

Characterization of Supported Palladium Catalysts¹

II. Pd/SiO₂

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The isomerization of neopentane has been investigated over the 0.76 wt% Pd/SiO₂ catalyst. It is found that after high temperature reduction (HTR, at 873 K) the selectivity for isomerization is much higher than that after low temperature reduction (LTR, at 573 K). A variety of experiments, including kinetic, chemisorption (O₂, H₂, and CO), temperature-programmed desorption of H₂, and X-ray diffraction, showed that this selectivity enhancement cannot be interpreted in terms of H₂ retention by the catalyst. Instead, the formation of Pd-Si compound(s) (most probably Pd₃Si) during HTR seems immediately responsible for the catalytic behavior of HTR Pd/SiO₂ catalysts. A mechanism is proposed for the Pd-SiO₂ interactions in which Pd atoms (or ions) are incorporated into the silica support (via oxygen vacancies) and a new phase of palladium silicide is formed. Regeneration by an oxygen treatment of the HTR sample does not fully restore the low isomerization selectivity typical of LTR samples. The additional selectivity is attributed to an overlayer of oxidized silicon species (after oxidation of the HTR sample) which partially cover the metal.

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INTRODUCTION

Recently we found that the reaction of neopentane with hydrogen may serve as a probe reaction for the characterization of Pd surfaces in various supported Pd catalysts (1). The selectivity toward isomerization (production of isopentane) vs cracking (formation of CH₄, C₂H₆, C₃H₈, and *i*-C₄H₁₀) appeared to be a convenient diagnostic parameter toward determining whether Pd interacts with a support. From our earlier work, we adopted the value of ca. 30% as the upper limit of isomerization selectivity for severely sintered Pd powders (2). Accordingly, an isomerization selectivity > 30%, especially near ca. 80-90%, has to be attributed to other causes, of which the more important seem to be metal-support interactions (3-10) and hydrogen retention in the Pd/support catalysts (11-14).

Both effects might operate after high temperature reduction (HTR).

Our attention was focused mainly on the Pd-silica system (1), because relatively little is known about the interaction between silica and palladium. In contrary, there is an enormous volume of literature on Pd-Si interactions leading to the formation of various Pd silicides (15-17). Although the formation of Pd silicides from Pd and SiO₂ at very high temperatures is expected both from thermodynamic considerations (18) and from research for device technology (15, 16), its importance in the field of heterogeneous catalysis seems somewhat underestimated. A noticeable exception is the work by Moss *et al.* (19) who found in their X-ray diffractometry (XRD) study that a 10 wt% Pd/SiO₂ catalyst subjected to HTR (873 K) underwent considerable transformation resulting in the formation of an unspecified Pd-Si phase(s). They assumed that interaction between Pd and SiO₂ occurred even at 723 K as their Pd/SiO₂ cata-

¹ Reference (1) is regarded as Part I of this series.

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lysts were less active for benzene hydrogenation than the same samples reduced at 573 K. However, other recent works concerning severely reduced (at 873 K and above) Pd/SiO₂ catalysts either do not report any serious interaction between both catalyst components (20) or do not refer to the formation of Pd silicides even if abnormal chemisorptive/catalytic properties of Pd/SiO₂ catalysts (after HTR) have been found (21). The main conclusion of our recent report (1) was that Pd interacts with SiO₂ at higher reduction temperatures (873 K and also even at 723 K) giving some palladium silicide species on the catalyst surface and this fact seems to be responsible for the increase of isomerization selectivity in neopentane conversion (up to ca. 70–90%).

We decided to continue this study for the following reasons. First, we felt that the problem of the effect of residual hydrogen in silica-supported Pd catalysts after HTR had not been properly considered in Ref. (1). Our statement that *all* residual hydrogen was removed from the catalyst after HTR by flushing with argon (or helium) at 873 K for 1 h could be not strictly valid. Although oxygen pulses did not produce water at 293 K, it could not be ruled out that strongly bound residual hydrogen may not react with oxygen at room temperature. It is known that silica pretreated with hydrogen at very high temperatures contains large amounts of "dissolved" hydrogen existing mainly in hydroxyl groups (22). Infra-red spectroscopy also shows a presence of Si–H bonds in hydrogen-pretreated silicas (23, 24).

A part of the present work is dedicated to the problem of determining the possible effect of residual hydrogen. We also try to furnish more solid evidence as to the absence of the effect of retained hydrogen in the HTR sample. Second, it appeared interesting to collect more experimental information which could give further insight into the nature of palladium–silica interactions. We did not have EXAFS, ESCA, or other

more sophisticated methods at our disposal, therefore our approach had to remain more "chemical." By properly designed kinetic and chemisorption studies, as a continuation of our chemical probes, we expected to obtain relevant information concerning Pd/SiO₂ catalysts.

EXPERIMENTAL METHODS

The preparation of 0.76 wt% Pd/SiO₂ catalyst has been described in an earlier paper (1). A few experiments were also performed with Pd and Pd–Ag powders. Both powders were Alfa Ventron products: Pd, 99.95% pure, fraction 0.25–0.55 μm and Pd–Ag alloy (35 : 65 ratio by weight), 99.9% pure.

The fractions exposed exhibited by the 0.76 wt% Pd/SiO₂ catalyst after various pretreatments were determined from chemisorption of H₂ (at 343 K) and CO (at 293 K) using a pulse technique. All gases used, except oxygen, i.e., H₂, CO, Ar, and He, were purified by passing through drying traps with final purification over MnO/SiO₂. Carbon monoxide was 99.995% pure (Van Eeghen, The Netherlands).

In a few experiments using temperature-programmed desorption (TPD) of H₂ from the 0.76 wt% Pd/SiO₂ catalyst following various pretreatments, the temperature was increased at a rate of 25 K/min from room temperature to ca. 1300 K. Between the reactor and the katharometer cell (Gow-Mac) a trap with degassed 4A molecular sieves was inserted in order to eliminate any traces of water released from the catalyst during TPD run.

