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Journal of Catalysis 220 (2003) 299–308
JOURNAL OF CATALYSIS
www.elsevier.com/locate/jcat

Transformation of Pd/SiO_2 into palladium silicide during reduction at 450 and 500 °C

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Received 18 February 2003; revised 22 May 2003; accepted 29 May 2003

Abstract

This work provides evidence that reduction of Pd/SiO_2 catalysts in dihydrogen at temperatures as low as 450 and 500 °C may already lead to a considerable interaction between palladium and silica, identified by the formation of palladium silicides (Pd_4Si and Pd_3Si). This result seems significant in view of the frequent usage of this temperature level in activation and pretreatment of Pd/SiO_2 catalysts. Application of a high flow of a reducing gas mixture and different reduction time periods indicates that an efficient removal of water vapor from the catalyst zone during hydrogen pretreatment facilitates reduction of silica to silicon, which, in turn, interacts with nearby palladium species. Silation of palladium in Pd/SiO_2 catalysts during a prolonged reduction at 450 and 500 °C has a considerable effect on the catalytic properties in the reaction of 2,2-dimethylbutane with dihydrogen. Incorporation of silicon into palladium lowers the catalytic activity, decreases the activation energy, increases the selectivity toward isomerization (at the expense of hydrogenolysis), and also changes the type of 2,2-dimethylbutane interaction with the surface of catalyst (from $\alpha\gamma$ to $\alpha\gamma'$ mode).

Keywords: Pd/SiO_2 catalysts; XRD; Palladium silicide formation; Effect of reduction at 450 and 500 °C; 2,2-Dimethylbutane conversion; Effect of silation on

1. Introduction

Compared to several more readily reducible oxide supports, like TiO_2, CeO_2, or V_2O_5, silica is considered as essentially a "nonreducible" oxide [1]. Nevertheless, the literature reports formation of a variety of Pd silicides during high-temperature reduction (HTR, at ∼ 600 °C and above, in the presence of hydrogen) of Pd/SiO_2 catalysts [2–7]. It is also known that introduction of silicon onto a palladium surface, either via HTR of Pd/SiO_2 or by intentional deposition (and subsequent decomposition) of silicon-containing compounds (SiH_4, Et_3SiH), greatly changes the catalytic reactivity with respect to saturated and unsaturated hydrocarbons [2–4,7–12]. As a matter of fact, the problem of metal silicide formation in catalysis is not new. It has also been appreciated by surface scientists who investigated metal samples in ultrahigh vacuum systems equipped with some quartz parts. For instance, the AES results showed that one of the contaminants (of studied samples) which caused some decrease of work function was silicon [13]. For a catalytic chemist, who wants to avoid problems with metal silicide formation, the question of primary importance is what is the highest temperature which can be used in the pretreatment and performance of silica-supported metal catalysts. It must be stressed that the reduction temperature level of ∼ 600 °C, applied in our earlier studies [3,4,7], is definitely too high to be regarded as that typically used in activation of supported palladium catalysts. It would be far more interesting to check if palladium interacts with silica at temperatures more frequently used for reduction of silica-supported palladium catalysts. In this respect one observes that, even if supported palladium precursors are generally reducible at relatively low temperatures (< 300 °C, see, e.g., Refs. [14–17]), there are numerous examples of using temperatures around 450 °C, and higher, for reduction of silica-supported palladium catalysts [17–26]. If, for example, a reaction is carried out on Pd/SiO_2 catalysts at > 300 °C, in order to avoid unwanted metal sintering during reaction, one would prefer to pretreat such catalysts at a temperature rather higher than the reaction temperature. Such Pd/SiO_2-

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0021-9517/$ – see front matter
doi:10.1016/S0021-9517(03)00246-X

catalyzed reactions certainly are (cyclo)alkane dehydrogenation (followed typically up to 450 °C [27]), methanol synthesis from CO and H_2 (followed up to 330–340 °C [28,29]), and alkane hydrogenolysis (measured at up to 377 °C [30] or even 405 °C [31]). Another reason for using somewhat higher reduction temperatures is an attempt to adjust (increase) palladium particle size, often employed in studies of the catalytic effect of metal particle size [32]. One more reason is associated with preparation and testing of silica-supported bimetallic catalysts containing palladium. The use of higher reduction temperatures is rationalized by the aim of preparing well-mixed bimetallic particles. However, it is not clear if such high temperatures of reduction bring about a stronger Pd–silica interaction. Finally, in comparative studies one would eventually pretreat an undoped Pd/SiO_2 catalysts under similar reduction conditions as bimetallic samples [33–47].

Thus, we believe that there are several solid reasons for studying the possibility of Pd–SiO_2 interactions at $T \sim 450$ °C. In this respect it should be noted that previous catalytic tests indicated that some Pd–silica interactions would take place in effect of Pd/SiO_2 reduction at $T = 450$ °C [2,3]. Indeed, large differences in catalytic activity between Pd/SiO_2 catalysts reduced at $T = 300$ and 450 °C in benzene hydrogenation [2], which is regarded as a structure-insensitive reaction, clearly imply that reduction at $T = 450$ °C must already generate some chemical changes in the catalysts. However, in those studies [2], no evidence from X-ray diffraction of any palladium–silicon interaction in catalysts reduced at $T = 450$ °C was detected. We have decided to reinvestigate this problem after our recent finding [48] that during reduction in dihydrogen at $T = 600$ °C, a silica-supported palladium catalyst is initially converted to Pd_4Si which subsequently reacts with silicon-containing species to form a Pd_3Si phase. However, if a more efficient removal of water vapor from the catalyst during reduction (brought about by using a higher flow of reducing mixture) is applied, Pd_3Si is directly formed [48]. In our present study of reduction of Pd/SiO_2 at $T = 450$ and 500 °C we decided to intensify the removal of water vapor from the catalyst zone by using a higher flow of a reducing mixture. Incidentally, since it is known that the influence of water vapor during reduction of supported metals is generally unfavorable (resulting in a sintering of metal particles [49]), we are hoping that experiments presented here with higher flows of reducing gas would be of more general interest for those working with supported metal catalysts.

