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Pd–Au/SiO_2: Characterization and Catalytic Activity

W. Juszczyk, Z. Karpiński,[1] D. Łomot, J. Pielaszek, and J. W. Sobczak

Institute of Physical Chemistry of the Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland

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A series of Pd–Au/SiO_2 catalysts was prepared by incipient wetness coimpregnation of silica with respective chloride solutions, followed by calcination in air and reduction in hydrogen at 380°C for 15 h. A variety of techniques, chemisorption of hydrogen and carbon monoxide, temperature-programmed reduction, X-ray diffraction, X-ray photoelectron spectroscopy, and neopentane conversion as a catalytic probe, were employed to characterize metal dispersion and interaction between two metal components and the support. It has been discovered that the prepared materials are not uniform: a palladium-rich phase of very high metal dispersion (particle size ~1.3 nm) coexists with much less dispersed gold-rich phase (particle size ~15 nm). X-ray photoelectron spectroscopy revealed some presence of $Si^{<IV}$ species (as reduced silicon or ex-palladium silicide) in reduced silica-supported Pd–Au catalysts. Because the amount of $Si^{<IV}$ positively correlates with metal dispersion it is suggested that these species are in a close vicinity to the highly dispersed Pd (Pd-rich) material, forming a kind of "chemical glue" between metal and support. In contrast to other Pd-based systems (e.g., Pd–Cu and Pd–Zn), coimpregnation of silica with aqueous solutions of palladium and gold chlorides does not produce well-homogenized bimetallic material.

INTRODUCTION

A wide interest in bimetallic systems in catalytic research is motivated by the superiority of many alloy catalysts in several technological processes (better stability and/or selectivity). Catalytic reforming of naphtha represents an important example: bimetallic Pt-based systems appear much better than traditional monometallic platforming catalysts (1, 2).

The preparation leading to the formation of a well-homogenized bimetallic system and its characterization in the case of highly dispersed, low-loaded bimetal/support catalysts still presents very real difficulties (3). Both physical and chemical *in situ* methods should be employed to achieve the most complete characterization. Recently, we characterized Pd–Co catalysts supported on silica (4, 5) and zeolite Y (6). X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) in combination with chemisorption, temperature-programmed reduction (TPR), and catalytic studies made examination of the alloy bulk homogeneity and estimation of the surface composition of Pd–Co particles supported on silica possible (5). Those results encouraged us to investigate other important Pd-based alloy combinations.

We also employed the reaction of neopentane with hydrogen as a catalytic probe for characterization of Pd surfaces both in supported and in unsupported catalysts. The course of this reaction over well-homogenized epitaxially oriented Pd–Au (111) alloy films (7) suggests that neopentane conversion would be a useful reaction for probing surfaces of supported Pd–Au particles. Namely, Pd-rich alloy films (of ~12 at% Au) exhibit a maximum of the isomerization activity vs Pd–Au alloy composition (7). It is conceivable that for poorly mixed alloy samples, the catalytic probing may not reveal such a maximum, as inhomogeneous samples should behave like physical mixtures of two metal components. Bearing in mind the problem of probing small bimetal particles on a support, one has to be very careful in attributing possible catalytic variations only to changes in sample homogeneity. Other variables, such as metal particle size and extent of metal–support interactions may influence catalytic properties and, therefore, should also be considered. In the case of silica-supported Pd catalysts, the effect of metal particle size in neopentane conversion is rather unimportant (8); however, one must take into account the danger of modification of catalytic properties of palladium by metal–support interactions. As a matter of fact, the selectivity for isomerization (versus cracking) appears to be a convenient diagnostic parameter in determining whether Pd interacts with a support (9, 10). Thus, in the present characterization of Pd–Au bimetal particles our intention was to employ such catalyst pretreatment in order to eliminate any stronger metal–support interactions. Then, any catalytic variations obtained could, hopefully, be attributed to changes in composition of bimetallic Pd–Au particles. For the preparation of a series of Pd–Au/SiO_2 catalysts we chose incipient wetness coimpregnation of silica with an aqueous solution of respective metal chlorides. This simple technique was found to be effective for prep-

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[1] To whom correspondence should be addressed. E-mail: zk@alpha.ichf.edu.pl.

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aration of several Pd-based bimetallic particles on supports (4, 5, 11–15).

It should also be noted that neopentane conversion has not been studied on silica-supported Pd–Au alloys. Therefore, the undertaking of these studies was justified for their own sake.

METHODS

Catalyst Preparation and Pretreatment

First, palladium and gold (both spectrographically standardized, 0.2-mm-diameter wires from Johnson Matthey) were dissolved in *aqua regia* freshly prepared from concentrated HCl and HNO_3 (analytical reagents from POCh, Gliwice, Poland). The Pd–Au/SiO_2 catalysts were prepared by incipient wetness coimpregnation of silica (Serva, puriss, 80–100 mesh) with appropriate amounts of dissolved metals. During impregnation and drying with infrared lamps a good mixing was assured by the rotary motion of a beaker containing catalyst precursor components. Overall metal loading was 2 wt% (a series of eight catalysts with different ratios of Pd to Au). For comparison, two high metal-loaded (10 wt%) catalysts were also prepared: pure Pd/SiO_2 and Pd70Au30/SiO_2 (the notation expresses atom percentage of Pd and Au in metal phase of the catalysts).

After impregnation, the catalysts were dried in an air oven at 120°C for 8 h. Then they were precalcined in a fluidized bed, ramping the temperature from 20 up to 450°C at 3°C/min, and kept at 450°C for 3 h. After calcination the catalysts were transferred to glass-stoppered bottles and were stored in a desiccator.

The final step of pretreatment was carried out before chemisorption, TPR, XRD, and kinetic experiments and consisted of calcination in an O_2 flow at 300°C for 30 min and purging in Ar (or He) at 300°C for 5–10 min. Next, samples pretreated before chemisorption, kinetic, and XRD experiments were reduced in a flow of pure H_2, ramping the temperature from 20 to 380°C at 8°C/min, and kept at this level for 15 h. Chlorine content after the reduction was always very low, i.e., below 0.05 wt%, as checked by titration against $AgNO_3$.

