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Conversion of Methylcyclopentane, Hydrogenation of Benzene, and Deactivation by Thiophene on Supported Pd–Rh Metallic Catalysts

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The catalytic properties of PdRh/Al_2O_3 catalysts were investigated for the hydrogenolysis of methylcyclopentane, the hydrogenation of benzene and 1-hexene, and the deactivation by thiophene of benzene hydrogenation. These results are compared with surface compositions reported in the literature for Pd–Rh films. When Pd is added to Rh, the variations of activity for these different reactions suggest that a segregation of palladium toward the surface occurs on the small particles of the supported catalysts to a similar extent as on films. The changes of selectivity in methylcyclopentane hydrogenolysis further suggest a topological segregation of Pd at edge and corner sites. At low Rh content, no segregation is observed on films, the activity for 1-hexene is normal, but the activity for benzene is low and depends on the size of the alloy particle: this may be interpreted by the requirement of a site containing more than one rhodium atom for benzene hydrogenation. Pd–Rh bimetallics show a decrease by two orders of magnitude of the rate of poisoning by thiophene. While the properties of the Pd–Rh bimetallic for the conversion of hydrocarbons are well explained by the ensemble theory of metals, the increased sulfur tolerance seems better explained by a modification of the electronic properties of rhodium. © 1985 Academic Press, Inc.

INTRODUCTION

Most of the recent advances in catalysis by metals have come from the widespread use of alloys. However, a detailed description of catalysis by bimetallics encounters two difficulties, namely, lack of information on the surface composition of supported bimetallic clusters and interpretation of the origin of the beneficial effects.

Segregation toward the surface of one component can occur in order to minimize the surface energy (*1*). This phenomenon has been clearly evidenced on films, but becomes more difficult to observe on small supported particles. Different microstructures may exist in that case (*2*), which complicates the interpretation of the results: for instance, the two components may be present as separate phases and bimetallic clusters (*2–4*). If we suppose a simple situation where the two metals form an alloy, the surface segregation on small particles is still a matter of discussion (*2–5*); however, recent EXAFS investigations of Ru–Cu, Rh–Cu, and Rh–Ir systems (*6*) confirm theoretical calculations (*2*) predicting the existence of a surface enrichment on highly dispersed alloys of miscible or immiscible components.

It is then sometimes difficult to interpret the effect of alloying due to the difficulties in determining the composition and topology at the surface of a small bimetallic particle. The ensemble theory is often used to explain the lesser ability for C—C bond cleavage and self-poisoning (*7, 8*). When a reaction does not require a multiple site to proceed, the modifications of rate might be accounted for by an electronic or ligand effect (*7, 8*). However, the occurrence of a ligand effect requires that, in the alloy, some electronic transfer occur between the components, which causes a shift in the *d*-band position. Unfortunately, in the case of most transition metals used in catalysis, the reality of these electronic transfers is questionable. Most of the modifications are re-

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stricted to a narrowing of the *d*-band by the phenomenon of dilution, and a rehybridization of orbitals. One of the rare systems which can be described by the Rigid Band Theory of metals is the Rh–Pd alloy (*9*). This system is therefore an interesting one on which to check the possible influence of the electronic interactions on the catalytic properties of the alloy.

Up to now this system has been studied for the oxidation of CO and ethylene by Moss *et al.* (*10, 11*). These authors worked on films and observed a surface enrichment of Pd in the composition range 20–90% Rh, corresponding to the miscibility gap of the alloy. The results of McKee and Norton (*12*) on the CH_4/D_2 exchange fit well with this hypothesis of a Pd-rich surface layer.

In previous work we investigated the influence of the dispersion and of the support on the catalytic properties of Pd and Rh for the hydrogenation of benzene, the hydrogenolysis of cyclopentane (CP) and methylcyclopentane (MCP), and the poisoning by thiophene of the hydrogenation of benzene (*13–16*). The main point was that no influence of particle size or support could be observed on palladium, while a structure sensitivity was noticed for sulfur poisoning and MCP hydrogenolysis over Rh.

It was therefore interesting to compare the Pd–Rh bimetallics to these monometallic catalysts of widely varying dispersion. However, due to the structure sensitivity of many reactions on Rh catalysts, we have attempted to compare samples of equivalent particle size.

EXPERIMENTAL

Catalysts. The catalysts were prepared by impregnation according to the incipient wetness technique. The supports used were γ-alumina from Rhône Poulenc (200 $m^2\ g^{-1}$) and Woehlm (205 $m^2\ g^{-1}$). The salts used were $RhCl_3$, $3H_2O$ and $PdCl_2$ from Merck. The support was previously acidified at pH ≅ 2 with hydrochloric acid (1 g/10 ml). After 1 hr the requisite quantities of the two solutions of salts were simultaneously added. The solution was kept for 2 hr under stirring. Then it was gently evaporated at 343 K and oven-dried overnight at 383 K.

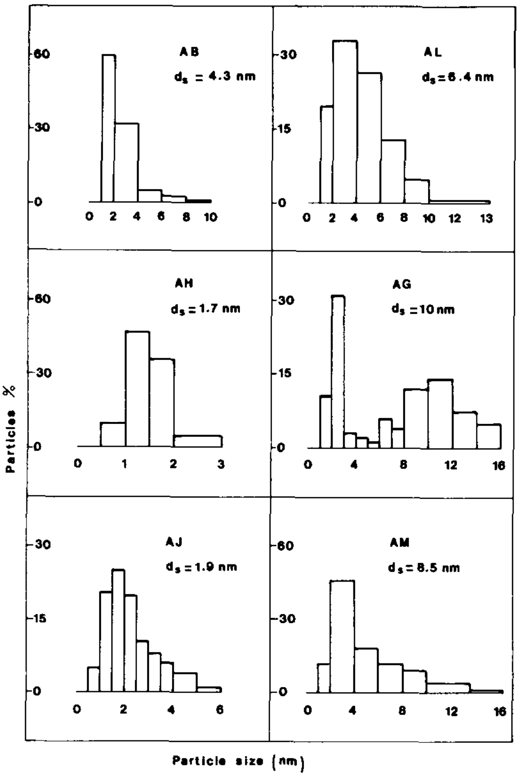

FIG. 1. Particle size distributions for different samples of $PdRh/Al_2O_3$.