After verification (by XRD) that there is a definite modification of Pd/SiO_2 catalysts after reduction at $T = 450$ and 500 °C, we decided to test these samples in 2,2-dimethylbutane conversion, the reaction which proved to be a convenient probe, sensitive to changes caused by various factors, such as metal dispersion or the presence of catalytically inactive alloying elements [50,51].

2. Experimental methods

2.1. Catalyst preparation, pretreatment, and characterization by X-ray diffraction and hydrogen chemisorption

The support was Davison 62 silica gel (specific surface area 340 m^2/g, pore volume 1.15 cm^3/g, 75–120 mesh) washed with diluted HCl and redistilled water, dried in an air oven at 120 °C for 21 h, and, finally, calcined in air in an oven at 450 °C for 4 h. Such a pretreatment results in a substantial purification of the silica (from Fe, Na, Ca, Ti, and Zr), leaving iron as an exclusive residual contaminant, at ~ 50 ppm level [52,53].

The 10 wt% Pd/SiO_2 catalyst was prepared by incipient wetness impregnation of silica with an aqueous solution of palladium dichloride (analytical reagent from POCh Gliwice, Poland). After impregnation, the solid was dried in an air oven at 120 °C for 8 h, transferred to glass-stoppered bottle, and kept in a desiccator.

Sample preparation for XRD measurements was as follows. A portion the predried catalyst precursor (~ 0.225 g) was subjected to calcination in air flow at 500 °C for 1 h (upon a 20 °C/min ramp), under fluidized bed conditions. After cooling to room temperature (RT) the precalcined samples were purged in argon flow and designated to reduction at 450 °C (or 500 °C) for different periods of time. However, in order to make interpretation of XRD spectra easier, it appeared reasonable to prepare Pd/SiO_2 samples characterized by low metal dispersion. For that purpose, prior to reduction, the samples were wetted with ~ 0.3 cm^3 of redistilled water and purged with argon. Then, each sample was subjected to a different reduction time, from 5 min to 140 h (for reduction at 450 °C) and from 5 min to 67 h (for reduction at 500 °C). The temperature was ramped from RT to 450 °C (or 500 °C) at 8 °C/min. An H_2/He (1/2) mixture was used as a reducing agent at total flow of 150 cm^3/min ($W/F = 0.0015$ g_{cat} min/cm^3). After reduction, the flow of hydrogen was stopped, and the reduced sample was cooled to RT in helium flow and immediately subjected to XRD examination. A standard Rigaku-Denki diffractometer with Bragg–Brentano focusing geometry and Ni-filtered CuK_α radiation and a step-by-step scanning technique ($\Delta(2\Theta) = 0.05°$) were used. For separate XRD studies, prereduced samples were purged with helium at the final reduction temperature (450 or 500 °C) for 1 h. Hydrogen and helium (both of 99.99% purity) were further purified over a 15 wt% MnO/SiO_2 and drying traps. Oxygen impurity in these gases was being checked regularly by replacing the reactor with a U-tube filled with a low-loaded MnO/SiO_2 catalyst, and never exceeded 0.1 ppm [54].

In separate experiments, after reduction and Ar purge for 1 h at a given reduction temperature, some samples were cooled to 70 °C and subjected to metal dispersion measurements by hydrogen pulse chemisorption. Table 1 lists the catalyst (Pd1, Pd2, and Pd3) and reduction codes (SR, short

Table 1
Sample codes and metal dispersions in 10 wt% Pd/SiO_2 catalyst after different pretreatments used before catalytic screening experiments

Catalyst code	Details of preparation[c]	Reduction code	H/Pd[h]
Pd1[a]	Reduction of a precalcined sample	SR[d]	0.33
		LR[e]	0.32
		Regeneration[f]	0.35
Pd2[b]	Wetted between calcination and reduction	SR[d]	0.04
		LR[e]	0.035
		Regeneration[f]	0.05
Pd3[b]	Wetted between calcination and reduction	SR[g]	0.01
		LR[g]	0.005
		Regeneration[f]	0.005

[a] A 0.225-g sample of 10 wt% Pd/SiO_2 not wetted before reduction.
[b] A 0.225-g sample of 10 wt% Pd/SiO_2 wetted between calcination and reduction.
[c] All samples precalcined in a fluidized bed regime in air flow ($\sim$ 250 cm^3/min).
[d] SR stands for a short-term reduction (5 min) at 450 °C.
[e] LR stands for a long-term reduction (17 h) at 450 °C.
[f] Regeneration denotes: sample investigated after LR was oxidized in O_2 flow at 500 °C, then after a short purge in helium at 500 °C, reduced at 300 °C for 1 h.
[g] Reduction at 500 °C (SR for 5 min; LR, 17 h).
[h] Metal fraction exposed (metal dispersion) from hydrogen chemisorption.

reduction, at 5 min; LR, long reduction, at 17 h; and regeneration, oxidation of LR sample and reduction at a lower temperature) and metal dispersions (H/Pd) obtained after specific pretreatments.