The reaction of neopentane (Merck) with hydrogen (palladium-diffused) was investigated in a static circulation system in the manner described previously (1, 2, 25). The alkane partial pressure was always kept at ca. 6 Torr (1 Torr = 133.3 Pa). The ratio of hydrogen-to-alkane was usually 10 : 1. In order to determine how hydrogen pressure influences the reaction rate, in some kinetic experiments H₂ pressure was changed between 20 and 120 Torr.

Turnover frequencies (N_t 's) were calculated on the basis of the fraction exposed measured by H₂ chemisorption. Initial product distributions (= selectivities) were calculated as the carbon percentage of neopentane consumed in the formation of a designated product, for example, mole percent of methane from neopentane would be divided by 5 and normalized in deriving the product distribution (25).

RESULTS

Chemisorption of Hydrogen, CO, Oxygen, and O₂/H₂ Titration

Table 1 presents data regarding fractions exposed (H/Pd_t and CO/Pd_t) exhibited by the 0.76 wt% Pd/SiO₂ catalyst after various pretreatments. In the pretreatment code (Table 1), O₂,573,0.5;H₂,573,1;Ar,723,1 means that the catalyst was exposed to flowing oxygen at 573 K for 0.5 h, then to hydrogen at 573 K for 1 h and, finally, to argon at 723 K for 1 h.

After chemisorption of H₂ on one HTR sample (pretreatment: O₂,573,0.5;H₂,873,

17;Ar,873,1; and H/Pd_t = 0.19) chemisorbed hydrogen was titrated with O₂ pulses at 293 K. The course of O₂/H₂ titration is presented in Fig. 1. It can be seen that second and third pulses of oxygen were consumed to a greater extent than the first one. The overall consumption of oxygen was (O/Pd_t)_o = 0.76. In order to calculate the amount of adsorbed oxygen it is necessary to subtract the expected uptake of oxygen needed for water production (O/Pd_t)_w = $\frac{1}{2}$ (0.19) = 0.095. Thus, the amount of adsorbed oxygen is (O/Pd_t)_a = 0.665. A somewhat lower consumption of O₂ on a similar sample (but without the preceding H₂ chemisorption) was found at 293 K, (O/Pd_t)_a = 0.58.

Temperature-Programmed Desorption of Retained Hydrogen from 0.76 wt% Pd/SiO₂ after HTR

Determinations of retained hydrogen by TPD were run on two samples of the Pd/SiO₂ catalysts. Both samples were reduced at 873 K for 17 h and flushed with an argon

TABLE 1
Fraction Exposed of 0.76 wt% Pd/SiO₂ Catalyst
after Various Pretreatments

Pretreatment ^a	H/Pd _t		CO/Pd _t ^d
	Adsorption ^b	Desorption ^c	
"Standard": O ₂ ,573,0.5; H ₂ ,573,1;Ar,723,1	0.70	0.69	0.62
O ₂ ,573,0.5;H ₂ ,573,1;Ar,873,18	0.49 (0.39) ^e	0.34	0.29
O ₂ ,573,0.5;H ₂ ,723,3;Ar,773,1	0.68	0.69	0.63
O ₂ ,573,0.5;H ₂ ,723,21;Ar,773,1	0.35	0.35	0.52
O ₂ ,573,0.5;H ₂ ,873,17;Ar,873,1	0.19	0.13	0.29
O ₂ ,723,1;H ₂ ,573,1;Ar,723,1 ^f	0.41	0.37	0.34
O ₂ ,573,0.5;H ₂ ,873,17;Ar,873,17	0.28	0.19	0.27

^a For the pretreatment code, see text.

^b Fraction exposed measured by hydrogen chemisorption at 343 K.

^c Fraction exposed measured by hydrogen desorption at 723 K.

^d Fraction exposed measured by CO chemisorption at 293 K.

^e The first number concerns H₂ uptake after the catalyst pretreatment, whereas the value in parentheses concerns H₂ consumption after H₂ desorption at 723 K. The value in parentheses is used in calculation of turnover frequency.

^f This pretreatment was applied to the catalyst previously reduced at 873 K for 17 h and flushed with Ar at 873 K for 1 h.

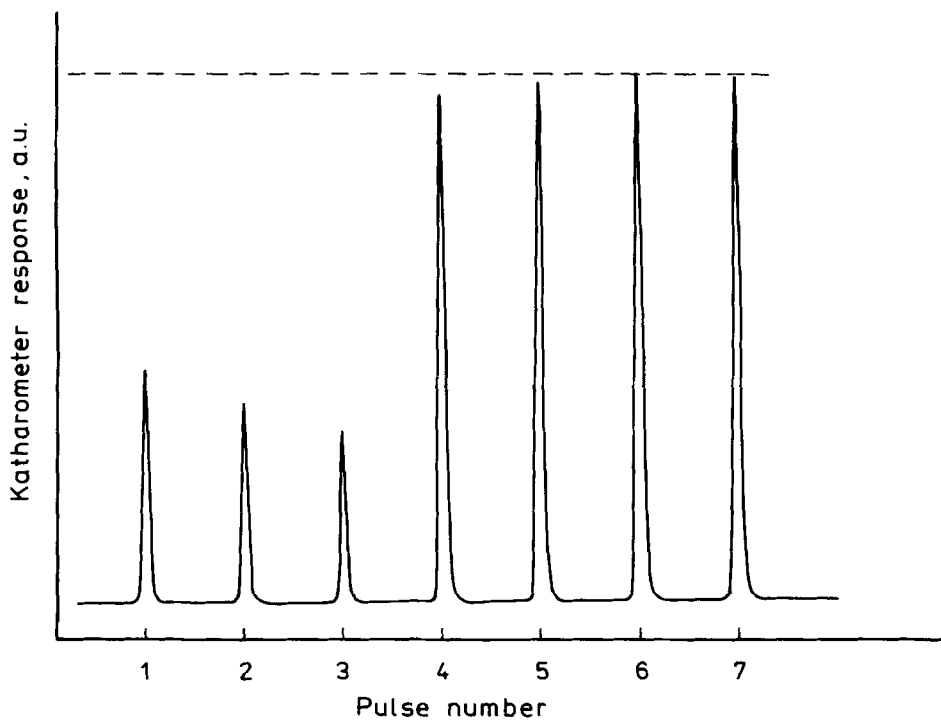


FIG. 1. The course of O_2/H_2 titration (at 293 K) of the 0.76 wt% Pd/SiO₂ catalyst after $O_2, 573, 0.5; H_2, 873, 17; Ar, 873, 1$. Catalyst weight, 0.340 g; He flow, 20 ml/min; a pulse of 4.7 μ mole of O_2 every 5 min.

