

Monodisperse Colloidal Metal Particles from Nonaqueous Solutions: Catalytic Behavior in Hydrogenation of But-1-ene of Platinum, Palladium, and Rhodium Particles Supported on Pumice

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Metal catalysts have been prepared by depositing monodisperse particles of platinum (2–3 nm), rhodium (2–3 nm), or palladium (5 nm) prepared in reversed micellar solutions on pumice. The particles are well dispersed on the support whereas particles deposited from aqueous or alcoholic solution give large aggregates. The catalytic properties of these different catalysts in the deuteration, isomerization, and hydrogen–deuterium exchange of but-1-ene have been compared. The activities calculated per metal surface atom are similar. However, platinum prepared from microemulsions show unusually high selectivity in the isomerization reaction, and for such particles dehydrogenated species are active in the exchange reaction. The specificity of rhodium and palladium catalysts is independent of the mode of preparation. The reaction mechanisms are discussed. © 1987 Academic Press, Inc.

INTRODUCTION

We have previously studied the catalytic behavior of platinum particles dispersed in reversed micellar solutions (microemulsions) containing an aliphatic hydrocarbon or a long chain alcohol as the main solvent, water, and a cationic or nonionic surfactant (1). We have shown that, in the temperature range where the suspensions are stable (around 20°C), the platinum particles are active for butene hydrogenation, whatever the micellar environment. However, the most stable and active catalysts consisted of reversed micelles formed by a nonionic surfactant (pentaethyleneglycoldodecyl ether), water, *n*-hexane, or *n*-hexadecane.

In such a system, because of isotopic dilution due to the too rapid exchange between deuterium gas and hydroxyl groups of the surfactant, it was impossible to study the isotopic olefin exchange reaction in order to obtain mechanistic information.

The preparation of platinum, palladium and rhodium particles suspended in microemulsions has already been described (2). In this paper we report on the method of depositing such particles on a support and on studies of the catalytic behavior of the dried catalysts in isotopic exchange, isomerization and deuteration of but-1-ene. It has now been possible to carry out the investigations without isotopic dilution; a comparison is made with the catalysts prepared by the classical impregnation method (3). Mechanistic information is derived from these results.

In the study of the mechanisms of olefin hydrogenation and related reactions the identification of the location of deuterium atoms in the reaction products is an essential element in the elucidation of the reac-

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tive adsorbed species (4). In most papers dealing with olefin hydrogenation on metal catalysts, the results are interpreted in term of the "associative mechanism" proposed by Horiuti and Polanyi (5). This mechanism is supported by the *cis* ligand insertion well known in homogeneous catalysis involving interconversions between π -olefinic and σ -alkyl ligands (6); hence it was assumed to occur universally on metals whatever their nature (7). However, by using perdeuteropropene as the deuterium source instead of D_2 the exchange and isomerization of olefins could be separated from the hydrogenation which tends to mask these reactions on most transition metals. It was then found that the hydrogen-deuterium exchange in but-1-ene depends on the nature of the metal (4, 8-10) and several other mechanisms were proposed depending on the metal.

On Pd and Ni supported on silica the location of the deuterium atom in but-1-ene, after reaction between deuterium gas and but-1-ene was found to be so specific to the metals that it was possible to correlate the deuterium distribution of but-1-ene with the surface segregation when the reaction was performed on PdNi alloys (11). For this reason it appears that the study of the exchange between deuterium and hydrogen in but-1-ene using microwave spectrometry to locate the deuterium atom at the initial stage of the reaction is a suitable method to characterize metal catalysts. We have applied this method to test the new type of catalysts that we have prepared in non-aqueous solutions and to compare them with the ones prepared by the classical impregnation method.

EXPERIMENTAL

Catalysts

1. *Catalysts prepared by classical impregnation method* (3). Pumice (Prolabo) in granular form, crushed, washed, and sieved (35-40 mesh) was impregnated with an aqueous solution of metal chloride salts; after a slow evaporation of water the powder

was dried overnight at 100°C and then reduced in a flow of hydrogen during 20 h at the following temperatures:

2% Pt/pumice from H_2PtCl_6 (Johnson Matthey) reduced at 200°C;

2.3% Pd/pumice from $PdCl_2$ (Johnson Matthey) reduced at 350°C;

10% Rh/pumice from $(NH_4)_2[RhCl_5 \cdot H_2O]$ (Johnson Matthey) reduced at 350°C.

