JOURNAL OF CATALYSIS **119**, 521–524 (1989)

Reaction of Neopentane with Hydrogen over Pd/SiO$_2$

INTRODUCTION

Recently we suggested that the reaction of neopentane with hydrogen would be a good probe for the activity characterization of supported Pd catalysts (*1, 2*); in particular, the selectivity toward isomerization appears to be a good measure of the interaction of Pd with the support. For example, with Pd/SiO$_2$ and Pd/TiO$_2$ reduced at higher temperatures, there is a considerable growth in isomerization selectivity compared to lower temperature-reduced materials.

However, it is important to distinguish between chemical and topographical effects in such modifications, and we have investigated both (*1, 3, 4*). Some earlier work (*3*) with neopentane/H$_2$ indicated that (111)-oriented Pd films are very selective toward isomerization (~70% at T ~ 275°C), but lose this selectivity after various pretreatments that lead to formation of a defect structure. However, Pd powders do not exhibit this selectivity even after high-temperature reduction (*1*). In view of this, and the results presented here, it seems clear that the prior work on Pd(111) was affected by extraneous surface effects, possibly the formation of Pd silicides after annealing in H$_2$ at 500°C. Still, there appears to be a large effect of morphology of Pd on the neopentane reaction, but little is known about the effect of particle size, particularly with respect to supported catalysts. In the present study we use a well-characterized series of Pd/SiO$_2$ to look further at this question in a situation where metal–support interactions should be absent.

EXPERIMENTAL

The catalysts investigated are described in Table 1. These were prepared by ion exchange from Pd(NH$_3$)$_4$(NO$_3$)$_2$ onto 80–100 mesh Davison grade 62 silica gel; details of preparation and characterization are given in (*5–7*). The neopentane (Matheson research grade) reaction was conducted in an automated fixed-bed reactor (Xytel, Max II) in the temperature range 250–300°C. Feed partial pressures were 6 and 60 Torr neopentane and hydrogen in a helium carrier, with total pressures ca. 1.2 atm at reactor inlet. Conversions were calculated on the basis of fraction exposed via hydrogen chemisorption (D_H, Table 1), and selectivities on the basis of neopentane consumed in the formation of an individual product. An *in situ* "standard" pretreatment procedure was employed for all runs as listed in Table 1 and described in detail in (*5*). After pretreatment the catalysts were cooled in He to reaction conditions and reactants introduced. Data were obtained in a series of runs at increasing temperature; check runs at lower temperature at various points in the sequence reproduced activity/selectivity within ±15%, indicating negligible influence of coke formation.

RESULTS AND DISCUSSION

Results for the seven Pd/SiO$_2$ catalysts investigated are given in Table 2. There is only a small effect (if any) of D_H on activity over the temperature levels investigated, with the exception of D_H = 0.856. For example, at 265°C an average N_t is $(4.07 \pm 1.33) \times 10^{-5}$ s^{-1} with an uncertainty level of ±30% of the overall activity (excluding D_H = 0.856). Similar trends pertain for the higher temperatures as well, with D_H = 0.856 always showing somewhat higher activity. Isomerization selectivities also exhibited minor changes with D_H. Usually, higher isomerization selectivities (25–45%)

0021-9517/89 $3.00

were observed at lower temperatures, where it was possible to control conversions at very low levels (<2.5%). At higher conversions an abrupt decline in isomerization occurred, suggesting that hydrogenolysis of isopentane (product of isomerization) goes faster than its formation. This point may be open to debate, but supports prior work (*1*, *8*). For the lowest dispersed catalyst ($D_H = 0.071$) the selectivity for isomerization (<30%) resembles the behavior of Pd powder, and there is a significant increase (to 45%) for $D_H = 0.498$ and 0.655 which is maximum for this series.

