

Pd–Au/Sibunit Carbon Catalysts: Characterization and Catalytic Activity in Hydrodechlorination of Dichlorodifluoromethane (CFC-12)

M. Bonarowska,* J. Pielaszek,* V. A. Semikolenov,† and Z. Karpiński*,‡¹

*Department of Catalysis on Metals, Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, PL-01224 Warsaw, Poland;

†Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Prosp. Akad. Lavrentieva 5, Novosibirsk 630090, Russia;

and ‡Faculty of Mathematics and Natural Sciences, Cardinal Stefan Wyszyński University, ul. Dewajtis 5, PL-01815 Warszawa, Poland

Received February 14, 2002; revised April 15, 2002; accepted April 18, 2002

A series of Sibunit carbon-supported palladium–gold catalysts prepared by different methods (wet and incipient wetness impregnation and direct redox reaction) were characterized by various techniques and investigated in the reaction of dichlorodifluoromethane with dihydrogen. The direct redox method resulted in a higher degree of Pd–Au alloying than the impregnation procedures. A temperature-programmed hydride decomposition (TPHD) study appears to be a very promising technique for characterization of Pd–Au bimetal. A clear correlation between TPHD spectra and X-ray diffraction data for Pd–Au catalysts allows proposal of the former technique for diagnosing the quality of Pd–Au alloying. The selectivity toward difluoromethane (desired reaction product) was increased upon introducing gold to palladium; however, this enhancement depended very much on the degree of Pd–Au alloying. For the catalysts prepared by the direct redox reaction method the selectivity for difluoromethane increased from <70 (for Pd) to nearly 90% for bimetallic samples at the highest temperature of screening, 180°C. Such a high selectivity enhancement was not observed for Pd–Au/C catalysts prepared by impregnation methods, which showed a lesser degree of Pd–Au alloying. During the reaction of dichlorodifluoromethane hydrodechlorination substantial amounts of carbon dissolve in the bulk of the palladium (or Pd-rich alloy) phase. Independent studies with a model Pd/SiO₂ catalyst showed that this carbon originates from the CFC molecule, not from the carbon support. It is interesting that a massive carbiding of palladium takes place at a very early stage of the reaction, when also the most important changes in catalytic behavior occur. Thus, it may be speculated that the surface state of the working catalyst must be correlated with the extent of the bulk carbiding. An easy removal of carbon from palladium by hydrogen at the reaction temperature confirms our earlier idea that methane formation from dichlorodifluoromethane may occur via hydrogenation of C₁ surface species. © 2002 Elsevier Science (USA)

Key Words: CCl₂F₂ hydrodechlorination; Sibunit carbon-supported Pd–Au catalysts; temperature-programmed hydride decomposition (TPHD) in assessing alloy homogeneity; selectivity to CH₂F₂ (HFC-32); effect of PdC_{0.13} formation.

1. INTRODUCTION

The Montreal Protocol (1987), followed by a number of important amendments, declared the necessity of immediately phasing out the production of chlorofluorocarbons (CFCs), which had been implicated in depletion of the ozone layer. This provided two challenges for scientists: (i) how to safely dispose of existing CFCs in a manner which is environmentally and economically acceptable, and (ii) how to obtain suitable replacements for these CFCs in their numerous applications (air conditioning, refrigerators, foam blowing agents, etc.) (1, 2). As a consequence, more intensive work on catalytic hydrodechlorination of CFCs was launched in the early 1990s. In the presence of hydrogen and an appropriate catalyst, CFCs can be converted into HCFCs (hydrochlorofluorocarbons) or HFCs (hydrofluorocarbons), regarded as benign CFCs replacements. However, other (less desirable) products are also formed. Apart from unavoidable HCl formation, a part of the CFC molecules may also be fully hydrodehalogenated, giving much less valuable saturated hydrocarbons (e.g., methane). Palladium was found to be unique among the catalytic metals for its activity and, especially, selectivity in this process, and as a consequence most fundamental work was done with this metal (3–17). Recent patents and scientific literature deal with palladium catalysts modified by doping other elements, among which gold is often mentioned (18–20). Such doping improves the selectivity for partial hydrodehalogenation (19, 20).

The role of support for monometallic palladium or bimetallic Pd-based systems seems also very important. Carbon is the support of industrial choice for a number of reasons, including high specific surface area and stability against corrosion by halogen-containing species. Research with the use of other supports, such as silica or alumina, serves mainly for short-term model studies, when the functioning of various metallic (active) phases is tested. Our previous results on supported Pd–Au in catalytic hydrodechlorination can be summarized as follows. Initial comparative studies with MgF₂- and C-supported Pd–Au catalysts

¹ To whom correspondence should be addressed. Fax: 48-22-6325276. E-mail: zk@ichf.edu.pl.

(21, 22) have already indicated that an intimate contact between Pd and Au is essential for improving the selectivity to CH₂F₂. Those studies also showed that a considerable extent of Pd–Au mixing was achieved in the case of MgF₂-supported Pd–Au catalysts whereas it was not the case for Pd–Au/C (22). Since those alloy catalysts had been prepared by impregnation, further progress in this research could be made only by application of another catalyst's preparation technique which would lead to a better Pd–Au alloying. Therefore, we decided to use direct redox reaction for preparation of (model) silica-supported Pd–Au catalysts. This method, developed by Barbier (23), results in a reductive deposition of gold onto pre-reduced palladium particles. In effect, a significant Pd–Au alloying was achieved in reduced bimetallic catalysts (24), which, furthermore, appeared much more selective toward CH₂F₂ formation than monometallic Pd/SiO₂ (a CH₂F₂ selectivity increase from ~50 to ~95% (25)). Such promising results led us to the replacement of silica (which is vulnerable to HF, an unavoidable hydrodehalogenation product) by carbon. Because the purity of active carbon support seemed crucial for the catalytic performance of Pd/C in CCl₂F₂ hydrodechlorination (7), we used Norit carbon which was pre-treated in helium at a very high temperature (1800°C) to remove a vast majority of impurities (26). The same pre-treated carbon was used in our previous study (22), when our failure to obtain well-mixed (and, hence, very selective) Pd–Au/C catalysts had to be related to the weakness of the incipient wetness coimpregnation method in preparation of supported bimetallic catalysts. Accordingly, our further studies concerned the catalytic behavior of Pd–Au/Norit carbon catalysts prepared by the direct redox reaction method (27). For those catalysts the selectivity for difluoromethane increased from ~72 (for Pd) to 86% (for bimetallic samples) at the highest temperature of catalysts' screening, i.e., 180°C. Such a high-selectivity improvement encouraged us to check how the direct redox method works for preparation of Pd–Au alloys supported on active carbons, characterized by higher surface areas and a more developed pore structure. Thus, a number of Pd–Au catalysts supported on Sibunit carbon (product commercialized by the Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences) were prepared using the direct redox reaction method and compared with their analogues produced by various impregnation techniques.

2. EXPERIMENTAL

2.1. Catalysts Preparation and Characterization

Different series of bimetallic Pd–Au/C catalysts were prepared using impregnation and direct redox method techniques. The latter method is driven by the difference in standard potentials of two metals, i.e., it profits from the fact that

noble metal ions are reduced by (and deposited onto) zerovalent species of less noble metals (23). The support was Sibunit carbon, washed with a boiling mixture of concentrated HCl and HF. Then, after a subsequent purge with a large amounts of redistilled water and drying in an air oven, the support was stored in a glass-stoppered bottle kept in a desiccator. Its nitrogen BET surface area measured with a ASAP 2010 Micromeritics instrument was 387 m²/g, BJH pore volume (from desorption branch) was 0.75 cm³/g, and average pore diameter was ~7 nm. The cumulative micropore volume (Horvath–Kawazoe) was 0.11 cm³/g, as estimated at relative pressure 0.012, and the median micropore diameter was 0.59 nm.

In all preparations of Pd/C and Pd–Au/C, catalysts palladium dichloride (analytical reagent from POCh, Gliwice, Poland) and ammonium chloroaurate (specpure from Johnson Matthey, England) were used. The 3 wt% Pd/C catalyst was prepared by impregnation of the activated carbon with an aqueous solution of palladium dichloride (acidified with HCl; Cl⁻/Pd²⁺ = 3.89) using the incipient wetness technique. The 1.5 wt% Pd/C catalyst was prepared by wet impregnation. After impregnation and drying, the resulting solids were transferred to glass-stoppered bottles and kept in a desiccator.

