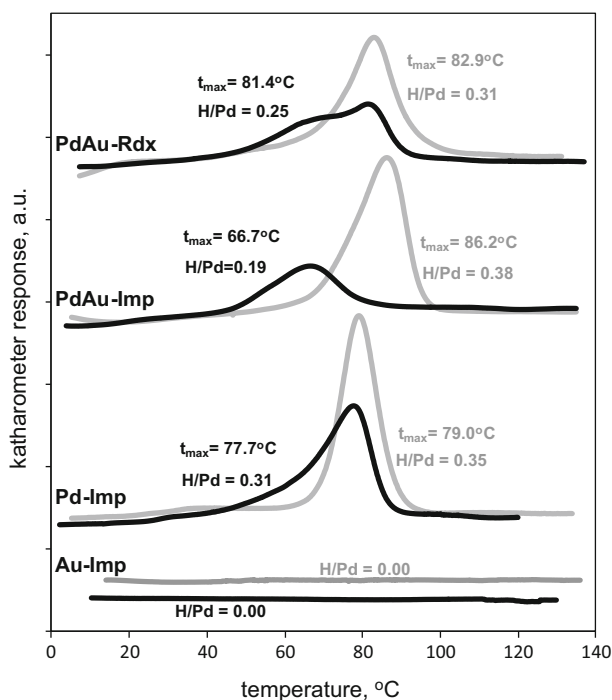


Fig. 1 Temperature-programmed hydride decomposition (TPHD) profiles of Pd-Au/C_{Sibunit} catalysts prepared by impregnation and redox method, activated by MW radiation (MW) and conventional H₂ reduction (red). TPHD runs carried out in 10% H₂/Ar flow 25 cm³/min, at temperature ramp of 8 °C/min from 0 to 130 °C. Black lines—catalysts after activation in H₂/380 °C/3 h; grey lines—catalysts after activation by MW irradiation 1050 W/10 s

is not accompanied by decrease in H/Pd ratio, what could be related with the increasing of particles size of Pd-rich metallic phase.

PdAu-Imp-red prepared using conventional impregnation and reduced in H₂/Ar mixture showed TPHD maximum shift towards lower temperature (66.7 °C). In this case, the crystallites of the palladium-rich metallic phase are almost twice smaller than in the catalyst PdAu-Imp-MW (5.1 and 9.4 nm, respectively). It means that the presence of small palladium crystallites reduces the effect of the increasing of the stability of this phase caused by the addition of gold to palladium. Simultaneously, for each pair of catalysts (catalyst reduced in hydrogen at 380 °C and catalyst prepared by MW irradiation) metal particles are larger for catalysts after treatment in MW oven. This explains the increase in the amount of released hydrogen (manifested as the H/Pd ratio in Table 2, Fig. 1) for catalysts marked with suffix – MW. On the other hand, a significant decrease of H/Pd ratio could confirm strong interaction between palladium and gold.

The TPHD profile of the PdAu-Rdx-red catalyst exhibits two maxima: a less intense one at 68 °C (related with the presence of Pd-rich phase) and more visible one at 81 °C, associated with decomposition of hydride of more Au-rich phase (Fig. 1). However, application of MW radiation for PdAu-Rdx catalyst, instead of typical reduction, leads to formation of only one TPHD maximum. This phenomenon could suggest the beneficial role of the MW radiation on a better distribution of both metal in the support, which was also confirmed by STEM measurements for PdAu-Rdx-red and PdAu-Rdx-MW (Figs. 2, 3). The elemental mapping results for the PdAu catalyst activated in 10% H₂/Ar (Fig. 2) and the catalyst activated by MW irradiation (Fig. 3) clearly show better distribution of Pd and Au particles and homogeneity of the PdAu-Rdx-MW catalyst. Our results confirmed that application of MW irradiation excites the dipoles of the molecules to intensify their rotations and vibrations, generates heat that is homogeneous and quickly dispersed within the entire reactor because of the increased friction between molecules. Uniform heating results in shorter crystallization time [26] leading to formation of homogenous PdAu alloys.

Fig. 4 shows the CCl₄ conversion after 10, 15 and 20 h of HDC reaction for all studied catalysts. Due to the ambiguity of the concept of turnover frequency (TOF) [27, 28, 30] Pd and PdAu catalyst activity is presented as overall CCl₄ conversion (Table 3).

