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Skeletal Rearrangement of Hydrocarbons on the Rare Earth Mixed Valence Intermetallic Compound $CePd_3$

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The skeletal rearrangements (isomerization, hydrogenolysis, dehydrocyclization) of methylcyclopentane, 2-methylpentane, and 3-methylhexane have been studied on the intermetallic compound $CePd_3$ and compared with results obtained on classical supported palladium catalysts prepared by impregnation. $CePd_3$ exhibited a very low activity; the reaction mechanisms involved were quite different from what is known of palladium catalysts and they were attributed instead to cerium atoms present in an oxidized form. However, an activation with air at room temperature or at 120°C dramatically increased the catalytic activity and the reactions involved were characteristic of palladium atoms, with a surprising selectivity toward aromatization and 1-5 ring closure. This enhancement was interpreted as due to a complete rearrangement of the surface, yielding active palladium sites on the surface. This phenomenon was related to the specific properties of cerium atoms which can undergo fast fluctuations of valence as revealed by photoelectron spectroscopy.

INTRODUCTION

Intermetallic compounds of the type A-M_x, where A is a rare earth or an actinide and M a transition metal atom, are well known for absorbing hydrogen in a dissociative way, at low pressure and temperature. This peculiarity and others led many investigators in the past few years to catalytic studies using this type of compound. Ammonia synthesis (*1*), methanation (*2–7*), hydrogenation of olefins (*8–10*), and dealkylation of aromatics with hydrogen or water (*6, 11*) were the main reactions performed.

These previous works showed that the surface of the intermetallic compound could undergo drastic changes during the course of the reaction, such as formation of a rare earth nitride or oxide and coalescence of the transition metal atoms into aggregates of up to several hundreds of Ångstroms in size. This might explain why the reactivity of these intermetallic compounds showed an induction period, while the same catalysts, pretreated in an oxygen atmosphere, reached a steady state very quickly (*2, 7*). This surface transformation, as indicated by CO chemisorption measurements, led to an increase of the specific area, which was very low initially, since the temperature of preparation of the intermetallic was very high. The catalytic activity was thus comparable to catalysts prepared by the classical impregnation method. This was particularly the case with intermetallic compounds of cerium or thorium, the oxides of which possess a valence +4, contrary to the other elements of the same series.

In this paper we report on the catalytic behavior of cerium-based compounds which exhibit remarkable physical properties due to the 4f electrons of cerium. For example stoichiometric $CePd_3$ is characterized by an extremely low lattice parameter as compared to compounds of other rare earths (*12*), a maximum of magnetic susceptibility at 140 κ (*13*), and a very high specific heat coefficient γ (38.5 mJ/mole κ^2) (*14*).

These physical properties, as well as

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spectroscopic results (*15*) (photoemission, X-ray absorption edges), show that the electronic structure of cerium is intermediate between $4f^05d^26s^2$ (valence 4) and $4f^15d^16s^2$ (valence 3). A first model, of fast fluctuations (*16*) between the two configurations $4f^0$ and $4f^1$, suppose that the 4f electrons are close to the Fermi level, which implies a high density of states near the Fermi level; it is worth noting that the density of states at the Fermi level, as deduced from the specific heat coefficient γ, is 16 eV^{-1} for $CePd_3$ and only 1.2 eV^{-1} for Pd (*17*). A delocalized model (*18*), which assumes that the 4f level is band-like, predicts an electronic behavior similar to d electrons in a transition metal.

Whatever the physical intepretation, interesting catalytic properties may be expected and it is important to emphasize that this phenomenon of fluctuating valences seems to be extremely sensitive to parameters such as chemical environment, presence of impurities, or deviation from stoichiometry (*19*).

We present here catalytic studies on $CePd_3$, oxidized or not, in comparison with other catalytic systems such as CeO_2, 10% Pd/Al_2O_3, and 10% Pd/CeO_2. The reactions chosen were hydrogenolysis of methylcyclopentane, isomerization of 2-methylpentane, and aromatization of 3-methylhexane.

On the basis of their interesting physical properties and of their hydrogen absorbing power, one could expect with these catalysts hydrogenating–dehydrogenating properties leading to modifications of selectivities, especially toward the formation of aromatics. It was also interesting to check whether the transition metal atom was still the active site, depending on different treatments, as in the preceding studies on intermetallic compounds. The variations of the specific activity of palladium obtained by partial or total decomposition of the intermetallic were then followed and compared to what was known on palladium catalysts prepared by classical means (*20, 21*).

The modifications of the surface were also examined by X-ray photoelectron spectroscopy.