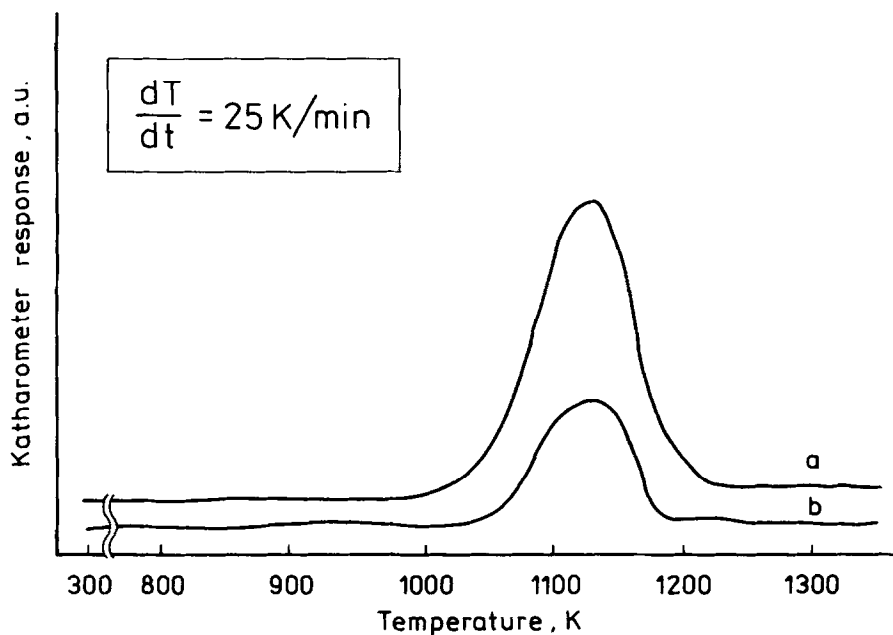


FIG. 2. TPD determination of retained hydrogen from two HTR samples of the 0.76 wt% Pd/SiO₂ catalyst. Curve (a) concerns a sample which has been flushed with Ar at 873 K for 1 h after HTR, whereas curve (b) concerns a HTR sample after a 17-h period of purging with argon at 873 K. Ar flow, 20 ml/min.

stream at 873 K. However, in the case of one sample this flushing was rather short, 1 h, whereas for another it was long, 17 h. Temperature program, $dT/dt = 25$ K/min was applied in both cases. Figure 2 shows the results. Only one form of desorbed hydrogen is seen, with maximum at ca. 1120–1130 K. The amount of released hydrogen ($(H/Pd)_d$) after the shorter flushing time was 1.2 which is ca. 2.5–3 times higher than the appropriate value after longer Ar flushing.

Reaction of Neopentane with H₂ on 0.76 wt% Pd/SiO₂ and on Pd and Pd–Ag Powders

Table 2 shows the results of kinetic studies 0.76 wt% Pd/SiO₂ after various pretreat-

ments (alkane pressure = 6 Torr, H₂/alkane = 10).

Table 3 is concerned with catalytic results for the catalyst which was oxidized, after HTR, at various conditions.

Figure 3 presents the hydrogen pressure dependence of the rates of hydrogenolysis and isomerization of neopentane over HTR catalyst (1 h Ar flushing at 873 K). Figure 4 presents a similar relation for the same catalyst but reduced at 723 K for 3 h and cooled in hydrogen to 523 K and briefly evacuated at 523 K before the reaction.

Table 4 shows kinetic results collected for unsupported samples: Pd (mixed with SiO₂, Davison grade 62, 100–120 mesh) and Pd–Ag (35 : 65) alloy powders.

It should be mentioned that pure (and

TABLE 2
Reaction of Neopentane on the 0.76 wt% Pd/SiO₂ Catalyst after Various Pretreatments

Catalyst pretreatment	Reaction temperature (K)	N_t (s ⁻¹)	Initial product distribution (%)				
			CH ₄	C ₂ H ₆	C ₃ H ₈	<i>i</i> C ₄ H ₁₀	<i>i</i> C ₅ H ₁₂
O ₂ ,573,0.5;H ₂ ,573,1;He,573,0.5	521	9.60×10^{-6}	42.4	—	3.7	43.0	11.0
	531	2.70×10^{-5}	36.4	0.4	12.9	50.3	—
	518	5.90×10^{-6}	27.2	1.0	3.8	49.8	18.7
	539	7.90×10^{-5}	36.4	1.0	22.0	39.8	0.7
	522	4.30×10^{-6}	52.7	1.6	3.1	28.2	14.4
	530	3.00×10^{-5}	32.4	0.4	10.5	51.5	5.6
O ₂ ,573,0.5;H ₂ ,573,1;He,873,17	525	1.39×10^{-5}	24.7	0.9	4.3	29.4	40.7
	534	3.12×10^{-5}	14.3	0.1	0.5	37.5	47.6
	544	6.48×10^{-5}	19.5	0.5	2.5	39.3	38.1
O ₂ ,573,0.5;H ₂ ,723,24;He,773,1	514	5.20×10^{-6}	6.3	0.7	1.2	26.4	65.3
	524	1.85×10^{-5}	7.8	0.4	1.3	36.0	56.4
	533	4.42×10^{-5}	12.5	0.5	1.0	30.7	55.3
O ₂ ,573,0.5;H ₂ ,873,17;He,873,1	575	7.90×10^{-5}	4.1	0.7	0.6	9.5	85.1
	593	2.15×10^{-4}	9.0	1.2	1.4	15.7	72.7
O ₂ ,573,0.5;H ₂ ,873,17;He,873,6	533	8.20×10^{-6}	7.2	0.7	2.4	12.3	77.4
	542	1.44×10^{-5}	4.7	0.6	1.5	13.1	80.1
	551	4.11×10^{-5}	4.9	0.3	—	14.0	80.7
O ₂ ,573,0.5;H ₂ ,873,17;He,873,17	534	1.95×10^{-5}	11.5	1.1	2.2	16.6	68.7
	543	4.29×10^{-5}	7.9	0.2	0.2	18.4	73.2
	553	6.82×10^{-5}	12.5	1.0	1.3	22.6	62.6
	534	2.06×10^{-5}	8.8	0.6	1.8	16.0	72.8
	544	4.20×10^{-5}	7.4	0.3	0.2	21.3	70.8
	553	6.87×10^{-5}	10.7	0.8	1.4	29.4	57.7
O ₂ ,573,0.5;He,873,17;H ₂ ,873,17;He,873,1	559	1.03×10^{-5}	0.2	0.2	1.5	6.2	91.9
	569	1.88×10^{-5}	1.8	0.4	—	5.6	92.2
	578	4.49×10^{-5}	3.2	0.5	0.8	8.8	86.8