2. *Catalysts prepared in ethanolic solution*. This type of catalyst consists of Pt particles deposited on pumice. The preparation is described in Table 1. It was found that it is very easy to reduce Pt^{IV} (from H_2PtCl_6) to Pt^0 using hydrogen at 20°C when the acid is dissolved in a water-free aliphatic alcohol. However, the Pt particles immediately after preparation aggregate irreversibly, i.e., it is impossible to redisperse them again. Therefore the H_2 reducing process was carried out in the presence of the carrier. However, large aggregates were still formed on the support (catalyst A). The use of hydrazine as reducing agent gave a more dispersed catalyst (catalyst B, 6 nm).

3. *Catalysts prepared in microemulsion*. The detailed description of the preparation

TABLE I
Preparation of Platinum on Pumice Catalysts in
Ethanolic Solution

Pt in catalyst, weight%	Method of deposition	Mean particle size (nm)
A, 2	Pumice is added to ethanolic solution of H_2PtCl_6 . Pt^{IV} reduced by H_2 flow at 20°C, during 15 min. Alcohol removed by evaporation at 20°C	Large aggregates
B, 2	Same process but reduction is done by N_2H_4 at 70°C during 10 min and H_2O_2 is added to take away the excess N_2H_4	6

TABLE 2

Preparation of Platinum on Pumice Catalysts in Microemulsion

Pt in catalyst, weight%	System	Method of deposition	Mean particle size (nm)
C, 2	PEGDE 10% Hexadecane 90% H ₂ PtCl ₆ · xH ₂ O (3.8 g Pt/kg)	Pt ^{IV} reduced by N ₂ H ₄ at 20°C in microemulsion, then pumice is added and deposition is done by shaking and by adding N ₂ H ₄ (pH 8). After washing with ethanol, catalyst is dried at 120°C	2.5
D, 0.5	PEGDE 5.2% n-hexane 94.8% H ₂ PtCl ₆ · xH ₂ O (0.4 g Pt/kg)	The colloidal solution is progressively deposited on pumice. Between the steps, n-hexane is evaporated.	Not studied

of the metal particles dispersed in microemulsions has been given previously (2). In Tables 2 and 3, we have summarized the specific preparation of each catalyst (Pt, Pd, Rh) and have given details about the method of deposition. In all cases, the microemulsions used as initial solvent consisted of distilled water, highly purified nonionic surfactant (pentaethyleneglycoldodecyl ether, PEGDE) and analytical grade hexane or hexadecane. The resulting particle sizes are obtained from electron transmission microscopy (Philips EM 300 type).

We wish to emphasize the particular features of this way of preparation. In the classical impregnation method the metallic salt is deposited on the support, the catalyst is dried and the reduction is carried out afterward. In our method the metallic salt is reduced in ethanol or in a microemulsion. This may take place either with the solution in contact with the support or, in most cases, by depositing the particles on the support after reduction. The salts are reduced by hydrazine at 20 or 70°C or by hydrogen at 20°C.

Apparatus, Procedure, and Analysis for Catalytic Reactions

The catalytic reaction was carried out in all-glass grease-free system including a re-

actor operating under differential conditions. Before each run, the catalyst was reduced overnight, *in situ*, at 200°C for Pt and 350°C for Pd and Rh under hydrogen flow followed by deuterium flow for 2 h to remove any hydrogen retained on the catalyst. In each case, a 200-mg load was used; if a lower quantity of catalyst had to be used, it was diluted by the carrier. It was checked that pumice under the same pretreatment conditions was totally inactive. For each run 4 mg of but-1-ene (Puriss grade purchased from Fluka) was carried through the reactor by deuterium gas (753 Torr) at a constant partial pressure (7 Torr). Deuterium (99.4% pure) from Air Liquide dried on molecular sieves at 77 K was used. The hydrocarbon mixture was collected at 77 K and then analyzed and separated by gas-liquid chromatography on a column consisting of firebrick (60–80 mesh) coated with 30% dimethylsulfolane, operating at 0°C. Each isomer was analyzed by mass spectrometry (using a CH7 type Varian spectrometer) and for but-1-ene and *cis*-butene by microwave spectrometry (using a

