

Modification of the catalytic properties of palladium by rare earth (La, Ce) addition

Catalytic activity and selectivity in hydrocarbon conversion

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Abstract

Pd/Al₂O₃ catalysts modified by cerium or lanthanum promoters are tested for hydrocarbon conversion: methylcyclopentane (MCP) hydrogenolysis, 2-methylpentane (2MP) isomerization and 3-methylhexane (3MH) hydrocracking, deshydrocyclization and aromatization. The following parameters are reviewed: (i) precursor salt of palladium (chloride or nitrate), (ii) rare earth nature (La or Ce), (iii) rare earth content within the range 0–100% and (iv) impregnation mode (coimpregnation or successive impregnations). The influence of chloride coming from the precursor salt of palladium on the catalytic behaviour is strongly underlined. Chlorine anions are trapped by rare earth cations at the interface, as evidenced in a subsequent paper dealing with characterization studies of these same catalysts (K. Kili, L. Hilaire, F. Le Normand, submitted). Although the reactions readily occur on metallic sites, as evidenced by ¹³C labelled experiments, the addition of rare earth increases the activity and modifies the selectivity, especially for 2MP isomerization. These changes are rationalized in terms of significant modification of the kinetic surface parameters (competitive hydrogen and hydrocarbon coverages). This is explained by (i) lowering of the hydrogen coverage of the palladium sites accompanying surface diffusion on the interface with the support and (ii) creation of new selective sites at the transition metal–rare earth interface. The other parameters investigated yield only minor changes of the catalytic behaviour. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Transition metal catalysts promoted by addition of a rare earth such as cerium or lanthanum

have been widely studied for two important groups of catalytic reactions:

- Automotive exhaust gas depollution where they allow a broadening in the Air/Fuel acceptance window of the gas composition and thus increase the performance and the stabilization of the three-way catalysts [1,2].
- Syngas conversion where they change the selectivity towards methanol and higher alcohols formation [3].

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Most explanations on the properties of such catalysts generally point out the creation of new sites at the interface between the metallic particle and the promoter by formation of an anionic vacancy on ceria. As such, these oxophile centers could help to a stronger adsorption and even to a partial decomposition of carbon monoxide, providing a new pathway towards the formation of higher alcohols [4–11]. This is now the most widely accepted view in the literature, although some authors have discussed other explanations, such as a direct electronic transfer up to an alloy formation [12,13] or a modification of the size and the texture (surface plans) of the metallic particle induced by interaction with the rare earth [4].

However today, a more complete view of the subject lacks as both the reducibility–oxidability and the acido-basicity of rare earth oxides are addressed in the occurrence of such an interaction. Characterization studies of these catalysts, with a special insight to these new sites, were carried out by FTIR of adsorbed CO [14], oxygen storage capacity measurements [15], thermo-programmed desorption [16,17], thermo-programmed reduction and oxydation [18], and X-ray photoemission (XPS) [19]. Important modifications of the C–O stretching vibrations were assigned to the creation of surface anion vacancies. In preceding papers [20–23], we used XPS on the Pd and Ce core levels and X-ray absorption (XAS) on the cerium L_{III} edge to fully characterize Pd–Ce(La)/Al₂O₃ catalysts. Surprisingly, we report that the precursor salt of the transition metal is an important parameter that governs the interaction between the transition metal and the rare earth. Thereby, by introducing a chloride salt precursor, an interaction has been proposed to occur through a chlorine bridge which allows to fast reoxidize palladium or reduce cerium, according to the oxidative or reductive conditions, respectively. By contrast, when starting from nitrate salt precursor, no such interaction does occur at all [22].

To further investigate the exact nature of this interaction, we prepared Pd/Al₂O₃ catalysts

modified by cerium and lanthanum additives that we test for hydrocarbon conversion. The catalytic probes include both the activity and the selectivity in the following reactions: methylcyclopentane (MCP) hydrogenolysis, 2-methylpentane (2MP) and 3-methylhexane (3MH) isomerization, hydrocracking, deshydrocyclization and aromatization. The specific mechanistic pathways were previously determined in our laboratory for unmodified Pd/Al₂O₃ in a wide range of metallic dispersion by a proper use of the ¹³C labelling technique in the 2MP and 3MH isomerization [24,25] and they had probed to be sensitive to size effects of the palladium particle size [26].

In this paper the effect of the following parameters have been addressed:

- Palladium precursor salt (chloride Pd(NH₃)₄Cl₂ or nitrate Pd(NO₃)₂)
- Rare earth nature (La or Ce)
- Rare earth content (the rare earth promotion ranges from 0 to 100% molar)
- Impregnation mode (coimpregnation or successive impregnations by two different procedures).

The physico-chemical properties of such catalysts have been elsewhere reported [20]. The influence of (i) the calcination temperature and (ii) the palladium loading and reduction temperatures has been elsewhere reported [27,28].