A 12% H_2/Ar mixture was used in TPR experiments. Conditions of TPR runs (flow, catalyst weight, temperature ramp) were optimized so as to match criteria suggested by Monti and Baiker (16). The temperature was ramped from −50 up to 400°C at 8°C/min. The thermal conductivity detector (TCD, Gow-Mac) was kept at 20 ± 0.05°C (thermostatting bath), providing constant response during each run. The analog signals from the thermocouple and TCD were passed through digital voltmeters (4 and 5½ digit, respectively) and monitored using an 8255 I/O card in a microcomputer. All gases, except oxygen, were purified by passing through drying traps with final purification over MnO/SiO_2. Carbon monoxide for chemisorption was 99.995% pure (Van Eeghen, The Netherlands) and also further purified by passing through drying and MnO/SiO_2 traps.

In a few experiments, two 10 wt% loaded samples (Pd100 and Pd70Au30) were investigated after the pretreatment described for 2 wt% loaded samples and also after prefiring in an air flow at 750°C for 3 h and reduction at 380°C for 15 h.

X-Ray Diffraction and X-Ray Photoelectron Spectroscopy

XRD experiments were performed on a standard Rigaku–Denki diffractometer using Cu$K\alpha$ radiation. An X-ray diffraction camera–gradientless reactor (17) was used for measurements in a controlled atmosphere. After reduction at 380°C for 15 h, samples were scanned by a step-by-step technique in the 2θ range of 30 to 72°. Resulting diffraction profiles originating from the metal phase were obtained by the method of subtraction of the support background profile (18) with appropriate data smoothing (19).

XPS experiments were performed on a Fisons Instruments VG ESCALAB-210 spectrometer using unmonochromatized Mg$K\alpha$ radiation. The experiments were performed *ex situ*; i.e., a sample after reduction at 380°C for 15 h in a separate apparatus was transferred through air and installed in the analytical XPS chamber. We looked at the following elements: Pd, Au, C, Cl, Si, O and N. Only traces of chlorine were detected in the pretreated catalysts. The intensities of peaks characteristic for Pd were much higher than those for Au, even for Au-rich Pd–Au/SiO_2 samples. The last finding is not, however, relevant for estimation of surface composition of the catalysts after reduction, as Pd is likely to segregate on the surface of Pd–Au alloys in oxidizing atmospheres (20–22). Therefore, our attention was turned mainly to the presence and state of silicon, as we found two kinds of silicon species, Si^{IV} and $Si^{<IV}$, in the samples. The surface Si(IV)-to-Si(<IV) atomic ratio was estimated from the integral intensities of Si 2*p* lines. The intensities were corrected for photoelectron cross section and for analyzer transmission, and relative concentrations were determined using the manufacturer's standard program.

Chemisorption of Hydrogen and Carbon Monoxide

The fractions exposed (dispersions) for Pd–Au/SiO_2 catalysts were determined from chemisorption of H_2. H_2 and CO chemisorptions were measured in a static greaseless glass system at room temperature. A portion of reversibly adsorbed hydrogen (or CO) was measured in the manner described by Leon y Leon and Vannice for chemisorption on Pd–Cu/SiO$_2$ (14) and subtracted from the total uptake to give an irreversible part. Gas pressure changes were monitored with a Setra pressure transducer, ranging from a few to 250–300 Torr (1 Torr = 133.3 Pa).

Neopentane Conversion

The reaction of neopentane (Merck) with hydrogen was investigated in a static-circulation system in the manner described previously (4, 5). The only impurity in the feed was *n*-butane at ~0.02% level; its presence was rather of minor importance (a constant level during catalytic runs). The alkane partial pressure was always kept at ~10 Torr. The ratio of hydrogen to alkane was ~10:1. The composition of the reaction mixture was measured by a Barocel Electronic Manometer (Model 1174). The reaction was followed by gas chromatography (HP 5890 Series II with FID, 6-m squalane/Chromosorb P column, with a HP 3396 Series II integrator). After the first 60–120 min of the reaction (5–6 "injections" to the gc system), the temperature of the furnace was raised as quickly as possible to study the course of the reaction at higher temperature. The degree of conversion was never higher than 0.3% for the lowest temperature and 2.8% for the highest one. It was established by examining the effect of a variable mixing of the gas mixture (by changing amplitude of the piston motion of the circulation pump) that there was no effect of external diffusion. One experiment with more crushed 2 wt% Pd/SiO$_2$ (most active catalyst) showed no extra effect of the catalyst grain size on the reaction course, which is suggestive of the lack of the effect of an internal diffusion process.

Turnover frequencies (TOFs) were calculated on the basis of the dispersion measured by H$_2$ chemisorption (D_H, see Tables 1 and 2). Initial product distributions (selectivities) were calculated as the carbon percentage of neopentane consumed in the formation of a designated product; for instance, mol% of methane from neopentane would be divided by 5 and normalized in deriving the product distribution. Isopentane was a primary product, whereas *n*-pentane was detected only after getting considerable amounts of isopentane (>0.5%). However, the ratio of *n*-pentane to isopentane was never higher than 1:5. Methane and isobutane were primary hydrogenolysis products, and propane and small amounts of ethane were only observed at conversions levels >0.5%.

A few experiments were also performed with Pd and Pd–Au powders. The powders were Alfa Ventron products: Pd, 99.95% pure, fraction 0.25–0.55 μm and two Pd–Au alloys, 99.9% pure, characterized by nominal Pd-to-Au weight ratios 25:75 (fraction 0.45–0.90 μm) and 20:80 (fraction 0.40–0.80 μm).

