

## Isomerization and Hydrogenolysis of Hexanes on an Alumina-Supported Pt-Ru Catalyst

G. DIAZ, F. GARIN, AND G. MAIRE

*Laboratoire de Catalyse et Chimie des Surfaces, Equipe de Recherche Associée au CNRS N° 385, Université Louis Pasteur, 4 Rue Blaise Pascal, 67008 Strasbourg, France*

Received March 29, 1982; revised July 20, 1982

Methylcyclopentane hydrogenolysis and 2-methylpentane isomerization were studied. On ruthenium/alumina catalysts, no isomer products were detected in C<sub>6</sub> hydrocarbon reactions. Methylcyclopentane hydrogenolysis was selective as confirmed by the high 3-methylpentane/n-hexane ratios. Isomerization reactions on Pt(9.6 at.%)–Ru(0.4 at.%) / Al<sub>2</sub>O<sub>3</sub> were studied between 220 and 300°C. Skeletal rearrangements proceeded from 220°C where Pt is inactive for this type of reactions. Very low apparent activation energies in isomerization reactions of C<sub>6</sub>-labeled hydrocarbons were found for selective and nonselective cyclic mechanisms: [2-C<sup>13</sup>]-2-methylpentane → [3-C<sup>13</sup>]-3-methylpentane and [4-C<sup>13</sup>]-2-methylpentane → [3-C<sup>13</sup>]-n-hexane, respectively. The results were explained using a bimolecular kinetic model which can take into account the phenomenon as an increase either in hydrocarbon coverage or in hydrocarbon adsorption strength on the catalyst surface.

### INTRODUCTION

It is well known that ruthenium is one of the most active metals in hydrogenolysis reactions. Carter *et al.* (1) studying the hydrogenolysis of n-heptane over a series of unsupported metals found that the activities of these various metals were as follows: Ru > Ir > Rh ~ Pt ≫ Pd. This order of activities corresponds closely to the pattern of variation of the percentage *d*-character of the metallic bond.

Alloying platinum with a metal which, like ruthenium, is only active in hydrogenolysis (hydrocracking) of hydrocarbons, leads to a remarkable improvement in the selectivity of platinum for isomerization in reforming reactions, as observed by Gray *et al.* (2) in the isomerization of n-pentane. Nevertheless, very little has been published concerning Pt–Ru catalysts for isomerization reactions (2) although more extensive work has been done on this system for hydrogenation (3, 4) and dehydrogenation (5) reactions. The main results show a synergistic effect in catalytic reductions of car-

bonyl compounds at low pressures and for aromatic systems at higher pressures where hydrogenolysis is to be avoided (3). On the other hand, in the hydrogenation of benzene a maximum of the rate has been observed for a percentage of 55 at.% Ru (4). Bond and Webster (6) observed in nitrobenzene and nitroaniline hydrogenation in the liquid phase a maximum of activity at 30 at.% Ru. Engels *et al.* (5), studying the dehydrogenation of cyclohexane on unsupported Pt–Ru catalysts, have found a maximum in activity for 20 at.% Ru or 40 at.% Ru depending on the treatment by hydrogen of the catalyst at 500 or 650°C, respectively.

One may expect that the very different catalytic properties of platinum and ruthenium will magnify some collective effects between these two metals and will influence or modify the cracking sites of Pt.

The aim of this work is to present results concerning the catalytic behaviour of the Pt–Ru/Al<sub>2</sub>O<sub>3</sub> system at very low Ru concentration in hydrogenolysis and isomerization reactions of alkanes. The isomerization of



FIG. 1. Dark field image superimposing in the print of the focussed and defocussed images. Magnification  $\times 500\,000$ .

$C^{13}$ -labeled hexanes was studied and the activation energies for the different reaction mechanisms involved were determined.

#### EXPERIMENTAL

(a) *Catalyst preparation.* The catalysts used for this study were prepared by the classical impregnation method of an inert alumina from Woelm (specific area 160–170  $m^2/g$ , mean pore diameter 30–40 Å, no metal detected by ESCA). The impregnating solutions were  $RuCl_3$  hydrate (Johnson Matthey) and  $H_2PtCl_6$  (Caplain St. André)

at appropriate concentration. The metal loading was fixed at 10% in weight, and the atomic percentages of Ru in the bimetallic samples varied from 3.8 to 55%. The reduction of the samples was performed at 400°C (except for one sample at 200°C) with a hydrogen flow rate of 20 ml/min during 24 h. The catalytic work presented here is focussed on the catalyst Pt–Ru/ $Al_2O_3$  with 3.8 at.% ruthenium, but other compositions have been studied.

(b) *Catalyst characterization.* Transmission electron microscopy experiments were

performed on monometallic Ru/Al<sub>2</sub>O<sub>3</sub> and on Pt-Ru/Al<sub>2</sub>O<sub>3</sub>. Two techniques were used, namely direct examination and the extractive carbon replica method (7).

Concerning direct examination, the method of Yacaman *et al.* (8), which is based on high-resolution weak beam images which are defocussed, was used to study the state of alloying on the bimetallic metal clusters. The fact that we observed a constant displacement between the focussed and defocussed images (Fig. 1) shows that the Pt-Ru particles are forming an alloy. On the other hand, dark field techniques, i.e., images which are formed using beams diffracted in either the particle or the support, can yield information about the shape and the crystallography of the particles (9). Results obtained for the Pt-Ru alumina catalyst with 3.8 at.% Ru have shown an epitaxial growth in the (111) direction.