Regardless of the activation method (conventional reduction or microwaves irradiation), monometallic Au/C catalysts show only negligible activity in CCl₄ HDC. Comparative studies of two monometallic palladium catalysts indicated that Pd/C subjected to short MW irradiation shows higher activity than the sample after 3 h of reduction in H₂/Ar flow at 380 °C (Pd-Imp-red) (Fig. 4). Higher activity and higher resistance for deactivation of Pd-Imp-MW could result from the presence of larger palladium nanoparticles than in the case of Pd-Imp-red (Tables 1, 2). This is in line with previous studies pointing at higher activity for larger particle sizes in the gas phase HDC process [4, 31, 32]. Additionally, MW activation resulted in increase of selectivity towards C1–C5 hydrocarbons (to the level 53%), the desired products of CCl₄ HDC, in comparison with the 33% selectivity obtained for Pd-Imp-red (Table 3, Fig. 4).

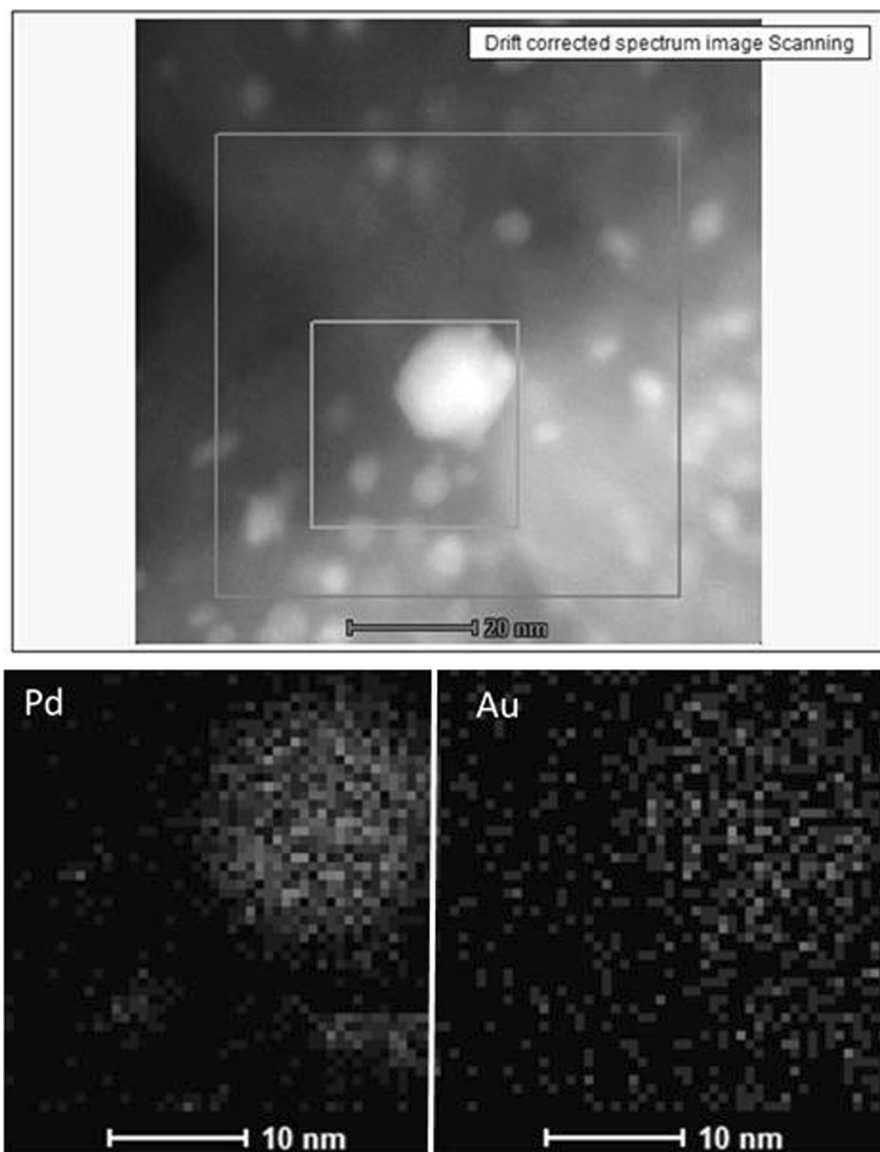


Fig. 2 STEM image and elemental mapping result of PdAu-Rdx-red catalyst