RESULTS

X-Ray Diffraction and Chemisorption Data

Figure 1 shows X-ray diffraction profiles for two high (10 wt%) metal-loaded samples: Pd100/SiO$_2$ and

TABLE 1

Chemisorption and XRD Data of 2 wt% Pd–Au/SiO$_2$ Catalysts after Calcination at 450°C and Reduction at 380°C

	Metal dispersion[b]		Apparent Pd dispersion[c]		Pd particle size[d] (nm)	Metal phase composition and crystallite size (nm) from XRD[e]
Catalyst[a]	D_H	D_{CO}	H/Pd	CO/Pd		
Pd100	0.87	0.94	0.87	0.94	1.3	Pd (<2.0)[f]
Pd96Au4	0.80	0.93	0.83	0.97	1.3_5	Pd-rich (<2.0)[f]
Pd90Au10	0.65	0.77	0.72	0.86	1.5_5	Pd-rich (<2.0)[f]
Pd85Au15	0.75	0.80	0.88	0.94	1.3	[g]
Pd70Au30	0.53	0.67	0.76	0.96	1.5	Pd-rich (<2.0)[f]; 91%Au (6.0)
Pd50Au50	0.43_5	0.47	0.87	0.94	1.3	Pd-rich (<2.0)[f]; 95%Au (8.0)
Pd25Au75	0.20	[g]	0.80	[g]	1.4	[g]
Au100	None	None	—	—	—	Au (7.7)

[a] Nominal composition in at%: Pd90Au10 denotes 90 at% of Pd and 10 at% Au in metal phase.

[b] D_H = H/Me, D_{CO} = CO/Me [amounts of adsorbed H or CO in moles per mole of metal (Pd+Au)].

[c] We assume there is no adsorption on Au in Pd–Au bimetallics.

[d] Palladium particle size from hydrogen chemisorption, $d_{Pd} = 1.12/D_H$, (23), assuming that chemisorbed hydrogen titrates only surface Pd atoms (1 H per 1 Pd surface atom).

[e] Crystallite size calculated from XRD (Scherrer method) from the (111) diffraction peak.

[f] Extremely diffused or invisible X-ray diffraction peaks.

[g] Not measured.

TABLE 2

Chemisorption and XRD Data of 10 wt% Pd–Au/SiO$_2$ Catalysts

Catalyst^{a}	Metal dispersion^{b} D_H	Metal dispersion^{b} D_{CO}	Apparent palladium dispersion^{c}	Pd particle size^{d} (nm)	Metal phase composition and crystallite size (nm) from XRD^{e}
	calc. 450°–red. 380°C				
Pd100	0.50	0.44	0.50	2.2	Pd (2.2)
Pd70Au30	0.39	^{g}	0.55	2.0	Pd-rich (<2.0); 70%Au (15)
	calc. 750°–red. 380°C				
Pd100	0.13	^{g}	0.13	8.6	Pd (7.0)
Pd70Au30	0.05	^{g}	0.07	16.0	4% Au (12); 56% Au (13)

Note. $^{a-g}$ are as in Table 1.

Pd70Au30/SiO$_2$. X-ray diffraction peaks representative for metal phases are superimposed on a descending featureless background characteristic of pure silicagel. After appropriate numerical treatment (see Methods), mean crystallite sizes and alloy bulk composition (from a change in lattice constant with the Pd–Au alloy composition) can be estimated from the resulting diffraction peaks. These results are included in Tables 1 and 2.

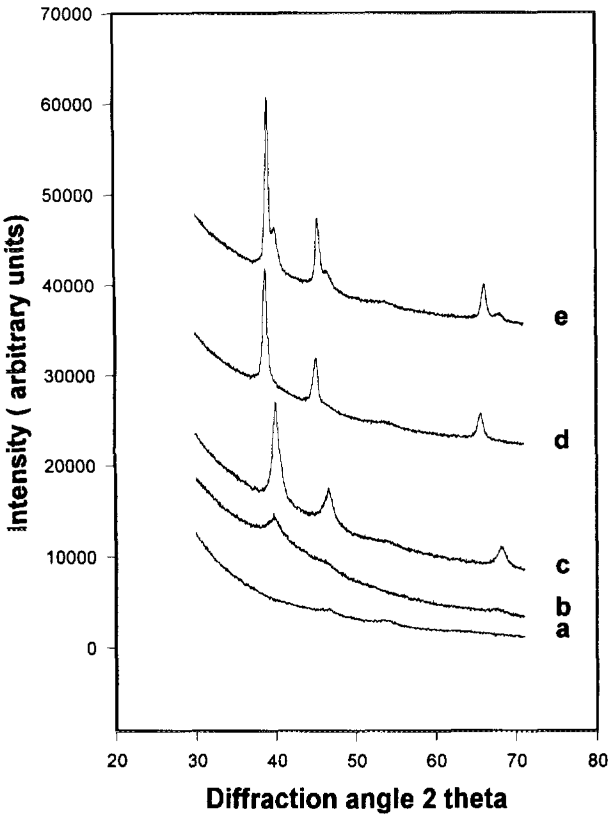

FIG. 1. XRD profiles of 10 wt% Pd-Au/SiO$_2$ catalysts: (a) pure silica gel, (b) 10 wt% Pd/SiO$_2$, after calcination at 450°C and reduction at 380°C, (c) 10 wt% Pd/SiO$_2$, after prefiring at 750°C and reduction at 380°C, (d) 10 wt% Pd70Au30/SiO$_2$, after calcination at 450°C and reduction at 380°C, and (e) 10 wt% Pd70Au30/SiO$_2$, after prefiring at 750°C and reduction at 380°C.

In the case of 2 wt% loaded bimetallic samples, the respective profiles originating from metal phases were very broad and much less intense than for the 10 wt% loaded series. Accordingly, crystallite sizes calculated by the Scherrer method are subjected to a considerable error, due to a very low signal-to-noise ratio.