2. Experimental part

2.1. Catalysts preparation

The support is a Woelm alumina of surface area 169 m²/g. The ceria support was prepared by precipitation of cerium nitrate into hydroxide at pH = 9, followed by calcination at 200°C within 4 h. The La₂O₃ (lanthana) support was prepared in the same way, except that calcination is operated at 550°C within 6 h. Surface areas were 38 and 19 m²/g, respectively.

Catalysts were prepared by coimpregnation or successive impregnations of aqueous solu-

tions (10^{-1} N) of $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ (purity 99.99%) (series I to IV, Table 1) or $\text{Pd}(\text{NO}_3)_2$ (series V) with $\text{Ce}(\text{NO}_3)_3$ (series I, III–V) or $\text{La}(\text{NO}_3)_3$ (series II). All reagents were purchased by Johnson Matthey and the purity was better than 99.99%. After wet impregnation, catalysts were dried 24 h in an oven at 120°C . Catalysts prepared by coimpregnation were calcined in the catalytic reactor for 4 h at 200°C in a flux of 20 ml/mn of dried air. At such calcination temperature it has been previously shown that the catalytic activity is high [27]. Two modes of successive impregnations were carried out. When rare earth was first impregnated (Series IV), the catalyst was calcined at 200°C 4 h after drying before subsequent palladium impregnation. When palladium was first impregnated (Series III), the catalysts were subsequently cal-

culated 4 h at 400°C followed by rare earth impregnation. The palladium content was roughly kept constant around $8 \pm 2\%$ whereas the rare earth content is continuously increased. For brevity's sake, the catalysts Pd–Ce(La)/ Al_2O_3 will be hereafter referred by the code indicated in Table 1. The weight contents of palladium, rare earth and chlorine after the catalytic tests are reported in Table 1, together with the palladium mean particle size determined by transmission electron spectroscopy. Other physical properties (surface area, X-ray diffraction, X-ray photoemission, ...) have been elsewhere reported [20]. Two important indications can be extracted from the data of Table 1. First, the chlorine content increases with the rare earth addition. This is the result of a chlorine trapping by the rare earth, as the occurrence

Table 1
Catalysts Pd–TR/ Al_2O_3

Series no.	Impregnation mode	Precursor salt	Ce(La) (wt.%)	Pd (wt.%)	Cl (wt.%)	<i>d</i> (TEM, nm)
I-1	Coimpregnation	$\text{Pd}(\text{NH}_3)_4\text{Cl}_2$	0.00	9.3	0.7	4.5
I-2	«	«	0.02	8.1	–	–
I-3	«	«	0.3	6.9	1.0	–
I-4	«	«	0.5	7.8	1.0	–
I-5	«	«	1.0	8.5	–	–
I-6	«	«	1.5	8.5	0.9	6.5
I-7	«	«	3.2	7.0	1.1	–
I-8	«	«	12.5	6.4	3.2	8.0
I-9	«	«	CeO_2	8.5	4.7	$\approx 15\text{--}20$
II-10	«	«	(0.02)	8.9	0.5	–
II-11	«	«	(0.5)	9.7	–	–
II-12	«	«	(1.1)	9.1	1.1	–
II-13	«	«	(7.0)	6.4	2.2	–
II-14	«	«	(La_2O_3)	7.7	5.5	≥ 10
III-15	Successive impregnations (Pd → Ce)	«	0.0	8.5	–	–
III-16	«	«	0.6	8.4	–	–
III-17	«	«	(0.6)	7.2	–	–
III-18	«	«	8.5	5.2	–	–
III-19	«	«	13.8	5.6	–	–
IV-20	Successive impregnations (Ce → Pd)	«	0.1	8.0	–	–
IV-21	«	«	0.5	7.9	–	–
IV-22	«	«	1.0	8.0	–	–
IV-23	«	«	2.2	8.6	–	–
IV-24	«	«	10.9	7.5	–	–
V-25	Coimpregnation	$\text{Pd}(\text{NO}_3)_2$	0.0	0.8	–	–
V-26	«	«	0.7	5.8	–	–
V-27	«	«	2.6	8.1	–	4.0
V-28	«	«	9.2	8.9	–	–
V-29	«	«	CeO_2	1.1	–	–

of oxychloride was detected [20,23,27]. Second, the mean palladium particle size increases with the rare earth addition due to a strong decrease of the surface area of the catalyst [20].

2.2. Catalytic tests

Hydrocarbon conversion was tested under atmospheric hydrogen in a pulsed catalytic microreactor already described [29]. Unless otherwise specified, catalysts (generally 50–200 mg) were treated by the following procedure: after drying and calcination in the microreactor, they were flushed by nitrogen at room temperature during 10 min before hydrogen was admitted. Reduction was operated while the temperature rose (2°C/min) up to 400°C followed by an hour at the reaction temperature (300°C for MCP and 2MP and 360°C for 3MH reactivity, respectively). In all cases the gaseous flux was 20 ml/min. Before any test, the catalyst was first precovered by a 3 µl injection of the reagent.

