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Catalytic Reactions of Hydrocarbons over Pt–Pd Alloys

IV. Hydrogen Effects in the Conversion of Saturated C_6 Hydrocarbons over Pt–Pd/SiO_2 Catalysts

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The activities and selectivities of a series of Pt–Pd/SiO_2 catalysts have been determined for the conversion of *n*-hexane (*n*H), 3-methylpentane (3MP), and methylcyclopentane (MCP). Saturated C_6 products predominate under high hydrogen pressures whereas benzene and olefin formation prevails under hydrogen-deficient conditions. The overall activity has a minimum for alloys; at the same time, isomerization selectivity (at the expense of C_5-cyclization and hydrogenolysis) had a maximum at similar compositions. On the basis of the hydrogen dependence of yields as well as of the isomer ratios obtained from alkanes and methylcyclopentane, the possible reaction mechanisms are discussed. These are in agreement with data published earlier for both pure metals and alloys. The contribution of the bond shift mechanism is important especially for 3MP isomerization. This is supported also by the formation of 2,2-dimethylbutane over each catalyst. This bond shift as well as the C_5-cyclic mechanism of isomerization requires less dissociated surface species as distinct from dehydroisomerization producing benzene from 3MP and MCP. Possible ensemble and hydrogen effects are discussed.

INTRODUCTION

Our interest in Pt–Pd alloy catalysts in skeletal reactions of hydrocarbons has been initiated by both practical and theoretical reasons. Both catalysts, in supported or unsupported forms, are active in skeletal isomerization, C_5-cyclization, aromatization, and, to a lesser extent, hydrogenolysis (*1–5*). Of the two metal blacks, Pd was more selective toward C_6 product formation from various hexane isomers than Pt (*6*). The catalytic behavior of Pt–Pd alloys represents a particular interest because of the close physical and catalytic properties of the two component metals.

Earlier studies [Parts I and II, (*7, 8*)] concerned the catalytic activity and selectivity of evaporated Pt–Pd films. Here alloys showed somewhat higher selectivity in *n*-hexane aromatization than pure metals.

Part III (*9*) has dealt with conversion of *n*-pentane and *n*-hexane on highly dispersed Pt–Pd/SiO_2 catalysts. Alloys were found to be more selective in C_5-cyclization of *n*-pentane than pure metals. Isomerization and hydrogenolysis were the major reactions of *n*-hexane (in excess hydrogen); of these, isomerization predominates, except for Pd/SiO_2 alloys (which were more selective in isomerization than pure metals), and probably takes place via the cyclic mechanism (*10*). In another study (*11*), the Pt–Pd/SiO_2 system showed a synergistic enhancement of selectivity in neopentane isomerization [necessarily by the bond shift mechanism (*10*)] although both components alone are also active in this reaction (*12–14*).

In the present work we have attempted to contribute to the problem of the mechanism of skeletal reactions of hexane isomers. Unfortunately, the ^{13}C labeling technique (*15*) so useful for mechanistic studies was not available to us. Our main approach was to study the effect of H_2 pressure on the

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various parallel pathways as was done recently with various hydrocarbons over various Pt catalysts (*16–18*). Briefly, the comparison of 2MP/3MP and 3MP/*n*H ratios from *n*-hexane, 3-methylpentane, and methylcyclopentane feeds can be regarded as a good measure for separating the bond shift and C_5-cyclic pathways (*19*). Moreover, the H_2 pressure dependence of yields of individual products [characteristic maxima, (*16, 18*)] can give information about the possible degree of dissociation of surface intermediates. We believe that the results on hydrogen effects can throw more light on the explanation of the combined effects of the Pt–Pd system (*3, 4*).

EXPERIMENTAL

The Pt–Pd/SiO_2 catalysts with an overall metal loading of 1% by weight were the same as used in earlier work (*9*); 0.5 g catalyst was used except for Pt/SiO_2 where 0.2 g was weighed into the reactor. The catalyst reduction was carried out in the reactor at 673 K, in a hydrogen flow (60 $cm^3\ min^{-1}$) for 2 hr. Then the hydrogen stream was replaced by another carrier gas (H_2–He mixtures containing 100, 50, 20, 5, and 0% H_2, respectively) and 3-μl pulses of the feed were introduced. The pulse-microcatalytic system was described previously (*20*).