Figure 2 exemplifies H$_2$ and CO chemisorption isoterms obtained for 2 wt% Pd–Au/SiO$_2$. The amount of chemisorbed hydrogen (or CO) served for estimation of fraction exposed (metal dispersion) seen as H/Me (or CO/Me). Metal particle sizes were further calculated from the hydrogen consumption and compared with respective crystallite sizes from the X-ray diffraction study (Tables 1 and 2).

TPR Data

Figure 3 presents TPR profiles of 2 wt% Pd–Au/SiO$_2$ catalysts after calcination at 450°C. Only single TPR

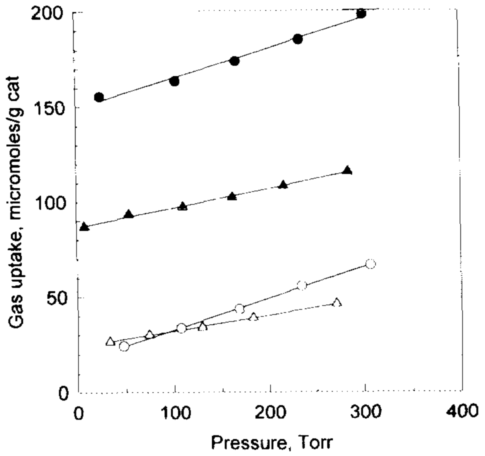

FIG. 2. Adsorption isoterms for hydrogen (triangles) and CO (circles) at 20°C on 2 wt% Pd85Au15/SiO$_2$. Total uptake, closed symbols; reversible uptake, open symbols.

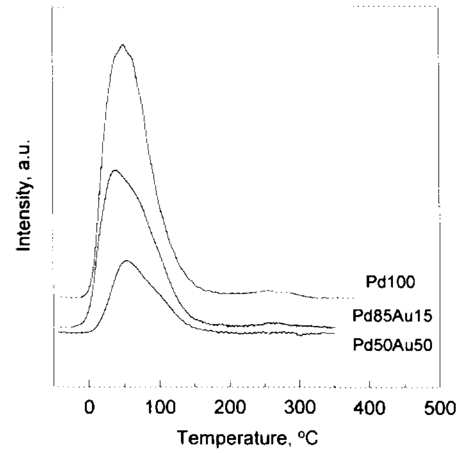

FIG 3. TPR profiles for 2 wt% loaded Pd–Au/SiO$_2$ catalysts.

peaks (for each catalyst) were seen, with a common maximum at ~50°C. The 2 wt% Au/SiO$_2$ sample after calcination at 450°C did not show any TPR peaks (not presented in Fig. 3), suggesting that gold is either in a reduced state already after calcination or instantaneously reduced at the beginning of the TPR run, i.e., at −50°C. XRD confirms the presence of reduced gold after reduction at 380°C (see Table 1).

XPS Data

Figure 4 shows XPS profiles of the Si 2*p* signal for the 10 wt% Pd70Au30/SiO$_2$ after calcination at 450°C and reduction at 380°C for 15 h (Fig. 4a) and after prefiring at 750°C and reduction at 380°C for 15 h (Fig. 4b). The appearance of a small peak at ca. 99.2 eV in the vicinity of the major peak at 103.4 eV manifests some presence of reduced silicon species in the former case. The ratio of relative intensities of two silicon lines, Si^{IV}:Si$^{<IV}$, was found to be ~93:7.

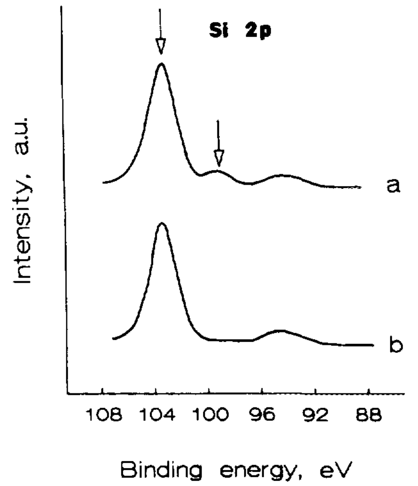

FIG. 4. Si 2*p* XPS lines for 10 wt% Pd70Au30/SiO$_2$ catalysts: (a) after calcination at 450°C and reduction at 380°C, and (b) after prefiring at 750°C and reduction at 380°C.

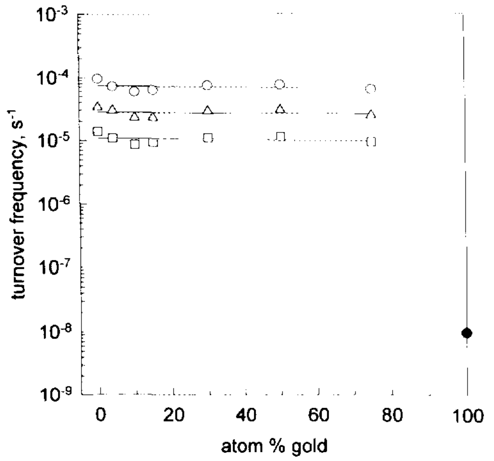

FIG. 5. Activities of 2 wt% Pd–Au/SiO$_2$ catalysts for neopentane conversion at 240°C (squares), 250°C (triangles), and 260°C (circles). The 2 wt% Au100/SiO$_2$ sample was inactive at reaction temperatures up to 350°C. A rough estimation of catalytic activity of gold at 250°C (10^{-8} s^{-1}) is shown as a closed circle. All samples were calcined at 450°C and reduced at 380°C.

Neopentane Conversion

Figures 5–7 show dependences of turnover frequency, isomerization selectivity, and activation energy vs the bimetal composition for 2 wt% Pd–Au/SiO$_2$ samples. Reproducibility of results was good, ~10–15%. Catalytic activity of the 2 wt% Au/SiO$_2$ was negligible at least at temperatures up to 350°C.