2.3. Products

The preparation and purification of the labelled reagents (2 and 4-¹³C-2MPs and 3-¹³C-3MP) together with the analysis of the label in the reaction products have been previously described in details [29,30]. All other hydrocarbons (MCP, 2 and 3MP, 3MH) were Fluka puriss products and were used without further purification. Frequent chromatographic tests showed that MCP contained both 0.06 ± 0.01% of *n*-hexane and cyclohexane as main impurities. They were subtracted from the analysis of the products. The chromatographic analysis were elsewhere described [26].

2.4. Activity

Activity A_1 , expressed in micromoles per second and per gram of palladium, were calcu-

lated for a low conversion level α_T , according to:

$$A_1 = (\alpha_T * F) / W \quad (1)$$

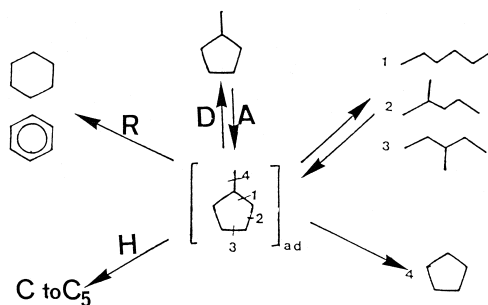
where F is the hydrocarbon flux (µmol/s) and W the palladium weight (g) of the catalysts. For small conversions, within the range 1–5%, the accuracy in the determination of the conversions from the formula (Eq. (1)) was about 10% but larger than 10% for larger conversions. We did not measure activities for conversions larger than 20% where repeating processes did not validate the formula (Eq. (1)). We checked on each sample, by plotting the contact time W/F as a function of the conversion α_T , that diffusional limitations did not restrict the determination of the activity.

3. Results

3.1. Methylcyclopentane (MCP) hydrogenolysis

According to Scheme 1, MCP yields by hydrogenolysis of the cycle the following initial products:

- *n*H, 2MP and 3MP (pathways 1, 2, 3 in Scheme 1, respectively) by rupture of the endocyclic carbon–carbon bond. It had been shown that these reactions are reversible on palladium at 300°C [24–26];
- *c*P (pathway 4 in Scheme 1) by irreversible rupture of the exocyclic carbon–carbon bond.



Scheme 1. Hydrogenolysis of MCP.

Table 2
Activity and selectivity in MCP hydrogenolysis Pd-RE/Al₂O₃ catalysts (RE = Ce or La)

Series no.	A_H ($\mu\text{mol/s.g Pd}$)	cP	2MP	3MP	nH
I-1	4.2	2	48	28	22
I-3	4.7	4	46	25	21
I-5	5.1	5	47	26	22
I-6	6.0	4	47	27	22
I-7	3.5	1	49	27	23
I-8	1.5	3	50	25	22
I-9	0.1	2	56	23	19
II-12	2.8	3	49	26	23
II-13	1.5	3	52	25	20
III-15	0.6	2	55	25	18
III-17	0.1	4	45	27	24
III-18	0.01	6	50	27	16
IV-20	5.3	7	50	25	18
IV-22	6.0	6	47	25	22
IV-23	3.2	5	50	25	20
IV-24	2.2	3	52	24	21
V-26	3.2	1	56	23	20
V-27	4.3	3	48	27	22
V-28	2.9	4	50	25	21
V-29	3.3	2	53	25	20

Ring enlargement to cyclohexane (R) and hydrocracking (H) by multiple breakings of the carbon-carbon bond are generally negligible at low conversions and at 300°C.

Table 2 displays some characteristic results obtained on the five series. In Fig. 1 the variation of the activity A_H is plotted with the rare earth to palladium molar ratio (RE/Pd). The Pd/Al₂O₃, Pd/CeO₂ (Pd/La₂O₃) catalysts are the lower and the upper limits of this ratio, respectively.

The striking feature of these results is the large difference of activity according to the palladium precursor salt: chloride or nitrate, corresponding to series I-IV and V, respectively. With a chloride precursor, the activity is enhanced by about one order of magnitude compared to the nitrate precursor. This difference tends to increase with the addition of a rare earth promoter, so that activity is vanishingly small for the nitrate precursor catalyst above (Ce/Pd) ≥ 1 . A decrease in activity down to three orders of magnitude is noted when palladium is deposited on the rare earth oxides. This effect is more pronounced on the lanthanum-promoted catalysts (series II) or on the nitrate-precursor catalysts (series V). In the range of medium rare earth content, there is a small difference in the promotion by lanthanum (series II) or cerium (series I and IV). At low cerium

