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Transformation of Pd/SiO_2 catalysts during high temperature reduction

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During reduction in dihydrogen at 873 K, a silica-supported palladium catalyst is initially converted to Pd_4Si which further reacts with silicon-containing species to a Pd_3Si phase. Such a stepwise phase change suggests that the mechanism of Pd silicide formation involves incorporation of silicon into a palladium phase, not *vice versa*, as was suggested in our previous work. This transformation has a great effect on catalytic properties of Pd–silica-containing systems in 2,2-dimethylpropane hydroconversion.

KEY WORDS: high-temperature reduction (HTR) of Pd/SiO_2; Pd silicides (Pd_4Si, Pd_3Si) formation; 2,2-dimethylpropane conversion; isomerisation selectivity

1. Introduction

Compared to some more readily reducible oxides, such as TiO_2, CeO_2 or V_2O_5, which serve as typical supports of active phases in heterogeneous catalysis, silica is regarded as an essentially “nonreducible” oxide [1]. However, literature reports the formation of Pd silicides during high temperature reduction (HTR, in the presence of hydrogen) of Pd/SiO_2 catalysts [2–7]. This transformation may have a considerable effect on the catalytic behaviour of reduced Pd/SiO_2 samples [2–4,7]. For instance, the selectivity for alkane isomerisation is much higher after HTR of Pd/SiO_2 catalysts than that after reduction at 573 K [3,4,7]. XRD investigations [4,6,7] as well as TEM studies [5] showed the presence of a variety of palladium silicides, such as Pd_2Si [5], Pd_3Si [4,7], Pd_4Si [6] or Pd_5Si [4], in highly reduced Pd/SiO_2 samples. Although variations in the reduction conditions and form of the Pd–SiO_2 specimen would justify the differences in the composition of obtained Pd_xSi_y phases, such a general statement is not satisfactory. More systematic studies can give important information as to a possible mechanism of palladium silicide formation in Pd/SiO_2 catalysts. The knowledge about the state of Pd/SiO_2 after a specified reduction pretreatment would better explain, and give the possibility for tuning, catalytic properties of silica-supported palladium systems. In this respect it should be mentioned that an intentional introduction of silicon onto the surface of palladium greatly changes the catalytic behaviour in various reactions of saturated and unsaturated hydrocarbons [2–4,7–12].

This report presents results obtained for 10 wt% Pd/SiO_2 prepared by impregnation of silica with palladium dichloride. It was our hope that characterisation (by XRD) of different Pd_xSi_y phases generated in Pd/SiO_2 catalysts by various reduction conditions would be much easier if a higher Pd loading was used. In particular, we were interested in finding reasons for reported differences in the composition of Pd silicide phases caused by apparently similar pretreatments [4–8]. Evolution of one Pd silicide to another would give indications as to the mechanism of Pd–silica interactions generated by high temperature reduction. Finally, the most significant structures of highly reduced Pd/SiO_2 samples were tested as catalysts in hydroconversion of 2,2-dimethylpropane, the reaction which appeared so useful in diagnosing changes in differently pretreated supported palladium catalysts [3,4,7,8].

2. Experimental

The carrier employed in the preparation of a palladium catalyst was Davison Grade 62 silica gel, 75–120 mesh, acid washed, with surface area of 340 m^2/g and pore volume of 1.15 cm^3/g. 10 wt% Pd/SiO_2 catalyst was prepared by the method of incipient wetness impregnation, using an aqueous solution of palladium dichloride (analytical reagent from POCh, Gliwice, Poland). In order to increase metal particle size (to facilitate XRD studies) the catalyst was sintered by precalcination in air at 1023 K for 3 h. For further pretreatment (reduction in H_2, purified over MnO/SiO_2 and drying traps, flow 25 cm^3/min) the catalyst ($\sim$1.5 g sample of 10 wt% Pd/SiO_2) was placed in the U-tube reactor equipped with a fritted disc, two closing Young stopcocks and a side arm (1/4″ tubing) which was connected, *via* Cajon ultra-Torr fitting, with a long tubing with closed end for successive collection of hydrogen-pretreated samples. After each reduction step (*i.e.*, after 1, 3, 5, 15, 17, 60 and 200 h) at 873 K, the reactor was cooled down to room temperature, closed, detached from the glass system and turned upside down in order to transfer a small portion ($\sim$0.1 g) of the