It is well known that PdO/Al_2O_3 is easier to reduce than Rh_2O_3/Al_2O_3. In order to obtain similar dispersion for all the samples the reduction temperature was gradually decreased from 773 K for Rh/Al_2O_3 to 673 K for Pd/Al_2O_3. At the same time the hydrogen flow rate was increased. To obtain a better dispersion two samples (AH and AJ) were calcined before the reduction step.

Characterization. Adsorption measurements were performed in a conventional volumetric apparatus. Prior to any determination the sample (≅1 g) was reduced *in situ.* The pressure range used was 0–10 Torr. The hydrogen used was a high pure grade from Air Liquide (99.9995%).

The results of chemisorption were checked by transmission electron micros-

TABLE 1

Physicochemical Characteristics of the Catalysts

Sample	Total metal loading	%Rh–%Pd	Dispersion (%)	Mean particle size (nm)		$T_{\text{reduction}}$ (K)
				Chemisorption	TEM	
AF	1.80	100–0	27	4.3	—	773
AE	1.69	90–10	27	4.3	—	773
AA	1.64	88–12	37	3.1	—	773
AB	1.70	76–24	38	3.1	4.3	773
AC	1.78	62–38	28	4.2	—	773
AD	1.78	54–46	26	4.4	—	723
AL	2.23	39–61	19	6.1	6.4	723
AK	2.20	23–77	22	5.2	—	673
AH	2.05	16–84	55	2.1	1.7	673
AG	2.00	10–90	9	12.8	10	723
AJ	2.10	5–95	64	1.8	1.9	673
AM	2.05	5–95	17	6.8	8.4	673
AI	2.00	0–100	47	2.4	—	673

copy. Size distribution of some samples are presented in Fig. 1. It can be seen that the agreement is generally good between chemisorption and microscopy (Table 1). However, sample AG exhibits a bimodal distribution with small particles in the range 10–20 Å; nevertheless, the contribution of these particles to the overall metallic surface is negligible. Chemical analysis of the samples was performed by atomic absorption by the Service Central d'Analyse (Solaize, France).

Activity experiments. A conventional flow reactor was used in the differential mode, with conversions usually less than 10%. Reactants were benzene (Bz) and 1-hexene from Fluka (thiophene-free grade), and methylcyclopentane from Carlo Erba; the only contaminant for the latter was *n*-hexane (nH) at the constant level of 0.05 ± 0.01% and this could be subtracted with good accuracy. Hydrogen was saturated with the vapor pressure of benzene at 287 K (60 Torr), of 1-hexene ($1H^{=}$) at 273 K (50 Torr), or of MCP at 273 K (41.2 Torr) and passed through the reactor. The products were analyzed by on-line gas chromatography. For the hydrogenation of benzene, the column (6 m × 2.2 mm i.d.) was packed with 10% Carbowax 20M on gas Chromosorb Q (120–140 mesh). For the conversion of methylcyclopentane the column (6 m × 2.2 mm i.d.) was packed with 10% squalane on Chromosorb W (80–100 mesh). In these reactions no significant deactivation occurs at the temperatures investigated here; otherwise, the initial activity was taken on a fresh catalyst.

An aliquot of the sample used for dispersion measurements was reactivated under flowing H_2 at 673 K before the catalytic measurements. Since Rh/Al_2O_3 is much more active than Pd/Al_2O_3, the weight of sample ranged from 10 mg (Rh/Al_2O_3) to 500 mg (Pd/Al_2O_3).

Sulfur poisoning. Poisoning was investigated by adding thiophene (40 ppm) to benzene. The conversion follows an exponential decay, characterized by a rate constant k_d such that $r/r_0 = \exp(-k_d \cdot t)$, where r and r_0 represent the rate at time t and time zero, respectively (*14*). k_d represents the rate constant of the conversion of thiophene on the metal.

RESULTS

Hydrogenation of benzene. The reaction rates and specific activities are reported in

TABLE 2

Activity and Deactivation Rate Constant in the Hydrogenation of Benzene at 353 K (P_{Bz} = 60 Torr)

Catalyst (%Rh–%Pd)	Total conversion (%)	Reaction rate (mol · sec^{-1} · $(g\ cat)^{-1}$ × 10^6)	Specific activity (hr^{-1})	k_d ($l^{0.6}$ $mol^{-0.6}$ min^{-1})
AF(100–0)	7.3	47	3000	170
AE(90–10)	4.0	24	1930	135
AA(88–12)	7.9	9.1	1800	130
AB(76–24)	9.0	23	1340	160
AC(62–38)	5.6	16.2	1220	75
AD(54–46)	5.8	9.3	760	70
AL(39–41)	7.4	2.4	220	30
AK(23–77)	6.3	1.3	100	25
AG(10–90)	7.1	0.5	140	6.7
AH(16–84)	3.0	0.6	21	5.4
AJ(5–95)	8.0	0.41	12	1.2
AM(5–95)	4.7	0.14	16	5.2
AI(0–100)	3.33	0.18	7.4	3.7

Table 2. The specific activity is defined here as the rate per surface metal atom, including Rh and Pd, which cannot be discriminated by H_2 adsorption. This specific activity decreases steadily from Rh to Pd in agreement with their respective activities, and no synergy is noticed. Since the activity of rhodium is two orders of magnitude larger than that of palladium, the specific activity of the samples containing more than 10% Rh may be ascribed to the surface rhodium atoms. The only peculiar behavior concerns the samples AG and AH, obtained from the same precursor reduced under different conditions. The high activity of sample AG is not an artifact since it has been reproduced several times. This must be related to the difference in particle size between the two samples. We have plotted in Fig. 2 the surface compositions reported by Moss and Gibbens (*11*) for Pd–Rh films, and the specific activities against the bulk composition of the catalysts.