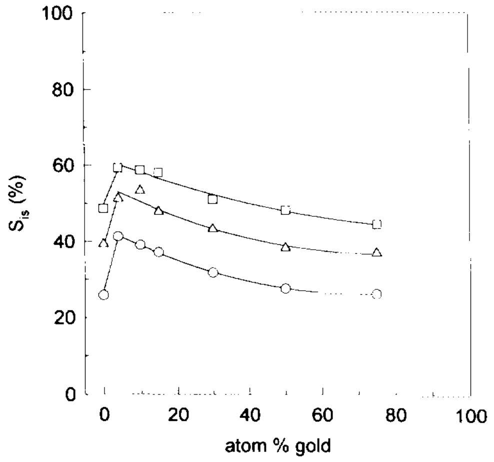

FIG. 6. Isomerization selectivity vs the Au bulk content for 2 wt% Pd–Au/SiO$_2$ at 240°C (squares), for conversion level of 0.05–0.14%; at 250°C (triangles), for conversion level of 0.11–0.34%; and at 260°C (circles), for conversion level of 0.21–0.90%. Sample pretreatment is as in Fig. 5.

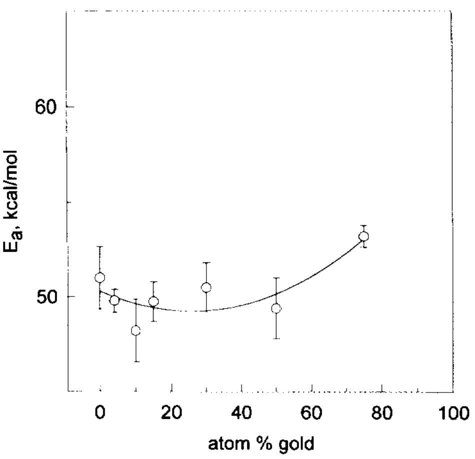

FIG. 7. Activation energy of neopentane conversion vs the Au bulk content for 2 wt% Pd–Au/SiO_2. Sample pretreatment is as in Fig. 5.

Table 3 shows results of kinetic studies of the reaction of neopentane with H_2 over 10 wt% Pd–Au/SiO_2 catalysts.

Table 4 shows results obtained for Pd and two Pd–Au powders after calcination at 300°C (15 min) and two-stage reduction at 300°C (1 h) and 400°C (1 h). It is evident that two bimetallic powders are more selective for isomerization than the Pd powder.

DISCUSSION

Preparation of highly dispersed, well-homogenized bimetallic supported catalysts still presents a real challenge (3). The extent of interaction between two metal components should always be high as unique synergistic catalytic properties of bimetallic catalysts can hardly be associated with the presence of a physical mixture. Optimizing the preparation method was, however, outside the scope of the present work, which was aimed toward evaluating methods which permit one to diagnose whether two highly dispersed metals (Pd and Au) interact with each other on a support.

In order to intensify alloying of two metal components one tends to employ rather severe catalyst pretreatment (temperature and duration). In this work we reduced Pd–Au/SiO_2 samples at 380°C for 15 h. Such conditions were suggested by our preliminary studies: reduction temperatures higher than 380°C led to considerable metal sintering and to the formation of palladium silicides from Pd/SiO_2 (9, 10). In particular, the latter fact had to be avoided because in the opposite case our catalytic probing would be inconclusive: it would be difficult to separate catalytic variations caused by metal–silica interactions from those originated from the bimetal alloying (see Introduction).

Probing Pd–Au/Silica Catalysts by XRD, Chemisorption, and TPR

X-ray diffraction study of 2 and 10 wt% metal-loaded Pd–Au/SiO_2 uncovered that the obtained catalysts are not homogeneous. Figure 1 illustrates this fact for 10 wt% loaded samples. After calcination at 450°C and reduction at 380°C, the alloy sample characterized by a nominal atomic Pd-to-Au ratio of 70/30 exhibits an XRD diffraction profile which can be ascribed to the presence of one *fcc* phase with the Pd-to-Au ratio of 30/70. The presence of phases considerably enriched in gold with respect to nominal compositions of prepared Pd–Au materials appears to be a rather general phenomenon (Tables 1 and 2). This fact suggests that some highly dispersed metallic material, apparently undetectable by XRD, must be considerably enriched in palladium. The presence of such

TABLE 3

Neopentane Conversion over 10 wt% Pd–Au/SiO_2: Turnover Frequencies and Initial Product Distributions

Catalyst		Reaction temperature	Initial product distribution (%)[a]					Turnover frequency
at%Pd	at%Au	(°C)	Me	Et	Pr	*i*B	*i*P+*n*P	(1/s)
			calc. 450°-red. 380°C					
100	—	240	10.7	0.1	0.3	32.8	56.9	1.06×10^{-5}
		263	17.6	0.4	2.5	48.1	31.4	9.63×10^{-5}
70	30	239	4.1	—	0.4	15.4	80.2	4.93×10^{-6}
		261	9.6	0.6	0.9	27.6	61.3	3.37×10^{-5}
			calc. 750°-red. 380°C					
100	—	240	15.9	2.6	5.0	40.4	36.1	8.50×10^{-7}
		261	14.0	0.4	1.1	47.6	36.9	9.17×10^{-6}
70	30	241	15.1	1.0	2.9	46.3	34.6	5.77×10^{-7}
		262	16.4	0.3	0.5	57.2	25.6	6.19×10^{-6}

[a] Me, methane; Et, ethane; Pr, propane; *i*B, isobutane; *i*P, isopentane; and *n*P, *n*-pentane.

TABLE 4

Neopentane Conversion over Pd and Pd–Au Powders: Initial Reaction Rates and Product Distributions

Catalyst at%Pd	Catalyst at%Au	Reaction temperature (°C)	Initial product distribution (%)[a] Me	Et	Pr	*i*B	*i*P+*n*P	Initial reaction rate[b]
100	—	290	13.6	0.3	0.3	49.5	36.2	22.63
		300	13.4	0.4	0.6	49.2	36.4	74.04
25	75	290	5.5	—	—	23.3	71.2	0.71
		300	6.4	0.1	0.3	24.5	68.6	1.51
20	80	330	3.2	0.6	4.1	8.8	83.4	0.15
		350	1.8	—	3.3	11.3	83.6	0.50

[a] Abbreviations are as in Table 3.