TABLE 3

Effect of Oxidation Conditions on Regeneration of the 0.76 wt% Pd/SiO₂ Catalyst after HTR^a

Oxidation temperature, duration	Reaction temperature (K)	N_t (s ⁻¹)	Initial product distribution (%)				
			CH ₄	C ₂ H ₆	C ₃ H ₈	<i>i</i> C ₄ H ₁₀	<i>i</i> C ₅ H ₁₂
298 K, 0.25 h	545	3.20×10^{-4}	19.8	1.3	2.9	42.9	33.3
	558	4.40×10^{-4}	26.6	2.3	8.8	41.6	20.7
298 K, 0.25 h	528	6.90×10^{-5}	20.4	0.8	2.0	25.5	51.3
	537	1.19×10^{-4}	16.9	0.7	0.7	37.8	43.9
573 K, 0.5 h	545	1.78×10^{-4}	24.0	1.8	3.8	40.4	30.0
	536	9.10×10^{-5}	16.6	0.7	1.1	35.3	46.3
723 K, 1 h	555	4.71×10^{-4}	23.8	1.1	5.2	43.5	26.4
	524	1.40×10^{-5}	13.7	2.4	2.7	27.7	53.5
	534	4.60×10^{-5}	13.1	—	0.1	33.8	52.5
	553	3.11×10^{-4}	25.9	1.2	4.1	43.2	26.5

^a All oxidations followed by H₂, 573, 1.

washed with HCl) SiO₂ pretreated as our Pd/SiO₂ (both after low temperature reduction (LTR) as well as after HTR) did not show any catalytic activity at temperatures up to 673 K. After the reaction, HTR sam-

ples of the Pd + silica mixture were analyzed by XRD. Figure 5 shows a typical spectrum. The samples were scanned in the 2θ range of 30° to 50° (Rigaku-Denki diffractometer, CuKα, Ni-filtered radiation). The

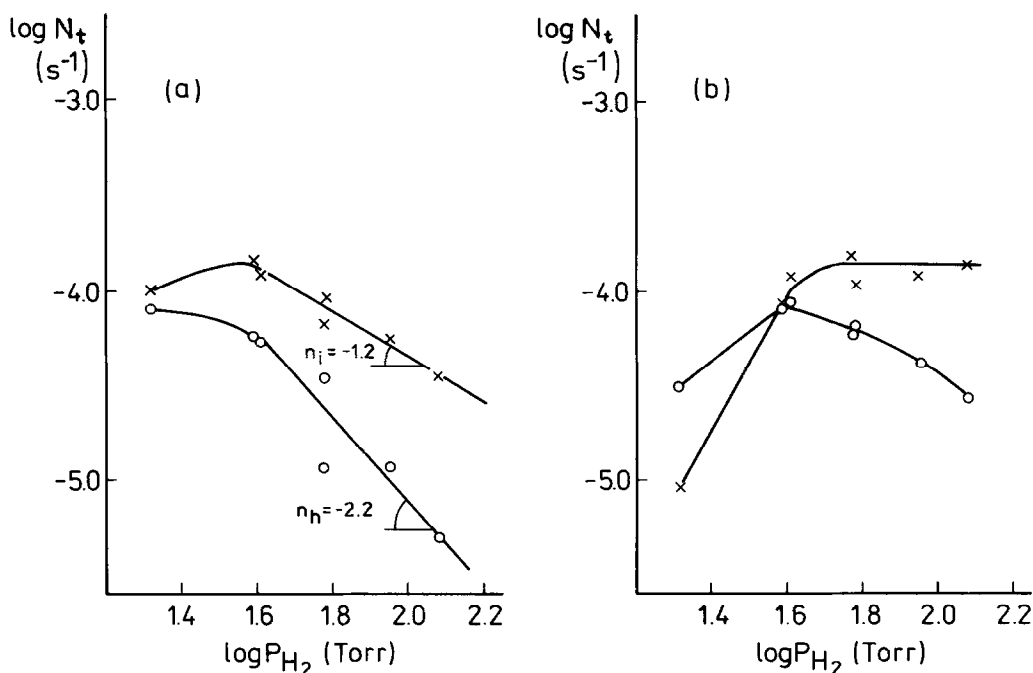


FIG. 3. Effect of hydrogen pressure on the rates of hydrogenolysis (O) and isomerization (X) over a HTR sample of the 0.76 wt% Pd/SiO₂ catalyst (flushed with He at 873 K for 1 h). Reaction temperature, (a) -573 K; (b) -593 K. n_h and n_i are reaction orders versus hydrogen for hydrogenolysis and isomerization, respectively. Each data point represents a fresh sample.

