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Catalytic Reactions of Hydrocarbons over Pt–Pd Alloys

III. Skeletal Reactions of *n*-Pentane and *n*-Hexane over Pt–Pd/SiO_2 Catalysts

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Isomerization, cyclization, and hydrogenolysis reactions of *n*-pentane and *n*-hexane were studied on silica-supported Pt–Pd alloy catalysts. From the results of the kinetic studies it can be inferred that the surface composition of highly dispersed Pt–Pd/SiO_2 catalysts is not substantially different from the bulk composition. The selectivity of the *n*-pentane cyclization is higher for the Pt–Pd alloys than for pure metals. This synergistic effect was not seen for the Pt–Pd films, which, among others, is due to a different surface composition of the samples examined. Self-poisoning of the Pt–Pd/SiO_2 catalysts was observed, the cyclization and hydrogenolysis reactions being the most suppressed, whereas the isomerization process was relatively insensitive to this effect. For the *n*-hexane conversion the major reactions were isomerization and hydrogenolysis, whereas the dehydrocyclization products were found in minor amounts. A suggestion is advanced (without special proof) that the *n*-hexane isomerization on Pt–Pd/SiO_2 catalysts runs primarily by the cyclic mechanism.

INTRODUCTION

The reasons for our interest in the study of the alkane conversion reaction on Pt–Pd alloys can be found in our previous paper (Part I (*1*)). We recall briefly that the objectives were both to find catalytically novel alloy systems, to be further used in the oil reforming process, and, in the first place, to use the platinum alloy in a study of the stereochemical aspects of alkane conversion reaction mechanisms. The paper referred to above is concerned with the conversion of the C_5 and C_6 alkanes over highly sintered Pt–Pd alloy films. Part II of this research (*2*) is dedicated to an attempt to estimate the surface composition of the Pt–Pd alloy films examined. The crystallite size of the sintered films could be estimated at ca. 1000 Å. In this present paper we examine a more highly dispersed system, namely, Pt–Pd/SiO_2 catalysts. It is a matter of common knowledge that the participation of the cyclization mechanism in the C_6 alkane isomerization increases with dispersion of the catalyst (*3*), while the cyclization reaction itself is favored by the presence of low coordination centers on the platinum surface (*4*). With dispersion of the Pt/SiO_2 catalyst a decline in selectivity toward isomerization vs hydrogenolysis is observed (*5*). Some differences in the catalytic behavior of Pt–Pd films and Pt–Pd/SiO_2 catalysts in the neopentane conversion reaction were also found in our study (*6*). For the silica-supported catalysts a synergistic effect occurred for the neopentane isomerization, whereas no such effect could be noticed for the Pt–Pd films.

In this experimental series in our study of the *n*-pentane and *n*-hexane conversions on Pt–Pd/SiO_2 catalysts, attempts were made to ensure such reaction conditions as to make the selectivity toward individual partial reactions of interest (i.e., cyclization, isomerization, and hydrogenolysis) be determined by the process kinetics alone. For it often happens that the cyclization can be thermodynamically inhibited (*5*); at large conversions the value of selectivity toward cyclization of *n*-pentane may not be a figure of merit in the appraisal of the behavior of

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the active centers of the catalyst. For that reason in the study on Pt–Pd/SiO_2 catalysts in a continuous-flow system, efforts were made to work under conditions of very low conversions.

EXPERIMENTAL METHOD

Five Pt–Pd/SiO_2 catalysts with an overall metal loading of 1 wt% were obtained by impregnation of an inert silica (270 m^2/g) with aqueous solution of $Pt(NH_3)_4Cl_2$ and $Pd(NH_3)_4Cl_2$. Two series of catalysts were investigated: series I, noncalcined, and series II, precalcined (prior to reduction) in an air oven for 25 h at 600°C. The weight of catalyst taken for one experiment was 0.5 g. Composition of the metal phase of the catalyst was determined by the X-ray fluorescence method.