EXPERIMENTAL

Catalysts

Intermetallic compound. An appropriate mixture of cerium and palladium (purity 3 *N* and 5 *N*, respectively) was melted in an arc oven and crushed under argon atmosphere into a 50 μm powder (*15*). X-Ray diffraction was used to check the absence of other phases in addition to the partially ordered close-packed $AuCu_3$ structure with *a* = 4.126 Å (*14, 19*). The samples were kept in a dry, inert atmosphere.

Supported catalysts. Ten percent Pd/Al_2O_3 and 10% Pd/CeO_2 were prepared by impregnating γ-alumina from Woelm and 4 *N* cerium dioxide with a solution of palladium chloride tetrammine $Pd(NH_3)_4Cl_2$. The powder was then dried for 20 h in an oven at 120°C.

Before any catalytic experiment, the samples were reduced under 1 atm. of hydrogen for 24 h at 150°C. The temperature was then increased up to the reaction temperature at a constant rate of 2°C/min.

Metallic cerium and cerium oxide were tested without any treatment.

Catalytic Experiments

The experiments were performed in a flow of hydrogen in a pulse microreactor which has already been described (*22*). The pretreatment in air of $CePd_3$ was made in static atmosphere during 2 days.

The reaction products were hydrogenated on Adams platinum at 80°C and then analyzed by gas chromatography on a DC 200 or on a capillary 0V 101 column and by mass spectrometry.

Labeled Molecules

The details on the synthesis, the purification, and the mass spectrometry of 2-[2-

^{13}C]methylpentane have been reported elsewhere (*23*).

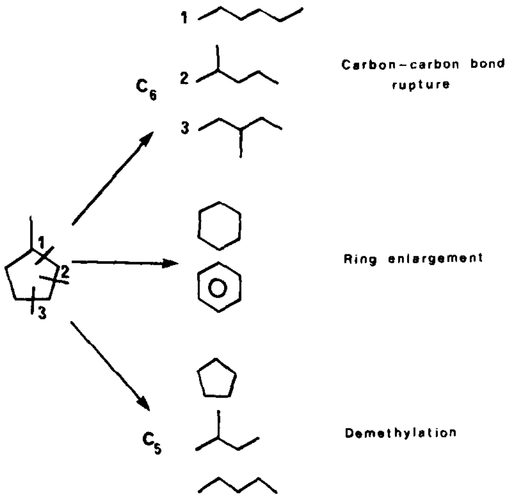
Photoemission

Photoelectron spectroscopic studies were performed in a VG ESCA III apparatus which has already been described (*24*). Let us mention only that the analyses were made using the 1486.6 eV Al$K\alpha$ radiation as X-ray source and that the treatments under gaseous atmospheres were made in a separate chamber. UHV down to 10^{-10} Torr was achieved in both chambers.

RESULTS

Catalytic Reactions

Hydrogenolysis of methylcyclopentane. The interaction of methylcyclopentane and hydrogen may lead to different reaction products which are given in Scheme 1:



The rupture of a secondary–secondary carbon–carbon bond gives 2-methylpentane (2-MP) and 3-methylpentane (3-MP) while the rupture of a tertiary–secondary bond leads to *n*-hexane (*n*-H). The ratio r = 3-MP/*n*-H will then be characteristic of the bond breaking mode. A ring enlargement will give cyclohexane and benzene (and sometimes methylcyclopentenes when the reaction products are not hydrogenated). A demethylation will result in cyclopentane which is quickly hydrogenolyzed to form *n*-pentane and successive isomerization and cracking reactions will give all the series of hydrocarbons from C_5 to C_1.

In Table I we have reported the selectivity ratios 2-MB/*n*-P and 3-MP/*n*-H together with the total activity (A_T) and the activity for the reaction of ring enlargement (A_A) in μmol/min · g-Pd. Activities have been calculated for conversions lower than 20% using the following relationship:

$$A_i = \frac{\alpha_i F}{w_{Pd}} \text{ in } \mu\text{mol/min} \cdot \text{g-Pd}$$

where α_i is the conversion for a given reaction i, F the hydrocarbon flow rate and w the weight of palladium. These activities have been calculated per mass unit in view of the present lack of accurate surface data on intermetallics (*7*).

It is quite clear that a treatment in air, especially at 120°C, had a very important effect on the catalytic activity (up to several orders of magnitude). However, the initial activity of $CePd_3$ was very low since a temperature as high as 350°C was necessary to obtain the same conversion as on cerium dioxide at 300°C and anyway the activity was much lower than on a classical supported palladium catalyst.

Important changes were also observed in the product distribution. Initially $CePd_3$ gave, as a major product, hexane and, surprisingly enough, isopentane, the amount of which decreased rapidly with time and eventually became negligible. On the other hand, the selectivity ratio 3-MP/*n*-H increased under hydrocarbon flow to reach a steady state after 30 min of reaction (Fig. 1). These two results show that an induction period was necessary to stabilize the $CePd_3$ surface. The same variations, without noticeable deactivation, were observed on the same catalyst after a few days under a hydrogen flow.