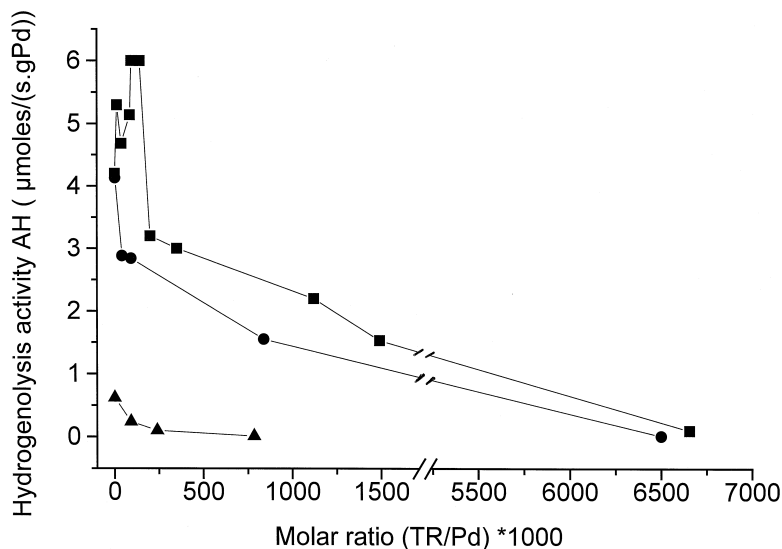


Fig. 1. Variation of the MCP hydrogenolysis activity A_H with the molar RE/Pd content for Pd-Ce (La)/Al₂O₃ catalysts. (Square) Series I-II; (Circle) series IV and (Up triangle) series V, respectively.

content, the activity rate A_H exhibits a maximum for ca. 1–2% cerium content (series I and IV) instead of a continuous decrease in activity for the lanthanum-promoted catalysts (series II). Catalysts I and IV displays the same behaviour with cerium content. By contrast, the activity still remains large even at high cerium

content for the catalysts of the series III (not shown).

The distributions of the initial products are determined by extrapolation to zero conversion level (Table 2). Fig. 2 displays two examples of such extrapolation for catalysts I-1 and II-13, respectively. The error in the initial product

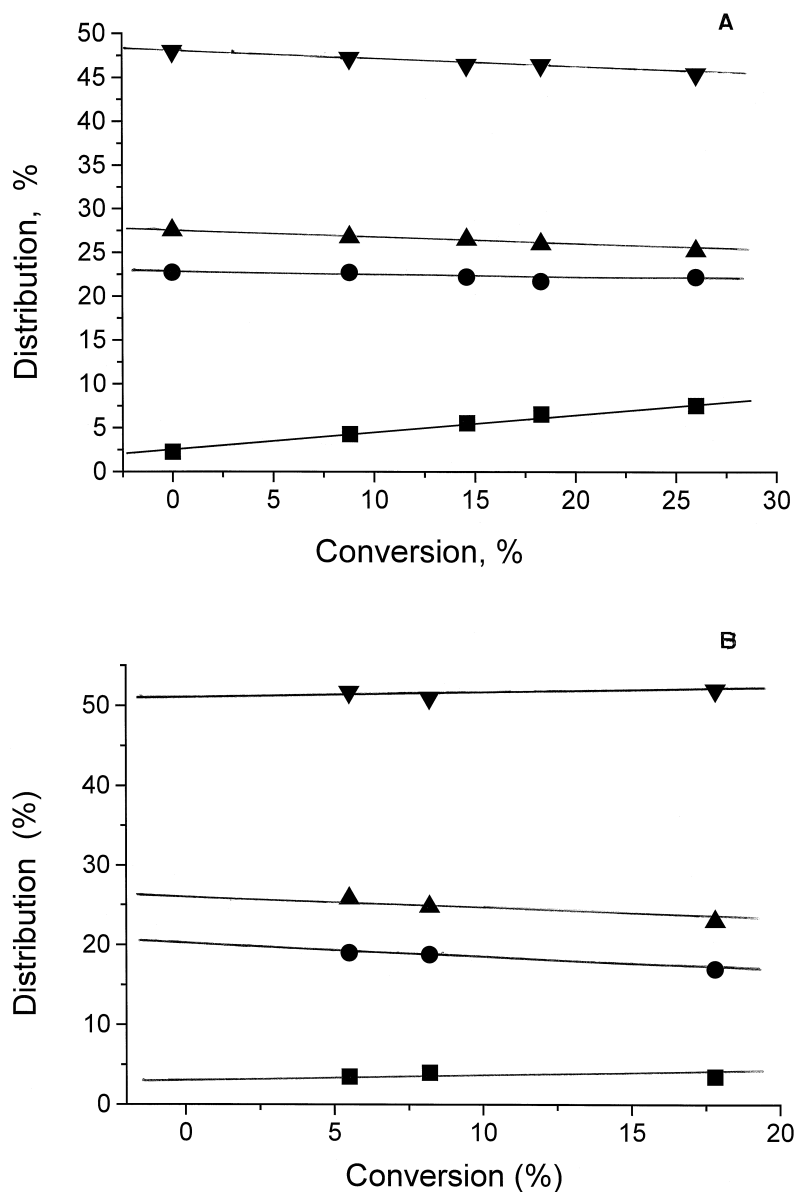


Fig. 2. Extrapolation to zero conversion of the products distribution: (a) Sample no. I-1 and (b) Sample no. II-13. (Down triangle) 2MP; (Up triangle) 3MP; (Circle) nH and (Square) cP.