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pretreated sample from the fritted disc to the collecting tubing. Part of the tubing with the solid was then flame sealed and detached from the reactor using a gas torch. In this way seven differently pretreated samples of the 10 wt% Pd/SiO_2 were collected and then subjected to X-ray diffraction studies (a standard Rigaku-Denki diffractometer with Ni-filtered Cu K_α radiation). The samples were scanned by a step-by-step technique in the 2θ range from 30° to 75°. At the beginning of HTR, the crystallite size of palladium (d_{Pd}) was ~35 nm, based on the broadening of 111 and 200 reflections of Pd (from the Scherrer formula). According to the formula proposed by Ichikawa *et al.* [13] this value is equivalent to the metal fraction exposed ~0.03 ($\mathrm{MFE} = 1.12/d_{Pd}$).

It is known from the study of temperature-programmed reduction that reduction of metal oxides is markedly hampered when it is performed in the presence of wet hydrogen [14–16]. A similar effect is obtained when one reduces a bigger sample of a metal oxide [14]. In order to study the effect of reduction conditions on the formation of Pd silicides from Pd/SiO_2, a smaller, than in the preceding experiment, sample (~0.14 g) of the 10 wt% Pd/SiO_2 was subjected to reduction at 873 K, using a higher, than previously, flow of hydrogen (~55 cm^3/min) and variable reduction time. A few samples pretreated in this fashion were also investigated by XRD.

The reaction of 2,2-dimethylpropane (Merck) in excess hydrogen (purified over MnO/SiO_2) on differently pretreated Pd/SiO_2 was conducted in a flow system under atmospheric pressure. 2,2-dimethylpropane was purified by passing it through a 5A molecular sieve trap to remove any *n*-butane impurity from the reactant stream. Feed partial pressures were: 2,2-dimethylpropane, 0.8 kPa, and hydrogen 8.0 kPa. Helium was a diluent gas. Total flow was 75 cm^3/min. The reaction was followed by GC (HP5890 with FID and 6 m squalane/Chromosorb P column). To avoid secondary reactions, overall conversions were kept low, *i.e.*, below 1%. In all cases, turnover frequencies (TOFs) were calculated on the basis of palladium dispersion estimated from the crystallite size of Pd-containing phase (from the broadening of the most intense XRD reflection). At the beginning of high temperature reduction (at 873 K) of 10 wt% Pd/SiO_2, the metal fraction exposed was estimated by H_2 chemisorption at 343 K (by pulse method) was in fair agreement with the corresponding value estimated from XRD profiles (~0.03). However, long term pretreatments in hydrogen at 873 K led to extremely low, practically not measurable hydrogen uptakes noticed in chemisorption measurements. On the other hand, the XRD profiles did not show large changes in the broadening of relevant XRD peaks originating from Pd_xSi_y phases, *vide infra*. These observations are in line with an earlier finding [3,4] that introduction of silicon onto a Pd surface leads to a large suppression of hydrogen chemisorption. The problems mentioned above (very low Pd dispersion and the presence of Si in Pd phase) cause the TOF values reported in this work to be probably subjected to a larger error. This is why in discussion of catalytic results more attention will be attached to changes in the selectivity.