One series of Pd–Au/C catalysts was prepared from the monometallic 3 wt% Pd/C. Gold (from an aqueous solution of ammonium chloroaurate) was deposited onto the Pd/C using the direct redox method (27). The 3 wt% Pd/C catalyst was pre-reduced at 300°C for 3 h in a special reactor in flowing 67% H₂–Ar (300 cm³/min), then purged in an argon flow at 300°C for 1 h, cooled to room temperature in Ar, and, finally, immersed in de-aerated redistilled water. The solution was continuously stirred by bubbling argon, at 200 cm³/min. Then, an aqueous solution of ammonium chloroaurate 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 60–65°C for 11 h. During preparation of Pd₈₀Au₂₀/C and Pd₇₀Au₃₀/C the total administered amounts of used metals (Pd and Au) were found in the catalysts. However, because the filtrates of Pd₆₀Au₄₀/C and Pd₅₀Au₅₀/C contained small amounts of dissolved metals (Pd and, especially, Au), the actual concentration in these catalysts had to be determined by atomic absorption.

Other Pd–Au/Sibunit catalysts were prepared by either wet coimpregnation or introduction of gold into 3 wt% Pd/C by incipient wetness impregnation. All the catalysts prepared in this work are listed in Table 1.

The prepared catalysts, after pretreatment identical to that used prior to the reaction tests (see next subsection), were characterized by H₂ chemisorption, temperature-programmed (palladium) hydride decomposition (TPHD), and XRD.

TABLE 1

Sibunit Carbon-Supported Pd–Au Catalysts Used in This Work

Catalyst composition	Preparation method ^b	Metal dispersion ^c (H/Pd)	H/Pd from TPHD ^d
3 wt% Pd/C	Incipient wetness impregnation	0.136	0.45
4.3 wt% Pd80Au20/C ^a	Direct redox ^e	0.046	0.38
5.2 wt% Pd70Au30/C ^a	As above	0.034	0.34
6.4 wt% Pd60Au40/C ^a	As above	0.044	0.23
8.0 wt% Pd50Au50/C ^a	As above	0.061	0.25
6.5 wt% Pd60Au40/C ^a	Incipient wetness impregnation ^e	0.076	0.24
1.5 wt% Pd/C	Wet impregnation	0.076	0.38
2.2 wt% Pd80Au20/C ^a	Wet coimpregnation	0.064	0.32
3.2 wt% Pd60Au40/C ^a	Wet coimpregnation	0.061	0.31
2.7 wt% Pd70Au30/C ^a	Direct redox ^f	0.031	0.29

^a In the notation PdX AuY, X, and Y denote atomic percentages of Pd and Au.

^b For further details see text.

^c From hydrogen chemisorption at 70°C.

^d From the decomposition of a Pd(Au)H phase; see text.

^e Prepared from 3 wt% Pd/C.

^f Prepared from 1.5 wt% Pd/C.

Hydrogen chemisorption experiments were performed in a pulse-flow system, as described elsewhere (24, 28). The thermal conductivity detector (TCD, Gow–Mac) was kept at 0°C, providing constant response during each run. All the gases used (H₂, Ar, and 10% H₂/Ar mixture) were purified by passing through drying traps, with final purification over MnO/SiO₂. Hydrogen chemisorption was carried out at 70°C. After H₂ chemisorption, the samples were cooled to ~20°C in H₂/Ar flow (to be transformed into respective Pd(Au)H phases). Next, they were heated to ~150°C, at the temperature ramp of 8°C/min. Such runs, called temperature-programmed hydride decomposition (TPHD), carried out in 10% H₂/Ar mixture would reveal how the stability and composition of the β-hydride phase is dependent on gold introduction to Pd/C (24).

XRD experiments were performed on a standard Rigaku–Denki diffractometer using Ni-filtered CuKα radiation. Several samples of Pd–Au/SiO₂ catalysts (after preparation and reaction) were scanned by a step-by-step technique, at 2θ intervals of 0.05° and a recording time of 10 s for each step.

2.2. Catalytic Measurements

Prior to reaction, all catalysts were reduced in flowing 10% H₂/He (25 cm³/min), ramping the temperature from 20 to 400°C (at 8°C/min), and kept at 400°C for 3 h.

The reaction of dichlorodifluoromethane (CFC-12 from Galco S.A., Belgium; purity 99.9%) with hydrogen (purified over MnO/SiO₂) was conducted in a glass flow system under atmospheric pressure at 160, 170, and 180°C. Feed partial

pressures were 15 and 150 Torr (1 Torr = 133.3 N m⁻²) of dichlorodifluoromethane and hydrogen, respectively, in a helium carrier (also purified by MnO/SiO₂). The flow of all gases was metered by MKS mass flow controllers and the overall flow rate of the reactant gas mixture was 100 cm³/min. The reaction mixture leaving the reactor was introduced via stainless steel tubing onto a gas chromatograph (HP 5890 series II with FID) and analyzed using a 5% Fluorcol/Carbopack B column (10 ft) from Supelco. The results of GC analysis were elaborated using HP Chemstation.

In order to adequately establish changes in the catalytic behavior, a typical reaction run lasted ~24 h. The first stage of the reaction involved a 17- to 18-h period at 180°C. During this time the catalyst performance stabilized in a flow of the reaction mixture, as established by analyzing the reacting gas at 30-min intervals. After the first four or five analyses, all catalyst performance was found to be quite stabilized and changed only very insignificantly during next 15–16 h of time-on-stream (TOS). Steady state was defined as a change in conversion of less than 0.1% at a 300-min TOS interval and a change in product selectivities of less than 1% at a 300-min TOS. Accordingly, after 17–18 h of time-on-stream, the reaction temperature was lowered, in 10° steps, and the next experimental points were collected. After catalyst screening at the lowest reaction temperature (160°C) the catalyst performance was tested again at 180°C, giving, in most cases, a good return to the initial behavior at this temperature. To avoid secondary reactions, the overall conversion was kept low, i.e., below 5%, at the highest temperature of catalyst screening.

3. RESULTS AND DISCUSSION

3.1. Characterization of Pd–Au/Sibunit Catalysts

Sibunit is a family consisting of a microcrystalline graphitelike form of carbons produced by pyrolysis of C₁–C₄ hydrocarbons at 850–950°C (29,30), obtainable from the Institute of Catalysis of RAS in Novosibirsk. It is characterized by large surface area, high purity, and chemical stability. That is why it has already been selected as a promising support for palladium-based catalysts operating in hydrodechlorination (31).

Figure 1 shows XRD profiles in the vicinity of the (111) reflection for reduced 3 wt% Pd/C and those Pd–Au/C catalysts which were prepared by the direct redox reaction method. The background from the Sibunit carbon is very flat in this range of diffraction angle. The profile of the palladium catalyst appeared quite diffused; the mean crystallite size estimated from the profile broadening was ~4 nm. Palladium dispersion, as derived from hydrogen chemisorption data (H/Pd = 0.136; Table 1) appeared low compared to that judged from XRD profile broadening, 0.28 (= 1.12/4 nm, according to (32)). This difference would result from Pd–C interactions, which occur as an effect of