selectivity is then estimated to $\pm 2\%$. We observed only small change in the evolution of product distribution with conversion. This indicates that consecutive reactions are scarce even at a high conversion level.

In Fig. 3, the evolution of the initial product distribution with the rare earth/palladium molar ratio is plotted for the catalysts of the series I. The variations of the selectivity are small but still detectable. Thereby, the 2MP selectivity slowly rises with the cerium content from 48% on the Pd/Al₂O₃ catalyst up to 56% on the ceria support.

The activation energies for each single carbon–carbon bond rupture have been determined on catalysts of the series I in a small temperature range (275–310°C) at a low conversion level ($\alpha_T < 5\%$) (Table 3). The error is estimated at 4 kcal/mol. Arrhenius plots $\text{Log } A_i = f(1/T)$ are plotted on Fig. 4. Activities are determined both in the decreasing and the increasing temperature mode. Activation energies are nearly the same for each endocyclic carbon–carbon bond rupture on a given sample. However when promoted with cerium or supported on ceria, the activation energies of the rupture of the endocyclic bonds are lowered by

Table 3

Activation energies for carbon–carbon bond rupture in MCP hydrogenolysis on Pd–Ce/Al₂O₃ (series I)

Series no.	(RE/Pd) · 10 (molar)	EA (Kcal/mol)				ΔT (°C)
		cP	2MP	3MP	nH	
I-1	0.0	56	57	58	57	280–310
I-8	14.9	64	47	47	47	275–310
I-9	100	60	44	49	45	255–300

about 10 kcal/mol. The rupture of the exocyclic carbon–carbon bond is more activated by about 10 kcal/mol.

3.2. 2-Methylpentane isomerization

3.2.1. (a) Overall activity and selectivity

As depicted in Scheme 2, 2MP directly yields at 300°C as main reactions:

- Hydrocracking from C1 to C5 hydrocarbons with selectivity S_H .
- Isomerization according to the so-called bond shift mechanism with selectivity S_{BS} [30].
- Isomerization and deshydrocyclization according to the so-called cyclic mechanism with selectivity S_C [30].

The isomerization activity A_I is reported in Table 4 for some selected catalysts as well as

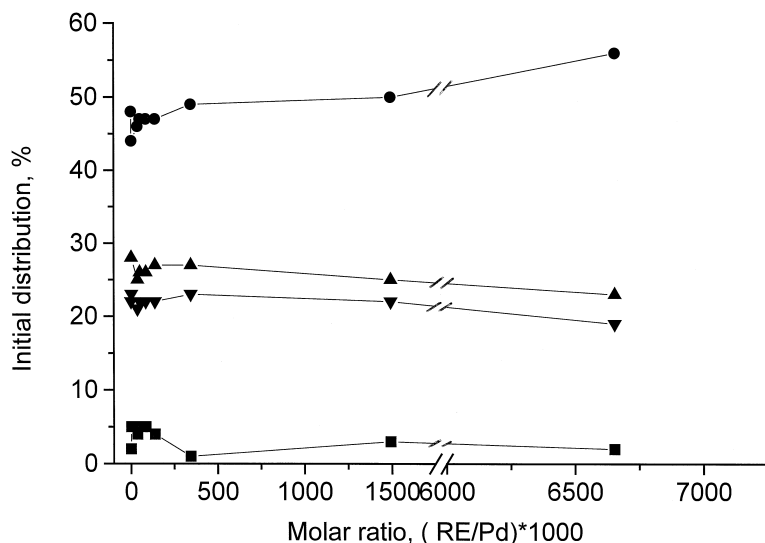


Fig. 3. Initial product distribution for Pd–Ce/Al₂O₃ catalysts of the series I as a function of the molar ratio (Ce/Pd). (Circle) 2MP; (Up triangle) 3MP; (Down triangle) nH and (Square) cP.