2.2. Catalytic conversion of 2,2-dimethylbutane

The reaction of 2,2-dimethylbutane (22DMB, Fluka AG, puriss, nominal purity $> 99.5\%$, actual purity $\sim 99.9\%$, as checked by GC) in excess hydrogen (purified over MnO/SiO_2) was conducted in a glass flow reactor under atmospheric pressure. Charges of ~ 0.225 g of differently pretreated samples of the 10 wt% Pd/SiO_2 were used. For catalyst reduction an H_2/He (1/2) mixture, at a total flow of 150 cm^3/min, was used, i.e., assuring the same sample pretreatment as prior to hydrogen chemisorption studies.

During catalytic runs the carrier gas (hydrogen, 8 cm^3/min) was passing through a saturator with 22DMB kept at -15 °C. The partial pressure of 22DMB was 51.5 Torr (1 Torr = 133.32 N/m^2). The reaction was followed by gas chromatography (HP 5890 Series II with FID and a 50-m PONA capillary column from Hewlett Packard). To avoid secondary reactions and limit self-poisoning, overall conversions (at steady state) were kept low, i.e., $< 4\%$ at the highest reaction temperature. After stable conversion at the highest reaction temperature was reached (3–6 h), the temperature was gradually decreased at ~ 10 °C intervals and next experimental points were collected. Turnover frequencies (TOFs) were calculated on the basis of metal dispersion values, H/Pd, known from hydrogen chemisorption. Initial product distributions (selectivities) were calculated as the carbon percentage of 22DMB consumed in the formation of a designated product. For instance, the mol% of methane from 22DMB would be divided by 6 and normalized in deriving the product distribution.

3. Results and discussion

Prior to presenting our results and their discussion a comment concerning sample preparation seems appropriate. In order to make use of X-ray diffraction for detecting subtle phase changes in our Pd/SiO_2 samples we decided to deal with a catalyst characterized by higher metal loading (here, 10 wt%) and relatively large metal crystallites. This is because the expected phase transformation ($Pd/SiO_2 \rightarrow$ a variety of Pd_xSi_y) leads to a gradual disappearance of a few relatively large XRD reflections from the fcc phase of palladium to a greater number of not very intensive reflections originating from various palladium silicides. In our previous work [48] we presintered a 10 wt% Pd/SiO_2 at 750 °C in air. Recent work [55] shows, however, that such a serious precalcination of Pd/SiO_2 would already lead to a considerable interaction between the metal and support resulting in formation of a mixed palladium–silicone oxide. It is logical to expect that this transformation would help in a more facile formation of palladium silicide(s) upon reduction. To avoid such a situation we preferred to enlarge palladium crystallites in our catalysts by prereduction of a wetted catalyst precursor. This procedure, without using very high temperatures in the precalcination step, led to a significant growth of palladium crystallites and, thus, made interpretation of our XRD spectra easier. In addition, this pretreatment (precalcination + reduction at > 400 °C) should remove, to the highest degree, chloride species (ex-$PdCl_2/SiO_2$), [16,56–61]. A single experiment with 10 wt% Pd/SiO_2 prepared from $Pd(NO_3)_2$ showed identical phase transformations after reduction at 450 °C for 24 h as the catalyst prepared from $PdCl_2$ (XRD not shown).

3.1. X-ray diffraction study of reduced Pd/SiO_2

The sample of the 10 wt% Pd/SiO_2 catalyst after reduction at $T = 450$ °C for 5 min showed a significant metal dispersion. Its XRD reflections (not shown) appeared quite broad and not intense. Application of the Scherrer formula resulted in estimation of average crystallite size $\sim$ 3–4 nm, from the (111) Pd reflection broadening. This level is compatible with the H/Pd ratio from chemisorption, ~ 0.33 ($d_{Pd}(nm) = 1.12/(H/Pd)$, according to Ichikawa et al. [62]). The long-term reduction (LR, for 17 h) as well as subsequent regeneration of this catalyst changed only insignificantly metal dispersion (H/Pd = 0.32 or 0.35, from chemisorption, respectively), again in accordance with Pd crystallite size estimated from the XRD profile broadening.

Unfortunately, a more detailed analysis of the diffused shape of palladium reflections in Pd1 samples which would

lead to detection of hypothesized phase changes (i.e., $Pd/SiO_2 \rightarrow Pd_xSi_y$) can hardly be ventured because of a low signal-to-noise ratio. The situation changed radically when we decided to increase palladium crystallite size by reduction of wetted catalysts.

Fig. 1 shows the XRD spectra of the samples reduced at 450 °C. Very large and narrow reflections from palladium manifest the presence of big palladium particles (~ 15 nm). After short reduction at 450 °C, only the XRD reflections from the fcc phase of palladium are seen (not shown in Fig. 1). However, a 17-h reduction at this temperature (profile a) brings about some indication of formation of another phase manifested by a tiny diffraction peak at $2\Theta \approx 38°$. Evolution of this diffraction peak and distortion of the right branch of the Pd (111) reflection obtained by a gradually increased reduction period are assigned to a continuing growth of a Pd_4Si phase [63]. This trend and appearance of other reflections characteristic of Pd_4Si phase are demonstrated by profiles c, e, g, and i, all of them collected for the catalyst reduced at 450 °C for 24, 40, 70, and 140 h. It is remarkable that the helium purge at 450 °C does not seem to destroy the palladium silicide (profiles b, d, f, and h).

Fig. 2 shows XRD data for the 10 wt% Pd/SiO_2 reduced at 500 °C. Here, the phase analysis is much easier than after reduction at $T = 450$ °C because respective XRD reflections characteristic of Pd_4Si are very pronounced already after a 17-h reduction period (profile a). A longer reduction (67 h) leads to some formation of a new phase, Pd_3Si [64], indicating even more profound incorporation of silicon into palladium. Again, as in the case of samples reduced at 450 °C, helium purge of the samples reduced at 500 °C does not seem to destroy the palladium silicide phase (profile b in Fig. 2).