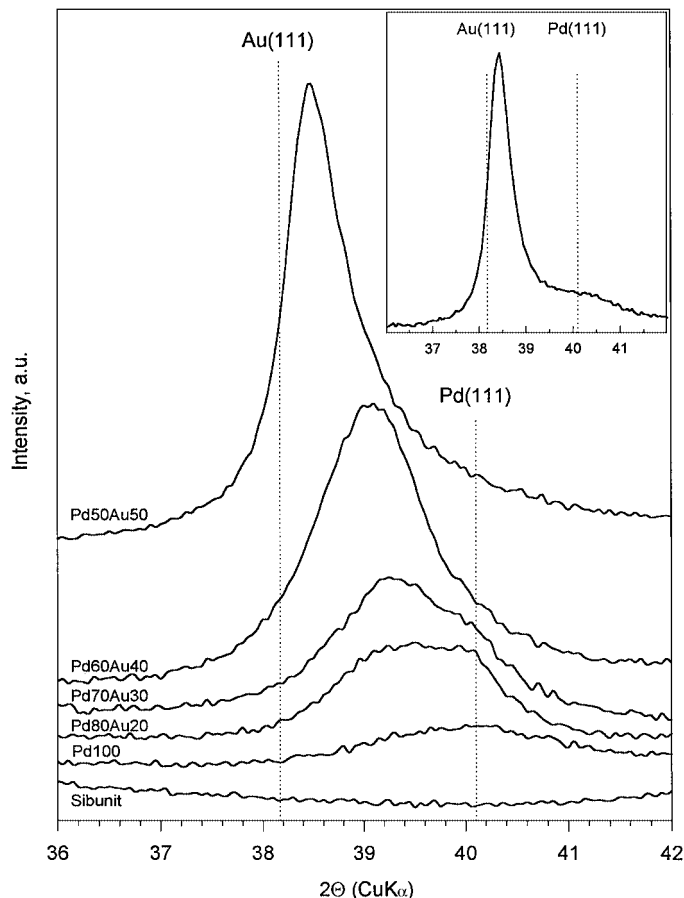


FIG. 1. XRD profiles of prereduced Sibunit-supported Pd–Au catalysts prepared by direct redox reaction. Inset: XRD from Pd60Au40/Sibunit prepared by incipient wetness impregnation. For catalyst code see Table 1. Positions of (111) reflections of fcc phases of palladium and gold are marked.

reduction in H₂ of Pd/C catalysts (33). Nevertheless, the H/Pd ratio from chemisorption studies (Table 2) as well as the crystallite size of Pd or Pd-rich phase from XRD profile broadening of reduced Pd–Au/C catalysts (Fig. 2) indicate that introduction of gold to Pd/C by the direct redox method does not lead to an appreciable decrease in metal dispersion.

XRD profiles furnish important results as to the composition of bimetallic Pd–Au particles supported on Sibunit (Fig. 1). It is seen that the best, although probably not perfect, alloying was achieved in the case of catalyst Pd60Au40/C, where a rather symmetric diffraction profile was obtained. For the remaining Pd–Au catalysts a distinct peak asymmetry is distinguished: the right branches of all profiles are noticeably distorted by the presence of Pd-richer phases. Decomposition of the (111) reflection profile into Pearson VII-type functions (not shown) allowed us to estimate the presence of various Pd–Au phases (Table 2). It should be stressed that the Pd60Au40/C catalyst which had been prepared by incipient wetness impregnation of 3 wt%

Pd/C displayed much lower degree of Pd–Au alloying than all the samples prepared by the direct redox reaction (Fig. 1, inset, and Table 2).

Temperature-programmed hydride decomposition (TPHD) has already been proposed as a suitable method for diagnosing the degree of alloying of bimetallic Pd-based catalysts (24, 34). In the majority of cases, introduction of another element to the palladium lattice (alloying) brings about a more-or-less serious decrease in hydrogen dissolution (i.e., a lower H/Pd ratio in respective hydride phase). Present work makes use of this observation. Figure 2 shows TPHD profiles from the catalysts prepared by the redox method. As seen, introduction of gold by the redox method moves gradually the principal TPHD peak toward higher temperatures. Such a shift is consistent with an earlier

TABLE 2

Metal-Phase Composition in Sibunit Carbon-Supported Pd–Au Catalysts: Comparison of TPHD with XRD data

Catalyst composition	Pd–Au phase composition	
	From TPHD	From XRD ^b
3 wt% Pd/C	Possibly bimodal distribution, fraction of lesser dispersion only slightly marked	Pd, crystallite size ~4 nm ^d
4.3 wt% Pd80Au20/C ^a	“Pd-like” + intermediary Pd–Au	<u>Pd54Au46</u> , <u>Pd94Au6</u>
5.2 wt% Pd70Au30/C ^a	Pd-like + intermediary Pd–Au	<u>Pd55Au45</u> , Pd96Au4
6.4 wt% Pd60Au40/C ^a	Pd-like + gold-richer Pd–Au + one “in-between” Pd–Au phase	<u>Pd34Au66</u> , <u>Pd56Au44</u> , Pd
8.0 wt% Pd50Au50/C ^a	Pd-like + one intermediary Pd–Au phase ^c	<u>Pd15Au85</u> , Pd34Au66, Pd94Au6
6.5 wt% Pd60Au40/C ^a	Pd-like phase ^c	<u>Pd13Au87</u> , Pd
1.5 wt% Pd/C ^a	Evident bimodal distribution; the ratio of low-to-high dispersed phase ~1:4	Two crystallite fractions: ~4 nm (prevailing) and ~20 nm ^d
2.2 wt% Pd80Au20/C ^a	Pd-like phase ^c	<u>Pd8Au92</u> , dispersed Pd
3.2 wt% Pd60Au40/C ^a	Pd-like phase ^c	<u>Au phase</u> , dispersed Pd
2.7 wt% Pd70Au30/C ^a	Similar to 1.5 t% Pd/C + one intermediary Pd–Au phase	Pd34Au66, Pd

^a In the notation Pd_XAu_Y, X and Y denote atomic percentages of Pd and Au. See Table 1 for other details.

^b From XRD study of reduced catalysts (Figs. 1 and 3). Atomic composition of detected Pd_XAu_Y phases based on the lattice parameter, calculated from (111) reflection. The presence of a variety of Pd–Au phases estimated from XRD profile decomposition into Pearson VII-type functions (not shown). The most abundant phases are underlined.

^c Gold-rich phases not noticed since they do not produce hydrides.

^d Palladium crystallite size from the broadening of (111) reflection (from Scherrer formula).

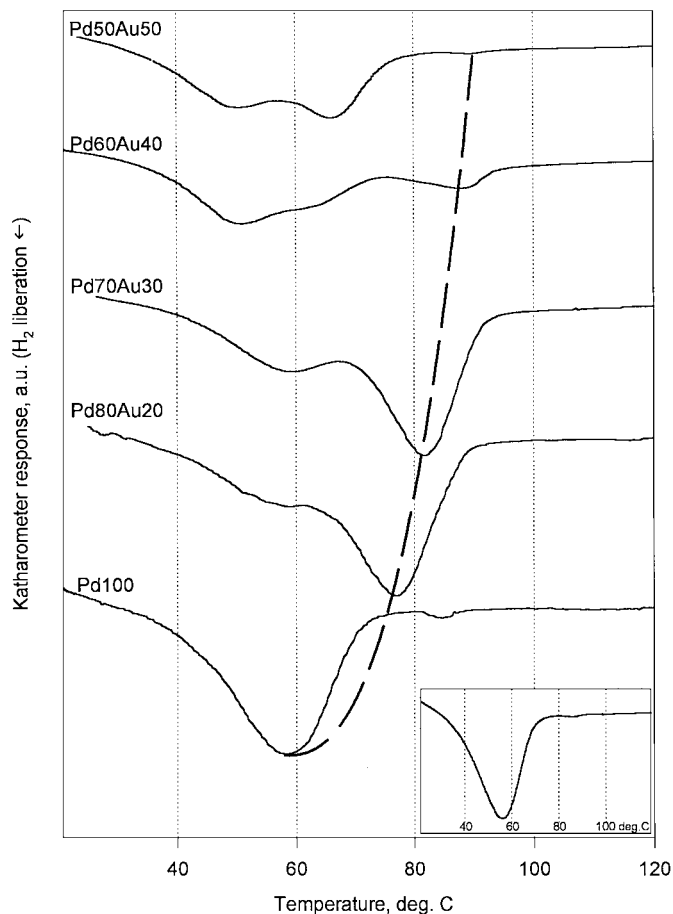


FIG. 2. Temperature-programmed hydride decomposition (TPHD) profiles of Sibunit-supported Pd–Au catalysts prepared by direct redox reaction from 3 wt% Pd/C. Inset: TPHD of Pd60Au40/Sibunit prepared by incipient wetness impregnation.

observation of Ziemecki *et al.* (35), who found that a commercial Pd–Au powder (of 20 wt% Pd) showed a TPHD peak at the temperature $\sim 35^\circ\text{C}$, higher than that exhibited for a physical mixture of Pd and Au powders. Our additional observation that the 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 1) indicates that a considerable amount of gold interacts with palladium in these catalysts (35). Nevertheless, the presence of a residual desorption peak at $\sim 60^\circ\text{C}$ shows that some palladium material is still not much influenced by gold. The inset in Fig. 2 presents, similarly as in Fig. 1, respective data for the Pd60Au40/C prepared by incipient wetness impregnation. The TPHD trace from this catalyst shows only decomposition of a Pd hydride phase. The presence of a gold-rich Pd–Au phase detected by XRD (Fig. 1, inset) cannot be observed by TPHD because gold-richer Pd–Au alloys do not form hydrides (36).