TABLE 3

Preparation of Rhodium and Palladium on Pumice in Microemulsion

Metal, weight	System	Method of deposition	Mean particle size (nm)
Rh _{MI} , 2	PEGDE 16.3%, n-hexane 78.5%, aq. sol. of RhCl ₃ 5.2% (2 g Rh/kg)	Rh ^{III} reduced by H ₂ at 20°C (in presence of Na ₂ CO ₃). Afterward pumice is added. Deposition by heating the solution to 60°C under N ₂ flow and evaporation of n-hexane. After washing with ethanol, catalyst is dried at 120°C	2–3
Pd _{MI} , 1.1	PEGDE 17.7%, n-hexane 70.7%, aq. sol. of PdCl ₂ 10.6%, NaOH N 1.3% (3.2 g Pd/kg)	Pd ^{II} reduced by N ₂ H ₄ at 20°C. Pumice is added. Deposition by flowing H ₂ through the solution and heating to 85°C in order to eliminate n-hexane. After washing by ethanol, catalyst is dried at 120°C	5 (in solution)

33.33-khz Hewlett-Packard microwave spectrometer). The analysis procedures are described in detail elsewhere (9).

RESULTS

Platinum

As mentioned under Experimental, to ensure complete reduction to metal, the catalysts were heated to 200°C under hydrogen flow prior to use. The results are given in Fig. 1 and Table 4.

We first consider the selectivity for isomerization compared to hydrogenation. The catalysts prepared by classical impregnation (2% Pt/pumice) showed very poor selectivity for isomerization (lower than 3%) at any conversion. For example, with a

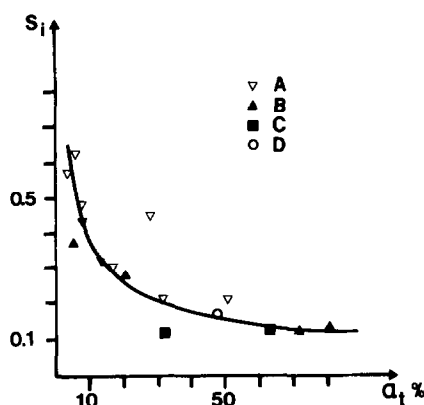
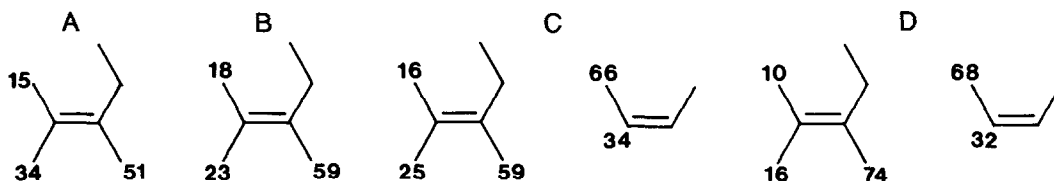


FIG. 1. Isomerization selectivity (S_i) as a function of total conversion (α_t) on platinum catalysts prepared: in alcoholic solution (∇ , A; \blacktriangle , B); in microemulsion (\blacksquare , C; \circ , D) ($S_i = \text{but-2-ene}/(\text{but-2-ene} + \text{butane})$).

TABLE 4
Hydrogenation, Isomerization, and Exchange of But-1-ene on Pt/Pumice at 20°C

Catalyst:	A	B	C	D												
Weight (mg):	60	60	10	40												
Flow rate ($\mu\text{mol/s}$):	0.11	0.11	0.48	0.66												
α_T^a (%)	52.3	82.9	66.1	54												
	$\begin{bmatrix} \text{Hydr.} \\ \text{Iso.} \\ \text{Exch.} \end{bmatrix}$	$\begin{bmatrix} 38.8 \\ 11.4 \\ 2.1 \end{bmatrix}$	$\begin{bmatrix} 69.7 \\ 11.3 \\ 1.9 \end{bmatrix}$	$\begin{bmatrix} 54.8 \\ 8 \\ 3.3 \end{bmatrix}$												
r^b	1	1.6	32	36												
Mass distributions																
(%)	but. 1 (49.8)	trans (9.0)	cis (2.4)	ane (38.8)	but. 1 (18.9)	trans (7.4)	cis (3.9)	ane (69.7)	but. 1 (37.2)	trans (4.8)	cis (3.2)	ane (54.8)	but. 1 (51.8)	trans (5.1)	cis (3.7)	ane (39.4)
d_0	95.8	61.1	61.4	7.8	90.1	53.0	53.0	—	91.1	42.5	41.6	3	88.8	47.6	46	3.2
d_1	3.7	27.8	28.5	26.1	8.5	30.1	30.4	7.6	7.6	38.7	38.4	19.7	9.7	35.2	36	18.9
d_2	0.5	7.5	8.4	42.4	1.4	10.7	10.8	64.9	1.1	12.4	13.3	47.8	1.3	11.4	11.9	51.1
d_3		2.8	1.7	12.8		3.8	3.3	15.2	0.2	3.9	4.2	16.4	0.2	3.6	3.9	15.9
d_4		0.8	0	5.3		1.4	1.4	5.1		1.4	1.4	6.5		1.3	1.4	5.6
d_5				2.6		0.6	0.7	3.2		0.5	0.5	3.2		0.4	0.4	2.6
d_6				1.4		0.4	0.4	1.7		0.3	0.3	1.6		0.3	0.2	1.2
d_7				0.7				0.9		0.2	0.2	0.8		0.1	0.1	0.7
d_8				0.4				0.5		0.1	0.1	0.5		0.1	0.1	0.4
d_9				0.3				0.4				0.3				0.2
d_{10}				0.2				0.4				0.2				0.2
$1/100 \sum_{i=1}^{10} idi$		0.5	0.5	2.0		0.7	0.7	2.5		0.9	0.9	2.3		0.8	0.8	2.2