3. Results and discussion

The results of XRD study of a larger sample (~1.5 g) of the 10 wt% Pd/SiO_2 catalyst subjected to a continuously more progressive reduction in H_2 at 873 K are presented in figure 1. The obtained diffraction patterns were confronted against the JCPDS files. However, a simple analysis of the vast majority of obtained XRD data allowed us to consider only three sets of crystallographic data: fcc phase of palladium, thin film of Pd_4Si data of Canali *et al.* [17][1] and orthorhombic phase of Pd_3Si [18]. It is clear from figure 1 that already a 1 h reduction of 10 wt% Pd/SiO_2 leads to visible changes in the XRD profile. Very small peaks, especially the reflection at ~40.8°, develop at further stages of the pretreatment indicating the formation of Pd_4Si at 873 K. It should be mentioned that an apparently similar specimen (5 wt% Pd/SiO_2 commercial catalyst from Degussa) investigated by Kępiński and Wołcyrz [6] did not show changes similar to ours, even after 40 h of reduction at 873 K (to see changes in the catalyst structure, those authors had to apply a considerably higher reduction temperature, 973 K). A dominant part of their XRD reflections were attributed to a Pd_4Si thin film phase earlier assigned by Canali *et al.* [17]. Our XRD profiles collected after 1, 3, 5, 15 and 17 h resemble very much the profiles from Kępiński and Wołcyrz work [6]. Therefore, we consider that at earlier stages of hydrogen treatment the Pd/SiO_2 catalyst successively transforms into Pd_4Si. After a 17 h reduction, the XRD profiles for fcc Pd phase are very weak, suggesting a substantial transformation of Pd into Pd_4Si.

Further reduction period extended to 60 h brings about considerable changes in the XRD spectrum. The reflections characteristic of Pd_4Si disappear and a new phase develops instead. This is an orthorhombic Pd_3Si phase, earlier noticed for 10 wt% Pd/SiO_2 (Serva SiO_2) after reduction at 873 K for 17 h [7] and for a physical mixture of Pd powder with Davison 62 silica gel, also after 17 h of reduction [4]. The presence of a greater number of Pd silicides in highly reduced Pd–SiO_2 catalysts (Pd_4Si, Pd_3Si or Pd_2Si [5]) may result from different factors, such as, *e.g.*, different Pd particle size, the presence of unspecified impurities in tested samples or different reduction conditions. The latter factor is addressed in the following paragraph.

XRD profiles of the smaller Pd/SiO_2 sample (0.14 g) pretreated at higher H_2 flow than the previous specimen (see section 2) are shown in figure 2. It is seen that a 5 h period of reduction at 873 K already leads to a dominant presence of Pd_3Si. It is recalled that in the preceding experiment, when we dealt with the larger sample of Pd/SiO_2 and lower hydrogen flow, such an effect was not observed even after a 17 h reduction period (only after 60 h, figure 1). This result

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[1] Data from table 1 (p. 5771) showing XRD results of Pd_4Si thin-film phase, after annealing at 923 K have been used in the present work.