Our sample regeneration procedure (see Experimental, Section 2.2) led to a complete disappearance of Pd_xSi_y reflections in the XRD spectra (not shown).

To sum up, the XRD studies of differently pretreated Pd/SiO_2 provide, for the first time to our best knowledge, direct evidence for the possibility of strong Pd–silica interactions induced by reduction in hydrogen at $T \leqslant 500$ °C. Observation of the phase transformation ($Pd/SiO_2 \rightarrow Pd_xSi_y$) was possible due to application of higher flows of reducing gas. Therefore, we suggest that modification of palladium properties by Pd–silica interactions should always be veri-

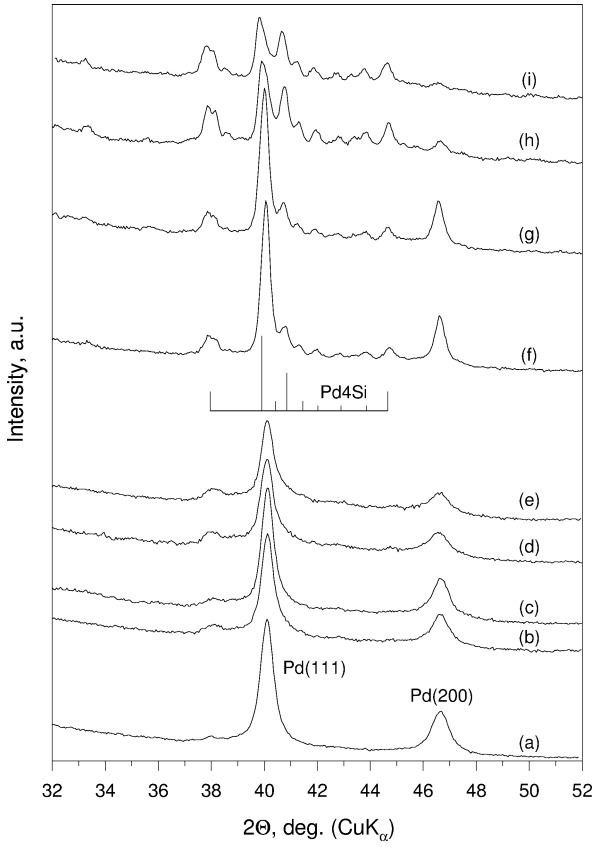


Fig. 1. XRD spectra of 10 wt% Pd/SiO_2 prereduced at 450 °C for different reduction periods: (a) 17 h, (b) 24 h, (c) 24 h + 1 h helium purge at 450 °C, (d) 40 h, (e) 40 h + 1 h helium purge at 450 °C, (f) 70 h, (g) 70 h + 1 h helium purge at 450 °C, (h) 140 h, (i) 140 h + 1 h helium purge at 450 °C. The bar diagram represents literature data for thin film of Pd_4Si from Ref. [63]; the reflections are visualized in a semiquantitative fashion according to their intensity (marked in Ref. [63] as *vvs*, *vs*, *ms*, *m*, and *mw*).

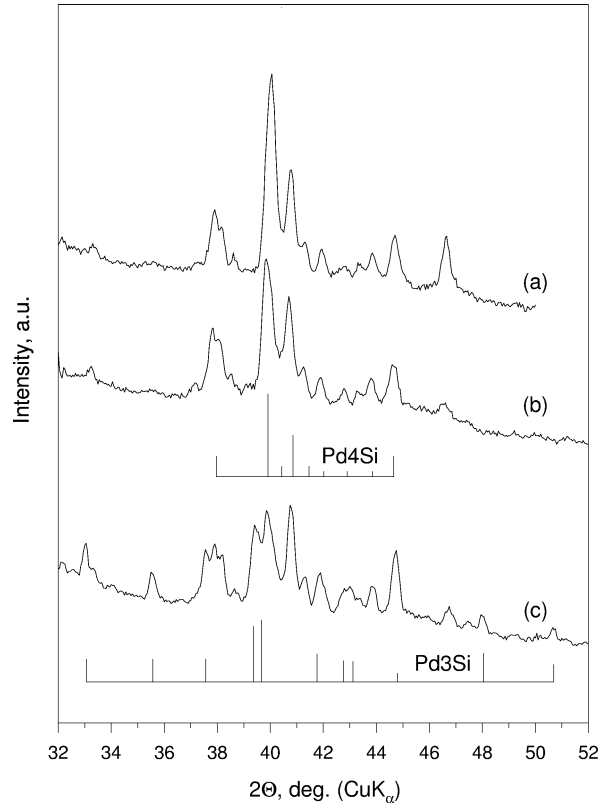


Fig. 2. XRD spectra of 10 wt% Pd/SiO_2 prereduced at 500 °C: (a) after reduction for 17 h, (b) after reduction for 17 h and subsequent helium purge at 500 °C for 1 h, (c) after reduction for 67 h. Two bar diagrams represent literature data for thin film of Pd_4Si from Ref. [63] and Pd_3Si (Ref. [64]). In the case of Pd_4Si data, the reflections are visualized in a semiquantitative fashion according to their intensity (marked in Ref. [63] as *vvs*, *vs*, *ms*, *m*, and *mw*).

fied in catalytic studies of Pd/SiO_2 when catalyst reduction at temperatures above 400 °C is employed.

3.2. Catalytic conversion of 2,2-dimethylbutane over differently pretreated Pd/SiO_2

The use of 2,2-dimethylbutane as a probe molecule for characterizing the nature of possible active sites on supported metal catalysts has recently been reviewed by Burch and Paál [51]. The results of screening Pd1, Pd2, and Pd3 samples after different pretreatments are presented in Tables 2, 3, and 4, respectively.