Figure 3 presents a closer comparison of TPHD and XRD data for a series of Pd–Au/Sibunit catalysts prepared by wet coimpregnation. Both characterization methods lead to the same conclusion: the extent of alloying in these catalyst is inadequate. The respective characteristics of the palladium-only phase are well recognized in both parts of Fig. 3. It is interesting that the TPHD trace from 1.5 wt% Pd/C is composed of two decomposition peaks with minima at ~ 65 and $\sim 90^\circ\text{C}$. Our earlier experiments with variously dispersed Pd/SiO₂ catalysts (24) suggest that the “high-temperature” peak must be associated with hydride decomposition from a poorly dispersed Pd phase. The conclusion about the presence of two (at least) Pd phases, differing in metal particle size, is strongly supported by the respective XRD data (left section of Fig. 3), where a complex (111) reflection of Pd can

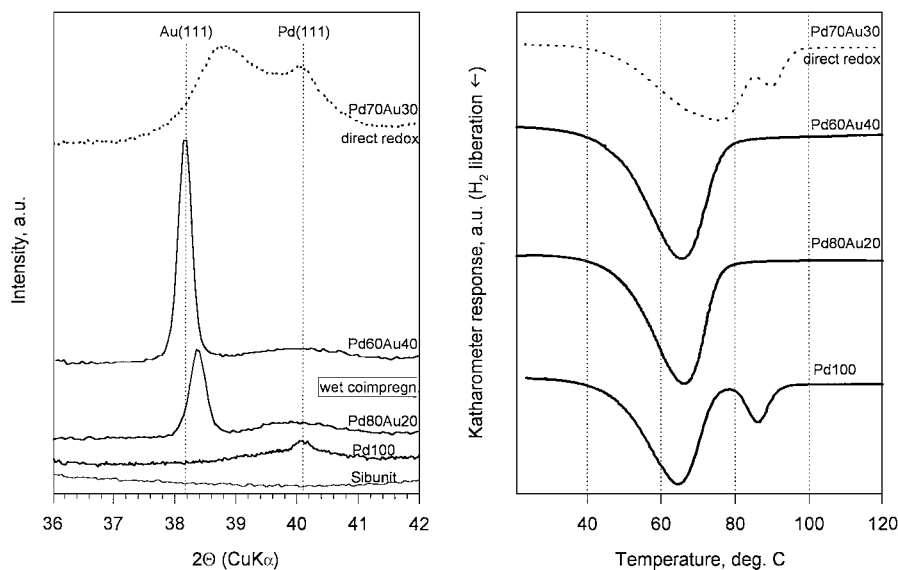


FIG. 3. Characterization of Sibunit-supported Pd–Au catalysts prepared from 1.5 wt% Pd/C by wet impregnation and direct redox methods. (Left) XRD; (right) TPHD. Broken lines denote the behavior of the catalyst prepared by the direct redox method.

be decomposed into two respective peaks, manifesting the presence of two crystallite size fractions: ~ 4 and ~ 20 nm (from XRD line broadening).

Summing up, the XRD and TPHD method applied in probing the degree of alloying in Sibunit-supported Pd–Au catalysts gave well-matched results. It is obvious that TPHD cannot detect gold-richer Pd–Au phases because they do not form β -hydride. On the other hand, application of this method in the case of probing of low-metal-loaded and more dispersed bimetallic systems may be advantageous. In such cases, XRD would give uncertain results, because of rather low signal-to-noise ratio.

3.2. Catalytic Behavior of Pd–Au/Sibunit in CCl₂F₂ Hydrodechlorination

Catalytic screening of all Pd–Au/C catalysts in CCl₂F₂ hydrodechlorination showed that stable conversions are achieved in a short time-on-stream (<1 h). It is exemplified in Fig. 4, where also product selectivities are shown to be quickly established at a constant level. The results of catalytic tests at steady state are presented in Table 3. Methane, difluoromethane (HFC-32), and, to a much lesser extent, chlorodifluoromethane (HCFC-22) were found to be the predominant products. The first two compounds make up usually more than 97% of all products. A noticeable exception is the 3 wt% Pd/C, for which the remaining products (mainly CHClH₂ and C₂H₆, CClF₃, CHF₃, and CHF₂CH₂F) make up 4.2% of all products at 180°C. It was observed that the selectivity to CH₄ was always lower at the very beginning of the reaction than at steady state. However, one has to admit that the total signal from the first

two analyses (FID detection) was somewhat reduced compared to that observed in subsequent GC analyses. This indicates that a part of the carbon material is missing in products, so it must be retained by the catalyst. Although a more quantitative treatment of this phenomenon is difficult (because the overall conversion was intentionally kept very low) it is considered that at least a part of “missing” carbon must be incorporated into palladium lattice. Such a thought is in line with earlier results (6, 7, 11, 17, 22, 25, 27, 34, 37) and is further discussed in more detail (*vide infra*).

Figures 5 and 6 display overall activity and selectivity toward CH₂F₂ (desired product) as a function of Pd–Au composition. Both figures indicate that the introduction of Au into Pd increases both the activity and the selectivity. However, this increase is small (TOF) or very small (selectivity) when impregnation methods were used in catalyst preparation. The most substantial improvement in the catalytic properties of Pd was achieved when gold was introduced into Pd/C by the direct redox method. In particular, Fig. 6 displays a gradual increase in selectivity toward CH₂F₂, from $<70\%$ for 3 wt% Pd/C to nearly 90% for 6.4 wt% Pd₆₀Au₄₀/C. On the other hand, the 6.5 wt% Pd₆₀Au₄₀ catalyst prepared by incipient wetness impregnation presents catalytic properties only insignificantly different from those exhibited by the monometallic 3 wt% Pd/C. This result can be rationalized in the light of characterization data presented in the previous subsection: The Pd–Au/C catalysts prepared by impregnation exhibited a rather poor degree of alloying compared to that shown by the samples that resulted from direct redox preparation. Similar results, although with somewhat lower selectivity enlargement, were found for Pd–Au catalysts deposited by

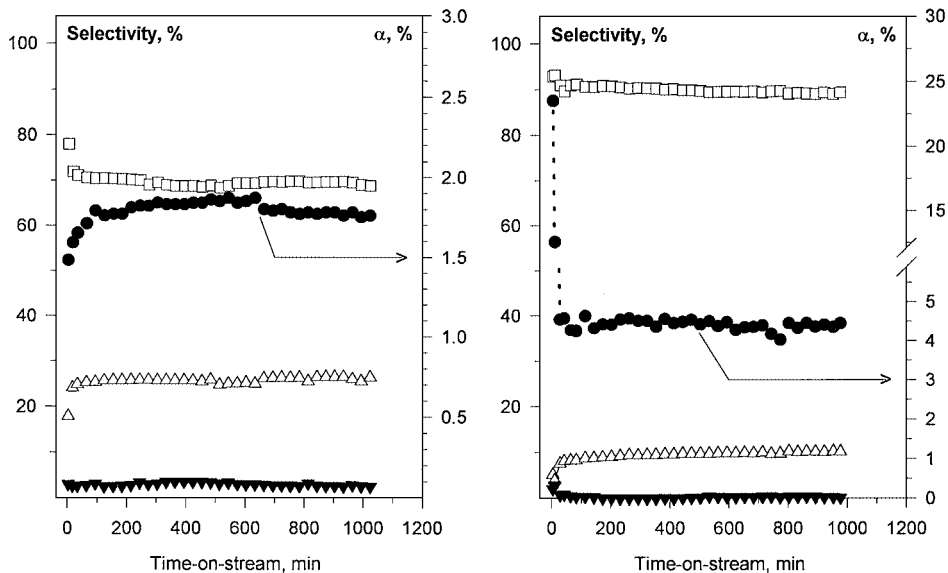


FIG. 4. Time-on-stream behavior in CCl₂F₂ hydrodechlorination at 180°C. (Left) 3 wt% Pd/C; (right) 6.4 wt% Pd₆₀Au₄₀/C. Conversion (α , %), ●. Selectivities to CH₂F₂, □; CH₄, △; CHClF₂, ▼.