The reduction was carried out *in situ* in the flow reactor (400°C, 12 h, 75 ml/min H_2 flow). After reduction the hydrogen was removed from the catalyst surface by flushing the catalyst bed with an argon stream at 400°C for 2 h. Subsequently, once the reactor was cooled down to room temperature, the metal surface area was measured by the pulse H_2 chemisorption method. The conditions of the H_2 chemisorption were so established as to make the maximum partial pressure of hydrogen at the "pulse" lower than 4 Torr (1 Torr = 133.3 N m^{-2}). This condition was critical as regards the uptake of hydrogen by the sample; at higher hydrogen pressure the β-palladium hydride phase could form, and the results of the measurement of the palladium and palladium-rich alloy surfaces by the chemisorption method could be biased (*7*). It was also assumed that it was merely the irreverisbly bonded hydrogen on the surface that was measured, while the reversibly dissolved hydrogen (referred to as α-phase) was leached out from the catalyst by the argon stream. The method of surface measurement by hydrogen chemisorption seemed attractive, as the metal surface area of each individual catalyst sample taken for the reaction could be estimated *in situ* immediately before the reaction.[1]

The whole reaction system was designed almost entirely in metal (except for the glass reactor, hydrocarbon saturator, and flow meters) and contained no mercury or grease. Hydrogen and argon were purified by passing them through a platinum catalyst and Deoxo BTS, respectively, followed by a molecular sieve.

The carrier gas used for the experiments with measurement of alkane conversion rate consisted of a 1/3 H_2/Ar mixture (under atmospheric pressure), and the hydrocarbon studied was fed into the carrier gas from the saturator maintained at a suitable temperature. For the reaction of *n*-pentane (chromatographically pure grade standard supplied by Chemipan, Poland, of purity >99.9%) a reaction mixture was obtained with *n*-pentane partial pressure of ca. 17 Torr by keeping the saturator with this hydrocarbon at −46°C; for *n*-hexane (pure standard grade supplied by Chemipan, Poland, purity min 99.98%) the vessel with this alkane was kept at −20°C to yield a partial pressure of *n*-hexane of ca. 14 Torr. The hydrogen-to-alkane ratio was 11.2/1 and 13.5/1 for *n*-pentane and *n*-hexane, respectively.

The alkane conversion reactions were studied successively at temperatures of 300, 330, and 360°C, returning to a temperature of 330°C and occasionally to 300°C.

It was established that there was no effect of external diffusion by examining the effect of a variable contact time. A linear relation was obtained for percent conversion vs contact time. Experiments with

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[1] Surprisingly high dispersion of the Pd/SiO_2 catalysts (as measured by H_2 chemisorption, Tables 1–4) leaves still some doubts as to the correctness of use of this method in spite of the numerous precautions mentioned in the text. Nevertheless, a possible overestimation of the palladium surface area, even as large as several hundred percent, does not change the basic character of the catalytic activity vs alloy composition relation (Figs. 1 and 3) because the specific activity of Pd/SiO_2 still remains rather low.

gradually more crushed catalyst showed no effect of the catalyst grain size on the percent conversion, which is suggestive of the lack of the effect of an internal diffusion process. It should be emphasized that in the entire series efforts were made to work under conditions of low conversions, $\alpha < 2\%$. This requirement was essential not only in the aspect of meeting the reactor differentiality condition but primarily to have the possibility of following the cyclization process (cf. the Introduction).

RESULTS

The catalytic activity and selectivity of the Pt–Pd/SiO_2 catalysts examined in the *n*-pentane and *n*-hexane conversion reactions with hydrogen are illustrated in Tables 1 and 2. Table 1 reports results for noncalcined catalysts and Table 2 results for catalysts calcined prior to the reduction.

Tables 3 and 4 report analogous results obtained in the *n*-hexane conversion reaction on both catalyst series.

TABLE 1

Rate of Conversion and Distribution of Reaction Products in *n*-Pentane Conversion on Noncalcined Pt–Pd/SiO_2 Catalysts