The formation of isopentane from methylcyclopentane was characteristic of metallic cerium where it largely predominated with

TABLE 1

Reactivity of Methylcyclopentane

Catalysts	Treatment	Total conversion α_T[a]	T(°C)	Total activity A_T (μmol/min · g-Pd)	Major products[b]	3-MP/n-H	2-MB/n-P	Aromatization activity A_A (μmol/min · g-Pd)
$CePd_3$ (I)	—	1 → 2	350		at first 2-MB > C_6 > $2C_3$			
$CePd_3$ (II)	I + 200 hr at 1 atm H_2 350°C		350	0.045–0.027	then $C_6 > 2C_3 \gg$ 2-MB	2.5 → 8	100 → 2	0.005
$CePd_3$ (III)	II + 2 days air 20°C	8.5	350	0.72	$C_6 \gg$ c-P	2.5	0.6	0.02
$CePd_3$ (IV)	III + 2 days air 120°C	16.8	350	30	C_6 > Bz + c-H > c-P	2.5	0.6	4.0
10% Pd/Al_2O_3	—	3.9	300	22	$C_6 \gg$ c-P	1.5	0.7	0.60
10% Pd/CeO_2	—	5.2	300	4.3	$C_6 \gg$ c-P	2.5	0.8	0.12
CeO_2	—	2.0	300	0.063	C_6 + stat. cracking[c]	3.6	2.0	0
Ce	—	0.5	300	0.020	2-MB	—	>100	0
Ce	Air 1 hr 300°C	8.8	300	0.26	C_6 + stat. cracking[c]	2.6	2.4	0

[a] α_T (%): overall conversions.

[b] 2-MB, 2-methylbutane; 3-MP, 3-methylpentane; n-H, n-hexane; c-P, cyclopentane; Bz, benzene; c-H, cyclohexane; n-P, n-pentane.

[c] Stat. cracking, statistical carbon–carbon bond rupture.

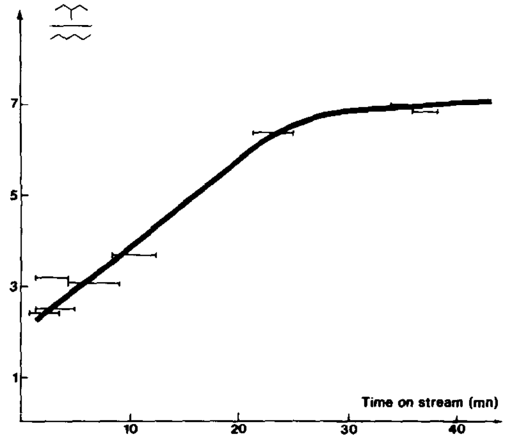


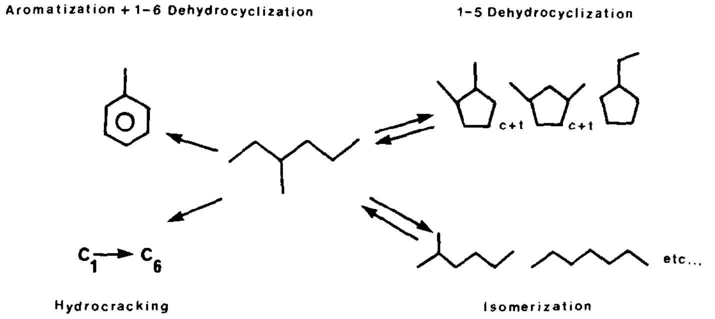
FIG. 1. Dependence of the selectivity ratio 3-methylpentane/*n*-hexane with time on stream of hydrocarbon for the intermetallic $CePd_3$.

a ratio 2-MB/*n*-P always higher than 100. On cerium oxide the reaction gave, together with hexanes, cracking products, the distribution of which was roughly statistical.

After a treatment under air atmosphere, the behavior of $CePd_3$ became stable in the flow of hydrocarbon. The ring enlargement was particularly enhanced after the treatment at 120°C. We shall refer to this effect in more detail when dealing with the aromatization of 3-methylhexane. The distribution of reaction products and the selectivity ratio 2-MB/*n*-P were quite close to those obtained on 10% Pd/Al_2O_3 and 10% Pd/CeO_2. However, the hydrogenolysis ratio 3-MP/*n*-H ($r = 2.5$) was comparable to that of 10% Pd/CeO_2 but substantially different on 10% Pd/Al_2O_3 ($r = 1.5$).