The catalysts were also examined by the extractive replica technique using a Philips EM 300C electron microscope. The separation of the metallic particles by destruction of the alumina carrier in a dilute solution of HF was controlled by TEM during 20 h to prevent any metallic particle loss. For each sample of Ru/Al<sub>2</sub>O<sub>3</sub> and Pt-Ru/Al<sub>2</sub>O<sub>3</sub>, more than 20 pictures were taken and histograms built up by measuring the size of at least 2500 particles.

Surface particle size distributions are shown in Figs. 2 and 3. The mean metallic particle sizes were 30 and 36 Å for 10% Ru/Al<sub>2</sub>O<sub>3</sub> and 0.2% Ru/Al<sub>2</sub>O<sub>3</sub> reduced at 400°C, respectively (Fig. 2).

A bimodal distribution was observed for the Pt-Ru/Al<sub>2</sub>O<sub>3</sub> catalyst with the lowest content in ruthenium. We can see two maxima (Fig. 3), one at 15 Å and the other at 75 Å. Electron microdiffraction analysis on these two distinct metallic distributions has shown that the larger particles were platinum, in contrast to the smaller ones which are Pt-Ru alloy. By this technique various Pt-Ru/Al<sub>2</sub>O<sub>3</sub> catalysts of different Pt/Ru atomic ratios were analysed (11). A constant alloy composition of Pt 44 at.%-Ru 56 at.% ( $\pm 5\%$ ) was found for the small parti-

cles. This means that in our case only the particles of a size lower than or equal to 15 Å, i.e., 8.7% of the total particles, are representative of this type of alloy.

Concerning the reduction state of the metals, Blanchard *et al.* (10) have observed a complete reduction of ruthenium in the bimetallic catalysts (Pt-Ru) at 500°C. In our case ESCA measurements have been done for all the Pt-Ru/Al<sub>2</sub>O<sub>3</sub> catalysts (11). No binding energy shift was observed, although a small broadening of the Ru 3d<sub>5/2</sub> peaks was present. On the other hand, no metal segregation was observed for the bimetallic samples. This result can be easily understood by the fact that only 8.7% of particles were alloyed.

(c) *Catalytic reactions.* The hydrogenolysis of methylcyclopentane and isomerization of C<sup>13</sup>-labeled hexanes were studied in a differential reactor system under 1 atm of hydrogen and small amounts of the respective hydrocarbon passing through the catalyst at constant pressure.

Part of the reaction mixture was analysed by gas chromatography and part was used for the location of the label in each molecule by mass spectrometry. The unlabeled hydrocarbons used as reactants were Fluka-puriss grade and the synthesis of the [2-C<sup>13</sup>]-2-methylpentane and [4-C<sup>13</sup>]-2-methyl pentane has been described elsewhere (12).

## RESULTS

A series of experiments were performed over various Pt-Ru/Al<sub>2</sub>O<sub>3</sub> catalysts where the atomic bulk percentages of Ru varied from 3.8 to 55% (11). We present in this paper the results given by the catalyst with the lowest content in Ru (3.8 at.%), which exhibits a noticeable isomerization behaviour. Some results obtained on 10 and 0.2% in weight Ru catalysts are also presented.

### I. HYDROGENOLYSIS OF METHYLCYCLOPENTANE

(a) *Ru/Al<sub>2</sub>O<sub>3</sub> Catalysts.* The catalytic behaviour of Ru/Al<sub>2</sub>O<sub>3</sub> catalysts for this reac-

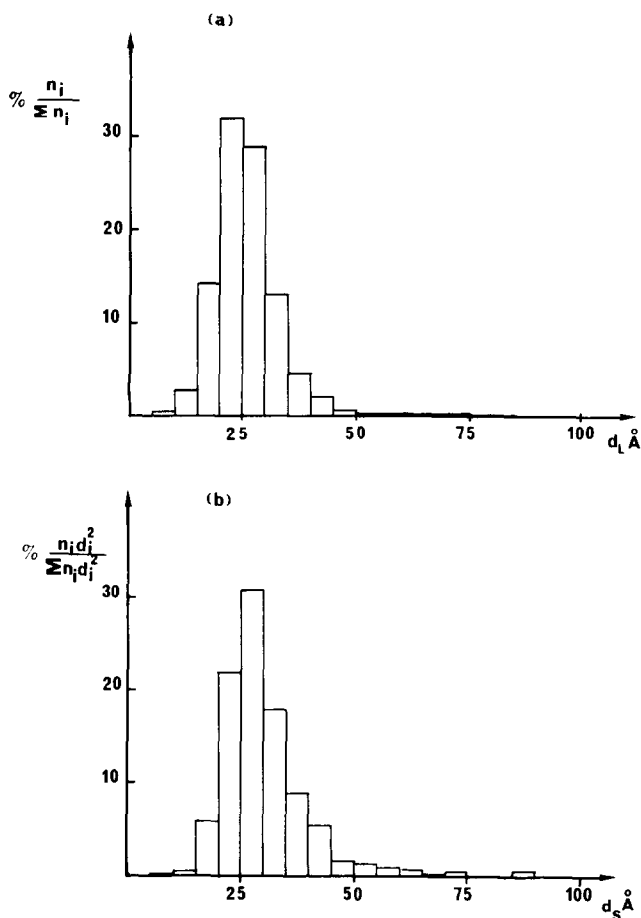


FIG. 2. Particle size distribution of ruthenium particles (a) 10% Ru/Al<sub>2</sub>O<sub>3</sub>, %  $n_i/\sum n_i$  vs.  $d_i$ . (b) 10% Ru/Al<sub>2</sub>O<sub>3</sub>, %  $n_i d_i^2/\sum n_i d_i^2$  vs.  $d_i$ . (c) 0.2% Ru/Al<sub>2</sub>O<sub>3</sub>, %  $n_i/\sum n_i$  vs.  $d_i$ . (d) 0.2% Ru/Al<sub>2</sub>O<sub>3</sub>, %  $n_i d_i^2/\sum n_i d_i^2$  vs.  $d_i$ .