Deuterium location in d_1 -but-1-ene and *cis*-butene (microwave analysis)



^a α_T is total conversion = exchanged but-1-ene + but-2-ene + butane.

^b r is relative number of transformed but-1-ene per second per g Pt of B, C, D cat. by comparison to A cat.

flow rate of 0.27 μmol but-1-ene/s on 10 mg 2% Pt/pumice, 27 mol% was converted to butane and 0.7 mol% to but-2-ene. In contrast the catalysts prepared in nonaqueous solution have a much *higher selectivity*, up to 60 at 4% conversion. Figure 1 shows the isomerization selectivity as a function of conversion for several experiments carried out on catalyst prepared in nonaqueous solutions. All the points fall on the same curve (Fig. 1). The decrease of the isomer selectivity with the highest conversions means that some consecutive isomer hydrogenation occurs during the reaction. However, in a large domain of conversion, the selectivity is more than 10%. This result is different from observations on classical supported platinum and on Pt particles dispersed in solution (1). The olefin isomers appear in sufficient amounts to be separated from hydrogenated products and analyzed by mass and microwave spectroscopy to find out the position of deuterium atoms entering into the molecules. Thus, for the first time on Pt catalysts, it becomes possible to investigate the exchange and isomerization mechanisms by using deuterium gas instead of hydrogen.

We now consider deuterium addition and exchange results and rates of reaction on different catalysts prepared by deposition of particles on pumice. In Table 4, catalysts A and B were prepared in the ethanolic solution, C and D in microemulsions, as described in Tables 1 and 2. In order to compare the catalytic behavior as a function of the catalyst preparation we have restricted the presentation of deuterium distributions to experiments in which the conversions to isomers (not including butane) were about 10% on any catalyst (Table 4). To obtain such constant isomer conversion, different weights of catalyst and flow rates of hydrocarbon were used depending on the specific activity of each catalyst. The activity of any catalyst may be roughly estimated by calculating the number of transformed but-1-ene molecules per unit time and unit weight of Pt. Comparing the activities of the B, C,

and D catalysts to the A catalyst (the relative rates are denoted by r in the tables) one finds that B is similar to A while C and D are about 30 times more active. The catalyst prepared by the classical way (the rate can be estimated from the results given at the top of this paragraph) is 7 times more active than A.

The deuterium distributions show the following important features:

Butane. A broad distribution is observed from d_0 to d_{10} with a maximum in d_2 . Usually, on Pt catalyst on which isomerization is not observed, the average number of deuterium atoms entering in one butane molecule is 2 (21). For catalysts B, C, and D 2.3, 2.5, and 2.2 are observed, confirming that consecutive deuteration of deuterated but-2-ene occurs at high conversion.

But-2-ene. The distributions in the *cis*- and *trans*-butene are quite similar. They show a very high percentage of d_0 (unexchanged molecules), i.e., 60% on A, 50% on B, 45% on D, and 40% on C. A control of purity of *cis* and *trans* isomers was made after the chromatographic separation in order to eliminate, when necessary, the influence of d_0 -but-1-ene which is difficult to remove completely due to the chromatographic tailing effect. The deuterated distributions smoothly decrease from d_1 to d_8 . There is only slight multiple exchange: on the average 1.5 deuterium atoms are incorporated in the deuterated isomer molecules

on any catalyst $\left(\sum_{i=1}^{10} i \cdot d_i = 1.5\right)$ The micro-

wave analysis of d_1 -*cis*-butene for the C and D catalysts shows identical distributions with 66% deuterium on C_1 and 33% on C_2 .