Isomerization of 2-[2-^{13}C]methylpentane. We give in Table 2 the result of an experiment on $CePd_3$ before activation as compared to Pd supported on Al_2O_3, SiO_2, and CeO_2. The major isotopic variety of the 3-methylpentanes was labeled on carbon 2 if the catalyst was $CePd_3$ and on carbon 3 with supported palladium. The percentage of *n*-[3-^{13}C]hexane was also surprisingly high among the different hexanes. It is clear that the behaviors of $CePd_3$ and of classical Pd catalysts are quite different.

Aromatization of 3-methylhexane. Four types of reaction, strongly dependent on the experimental conditions, may be observed with 3-methylhexane (Scheme 2):



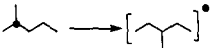
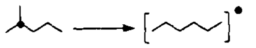
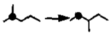
Isomerizaton (I) which leads to saturated heptanes and 1-5 dehydrocyclization (D) to give substituted cyclopentanes; these reactions are reversible.

Aromatization which gives toluene, 1-6 dehydrocyclization leading to methyl cyclohexane (A) and hydrogenolysis (C) yielding all the hydrocarbons from C_6 to C_1; these reactions are irreversible.

We have performed with this molecule a series of experiments on $CePd_3$ before and after treatment in air. In Table 3 we give (a) the total activity A_T, (b) the specific activity for aromatization (and 1,6-dehydrocyclization) A_A, and (c) the distribution of reaction products obtained on $CePd_3$ after treatment in air at 20 and 120°C, on 10% Pd/Al_2O_3 and 10% Pd/SiO_2 for the different reactions,

TABLE 2

2-[2-^{13}C]Methylpentane Isomerization: Distribution in Percentage of the Labeled Products

Catalysts	T(°C)	Total conversion (%)				
			Cyclic mechanism	Bond shift mechanism	Cyclic mechanism or n-propyl shift	Methyl shift
						
$CePd_3$	350	7.0	29	71	68	32
10% Pd/CeO_2	300	19.2	91	9	92	8
10% Pd/Al_2O_3[21]	360	29.4	90	10	95	5
10% Pd/SiO_2[21]	360	8.0	71	27	91	9

viz., hydrogenolysis (S_C) in which we include the demethylation selectivity percentage ($C_6 + C_1$), isomerization (S_I), dehydrocyclization (S_D), and aromatization (S_A).

As already seen with methylcyclopentane, air had a strong influence on the catalytic activity of $CePd_3$. This effect was noticeable even at 20°C, which shows how important it is to carefully avoid any contact with air if one claims to estimate the activity of the intermetallic compound. After treatment at 120°C, the activity per gram of metal was lower than that of a classical 10% Pd/Al_2O_3 but $CePd_3$ was more active than 10% Pd/CeO_2 and 10% Pd/SiO_2. The differences between 10% Pd/Al_2O_3 and 10% Pd/CeO_2 may be explained by a difference in the specific areas of the supports. Cerium oxide and metallic cerium exhibited a very low activity.

Demethylation as measured by percentage ($C_6 + C_1$) was the main reaction on palladium as already seen on unoriented films (*25*, *26*), on supported palladium (*19*), or palladium black (*27*, *28*). This was also the case with $CePd_3$ treated with air, but to a lesser extent compared with the palladium/alumina catalyst as seen in Table 3.

The selectivity for the production of aro-

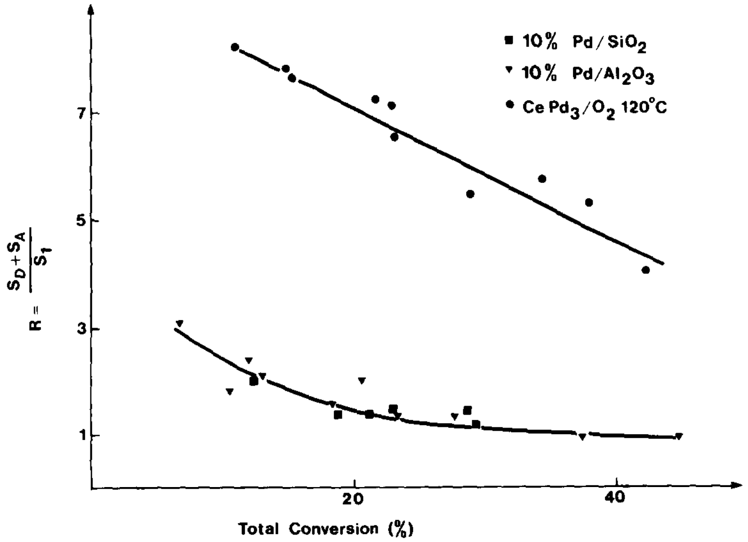


FIG. 2. Dependence of the selectivity ratio $R = (S_D + S_A)/S_I$ with the total conversion for various palladium catalysts. T = 360°C. ■, Pd/SiO_2; ▼, Pd/Al_2O_3; ●, $CePd_3$ treated with air at 120°C.