TABLE 3

Hydrodechlorination of CCl_2F_2 on Pd–Au/Sibunit Catalysts: Conversions, Product Selectivities, TOFs, and Apparent Activation Energies (E_a)

Catalyst	Reaction temperature (°C)	Conversion (%)	Selectivity ^a (%)			Turnover frequency ^b (s ⁻¹)	E_a (kJ/mol)
			CH ₄	CH ₂ F ₂	CHClF ₂		
3 wt% Pd/C	180	1.77	26.2	69.4	2.7	0.0465	58.2 ± 1.0
	170	1.24	24.3	71.7	3.1	0.0325	
	160	0.87	22.0	72.9	4.4	0.0228	
4.3 wt% Pd80Au20/C ^c	180	2.03	16.6	80.9	1.7	0.0653	53.9 ± 1.5
	170	1.45	15.3	81.9	2.1	0.0469	
	160	1.04	13.9	83.2	2.5	0.0335	
5.2 wt% Pd70Au30/C ^c	180	2.37	10.1	87.6	1.0	0.1130	62.1 ± 2.5
	170	1.58	9.2	89.1	1.1	0.0753	
	160	1.11	8.4	89.3	1.6	0.0531	
6.4 wt% Pd60Au40/C ^c	180	4.40	10.1	89.2	0.3	0.1201	60.9 ± 2.2
	170	2.97	9.4	90.2	0.1	0.0811	
	160	2.07	8.8	91.0	0.0	0.0565	
8.0 wt% Pd50Au50/C ^c	180	4.40	14.8	82.6	1.5	0.0906	67.9 ± 6.1
	170	2.64	12.8	83.6	1.8	0.0545	
	160	2.11	12.8	84.3	2.5	0.0434	
6.5 wt% Pd60Au40/C ^d	180	2.74	21.7	75.9	1.9	0.0376	60.1 ± 0.6
	170	1.90	19.9	77.6	2.2	0.0260	
	160	1.30	18.0	78.9	2.8	0.0178	
1.5 wt% Pd/C ^e	180	1.64	18.8	79.0	0.9	0.0759	57.2 ± 0.9
	170	1.17	17.3	80.4	1.0	0.0541	
	160	0.81	15.9	82.3	0.9	0.0377	
2.2 wt% Pd80Au20/C ^e	180	3.82	13.2	85.0	0.7	0.1175	56.2 ± 0.9
	170	2.79	12.2	85.8	1.2	0.0856	
	160	1.94	11.1	86.1	1.6	0.0595	
3.2 wt% Pd60Au40/C ^e	180	5.04	12.3	85.3	1.2	0.1234	56.3 ± 3.0
	170	3.62	11.4	86.3	1.4	0.0886	
	160	2.39	10.2	86.9	1.8	0.0586	
2.7 wt% Pd70Au30/C ^f	180	2.84	11.0	88.7	0.0	0.1400	61.8 ± 1.1
	170	1.97	10.5	89.2	0.0	0.0971	
	160	1.33	9.6	90.3	0.0	0.0657	

^a Minor products: C₂H₆, CClF₃, CHF₃, and CHF₂CH₂F ($\Sigma < 2\%$; most often $< 1\%$).

^b Based on H/Pd data shown in Table 1.

^c Pd–Au/C catalysts prepared from 3 wt% Pd/C by direct redox method.

^d Pd–Au/C catalyst prepared from 3 wt% Pd/C by incipient wetness impregnation.

^e Pd/C and Pd–Au/C catalysts prepared by wet (co)impregnation.

^f Pd–Au/C catalyst prepared from 1.5 wt% Pd/C by direct redox method.

direct redox reaction onto highly pretreated Norit carbon (from ~72 to ~86% at 180°C (27)). However, at that time, for unknown reasons, a better Pd–Au alloying caused some decrease in turnover frequency (catalysts: $A > B > C$ (27)), which is not the case for Sibunit-supported Pd–Au catalysts (Table 3). In any case, the level of TOF in both works was similar, ~0.05–0.1 s⁻¹, at 180°C.

A similar conclusion may be drawn from screening the catalysts prepared by wet (co)impregnation. Introduction of gold by this technique brings about only modest selectivity changes (Fig. 6). (This speaks once more against using impregnation methods for preparing well-mixed Pd–Au/support catalysts.) Therefore it is not surprising that when 1.5 wt% Pd/C was doped with Au using a direct redox reaction technique, the resulting catalyst (2.7 wt%

Pd70Au30) appeared to be more active (Fig. 5) and selective toward CH₂F₂ (Fig. 6) than the Pd–Au/C samples prepared by wet coimpregnation. It is interesting that the selectivity of monometallic Pd/C (a starting point in our search for more-selective catalysts) was found to be higher for 1.5 wt% Pd/C than for the 3 wt% sample. This result is rationalized in terms of a palladium dispersion (or particle size) effect. Earlier work with Pd/Al₂O₃ (36) and Pd/SiO₂ (25) catalysts (performed at the same screening conditions as used in this work) showed that less dispersed palladium catalysts are more selective toward CH₂F₂. In the previous subsection (Table 2) it was shown that the 1.5 wt% Pd/C prepared by wet impregnation contained two fractions of palladium: large (20 nm) metal crystallites mixed with highly dispersed Pd (4 nm in size) particles. It appears that higher palladium

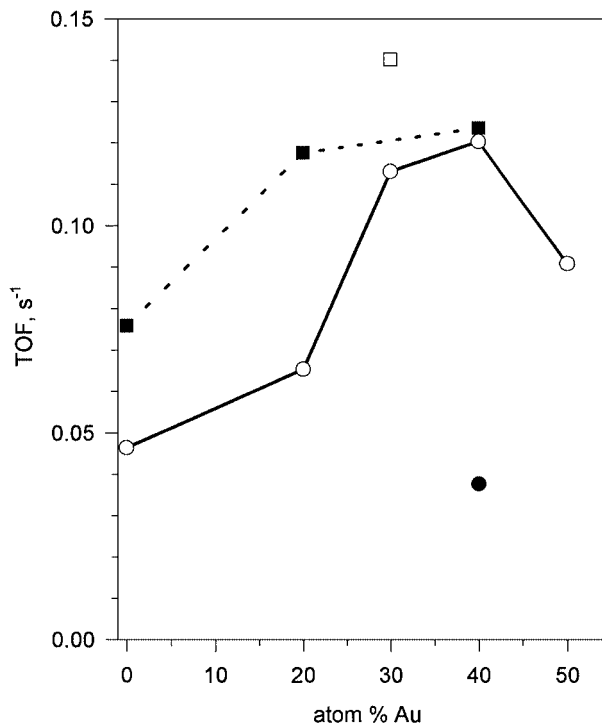


FIG. 5. The effect of Pd–Au alloying on overall activity in CCl₂F₂ hydrodechlorination at 180°C. Pd–Au/C catalysts prepared from 3 wt% Pd/C: ○, by direct redox reaction; ●, by impregnation. Pd–Au/C catalysts from 1.5 wt% Pd/C: ■, by impregnation; □, by direct redox reaction.

dispersions, most wanted for economic reasons, are not well suited for achieving highest selectivities to CH₂F₂; so one has to seek a reasonable compromise when dealing with technological application.