Metal-phase composition[a] (at.%)	Metal particle size[b] (Å)	Reaction temp. (°C)	Rate of overall conversion[c]	Product distribution[d] (%)					
				CH_4	C_2H_6	C_3H_8	C_4H_{10}	iC_5	cC_5
100% Pt	39	304	9.00	2	8	8	9	36.5	36.5
		333	25.38	2	8.5	8	6.5	45	30
		361	31.49	3	11	11	10	52	13
		335	14.32	2	7.5	7.5	6	39	38
		301	3.65	2	7.5	7	5.5	37	41
100% Pd	16.5	301	0.20	6	1.5	1.5	15.5	75.5	—
		331	1.81	7	2.5	3	28	21	38.5
		361	5.21	4	3	4	27	21	41
		334	0.65	2.5	2.5	4	20.5	50	20.5
85% Pd	15	300	0.28	12	6.5	6.5	10.5	43.5	21
		331	1.41	7.5	3.5	4	11.5	20.5	53
		361	3.12	7.5	2.5	3	11.5	18	57.5
		331	0.61	5.5	2.5	4	6	37.5	44.5
52% Pd	22.5	300	1.21	5.5	6	6	6.5	26	50
		332	3.76	5	5	5	7.5	23.5	54
		362	5.82	6	4	4	9	28	49
		329	0.97	4.5	3	3	7.5	42.5	39.5
		303	0.28	3.5	2	2	3.5	85	4
42% Pd	34.5	299	3.44	4	6	5.5	5.5	27	52
		330	9.07	3.5	4.5	4	4.5	34	49.5
		363	15.46	4	4.5	4.5	5	32	50
		324	2.16	3.5	4	4	5	35	48.5
		301	0.75	6	4.5	4.5	6	55	24

[a] As estimated by X-ray fluorescence.

[b] Metal particle size, $D = 6/\rho S$; where ρ is the alloy density and S is the metal surface area, measured by H_2 chemisorption in a pulse system.

[c] Expressed in 10^5 moles of *n*-pentane/h m^2 of metal surface.

[d] Product distribution is expressed as the percent of *n*-pentane consumed in the formation of a given product divided by total consumption.

TABLE 2

Rate of Conversion and Distribution of Reaction Products in *n*-Pentane Conversion on Pt–Pd/SiO_2 Catalysts. Catalysts Calcined at 600°C Prior to Reduction

Metal-phase composition[a] (at.%)	Metal particle size[b] (Å)	Reaction temp. (°C)	Rate of overall conversion[c]	Product distribution[d] (%)					
				CH_4	C_2H_6	C_3H_8	C_4H_{10}	iC_5	cC_5
100% Pt	80	299	9.00	3	6	6	4	31	50
		330	18.03	2.5	7.5	7	5	31	47
		360	27.63	3	8.5	8.5	4.5	28	47.5
		333	10.00	2.5	5	5	5	40.5	42
		304	4.06	2	2	2	15	45	47.5
100% Pd	10.5	301	0.29	7.5	9.5	9.5	23	23	27.5
		333	0.91	9	4.5	4.5	30	14	38
		365	2.02	9	3.5	4	32	10.5	41
		331	0.17	14.5	4	5	18	45	13.5
85% Pd	14.5	301	0.26	7	7.5	7	28.5	50	—
		331	1.39	7.5	6.5	6	26.5	19.5	34
		365	3.20	7.5	3.5	4	29.5	12.5	43
		330	0.28	4.5	4.5	10	19	43.5	18.5
52% Pd	21.5	302	0.28	7.5	7.5	15.5	10.5	59	—
		330	0.99	4.5	4	4	14	28.5	45
		361	2.88	4	3	2.5	11.5	28	51
		334	0.87	2.5	1.5	3.5	5.5	38.5	48.5
42% Pd	67	301	1.53	5	11.5	10	3.5	36	34
		330	6.61	3	6.6	5.5	8	18	59
		360	13.20	2.5	4	3.5	6.5	21	62.5
		334	2.96	2.5	6	4	10	24	53.5

[a–d] As in Table 1.

DISCUSSION

n-Pentane Reaction

Catalytic Activity. Platinum is the most active catalyst, while palladium and the palladium-rich alloy are the least active catalysts in the *n*-pentane conversion reaction. This fact agrees with the results obtained by Kikuchi *et al.* (*8*) who studied *n*-pentane hydrogenolysis on various transition metals. The absolute value of the catalytic activity of platinum expressed in moles of converted *n*-pentane per gram of Pt per hour is in close agreement with the results of the study by Brunelle *et al.* (Table 3 from (*5*), the data for the exchanged catalyst characterized by a Pt loading of ca. 1%). It should be emphasized here that both in the Kikuchi *et al.* work (*8*) and in that by Brunelle *et al.* (*5*) the authors were unable for thermodynamic reasons to follow the *n*-pentane cyclization. Similar objections may be raised as to the determination of selectivity of *n*-pentane cyclization on a Pt/SiO_2 catalyst in the study by Van Schaik *et al.* (*9*) who worked under relatively high conversions. Our results do not allow us to estimate the apparent activation energy in the *n*-pentane conversion reaction First, for a given temperature the percent conversion cannot be used in the determination of the activation energy as a measure of the stationary catalytic activity, as the process of continuous self-poisoning of the catalysts was involved here (usually the period of induction to achieve a relative stability of percent conversion was ca. 1 h). Second, this self-poisoning process in-