The hydrogenation of benzene previously was found to be "facile" on Pd or Rh/Al_2O_3 (*13*), and a discrepancy therefore appears between these two curves. The gap is small at high Rh content, but at low content the activity is 10 times lower than that expected from the segregation curve. The apparent activation energy, E_a, seems to go through a minimum value for Pd–Rh alloys, as illustrated in Table 3.

Sulfur poisoning. The variations of the deactivation rate constant k_d are reported in Fig. 3. As previously shown, benzene is mainly hydrogenated by rhodium, and k_d therefore represents the deactivation rate of the surface rhodium atoms. The initial

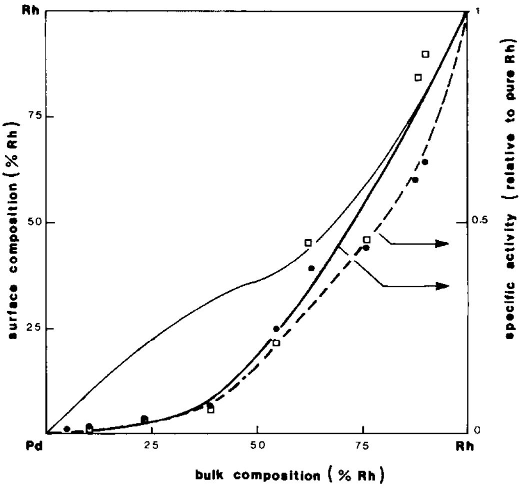

FIG. 2. Specific activity for benzene hydrogenation (●), MCP conversion (□), and surface composition (—), from Ref. (*11*), against bulk composition of PdRh/Al_2O_3.

TABLE 3

Apparent Activation Energy for the Hydrogenation of Benzene

Catalyst	Dispersion (%)	E_a (kcal · mol^{-1})
AF(100–0)	27	12.5
AA(88–12)	37	10.5
AL(39–61)	19	7.3
AK(23–77)	22	8.0
AJ(5–95)	64	10.0
AM(5–95)	17	7.6
AI(0–100)	47	14

value of 170 is in good agreement with the value of 160 obtained previously (*14*) on a 30% dispersed Rh/Al_2O_3 catalyst. With additions of Pd, k_d decreases steadily. It was previously reported that on Rh/Al_2O_3, the rate of poisoning decreases with the particle size, while it remains constant whatever the dispersion of Pd/Al_2O_3 (*14*). As for the hydrogenation of benzene, no synergy is observed, except for the well-dispersed sample AJ, for which the rate of poisoning becomes lower than that of Pd/Al_2O_3.

During the deactivation process, a particular phenomenon is observed in the earlier steps of the reaction (Fig. 4) For catalysts containing 20 to 100% Rh, the changes of conversion as a function of time are quite usual and present an exponential decay as soon as the poison is fed. For catalysts of lower rhodium content, the activity decreases sharply to a minimum value, then rises to an activity comparable to the initial one. The classical exponential decay occurs after this deactivation /reactivation sequence. k_d has been determined on this last part of the curve, after the initial fluctuations. This phenomenon is reproduced in an experiment made with benzene contaminated with 200 ppm of thiophene (Fig. 4e), and its is surprising that this large concentration of poison does not definitively deactivate the catalyst.

Hydrogenation of 1-hexene. The hydrogenation of 1-hexene to *n*-hexane has been performed on four samples (Table 4). The difference of activity between pure Rh and Pd is about 20, and the activities observed on the two bimetallics are proportional to their respective surface compositions, and no clear influence to particle size is noticed. The specific activities are high, as expected for a fast reaction such as olefin hydrogenation. Therefore, due to the large exothermicity of the reaction, the results are considered as more comparative than truly quantitative.

Conversion of methylcyclopentane. Table 5 shows the reaction rates and specific activities for the conversion of methylcyclopentane at 493 K. Specific activities decrease monotonically from Rh to Pd as illustrated in Fig. 2, and parallels the activity for benzene hydrogenation: it deviates clearly, at low Rh content, from the surface composition determined on films. The distribution of products is reported in Table 6: methylcyclopentane ring opening to hexanes is the predominant reaction at the temperature selected here. Whatever the catalyst, only trace amounts of cracking products were observed, among which C_1 and C_5 were the major products. Since cy-

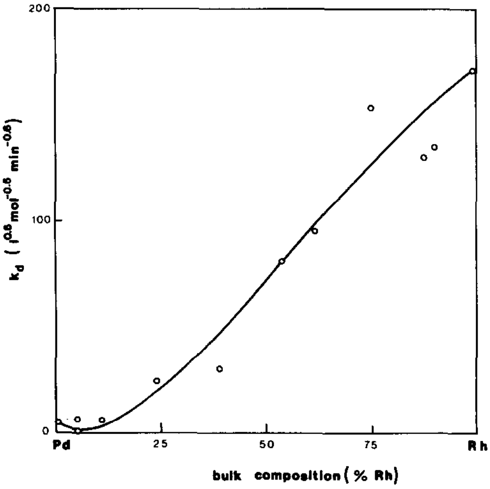

FIG. 3. Deactivation rate constant k_d determined for the hydrogenation of benzene at 353 K, as a function of bulk composition of PdRh/Al_2O_3; $P_{\text{thiophene}}$ = 40 ppm.