Carbiding of palladium-containing catalysts in the reaction of CCl₂F₂ is a well-known phenomenon. It is manifested in a substantial retention of carbon in a palladium lattice, as the presence of palladium–carbon solutions (up to a PdC_{0.13}) has been ascertained using XRD (6, 7, 11, 17, 22, 25, 27, 34, 37). We decided to investigate this problem in more detail for two reasons. First, 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. Therefore, XRD spectra of used catalysts, in comparison with those of reduced catalysts, should furnish additional information on the composition of an active phase of Pd–Au/C catalysts. Second, it was thought that if a substantial carbiding was found in this study, then it would be useful to look over the time scale of this phenomenon.

Figure 7 shows XRD spectra (only in the neighborhood of (111) reflections of Au and Pd) of used Pd–Au/C catalysts, prepared by direct redox method from 3 wt% Pd/C. A closer comparison with Fig. 1 (XRD of reduced catalysts) shows that the XRD reflections of used catalysts are much more symmetric. As mentioned in the previous subsection,

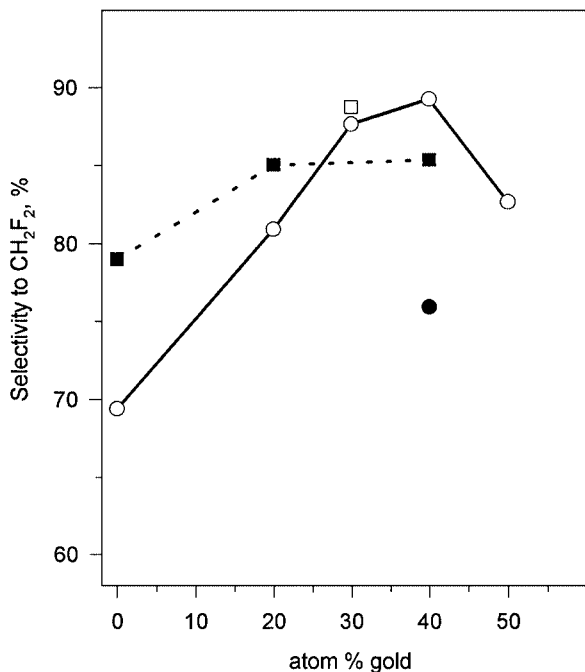


FIG. 6. The effect of Pd–Au alloying on CH₂F₂ selectivity in CCl₂F₂ hydrodechlorination at 180°C. Pd–Au/C catalysts prepared from 3 wt% Pd/C: ○, by direct redox reaction; ●, by impregnation. Pd–Au/C catalysts from 1.5 wt% Pd/C: ■, by impregnation; □, by direct redox reaction.

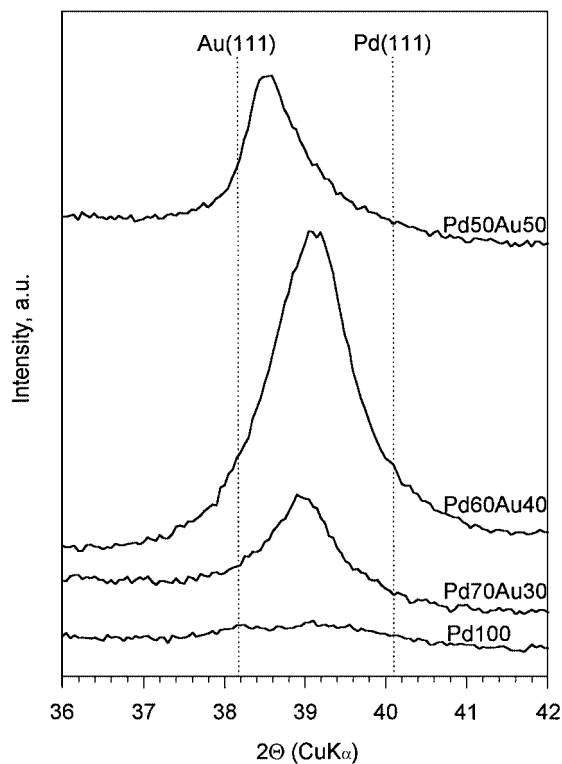


FIG. 7. XRD profiles of Sibunit-supported Pd–Au catalysts (prepared by direct redox reaction) subjected to CCl₂F₂ hydrodechlorination.

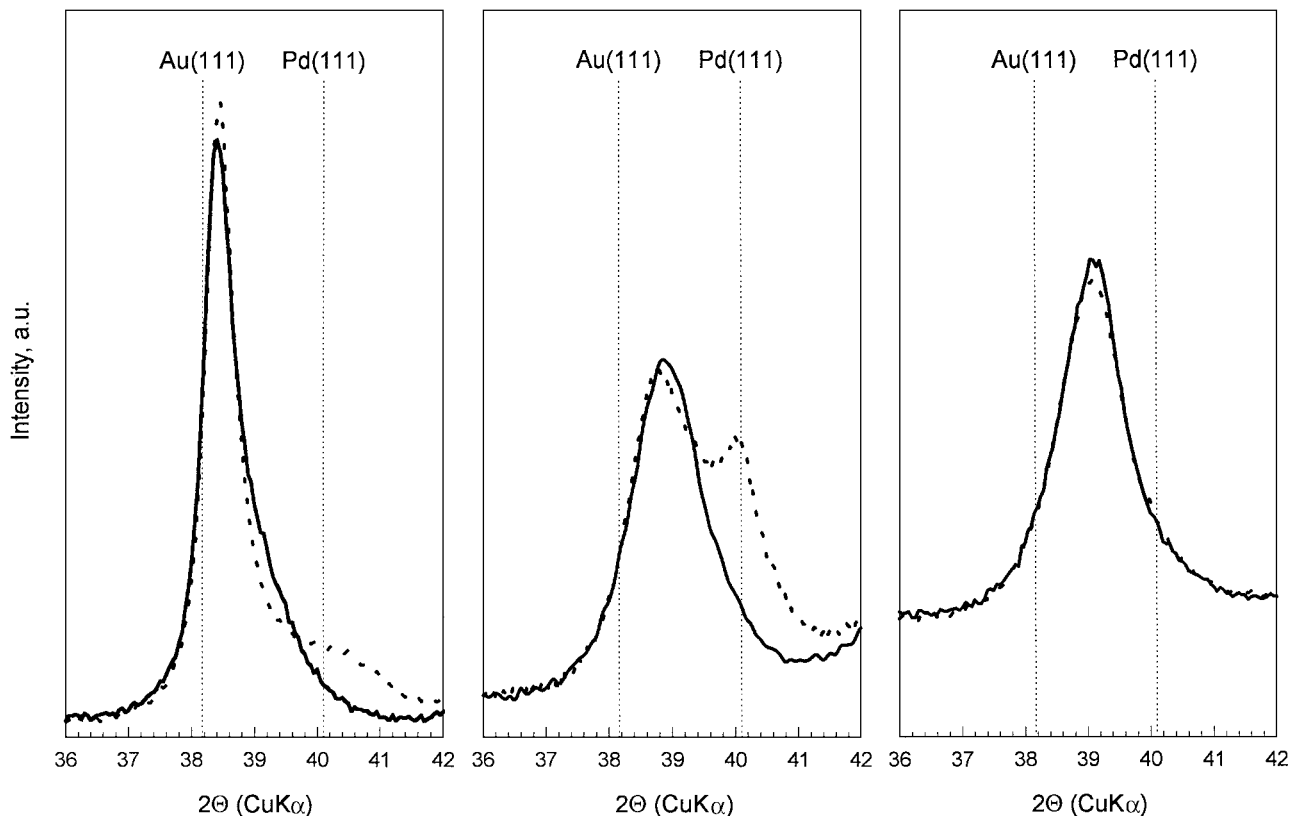


FIG. 8. The effect of CCl_2F_2 hydrodechlorination on XRD profiles of Sibunit carbon-supported Pd–Au catalysts. Comparison of used (solid line) with freshly reduced (broken line) catalysts. (Left) 6.5 wt% Pd60Au40/C prepared by incipient wetness impregnation; (middle) 2.7 wt% Pd70Au30/C prepared by direct redox method from 1.5 wt% Pd/C; (right) Pd60Au40/C prepared by direct redox method from 3 wt% Pd/C.