But-1-ene. A simple exchange is observed on all catalysts. This implies that during each adsorption/desorption step leading to the exchange reaction with but-1-ene, a single hydrogen is replaced by a deuterium atom. The location of the deuterium atom, however, depends on the catalyst. Exchange at C_2 represents 51, 59, 59, and 74% for catalysts A, B, C, D, respectively.

On all catalysts, exchange at the *trans* position on C₁ is higher than at the *cis* position, the difference being the highest on the A catalyst.

Palladium and Rhodium

The results of reactions on palladium and rhodium catalysts are given in Table 5. The catalytic behavior of metal particles prepared in microemulsion (Pd_{MI}, Rh_{MI}) is compared to particles prepared by the classical method (Pd_{WAT}, Rh_{WAT}). Palladium and rhodium show a specific behavior in the olefin deuteration reaction independently of the preparation method used. Table 5 gives the fine and the hyperfine distributions for exchanged, isomerized, and deuterated products of but-1-ene reactions on Pd and

Rh catalysts. On the Pd catalysts several runs were made at different degrees of conversion. The deuterium distributions were found to be identical for several runs. It is known (7) that palladium is the most selective metal for isomerization (50 to 60% selectivity observed up to 50% of total conversion) while on rhodium the deuteration of olefins is very fast by comparison to isomerization. Nevertheless, in the rhodium experiments, we succeeded in isolating olefins from the reaction products and found that the degrees of exchange and isomerization were low enough to allow us to derive information from the deuterium distribution in the olefins.

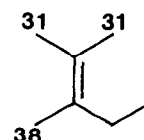
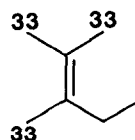
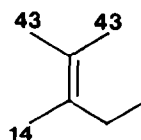
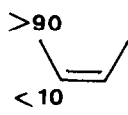
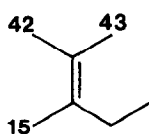
As on platinum, the hydrogen–deuterium exchange in but-1-ene mainly involves a

TABLE 5

Hydrogenation, Isomerization, and Exchange of But-1-ene on Pt/Pumice and Rh/Pumice at 20°C

Catalyst:	Pd _{MI} (Microemulsion)	Pd _{WAT} (Classical)	Rh _{MI} (Microemulsion)	Rh _{WAT} (Classical)																																																																																																																																																																																																																														
Weight (mg):	5	15	2.5	5																																																																																																																																																																																																																														
Flow rate (μmol/s):	0.71	1.25	0.52	1.39																																																																																																																																																																																																																														
α _T (%)	28	44.1	95	96.7																																																																																																																																																																																																																														
<div style="display: flex; align-items: center;"> <div style="border-left: 1px solid black; border-right: 1px solid black; padding: 0 5px; margin-right: 5px;"> Hydr. Iso. Exch. </div> <div style="display: flex; flex-direction: column; align-items: center;"> <div style="margin-bottom: 5px;">[9.7</div> <div style="margin-bottom: 5px;">[12.6</div> <div style="margin-bottom: 5px;">[5.7</div> </div> <div style="display: flex; flex-direction: column; align-items: center;"> <div style="margin-bottom: 5px;">[22</div> <div style="margin-bottom: 5px;">[19.9</div> <div style="margin-bottom: 5px;">[2.2</div> </div> <div style="display: flex; flex-direction: column; align-items: center;"> <div style="margin-bottom: 5px;">[94.1</div> <div style="margin-bottom: 5px;">[0.58</div> <div style="margin-bottom: 5px;">[0.28</div> </div> <div style="display: flex; flex-direction: column; align-items: center;"> <div style="margin-bottom: 5px;">[94.1</div> <div style="margin-bottom: 5px;">[2.1</div> <div style="margin-bottom: 5px;">[6.5</div> </div> </div>	r ^a Relative rate:	73	32	200	54	Mass distributions																	(%)	but. 1 (77.7)	<i>trans</i> (6.6)	<i>cis</i> (6)	ane (9.7)	but. 1 (58.1)	<i>trans</i> (11.7)	<i>cis</i> (8.2)	ane ^b (22)	but. 1 (5.32)	<i>trans</i> (0.38)	<i>cis</i> (0.2)	ane (94.1)	but. 1 (3.8)	<i>trans</i> (1.35)	<i>cis</i> (0.75)	ane ^b (94.1)	d ₀	92.7	39.9	45	14.4	96.2	89.1	83.9	94.8	61.5	64	0.7	86.6	44.3	44.3			d ₁	5.7	34.8	33.7	29.7	3.1	8.5	12.4	4.2	20.5	19.9	9.7	9	23.7	24.1			d ₂	1.3	13.1	12	27.8	0.5	1.7	2.5	0.8	8.7	8	35.4	2.3	13.6	12.9			d ₃	0.2	6.7	5.7	12		0.4	2.5	0.1	4.5	3.6	18.6	0.7	8.3	7.6			d ₄	0.1	2.9	2	5.9		0.2	0.7	0.1	2.5	2.7	12.7	0.6	4.9	4.9			d ₅		1.5	0.6	3.3			0.3		1.2	0.9	7.4	0.3	2.3	2.0			d ₆		0.9	0.6	2.5			0.1		0.6	0.9	4.2	0.2	1.3	1.0			d ₇		0.5	0.4	2.1					0.5		3.2	0.1	0.8	1.4			d ₈		0.2		1.2					0.4		2.3		0.5	0.8			d ₉				0.7							2.9						d ₁₀				0.5							3.1					
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d ₇		0.5	0.4	2.1					0.5		3.2	0.1	0.8	1.4																																																																																																																																																																																																																				
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Deuterium location in *d*₁-but-1-ene and *cis*-butene (microwave analysis)