[b] Expressed as 10^{-10} mol $g_{Pd(orPdAu)}^{-1}$ s^{-1}.

Pd-rich phase *is speculated from the mass balance*. The possibility that the invisibility of a Pd-rich phase is caused by its oxidation must be rejected as we performed our XRD study in an *in situ* XRD camera–reactor, after reduction in H_2. An important question arises as to whether some gold is yet incorporated into that highly dispersed phase.

The same catalyst, i.e., 10 wt% Pd70Au30/SiO$_2$, after firing at 750°C and subsequent reduction at 380°C, exhibits two XRD-detectable phases, as seen in Fig. 1e (two (220) reflections at $2\theta \approx 66°$). A gold-richer phase (of ~56 at% Au) is more abundant than a Pd-richer phase (of ~4 at% Au). It is obvious that the prefiring at 750°C effectively sinters metal particles and produces big changes in the phase composition. The composition of the Au-richer phase shifts from 70 to 56 at% Au. This may suggest that some palladium (but not gold) from an "amorphous Pd-rich" phase incorporates into the Au-richer phase on firing at 750°C. However, such an explanation is not acceptable, as one expects rather higher mobility of gold than palladium at higher temperatures. In addition, a closer comparison of integral intensities of (220) peaks originating from Au-richer phases in the 10 wt% Pd70Au30/SiO$_2$ catalyst after two employed pretreatments (Fig. 1, profile d vs profile e) allows one to believe that also some gold incorporates into the big Au-rich particles. This conclusion together with the fact of appearance of another Pd-Au (with 4 at% Au) phase after prefiring at 750°C speaks for nonnegligible amounts of gold in the "amorphous Pd-rich" phase in the catalysts after calcination at 450°C and reduction at 380°C.

Temperature-programmed reduction study of 2 wt% Pd–Au/SiO$_2$ catalysts showed that reduction of all samples is essentially complete below 150°C (Fig. 3). A featureless background spectrum observed in TPR of 2 wt% Au/SiO$_2$ sample (not shown in Fig. 3) indicates that the gold catalyst is already reduced before the commencement of the TPR run. The TPR peaks presented in Fig. 3 exhibit maxima at approximately identical temperature, i.e., at ~50°C. This finding suggests that we deal with reduction of only one precursor. This must be a precalcined Pd chloride precursor, all the more so as integrated areas of the TPR peaks are roughly proportional to the Pd content in the samples.

In the case of Pd/SiO$_2$ and Pd–Au/SiO$_2$, TPR profiles do not confirm any evolution of hydrogen, often seen as negative peaks related to the decomposition of β-PdH phase (5). The absence of the "PdH decomposition" peak would suggest a presence of highly dispersed palladium (or Pd–Au alloy) phase.

The results of hydrogen chemisorption on Pd–Au/SiO$_2$ catalysts are compatible with our speculation as to poor homogeneity of the catalysts. Tables 1 and 2 show that hydrogen uptake calculated per Pd content does not change with the nominal composition of the Pd–Au bimetal, which for 2 wt% loaded samples is equal to 0.819 ± 0.046 (at a 95% confidence level). This result in combination with the XRD data suggests that a dominant part of adsorption proceeds on the highly dispersed Pd-rich material not "seen" by XRD. We think that this material is responsible for catalysis (neopentane conversion, see next subsection).

Neopentane Conversion

a. Pd–Au powders. Our earlier work on neopentane conversion on epitaxially oriented Pd–Au (111) alloy films displayed the presence of a maximum in the isomerization activity at ~12 at% Au (7). That result stimulated the present probing of Pd–Au bimetal particles dispersed over a silica support. If catalytic properties of prepared Pd–Au/SiO$_2$ samples were *additive*, one would come to conclusion that the bimetal homogeneity is *poor*. However, it must be recalled here that the Pd–Au (111) films were prepared by evaporation of two metals on a mica base with subsequent annealing in H_2 at 500°C (7). Such a severe pretreatment would lead to some contamination of Pd–Au films by mica ingredients (e.g., K, Al, Mg, Si?). Until now our results obtained on Pd–Au (111) films (7) have not been verified by any work on real single crystals, with an adequate control of surface composition and cleanliness. On the other hand, it is known that high-temperature (≥450°C) reduction of the Pd–SiO_2 system leads to the formation of palladium silicides, which, in turn, exhibit quite different catalytic properties than pure Pd (9, 10). During high-temperature reduction, isomerization selectivity (S_{is}) grows from ~30% up to 80–90%. In effect, some skepticism to the relevance of our previous results on Pd–Au (111) films (7) motivated us to get some verification from the work on Pd–Au powders.

Table 4 shows that, in fact, alloying Pd with Au produces an enhancement in isomerization selectivity. A moderate selectivity level, ~30% for Pd powder at low conversions (<1.5%) is considerably increased to 70–80% for two Pd–Au alloy powders. Such a selectivity growth makes a promising basis for subsequent probing supported bimetal Pd–Au particles: Pd–Au alloy composition should have a primary effect on catalytic behavior in the reaction of neopentane with hydrogen. Other variables, such as metal dispersion and metal–support interactions should also be considered. It is advantageous here that in the case of neopentane conversion over Pd/SiO_2, the effect of metal dispersion is rather insignificant (8). On the other hand, our intention was to avoid significant metal–silica interactions by carrying out the reduction at temperatures well below that found for obtaining Pd silicides (450–600°C, (9, 10, 24)).