The reagents used were *n*-hexane (*n*H), 3-methylpentane (3MP), and methylcyclopentane (MCP), which were chromatographically pure substances.

The reactions were studied between 330 and 420°C (603 and 693 K). In the case of mixtures of low hydrogen percentages (0, 5, and 20% H_2, respectively) the catalytic activity was regenerated after each pulse by an air slug at reaction temperature followed by hydrogen flow for several minutes. The metal surface areas of our catalysts were measured by oxygen chemisorption using a Sartorius microbalance. Crystallite sizes have been compiled in Table 1.

TABLE 1

Properties of Various Pt–Pd/SiO_2 Catalysts

Metal phase composition[a] (atom%)		Specific surface of metal[b] (m^2/g)	Metal particle size[c] (nm)
Pt	Pd		
100	0	0.46	5.8
58	42	0.73	4.4
48	52	0.43	7.9
15	85	0.33	12.7
0	100	0.17	29.4

[a] As estimated by the X-ray fluorescence method.

[b] Determined by oxygen chemisorption.

[c] Metal particle size, $D = 6/\rho S$, where ρ is the density of the alloy and S the metal surface area.

RESULTS

a. Activity

The conversion rates have been calculated as molecules reacted per pulse per metal surface unit. This was obtained by multiplying the number of molecules per standard 3-μl pulses (1.37×10^{19} molecules for *n*H, 1.38×10^{19} for 3MP, and 1.59×10^{19} for MCP) by the corresponding conversion. Here mole number increases (for hydrogenolysis only) and losses (coke formation) were neglected.

Figure 1a shows overall conversions for all three feed hydrocarbons as a function of the catalyst composition. A minimum is seen in the range between 50 and 85 atom% Pd. Such a minimum was not observed for *n*-hexane conversion on Pt–Pd/SiO_2 in a flow reactor study [Part III, (*9*)]. However, we believe that, on that occasion, the estimation of the metal surface area for Pd and 85% Pd alloy by the H_2 chemisorption method was not correct [see the footnote in Ref. (*9*), p. 314], although the results obtained in both parts for Pt and Pt-rich alloy are in reasonable agreement. Now if one considers a possible ca. 10-fold overestimation of crystallite size [for Pd: 294 Å in this work vs 27.5 Å in Ref. (*9*), Table 3] a minimum in the relation between catalytic activity and alloy composition should, in fact, exist. Obviously any more conclusive reasoning can hardly be ventured as the metal

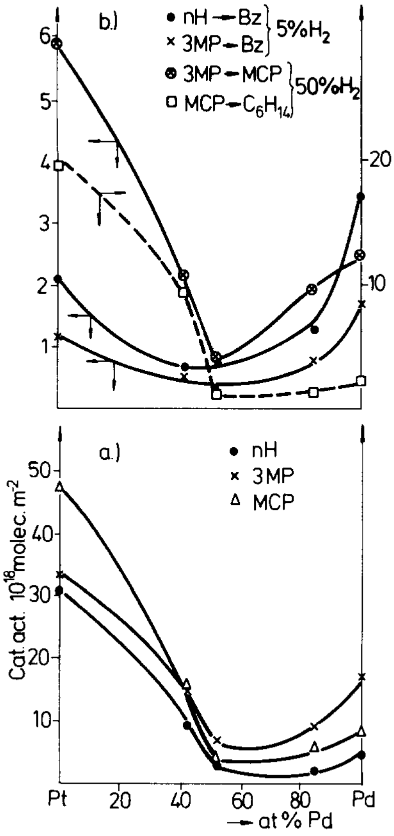

FIG. 1. Catalytic activity of various catalysts, as a function of their composition. $T = 663$ K. (a) Overall activity in hydrogen carrier gas. (b) Benzene formation from n-hexane and 3-methylpentane in 5% hydrogen; ring closure of 3-methylpentane and ring opening of methylcyclopentane in 50% hydrogen (see symbols on the figure).

surface area of the catalysts as used in Part III seems to be not known. The curve is composed of a convex descending branch in the Pt-rich range and (much less steep) concave ascending branch toward pure Pd. These data were measured in pure hydrogen. Figure 1b shows yields of selected reaction types in the presence of other gas atmospheres, favorable for the given reaction. The composite character of the curves can be recognized for reactions producing saturated products (C$_5$ ring closure and opening). Another type of curve appears for aromatization where the activity of palladium is higher than that of platinum.