TABLE 3

Aromatization of 3-Methylhexane: Reactivity at 360°C

Catalysts	Treatment	Total activity A_T (μmol/min · g-Pd)	Aromatization activity A_A (μmol/min · g-Pd)	Total conversion α_T	Hydrogenolysis		Isomerization	Dehydrocyclization	Aromatization
					$\%S_c$[a]	$\%C_6 + C_1$[b]	$\%S_I$[a]	$\%S_c$[a]	$\%S_A$[a]
$CePd_3$	—	0.14	0.01	1.0	88	42		12	
$CePd_3$	Air 2 days 20°C	0.42	0.05	4.8	58	43	7	24	12
$CePd_3$	Air 2 days 120°C	26.5	5.8	15.4	61	40	5	15	19
10% Pd/Al_2O_3	—	54.6	5.6	16.9	69	61	12	10	9
10% Pd/SiO_2	—	9.3	0.4	18.8	65	57	15	16	4
10% Pd/CeO_2	—	4.8	0.5	2.4	58	42	11	21	10
CeO_2	—	0.14[c]	0.01	3.8	65	21		35[d]	
Ce	—	0.07[c]	tr	3.0	67	42		33[d]	

[a] $\% S_c + \% S_I + \% S_D + \% S_A = 100$.

[b] $\% (C_6 + C_1)$ = selectivity in the demethylation cracking.

[c] Activity in μmol/min · g (catalyst).

[d] Some olefins in the products.

matics or cyclics was also very sensitive to the air treatment. We have followed the variation of the ratio $R = (S_D + S_A)/S_I$ as a function of the total conversion for $CePd_3$ activated in air at 120°C and for 10% Pd/Al_2O_3 and 10% Pd/SiO_2 (Fig. 2). This ratio is actually a measurement of the possibility for the catalyst to give cyclization (1-5 and 1-6) rather than isomerization. R was strongly dependent on the conversion and a careful study was necessary. The hydrogenolysis selectivity was important so that it was not possible to lower the total conversion further than 10% for a detailed study of isomerization.

Whatever the support, Al_2O_3 or SiO_2, the activity for different reactions, isomerization or aromatization and dehydrocyclization, remained at a comparable level. As we supposed that the rate of hydrogenolysis of the ring was higher than the rate of dehydrocyclization (*29*), we are not surprised that R increased with decreasing conversion. By extrapolating to zero conversion we found $R \sim 4$–5 for Pd/Al_2O_3 and Pd/SiO_2 and $R \sim 9$ for $CePd_3(O_2)$.

Photoemission Studies

A $CePd_3$ sample, already used in catalytic studies, was studied by photoelectron spectroscopy. In Fig. 3 we give the 3d core level spectra of palladium recorded before and after a reduction in 1 atm H_2 at 350°C followed by an oxygen treatment at 20°C. Initially two maxima at 335 and 340 eV, characteristic of Pd^0, were recorded but shoulders at approximately 2 eV toward higher binding energies indicated a partial oxidation. These shoulders disappeared after reduction by H_2 and they were not detected after the oxygen treatment. The 0 1s peak at 529.6 ± 0.3 eV was too complicated to speculate on the possible presence of hydroxides or carbonates on the surface, as sometimes observed (*30*). This complexity comes in particular from the fact that it overlaps the $3p_{1/2}$ transition of palladium.

The interpretation of the 3d core levels of cerium is also difficult since many satellite peaks are detected (Fig. 4). Apart from a final state obtained by screening of the 3d core hole by 5d or 6s electrons of the conduction band (final state $4f^0$ in the case of CeO_2), one has to assume the presence of other final states with supplementary electrons on the 4f level (final states $4f^1$ and $4f^2$ in the case of CeO_2) arising from internal transitions of 5d–6s electrons or electrons of the filled 2p level of oxygen.

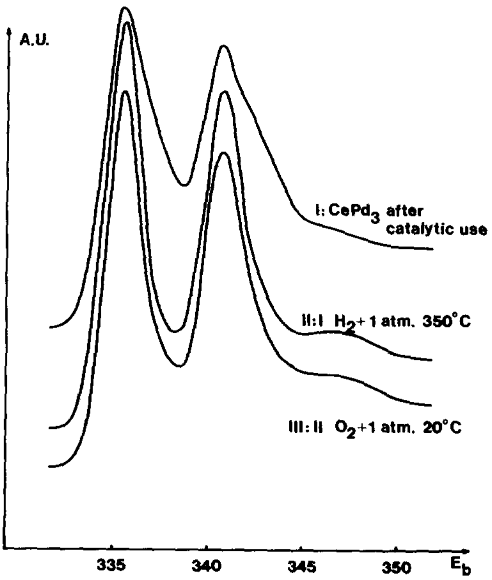


FIG. 3. Palladium 3d core levels in $CePd_3$ (E_B in eV). Variations with treatment.