Activation energies and preexponential factors obtained here are linearly correlated; however, due to the rather generous experimental error we prefer not to talk about compensation, but call attention to

TABLE 1

Fraction Exposed of the Pd/SiO_2 Catalysts

Catalyst[a]	wt% Pd	D_H[b]	Origin[c] (Ref)
7.1-SiO_2–$PdNO_3$	1.91	0.071	(*6*)
13.8-SiO_2–$PdNO_3$	2.09	0.138	(*5*)
29.3-SiO_2–$PdNO_3$	2.09	0.293	(*5*)
49.8-SiO_2–$PdNO_3$	1.56	0.498	(*5*)
65.5-SiO_2–$PdNO_3$	2.09	0.655	(*5*)
71.9-SiO_2–$PdNO_3$	0.49	0.791	(*5*)
85.6-SiO_2–$PdNO_3$	0.51	0.856	(*7*)

[a] Designation from Ref. (*5*).

[b] Fraction exposed measured by H_2 pulse chemisorption at 70°C after "standard" pretreatment: O_2, 300°C, 0.5 h; H_2, 300°C, 1 h; He, 450°C, 1 h.

[c] Description of preparation.

TABLE 2

Reaction of Neopentane with H_2 over Pd/SiO_2

Catalyst (D_H)	Reaction temp (°C)	N_t (s^{-1})	Product distribution (%)[a]					E_A[b] (kcal/mol)
			CH_4	C_2H_6	C_3H_8	iC_4H_{10}	iC_5H_{12}	
0.071	265	4.81×10^{-5}	20.0	29.7	—	29.1	21.2	
	273	1.11×10^{-4}	16.1	10.5	5.5	42.1	25.8	63.9 ± 3.8
	287	4.23×10^{-4}	16.6	1.9	5.9	47.8	27.7	
0.138	266	3.29×10^{-5}	24.9	20.7	7.5	23.7	23.2	
	276	8.63×10^{-5}	19.4	5.2	9.5	37.3	28.6	60.4 ± 2.0
	288	3.18×10^{-4}	21.7	1.6	12.8	46.5	17.4	
0.293	264	4.78×10^{-5}	16.3	10.9	7.0	29.3	36.6	
	277	1.47×10^{-4}	20.0	2.7	11.1	43.1	23.2	59.1 ± 1.8
	286	3.87×10^{-4}	25.9	1.7	17.8	44.5	10.5	
0.498	265	5.15×10^{-5}	18.4	5.2	2.7	30.8	42.9	
	275	1.37×10^{-4}	17.8	2.7	5.8	42.5	31.3	57.1 ± 1.0
	288	4.35×10^{-4}	25.8	1.9	14.2	46.1	12.0	
0.655	265	2.48×10^{-5}	15.7	3.9	6.0	28.2	46.1	
	275	6.37×10^{-5}	17.0	1.9	5.1	36.2	39.8	56.1 ± 2.4
	287	2.04×10^{-4}	24.6	1.3	12.0	44.0	18.1	
0.791	264	3.91×10^{-5}	27.8	17.1	7.5	26.2	21.4	
	276	1.43×10^{-4}	21.6	2.9	11.5	43.7	20.3	61.8 ± 2.4
	286	3.78×10^{-4}	25.5	1.4	18.2	46.4	8.5	
0.856	264	6.80×10^{-5}	25.8	—	6.6	41.9	25.7	
	274	1.97×10^{-4}	25.2	1.3	11.0	49.6	12.9	66.4 ± 1.5
	286	7.03×10^{-4}	30.3	1.4	23.6	41.4	3.3	

[a] Via GC analysis, 50-m capillary fused silica column with crosslinked methyl silicone (Hewlett–Packard No. 19091S).

[b] From least-squares Arrhenius analysis; average number of points: ca. 10–12.