Overall yields for all reactants over each catalyst have been included in Tables 2–4.

In agreement with the literature (*6*, *16–18*) the yields of various products (or types of products) have, as a rule, maxima as a function of the hydrogen pressure. Figure 2 shows conversions to saturated products: isomer and methylcyclopentane formation from n-hexane. Figure 3 shows analogous plots for three of the catalysts obtained with 3MP reactant. With methylcyclopentane feed (Fig. 4) Pt and 42% Pd show a monotonic increase in ring opening yield whereas the other metals exhibit more or less pronounced maxima.

Olefin formation has maxima at low H$_2$ pressures over each catalyst. Figure 5a shows the yields for pure Pt and Pd as examples. Maxima at various hydrogen pressures have been reported for aromatization over Pt catalysts on different supports (*18*) as well as over Pd-black (*6*). Here (Fig. 5b) Pd shows highest yields at 0 and 5% H$_2$ content, respectively; a monotonic decrease of the yield is observed with 85% Pd whereas pure Pt exhibits a very flat maxi-

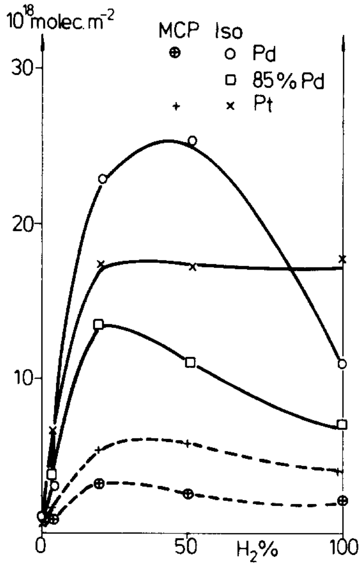

FIG. 2. Formation of isomers (solid lines) and methylcyclopentane (dashed lines) from n-hexane, as a function of the composition of the carrier gas. $T = 663$ K.

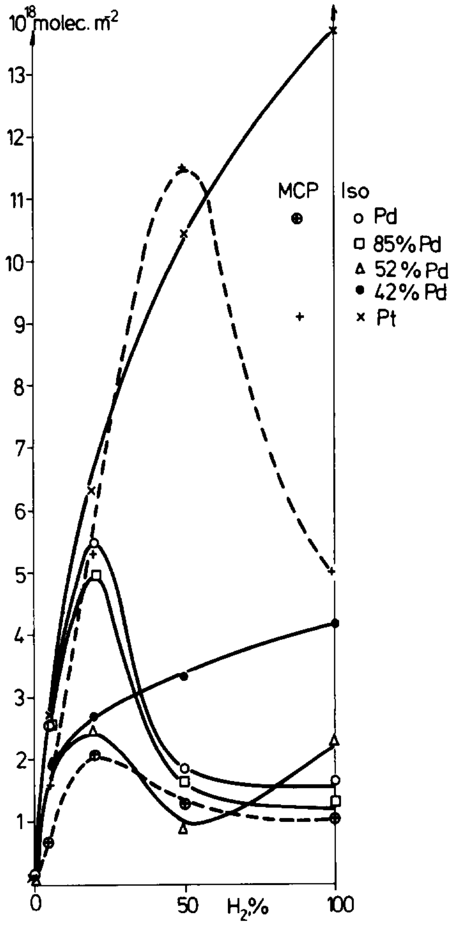

FIG. 3. Formation of isomers (solid lines) and methylcyclopentane (dashed lines) from 3-methylpentane, as a function of the composition of the carrier gas. $T = 663$ K.

mum. The other two alloys show somewhat similar curves to that shown for 85% Pd.