All catalysts (Pd1, Pd2, and Pd3) subjected to SR and regeneration pretreatments showed a considerable deactivation during first few hours on stream (Fig. 3, left and middle sections). Such a relatively high tendency of palladium to self-poisoning was previously reported by Vogelzang et al. [50], who studied 22DMB reaction over a variety of metals. In agreement with that work we also observed that this deactivation is accompanied by an increase in isomerization selectivity, at the expense of hydrogenolysis. At the same time, the type of Pd–22DMB interaction changes. It is recalled that the structure of 22DMB offers three basic types of interactions: $\alpha\beta$, $\alpha\gamma$, and $\alpha\gamma'$ with metal surfaces [50,51], (Scheme 1: in this notation only positions of bonded carbon atoms are pointed out, without specifying the character of carbon–metal bond, e.g., $\alpha\alpha\gamma$ or $\alpha\alpha\beta\beta$, i.e., tri- or tetraadsorbed species are not marked). The $\alpha\beta$ type leads to hydrogenolysis (with 2,2-dimethylpropane as a distinguishing product), whereas the $\alpha\gamma$ and $\alpha\gamma'$ types may result in hydrogenolysis and isomerization. As far as isomerization is concerned, the $\alpha\gamma$ type of interaction leads to 3-methylpentane, whereas the $\alpha\gamma'$ gives 2-methylpentane and 2,3-dimethylbutane, as primary products, respectively. Vogelzang et al. [50] found that, in addition to higher isomerization selectivity, a carbonized Pd/SiO_2 shows higher proportion of products resulting from an $\alpha\gamma'$ type of interaction (at the expense of $\alpha\gamma$). The same effects were observed by alloying palladium with silver [50]. Our work shows that silicon incorporation to palladium leads to analogous changes, vide infra.

Considering different types of 22DMB interaction with palladium surface, the LR pretreatment results in a pronounced decrease of the $\alpha\gamma$ hydrogenolysis mode, whereas all other types are only slightly changed (Fig. 4). The question arises why the $\alpha\gamma$ hydrogenolysis type is more altered than the respective $\alpha\gamma'$ or $\alpha\beta$ modes? Palladium is known as an exceptionally effective metal for multiple exchange of any hydrocarbon for which an $\alpha\beta$ process is possible [65,66]. It is also known that even at higher temperatures Pd is a rather poor catalyst for forming $\alpha\alpha$ or $\alpha\gamma$ intermediates [67]. However, the role of $\alpha\beta$ mode, so important for rationalizing a very high extent of D_2 exchange of linear alkanes or so-called one-set exchange of cyclopentane on palladium at lower temperatures, is suppressed, at $T \sim 300$ °C, by higher contributions from $\alpha\gamma$ and $\alpha\gamma'$ modes. Indeed, it was found [68] that on Pd, demethylation (i.e., the dominating mode of hydrogenolysis on Pd catalysts [31,69–73])

Table 2
2,2-Dimethylbutane reaction on silica-supported Pd1 catalyst (metal dispersion ∼ 0.33): Turnover frequencies, selectivities, and types of interaction

Reaction	Selectivity[a] (%)			Conversion	Type of interaction[b] (%)					TOF[c]
temperature (°C)	$S_{<6}$	S_{is}	S_{cycl}	(%)	$\alpha\gamma_{<6}$	$\alpha\gamma_{is}$	$\alpha\gamma'_{<6}$	$\alpha\gamma'_{is}$	$\alpha\beta_{<6}$	(s^{-1})
SR[d]										
310	37.0	62.8	0.2	3.70	27.0	13.2	2.7	51.3	5.8	2.18E–04
300	28.8	70.7	0.5	1.55	19.9	16.2	2.4	56.7	4.7	9.17E–05
290	23.2	76.1	0.6	0.62	14.5	17.6	2.5	61.4	4.0	3.68E–05
280	19.0	79.5	1.5	0.24	10.2	18.6	2.5	65.4	3.3	1.42E–05
270	15.1	81.2	3.7	0.12	6.7	16.4	4.6	68.0	4.3	7.00E–06
LR[d]										
320	15.9	83.1	1.0	3.76	10.1	15.6	2.8	70.8	0.7	2.24E–04
310	11.5	87.9	0.6	1.60	6.3	17.6	2.3	73.2	0.6	9.58E–05
300	9.5	89.5	1.0	0.75	4.5	18.6	1.9	74.5	0.5	4.46E–05
290	8.0	90.1	2.0	0.37	3.2	18.9	2.4	75.5	–	2.21E–05
280	6.8	90.9	2.3	0.17	0.8	18.6	3.9	76.7	–	1.03E–05
Regeneration[d]										
310	27.4	71.8	0.8	2.92	20.7	15.1	3.1	59.1	1.9	1.65E–04
300	21.5	77.6	0.9	1.29	14.8	18.0	2.8	62.7	1.7	7.33E–05
290	17.2	82.1	0.7	0.49	10.0	20.4	2.7	65.3	1.5	2.79E–05
280	12.3	84.9	2.8	0.20	3.7	22.2	2.9	68.9	2.2	1.12E–05
270	7.2	83.3	9.5	0.08	–	26.8	5.9	67.2	–	4.63E–06

[a] Selectivities for hydrogenolysis ($S_{<6}$), isomerization (S_{is}), and C_6 cyclic products (S_{cycl}; mainly cyclohexane and benzene, small amounts of methylcyclopentane only at higher reaction temperatures).

[b] According to Vogelzang et al. [50], see also Scheme 1. Subscripts stand for products associated with a specific type of interaction: < 6, hydrogenolysis products (*i*-butane, *i*-pentane, 2,2-dimethylpropane); is, isomers (2-methylpentane, 3-methylpentane, 2,3-dimethylbutane).