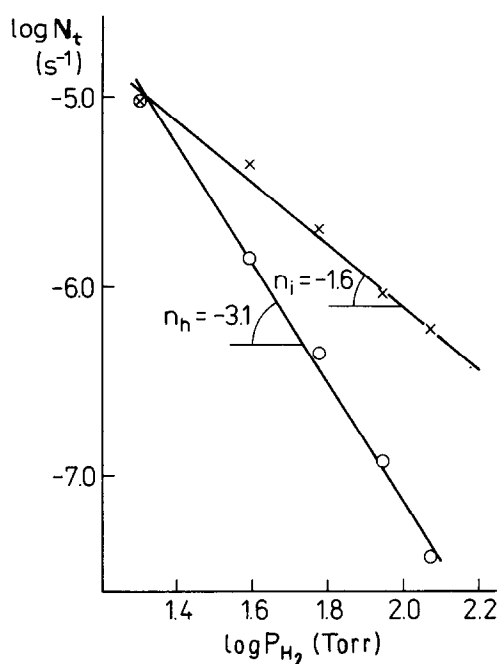


FIG. 4. Effect of hydrogen on the rates of hydrogenolysis (O) and isomerization (X) over the 0.76 wt% Pd/SiO₂ catalyst after reduction at 723 K for 3 h, without vigorous removal of H₂. n_h and n_i are as in Fig. 3. Each data point represents a fresh sample.

majority of the observed peaks were assigned to pure Pd and Pd₃Si phases (26, 27).

DISCUSSION

The results presented in this paper concern the same 0.76 wt% Pd/SiO₂ catalyst which was used in our previous study (1). Very pronounced differences in catalytic behavior, especially in isomerization selectivity (variations between 0 and 90%), resulted from different pretreatments of this catalyst (Table 2). In this paper we shall discuss two problems. First, we shall determine the extent to which residual hydrogen in the catalyst after HTR influences catalytic behavior. We shall present evidence that a high level of isomerization selectivity obtained after helium flushing (at 873 K) of a HTR sample is not due to retained H₂, but due to metal-support interactions. Second, we shall present our picture of transformation of Pd/SiO₂ catalysts during HTR and regeneration.

TABLE 4

Reaction of Neopentane on Pd and Pd-Ag (35:65) Alloy Powders

Sample pretreatment	Reaction temperature (K)	Initial reaction rate ^a	Initial product distribution (%)					
			CH ₄	C ₂ H ₆	C ₃ H ₈	<i>i</i> C ₄ H ₁₀	<i>i</i> C ₅ H ₁₂	
Pd + SiO₂								
O ₂ ,573,0.5;H ₂ ,573,1	528	17.50	21.1	2.8	4.9	46.0	25.3	
	537	60.20	19.4	1.1	4.1	53.5	21.9	
	547	207.00	27.7	4.1	15.8	50.7	1.6	
O ₂ ,573,0.5;H ₂ ,573,1;He,873,17	571	16.00	18.4	1.6	2.2	53.9	23.9	
	586	60.00	16.8	7.3	11.2	60.1	4.5	
O ₂ ,573,0.5;H ₂ ,723,17;He,773,17	555	38.90	19.5	1.1	2.1	61.9	15.4	
	565	69.80	20.8	3.8	5.7	62.9	6.8	
	642	11.00	4.5	0.5	—	48.5	46.5	
O ₂ ,573,0.5;H ₂ ,873,17;He,873,1 ^b	662	13.00	8.8	0.3	3.3	63.1	24.4	
	580	6.48	4.9	—	—	18.7	76.4	
	589	12.50	4.1	0.7	1.0	13.1	81.0	
O ₂ ,573,0.5;H ₂ ,873,17;He,873,22 ^c	599	22.70	5.0	0.2	1.8	15.0	78.0	
Pd-Ag alloy powder								
O ₂ ,573,0.25;H ₂ ,673,1	682	2.86	8.7	—	—	32.9	58.5	
	691	2.88	14.1	—	1.9	36.0	56.4	

^a Expressed as 10⁻¹⁰ mol · g_{Pd (or PdAg)}⁻¹ · s⁻¹.

^b Sample prepared by inadequate mixing of Pd powder with silica, designated as (a) in the text.

^c Sample prepared by very careful mixing of both components, designated as (b) in the text.