Data for apparent activation energies of aromatization and saturated C_6 formation (isomerization plus ring closure) from both hexane isomers have been compiled in Table 5. Here the two classes of reaction were measured under conditions favorable for each of them: aromatization in helium and saturated C_6 formation in hydrogen. Aromatization proceeds with higher activation energy in the presence of hydrogen. Almost identical values (78 kJ mol^{-1}) were obtained over pure Pt and Pd. Composite catalysts show similar values in higher hydrogen content, too. The E_A values for saturated C_6 formation do not decrease significantly in H_2–He mixtures.

b. Selectivity

Percentage selectivity values have been compiled in Tables 2–4 in addition to overall activities. Figure 6 shows the same values at a higher temperature: 663 K, in pure hydrogen. Here monotonically decreasing benzene selectivities are observed with increasing Pd content. Under hydrogen-deficient conditions (Tables 2 and 3) where benzene formation is favorable, highest selectivities are achieved in the Pd-rich region. Olefin formation is most enhanced over Pt-rich catalysts (Table 3).

The ring opening of methylcyclopentane has maximum selectivity over Pt-rich catalysts from 52% Pd upward, with benzene

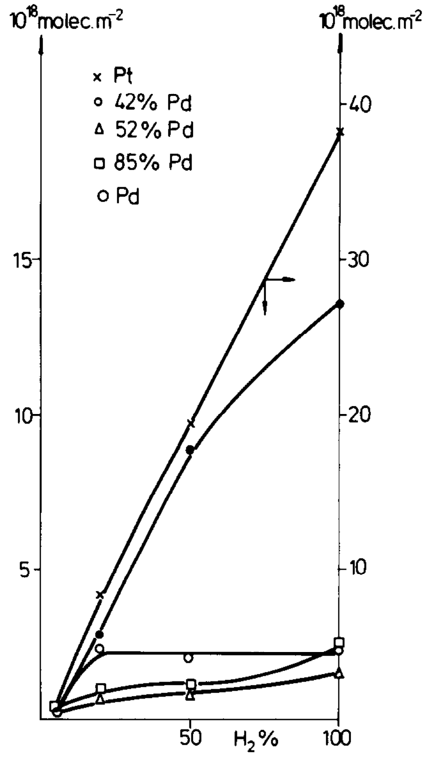

FIG. 4. Ring opening activity as a function of the composition of the carrier gas. Feed: methylcyclopentane, $T = 663$ K.

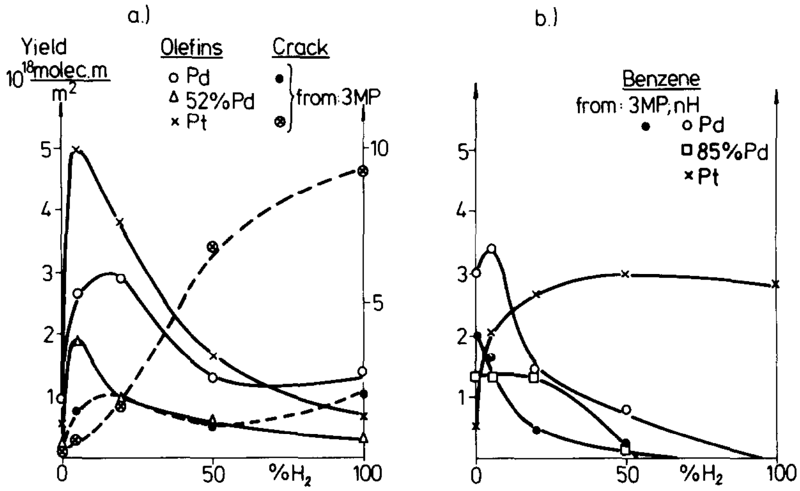

FIG. 5. Formation of various products as a function of the carrier gas. $T = 663$ K. (a) Cracking and olefin formation from 3-methylpentane. (b) Aromatization of *n*-hexane and 3-methylpentane.

and olefin formation predominating (Fig. 6). At higher temperatures (e.g., 663 K) benzene selectivity is around 60–65% irrespective of the catalyst composition.