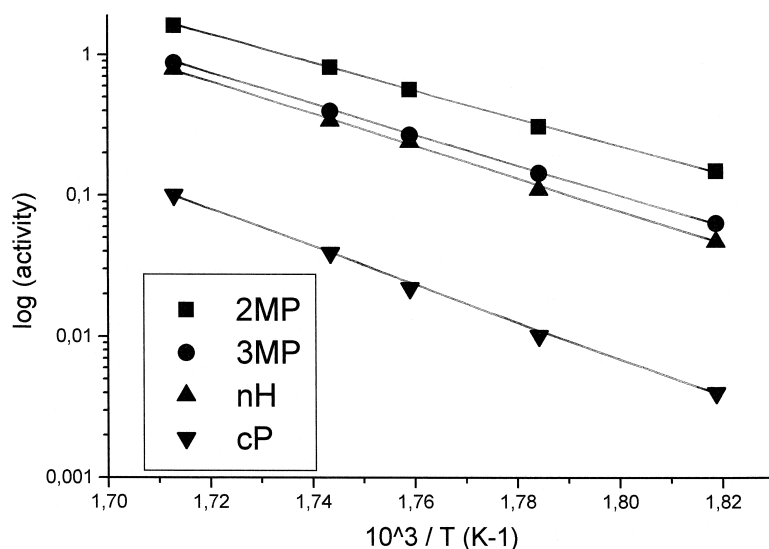
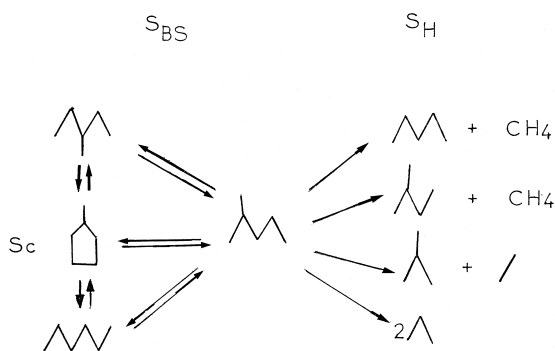


Fig. 4. Arrhenius plots $\text{Log } A = f(1/T)$ in MCP single carbon–carbon bond rupture for catalyst no. I-8. (Square) 2MP; (Circle) 3MP; (Up triangle) nH and (Down triangle) cP.

the conversion α_T , the selectivity for hydrocracking S_H and the selectivity for isomerization S_I . As the two isomerization pathways cannot unambiguously be determined with the use of unlabelled hydrocarbons, the overall selectivity for isomerization is $S_I = S_{BS} + S_C$ including MCP. A trend towards a decrease in activity is observed when increasing the rare earth content. The precursor salt of palladium significantly affects the isomerization selectivity. These variations must be considered with care however as, unlike MCP hydrogenolysis, S_I strongly depends on the overall conversion. By contrast the isomerization selectivity strongly decreases



Scheme 2. 2MP reactivity.

when using the nitrate precursor salt of palladium.

Also reported in Table 4 are the isomerization ratios 3MP/nH obtained by the MCP hydrogenolysis and the 2MP isomerization, respectively. The similarity of these two ratios strongly suggests that, whatever the series, the main isomerization process occurs through a cyclic mechanism, which is the main pathway described on pure palladium [24].

Anyway the high ratio isobutane to *n*-butane indicates that consecutive reactions are negligible as *n*-butane could be obtained only by multiple carbon–carbon bond rupture.

We compare the activity in 2MP isomerization A_I [$A_I = \alpha_T \cdot (S_{BS} + S_C)$] vs. the activity in MCP hydrogenolysis A_H by plotting the ratio $r = A_I/A_H$ as a function of the RE/Pd molar content (Fig. 5). We find then a similar behaviour for the catalysts prepared from the palladium chloride precursor salt, whatever the impregnation mode (series I, II and IV). The ratio r passes through a smooth minimum at low rare earth content, then steeply increases to reach a value about five-fold larger on the ceria support. On the contrary for the catalysts prepared with a

Table 4
2MP isomerization at 300°C on Pd–RE/Al₂O₃ catalysts: activity and selectivity

Series no.	(Re/Pd) · 10 (molar)	α_T (%)	(3MP/nH) _{MCP}	(3MP/nH) _{2MP}	S_H	S_I	$r = A_I/A_{II}$	A_I (μmol/s.g Pd)
I-1	0.0	14	1.00	1.30	63	37	0.29	2.4
I-4	0.5	6	1.20	1.20	56	44	0.14	1.2
I-6	1.4	6	1.25	1.25	55	45	0.10	1.3
I-8	14.9	6	1.10	1.15	36	64	0.50	1.2
I-9	100.0	1	–	1.20	14	86	1.10	0.13
II-12	(0.9)	7	1.30	1.15	60	40	0.18	1.3
II-13	(8.4)	9	1.40	1.15	45	55	0.33	1.5
IV-22	0.9	12	1.05	1.15	47	53	0.25	2.5
IV-24	11.2	3	1.15	1.15	39	61	0.29	1.1
V-25	0.0	0.1	1.20	1.40	50	50	0.08	0.10
V-26	0.9	2	1.05	1.30	65	35	0.22	0.15
V-28	7.8	0.2	–	1.70	76	24	0.12	0.006

palladium nitrate precursor (series V), r drops to a very small value (Table 4). As the main process on palladium is a cyclic mechanism with adsorbed MCP as a common intermediate in both isomerization and deshydrocyclization (Scheme 2), the ratio r is a true indication of the relative rate of deshydrocyclization compared to the hydrogenolysis of the same cycle. Thus an increase in r must imply an increase in the deshydrocyclization step yielding MCP and the isomers or an inhibition in the ring opening of

the adsorbed cycle. However, as pointed out by Gault [31], the distribution of 2MP products is strongly dependent on the conversion level, and further indications can only be gained by the use of ¹³C-labelled reagents.