b. Pd–Au/SiO_2: Catalytic activity. Turnover frequency for monometallic 2 wt% Pd/SiO_2 (Fig. 5) was found to be comparable with values reported earlier for 10 wt% Pd/SiO_2 of the Pd–Co/SiO_2 series (5) and for 2 wt% Pd/SiO_2 of the Pd–Cu/SiO_2 series (15). Figure 5 shows the relation of catalytic activity vs Pd–Au bimetal composition for 2 wt% loaded silica-supported samples. It is clear that turnover frequencies calculated on the basis of H/Me do not depend on the Pd/Au ratio. Because catalytic activity of 2 wt% Au/SiO_2 sample was immeasurably low, in agreement with (25), the possibility arises that the "catalytically working" surface of our Pd/SiO_2 and Pd–Au/SiO_2 samples possesses an almost identical chemical composition; Fig. 5 suggests that this must be very rich in Pd if not pure Pd material. This conclusion is compatible with the results of chemisorption and XRD studies, discussed in preceding subsections.

Activation energies shown in Fig. 7 indicate small variations with the Au content. However, this change, from ~50 kcal/mol (for a majority of samples) to 53 kcal/mol (for Pd25Au75) seems very small compared to variations in recently studied Pd–Cu/SiO_2 catalysts (15), where the E_A span was 8 kcal/mol. Because, in the case of Pd–Cu/SiO_2 catalysts, a good bimetal homogeneity was obtained, we think that the comparison of changes in activation energy makes another indication as to rather poor alloying in the case of Pd–Au/SiO_2 catalysts.

c. Pd–Au/SiO_2: Isomerization selectivity. Figure 6 shows respective changes in isomerization selectivity vs the Pd–Au bimetal content in 2 wt% loaded catalysts. The samples with a nominal Pd-to-Au ratio of 96/4, 90/10, and 85/15 are undoubtedly more selective than other samples. This result conflicts somewhat with our earlier conclusions coming from the analysis of the catalytic activity data. Apparently, the selectivity for isomerization seems to be even more sensitive than the overall activity as a diagnostic parameter in determining whether palladium interacts with gold. This is not surprising because Pd–Au alloys show higher than pure Pd isomerization selectivity in *n*-hexane (26, 27) and *n*-heptane conversions (28). It should be mentioned that the enhancement in S_{is} for 2 wt% Pd–Au/SiO_2 (by 10–15%) is not as high as in the case of Pd and Pd–Au powders (by 40–50%, Table 4). This accounts for the rather small gold content in the highly dispersed working phase of the catalysts. In the case of 10 wt% loaded samples, the Pd70Au30 was much more selective toward isomerization than 10 wt% Pd/SiO_2 (by ~25% after precalcination at 450°C, Table 3). This suggests somewhat better alloying in 10 wt% loaded samples than in the case of 2 wt% series. However, it must be stressed that in both silica-supported catalyst series, S_{is} level for Pd100/SiO_2 was somewhat higher than in the case of Pd powder. We think that, in spite of our approach, this difference must be due to some interaction of Pd with silica in effect of reduction at 380°C for 15 h. As was mentioned in the Introduction, our intention was to avoid such an effect because it would complicate the analysis of Pd–Au interactions from the catalytic probing. The employed reduction conditions appeared to be a good compromise for obtaining well-mixed within a metal particle and still well-dispersed Pd–Au particles, avoiding an excessive interaction of Pd with silica. A measure of such interaction would be a disagreement between hydrogen and CO chemisorption. Our earlier work showed that interaction of Pd with silica lowers hydrogen uptake, whereas CO chemisorption suffers only very little (9, 10). Our preliminary study showed that reduction at 380°C for 15 h does not lead to considerable differences between H_2 and CO uptakes (Table 1), whereas reduction at 450°C certainly brings about some complications (9, 10, 24). It appears that neopentane conversion is a more sensitive surface probe than chemisorption. The reaction study with 10 wt% loaded samples after prefiring them at 750°C and reduction at 380°C for 15 h (Table 3) exhibited rather moderate isomerization selectivities (30–40%). The fact that in this case the reduction at 380°C for 15 h does not produce any considerable enhancement in S_{is} (compared to Pd powder) results from the fact that after prefiring we deal with poorly dispersed metal phase and, hence, smaller metal–support interface.

Surprisingly, the prefired 10 wt% Pd70Au30/SiO$_2$ did not exhibit higher isomerization selectivity than the prefired 10 wt% Pd/SiO$_2$ catalyst (Table 3) although XRD analysis showed the presence of two Pd–Au alloy phases (one with ~4 at% Au and another with ~56 at% Au). Although we do not offer any definitive explanation of this result, we believe that such a severe prefiring at 750°C must influence in some way the Pd–Au bimetal particles. A profound surface segregation of palladium in Pd–Au alloys after calcination at 750°C is inevitable (21), and, perhaps, a subsequent reduction at 380°C does not cause much of a change in composition of the surface layer.

XPS

Our supposition that reduction at 380°C of highly dispersed Pd–Au catalysts leads to some interaction with silica was supported by comparative *ex situ* XPS study of 10 wt% Pd70Au30/SiO$_2$ sample after two pretreatments: (a) after calcination at 450°C and reduction at 380°C, and (b) after prefiring at 750°C and reduction at 380°C. As was shown in preceding subsections, the calcination at 750°C led to some improvement in alloy bulk homogeneity and, at the same time, to a considerable metal sintering (Table 2). The presence of a small peak at 99.2 eV in the vicinity of a major Si 2p peak at 103.4 eV in the XPS spectrum of unprefired (more dispersed) sample is seen (Fig. 4a). This small peak can be ascribed to a reduced silicon species or silicon in a palladium silicide. Because after similar reduction pretreatment the prefired sample does not display such a peak (Fig. 4b), we assume that the reduced silicon species must be in the vicinity of metal particles, possibly forming a "chemical glue" between metal and support.