The ring opening is definitely selective although less than observed with Pt catalysts of low dispersion (*6, 18, 21–23*). The selectivity has a minimum in the Pd-rich region of alloys (52 and 85% Pd): 42% Pd behaves again similarly to Pt. It decreases with decreasing hydrogen pressure. Table 6 presents these data together with isomer ratios obtained from *n*H and 3MP.

DISCUSSION

As in Part III (*7*), Pt/SiO$_2$ has been found more active than all other catalysts (Fig. 1). At the same time, the alloys are more selective for isomerization, owing to their lower activity in cracking and C$_5$ ring closure (Fig. 6, Tables 2–4). In this respect the results with our catalysts are at variance with the data reported by Matsumoto *et al.* (*24*) who found much lower isomerization (13–26%) and higher cyclization (42–62%) selectivity for *n*H and methylpentanes over

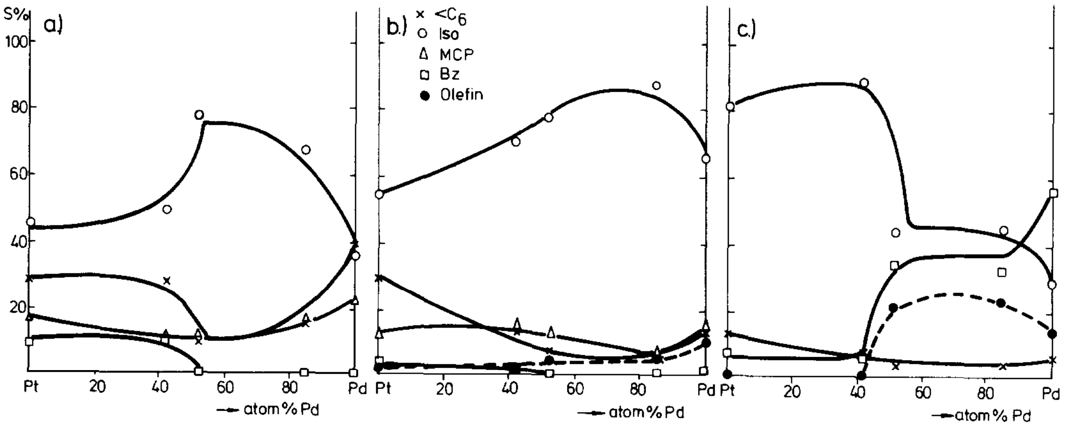

FIG. 6. Selectivities of various products from *n*-hexane (a); 3-methylpentane (b); methylcyclopentane (c). Carrier gas: hydrogen, $T = 663$K.

TABLE 2

Rate of Conversion and Product Distribution in *n*-Hexane Conversion on Pt–Pd/SiO_2 Catalysts at T = 633 K

Metal phase composition[a] (at.%)	H_2 content in the carrier gas (%)	Rate of overall conversion, (10^{18} mol m^{-2})	Selectivity[a] (%)				
			$<C_6$[b]	Isomers	MCP[c]	Bz[c]	Olefins
100% Pt	100	18.6	22.9	51.9	17.8	7.4	—
	50	18.7	20.1	47.1	24.3	8.5	—
	20	15.2	10.7	42.6	34.6	10.3	—
	5	16.8	7.5	43.0	33.1	16.4	—
	0	1.4	6.5	29.3	33.7	30.4	—
42% Pd	100	2.8	23.0	55.7	17.3	4.1	—
	50	2.8	14.2	55.0	26.1	4.7	—
	20	5.3	16.6	44.6	29.1	9.8	—
	5	4.2	15.1	34.1	28.9	21.9	—
	0	2.1	17.3	32.1	10.9	39.7	—
52% Pd	100	0.42	10.7	75.4	13.9	—	—
	50	0.40	8.4	91.6	—	—	—
	20	2.8	16.0	49.7	25.9	8.5	—
	5	2.9	11.5	57.2	16.2	15.1	—
	0	1.1	6.8	9.8			
85% Pd	100	0.63	11.9	88.1	—	—	—
	50	0.90	28.4	63.2	8.3	—	—
	20	3.7	22.6	46.5	21.7	9.3	—
	5	4.7	15.5	56.8	12.5	15.3	—
	0	2.0	13.1	27.9	9.4	49.6	—
100% Pd	100	2.8	4.4	32.8	21.1	—	4.7
	50	4.8	33.0	40.0	21.7	5.3	—
	20	6.7	30.1	34.9	23.7	11.2	—
	5	9.4	25.4	33.8	16.4	24.4	—
	0	3.9	27.8	21.2	2.8	48.2	—

[a] Σ all products = 100%.