Addition of gold to palladium catalyst leads to decrease in the overall CCl_4 conversion (Fig. 4). However, the presence of Au in Pd-Au catalysts activated using MW irradiation prevents strong deactivation of palladium under the reaction conditions. Finally, after 20 h of reaction, the bimetallic system subjected to MW irradiation has shown higher activity than both monometallic Pd and bimetallic Pd-Au catalysts activated by the conventional reduction in H_2 (Fig. 4). It should be stressed here that despite lower amounts of palladium as compared to monometallic

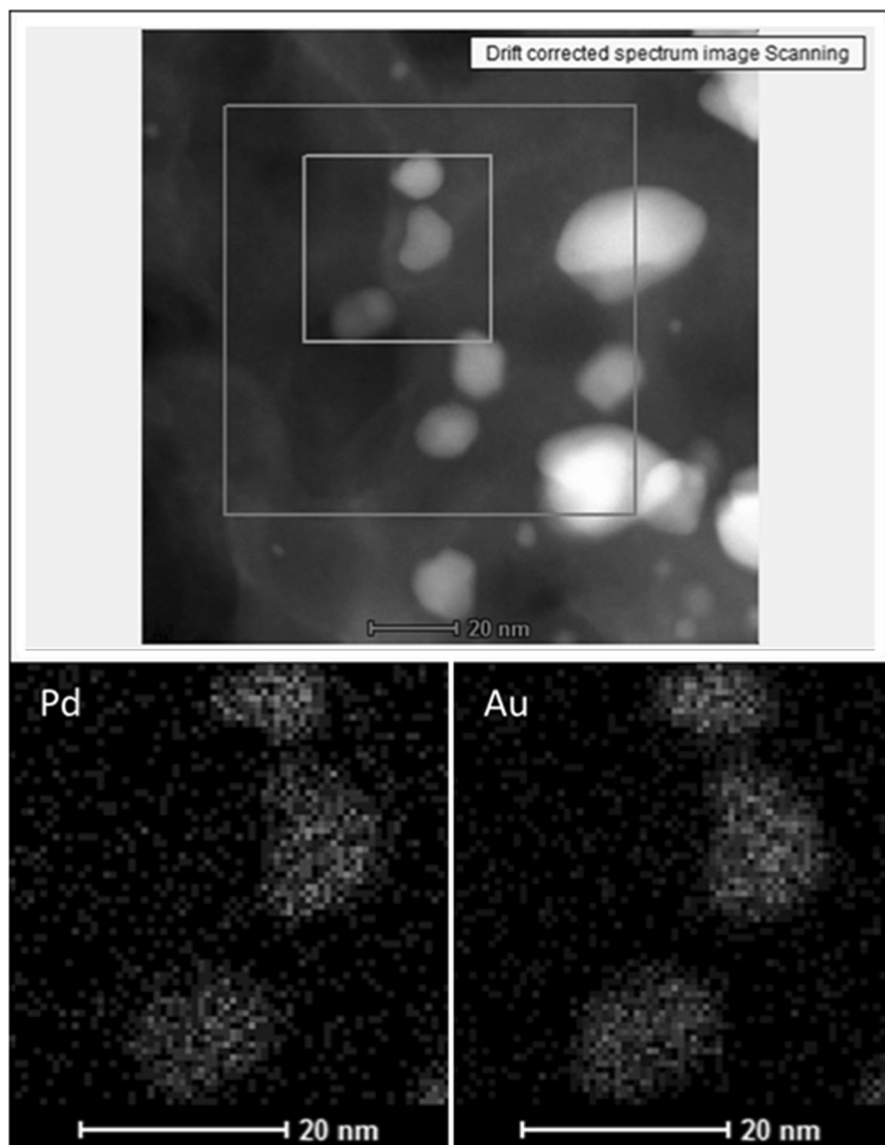


Fig. 3 STEM image and elemental mapping results of PdAu-Rdx-MW catalyst

Pd catalyst, the bimetallic systems activated by MW irradiation have shown similar activity expressed as overall conversion as monometallic Pd catalyst (Table 3), and the highest selectivity towards the desired products (C1–C5 hydrocarbons) (Fig. 5—synergistic effect). This synergistic effect on the catalytic activity depends on the surface electronic structure that can be modified by interactions between the two kinds of atoms in the Pd-Au bimetallic alloy owing to the strain and ligand effects [33]. Both effects result in changes in the width and average energy of the d-band