tion is summarized in Table 1. The distributions of the products obtained from methylcyclopentane hydrogenolysis are shown as percentages of reactant having

disappeared. It can be observed that Ru is a very selective catalyst in the methylcyclopentane hydrogenolysis reaction. Only secondary C–C bonds of the ring are ruptured

TABLE I

Hydrogenolysis of Methylcyclopentane over 0.2 g of Ru/Al<sub>2</sub>O<sub>3</sub> Catalyst

at.% Ru	Reduction temp (°C)	Reaction temp (°C)	$\bar{d}_s$ (Å)	$\alpha_T$ (%)	$\Sigma$ Cracking	C <sub>6</sub> Products			$\frac{3MP}{n-H}$
						2MP	3MP	n-H	
10	400	140	30	10	40	38	19	3	6.3
10	200	140	—	3.3	56	25	16	3	5.3
0.2	400	140	36	0.9	35	42	16	7	2.2

Note. Product distributions in mole percentage. % $\alpha_T$  = Overall conversion in percent;  $\bar{d}_s$  = mean metallic particle size; 2MP = 2-methylpentane; 3MP = 3-methylpentane; n-H = n-hexane.

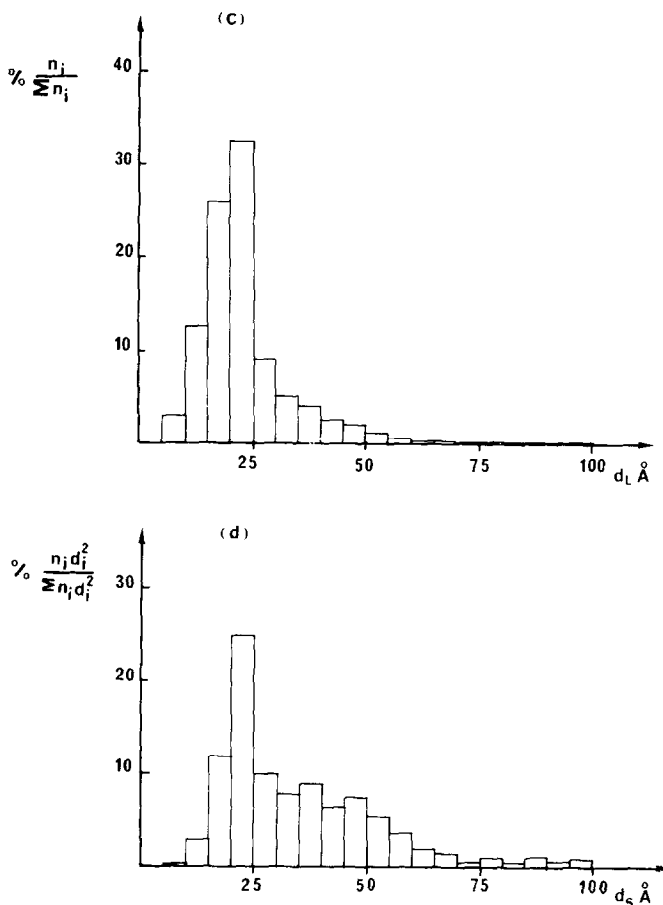


FIG. 2—Continued.

preferentially as shown by the high values of the ratio  $r = 3\text{MP}/n\text{-H}$ . On the other hand, no extensive cracking was observed at this very low temperature. Finally, an increase in the catalytic activity is observed when the catalyst is reduced at 400°C instead of 200°C.

(b) *Pt-Ru/Al<sub>2</sub>O<sub>3</sub> Catalyst.* Successive temperature treatments under hydrogen were performed on the Pt-Ru/Al<sub>2</sub>O<sub>3</sub> catalyst in the range 220 to 320°C and the catalytic behaviour was followed as a function of the temperature treatment. In all cases the hydrogenolysis reaction was carried out at 220°C on 0.2 and 0.02 g of catalyst as reported in Table 2. The first very interesting fact is the decrease of the cracking reactions compared to the pure ruthenium catalyst although the temperature of treatment

increased. The continuous decrease of the selectivity ratio 3MP/n-H when the catalyst is treated from 240 to 320°C could be explained by the fact that the rates of cracking of the n-hexane and the methylpentanes are different. This assumption is confirmed by the fact that (i) the ratio 3MP/n-H does not vary between 220 and 320°C when the cracking reaction does not occur (second part in Table 2) and (ii) the ratio 2MP/3MP is remarkably constant whether the cracking reactions take place or not.

The ratio  $3\text{MP}/n\text{-H} = 1.2 \pm 0.1$  obtained at low conversion corresponds to the value observed on a pure dispersed Pt catalyst (13). The catalyst is stable in the temperature range of treatment (220 to 320°C). On the other hand a low percentage of cyclohexane is obtained at low conversions.