[c] Turnover frequency based on metal dispersion from hydrogen chemisorption (H/Pd).

[d] For catalyst pretreatment see Table 1.

Table 3
2,2-Dimethylbutane reaction on silica-supported Pd2 catalyst (metal dispersion ∼ 0.04): Turnover frequencies, selectivities, and types of interaction

Reaction	Selectivity[a] (%)			Conversion	Type of interaction[b] (%)					TOF[c]
temperature (°C)	$S_{<6}$	S_{is}	S_{cycl}	(%)	$\alpha\gamma_{<6}$	$\alpha\gamma_{is}$	$\alpha\gamma'_{<6}$	$\alpha\gamma'_{is}$	$\alpha\beta_{<6}$	(s^{-1})
SR[d]										
330	49.1	50.6	0.3	1.70	42.9	9.5	1.3	42.2	4.0	7.29E–04
320	47.0	53.0	–	0.63	40.6	10.6	1.2	43.4	4.2	2.69E–04
310	45.3	54.7	–	0.24	37.8	10.2	2.0	44.3	5.6	1.02E–04
LR[d]										
341	43.3	56.7	–	0.28	33.5	12.8	3.7	46.1	3.8	1.54E–04
330	37.5	62.5	–	0.12	26.1	15.4	5.9	49.1	3.5	6.53E–05
321	23.3	71.2	5.5	0.05	14.0	20.6	–	60.7	4.7	2.84E–05
Regeneration[d]										
330	58.7	41.0	0.3	1.73	50.0	6.5	2.5	36.0	5.0	6.41E–04
320	55.0	45.0	–	0.52	46.9	8.1	1.9	38.3	4.9	1.94E–04
310	48.7	50.7	0.6	0.19	41.3	10.7	–	41.9	6.1	6.99E–05

[a–d] As in Table 2.

Table 4
2,2-Dimethylbutane reaction on silica-supported Pd3 catalyst (metal dispersion ∼ 0.01): Turnover frequencies, selectivities, and types of interaction

Reaction	Selectivity[a] (%)			Conversion	Type of interaction[b] (%)					TOF[c]
temperature (°C)	$S_{<6}$	S_{is}	S_{cycl}	(%)	$\alpha\gamma_{<6}$	$\alpha\gamma_{is}$	$\alpha\gamma'_{<6}$	$\alpha\gamma'_{is}$	$\alpha\beta_{<6}$	(s^{-1})
SR[d]										
330	48.5	51.1	0.4	1.22	41.9	9.3	1.8	43.4	3.6	1.37E–03
321	47.0	53.0	–	0.44	39.8	9.6	1.8	44.8	4.1	4.98E–04
310	44.0	56.0	–	0.15	37.4	10.0	–	47.7	4.9	1.65E–04
LR[d]										
350					No activity					
Regeneration[d]										
331	55.3	44.7	–	0.40	46.0	7.8	3.2	37.9	5.1	9.41E–04
320	51.4	48.1	0.5	0.14	42.1	9.9	2.4	39.5	6.1	3.25E–04
311	47.3	52.7	–	0.05	36.7	10.3	–	44.0	9.0	1.21E–04

[a–d] As in Table 2.

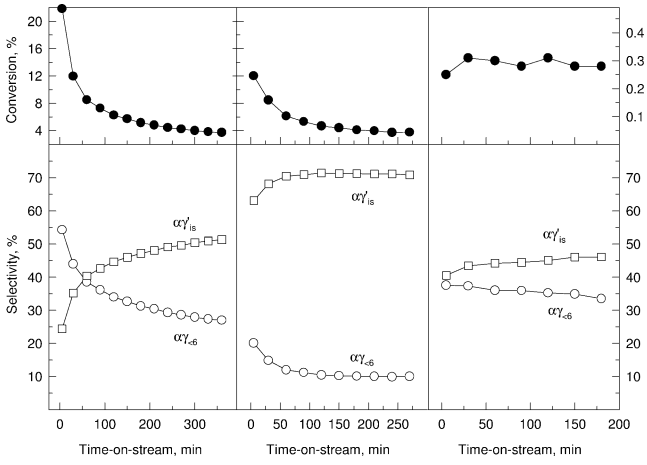
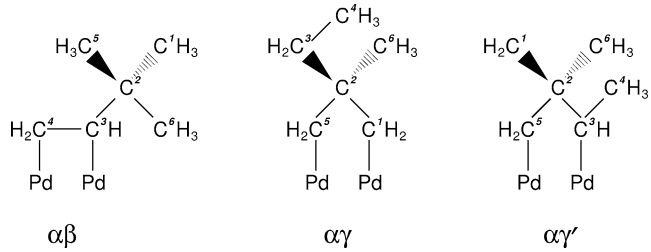


Fig. 3. Time-on-stream behavior (conversion and selectivity) in 2,2-dimethylbutane conversion for 10 wt% Pd/SiO_2 subjected to different pretreatments. Left section, for catalyst Pd1 after SR, reaction at 310 °C; middle section, for catalyst Pd1 after regeneration, reaction at 320 °C; and right section, for catalyst Pd2 after LR, reaction at 341 °C. For symbol designation, see text and Table 1.



Scheme 1. Principal modes of interaction of 2,2-dimethylbutane with metal surfaces, according to Burch and Paál [51].

is equally effective in the reactions of both 2-methyl- and 3-methylpentane, for primary, secondary, and tertiary C–C bonds.