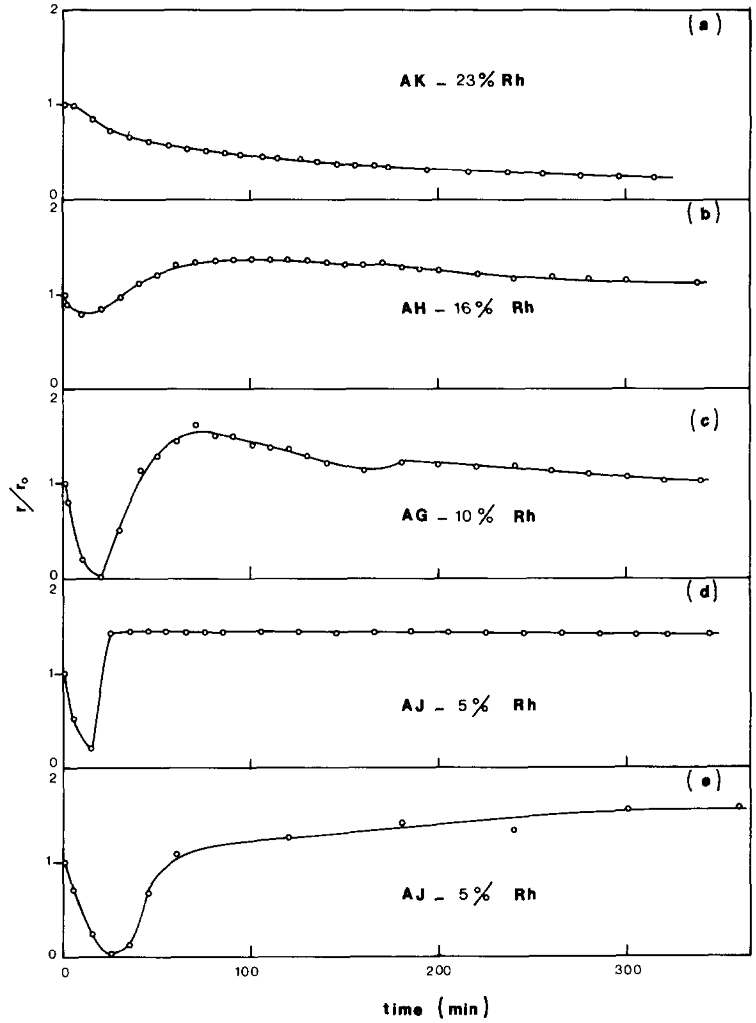

FIG. 4. Variation of the relative activity as a function of time for different catalysts. (a–d) $P_{\text{thiophene}}$ = 40 ppm; (e) $P_{\text{thiophene}}$ = 200 ppm.

clopentane ring opening is 10 times faster than methylcyclopentane ring opening on Rh and Pd/Al_2O_3 (*13*, *16*), these products can be formed by the sequence

$$MCP \rightarrow CP + CH_4$$

$$CP \rightarrow n\text{-}C_5.$$

No other product was detected, such as benzene or olefins reported by Koscielski *et al.* (*17*) on Pd/Al_2O_3 at 633 K.

The selectivity pattern of Rh/Al_2O_3 reproduced that previously reported under similar conditions (*15*). Pd/Al_2O_3 has not been extensively studied in the low-temperature conversion of hexanes. At 496 K,

TABLE 4

Activity in the Hydrogenation of 1-Hexene at 273 K ($P(1H^{=})$ = 50 Torr)

	Catalyst			
	AF	AG	AH	AI
Specific activity (hr^{-1})	8×10^5	1.7×10^5	1.3×10^5	5×10^4

TABLE 5

Activity in the Conversion of Methylcyclopentane at 493 K (P_{MCP} = 41 Torr)

Catalyst	Total conversion (%)	Reaction rate (mol · sec^{-1} (g cat)$^{-1}$ × 10^9)	Specific activity (hr^{-1})
AF(100–0)	6.6	6500	500
AE(90–10)	6.4	5700	460
AA(88–12)	16.2	7200	440
AB(76–24)	9.1	4000	230
AC(62–38)	7.0	3100	230
AD(54–46)	11.3	1300	110
AL(39–61)	8.5	360	34
AK(23–77)	3.4	220	17
AH(16–84)	3.1	10	0.3
AG(10–90)	3.0	23	6.3
AJ(5–95)	2.8	1.4	0.04
AM(5–95)	3.0	0.84	0.084
AI(0–100)	0.42	0.7	0.03

MCP hydrogenolysis on large Pd particles yields 2MP to a lesser extent and more *n*-hexane (*18*). At 553 K, the product distribution is quite similar to the present ones. The discrepancy observed at 493 K may be accounted for by either a lack of precision in the determination of *n*-hexane or an influence of the particle size of Pd. In a recent work, we observed no influence of particle size on the selectivity of MCP ring opening in the case of Pd (*19*).

The change in selectivity from Rh to Pd is restricted to the internal ratio between hexanes. Above 50% Rh, the ratio 2MP/nH is roughly constant, whereas it decreases at low Rh content, as illustrated in Fig. 5. The yield of 3MP remains constant and the decrease of 2MP is balanced by the increase of *n*-hexane.