Our spectra were quite similar to that of CeO_2 (see Fig. 4 and the binding energies in Table 4) and they were largely different from a pure $CePd_3$ sample where both the O 1s transition and the KLL Auger peak of oxygen at 975 eV could not be detected. However, after reduction by H_2 at 350°C (that is under out catalytic conditions), two shoulders were detected at 884.5 and 903 eV which might be attributed to the intermetallic compound itself. Nevertheless, it is not possible to discard a partial reduction giving small amounts of an intermediary oxide, Ce_2O_3 for example, or metallic cerium, or even some cerium hydride.

The ratio Pd/Ce was estimated from the ionization cross-sections given in the litera-

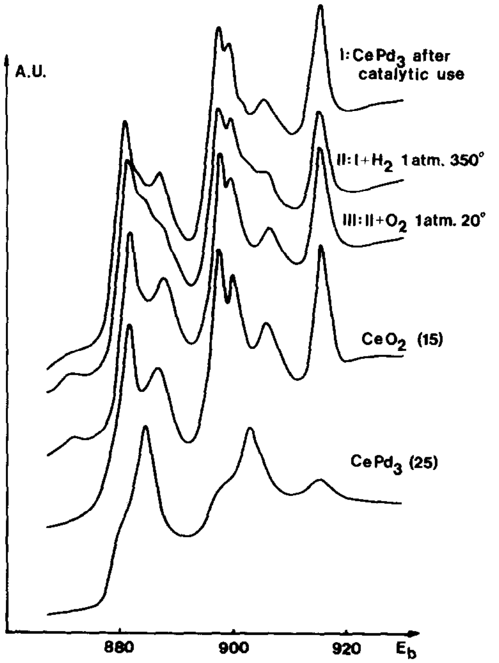


FIG. 4. Cerium 3d core levels in $CePd_3$ (E_B in eV). Variations with treatment. Comparison with CeO_2 and $CePd_3$.

ture (*33*). The values thus obtained showed a very small variation (0.7–0.8) from one spectrum to the other and were very different from the expected ratio (Pd/Ce = 3). However, one has to point out that the complexity of the cerium spectrum caused a large uncertainty on these values.

DISCUSSION

Nature of the Active Sites

We believe that the product distribution resulting from the complex reactions we have studied can give valuable information on the nature of the active sites involved. Since we have seen that the behaviour of $CePd_3$ was drastically changed after a treatment under air atmosphere, we shall deal with the two situations successively.

Reactions of $CePd_3$ without air treatment. From our results it is clear that the active sites involved in all our reactions include preferentially cerium species and that palladium atoms play a minor part. Several pieces of evidence support this conclusion:

(1) The catalytic activity is always very small and quite close to that of cerium oxide or metallic cerium.

(2) The steady state is reached after an induction period under the hydrocarbon flow, which is often the case with oxides but not with metals.

(3) The product distribution is close to that found for Ce catalysts.

(4) As with metallic cerium, the initial reaction of methylcyclopentane is the selective formation of isopentane, which is never observed on palladium. This reaction quickly disappears in favor of a classical hydrogenolysis, as on CeO_2.

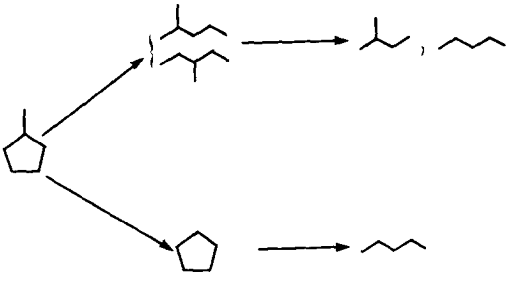
TABLE 4

Cerium 3d Core Level Binding Energies (eV)[a]

Compounds	Reference	$3d_{3/2}$			$3d_{5/2}$			Others	
		f^0	f^1	f^2	f^0	f^1	f^2		
$CePd_3$ (I)	This work	915.9	906.5	899.8	897.7	888.0	881.5		
(II): (I) + H_2 350°C	This work	916.0	906	900.3	898.0	887.5	881.3	884.5	903
(III): (II) + O_2 20°C	This work	916.1	906.8	900.2	897.9	888.2	881.9		
CeO_2	*31*	916.7	907.3	900.2	898.2	888.4	882.4		
Ce_2O_3	*31*	—	904.5	899.9	—	886.1	881.3		
$CePd_3$	*19*	914.7	902.9	898.5	—	884.3	879.6		
Ce	*32*	—	901.7	—	—	883.7	878.5		
$CeH_{2.1}$	*32*	—	904.0	900	—	885.7	882		

[a] Reference: carbon 1s line at 284.6 eV.