Preparation and Morphology of Pd–Au/Silica Catalysts

Preparation of supported Pd–Au alloys has been a subject of numerous studies for many years; the review of Allison and Bond (29) covers the period until 1972. It appears that when a classical (co)impregnation is employed, a complete alloying may be achieved only when a high-temperature pretreatment is employed. Pretreatment (calcination, reduction, or degassing) temperatures even as high as 700–900°C were used. Such a drastic treatment causes a severe metal sintering: in fact, Pd–Au alloy particles as large as 40 nm were often reported (30). A noteworthy exception in the search for preparation of highly dispersed and well-homogenized supported Pd–Au particles is the work by Lam and Boudart (31): small Pd–Au particles (2.0–4.5 nm in size) were prepared by ion exchange of $[Au(en)_2]^{3+}$ and $[Pd(NH_3)_4]^{2+}$ with silica and reduction at temperatures up to 300°C.

Impregnation of silica with an aqueous solution of respective metal chlorides gives good results in the case of several Pd-based alloys: Pd–Co (5, 12), Pd–Fe(Ag) (12), Pd–Zn (13), and Pd–Cu (14, 15). However, in preparation of Pd–Au/SiO$_2$, it results in the formation of poorly mixed metals. Inhomogeneous distribution of Pd and Au over silica may follow from a large difference between solubilities of two metal salts. At the beginning of solvent (water) removal, the gold precursor rapidly precipitates, possibly at pore outlets. During further drying, palladium chloride tends to cover the support evenly. In effect, calcination at moderate temperatures (up to 450°C) and reduction leads to two metal fractions, one consisting of large crystallites of Au-rich material, the other, of highly dispersed Pd-rich phase. For higher metal loadings (10 wt%), due to a somewhat greater surface crowding the interaction between these two phases is stronger. In effect, 10 wt% Pd70Au30/SiO$_2$ is much more selective toward isomerization than 10 wt% Pd/SiO$_2$ and 2 wt% bimetal series.

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REFERENCES

1. Kluksdahl, H. E., U.S. Patent 3,415,737 (1968).
2. Sinfelt, J. W., U.S. Patent 3,953,368 (1976).
3. Bond, G. C., *Chem. Soc. Rev.* **20,** 441 (1991).
4. Juszczyk, W., Karpiński, Z., Paál, Z., and Pielaszek, J., *in* "Proceedings, 10th International Congress on Catalysis, Budapest, 1992" (L. Guczi, F. Solymosi, and P. Tétényi, Eds.), Part B, p. 1843. Akadémiai Kiado, Budapest, 1993.
5. Juszczyk, W., Karpiński, Z., Łomot, D., Pielaszek, J., Paál, Z., and Stakheev, A.Yu., *J. Catal.* **143,** 583 (1993).
6. Karpiński, Z., Zhang, Z., and Sachtler, W. M. H., *Catal. Lett.* **13,** 123 (1992).
7. Karpiński, Z., *J. Catal.* **77,** 118 (1982).
8. Karpiński, Z., Butt, J. B., and Sachtler, W. M. H., *J. Catal.* **119,** 521 (1989).
9. Juszczyk, W., Karpiński, Z., Pielaszek, J., Ratajczykowa, I., and Stanasiuk, Z., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 3, p. 1238. Chem. Institute of Canada, Ottawa, 1988.
10. Juszczyk, W., and Karpiński, Z., *J. Catal.* **117,** 519 (1989).
11. Choi, K. I., and Vannice, M. A., *J. Catal.* **131,** 36 (1991).
12. Coq, B., Hub, S., Figueras, F., and Tournigant, D., *Appl. Catal. A* **101,** 41 (1993).
13. Green, B. E., Sass, C. S., Germinario, L. T., Wehner, P. S., and Gustafson, B. L., *J. Catal.* **140,** 406 (1993).

14. Leon y Leon, C. A., and Vannice, M. A., *Appl. Catal.* **69,** 291 (1991).
15. Juszczyk, W., Karpiński, Z., Łomot, D., and Pielaszek, J., *Pol. J. Chem.* **67,** 1183 (1993).
16. Monti, D. A. M., and Baiker, A., *J. Catal.* **83,** 323 (1985).
17. Zieliński, J., and Borodziński, A., *Appl. Catal.* **13,** 305 (1985).
18. Pielaszek, J., *in* "Advanced Methods in X-Ray and Neutron Structure Analysis of Materials" (J. Hasek, Ed.), p. 209. Plenum, New York, 1989.
19. Pielaszek, J., *Z. Kristallogr.* **185,** 703 (1988).
20. Wood, B. J., and Wise, H., *Surf. Sci.* **52,** 151 (1975).
21. Maire, G., Hilaire, L., Legare, P., Gault, F. G., and O'Cinneide, A., *J. Catal.* **44,** 293 (1976).
22. Mezey, L. Z., Giber, J., Hofer, W., and Varga, P., *Surf. Sci.* **234,** 197 (1990).
23. Ichikawa, S., Poppa, H., and Boudart, M., *J. Catal.* **91,** 1 (1985).
24. Moss, R. L., Pope, D., Davis, B. J., and Edwards, D. H., *J. Catal.* **58,** 206 (1979).
25. Balakrishnan, K., and Schwank, J., *J. Catal.* **132,** 451 (1991).
26. Visser, C., Zuidwijk, J. G. P., and Ponec, V., *J. Catal.* **35,** 407 (1974).
27. O'Cinneide, A., and Gault, F. G., *J. Catal.* **37,** 311 (1975).
28. Sinfelt, J. H., *in* "Bimetallic Catalysts. Discoveries, Concepts, and Applications", p. 10. Wiley, New York, 1983.
29. Allison, E. G., and Bond, G. C., *Catal. Rev.* **7,** 233 (1973).
30. Sancier, K. M., and Inami, S. H., *J. Catal.* **11,** 135 (1968).
31. Lam, Y. L., and Boudart, M., *J. Catal.* **50,** 530 (1977).