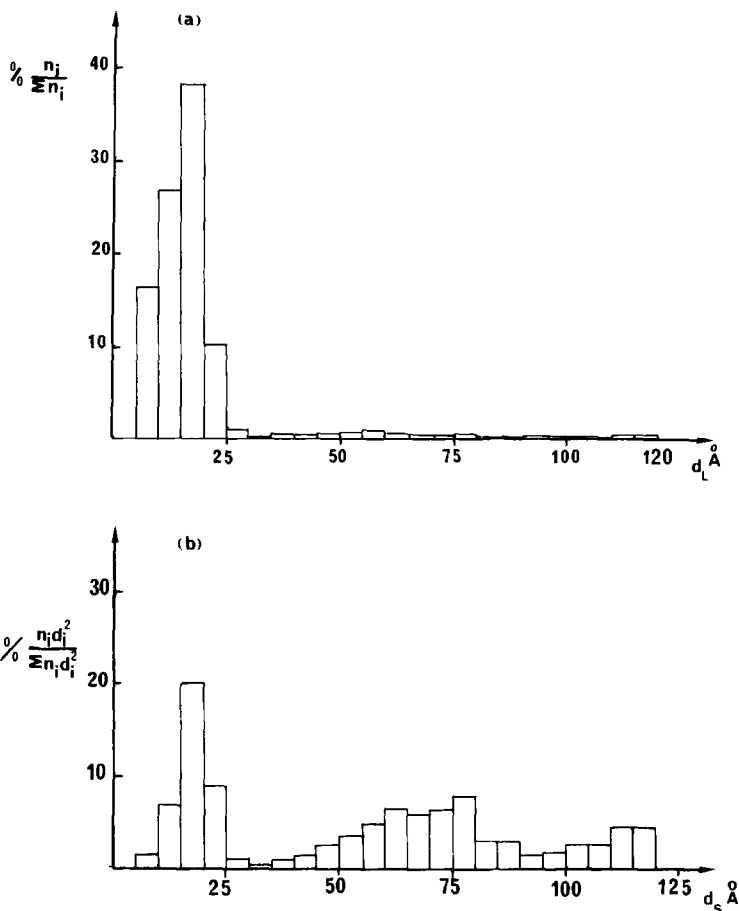


FIG. 3. Particle size distribution of Pt-Ru/Al<sub>2</sub>O<sub>3</sub> catalyst with 3.8 at.% Ru. (a)  $\% n_i/\Sigma n_i$  vs.  $d_L$ . (b)  $\% n_i d_i^2/\Sigma n_i d_i^2$  vs.  $d_s$ .

## II. HYDROCRACKING AND ISOMERIZATION OF 2-METHYLPENTANE

The three main reactions were (i) hydrocracking yielding pentanes, butanes, propane, ethane, and methane, (ii) isomerization, and (iii) dehydrocyclization to methylcyclopentane. In each experiment, the mole fractions of butanes and ethane, and those of methane and pentanes were exactly equal, except on pure Ru catalysts. In Tables 3, 4, and 5 the distributions of the products obtained from 2MP on pure Ru catalysts (Table 3) and on the Pt-Ru/Al<sub>2</sub>O<sub>3</sub> catalyst (Tables 4 and 5) are shown as percentages of reactants having disappeared.

### Hydrocracking

(a) *Ru/Al<sub>2</sub>O<sub>3</sub> catalysts.* The selectivity  $S$ , defined as the percentage of reacted molecules converted into C<sub>6</sub> products, shows that no significant isomerization reactions are involved on pure Ru catalyst whatever the reduction temperature and the metal loading (Table 3). We can observe very high values for the ratios isobutane/*n*-butane and isopentane/*n*-pentane which are specific to the behaviour of ruthenium.

(b) *Pt-Ru/Al<sub>2</sub>O<sub>3</sub> catalyst.* Experiments were made at high and low conversion between 220 and 300°C. Results obtained at low conversion (below 10%) are shown in Table 4. Several points can be emphasized:

TABLE 2

Hydrogenolysis of Methylcyclopentane at 220°C over 0.2 and 0.02 g of a Pt-Ru/Al<sub>2</sub>O<sub>3</sub> Catalyst as a Function of the Temperature of Treatment of the Catalyst

Weight (g)	Treatment temp (°C)	$\alpha_T^a$ (%)	Product distribution (mole %)					$\frac{3MP}{n-H}$	$\frac{2MP}{3MP}$
			$\Sigma$ Cracking	2MP	3MP	n-H	c-H		
0.2	220	29	9	66.4	19.1	5.5		3.5	3.5
	240	27	7	68	19	7		3.6	3.5
	260	26	5	69.6	18.1	7.8		2.3	3.8
	270	22	4	68.7	18.4	8.7		2	3.7
	280	18	4	68.4	18	9.9		1.8	3.8
	300	15	4	65.9	18.7	11.6		1.6	3.5
	320	23	7	63	18	12		1.4	3.5
0.02	220	0.87	0	58.4	20.3	14.9	6.5	1.3	2.9
	240	0.76	0	58.7	17.3	18.3	9.5	0.9	3.4
	260	1.02	0	60.0	18.6	15.2	6.1	1.2	3.2
	300	0.9	0	59.3	17.6	15.7	7.0	1.1	3.4
	320	1.2	0	61.1	19.2	14.9	5.0	1.3	3.2

<sup>a</sup> Overall conversion. c-H = cyclohexane.

- the selectivity  $S$ , defined as before, increases with increasing reaction temperature,

- the cracking pattern seems to be a very sensitive approach to the structural morphology of the metal crystallites in the catalyst. In fact the deethylation is the main reaction until 300°C, which is not the case on pure platinum catalysts (12). It can be seen that the amount of (C<sub>2</sub> + C<sub>4</sub>) molecules is higher than the (C<sub>1</sub> + C<sub>3</sub>) amount up to 260°C, but at higher temperatures the statistical value (i.e., 3(C<sub>2</sub> + C<sub>4</sub>) = (C<sub>1</sub> + C<sub>3</sub>)) is never reached. No repetitive processes are present as confirmed by the high value of the ratio isobutane/n-butane.

- the ratio isopentane/n-pentane is always higher than the theoretical value of 0.5. It seems that the high deethylation process and the selective rupture of the C<sub>4</sub>-C<sub>5</sub> bond in the molecule are specific to the Pt-Ru/Al<sub>2</sub>O<sub>3</sub> catalyst.