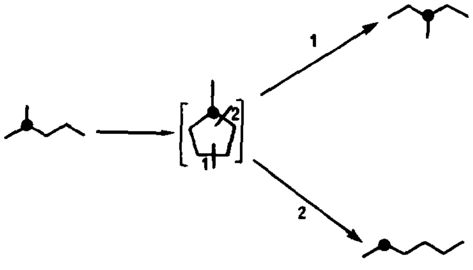
The initial formation of isopentane may be due either to fast consecutive reactions (Scheme 3)



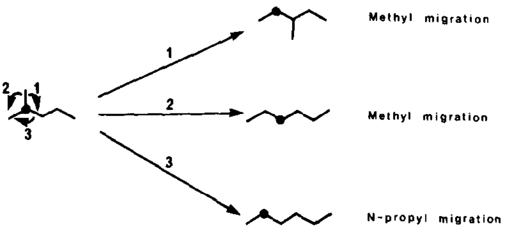
or to a concerted mechanism involving the rupture of two secondary–secondary carbon–carbon bonds (Scheme 4).

We believe that the latter mechanism is more probable since consecutive reactions would also lead to *n*-pentane (Scheme 3), which we have not detected. Moreover, if we remember that the formation of isopentane decreases rapidly under hydrocarbon flow, a concerted mechanism with the formation of a carbide Ce-C (*34*) provides a better explanation than consecutive reactions.

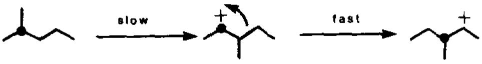
On palladium, whether supported on alumina or silica or alloyed with gold (*20*, *35*), the isomerization of 2-[2-^{13}C]methylpentane proceeds via a cyclic mechanism (Scheme 5).



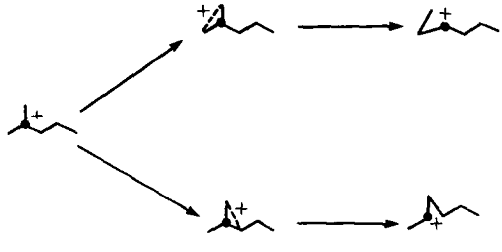
The bond shift mechanism (Scheme 6), involved in reactions on platinum catalysts with large crystallite sizes (*22*), plays a minor part on palladium.



Quite clearly, on CePd$_3$, the main reaction products come from a bond-shift mechanism to the extent of around 70%: methyl migration will give 3-[2-^{13}C]methylpentane (path 1) or *n*-[3-^{13}C]hexane (path 2) while an *n*-propyl shift (path 2) yields *n*-[2-^{13}C]hexane. On the other hand, supported palladium catalysts gave only 20% of a bond-shift mechanism from 2-[2-^{13}C]methylpentane. Naturally, one could also suppose that the sites responsible for the cyclization were strongly poisoned on CePd$_3$ and that the major pathway became a bond-shift mechanism on metals of the Gault–Garin type (*22*) or of the McKervey–Rooney–Samman type (*36*). However, we believe that the labeling of all our reaction products can be best explained by an acid type mechanism involving a carbocation formed on the acidic sites of the oxide CeO$_2$. A 1-2 methyl shift will then explain the formation of 3-[2-^{13}C]methylpentane while the minor product (3-[3-^{13}C]methylpentane, 29%) would result in a very fast ethyl migration (*37*) (Scheme 7).



In the same way, a protonated intermediary of cyclopropane type will provoke a chain lengthening yielding *n*-[2-^{13}C]hexane, by propyl migration, rather than *n*-[3-^{13}C]hexane by methyl migration (Scheme 8).



We prefer to invoke an acidic mechanism rather than ametallic one for several other reasons.

First, the activity for $CePd_3$ is of the same order of magnitude as for cerium dioxide.

Second, the product distribution of methylcyclopentane and 3-methylhexane is close to that given by cerium dioxide.

Third, our photoelectron spectroscopic results show that the ratio Pd/Ce in the topmost layers is much lower than that which the stoichiometry would foresee (0.7 instead of 3). Such a segregation has previously been reported in lanthanum compounds (*30*). Palladium atoms are still detected but one has to remember that XPS probes several atom layers under the surface. We have recorded Auger spectra on the same sample and with this technique, which is more sensitive to the surface layer, we could not detect palladium at all (*38*) before any treatment. The XPS spectra of the 3d core levels of cerium seem to indicate the presence of a small amount of the intermetallic itself but this will not induce necessarily a catalytic activity.