^a The reference catalyst for the relative *r* values in catalyst A (Table 4).

^b Not analyzed.

single hydrogen. The location of the deuterium atom in d_1 species is very specific to the metal: on palladium, 85% of the deuterium is attached to C_1 with almost equal amounts on the *trans* and *cis* positions (43 ± 3). The remaining 15% are located on C_2 . On rhodium, deuterium atoms are equally distributed on all the vinylic positions. Deuterium atoms were not found on C_3 and C_4 for any catalyst.

In the isomerization reaction, the migration of the double bond without introduction of deuterium atoms is always the main reaction path whatever the metal. However, the percentage of d_0 isomers varies strongly from one catalyst to another. For example, it represents around 40% of the isomer distributions on Pd_{MI} and 85% on Pd_{WAT} ; on Pd_{MI} the hyperfine distribution of deuterium in d_1 -*cis*-butene is 90% on C_1 and less than 10% on C_2 .

DISCUSSION

The discussion will be devoted mainly to the mechanisms of the reactions; however, some remarks can first be made regarding the activities of the different catalysts.

Activities

As is evident from Tables 2 and 3, the method of preparation of catalysts from microemulsion involves the use of considerable amounts of surfactant (pentaethyleneglycoldodecyl ether) which, at least as long as the particles remain dispersed in the microemulsions, is adsorbed on them. It is clearly conceivable that the surfactants may have a poisoning effect on the final catalysts. As a matter of fact it has none and it was found instead that the catalysts Pt, Pd, Rh prepared from salts dissolved into microemulsion were rather more active in the hydrogenation and isomerization of but-1-ene (activity by metal weight unit) than the ones prepared from salts dissolved in alcoholic solution or prepared by the "classical way" (see the r values in Tables 4 and 5). This high activity can be easily explained if we take into account the dispersion of the

catalysts. The Pt, Pd, and Rh catalysts supported on pumice with a high metal loading (2 to 10%) and prepared from aqueous solutions in the classical way have a low dispersion (by X-ray broadening 200 Å was found as particle size), Pt catalysts prepared in alcoholic solution show also large particles while the particle size of the catalysts prepared from microemulsion range from 20 to 30 Å for Pt and Rh and 50 Å for Pd. Although no systematic kinetic studies were made, a turnover number (TON) can be estimated (transformed molecules per second per metal surface atom): on Pt (catalyst C) TON is about 0.63, on Pd_{MI} 1.9, on Rh_{MI} 2.