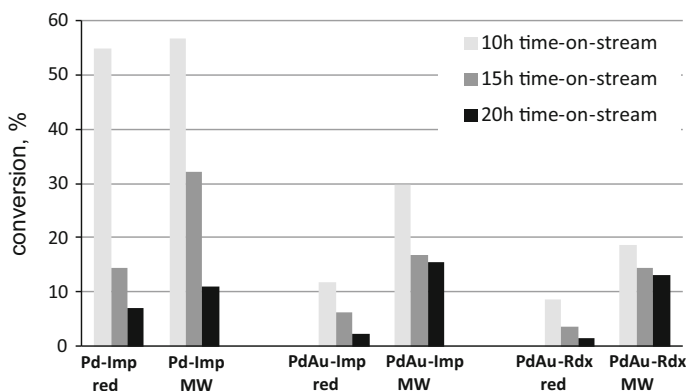


Fig. 4 Total conversion in CCl_4 hydrodechlorination, (at $90\text{ }^\circ\text{C}$, $\text{H}_2/\text{CCl}_4 = 14$, H_2/Ar mixture flow $29\text{ cm}^3/\text{min}$, weight of catalysts 0.2 g) on different prepared PdAu/ $\text{C}_{\text{Sibunit}}$ catalysts

Table 3 Hydrodechlorination of tetrachloromethane on PdAu/ $\text{C}_{\text{Sibunit}}$ catalysts

Catalyst	$\text{HdCl CCl}_4, \text{H}_2: \text{CCl}_4 = 14:1, 90\text{ }^\circ\text{C}$				$\alpha\text{ } \%$ ^a
	Selectivity (%)				
	C_{1-3}H_y ^b	$\text{C}_{>3}\text{H}_y$ ^c	CHCl_3	$\text{C}_{x>1}\text{H}_y\text{Cl}_z$ ^d	
Pd-Imp-red	32.8	0.3	35.7	31.2	6.7
Pd-Imp-MW	34.7	17.9	8.1	39.4	16.0
PdAu-Imp-red	37.2	4.7	12.0	46.1	4.4
PdAu-Imp-MW	51.6	19.9	4.4	24.2	15.6
PdAu-Rdx-red	28.0	2.9	6.5	62.5	1.5
PdAu-Rdx-MW	43.1	8.8	6.6	41.5	13.1
Au-Imp-red	100.0	0.0	0.0	0.0	< 0.1
Au-Imp-MW	100.0	0.0	0.0	0.0	< 0.1

^aFinal conversions and product selectivities after ca.20 h of time on stream

^bAggregated selectivity towards: $\text{CH}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_8$

^cAggregated selectivity towards: $\text{C}_4\text{H}_8, \text{C}_4\text{H}_{10}, \text{C}_5\text{H}_{10}$ and C_5H_{12}

^dAggregated selectivity towards: $\text{C}_2\text{Cl}_6, \text{C}_2\text{HCl}_5, \text{C}_2\text{H}_2\text{Cl}_4, \text{C}_3\text{H}_x\text{Cl}_3, 1,1,1\text{-C}_2\text{HCl}_3, \text{C}_2\text{H}_3\text{Cl}$ and $\text{C}_2\text{H}_5\text{Cl}$

that may account for the enhancement in catalytic activity [34]. The mechanisms of MW activations, which are more closely related to the molecular structures and properties than those of the conventional heating [35], greatly facilitates Pd-Au interaction and plays a beneficial role in formation of homogeneous alloys. Furthermore, comparison of activity of our bimetallic PdAu catalysts with other palladium-gold catalysts in CCl_4 HDC clearly showed that the catalytic properties of PdAu-Rdx-MW are better or comparable to the activity of previously investigated PdAu catalysts in the same process [9, 10].