The results at high conversion are summarized in Table 5. When the total conversion reaches 30%, consecutive cracking reactions take place, as shown by the continuous decrease of the ratio isobutane/

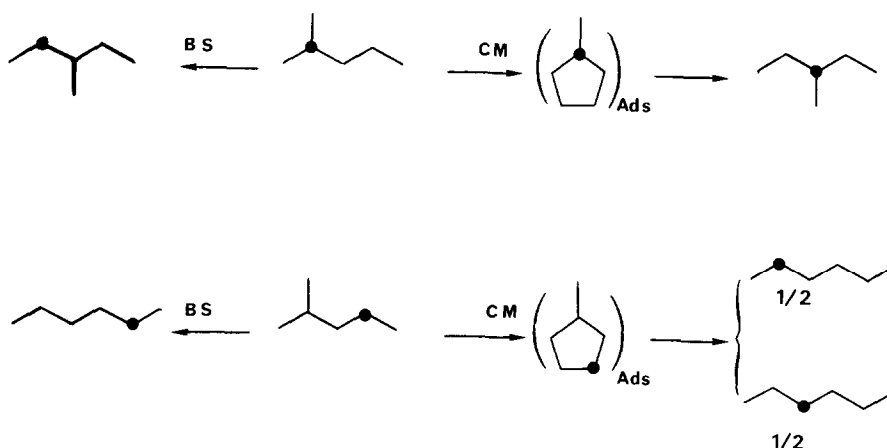
n-butane. The most striking result is perhaps the absence of extensive hydrocracking reactions (C<sub>1</sub> = C<sub>5</sub>, C<sub>2</sub> = C<sub>4</sub>) even at high conversions. The predominance of the deethylation process and the very high isopentane/n-pentane ratio are also observed when the reaction is performed at higher conversions.

#### Isomerization and Dehydrocyclization (Tables 4 and 5)

The percentage of methylcyclopentane in the reaction products is very high and its amount is a function of the conversion. The ratio 3MP/n-H in 2-methylpentane isomerization decreases continuously when the reaction temperature increases. This variation can be observed for reactions occurring at low or high conversions.

### III. ISOMERIZATION OF LABELED HEXANES

The isomerization of [2-C<sup>13</sup>]-2MP and [4-C<sup>13</sup>]-2MP has been studied between 220 and 300°C on the Pt-Ru/Al<sub>2</sub>O<sub>3</sub> catalyst. In Tables 6 and 7 we report the distribution of the expected isotopic varieties and the per-



SCHEME 1. BS, bond shift; CM, cyclic mechanism.

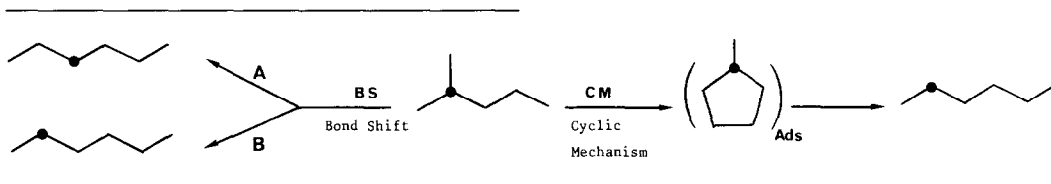
centages of cyclic mechanism calculated according to Reactions 1 and 2 in Scheme 1.

The repetitive process which is present at high conversion does not influence the isomerization distribution as seen in Table 6 where only 3.5 and 4.5% of [methyl- $C^{13}$ ]-3-pentane is obtained when the conversion is 46 and 55%, respectively.

(a) *Isomerization of 2MP to 3MP (Table 6)*. The percentage of cyclic mechanism varies in an erratic way and its amplitude of variation in a range of 80°C (220 to 300°C) is only of 30 to 46%. Nevertheless, it is important to mention that at 220°C we obtain 40%

of cyclic mechanism which is not the case on pure platinum catalysts where isomerization does not proceed at this very low temperature.

(b) *Isomerization of 2MP to n-H (Table 7)*. We can see that the percentage of cyclic mechanism obtained for this reaction varies in the same way as in the preceding case. Except for the reaction at 240°C which gives a low value for the cyclic mechanism, the other results are between 77 and 86%. The second part of Table 6 gives the percentage of bond shift A in chain lengthening (Scheme 2).



All the values are in the same range and equal to  $10 \pm 2.5$  except for the experiment at 220°C where the value is twice as high. This result is in disagreement with those obtained on Pt/alumina catalysts where the contribution of this mechanism is equal to 1 (13).

The second part of Table 7 shows the percentage of bond shift B mechanism. We can notice that in all cases it is always lower

than the bond shift A (Table 6) which is never observed on supported Pt catalysts. This phenomenon has only been observed with catalytic experiments on stepped surfaces of platinum (14) where this particular situation seems to be due to the presence of (111)-oriented planes. In our case, an epitaxial growth in the (111) direction was observed by TEM for the Pt and Pt-Ru metallic particles on this Pt-Ru/ $Al_2O_3$  catalyst.