Such values, near to unity, are in good accordance with the kinetic studies performed for hex-1-ene hydrogenation on Pt catalyst prepared from microemulsion or on Euro Pt catalyst for which TON of 0.85 is obtained (metal particles size 30 and 18.5 Å, respectively (23)). Therefore it can be concluded that the *surfactant has no poisoning effect* in the catalytic reaction; it is apparently eliminated completely by the washing with alcohol followed by the pretreatment of the catalyst by heating. However, the role of the surfactant is essential for obtaining well-monodispersed metal particles; it has a stabilizing effect, first around water pools to form inverted micelles, then to maintain a stable dispersion of suspended metal particles and finally also during the deposition process on the support.

Exchange Reaction

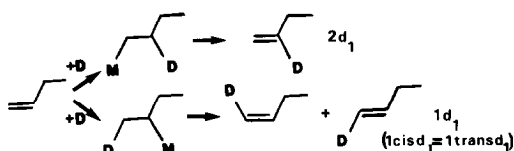
We will now consider the mechanisms of the reaction, mainly deduced from the hyperfine distribution of but-1-ene.

It is noticeable that this distribution is determined by the nature of the metal but independent of the metal particle preparation. Moreover, with the exception of palladium, it is independent of the presence or absence of deuterium in the gas phase as will here be discussed. The distribution, with about 60% deuterium atoms on C_2 plus 40% unequally distributed on C_1 , with a

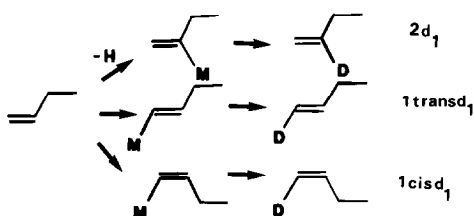
larger part on the *trans* position than on *cis*, is exactly the same as that obtained on Pt supported on pumice (12) or on Pt film (8) when perdeuteropropene was used as the source of deuterium atoms instead of deuterium gas. The same observation can be made on rhodium catalyst: an equal distribution of deuterium atoms on the three vinylic positions is found on rhodium pumice under hydrogenation conditions (under D_2 flow) whatever the genesis of the catalysts (this work) and on rhodium film in the presence of perdeuteropropene (8). On the contrary, however, on palladium catalysts, when deuterium gas is used to carry out the olefin-exchange reaction, a characteristic distribution with 85% deuterium atom on C_1 (equal distribution on *cis* and *trans* position) and 15% on C_2 is observed on palladium pumice (this work) and on palladium/silica (11), while, if perdeuteropropene is used instead of deuterium gas, the exchange of allylic hydrogen (on C_3) is observed on palladium/pumice (13) and becomes even dominating (more than 60%) on palladium film (14).

Three mechanisms have been invoked to explain the exchange reaction. The different locations of deuterium in monodeutero butene resulting from each mechanism are as follows:

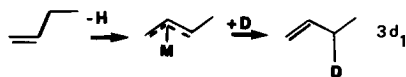
(1) associative mechanism (Horiuti-Polanyi) giving equal amounts of *cis* and *trans* exchange on C_1 (5):



(2) vinylic dissociative mechanism (Farkas, Ref. (15)):



(3) allylic dissociative mechanism (16):



Allylic dissociative mechanism. From the above scheme it is seen that this mechanism is characterized by the exchange of D on C_3 ; it was never found on any metal under hydrogenation conditions. It is observed only on palladium when but-1-ene and perdeuteropropene interact (13, 14). Thus the presence of *deuterium gas on palladium prevents the formation of allylic species*. This leads us to suspect an influence of palladium hydride formation, but further work is in progress to confirm this point.

Vinylic dissociative mechanism. This mechanism is characterized by the inequality between C_1 *trans* d_1 and C_1 *cis* d_1 with C_1 *trans* $d_1 > C_1$ *cis* d_1 since, in the associative mechanism, the free rotation around C_1-C_2 in secondary half-deuterated species leads to the same amount of C_1 *trans* d_1 and C_1 *cis* d_1 after desorption. In the Farkas mechanism, the larger amount of *trans* d_1 is explained by a steric hindrance between the surface atoms and the adsorbed butene molecule.