[b] Hydrogenolysis products.

[c] MCP, methylcyclopentane; Bz, benzene.

4% Pd/SiO_2. Selectivities were, in general, closer to those found for *n*-hexane conversion in Part III (9), in spite of the different overall conversion values (up to 20% here and 2% in Part III).

The higher selectivity of alloys is exhibited at the expense of their lower activity. The number of active ensembles is, however, a function of hydrogen pressure. Apparently, hydrogen and metal produce active sites in the appropriate form and their amount is lower with alloys. At the same time, cracking ensembles are almost eliminated. The utilization of the hydrogen depends on the composition: let us investigate hydrogen effects in detail.

Under hydrogen-deficient conditions (0 and 5% H_2 in the carrier gas) the overall activity drops to very low level (Tables 2–4) and is practically independent of the alloy composition. The synergistic effect for enhanced isomer selectivity disappears and benzene plus olefins represent the main (or, eventually only) products. The activation energy values (Table 5) suggest that all alloys have a similar, low energy barrier for benzene formation from *n*-hexane in helium.

It is reasonable to assume that the catalysts are heavily carbonized and their metal composition plays a minor role in determining the selectivity. Benzene must be produced over heavily carbonized centers where presumably M–C ensembles represent the active sites, containing mainly single metal atoms (*25*).

Earlier results (*26*) give us some basis to estimate the amount of surface carbon. The amounts of gas phase products and "retained" hydrocarbons were close to each other when a 3-μl pulse of radioactive 3-methylpentane was injected on to Pt-black in helium. This amount of retained hydrocarbon led to the blocking of 70–80% of the surface metal atoms if a C : Pt = 1 : 1 ratio was assumed; the yields of saturated C_6 products and fragments decreased nearly to the same extent. At the same time, the loss of aromatizing activity was much less, up to 30%. In 5% H_2, the amount of surface atoms blocked was 15–20%; with even more hydrogen present, this could not even be measured. No detectable loss of aromatizing activity was observed in the presence of hydrogen-containing carrier gas. We may assume, therefore, the blocking of at least 70–80% of metal atoms in helium, independently of the composition of the catalyst. When the M metal is Pd, the energy barrier increases (Table 6).

At higher hydrogen pressures, the state of the catalysts changes from carbonized surfaces to those containing more hydrogen, and this is reflected on the selectivities (*27, 28*) and E_a values.

The character of the curves depends on the catalyst composition as well as on the reaction to be studied.

TABLE 3

Rate of Conversion and Product Distribution in 3-Methylpentane Conversion on Pt-Pd/SiO_2 Catalysts at $T = 633$ K