The selectivity pattern remains approximately the same when the dispersion of the metallic phase changes at the same compo-

TABLE 6

Selectivities of Methylcyclopentane Hydrogenolysis on PdRh/Al_2O_3 at 493 K

Catalyst	Selectivity (%)								
	C_1	C_2	C_3	C_4	C_5	2MP	3MP	*n*-hexane	Other
AF(100–0)	5.0	0.2	0.1	0.5	2.9	62.2	25.4	3.7	—
AE(90–10)	2.1	0.3	0.1	0.5	2.4	66.2	22.9	5.0	—
AA(88–12)	1.7	0.1	0.1	0.2	1.5	71.3	22	2.8	—
AB(76–24)	1.8	0.2	0.1	0.3	2.0	68.7	22.7	4.2	—
AC(62–38)	3.4	0.3	0.1	0.4	2.7	64.5	23.9	4.6	—
AD(54–46)	5.0	0.3	0.1	0.7	2.9	62.2	25.4	3.7	—
AL(39–61)	5.3	—	—	0.5	4.1	58.4	24.0	8.0	—
AK(23–77)	7.6	—	—	0.6	5.5	54.2	24.0	8.1	—
AH(16–84)	8.3	0.5	0.3	0.6	4.3	51.0	25.2	9.4	—
AG(10–90)	6.7	—	0.3	0.7	4.7	54.5	22.6	10.6	—
AJ(5–95)	7.9	—	—	—	0.5	50.6	25.7	11.8	3.4
AM(5–95)	7.1	0.5	0.3	0.7	4.5	50.5	24.4	9.7	—
AI(0–100)	9.0	—	—	—	5.0	45.0	23.0	18.0	—

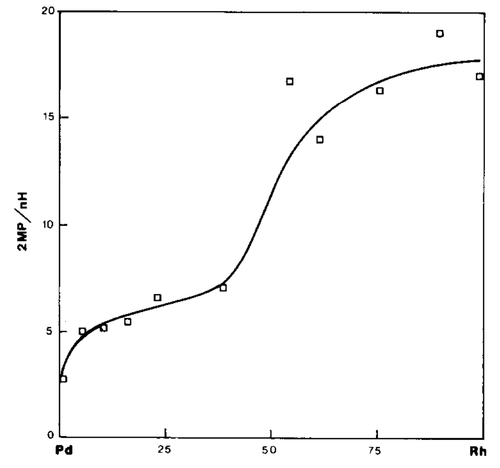

FIG. 5. 2MP/nH ratio for MCP conversion against bulk composition of PdRh/Al_2O_3.

sition (samples AG and AH, AJ and AM). In that case, the specific activity for benzene hydrogenation and MCP hydrogenolysis decreases noticeably with the particle size.

The apparent activation energies measured from the rate of formation on the hexanes are reported in Table 7. The general trend is an increase from Rh to Pd. The activation energy for the formation of *n*-hexane is larger than that obtained for the other hexanes on Rh-rich samples, as was observed previously on Rh/Al_2O_3 (*15*).

A few experiments were made using MCP contaminated by 10 ppm of thiophene. In this case a special device was used: the effluents of the reaction were stored in a 16-loop valve, which allowed us to make a complete analysis of a sample trapped in the earlier stages of the deactivation. An example is reported in Fig. 6 for sample AL. The conversion of MCP as a function of time follows the same trend as that observed for benzene hydrogenation. The selectivity also changes: during the initial decrease of activity, the ratio 2MP/nH also decreases, increases, and then remains roughly constant during the long-term deactivation, after 100 min.

TABLE 7

Apparent Activation Energy

Catalyst	E_a (kcal · mol^{-1}) from the rate of formation of		
	2MP	3MP	nH
AF(100–0)	18.9	21.6	25.5
AE(90–10)	21.0	31	35
AL(39–61)	17.0	22	29
AH(16–84)	29.0	26	27
AJ(5–95)	43.0	40	51
AM(5–95)	38.0	38	56
AI(0–100)	47.0	47	46

DISCUSSION

From the experimental results we can conclude that the addition of Pd to Rh modifies the catalytic properties in many respects, the most interesting being probably the increase in selectivity to *n*-hexane in the hydrogenolysis of MCP and the better sulfur resistance in the hydrogenation of benzene.

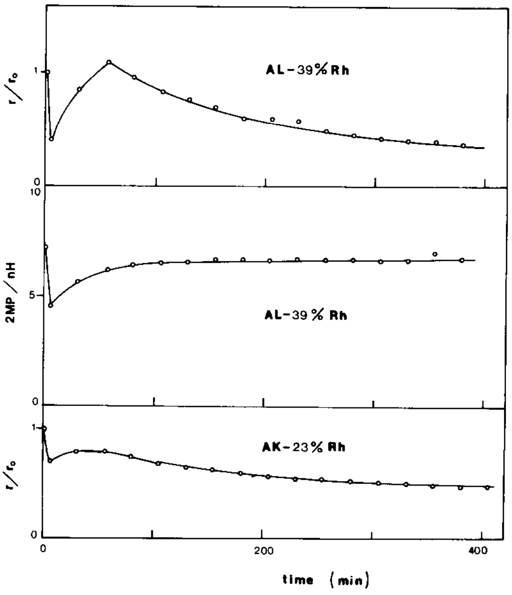

FIG. 6. Poisoning of the conversion of methylcyclopentane by thiophene (40 ppm): variation of the relative activity and of the 2MP/nH ratio, as a function of time for different catalysts.