TABLE 3

Rate of Conversion and Distribution of Reaction Products in *n*-Hexane Conversion on Noncalcined Pt–Pd/SiO$_2$ Catalysts

Metal-phase composition[a] (at.%)	Metal particle size[b] (Å)	Reaction temp. (°C)	Rate of overall conversion[c]	Product distribution[d] (%)							
				C_1	C_2	C_3	C_4	C_5	iC_6	MCP	Bz
100% Pt	30.5	301	3.42	2	3.5	7	5.5	8	71	2.5	0.5
		333	8.50	2	3.5	6	5	5	63	13.5	2
		362	14.84	2	3.5	5.5	5.5	5.5	56	18	4
		330	3.49	1.5	3.5	9	7.5	7	63	8	0.5
		300	0.71	3	5.5	13.5	11	8.5	58.5	—	—
100% Pd	27.5	299	0.06	10	6.5	13.5	10	20	40	—	—
		327	0.40	5	4	7.5	7	39.5	37	—	—
		360	1.30	1.5	2	4.5	3.5	32.5	53	0.5	2.5
		327	0.26	1	1.5	5.5	5	17	70		
85% Pd	14.5	303	0.13	4	10	18	16	19.5	32.5	—	—
		333	0.44	3	4.5	6.5	6.5	18.5	49	12	—
		365	1.60	1.5	1.5	2	2.5	11	57	18.5	6
		334	0.24	1	2.5	5	4	8	79.5	—	—
52% Pd	21.5	304	0.22	2.5	9.5	15.5	14.5	18	40	—	—
		330	0.73	2.5	5.5	8.5	8	15	54	3.5	3
		360	1.52	1.5	2.5	4.5	4	9.5	66.5	8	3.5
		332	0.31	1.5	3.5	7.5	5	5.5	77	—	—
42% Pd	31.5	298	0.50	2.5	9.5	14.5	14.5	14.5	44.5	—	—
		334	2.70	1	4	6.5	6	7	62	13	0.5
		361	5.00	1	3	5	4.5	8.5	52	21.5	4.5
		329	0.78	1	3.5	8.5	7	9	71	—	—
		304	0.23	1.5	8.5	11.5	13.5	11.5	53.5	—	—

[a,b] As in Table 1.

[c] Expressed in 10^5 moles of *n*-hexane/h m^2 of metal surface.

[d] Product distribution is expressed as the percent of *n*-hexane consumed in the formation of a given product divided bytotal consumption. MCP, methylcyclopentane; Bz, benzene.

creases with temperature, particularly so when passing from 330 to 360°C, and the "return" from 360 to 330 or 300°C yields much lower values of the percent conversion than the original conversion values in those temperatures (i.e., at the beginning of the 300 → 330 → 360 → 330 → (300°C) cycle). This poisoning, expressed as percent loss of activity after the 330 → 360 → 330°C cycle, is different for various catalysts, but nearly always the highest for palladium and an alloy containing 85 at.% Pd.

Despite the hindering effect of the catalyst poisoning with time the relation of catalytic activity vs composition of the Pt–Pd alloy is invariably similar, independent of the temperature. Figure 1 illustrates this relation for a temperature of 330°C. Of a similar character was the relation of the catalytic activity of the Pt–Pd alloy films (cf. Fig. 2 in (*1*)). This similarity may be a matter of chance, and any more conclusive reasoning can hardly be ventured, as the surface composition of our catalysts is not known. It can merely be suggested that the highly dispersed Pt–Pd/SiO$_2$ catalysts have on their surface a composition which is closer to that of the bulk composition, as compared with the films. This concept

TABLE 4

Rate of Conversion and Distribution of Reaction Products in *n*-Hexane Conversion on Pt–Pd/SiO_2 Catalysts. Catalysts Calcined at 600°C Prior to Reduction