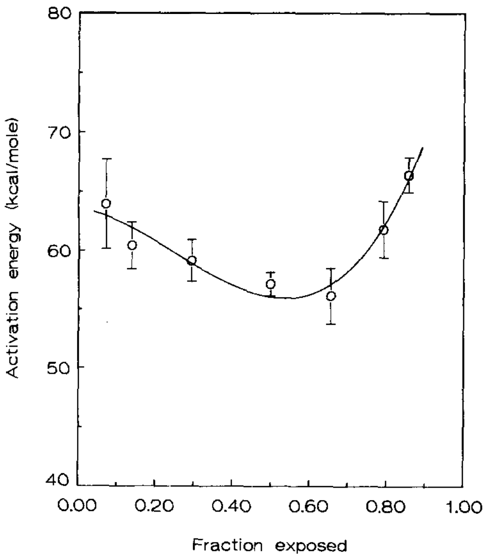

FIG. 1. Reaction of neopentane with H_2 over Pd/SiO_2 catalysts. Activation energy as a function of fraction exposed.

the variation in activation energy with D_H (Fig. 1). E_A is minimum for $D_H = 0.498$–0.655, where isomerization activity is maximum, and the two findings seem to be correlated. For hydrogenolysis, energy for C–C bond rupture is required, while for isomerization only partial bond breaking is required. This has already been reported for this reaction on supported Pt (*9*). In addition, Dominquez and Yacaman (*10*) showed that N_t (360°C)/N_t (300°C) was about 2, while the same ratio for isomerization was <1.5 (for Pt/C, Table 1 in *10*). The inference that hydrogenolysis and isomerization proceed via a similar intermediate contradicts an earlier conclusion based on published data (*11*) on hydrogen dependence, and at present the reasons for this are not known; however, the selectivity data here are better defined than those presented before. Additional experimentation on this point is clearly required.

The minimum in E_A combined with increased selectivity for isomerization recalls similar results for methylcyclopropane hydrogenolysis over the same series of catalysts (*5*); some variation in N_t can be identified, but nothing is particularly pronounced. This is in accord with considerable prior literature on Pd/SiO_2 (*12*). However, that reaction is quite structure-sensitive on Rh/Al_2O_3, somewhat sensitive on Pt/SiO_2, but is also structure-insensitive on Pd/Al_2O_3 (*13*). Cyclopentane hydrogenolysis follows the same pattern (*14*). Benzene hydrogenation is typically classified as a "structure-insensitive" reaction (*15, 16*), and indeed it is so on Pd/SiO_2, but not on Rh/Al_2O_3 (*13*). The sum of this and much more literature is that supported Pd seems to be a structure-insensitive catalyst under conditions or for reactions where other Pt-group metals are structure-sensitive. Neopentane is a good reaction probe here since there is almost nowhere it can go except on the metal.

The question then arises how to explain the rather general structure-insensitivity of supported Pd for this fairly wide range of reactions. We incline to the suggestions of Burwell *et al.* (*17, 18*) who propose the effect of extractive chemisorption to explain the results of di-*t*-butylacetylene hydrogenation on supported Pt. This reaction was also structure-insensitive but should not have been so on the basis of steric considerations; one would think that high D_H catalysts would be much more active, but it is not so. It was proposed that in chemisorption one or two atoms of Pt were displaced above the initial planar level leading to increased bonding to the surface for low dispersion catalysts. If the strength of the *M*–H bond is similar for the noble metals, then one can expect much easier extractive chemisorption for Pd compared to other metals (lattice energy in kcal/mol is 90 = Pd; 127 = Rh; 152 = Ir; 122 = Pt). This view then goes in the direction of explaining higher N_t on the lower dispersion catalysts.

The remaining question has to do with the high N_t observed for $D_H = 0.856$. In fact, we have no explanation for this and thus leave it as a reported number. The conclusion, then, is that neopentane hydrogenolysis, reported to be structure-sensitive on other supported metals, is not so on supported Pd. Obviously metal–metal energies do not explain the whole problem, but the lower lattice energy of Pd may be important in determining its structure-insensitivity.

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Received October 3, 1988; revised May 31, 1989

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