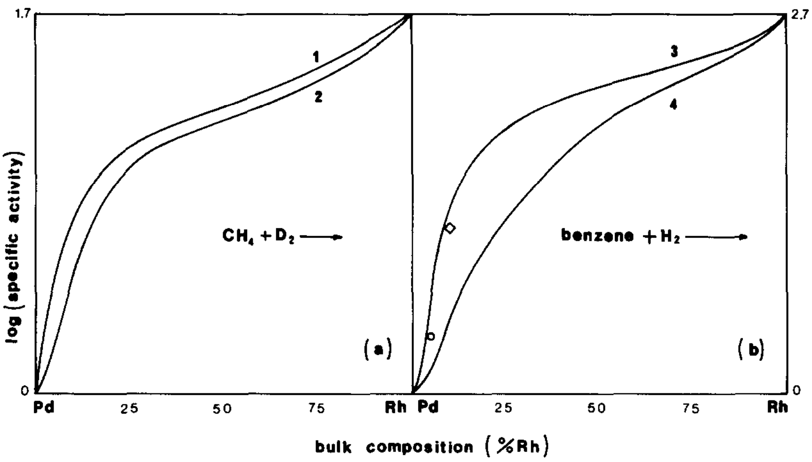

FIG. 7. Specific activity, in arbitrary log units, as a function of bulk composition of PdRh/Al_2O_3. (a) CH_4 + D_2 exchange; curve 1, calculated for a film with a surface composition according to Ref. (*11*), assuming that the specific activities of Pd and Rh are additive; curve 2, experimental results from Ref. (*12*); (b) hydrogenation of benzene; curve 3, specific activity calculated, as for curve 1, from the activities of pure Rd and Rh; curve 4, experimental results for supported catalysts. ◇, sample AG; ○, sample AM.

The variations of activity for benzene and methylcyclopentane also suggest that some alloying does occur, since the activity is not proportional to the respective content of the two metals. It is likely that Pd and Rh are in the same metallic particle. No direct determination of the surface composition was attempted, but we can find significant information in the catalytic data. Let us compare the hydrogenation of benzene with the results of CH_4/D_2 exchange on Pd–Rh films (*12*) and the surface composition of Pd–Rh films determined by Moss and Gibbens (*11*).

These two reactions have been claimed to be facile, or less structure dependent, especially the CH_4/D_2 exchange, which can proceed at a single metal atom (*7*). Indeed, good parallelism is observed between the activity data of CH_4/D_2 exchange and the surface composition of the film determined by Moss and Gibbens (*11*), as shown in Fig. 7. However, the simplicity of this exchange reaction is only apparent, since if the overall activity follows the surface composition, and might be attributed mainly to Rh, the selectivity of the exchange, with the absence of *d*-2 and *d*-3 methanes, remains characteristic of Pd over the whole composition range. This effect may be accounted for by modification of the electronic characteristics of the rhodium atoms which affects the exchange reaction. Therefore it may be inferred that the surface composition of Pd–Rh films, and powders under reductive atmosphere, are reasonably reproducible. Then the rapid decrease of the specific activities observed in Fig. 2, upon Pd addition to Rh, may be ascribed to a surface enrichment in palladium as observed on the films. It is, however, surprising that in the range 0–20% Rh, where no surface enrichment is noticed on the films, the hydrogenation of benzene does not parallel the surface composition.

Two possibilities then appear:

(i) The small particles behave differently from films with respect to surface enrichment. This possibility is based on the idea that the volatile component, here Pd, prefers a low coordination which can be found at the surface. Then, small particles possessing a higher proportion of edge and corner sites could present a higher surface con-

TABLE 8

Number of Atoms of Different Environments for Cubooctahedral Clusters

m	N_T	N_S	$N_c + N_e$	$N(111)$	$N(100)$	N_S/N_T	Size (Å)
4	147	92	60	10	16	0.63	18.9
5	309	162	84	15	25	0.52	24.3
6	561	252	108	21	36	0.45	29.7
7	923	362	132	28	49	0.39	35.1
8	1,415	492	156	35	64	0.35	40.5
9	2,057	642	180	44	81	0.31	45.9
10	2,869	812	204	54	100	0.28	51.3
40	≃190,000	15,200	916	780	1600	0.08	150

Note. m = number of atoms on an edge; N_T = total number of atoms; N_S = number of surface atoms; $N_c + N_e$ = number of corner and edge atoms; $N(111)$ and $N(100)$ = number of atoms on one (111) or (100) plane, respectively. The size is calculated assuming 2.7 Å as the interatomic distance.

centration of palladium. This hypothesis is not supported by the results obtained in the hydrogenation of 1-hexene: in that case the specific activity is proportional to the bulk content of rhodium (Table 4), and it must therefore be concluded that the surface composition is not drastically different from that of films.

(ii) The hydrogenation of benzene requires more than a single rhodium atom. The turnover frequency for the hydrogenation of benzene is approximately constant for Rh particles larger than 10 Å, but several experimental results (*13, 19–21*) show that the activity falls when the particle size is less than 10 Å. These very small particles behave as organometallic compounds which can hydrogenate double bonds but are unable to hydrogenate aromatic rings. This behavior has been interpreted as an electronic modification of the particles by the support (*21*) but can also be accounted for by the ensemble theory. Indeed the hydrogenation of 1-hexene shows that rhodium atoms are present at the surface. If we compare the samples AG and AH, we reach the conclusion that sample AG, with particles as large as 150 Å, behaves like a film, whereas the 17-Å particles of sample AH are much less active, despite a larger rhodium content. The sample phenomenon is observed for the samples AJ and AM.

Rh and Pd both have fcc structures and favor the same cubooctahedral habit (*22, 23*). It may be hypothesized that the alloy will follow the same trend. Let us consider in Table 8 the distribution of the metallic atoms in that case. We assume for simplicity that the surface compositions are identical to those determined by Moss and Gibbens (*11*). Due to the low dispersion, the great majority of surface atoms in the sample AG are distributed in (100) and (111) planes which contain approximately 800 and 1600 atoms, among which 40 to 80 are rhodium atoms. This number is large enough to allow the formation of a site formed by several neighboring atoms. By contrast, on sample AH, the total number of atoms in the (100) and (111) planes is only 15 to 25, which corresponds to one or two rhodium atoms per plane. In this case the probability of finding a small ensemble of neighboring rhodium atoms falls drastically even if the surface concentration is the same in both cases. Then the activity for reactions proceeding at a multiple site is severely affected. Recently this point has received special attention in a theoretical study by Martin *et al.* (*24*). Since the hydrogenation of benzene behaves differently in this respect from the hydrogenation of olefins, it may be concluded that this reaction needs more than one surface rhodium atom to proceed.