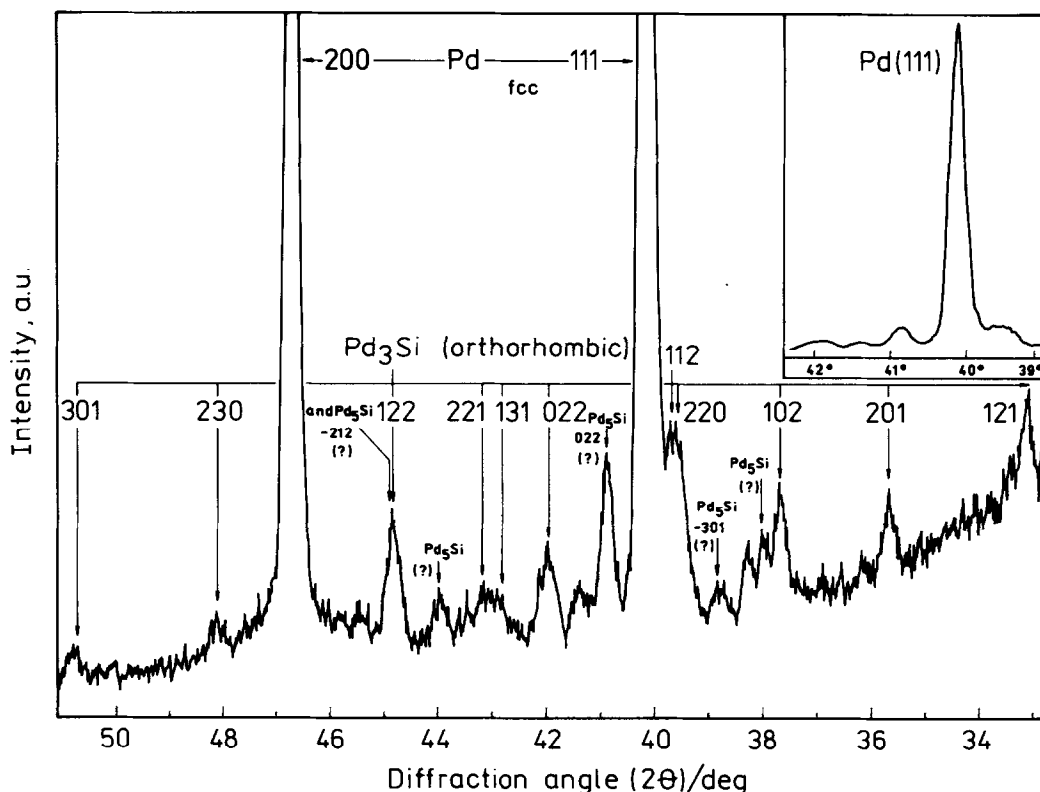


FIG. 5. XRD spectrum of a mechanical mixture of Pd powder and silica gel after HTR. The assignment of Pd_3Si (and Pd_5Si) by Wysocki and Duwez (26) and nonindexed reflections by Röschel and Raub (27). Inset, a part of XRD spectrum showing the vicinity of (111) reflection of Pd, intensity scale lowered by factor of ca. 10.

Hydrogen Effect or Its Absence?

A Pd/SiO₂ catalyst, which is highly selective (toward isomerization) is produced upon HTR ((1) and present results). Table 1 taken from Ref. (1) shows that the catalyst reduced at 873 K for 17 h without flushing with He is very selective but also not very active. Flushing with He at 873 K for 1 h produces a more active sample (activity level judged from the reaction temperature needed to obtain a similar level of conversion). At the same time isomerization selectivity decreases only slightly (85 vs 92%, Table 1 in (1)). Prolonged duration of the He flush at 873 K (6 or 17 h vs 1 h) seems to increase the activity slightly but with no significant decrease in the isomerization selectivity (Table 2, this work). Thus, when a

HTR sample of Pd/SiO₂ was not flushed with He at 873 K the effect of the treatment with H₂ at 873 K appeared as a drop in overall activity. However, in cases when catalysts are flushed with inert at least for 1 h, as will be shown, retained hydrogen, if any, does not influence kinetic results.

First, as was stated previously (1), O₂ pulses introduced at 293 K onto a HTR sample (flushed out with Ar at 873 K for 1 h) did not produce water. Whether or not oxygen reacts with strongly bound hydrogen at 293 K is a problem which cannot be solved here. However, Table 3 shows that oxygen pretreatment of the HTR sample "regenerates" the catalyst to an extent which is independent of the severity of the O₂ treatment.

Second, TPD experiments carried out on

two HTR samples which had been exposed to different Ar flushing periods (1 or 17 h) showed that both samples released only one form of strongly bound hydrogen (peak maximum at ca. 1130 K, Fig. 2). Let us consider potential sources of hydrogen in a Pd/SiO₂ catalyst which has been exposed to HTR: OH groups, Si-H bonds, and hydrogen dissolved in the metal. The equilibrium concentration of OH groups depends on the temperature of hydrogen pretreatment of silica and acquires the highest level for the temperature range of 873–1173 K ((22), for a modified chemical vapor deposition-made silica). HTR might conceivably also cause hydrogen dissolution in Pd particles (29) and produce Si-H bonds (23, 24, 28). It was shown that Si-H bonds produced on hydrogen uptake at 573 K dissociated at 873 K even in a H₂ atmosphere (28). Thus, it seems safe not to consider any presence of Si-H bonds in the catalyst after flushing it with Ar at 873 K. The solubility of hydrogen in palladium under 760 Torr at 873 K is rather low, H/Pd < 0.01 (29). Ar flushing at the same temperature for 17 h, and also for 1 h, should further diminish this low level of retained hydrogen in unsupported Pd samples. On the other hand, the amount of released H₂ during TPD exceeds considerably the level expected for dissolution of H₂ in Pd (H/Pd_t = 1.2 for the shorter exposure to Ar at 873 K and ca. 0.45 for the longer Ar flushing).

It is striking that both TPD spectra (Fig. 2) show one form of released H₂ with the maximum at ca. 1130 K. This suggests that hydrogen originates from only one source: hydroxyl groups. Myers (28) showed that hydrogen from dissociation of OH groups (in H₂-treated silicas) appeared in the gas phase at ca. 1073 K. The OH groups are, naturally, more plentiful in HTR catalysts which experienced shorter exposure to flowing Ar at 873 K. However, it seems doubtful that this strongly bound hydrogen in the form of OH groups influences the catalytic properties of a Pd/SiO₂ catalyst in the sense of being a reservoir of hydrogen

which could be further used in the reaction of neopentane. As a matter of fact we should rather expect quite the opposite phenomenon: due to a "sucking" power of highly dehydrogenated (and dehydroxylated) silica support our reaction mixture (neopentane in excess of hydrogen) introduced onto such a catalyst should become poorer in hydrogen (formation of new Si-H and O-H bonds at reaction temperatures of ca. 550–580 K). Kinetic results confirm this expectation. Figure 4 shows hydrogen pressure dependences of rates of hydrogenolysis and isomerization over the 0.76 wt% Pd/SiO₂ catalyst reduced at 723 K for 3 h, cooled in H₂ to ca. 540 K, and briefly evacuated at 540 K. Here we deal only with the "right-hand branches" of bell-shaped curves, typical of hydrocarbon reactions (12–14). This is an example of the hydrogen pressure effect. Good straight-line relations suggest that we worked at pressures of H₂ considerably larger than that of P_{H_2} at the maximum in the bell-shaped curve. On the other hand, the H₂ pressure relations obtained for HTR Pd/SiO₂ (Fig. 3) clearly indicate that we approached conditions of relative deficiency of hydrogen (for interpretation of bell-shaped curves in the kinetics of hydrocarbon reactions, see Paál *et al.* (12–14, 30)). In this work we obtained negative apparent energies of activation for the H₂/alkane ratio of 40/6 and 20/6 (values not presented) for a HTR Pd/SiO₂. This also indicates a serious deficiency of hydrogen (30).

Summing up, we are confident that metal-support interactions and not strongly held hydrogen are responsible for modification of catalytic properties of Pd/SiO₂ catalysts by HTR (followed by Ar flushing at 873 K). In the next subsection a possible character of these interactions will be discussed.