Metal phase composition (at.%)	H_2 content in the carrier gas (%)	Rate of overall conversion (10^{18} mol m^{-2})	Selectivity (%)				
			$<C_6$	Isomers	MCP	Bz	Olefins
100% Pt	100	18.6	28.2	62.1	7.0	0.8	1.9
	50	19.6	19.8	54.6	18.3	2.1	5.2
	20	17.0	8.0	53.4	27.5	3.4	7.7
	5	14.8	2.5	62.3	14.4	3.2	17.7
	0	11.0	8.1	40.5	13.6	—	37.8
42% Pd	100	4.4	11.9	71.0	15.2	—	1.9
	50	4.3	5.6	68.0	23.6	—	2.8
	20	9.0	7.7	64.4	23.5	1.7	2.7
	5	8.8	3.9	68.3	16.8	3.2	7.8
	0	1.9	11.4	31.9	9.0	14.3	33.5
52% Pd	100	1.7	5.1	87.4	2.7	—	4.7
	50	1.3	4.7	85.3	2.6	—	7.4
	20	11.9	2.9	78.4	13.7	0.6	4.5
	5	7.2	3.1	75.1	7.1	2.0	12.7
	0	1.4	38.9	23.4	6.8	19.1	11.7
85% Pd	100	2.7	3.4	85.5	8.0	—	3.1
	50	5.0	3.0	88.7	5.2	—	3.2
	20	11.1	5.1	77.9	1.2	0.4	4.3
	5	11.6	3.9	77.0	9.8	2.8	6.4
	0	1.1	24.1	22.7	8.5	29.0	15.6
100% Pd	100	8.1	23.3	53.8	21.1	—	1.8
	50	13.1	10.9	69.4	16.5	—	3.2
	20	15.4	8.0	72.9	14.4	0.8	3.9
	5	22.5	7.8	55.7	10.3	5.3	20.9
	0	3.5	23.2	24.7	6.5	29.8	15.8

TABLE 4

Rate of Conversion and Product Distribution in Methylcyclopentane Conversion on Pt–Pd/SiO_2 Catalysts at $T = 633$ K

Metal phase composition (at.%)	H_2 content in the carrier gas (%)	Rate of overall conversion (10^{18} mol m^{-2})	Selectivity (%)			
			$<C_6$	Isomers	Benzene	Olefins
100% Pt	100	39.5	8.9	87.9	3.2	—
	50	36.9	6.5	59.4	34.1	—
	20	17.3	7.3	61.0	23.3	8.3
	5	10.0	1.6	9.4	65.7	23.4
42% Pd	100	10.0	2.2	94.3	3.6	—
	50	8.2	4.2	87.1	7.0	1.7
	20	6.4	8.3	63.8	20.3	7.6
	5	3.8	2.7	16.7	62.1	18.5
52% Pd	100	0.8	3.8	12.6	35.1	48.5
	50	1.4	—	37.4	38.0	24.6
	20	3.0	1.3	24.4	53.9	20.4
	5	2.4	1.9	9.7	65.2	23.2
85% Pd	100	1.7	3.4	56.4	20.6	19.5
	50	2.0	2.9	37.9	46.1	13.1
	20	3.0	—	26.8	50.2	23.0
	5	4.3	3.3	9.6	65.7	21.4
100% Pd	100	4.3	3.5	52.6	38.2	5.7
	50	5.0	—	44.3	38.3	17.4
	20	7.2	—	25.9	52.6	21.5
	5	6.0	7.2	19.8	32.4	40.6

Benzene production decreases for all compositions; in Fig. 5b the benzene yield vs H_2 pressure curves for pure Pd/SiO_2 are very similar to those reported for Pd-black (*6*) whereas the flat maximum obtained for Pt/SiO_2 resembles that obtained for another Pt/SiO_2 sample (*18*). One may wonder whether this difference is due to the intrinsic differences of the metals or to the fact that our Pd catalyst had rather large crystallites whereas Pt was a dispersed sample (Table 1). If the latter version is true, it would represent another type of crystallite size effect in addition to that reported for isomerization (*29*).

Three types of curve can be distinguished for saturated C_6 formation (Fig. 2):

(i) Isomer yield increased monotonically with platinum-rich catalysts (Pt and 42% Pd).

(ii) A sharp maximum was observed at about 20% H_2 content with the two Pd-rich catalyst [in agreement with literature data reported for Pd-black (*6*)].

(iii) The 52% Pd catalyst represented a peculiar transition species: it had the maximum characteristic of Pd-rich alloys but, with more hydrogen present, a second increase of the yield appears. This could be observed at each temperature.

Thus, the hydrogen dependence of isomerization yields changes gradually with catalyst composition. The transition of "Pt-type" to "Pd-type" isomerization takes place around 50% Pt content.