the asymmetry of the profiles of reduced catalysts was caused by the coexistence of different $\text{Pd}_x\text{Au}_{1-x}$ phases; more specifically, in addition to a more intensive diffraction peak from a gold-richer phase, a more diffuse reflection from a palladium-rich phase should be recognized. When palladium dissolves carbon, its lattice constant increases from ~ 0.389 to ~ 0.399 nm (38–40), resulting in a downward shift in the XRD spectrum. An analogous shift is expected when Pd is alloyed with Au. So, carbon dissolution in Pd (or Pd-very-rich samples) as an effect of the reaction must bring about more narrow diffraction profiles because Au(111) reflection (at $2\theta \approx 38.2^\circ$, for $\text{CuK}\alpha$ radiation) is closer to PdC_x (111) (at $2\theta \approx 39^\circ$) than to the Pd(111) ($2\theta \approx 40.1^\circ$). Figure 8 exemplifies this shift for two Pd–Au/C catalysts prepared by incipient wetness impregnation, 6.5 wt% Pd60Au40, and direct redox reaction, 2.7 wt% Pd70Au30. However, the right part of Fig. 8 indicates a different situation for 6.4 wt% Pd60Au40/C prepared by the direct redox method from 3 wt% Pd/C, where the profile from a used sample almost matches that obtained after prereduction. This catalyst showed the best alloy homogeneity (and catalytic behavior in CCl_2F_2 hydrodechlorination), as the amount of Pd-like phase in the reduced sample was rather small. This confirms our thought that,

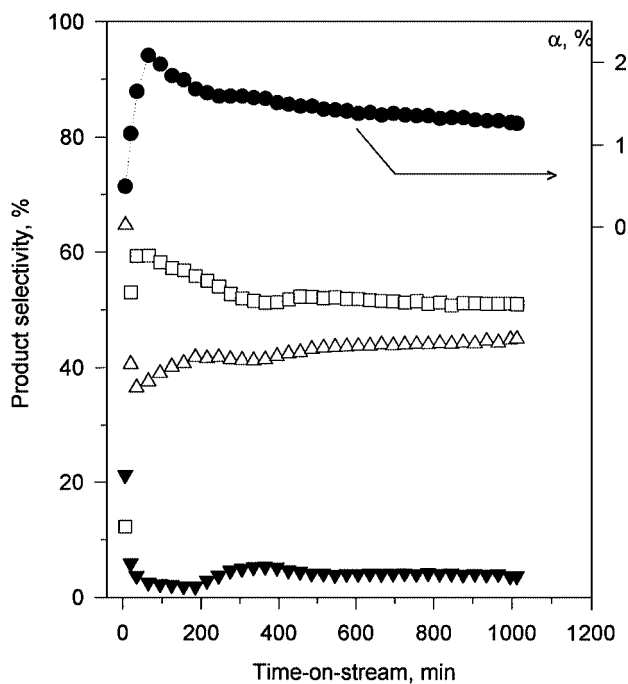


FIG. 9. Catalytic behavior of 10 wt% Pd/SiO₂ in CCl_2F_2 hydrodechlorination at 180°C. Symbols as in Fig. 4.

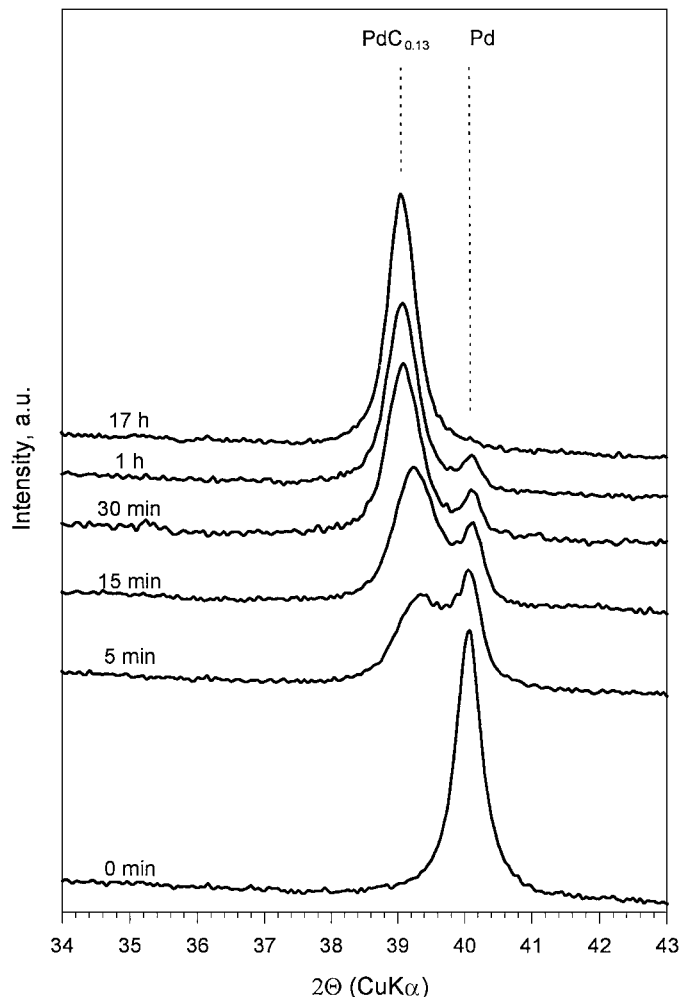


FIG. 10. XRD profiles of 10 wt% Pd/SiO₂ subjected to CCl₂F₂ hydrodechlorination at 180°C: the effect of time-on-stream (in minutes). Positions of (111) reflections of fcc phases of palladium and PdC_{0.13} phases (40) are marked.

similarly to hydrogen dissolution, gold-richer Pd–Au alloys dissolve much less carbon than pure does palladium.

After finding large amounts of carbon in our catalysts subjected to CCl₂F₂ hydrodechlorination, it was interesting to check how fast the process of carbon dissolution is. To eliminate a possible participation (in this process) of carbon originating from the support, we used a silica-supported catalyst (10 wt% Pd/SiO₂, metal dispersion, H/Pd = 0.04). It must be said that the behavior of 10 wt% Pd/SiO₂ (activity, selectivity) still exhibited some variations at the end of the reaction screening, indicating that steady state was not attained in this case. Nevertheless, its catalytic performance in CCl₂F₂ hydrodechlorination at 180°C (Fig. 9) does not differ much from that reported in our earlier work (25) and is not discussed here. We wish only to emphasize the fact that the most important changes in catalytic behavior (activity, selectivity) occur at an early stage of reaction and to correlate it with changes in the catalyst' structure.

Figure 10 displays XRD spectra of the 10 wt% Pd/SiO₂ catalyst subjected to different time intervals of reaction. Surprisingly, even as short a time-on-stream as 5 min results in the formation of a very substantial amount of the PdC_x phase. After a usual reaction run (several hours), the catalyst seems to be completely converted PdC_x. Therefore, we conclude that carbon originating from the organic molecule vastly modifies the catalytic behavior. Easy removal of carbon by a mild hydrogenative treatment (37) led us to the proposition that the working state of palladium catalysts depends on carbon inventory. The C₁ adspecies created as an effect of CCl₂F₂ dissociation swiftly enter the palladium bulk, giving Pd–C solutions up to 13 at% C. These solutions make an efficient carbon sink, which regulates the population of surface C₁ species, which in turn are hydrogenated off to methane (decreasing the selectivity to CH₂F₂). Therefore, surface and bulk carbon seems to play an important role in determining catalytic properties of Pd catalysts. Introduction of gold to palladium reduces surface (and bulk) carbiding as well as weakens binding of CF₂ adcarbenes, which are generally accepted reaction intermediates (3–8). Such an effect would be advantageous for avoiding undesirable defluorination to C₁ surface species, and, in consequence, methane formation.