Metal-phase composition[a] (at.%)	Metal particle size[b] (Å)	Reaction temp. (°C)	Rate of overall conversion[c]	Product distribution[d] (%)							
				C_1	C_2	C_3	C_4	C_5	iC_6	MCP	Bz
100% Pt	135	300	0.60	10.5	8	18.5	6.5	10.5	4.6	—	—
		331	2.96	4.5	5.5	7.5	10	19	53.5	—	—
		360	7.60	1.5	5.5	10.5	10	11	57	—	4.5
		330	1.75	3	4	9.5	7.5	15.5	60.5	—	—
100% Pd	14	300	0.16	5.5	12.5	21.5	18.5	34.5	7.5	—	—
		333	0.38	7.5	6.5	10	11	49.5	15.5	—	—
		363	0.80	11.5	2.5	3	4.5	45.5	26	3	4
		331	0.08	8	2.5	8	12	33	36.5	—	—
85% Pd	14	300	0.15	6.5	5	8	5.5	57.5	17.5	—	—
		330	0.37	5	2.5	2.5	5.5	39.5	45	—	—
		359	0.84	3.5	1.5	2.5	3.5	23.5	61	—	4.5
		333	0.18	1.5	1.5	2.5	3.5	22.5	68.5	—	—
52% Pd	23	305	0.17	5.5	9.5	11	12	30.5	31.5	—	—
		330	0.30	3.5	4	5	5	21.5	61	—	—
		365	0.85	1.5	2	3.5	4	14	65	—	10
		333	0.17	1.5	3	5.5	5.5	4.5	80	—	—
42% Pd	66.5	302	0.36	6	12	12	23.5	22	24.5	—	—
		333	0.80	3.5	5.5	9	11	21	50	—	—
		364	1.85	2.5	3.5	5.5	5.5	12	71	—	—
		334	0.61	2.5	3.5	6.5	3.5	6.5	77.5	—	—

[a–d] As in Table 3.

would be favored by the results of the work by Gómez *et al.* (*10*) who dealt with Pt–Pd/Al_2O_3 catalysts of a dispersion close to that of our catalyst systems. On the other hand, from the theoretical considerations by Burton *et al.* (*11*), it follows that the more volatile element (in our case Pd) may segregate on the surface at the sites of low coordination number, such as ledges or kinks. In such a case, however, a rather different run of the catalytic activity vs alloy composition should be expected, namely, a high activity of pure platinum, which falls sharply even at a low Pd content to low values of the activity characteristic of pure palladium. In our case the alloy containing 42 at.% Pd has an activity which is almost an order of magnitude higher than the activity of pure palladium and the alloy of a Pd content of 85 at.%.

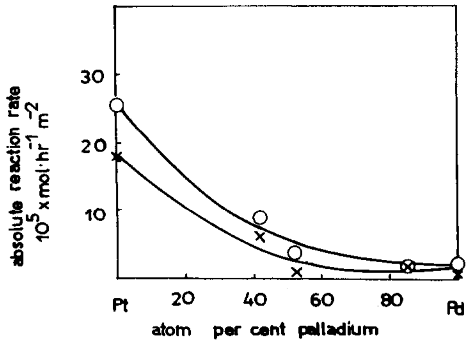

FIG. 1. *n*-Pentane conversion rate vs Pt–Pd alloy composition at 330°C. Noncalcined Pt–Pd/SiO_2 catalysts (○); catalysts calcined at 600°C (×).

Calcination of the catalysts (prior to the reduction) has no effect on the course of the activity vs composition relation. With relatively minor changes in the metal particle size effected by calcination (Tables 1 and 2)

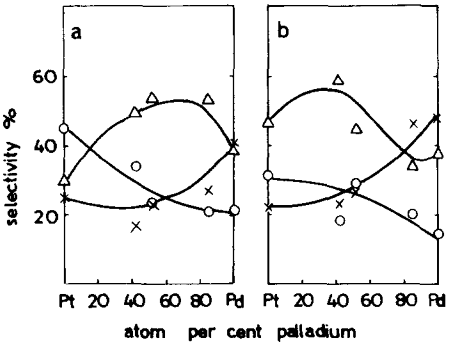

FIG. 2. Selectivity parameters for *n*-pentane reaction at 330°C. Isomerization (○); cyclization (△); hydrogenolysis (×). (a) Noncalcined Pt–Pd/SiO_2 catalysts; (b) calcined catalysts.

a similar course of both the curves in Fig. 1 may suggest that in either case we have a similar surface composition involved which is possibly close to the bulk composition. The character of the activity vs composition relation for Pt–Pd alloy obtained here is similar to that obtained by Gómez *et al.* (*10*) in the reaction of benzene hydrogenation on Pt–Pd/Al_2O_3 catalysts.