Fig. 6 shows the XRD results obtained for the activated (thick line) and spent (thin line) PdAu/C catalysts. Independently on the activation procedure, Pd-Au alloying is far from being perfect in the case of all bimetallic samples. The presence of separate crystalline phase of gold in PdAu-Imp-red and PdAu-Imp-MW catalysts might suggest that separation between deposited gold and palladium material is so substantial that a noticeable alloying during the activation by conventional reduction or MW irradiation can occur only to a moderate extent.

XRD profiles of fresh PdAu-Rdx catalysts and PdAu-Imp catalysts (both -MW and -red) are very different, but the difference in catalytic performance is no so marked (Fig. 4). This phenomenon could be the consequence of an application of different synthesis method of the catalysts. Based on our earlier experience, conventional co-impregnation leads to the formation separately existing palladium and big gold particles on carbon support (unsatisfactory mixing of both metals is observed) [8, 10]. On the other hand, application of direct redox method (described in details by Barbier, et al. [36] usually leads to formation of lower particles size of dopant (Au in our case) and better mixing of dopant and “parent” metal (Pd in our case). However, besides of well visible in XRD profiles Pd-Au phases, both synthesis methods lead to formation of very low crystallites of Pd-Au alloys (< 2 nm). Hence, we suppose that well dispersed Pd-Au phase plays the significant role in catalytic behavior of our catalysts. Due to the fact that the amount of this fine crystalline phase is comparable in the PdAu-Rdx and PdAu-Imp catalysts, so the differences in catalytic properties of both catalysts are not spectacular. Homogenization of bimetallic particles by microwave irradiation results in further improvement of catalytic properties, which is accompanied by some increase in the size of metallic particles.

For all tested catalysts, metal particles size obtained from XRD measurements are higher than from CO chemisorption (Table 2). This difference between XRD and chemisorption results indicates that the part of the Pd-Au alloy phase is in the fine crystalline form, invisible in XRD profiles, however, having expanded surface increases the chemisorption result. The presence of very low Pd-Au particles was

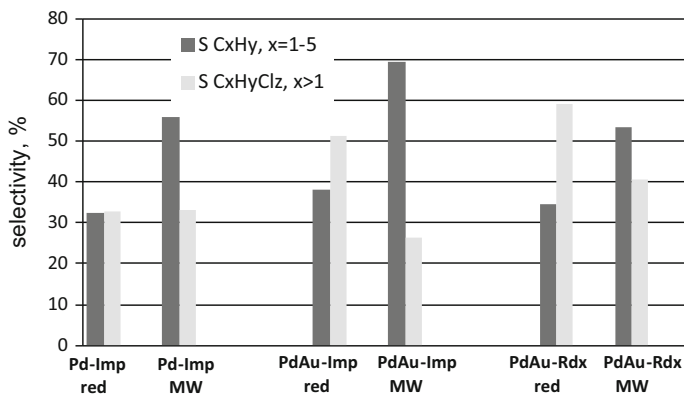


Fig. 5 Final selectivity after 20 h time-on-stream in CCl_4 hydrodechlorination (at 90°C , $\text{H}_2/\text{CCl}_4 = 14$, H_2/Ar mixture flow $29\text{ cm}^3/\text{min}$, weight of catalysts 0.2 g) on different prepared PdAu/C_{Sibunit} catalysts