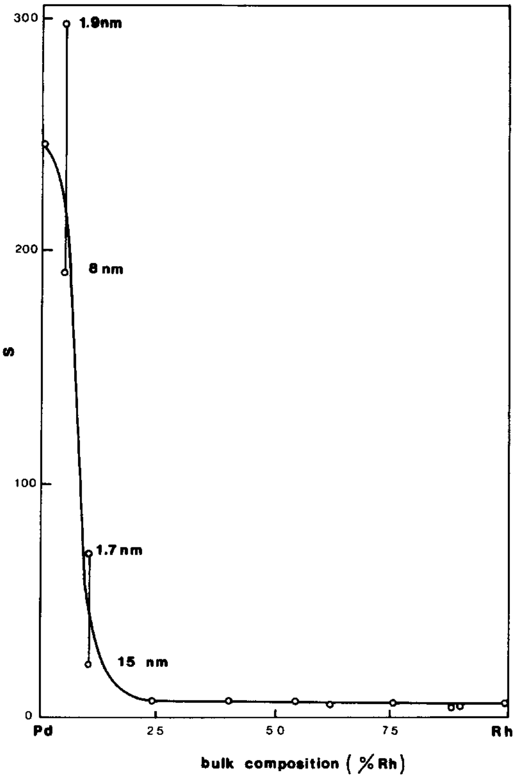

FIG. 8. Ratio S between the specific activities in the hydrogenation of benzene and the conversion of methylcyclopentane against bulk composition of $PdRh/Al_2O_3$. Vertical lines join values obtained on pairs of samples of different particle sizes AG and AH, and AJ and AM.

The results obtained with the conversion of methylcyclopentane can give some additional information on the coordination of surface rhodium atoms. The specific activity for the hydrogenolysis of MCP follows the same trend as the activity for benzene hydrogenation, as shown in Fig. 8 by the plot of the ratios of these activities. Surprisingly, the ratio remains approximately constant in the range 20 to 100% Rh. On supported rhodium catalysts, it was previously observed that the turnover frequency decreased with the particle size (*15*). This result was interpreted in terms of changes in the coordination of the surface atoms: the turnover number was found to be high (≃500 at 493 K) when the coordination of rhodium was high, as for large cubooctahedra of Rh/Al_2O_3 or small icosahedra of Rh/SiO_2. In the present case, with $PdRh/Al_2O_3$, the specific activity for MCP conversion parallels the specific activity for benzene hydrogenation, which is independent of the coordination of rhodium since no influence of particle size has been observed above 10 Å. That means that Rh keeps a high coordination, like the initial one for a 50-Å rhodium particle where 80% of the surface atoms are located on dense planes. Then this constancy of the ratio of activities suggests that Rh occupies central positions in the (111) and (100) planes in order to keep a high coordination.

The changes of the internal selectivity between hexanes agree with this model: the 2MP/*n*-hexane ratio remains the same between 100 and 50% Rh, in the bulk (which corresponds to a range 100–35% Rh at the surface), and is characteristic of large Rh particles (*15*).

The results of the conversion of methylcyclopentane therefore suggest that the particles can be described as a Pd-rich layer, where Pd atoms are located preferentially at corner and edge sites, and Rh forms "islands" of a size large enough to behave like Rh/Al_2O_3 big clusters. That nonrandom distribution of Rh in the surface layer is consistent with the thermodynamic properties of Pd–Rh alloys (*25*), which show a miscibility gap, and with the theoretical predictions of Burton *et al.* (*2*), for which edge and corner sites would be expected to be richer than the plane sites in the more volatile component.

In the range 20–50% Rh, the ratio S, namely, activity of Bz/activity of MCP, stays constant and the selectivity ratio 2MP/*n*-hexane decreases from 17 to 6. The latter value is typical of ring opening on small Rh/Al_2O_3 particles (*15*). When the Rh content decreases in the sample, the size of Rh islands should decrease also. The fact that these smaller islands behave like larger ones with respect to the conversion of MCP may be explained by a cooperative action of the surrounding Pd atoms which would accommodate the hydrogen needed for the reaction. However, the rupture of the C—C bond should occur on Rh only, and the selectivity of ring opening should then depend only on the environment of the rhodium site, as on Rh/Al_2O_3 catalysts (*15*).

Below 20% Rh the ratio *S* of activities between benzene and methylcyclopentane increases very clearly and the resistance to sulfur poisoning also increases. The former effect can be interpreted within the framework of the ensemble model, assuming that the size of the site required to hydrogenolyze MCP is larger than the site needed to hydrogenate benzene. This assumption appears likely since it is now well established that reactions involving C—C bond rupture are more demanding than hydrogenation/dehydrogenation reactions involving C—H bonds (*26*). For instance, dilution of the Pt surface into small ensembles by different modifiers, such as Sn, Au, Re, C_{ads}, S_{ads}, drastically reduces the hydrogenolytic activity, while mild dehydrogenation reactions are affected to a lesser extent (*27*). In other respects on Rh/Al_2O_3 catalysts the hydrogenation of benzene has been found to have little dependence on the metal particle size, while the activity of MCP ring opening increases with the particle size (*15*). The results obtained on samples AG and AH agree well with that hypothesis, since by going to small metallic particles on the AH sample, the specific activity for hydrogenolysis decreases faster than that for hydrogenation. As previously emphasized, the probability of encountering, on a bimetallic cluster, an ensemble having *n* neighboring atoms of the same metal increases when the size of the cluster increases (*24*). Indeed, the two samples AG and AM which have a low dispersion give for the hydrogenation of benzene a turnover frequency which is similar to that expected for Pd–Rh films of the same bulk composition, assuming that the catalytic activity is proportional to the surface composition (Fig. 7).