TABLE 3  
Reactions of 2-Methylpentane on Ru/Al<sub>2</sub>O<sub>3</sub> Catalysts

Ru %	Reduction temp (°C)	Reaction temp (°C)	$\bar{d}_s$ (Å)	$\alpha_T$ (%)	S %	Products (mole %)						$\frac{iC_4}{nC_4}$	$\frac{iC_5}{nC_5}$	
						6C <sub>1</sub>	3C <sub>2</sub>	2C <sub>3</sub>	C <sub>2</sub> + C <sub>4</sub>	C <sub>1</sub> + C <sub>5</sub>	3MP			n-H
10	200	160	—	3	0	5.3	—	1.8	54.2	38.7	—	—	36	17
10	400	160	30	14	0.8	3.1	—	4.7	47.8	43.5	0.6	0.2	28	14
0.2	400	200	36	7	4.5	10.5	—	6.6	56.5	21.5	2.3	2	15	4.8

Note.  $\bar{d}_s$  = Mean metallic particle size;  $\alpha_T$  = overall conversion; 3MP = 3-methylpentane; n-H = n-hexane; MCP = methylcyclopentane; iC<sub>4</sub> = isobutane; nC<sub>4</sub> = n-butane; iC<sub>5</sub> = isopentane; nC<sub>5</sub> = n-pentane.

#### IV. ACTIVATION ENERGIES

Apparent activation energies were determined for the isomerization of [2-C<sup>13</sup>]-2-methylpentane and [4-C<sup>13</sup>]-2-methylpentane in the temperature range of 220 to 300°C. The amounts of cyclic mechanism were taken as the sum of molecules formed by the cyclic mechanism and the methylcyclopentane desorbed. This can be done because the rate-determining step in this type of reaction is the C-C formation (i.e., dehydrocyclization) and not the C-C bond rupture (i.e., hydrogenolysis). Very low values of apparent activation energies were obtained for both types of cyclic mechanism:  $36.5 \pm 1.5$  kcal/mole for the nonselective mechanism and  $25.5 \pm 1.5$  kcal/mole for the selective one.

#### DISCUSSION

Two different reactions have been studied on Pt-Ru/Al<sub>2</sub>O<sub>3</sub> at low Ru bulk concentration, namely methylcyclopentane hydrogenolysis, which is a well-known structure sensitive reaction, and skeletal isomerization of C<sub>6</sub> alkanes.

The catalytic behaviour of this system will be discussed here, comparing the results to those obtained on pure platinum/alumina catalysts. Preliminary experiments on Pt (10%)/Al<sub>2</sub>O<sub>3</sub> were carried out between 220 and 240°C in 2-methylpentane isomerization reactions, and no isomer products were detected in this temperature range. This result clearly shows that platinum is catalytically inactive for isomerization reactions at these low temperatures. On the other hand, from methylcyclopentane hydrogenolysis data obtained at low conversions after thermal treatment of the bimetallic catalyst, we have shown that the ratio 3-methylpentane/n-hexane is constant. This means that the catalyst is not modified in the range 220 to 300°C.

These preliminary experiments have pointed out two phenomena:

- metal segregation can be excluded for

TABLE 4

Isomerization of 2-Methylpentane on 0.02 g of Pt-Ru/Al<sub>2</sub>O<sub>3</sub> Catalyst as a Function of Temperature. (Low Conversion)

Temp (°C)	$\alpha_T^a$ (%)	S <sup>b</sup> (%)	Products (mole %)						iC <sub>4</sub> /nC <sub>4</sub>	iC <sub>5</sub> /nC <sub>5</sub>	3MP/n-H
			2C <sub>3</sub>	C <sub>2</sub> + C <sub>4</sub>	C <sub>1</sub> + C <sub>5</sub>	3MP	n-H	MCP			
220	0.2	17.5	17.2	42.3	23	—	—	17.5	36	3.1	
240	0.48	35	11.1	31.7	20.7	3.8	2.8	28.3	42	2.6	1.4
260	2.8	49.5	5.9	25	20.5	17.5	12.0	20	25	2.6	1.45
270	2.6	66	2.6	15.6	15.4	24.5	18.2	23.6	22	1.4	1.3
280	4.1	67	3.5	14.3	15.2	21.3	25.4	20.2	13	1.4	0.8
290	8.5	69	3.3	13.0	14.7	23.5	30.3	14.9	6	1.4	0.77
300	8.7	74	3.1	9.8	13.3	24.2	33.3	15.8	4.8	1.12	0.72

<sup>a</sup> Total conversion.

<sup>b</sup> Selectivity.

this catalyst in the range of temperature considered.

(b) the ratio 3MP/n-H being constant and approximately equal to unity shows a high dispersion of metal particles. This fact has been confirmed by TEM where the total mean metal particle size is  $\bar{d}_s = 53 \text{ \AA}$  ( $\bar{d}_s = 18 \text{ \AA}$  for the small particles only). The isomerization of labeled hexanes ([2-C<sup>13</sup>]-2-methylpentane and [4-C<sup>13</sup>]-2-methylpentane) has shown that the percentage of cyclic mechanism in the reaction 2MP to 3MP is almost constant. The same behaviour is observed in the 2MP to n-H reaction. Nevertheless, it is important to mention that already at 220°C we obtain 40% of cyclic mechanism in the 2MP to 3MP reaction. To obtain the same distribution on pure platinum catalysts at 254°C, they must have a metal dispersion of 55% and a metal loading of 4.1% as previously seen in this laboratory (13). We arrive at the same conclusion concerning the 2MP to n-H reaction.

We underlined also that in chain lengthening reactions of 2MP to n-H, the methyl migration (bond shift A) is predominant compared to the propyl migration (bond shift B).

Isomerization reactions proceeding from 220°C are representative of the Pt-Ru alloy particles. On the other hand, when reac-

tions take place in the range 260 to 300°C, Pt-Ru alloy particles and Pt particles are involved.

One fundamental result obtained on the Pt-Ru/Al<sub>2</sub>O<sub>3</sub> catalyst studied in the present work, is the very low value found from Arrhenius plots for the apparent activation energies whatever the catalytic reactions are. For the cyclic mechanism we obtained:

- nonselective mechanism  $36.5 \pm 1.5$  kcal/mole
- selective mechanism  $25.5 \pm 1.5$  kcal/mole.