Selectivity. Consideration of variations in the selectivity vs Pt–Pd alloy composition is of much higher interest in the isomerization, cyclization, and hydrogenolysis reactions. These relations are shown in Fig. 2 for 330°C and for both catalyst series.

The selectivity toward hydrogenolysis is in both cases higher for palladium than for pure platinum. Also in both cases a substantial drop in that selectivity is observed on passing from palladium to the alloys richer in platinum; alloys containing 42 and 52 at.% Pd behave in this respect like pure platinum. This is one more piece of evidence (*1*) that for the hydrogenolysis reaction the most suitable are the Pd–Pd atomic doublets, whereas the so-called "mixed" Pt–Pd ensembles are not very effective here. The product distribution for the hydrogenolysis reaction (Tables 1 and 2) also shows that the Pd/SiO_2 catalysts and the alloy containing 85 at.% Pd behave similarly. This similarity manifests itself in a more selective *n*-pentane cracking process, as compared with this process run with the use of platinum alloys containing 42 and 52 at.% Pd; this is shown by a more selective demethylation of *n*-pentane which leads to the formation of butane in considerable amounts, whereas the amount of methane formed, as measured using a flame ionization detector, is possibly underestimated for the reasons given in the work by Garin and Gault (*14*).

Isomerization of *n*-pentane which occurs by a mechanism that goes without the formation of a five-membered ring is invariably more pronounced for platinum than for palladium and the Pt–Pd/SiO_2 alloys. The calcination of platinum at 600°C in air (cf. Fig. 2b), which results in a doubled size of the metal particles (Tables 1 and 2), affords a rather unexpected decrease in isomerization, whereas the selectivity toward cyclization increases. Unfortunately, for both the Pt/SiO_2 catalysts generally rather large crystallites were involved (80 and 39 Å, respectively). Brunelle *et al.* (*5*) demonstrated that the selectivity toward hydrogenolysis vs isomerization falls with larger crystallite size; this fall, however, is abrupt merely in the range of 0 to 50 Å. Again it should be stressed that Brunelle *et al.* (*5*) were unable to observe cyclization of *n*-pentane. In the case of *n*-pentane cyclization we observe, both for the calcined and noncalcined catalysts, some selectivity maxima for the alloys vs pure metals. It is of some interest that palladium here shows a similar selectivity to platinum (it should be borne in mind that palladium is much less active than platinum; cf. Fig. 1). This synergistic effect in the cyclization of *n*-pentane on the Pt–Pd/SiO_2 catalysts is likely to result not only from the effect of dispersion on the selectivity, but more so from the actual surface concentration of the alloy. If we compare the selectivity in the *n*-pentane cyclization on Pt–Pd alloy films (cf. (*1*), Fig. 2) with the present results, then the evident difference in the course of the selectivity vs composition relation may be interpreted as follows: for the films, as rationalized before (*1*, *2*), the alloy surface is enriched in palladium. Accordingly, a film of an alloy of a bulk content of ca. 30 at.% Pd should have on its surface ca. 60–70 at.% Pd (*2*). A qualitatively similar but somewhat less enrichment of the surface in palladium was concluded in the work by Kuijers *et al.* (*12*). It follows that for the films between Pt and the alloy contining ca. 30 at.% Pd (in the bulk), which in the *n*-pentane cyclization reaction behaves like platinum, a gap is formed that is not covered by the kinetic data for the surface composition of 0 to 60–70 at.% Pd. Some additional experiments with *n*-pentane on Pt–Pd films might show that somewhere in that region there is a maximum in selectivity for cyclization.

From comparison of the results obtained for the films and for the Pt–Pd/SiO_2 catalysts it also follows that highly dispersed palladium is more selective in the cyclization than the palladium film which, as shown in (*1*), exhibits a strong (111) texture. It therefore should be strongly emphasized that in the case of the Pd/SiO_2 catalyst examined in this study low coordination centers of the edge or corner atom type are responsible for its high activity in the cyclization reaction. This concept gains support from the findings of a recent work by Ledoux *et al.* (*13*), who assigned a different role to various surface centers in the alkene isomerization, hydrogenation, and deuterium exchange reactions.