4. CONCLUSIONS

A series of Sibunit carbon-supported palladium–gold catalysts manufactured by different methods (wet and incipient wetness impregnation and direct redox reaction method) were characterized by various techniques and investigated in the reaction of dichlorodifluoromethane with dihydrogen. The direct redox method resulted in a higher degree of Pd–Au alloying than the impregnation techniques. A temperature-programmed hydride decomposition (TPHD) study appeared to be a very promising technique for characterization of supported Pd–Au bimetal. The observed correspondence of TPHD and X-ray diffraction data for Pd–Au catalysts makes the former technique feasible for diagnosing the quality of Pd–Au alloying. The advantage of this method should especially be valuable when dealing with low-metal-loaded supported Pd–Au catalysts characterized by a considerable dispersion, i.e., when X-ray diffraction would not give reliable results.

Sibunit carbon has proved to be very useful support for the Pd–Au-active phase in CCl₂F₂ hydrodechlorination. A noticeable selectivity toward CH₂F₂ (desired reaction product) was achieved. This selectivity was increased upon introducing gold to palladium. This enhancement depended, however, very much on the degree of Pd–Au alloying. For the catalysts prepared by the direct redox reaction method the selectivity for difluoromethane increased from <70 (for Pd) to nearly 90% for bimetallic samples at the highest temperature of screening, 180°C. This is in contrast to Pd–Au/C

catalysts prepared by impregnation methods, which showed a lesser degree of Pd–Au alloying.

It was confirmed that in the course of the CCl_2F_2 reaction, substantial amounts of carbon are incorporated into the bulk of the palladium (or Pd-rich alloy) phase. Separate studies with a model Pd/SiO₂ catalyst revealed that this carbon originates from the CFC molecule, not from the carbon support. More important, it was found that a substantial amount of carbon is dissolved in palladium at the very beginning of the reaction. Because this carbon can be easily removed from the catalyst by a mild hydrogen treatment (at the reaction temperature) it is argued, in agreement with earlier works, that methane formation from dichlorodifluoromethane may result at least in part from an easy hydrogenation of bare carbon species present in the catalyst.

ACKNOWLEDGMENT

We thank Prof. Maria Wojciechowska (Adam Mickiewicz University, Poznań) for her help in the characterization of our Sibunit carbon sample (BET surface area and pore structure).

REFERENCES

- Manzer, L. E., *Catal. Today* **13**, 13 (1992).
- Manzer, L. E., and Rao, V. N. M., *Adv. Catal.* **39**, 329 (1993).
- Coq, B., Cognion, J. M., Figuéras, F., and Tournigant, D., *J. Catal.* **141**, 21 (1993).
- Coq, B., Figuéras, F., Hub, S., and Tournigant, D., *J. Phys. Chem.* **99**, 11159 (1995).
- Karpiński, Z., Early, K., and d'Itri, J. L., *J. Catal.* **164**, 378 (1996).
- van de Sandt, E. J. A. X., Wiersma, A., Makkee, M., van Bekkum, H., and Moulijn, J. A., *Catal. Today* **35**, 163 (1997).
- van de Sandt, E. J. A. X., Wiersma, A., Makkee, M., van Bekkum, H., and Moulijn, J. A., *Appl. Catal. A* **155**, 59 (1997).
- Wiersma, A., van de Sandt, E. J. A. X., den Hollander, M. A., van Bekkum, H., Makkee, M., and Moulijn, J. A., *J. Catal.* **177**, 29 (1998).
- Makkee, M., Wiersma, A., van de Sandt, E. J. A. X., van Bekkum, H., and Moulijn, J. A., *Catal. Today* **55**, 125 (2000).
- Moulijn, J. A., Makkee, M., Wiersma, A., and van de Sandt, E. J. A. X., *Catal. Today* **59**, 221 (2000).
- Öcal, M., Maciejewski, M., and Baiker, A., *Appl. Catal. B* **21**, 279 (1999).
- Ramos, A. L., Schmal, M., Aranda, D. A. G., and Somorjai, G. A., *J. Catal.* **192**, 423 (2000).
- Deshmukh, S., and d'Itri, J. L., *Catal. Today* **40**, 377 (1998).
- Early, K., Kovalchuk, V. I., Lonyi, F., Deshmukh, S., and d'Itri, J. L., *J. Catal.* **182**, 219 (1999).
- Karpiński, Z., and d'Itri, J. L., *Catal. Lett.* **77**, 135 (2001).
- Cao, Y. C., Jiang, X. Z., Song, W. H., Bai, Z. Q., and Fang, X. Q., *Catal. Lett.* **76**, 53 (2001).
- Morato, A., Alonso, C., Medina, F., Garreta, J. L., Sueiras, J. E., Cesteras, Y., Salagre, P., Tichit, D., and Coq, B., *Catal. Lett.* **77**, 141 (2001).
- Morikawa, S., Samejima, S., Yositate, M., and Tatsumatsu, S., Eur. Patent 0,347,830, A2 (1989), to Asahi Glass Co.
- Rao, V. N. M., U.S. Patent 5,447,896 (1995), to du Pont de Nemours.
- Rao, V. N. M., U.S. Patent 5,629,462 (1997), to du Pont de Nemours.
- Malinowski, A., Juszczak, W., Pielaszek, J., Bonarowska, M., Wojciechowska, M., and Karpiński, Z., *Chem. Commun.* 685 (1999).
- Malinowski, A., Juszczak, W., Pielaszek, J., Bonarowska, M., Wojciechowska, M., and Karpiński, Z., *Stud. Surf. Sci. Catal.* **130**, 1991 (2000).
- Barbier, J., in "Handbook of Heterogeneous Catalysis" (G. Ertl, H. Knözinger, and J. Weitkamp, Eds.), Vol. 1, p. 257. Wiley-VCH, Weinheim, 1997.
- Bonarowska, M., Pielaszek, J., Juszczak, W., and Karpiński, Z., *J. Catal.* **195**, 304 (2000).
- Bonarowska, M., Malinowski, A., Juszczak, W., and Karpiński, Z., *Appl. Catal. B* **30**, 187 (2001).
- Kowalczyk, Z., Sentek, J., Jodzis, Z., Diduszko, R., Presz, A., Terzyk, A., Kucharski, Z., and Suwalski, J., *Carbon* **34**, 403 (1996).
- Bonarowska, M., Burda, B., Juszczak, W., Pielaszek, J., Kowalczyk, Z., and Karpiński, Z., *Appl. Catal. B* **35**, 13 (2001).
- Juszczak, W., Karpiński, Z., Łomot, D., Pielaszek, J., and Sobczak, J. W., *J. Catal.* **151**, 67 (1995).
- Likhoholov, V. A., Fenelonov, V. B., Okkel, L. G., Goncharova, O. V., Avdeeva, L. B., Zaikovskii, V. I., Kuvshinov, G. G., Semikolenov, V. A., Duplyakin, V. K., Baklanova, O. N., and Plaksin, G. V., *React. Kinet. Catal. Lett.* **54**, 381 (1995).
- Fenelonov, V. B., Likhoholov, V. A., Derevyankin, A. Yu., and Mel'gunov, M. S., *Catal. Today* **42**, 341 (1998).
- Lokteva, E. S., Lunin, V. L., Golubina, E. V., Smagina, V. I., Egorova, M., and Stoyanova, I. V., *Stud. Surf. Sci. Catal.* **130**, 1997 (2000).
- Ichikawa, S., Poppa, H., and Boudart, M., *J. Catal.* **91**, 1 (1985).
- Krishnankutty, N., and Vannice, M. A., *J. Catal.* **155**, 312 (1995).
- Malinowski, A., Juszczak, W., Bonarowska, M., Pielaszek, J., and Karpiński, Z., *J. Catal.* **177**, 153 (1998).
- Ziemecki, S. B., Michel, J. B., and Jones, G. A., *React. Solids* **2**, 187 (1986).
- Maeland, A., and Flanagan, T. B., *J. Phys. Chem.* **69**, 3575 (1965).
- Juszczak, W., Malinowski, A., and Karpiński, Z., *Appl. Catal. A* **166**, 311 (1998).
- Stachurski, J., and Frąckiewicz, A., *J. Less-Common Met.* **108**, 241 (1985).
- Ziemecki, S. B., Jones, G. A., Swartzfager, D. G., Harlow, R. L., and Faber, J., *J. Am. Chem. Soc.* **107**, 4547 (1985).
- Kaszur, Z., Stachurski, J., and Pielaszek, J., *J. Phys. Chem. Solids* **47**, 795 (1986).