The comparison of isomer ratio permits us to draw conclusions about the prevailing pathway of skeletal rearrangement. The following facts should be recalled:

(a) Identical H_2 pressures belong to the

TABLE 5

Energy of Activation of Formation of Various Products over Different Catalysts

Catalyst	E_A (kJ mol^{-1})			
	Benzene[a] formation from		C_6 saturated[b] formation from	
	nH	3MP	nH	3MP
Pt	6	—	84	84
42% Pd	38	40	96	96
52% Pd	40	63	130	125
85% Pd	40	69	121	121
Pd	84	75	75	100

[a] Carrier gas, helium.
[b] Carrier gas, hydrogen.

maxima of isomerization and C_5 ring closure of n-hexane; these are at different pressures with 3-methylpentane (Figs. 2 and 3).

(b) Also, the isomer ratios are the same with nH and MCP and different with 3MP and MCP (Table 6).

(c) Finally, the different hydrogen dependences of isomer yields from nH and 3MP show also that two distinct pathways are responsible for skeletal rearrangement of these two hexane isomers. All these point to a predominant C_5-cyclic pathway of n-hexane isomerization over each catalyst (7), and to the prevailing bond shift pathway of 3-methylpentane → 2-methylpentane isomerization.

The occurrence of bond shift is supported also by the appearance of 2,2-dimethylbutane (about 1% of the 2MP yield). The minor role of the cyclic mechanism is shown also by the meager ring opening yields over alloys with more than 50% Pd content (Fig. 4) as well as the poor MCP yields from both alkanes. Gault and coworkers reported a predominant bond shift mechanism for 2MP isomerization over

TABLE 6

Selectivity of Methylcyclopentane Ring Opening and Alkane Isomerization as a Function of the Catalyst Composition and Hydrogen Pressure[a]

Metal phase composition (at.%)	Reactant	Ratio of 2MP/3MP if the carrier gas contains				Ratio of 2MP/nH if the carrier gas contains			
		100% H_2	50% H_2	20% H_2	5% H_2	100% H_2	50% H_2	20% H_2	5% H_2
100% Pt	nH	1.5	1.6	1.1	0.5	—	—	—	—
	MCP	2.4	1.8	1.3	—	1.9	1.6	4.5	—
	3MP	—	—	—	—	3.9	11	16	16
42% Pd	nH	1.5	1.5	1.4	1.1	—	—	—	—
	MCP	2.0	1.6	1.2	2.3	3.9	2.4	1.9	1.1
	3MP	—	—	—	—	6.7	11	14	14
52% Pd	nH	0.7	1.0	1.0	0.7	—	—	—	—
	MCP	1.0	1.3	1.4	—	1.2	0.8	0.9	—
	3MP	—	—	—	—	v.h.	12	9	5
85% Pd	nH	0.9	1.1	1.0	0.7	—	—	—	—
	MCP	1.0	1.4	1.3	0.6	1.0	2.1	0.9	—
	3MP	—	—	—	—	v.h.[b]	87	15	v.h.
100% Pd	nH	0.9	1.0	0.9	0.7	—	—	—	—
	MCP	1.8	1.4	1.0	—	2.5	1.0	1.4	—
	3MP	—	—	—	—	v.h.	260	300	30

[a] $T = 633$ K.
[b] v.h. = very high (100 or above).

both Pt and Pd on alumina (*22*), whereas the cyclic mechanism becomes predominant with heptane isomers over 10% Pt/Al_2O_3 (*30–32*).

As far as the main conclusions are concerned, our studies support the generalized mechanism proposed for hydrocarbon reactions on metals drawn on the basis of the hydrogen dependence of the yields (*33*). A reaction involving a less dissociated surface intermediate should have its maximum yields at higher hydrogen pressure. Our results support the view that two types of bond shift isomerization should exist (*6, 34*): one species having a strongly dissociated character is responsible for dehydroisomerization of isohexanes and methylcyclopentane while another, less dissociated species, gives skeletal isomers (*30, 35*).

Whereas the overall activity of Pt–Pd alloys is poorer than that of both pure components, a synergistic effect appears in the composite catalysts which is manifested in their high isomerization selectivity. This can be interpreted in the sense that they can utilize hydrogen in such a way that the formation of less dissociated surface species becomes very favorable. In this respect it is of minor importance whether this less dissociated species produces isomers via bond shift or the C_5-cyclic mechanism (*35*).

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