This result, in combination with the fact that metallocarbenes cannot be formed from tertiary carbon atoms, indicates that demethylation cannot be ascribed to an $\alpha\beta$-dicarbene mechanism. Therefore, demethylation (as well as isomerization) of 2-methylpentane must proceed via $\alpha\gamma$-adsorbed species [68]. However, the presence of only an

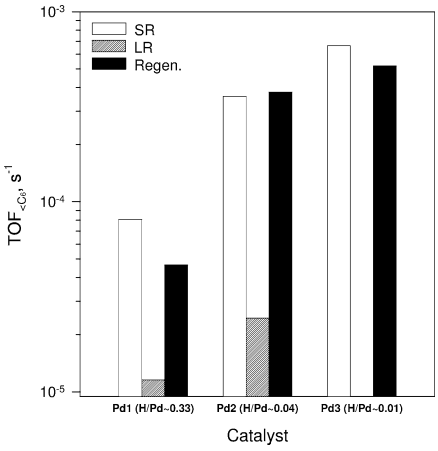


Fig. 4. Changes in turnover frequency for hydrogenolysis of 2,2-dimethylbutane conversion for differently pretreated 10 wt% Pd/SiO_2. Reaction temperature 310 °C (Pd1) or 330 °C (Pd2 and Pd3).

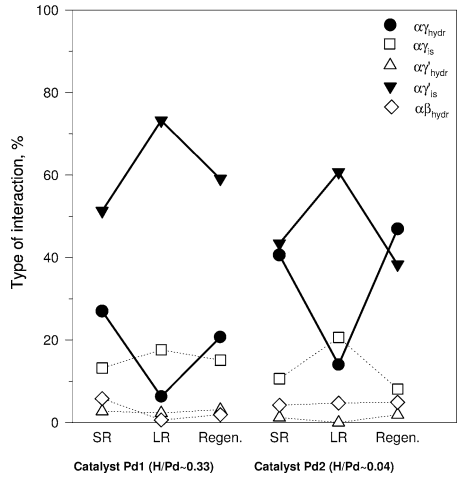


Fig. 5. Changes in type of interaction with the catalyst dispersion and pretreatment in the reaction of 2,2-dimethylbutane conversion. Reaction temperature 310 °C (Pd1) or 330 °C (Pd2).

ethyl (and not propyl) group in 22DMB does not allow activation of this molecule in a similar fashion as 2-methylpentane, so demethylation of the 22DMB chain from a longer side of this molecule can only proceed via an $\alpha\beta$ mode of interaction, giving neopentane and methane as primary products. Based on the above-noted arguments this process is less likely for palladium surfaces and, indeed, it was observed here only at a few percent level (Tables 2–4); instead the $\alpha\gamma$ type of interaction predominated.

At the beginning of the reaction, when the surface of palladium in SR samples is still not significantly contaminated, the bonding capacity of palladium surface atoms is high, both types of 1,3-interaction, $\alpha\gamma$ and $\alpha\gamma'$, operate (Fig. 3). The former type leads mainly to hydrogenolysis whereas the latter to isomerization. When the reaction proceeds, some Pd sites become "carbided," resulting in an extensive decrease of overall activity (Fig. 3). "Carbiding" also leads to changes in selectivity. Fig. 3 shows that the $\alpha\gamma'$ isomerization increases at the expense of $\alpha\gamma$ hydrogenolysis. This result, in agreement with Vogelzang et al. [50], suggests that the proportion of strongly adsorbing metal atoms is diminishing in the course of reaction. The reaction mechanism shifts from $\alpha\gamma$ to $\alpha\gamma'$ type. The activation of 22DMB via an $\alpha\gamma'$ state needs somewhat less energy than for $\alpha\gamma$ mode because the carbon–hydrogen bond in the $>CH_2$ group is weaker than in the $–CH_3$ group [74]. In general, a decreased bonding capacity of carbided Pd surface may favor the isomerization route over hydrogenolysis, which must require a stronger attachment of alkane molecule to palladium.

Compared to carbiding, silation of palladium surface caused by a long-term reduction at $T = 450$ and 500 °C results in even larger changes. The overall activity is very low (for Pd2) or completely vanished (for Pd3, most probably because of too extensive deposition of Si) already at the very beginning and does not alter much in the course of reaction. A similar stability characterizes the selectivity pattern. Fig. 3 (right section) illustrates this situation for catalyst Pd2 at the LR state. It appears that silation of Pd surface lowers the activity but also decreases (or completely eliminates) carbiding. Such a conclusion is in line with an earlier XRD study [6], that carbon introduction to palladium lattice is not observed after high-temperature reduction of Pd/SiO_2.

Tables 2 and 3 show that, at steady state, LR samples exhibit lower hydrogenolysis selectivities than SR and "regenerated" ones. This result, in combination with a significant decrease in overall activity, shows that upon Si addition to Pd, hydrogenolysis suffers much more than isomerization. Similar effects were already seen after carbiding palladium or alloying this metal with silver [50]. Changes in overall activity for hydrogenolysis (Fig. 4) upon LR are either nearly (for Pd1 and Pd3) or completely reversed (Pd2) upon regeneration. This suggests that silation of Pd particles during reduction at $T = 450$ and 500 °C is not as "deep" as after reduction at 600 °C, when only a partial "recovery" was reached [75].

Fig. 5 displays changes in the type of 22DMB interaction produced by catalyst pretreatment. Since the catalyst Pd3 lost its activity upon LR, it is not considered here. The most important changes are visible for the $\alpha\gamma$ (hydrogenolysis) and $\alpha\gamma'$ (isomerization) modes, so they are represented by thick solid lines. Other types of interaction alter slightly with catalyst pretreatment. The increase of $\alpha\gamma'$ (isomerization) mode at the expense of $\alpha\gamma$ (hydrogenolysis) is analogous to that achieved by carbiding. Accordingly, interpretation of this effect can again be rationalized by reduction of the bonding capacity of Pd/SiO_2 caused by blocking the metal surface, this time by silicon. Regeneration of LR samples by oxidation at 500 °C and reduction at 300 °C practically restores the catalytic behavior observed for SR samples (Fig. 5).