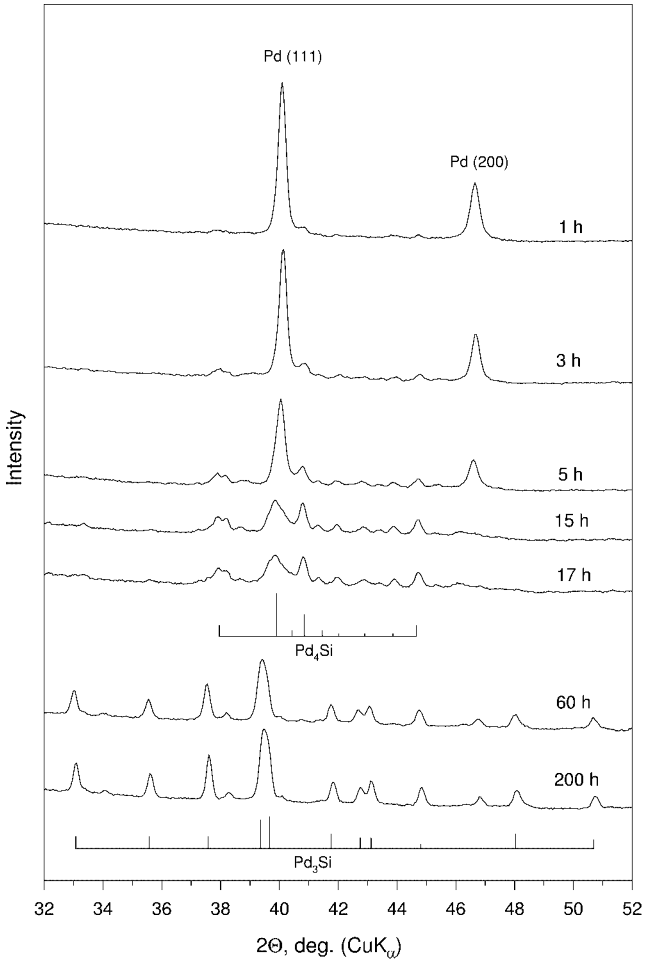

Figure 1. X-ray diffraction patterns obtained from a larger sample (1.5 g) of 10 wt% Pd/SiO$_2$ subjected to reduction in hydrogen at 873 K. All patterns are described by a reduction period (at right side of each profile), ranging from 1 to 200 h. Two bar diagrams represent literature data for: thin film of Pd$_4$Si from [17] and Pd$_3$Si [18]. In the case of Pd$_4$Si data, the reflections are visualised in a semiquantitative fashion according to their intensity (marked in [17] as vvs, vs, ms, m and mw).

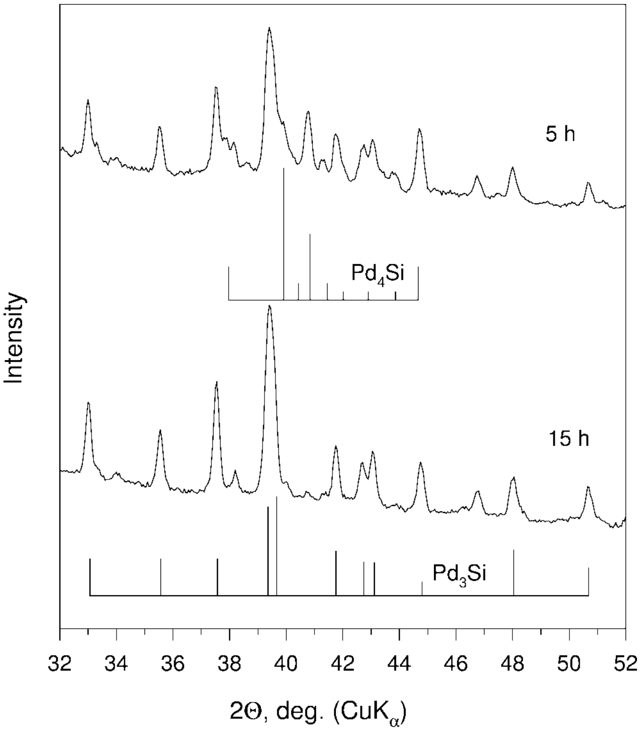

Figure 2. X-ray diffraction patterns obtained from a smaller sample (0.14 g) of 10 wt% Pd/SiO$_2$ subjected to reduction in hydrogen at 873 K for 5 and 15 h. The two bar diagrams represent literature data for thin films of Pd$_4$Si [17] and Pd$_3$Si [18] (see figure 1).

may rationalize the controversy in reported compositions of Pd$_x$Si$_y$ phases obtained after the high temperature reduction of Pd/SiO$_2$ catalysts [3–7]. The observation of Pd$_4$Si formation in the first experiment was possible because, most probably, reduction of Pd/SiO$_2$ was retarded by a slower removal of water vapor from the larger portion of the catalyst.

Previously [4] we assumed that palladium species enter the silica support *via* oxygen vacancies giving rise to palladium silicide formation. The Pd$_4$Si → Pd$_3$Si transformation during further stages of hydrogen treatment at 873 K sug-

Table 1
2,2-dimethylpropane conversion over 10 wt% Pd/SiO$_2$ (0.15 g) subjected to various reduction pretreatments: overall conversions, product selectivities, turnover frequencies and activation energies