3.2.2. ¹³C isotopic labelling

Three labelled hexanes have been used (Scheme 3). They allow to fully distinguish between the cyclic mechanism and the bond shift mechanism of 2MP and 3MP isomerization

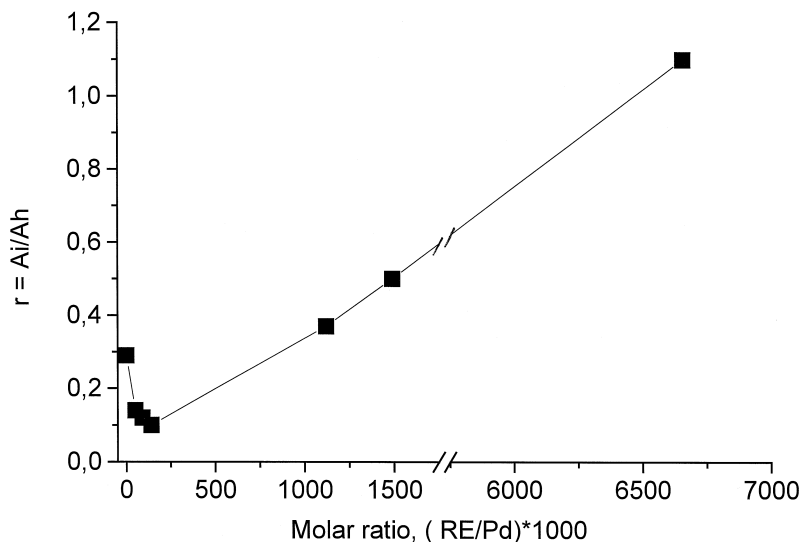
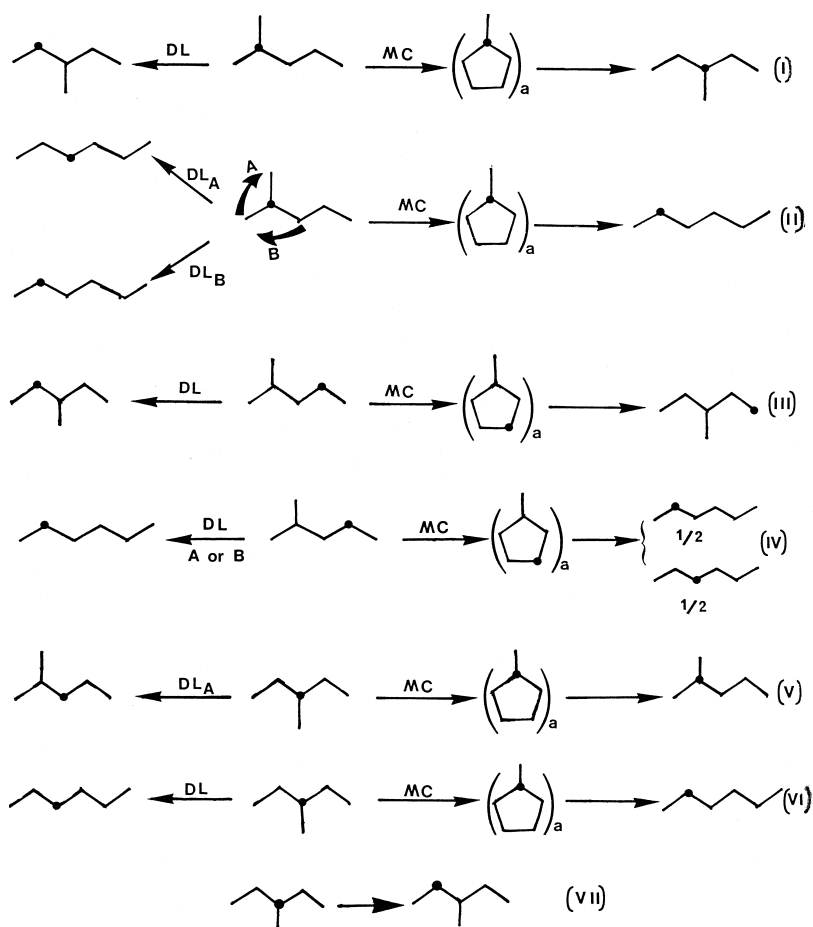


Fig. 5. Evolution of $r = A_I/A_H$ as a function of the molar ratio RE/Pd. Series I–II.