At present no kinetic data for C<sub>6</sub> alkane isomerization mechanisms on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts are available in the literature. Nevertheless on 10% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, the isomerization of C<sup>13</sup>-labeled pentanes has been studied (15) and the activation energy for cyclic mechanisms is around 70 kcal/mole. Assuming that the total activities of the catalytic reaction of C<sub>5</sub> and C<sub>6</sub> hydrocarbons are equal (i.e.,  $\alpha F/W$  are the same;  $\alpha$  = total conversion,  $F$  = hydrocarbon flow,  $W$  = weight of the catalyst), we can estimate the decrease of the activation energies for the C<sub>6</sub>-hydrocarbon reactions as never greater than 5 kcal/mole. This means, for example, that the activation energy for the C<sub>6</sub> alkanes in the cyclic mechanism is nearly equal to 65 kcal/mole. We never divide by a factor of 2 the values of  $E_a$  from C<sub>5</sub>

TABLE 5  
Isomerization of 2-Methylpentane on 0.2 g of a Pt-Ru/Al<sub>2</sub>O<sub>3</sub> Catalyst as a Function of Temperature (High Conversion)

Temp (°C)	$\alpha_T^a$ (%)	$S^b$ (%)	Products (mole %)						iC <sub>4</sub> /nC <sub>4</sub>	iC <sub>5</sub> /nC <sub>5</sub>	3MP/n-H
			2C <sub>3</sub>	C <sub>2</sub> + C <sub>4</sub>	C <sub>1</sub> + C <sub>5</sub>	3MP	n-H	MCP			
220	2	22.4	6.6	46.6	24.3	10.5	4.1	7.8	33.5	2	2.5
240	11	31	6	32.2	22	18.6	8.1	4.1	13.5	2.5	2.6
260	27.6	46.7	10.8	18.4	19	25.8	18.1	2.6	3.3	1.3	1.4
270	30	60	5.2	15	20	32	24.8	2.7	1.8	1.1	1.3
280	46	46	9.4	21	23.6	23.9	19.8	1.8	1.1	1.2	1.2
290	20	62	4.3	15.2	18.3	27.7	28.4	5.9	2.4	1.2	0.97
300	55	44	8.3	20.6	27.3	21.4	19.9	2.05	0.8	1.1	1.07

<sup>a</sup> Total conversion.

<sup>b</sup> Selectivity.

to C<sub>6</sub> hydrocarbons in isomerization reactions.

The lowering of the  $E_a$  has also been seen by Engels *et al.* (5) on Pt-Ru/Al<sub>2</sub>O<sub>3</sub> catalysts for the ethane hydrogenolysis reaction, which is a very activated one. In agreement with our results they observed a decrease in the activation energy for this reaction when it occurs on Pt-Ru catalysts compared to pure Pt catalysts.

Two series of catalytic experiments performed on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst have shown that when the apparent activation energies decrease, the coverage by hydrocarbon radicals increases. First, in a comparative study of the kinetic data obtained with C<sub>5</sub>, C<sub>6</sub>, and C<sub>7</sub> hydrocarbons, Gault *et al.* (16) could explain the variation in the order versus hydrogen from negative values for C<sub>5</sub> isomerization to positive values in C<sub>7</sub> isomerization by the multisite adsorption model proposed recently by Frennet *et al.* (17). We can conclude as they did that the changes from negative to positive order in the hydrocarbon series from C<sub>5</sub> to C<sub>7</sub> can be interpreted if one assumes an increase in the strength of hydrocarbon adsorption. We can underline that in parallel from C<sub>5</sub> to C<sub>7</sub> hydrocarbons the apparent activation energies for isomerization reactions decrease continuously. In addition, from C<sub>5</sub> to C<sub>6</sub> to C<sub>7</sub> hydrocarbon reactions, the percentage of bond shift B decreases from 75% with C<sub>5</sub> to 60% with C<sub>6</sub> and 45% with C<sub>7</sub>. Secondly, catalytic experiments done at low hydrogen pressures have shown that the apparent activation energies for C<sub>6</sub> hydrocarbon reactions are very low, about 15 kcal/mole (18, 19), and we know that the hydrocarbon coverage  $\theta_C$  in that case must be very high.

These two results suggest that on our Pt-Ru/Al<sub>2</sub>O<sub>3</sub> catalyst at low Ru concentration were the apparent activation energy is very low, and bond shift A > bond shift B, the hydrocarbon coverage or the adsorption strength of the hydrocarbon must be important. On the other hand, it is necessary to point out that though the hydrocarbon cov-

TABLE 6

Isomerization of [2-C<sup>13</sup>]-2-Methylpentane at High Conversions on Pt-Ru/Al<sub>2</sub>O<sub>3</sub> Catalyst. Distribution of the Various Isotopic Species as a Function of Temperature



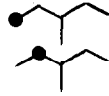
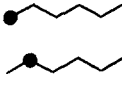
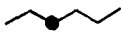
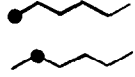

Temp (°C)	$\alpha_T$ (%)				% Cyclic mechanism			Bond shift A
220	2	0	40	60	40	80.6	19.4	19.4
240	11	1.7	46	52	46	92.3	7.7	7.7
260	27	1.5	32.5	66	32.5	90.5	9.5	9.5
270	30	0.5	31	68.5	31	91	9	9
280	46	3.5	30.5	65.5	30.5	87.5	12.5	12.5
290	20	0.3	43.0	56.3	44	92.5	7.6	7.6
300	55	4.5	42.5	53	42.5	—	—	—

TABLE 7

Isomerization of [4-C<sup>13</sup>]-2-Methylpentane on Pt-Ru/Al<sub>2</sub>O<sub>3</sub> Catalyst. Distribution of the Various Isotopic Species as a Function of Temperature

Temp (°C)	$\alpha_T$ (%)			% Cyclic mechanism	Bond shift B
220	4.8	61.5	38.5	77	3.5
240	10.8	76.8	28.9	58	—
260	39	56.7	43.3	86.6	4.5
270	27	57.5	42.5	85	6
280	39	58.7	41.2	82.5	5.5
290	20	57.8	42.2	84	7.9
300	56	59.8	40.2	80.4	—

erage  $\theta_C$  must be important in this catalyst, it does not mean that it can be easily deactivated, as confirmed by deactivation test reactions (11).