Palladium-Silica Interactions Induced by HTR

Our previous work (1) reports several indications (XRD, IR spectra of adsorbed CO

on a HTR sample) that the formation of palladium silicide species is feasible during HTR. The very high isomerization selectivities (ca. 70%, Table 2, this work) resulting from a longer period of flushing in Ar (17 vs 1 h) provides another important indication that some change in catalyst morphology rather than retained H₂ is primarily responsible for the change in catalytic behavior.

For elucidation of the nature of the HTR Pd/SiO₂ catalyst we shall make use of the following information:

(1) Kinetic results collected for Pd powder mixed with silica after LTR (573 K) and after HTR (873 K) (Table 4).

(2) XRD spectrum of the catalytic material studied in (1) (Fig. 5).

(3) The results of O₂ consumption by the catalyst during O₂/H₂ titration or O₂ chemisorption. The rather peculiar course of O₂/H₂ titration (Fig. 1).

(4) Kinetic results collected for the Pd-Ag powder (Table 4).

(5) Kinetic results with variously oxidized HTR samples of Pd/SiO₂ (Table 3).

Let us start with the results showing the interaction of Pd powder with SiO₂. Table 4 shows that two HTR samples were more selective for isomerization than the LTR sample. Also very careful purging in He (at 873 or 773 K) of the LTR sample does not produce a good isomerizing material. A similar situation was found with the 0.76 wt% Pd/SiO₂ catalyst (Table 2). HTR at 873 K seems to be a prerequisite for obtaining the highest selectivity for isomerization.

Let us compare the catalytic behavior of two HTR powders (Table 4). The sample designated as (a) (shorter Ar flushing) was intentionally rather poorly mixed with silica, whereas in the case of the sample designated as (b) (Ar, 873, 22) the mixing was performed as thoroughly as possible (without using a mortar). Sample (a) was less active and also *less selective* than sample (b). This again speaks against any special role of retained hydrogen in producing a

high level of isomerization selectivity. In our opinion, the extent of "mixing" of Pd with SiO₂ determines the resulting catalytic behavior. In sample (a) the overall catalytic behavior was the resultant of the activity of pure Pd and palladium silicide (this sample was somewhat more selective than LTR powder). Its activity, due to severe sintering of Pd, was low. On the other hand, sample (b) which was pretreated even more drastically exhibited higher activity. The better mixing of Pd with SiO₂ resulted in better interaction of two components; in this case the reaction of neopentane with H₂ goes on palladium silicide.

After kinetic runs both samples ((a) and (b)) were scanned on an X-ray diffractometer and gave almost identical XRD spectra. Figure 5 shows the XRD spectrum of sample (b). Among several phases it is easy to find reflections originating from palladium and the Pd₃Si orthorhombic phase (26). Thus we think that Pd, Pd₃Si, and SiO₂ are basic components of the HTR sample of the mixture of Pd with silica. However, in the case of sample (a), which was not properly homogenized, it was easy to detect large agglomerates of metal, whereas in the case of sample (b) all resulting catalytic material (after pretreatment) resembled rather "dirty" silica with a tiny amount of small Pd grains. After the XRD scan sample (b) was sieved through a 230-mesh screen in order to separate Pd grains from dirty silica. XRD analysis of both fractions revealed that the metallic phase was pure Pd whereas dirty silica, in addition to all palladium silicide(s) peaks, exhibited also very pronounced Pd reflections. Roughly estimated from the (111) peak width, the crystallite size of Pd is ca. 400 Å. The crystallite size of Pd₃Si seems at least similar (it is possible that one "silicide" peak may result from overlapping of a few peaks originating from other phases). Thus high temperature reduction of Pd powder mixed with silica produces a very extensive interaction between metal and silicon. Turning our attention to the highly dispersed Pd/

SiO₂ catalyst we would expect that the interaction between the two components on HTR would produce almost pure crystallites of Pd₃Si. The XRD spectrum of a 1.58 wt% Pd/SiO₂ was shown in Ref. (1). The apparent (111) peak of Pd, because of its very peculiar shape, could not be analyzed; all its distortion might originate from the presence of other phases. As a matter of fact, even the presence of pure Pd peaks might be questioned. EXAFS experiments with the HTR sample of Pd/SiO₂ should give a conclusive answer to this problem.

Table 2 shows that the HTR 0.76 wt% Pd/SiO₂ flushed with He at 873 K for 1, 6, or 17 h always exhibited a high level of isomerization selectivity. LTR followed by very long He flushing at 873 K also seems to give some moderate increase in selectivity with respect to the level of 30%, which has been somewhat arbitrarily taken as a measure of a selectivity of highly sintered Pd powder (without interactions) (1, 2). On the other hand, very long reduction (24 h) at 723 K followed by Ar, 773, 1 gives higher selectivity levels. This recalls earlier conclusions of Moss *et al.* (19), who suspected some interaction between Pd and SiO₂ even at 723 K, because these samples were less active in benzene hydrogenation than LTR samples.

Now the question arises as to how to visualize a Pd/SiO₂ catalyst in the state resulting from HTR. XRD analysis showed the presence of the Pd₃Si phase. However, the silicon content in the surface layer in this phase may differ from 0.25, since Si segregation to the surface of Pd-Si compounds at moderate temperatures is expected (in vacuum (31, 32)). Our earlier attempt to estimate the surface composition of a HTR sample of 0.76 wt% Pd/SiO₂ (1) should be treated with some reserve. O₂/H₂ titration (see Results) gave $(O/Pd)_a = 0.665$. Because the same sample after "regeneration" by oxygen (and LTR) adsorbed $(O/Pd) = 0.29$, then silicon should acquire $0.665 - 0.29 = 0.375$. If we assume that one

Si atom picks up two O atoms,³ then the Si/Pd ratio is equal to ca. 0.19. This would suggest the presence of Pd₄Si. However, if oxidation (at 293 K) is limited to the surface of palladium silicide then the oxygen balance should be counted differently. Because the fraction exposed after regeneration is $H/Pd_t = 0.29$ (Table 1), then the ratio of surface Si-to-surface Pd should be 0.19/0.29. Such a calculation was performed in Ref. (1) suggesting that the palladium silicide was Pd₂Si.