Fig. 6 presents the Constable plot constructed from activation energies and preexponential factors of differently pretreated Pd1, Pd2, and Pd3 catalysts. Although quite good correlation is found ($r^2 = 0.9918$), its interpretation does not appear straightforward. The 22DMB conversion, in which two reactions (hydrogenolysis and isomerization) charac-

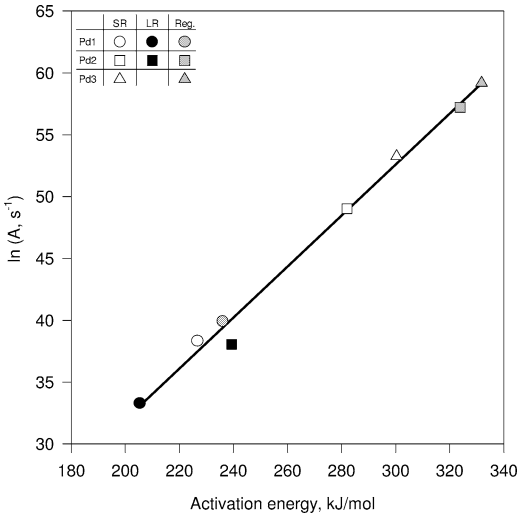


Fig. 6. Constable plot for 2,2-dimethylbutane conversion on differently pretreated Pd/SiO_2 catalysts.

terized by different structure-sensitivity occur, is probably influenced by palladium particle size as well by alloying (silation) effects. The problem is probably even more difficult because the extent of surface silation may depend on metal particle size. In any case, silation (LR samples of Pd1 and Pd2) markedly reduces both the activation energies and the preexponential factors. It is possible that the decreased preexponential factors indicate some reduction in the number of sites essential for 22DMB reaction. Apparently, silation decreases much more the number of these sites than the concentration of centers active in H_2 chemisorption. On the other hand, lower activation energies of LR samples would confirm our speculation of a decreased bonding capacity of "silaned" Pd surfaces. Recent work [76] showed that lower activation energies in alkane conversions on platinum catalysts may result from a decreased hydrogen coverage. Similarly, it was shown [77] that wide variations in apparent activation energy of alkane conversion may result from differences in chemisorption terms and in surface coverage, in the manner predicted by the Temkin equation. It is likely that diluting active Pd sites by silation weakens chemisorption bonds, leading to a decrease of hydrogen coverage and, as a consequence, to a decrease of apparent activation energies. It is possible that hydrogen is plentiful on palladium surfaces (even at "carbided" state) leading to higher values of E_a. Introduction of silicon onto a Pd surface must bring larger effects than carbiding. Adopting the idea of Vogelzang et al. [50] that deactivation of the "valley" positions in a palladium surface by deposited carbon species changes the catalytic behavior, we suggest that, due to much larger atomic radius, silicon should create even larger changes in the contiguity of palladium atoms, leading to more extensive modification of the catalytic behavior of palladium.

Fig. 6 suggests that silation brings about larger changes for low dispersed Pd/SiO_2 catalysts. This result is in line with recent studies of Smith et al. [10] who found that silation of palladium by Et_3SiH caused larger changes in the case of low metal dispersed Pd/SiO_2 catalysts. There are two reasons why the surface coverage of lowly dispersed palladium by silicon species is higher than that of highly dispersed Pd. First, the phenomenon of silicon incorporation into palladium bulk would be in some respects similar to that exhibited by absorption of hydrogen into bulk palladium: the lower Pd dispersion, the higher H/Pd_{bulk} ratio [78–80]. Thus, a low dispersed palladium would contain more silicon than a highly dispersed Pd. Second, the surface segregation of silicon in palladium silicides is known from the eighties [81–84]. The last finding combined with the Williams–Nason theory of alloy segregation [85] implies a more distinct silicon segregation in lowly dispersed Pd silicides than in highly dispersed ones. Both reasons lead to the conclusion that the surfaces of highly dispersed palladium are supposed to be less modified by silicon species.

4. Conclusions

We conclude that reduction of Pd/SiO_2 catalysts in dihydrogen at temperatures as low as 450–500 °C may already bring about considerable interactions between palladium and silica, recognized as the formation of palladium silicides. Previous literature data reported such a possibility, but achieved only at much higher temperatures ($\sim$ 600 °C and above). As the temperature level of 450 and 500 °C is commonly used in activation of silica-supported Pd-based catalysts [17–26,32–47], one can expect that, in a number of cases, $Pd–SiO_2$ interactions would have an effect on the catalytic behavior. Our observations, which were possible through application of a higher flow of a reducing gas mixture, indicate that an effective elimination of water vapor from the catalyst zone during H_2 pretreatment helps in reduction of silica to silicon, which interacts with nearby palladium species. Silation of palladium in Pd/SiO_2 catalysts during a prolonged reduction at $T = 450$ and 500 °C has a considerable effect on the catalytic properties in the reaction of 2,2-dimethylbutane with dihydrogen. Incorporation of silicon into palladium brings about similar catalytic consequences as carbiding or alloying with silver [50]. It lowers the catalytic activity, decreases the activation energy, increases the selectivity toward isomerization (at the expense of hydrogenolysis), and also changes the type of 2,2-dimethylbutane interaction with the surface of catalyst (from $\alpha\gamma$ to $\alpha\gamma'$ mode).

Acknowledgment

This work was partly supported by the Committee for Scientific Research of Poland (KBN) within Research Project 3 T09A 023 16.

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