A confirmation of this proposal is that there was relatively little cracking on the Pt-Ru catalyst, which would support the conclusion that deactivation due to carbiding is not to be expected on this catalyst, since extensive breakdown of the hexanes apparently does not occur.<sup>1</sup>

#### CONCLUSIONS

On pure ruthenium catalysts no isomer products were detected in the isomerization

<sup>1</sup> We thank one of the referees for having suggested this argument.

of 2-methylpentane. Extensive cracking reactions were present at temperatures above 200°C. The methylcyclopentane hydrogenolysis was selective.

On the Pt-Ru/Al<sub>2</sub>O<sub>3</sub> system at low ruthenium atomic concentration (Pt/Ru = 25) skeletal isomerization reactions proceed from 220°C, where platinum is inactive for this type of reaction, without extensive hydrocracking of the reaction products. A bimodal dispersion of the particles was obtained but a homogeneous dispersion of the small particles has been stated. An epitaxial growth in the (111) direction was also observed for the total metallic particles.

The combination of kinetic and tracer studies gave some ideas about the different

reactions occurring on a Pt-Ru surface. Very low values of apparent activation energies for the skeletal reactions were found. This fact has been interpreted by an increase of the hydrocarbon coverage or the adsorption strength of the hydrocarbon on the surface of the catalyst. We confirm, in addition, that the nonselective cyclic mechanism is more activated than the selective one, as is the case on Pt-alumina catalysts.

Further work is in progress on skeletal isomerization reactions over Pt-Ru catalysts of different ruthenium concentration and will be published soon.

#### ACKNOWLEDGMENTS

We thank Dr. M. José Yacaman (Instituto de Física, UNAM, México) for the Transmission Electron Microscopy determination. In the same way we thank Mr. J. L. Schmitt for the carbon replica examination of the samples. One of us (G.D.) thanks the Consejo Nacional de Ciencia y Tecnología de México (CONACYT) for financial support.

#### REFERENCES

1. Carter, J. L., Cusumano, J. A., and Sinfelt, J. H., *J. Catal.* **20**, 223 (1971).
2. Gray, T. J., Masse, N. G., and Oswin, H. G., Proceedings International Congress on Catalysis, 2nd Paper (Paris 1960), Vol. 2, p. 1697, Editions Technip, Paris, 1961.
3. Rylander, P. N., and Cohn, G., Proceedings International Congress on Catalysis 2nd (Paris 1960), Vol. 1, p. ■, Editions Technip, Paris, 1961.
4. Gómez, R., Corro, G., Díaz, G., Maubert, A., and Figueras, F., *Nouv. J. Chim.* **4**, 677 (1980).
5. Engels, S., Phuong Kue, N., and Wilde, M., *Z. Anorg. Allg. Chem.* **463**, 96 (1980).
6. Bond, G. C., and Webster, G., *Proc. Chem. Soc.* 398 (1964).
7. Dalmai-Imelik, G., Leclercq, G., and Mutin, I., *J. Micro. Elec.* **20**, 123 (1974).
8. Yacaman Jose, M., Zenith, J., and Contreras, J. L., *Appl. Surface Sci.* **6**, 1 (1980).
9. Yacaman Jose, M., "Growth and Properties of Metal Clusters" (J. Bourdon, Ed.), p. 225, Elsevier, Amsterdam, 1980.
10. Blanchard, G., Charcosset, H., Chenebaux, M. T., and Primet, M., "Preparation of Catalysts II" (B. Delmon, P. A. Jacobs, and G. Poncelet, Eds.), p. 197, Elsevier, Amsterdam, 1979.
11. Diaz, G., Ph.D. thèse Doctorat D'Etat, Strasbourg, 1982.
12. Chambellan, A., Dartigues, J. M., Corolleur, C., and Gault, F. G., *Nouv. J. Chim.* **1**, 41 (1979).
13. Dartigues, J. M., Chambellan, A., Corolleur, S., Gault, F. G., Renouprez, A., Moraweck, B., Bosch-Giral, P., and Dalmai-Imelik G., *Nouv. J. Chim.* **3**, 591 (1979); Gault, F. G., Garin, F., and Maire, G., "Growth and Properties of Metal Clusters" (J. Bourdon, Ed.), p. 451, Elsevier, Amsterdam, 1980.
14. Garin, F., Aeiyyach, S., Legare, P., and Maire, G., *J. Catal.* **77**, 323 (1982).
15. Garin, F., and Gault, F. G., *J. Amer. Chem. Soc.* **97**, 4466 (1975).
16. Gault, F. G., Amir-Ebrahimi, V., Garin, F., Parayre, P., and Weisang, F., *Bull. Soc. Chim. Belg.* **88**, N° 7-8, 475 (1979).
17. Frennet, A., Lienard, G., Crucq, A., Degols, L., *J. Catal.* **53**, 150 (1978).
18. Luck, F., Ph.D. thèse Doctorat d'Etat, Strasbourg, 1983.
19. Garin, F., Maire, G., and Gault, F. G., *Nouv. J. Chim.* **5**, 553 (1981).