As mentioned previously, the temperature relation obtained (Tables 1 and 2) does not allow us to determine the activation energy for the *n*-pentane conversion reaction. It is worthwhile, however, to take a closer look at the temperature effect on the selectivity of the process expressed as selectivity times the conversion rate, particularly after the 300 → 330 → 360 → 330°C temperature cycle. From the data obtained it follows that the hydrogenolysis and cyclization suffer the most, whereas isomerization is in general decreased to a minor extent. Again this is an indirect indication (*5*, *16*) that the alkane isomerization is a less structure-sensitive reaction than hydrogenolysis. This effect is most visible for palladium and an alloy containing 85 at.% Pd. These are, however, the most strongly dispersed catalysts, where the relative share of the edge or corner atoms is the largest. Possibly upon poisoning by the carbon residues the usefulness of these sites for cyclization or hydrogenolysis processes is decreased, and whether or not these sites participate in the isomerization reaction it would be too precocious to say. It seems likely, however, that for palladium exclusively highly coordinated sites, i.e., face atoms, are responsible for the isomerization (*1*).

For platinum the matter is much more involved. Here the relatively low poisoning sensitivity of Pt/SiO_2 in either cyclization, isomerization, or hydrogenolysis finds its explanation in that the Pt/SiO_2 catalysts examined in this study featured a relatively low dispersion. A similar situation occurs for an alloy of a Pd content of 42 at.%.

A much higher selectivity in the *n*-pentane cyclization for Pt films (ca. 80%, Ref. (*1*)) cannot, of course, be the result of an increased contribution of low coordination sites on the surface of strongly sintered film (actually there are none there) but this is a result of other experimental conditions employed in that study, as compared with this work, specifically a different partial pressure of hydrogen. In accordance with Garin and Gault (*14*) in the *n*-pentane cyclization the reaction order with respect to H_2 is ca. -3.4, whereas for isomerization and hydrogenolysis of this alkane it is ca. -1.8. In this connection the relatively high hydrogen pressure in this work will favor kinetically isomerization and hydrogenolysis. In the case of the study with Pt films (*1*) the hydrogen pressure applied was ca. 10 Torr, while in this work it was ca. 190 Torr. On the other hand, as follows from the study of Dartigues *et al.* (*15*) the participation of the cyclic mechanism in the *n*-hexane isomerization on Pt/SiO_2 catalysts falls with increasing size of the metal crystal grains, but it is fairly high at ca. 50% for large (>100 Å) particles of platinum.

n-Hexane Reaction

Catalytic activity. Figure 3 presents the relation of catalytic activity of Pt-Pd/SiO$_2$ catalysts vs alloy composition for the *n*-hexane conversion process. Here again catalyst Pt/SiO$_2$ is far more active than palladium or Pt-Pd alloys, and the character of the relation shown resembles that of Fig. 1 for the rection of *n*-pentane with hydrogen. Thus the conclusions relating to the surface composition of the Pt-Pd/SiO$_2$ catalysts will be analogous to those in the previous subsection.

Here, however, the Pt/SiO$_2$ catalyst, as a result of sintering and hydrogen reduction, suffered a serious decrease in the specific surface of the metal (crystal grains > 100 Å) and its specific activity fell so much as to become close to the low activity of other catalysts studied. Incidentally, for the Pt-Pd alloy films (Fig. 3 in Ref. (*1*)) the catalytic activity for all the catalysts examined was almost the same.

For the *n*-hexane conversion, as for the *n*-pentane reaction, a rather substantial poisoning of the catalysts is achieved after the 300 → 330 → 360 → 330°C cycle which depending on the sample manifests itself in a two- to fourfold drop in activity (Tables 3 and 4).

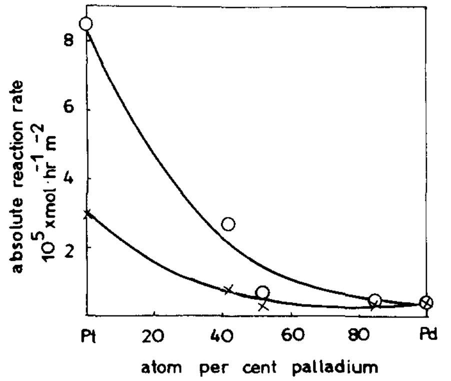

FIG. 3. *n*-Hexane conversion rate vs Pt-Pd alloy composition at 330°C. Noncalcined Pt-Pd/SiO$_2$ catalysts (○); catalysts calcined at 600°C (×).