Catalyst pretreatment[a]	Reaction temperature (K)	Conversion (%)	Selectivity[b] (%)		TOF[c] (s^{-1})	Activation energy (kJ/mol)
			$S_{<C_5}$	S_{iso}		
Red. 573 K, 1 h	544	0.15	53.5	46.5	1.43×10^{-4}	276 ± 2
	554	0.44	55.3	44.7	4.20×10^{-4}	
Red. 873 K, 3 h	574	0.10	42.9	57.1	9.50×10^{-5}	
	583	0.23	42.5	57.5	2.19×10^{-4}	251 ± 8
	594	0.64	44.5	55.5	6.10×10^{-4}	
Red. 873 K, 15 h	603	0.11	37.6	62.4	1.05×10^{-4}	
	613	0.25	36.0	64.0	2.38×10^{-4}	238 ± 3
	623	0.50	37.8	62.2	4.77×10^{-4}	
Red. 873 K, 60 h	614	0.14	34.2	65.8	1.33×10^{-4}	
	624	0.29	33.8	66.2	2.77×10^{-4}	249 ± 9
	633	0.55	34.6	65.4	5.25×10^{-4}	

[a] Reduction treatment in H$_2$ (temperature and duration). All samples were precalcined at 1023 K for 3 h.
[b] $S_{<C_5}$ = selectivity for hydrogenolysis; S_{iso} = selectivity for isomerisation.
[c] TOF (turnover frequency) assuming palladium dispersion 0.03 (see section 2).

gests a different mechanism. The stepwise enrichment in silicon of the silicide phase implies that silicon-containing species (Si, SiO or silane [19]) are the migrating species which enter the bulk of Pd-based material. We expected that our experiment with the reduction period increased to 200 h would show the formation of even more Si-rich silicides (*e.g.*, Pd_2Si, observed by others [5]). Unfortunately, such attempts failed. Probably, the ability towards dihydrogen dissociation of the Pd_3Si surface is markedly reduced compared to the behaviour of pure palladium. Such a situation would result from a simple extrapolation of the hydrogen chemisorption study of differently prereduced Pd/SiO$_2$ catalysts [3,4]. If it were so, the hydrogen atom flux needed for the reduction of silica would be considerably diminished.

Since our earlier reports indicated a considerable increase of alkane isomerisation selectivity of silica-supported palladium catalysts subjected to high temperature reduction [3,4,7,8,20] we decided to test the catalytic behaviour of present Pd/SiO$_2$ samples after different reduction periods. We were interested to examine if the $Pd_4Si \rightarrow Pd_3Si$ transformation, associated with silicon enrichment of Pd-based phase, would cause important changes in isomerisation selectivity (S_{iso}) of 2,2-dimethylpropane. Table 1 shows the results of catalytic screening. It is seen that extra time of catalyst reduction in H_2 at 873 K leads to a continuous growth in isomerisation selectivity. However, the most important increase in isomerisation selectivity is achieved already after a 3 h reduction period. At that stage, a significant portion of our catalyst is converted into Pd_4Si (figure 1 and discussion above). Further reduction (15 and 60 h) brings about some increase of S_{iso}; however, at the same time the overall activity decreases. Table 1 shows that for increasingly prolonged reduction periods, much higher reaction temperatures are needed for obtaining similar conversion levels. Therefore, one can speculate that addition of moderate amounts of silicon leads to a more useful tuning of Pd/SiO$_2$ catalysts. Although we do not dispose with the knowledge about surface composition of our Pd silicides it is reasonable to assume that Pd_3Si has more silicone than Pd_4Si at the surface. In this respect, it seems appropriate to note that adding larger amounts of silicon brings about a serious catalyst poisoning, as has been observed by Molnar *et al.* [21], who studied selective poisoning by Et_3SiH of various metals (Cu, Ni, Rh, Pd and Pt) in catalytic hydrogenation.

Table 1 also shows that HTR of 10 wt% Pd/SiO$_2$ lowers the activation energy in 2,2-dimethylpropane reaction. Apparently, the presence of silicon in palladium surface brings about similar changes in E_a as diluting palladium with gold [22].

To sum up, we report, for the first time, variations in the composition of the Pd_xSi_y ($Pd_4Si \rightarrow Pd_3Si$) during high temperature reduction of silica-supported palladium catalysts. Such changes are suggestive of the mechanism of a successive incorporation of silicon species into the palladium bulk. Efficiency of palladium–silica interactions strongly depends on the rate of water vapor removal during high temperature reduction. Consequences of this effect would be important for the state of silica-supported palladium catalysts reduced by others at somewhat lower temperatures (*e.g.*, at 773 K and below). Testing the above hypothesis is under way in our laboratory.

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