On the whole, before any air treatment, the catalytic activity of $CePd_3$ seems related to the presence of metallic cerium or cerium dioxide and not to palladium atoms. If really $CePd_3$ itself is involved in the reactions, its activity is probably very low. This is in agreement with other results published in the literature. For example, $CePd_3$ behaves like a poisoned palladium catalyst in the selective hydrogenation of alkynes (*39*). Other intermetallic compounds have shown a very low activity for hydrocarbon reactions even after successive reductions by hydrogen (*6*).

Reactions of $CePd_3$ treated in air. The action of air, even at room temperature, completely modifies the catalytic properties of the intermetallic compound. The activity is drastically enhanced, the hydrogenolysis ratio 3-MP/*n*-H becomes identical to values obtained with Pd/CeO_2, and the distribution of products of 3-methylhexane, as on the latter catalyst, is in the order demethylation > dehydrocyclization > isomerization.

Quite clearly, $CePd_3$ treated in air behaves like a classical palladium catalyst.

Activation Procedure

The most striking result of our studies is the difference in catalytic behaviour between $CePd_3$ before and after treatment in air. We believe that these differences are the result of a complete rearrangement occurring in the first layers of the surface when the intermetallic compound is submitted to a prolonged exposure to air. In this regard it is necessary to recall that $CePd_3$ was prepared and kept in an air-free atmosphere; it was inserted into the catalytic apparatus quickly but without special caution and this short exposure in the open air was sufficient to provoke an oxidation at least a part of the cerium; however, one may assume that the exposure was not long enough to result in a very important rearrangement of the surface. On the contrary, after 48 hr in air the oxidation was completed, palladium atoms were oxidized and a further reduction left catalytically active palladium atoms on the surface.

It is interesting to compare $CePd_3$ with other systems of the same series. Although we must be careful about the real significance of CO chemisorption results on intermetallics, it has been shown that cerium- or thorium-based intermetallic compounds absorb oxygen with a very important increase of the metallic area. The enhancement may reach 100 or even 1000 times for $CeNi_5(O_2)$ and $ThNi_5(O_2)$, respectively. On the contrary, the increase is much smaller, only one order of magnitude, for $LaNi_5(O_2)$ (*10*). The differences between $LaNi_5$ and $CeNi_5$ may be related to the properties of the oxides of the rare earth metals. On cerium oxide, where the fourth ionisation potential of the metal is low, empty anionic sites may be easily created while keeping the same geometric structure of the fluorite type. The great mobility of these empty sites, where two neighboring anions possess the valence +3, could be explained by the ability of cerium to shift from valence +4 to valence +3; the great affinity of oxygen toward cerium would result in an easy destruction of the intermetallic compound (ΔH formation of CeO_2 = −233 kcal/mole). The propagation of the oxide would create a great disorder on the surface resulting in the formation of dislocations, steps, kinks, etc. which might be occupied by the transition metal atoms responsible for a high catalytic activity. On the contrary, the absorption of oxygen in $LaNi_5$ is much less easy since the La^{3+} ion is much more stable and the rearrangement of the surface would be weaker.

A last interesting point to discuss is the high selectivity toward the cyclization reaction of 3-methylhexane, as compared to a classical palladium catalyst. The interpretation of these differences is not straightforward. One may tentatively invoke electronic effects including charge transfer or geometrical modification of the surface. Recent studies have shown that platinum and palladium exhibited different catalytic behaviors in the presence of cerium oxide and that an interaction between the transition metal atoms and cerium was occurring (*40*, *41*). Another possibility would include kinetic effects. These intermetallic compounds are well known to possess a great ability to absorb hydrogen. This absorption of hydrogen might modify the distribution of surface species, favoring the dehydrogenated ones which lead to the formation of aromatics. It has been shown that the hydrogen pressure strongly influences the selectivity of hexanes on platinum (*42*, *43*) or on palladium catalysts (*28*, *43*), aromatization being favored versus isomerization at low hydrogen pressure. Quite clearly further studies, including for example a comparison between these intermetallic compounds activated in air and catalysts prepared by the classical impregnation methods, as well as results on the particle sizes, are necessary to elucidate this problem.

CONCLUSIONS

We have shown that the intermetallic compound $CePd_3$ exhibits a very low catalytic activity, principally due to cerium atoms, unless it is activated in an air atmosphere. Such a treatment dramatically increases the catalytic activity and induces a catalytic behavior comparable to that known for classical palladium, with an enhanced selectivity toward aromatization and 1-5 ring closure. It seems that the increase of the catalytic activity in the presence of air is related to the peculiar properties of the cerium ion, which may undergo fast valence fluctuations.

Further work is in progress, on this system and others, to obtain a better insight into the mechanism of the activation, in particular to elucidate the different parts played by electronic and geometric effects.

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