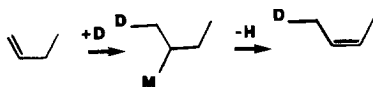
From our results, this mechanism would take place on platinum catalyst; at least it would explain the exchange on C_1 . This result agrees well with the studies of Ueda *et al.* (17) of the exchange reaction between propene and D_2 or D_2O on platinum black. They found that the ratio C_1 *trans* d_1/C_1 *cis* d_1 in monodeutero propene increases from 3 to 8 when they replace D_2 by D_2O as the deuterating agent. In the but-1-ene exchange reaction, the uneven *trans/cis* distribution was found to be larger when C_3D_6 was used instead of D_2 (12). This could be explained by the coexistence of several dehydrogenated and hydrogenated adsorbed species, all leading to the exchanged but-1-ene by, respectively, vinylic dissociative and associative mechanisms. The amount of the dehydrogenated species should be

higher on the surface in the absence of D_2 , leading to a higher *trans/cis* ratio. It is interesting to note that Demuth (18) in studies of the chemisorption and reaction of ethylene on Pt(111) at 300 K has demonstrated, by using temperature-programmed thermal desorption and UV photoemission spectroscopy, that ethylene dehydrogenates to form a C_2H_3 species which has ionization energy levels consistent with a vinyl-like species $CH=CH_2$. Fisher and Keleman (19) have proposed also this type of vinyl species on a 5×20 Pt(100) surface. These findings support the vinylic dissociative mechanism that we propose to take place on our platinum particles in the exchange of but-1-ene.

Associative mechanism. This mechanism is characterized by the equality between C_1 *cis* d_1 and C_1 *trans* d_1 species. Hence, this mechanism would take place on rhodium and palladium. However, the rates of formation of *n*-butyl and *sec*-butyl half-deuterated species have to be different in order to explain the predominance of C_1d_1 over C_2d_1 , mainly on palladium as was already discussed (11). More work is needed to affirm that the *sec*-butyl radical on palladium is more stable and/or reactive than *n*-butyl.

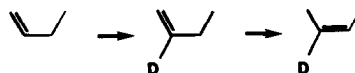
Double Bond Migration

In order to explain the large amount of d_0 isomers, it has to be assumed that this reaction takes place mainly by an intramolecular hydrogen shift, whatever the metal. However, an additional mechanism occurs that introduces nearly one deuterium atom in the molecule. This could be described as a Horiuti–Polanyi mechanism leading to C_1d_1 but-2-ene. The mechanism is dominant on palladium where more than 90% of the D is found on C_1 .



On platinum only 66% of the D is located on C_1 . The remaining 33% observed on C_2 can be explained by a consecutive isomeri-

zation (intramolecular hydrogen shift) of deuterated but-1-ene:



Thus, at least two mechanisms probably occur in the $\alpha\beta$ double bond migration. The presence of different types of surface sites depending largely on the preparation of the catalysts could explain the relative variations of the amount of d_0 -but-2-ene. In order to explain the unusual selectivity in isomerization found on supported platinum catalyst prepared from nonaqueous solution a similar explanation, involving different sites for hydrogenation and isomerization may also be invoked. It is possible that, as proposed by Siegel *et al.* (24) coordinatively unsaturated sites exist on metal surfaces and that their ability to adsorb hydrogen governs the reactions. Thus, MH_2 (M = metal) sites should be involved in hydrogenation, MH sites in $\alpha\beta$ double bond migration by the Horiuti–Polanyi mechanism, and M sites in the $\alpha\beta$ double bond migration by intramolecular hydrogen shift. The relative importance of these different sites should depend on the catalyst (nature of metal, method of preparation, pretreatment) but further work is necessary to have a better understanding of the nature of the active sites.

CONCLUSION

We have shown that for catalysts prepared from microemulsions the surfactant, which is a necessary part of the microemulsion, does not decrease the activity of the catalysts. Mild catalytic pretreatments are sufficient to eliminate the effect of these large molecules which might have been expected to act as a poison. Well-monodispersed supported catalysts, Pt (2.5 nm), Rh (2.5 nm), Pd (5.0 nm), are obtained from particles suspended in microemulsions and they are as active as catalysts prepared in the classical way.

Concerning the mechanisms of the hy-

drogenation, isomerization and exchange of but-1-ene, they have to be related to different types of surface sites. Hydrogenated and dehydrogenated species undergo reaction at 20°C. The method of preparation of the catalyst influences the behaviour of platinum catalysts while palladium and rhodium keep their specificity whatever the way they are prepared. The enhanced selectivity for isomerization of the Pt catalyst prepared from microemulsion has probably its explanation in the following observation. This catalyst when treated by hydrogen at 200°C shows some deactivation of the hydrogenation sites while the sites responsible for the isomerization are not affected by that treatment.

Further work on this particular type of catalyst might take advantage of their narrow size distribution to study their selectivity in structure-sensitive reactions, especially if one finds some way of decreasing the size of the metallic particles.

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