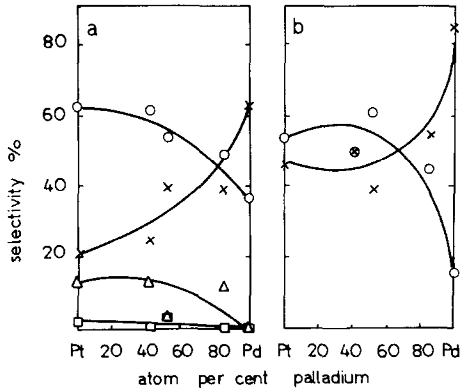

FIG. 4. Selectivity parameters for *n*-hexane reaction at 330°C. Isomerization (○); hydrogenolysis (×); benzene formation (□); methylcyclopentane formation (△). (a) Noncalcined Pt-Pd/SiO$_2$ catalysts; (b) calcined samples.

Selectivity. Figures 4 and 5 show the selectivity changes for the *n*-hexane conversion on Pt-Pd/SiO$_2$ catalysts at 330 and 360°C, respectively. Here again a dramatic fall in hydrogenolysis selectivity is observed on passing from pure palladium to Pt-Pd alloys. However, in the case of the calcined Pt/SiO$_2$ catalyst the selectivity toward isomerization increases at the expense of dehydrocyclization. Dehydrocyclization (the formation of both methylcyclopentane and benzene) is in general a less significant reaction, but it is completely eliminated by calcination of the catalysts. In the case of platinum-rich catalysts this may be due to a substantial rise in the metal crystallite size upon calcination (Tables 3 and 4).

For calcined catalysts a gentle maximum of isomerization selectivity vs alloy composition is observed. The analogy of this result to the earlier findings for neopentane isomerization on Pt-Pd/SiO$_2$ catalysts (*6*) would suggest that isomerization goes through a bond-shift mechanism (*16*). This conclusion, however, may be wrong, as only studies with ^{13}C-labeled hexane such as made by Garin and Gault (*14*) could afford decisive proof with respect to the participation of the cyclic and bond-shift mechanisms in the isomerization process.

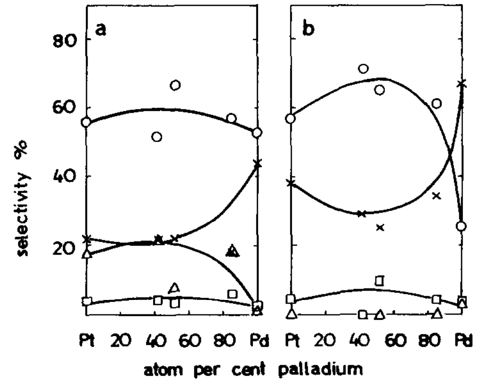

FIG. 5. Selectivity parameters for n-hexane conversion at 360°C. Isomerization (○); hydrogenolysis (×); benzene formation (□); methylcyclopentane formation (△). (a) Noncalcined Pt–Pd/SiO_2 catalysts; (b) calcined catalysts.

From the experiments made for n-pentane we are more inclined to believe that participation of the cyclic mechanism in the n-hexane isomerization prevails over the bond-shift mechanism, as the n-pentane cyclization predominates over isomerization of this alkane. For the n-hexane reaction the low concentration of the dehydrocyclization products may be due to their rapid cracking to C_1–C_5 products. It should be emphasized here that the selectivity toward hydrogenolysis is in general higher for n-hexane than for n-pentane (Figs. 2 and 4). A rapid hydrogenolysis of methylcyclopentane-like species to yield hexane isomers is another likely reaction path involved here. Aromatization of methylcyclopentane to benzene and a possible irreversible adsorption of the latter (to produce coke) should rather be left out of account here, despite that from a thermodynamic viewpoint benzene is likely to form. This is because the experiments were made under conditions of a large excess of hydrogen and, on the basis of the conslusions of Tétényi *et al.* (*17*) regarding the effect of various kinetic factors, we believe that aromatization is suppressed here. However, since the reaction course vs hydrogen pressure relation was not studied an unambiguous position cannot be assumed. Likewise, because the chromatographic analysis of the n-hexane conversion products failed in distinguishing 2-methyl- from 3-methylpentane (both the isomers are reported as one item in Tables 3 and 4), we are unable to determine unequivocally the contribution of the cyclic mechanism in the isomerization reaction. However, such more precise information could come from analogous studies on selective cleavage of the methylcyclopentane ring on our catalysts (*18*). Such experiments are our future target.

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