It may also be noted that Popova *et al.* (*28*) have previously shown that the amount of strongly bonded hydrogen decreases sharply with the first addition of Rh to Pd; then the decrease of the hydrogen coverage could explain the variations of catalytic properties observed on alloying. However, the different behaviors between samples AJ and AM, and AG and AH, which present similar rhodium contents and differ mainly by the particle size, do not favor this interpretation, and the conversion of hydrocarbons is therefore well described by simply using the ideas of the ensemble theory.

The results of poisoning by thiophene, however, are not well explained in this frame. In a previous work, we found that the deactivation rate constant k_d decreased with the size of the rhodium particles when alumina was used as support (*14*). The improvement of the sulfur resistance was interpreted by a decrease of the local density of states (LDS) at the Fermi level. This interpretation was based on two facts: the HDS of thiophene, which provides the poison, is controlled by electronic factors (*29*) and thiophene has been found to be an electron acceptor on platinum (*30*). The catalyst is therefore more resistant to thiophene if the ionization potential is high and the LDS at the Fermi level is low. This is the case for palladium catalysts and for small cubooctahedral particles of Rh/Al_2O_3. By contrast, the LDS is higher on the dense planes of rhodium and the resistance against poisoning is then lowered: this is the case for small icosahedra of Rh/SiO_2 or large cubooctahedra on whichever support.

In the present case, we can consider that the catalytic activity for hydrogenation, and hence the deactivation rate constant k_d, are representative of the surface rhodium atoms. Figure 3 shows that k_d decreases rapidly upon addition of Pd to Rh, and goes through a *minimum* value for sample AJ. This is a quite different behavior from that observed for the conversion of MCP, where the catalytic activity per surface rhodium atom is roughly constant in the range 50–100% Rh, since the specific activity parallels the surface rhodium content. Moreover, the variations of k_d by alloying reach two orders of magnitude, and this is a sufficiently large effect to be accounted for by an electronic modification of the catalytic site by alloying. Indeed, large variations of turnover numbers can also be explained by the ensemble theory (*26*), but here it is more difficult to justify a minimum of activity, which indeed does not exist in the conversion of MCP. We must also assume that the size of the ensemble needed to decompose thiophene is much larger than that required to convert methylcyclopentane, and this is not consistent with the results obtained by changing the particle size and support, in which similar structure sensitivities were observed in both cases (*14, 15*).

In a recent study of the electronic properties of Pd and Ni alloys, Fuggle *et al.* (*31*) reach the conclusion that when Pd or Ni is alloyed with an electropositive element, a slight electron transfer occurs from the latter to Pd or Ni, and the filling of the Pd *d*-band decreases the LDS at the Fermi level.

Rhodium is more electropositive than Pd since the ionization potential and work function of Pd are greater. Then by adding Pd to Rh we can expect, first, a decrease of the Pd *d*-states at E_F, and, second, a modification of Rh which becomes electron deficient, then less able to give electrons into the metal–sulfur bond. This model explains the better resistance of Pd–Rh catalysts compared to Rh, and is consistent with the mechanisms proposed for hydrodesulfurization (*29*).

The enhancement of the sulfur resistance of well-dispersed samples, in which the size of the rhodium islands decreases, is also consistent with this model since it may be expected that the electronic transfer between Pd and Rh will be favored when the Rh atoms are isolated in the Pd matrix (*9*).

The deactivation/reactivation phenomenon occurring in the first steps of the reaction shows a surface reconstruction by sulfur, as indicated by the change of the ratio 2MP/*n*-hexane (Fig. 7). However, after 50 to 100 min this ratio reaches the initial value and remains constant. It is then assumed that the surface has some common features with the initial one.

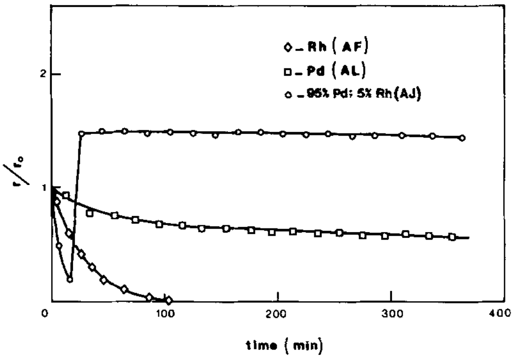

FIG. 9. Variation of the relative activity as a function of time for pure Rh, pure Pd, and a bimetallic PdRh/Al_2O_3 catalyst; $P_{\text{thiophene}}$ = 40 ppm.

In conclusion, the addition of palladium to rhodium has several effects, the most beneficial being an interesting enhancement of the resistance to sulfur poisoning by thiophene (illustrated in Fig. 9) and an inhibition of both hydrogenation of benzene and hydrogenolysis of methylcyclopentane, but not of the hydrogenation of 1-hexene.

These catalytic results, in association with the segregation curve reported for films, suggest that the surface composition of supported small particles are similar to that of Pd–Rh films. On the small particles, Pd preferentially occupies corner and edge sites and pushes Rh onto the dense planes. Rhodium tends to form islands at the surface.

The reactions investigated here can be divided into two groups:

(i) Benzene hydrogenation and MCP hydrogenolysis for which the catalytic results can be described by the ensemble theory of catalysis is one. The size of the ensemble required to hydrogenate benzene is lower than that needed to react with methylcyclopentane, but is probably larger than a single metal atom.

(ii) The poisoning of benzene hydrogenation by thiophene, which involves the HDS of thiophene, is better described by the electronic theory of catalysis in agreement with the reported physical properties of Pd–Rh alloys.

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