Figure 1 shows the unexpected course of O₂/H₂ titration of the HTR sample. The second and third pulses of O₂ were consumed to a greater extent than the first one. This suggests some acceleration of oxidation after passing the first pulse. O₂/H₂ titration of the LTR sample (not shown) does not exhibit such a behavior (only gradual decrease of O₂ consumption). It may suggest that the attack of oxygen meets initially some difficulties. If Si-H bonds are sufficiently strong not to be dissociated by molecular oxygen at 293 K, then we need some patches of free Pd (or Pd-Si) surface for accommodation and dissociation of oxygen molecules. Then atomic oxygen may readily react with Si-H bonds producing water and SiO₂. That initial "slow" oxygen uptake is not likely caused by inherent kinetics of silicon oxidation, i.e., due to differences in the rates of formation of different silicon oxides. It is known that oxidation of Ni silicides at room temperature proceeds via two-step process kinetics, in which the first step is faster than the second one (33). Oxidized silicon species (as SiO₂) should be located on top of Pd atoms (34). Apparently its presence modifies catalytic properties: regeneration by O₂ (Table 3) brings more selective catalysts than LTR samples. No matter how drastic

³ A less oxidized silicon species (Si₂O, SiO, and Si₂O₃), although possible as transient species, should not stay after the applied oxygen exposure (Ref. (33), our exposure ca. 10⁸ L (= Langmuir (unit of exposure, 1 L = 10⁻⁶ · Torr · S))).

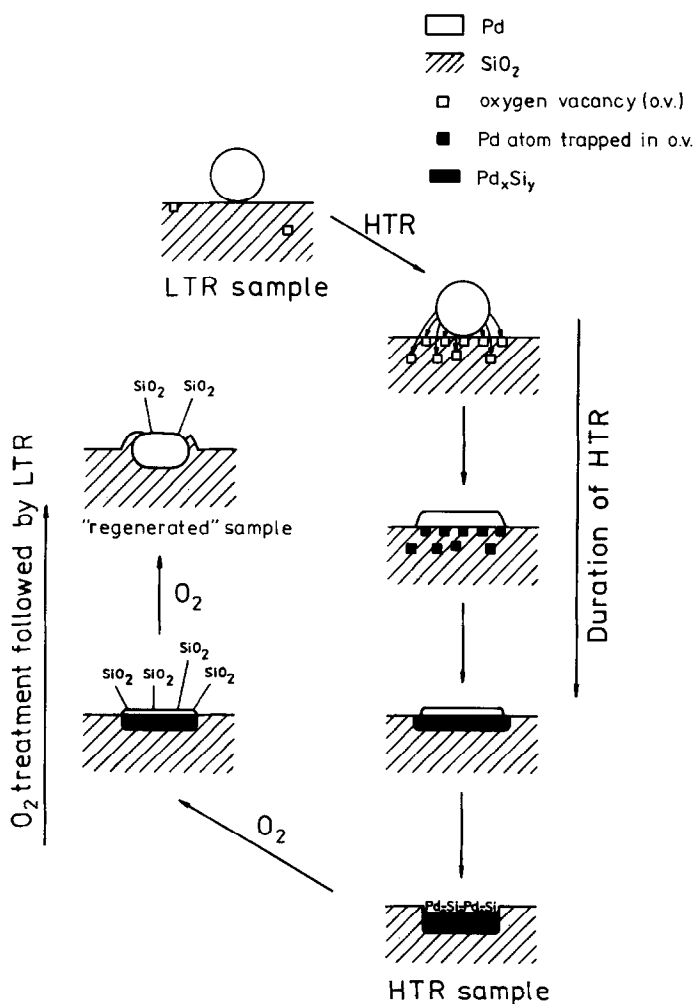


FIG. 6. Model of interactions between palladium and silica during HTR and "regeneration" of a HTR Pd/SiO₂ catalyst (by oxidation followed by LTR).

oxidation is applied, its result is always very similar (Table 3).

The result of XRD analysis of both sieved fractions of the mechanical mixture of Pd with SiO₂, especially the absence of silicide in the Pd-like fraction, suggests that the formation of silicide species by transport of silicon containing species (silane, SiO, SiO₂ ?) to Pd by gas or solid phase is unlikely. It is known that Pd easily diffuses through a 20-Å layer of SiO₂ to the silicon layer at moderate temperatures in order to form silicides (35, 36). The mechanism of Pd transport is via oxygen vacancies which

are always present in a defective SiO₂ material (32). In our case silicon atoms in the vicinity of such vacancies (produced by dehydroxylation and HTR) would be bonded to H atoms. However, Si-H bonds are rather weak at 873 K (28); thus, H atoms should be easily replaced by incorporating Pd species. A somewhat simplified situation on a Pd/SiO₂ catalyst showing HTR and regeneration by O₂ is presented in Fig. 6. This mechanism includes some steps involved in silicide formation from metal and silicon and silicide oxidation (encapsulation) suggested by Nuzzo and Dubois (37).

Somewhat less clear are initial steps of the mechanism. We do not even know what Pd species are captured in anion vacancies: atoms or, more probably, ions which owing to smaller size could more easily penetrate the bulk of defected SiO₂.

Finally, it should be mentioned that the very high isomerization selectivity in the reaction of neopentane on HTR samples of Pd/SiO₂ and the mixture of Pd with SiO₂ results from a considerable suppression of hydrogenolysis. It is known that the rate of alkane hydrogenolysis reactions is markedly lowered when Pd (or other Group VIII active metal) is alloyed with an inert element (e.g., Pd–Au (25)). Isomerization suffers with alloying much less than hydrogenolysis, because the first reaction requires much smaller active ensembles (38). Two experiments with Pd–Ag (35:65) alloy powder confirm again this expectation (Table 4). Apparently, both silicon and silver species make the surface of palladium more selective for isomerization.

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