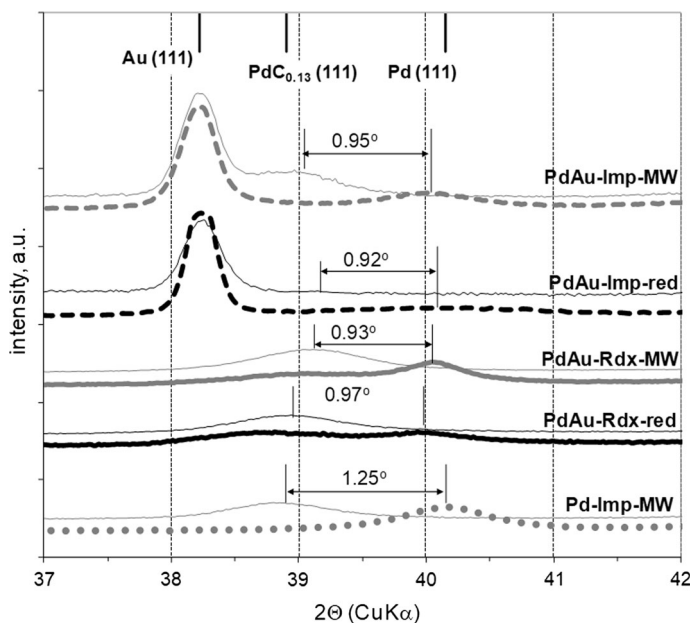


Fig. 6 XRD profiles of Pd and PdAu/C_{Sibunit} catalysts after activation and catalytic reaction. Positions of (111) reflections of *fcc* phases of Au, Pd and PdC_{0.13} are marked. Black lines—catalysts after conventional activation by reduction in H₂/380 °C/3 h; grey lines—catalysts after activation by microwave irradiation 1050 W/10 s; thick lines—catalysts after activation; thin lines—catalysts after HdCl of CCl₄

also confirmed by STEM results (Figs. 2, 3). It could suggest that the presence of very small, uniform Pd-Au alloy particles affects the catalytic behavior of Pd-Au systems.

Additionally, the comparison of XRD spectra obtained for activated (thick line) and spent Pd-Au samples (thin line) provides additional information about the composition of active phase in PdAu/C catalysts.

Formation of palladium-carbon solution (PdC_x) under HDC conditions for all bimetallic samples (Fig. 6) was detected. Pd-rich Pd-Au alloys (visible in XRD profiles) are sensitive to carbiding under reaction conditions. CCl₄ HDC led to the disappearance of Pd (111) diffraction peak and appearance of a new one—corresponding to the presence of PdC_x(111) solution, where $x \leq 0.13$ [37]. However, smaller distance between the position of Pd (111) diffraction peak (for all PdAu activated samples) and PdC_x peak (for spent catalysts) than that obtained for monometallic palladium catalyst could indicate partial alloying of palladium and gold in bimetallic catalysts. The presence of the Pd(111) diffraction peak and PdC_x (111) for spent samples (Fig. 6), confirm the presence of palladium species sensitive to carbiding. However, application of MW activation in the case of PdAu-Rdx-MW results in better alloying, which is manifested as decrease in the carbiding effect (Fig. 6).

As shown in Fig. 4, all tested catalysts undergo significant deactivation during the hydrodechlorination of CCl_4 , but this deactivation is the smallest in the case of bimetallic PdAu catalysts after MW irradiation. This deactivation most probably results from the carburizing of the Pd-rich metallic active phase. XRD studies of post-reaction catalysts showed a significant phase transformation for all Pd and PdAu catalysts. A considerable shift of XRD profiles toward lower diffraction angles (Fig. 6) suggests carbon incorporation into Pd/PdAu bulk. Evidently, bare C1 species (from the CCl_4 molecule after stripping off all chlorine atoms) enter Pd (or Pd-rich phase) bulk before being hydrogenated to methane. This effect was observed earlier for monometallic Pd/ $\text{C}_{\text{Sibunit}}$ catalysts subjected to CCl_4 hydrodechlorination at 363 K [10], but not noticed for Pd–Au/ $\text{C}_{\text{Sibunit}}$ catalysts, characterized by very good homogeneity of the Pd–Au alloy. Therefore, the extent of carbon incorporation was supposed to be a measure of Pd–Au nonhomogeneity as carbon, analogously to hydrogen, should be less soluble in well-mixed Pd–Au alloys than in pure Pd. When palladium dissolves carbon, its lattice constant increases from 0.389 to 0.399 nm [37], resulting in a downward shift in the XRD spectrum. For tested monometallic Pd catalysts this shift in 2θ value was 1.25° and for Pd–Au catalysts in the range $0.92\text{--}0.97^\circ$. This means that there is some mixing of gold and palladium in our PdAu catalysts, but the homogeneity of the PdAu alloy is nonsufficient. Thus, the catalysts, before its practical application still require optimization in terms of both active phase composition and its homogeneity.

Conclusions

The investigation performed within the scope of this work clearly shows that, independently on the synthesis way (impregnation or redox method), application of short-time MW activation is a more efficient method of Pd–Au alloy formation (or substantial degree of Pd–Au mixing on carbon support) than conventional activation by H_2 reduction at 380 °C. Pd–Au alloys subjected to MW irradiation show higher stability and higher selectivity towards the desired products (C1–C5 hydrocarbons) as compared to catalysts subjected to conventional reduction in 10% H_2/Ar flow.

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