Scheme 3. Isomerization pathways of ^{13}C -labelled hexanes. DL and MC stand for bond shift and cyclic mechanisms, respectively.

[24,31,32]. $2\text{-}^{13}\text{C}\text{-2MP}$, $4\text{-}^{13}\text{C}\text{-2MP}$ and $3\text{-}^{13}\text{C}\text{-3MP}$ yields by a cyclic mechanism $3\text{-}^{13}\text{C}\text{-3MP}$ (pathway I), $1\text{-}^{13}\text{C}\text{-3MP}$ (pathway III) and $2\text{-}^{13}\text{C}\text{-2MP}$ (pathway V), respectively, and by a bond shift mechanism $2\text{-}^{13}\text{C}\text{-3MP}$ (pathway I), $2\text{-}^{13}\text{C}\text{-3MP}$ (pathway III) and $3\text{-}^{13}\text{C}\text{-2MP}$ (pathway V), respectively. On the other hand, the use of $2\text{-}^{13}\text{C}\text{-2MP}$ and $4\text{-}^{13}\text{C}\text{-2MP}$ is required to determine the respective contributions of the bond shift A (or methyl shift), bond shift B (or isopropyl shift) and the cyclic mechanism of n -hexane (pathways II and IV). Therefore, $2\text{-}^{13}\text{C}\text{-2MP}$ yields the $3\text{-}^{13}\text{C}\text{-nH}$ by a bond shift A, but the $2\text{-}^{13}\text{C}\text{-nH}$ by a bond shift B or the cyclic mechanism (pathway II). However the $4\text{-}^{13}\text{C}\text{-2MP}$ can differentiate between the two last processes as the $2\text{-}^{13}\text{C}\text{-nH}$ is obtained by the bond

shift B and the $3\text{-}^{13}\text{C}\text{-nH}$ is obtained by half by the cyclic mechanism (pathway IV). The use of $3\text{-}^{13}\text{C}\text{-3MP}$ also determines the comparative rate in n -hexane formation by ethyl shift ($3\text{-}^{13}\text{C}\text{-nH}$) and cyclic mechanism ($2\text{-}^{13}\text{C}\text{-nH}$) (pathway VI). This molecule also allows to evaluate the rate of autoisomerization from $3\text{-}^{13}\text{C}\text{-3MP}$ to $2\text{-}^{13}\text{C}\text{-3MP}$ by an ethyl shift (pathway VII). Finally the occurrence of abnormal species, such as the $1\text{-}^{13}\text{C}\text{-nH}$ or the $1\text{-}^{13}\text{C}\text{-3MP}$ obtained from the $2\text{-}^{13}\text{C}\text{-2MP}$, provides some additional information on consecutive adsorptions–desorptions or on possible diffusional limitations.

We report in Table 5 the isotopic distribution in isomeric products of the three catalysts I-6, I-8 and IV-18. They are compared with an unpromoted 8.5% Pd/ Al_2O_3 sample of the lit-

Table 5

Isomerization of labelled 2 and 3 at 300°C on Pd–RE/Al₂O₃: distribution of the label in the products distribution

Reagent															
ref 24	24	76	0	0	96	4	0	62	38	0	75	25	-	-	-
I-6	26	74	0	0	95	5	0	62	38	0	80	20	3.4	96.6	0
I-8	26	74	0	0	100	0	0	67	33	0	87	13	6.7	93.3	0
III-18	22	78	0	0	93	7	0	59	41	-	-	-	-	-	-

erature [24]. We note no significant change in isotopic labelling of the products. The cyclic mechanism is largely the predominant process as 3-¹³C-3MP and 2-¹³C-nH are the main products in the isomerization of 2-¹³C-2MP and 3-¹³C-3MP, respectively.

Hence, the isotopic labelling allows to establish a complete mechanistic balance, including now hydrocracking, isomerization and deshydrocyclization products (Table 6). We also report for comparison the distribution on unpromoted Pd/Al₂O₃ catalysts [24,26]. When the cerium content increases, the selectivity in cyclic mechanism S_{CM} noticeably increases to the detriment of the hydrocracking selectivity S_H . This result is obtained in spite of the fact that a large conversion promotes irreversible hydrocracking and the conversion is larger on the

sample of Ref. [24] than on the sample I-6 and is close to the conversion on samples I-8 and V-28. The bond shift selectivity S_{BS} remains invariably low. We also note that the selectivities are not dependent on the mode of impregnation.

As we report on Table 5 that the proportion of labelled isomers obtained by a cyclic mechanism does not increase, we conclude that the increase in cyclic mechanism S_{CM} reported in Table 6 is essentially due to a MCP desorption faster than the rupture of the endocyclic carbon–carbon bond of the adsorbed MCP.

3.3. 3-Methylhexane reaction

According to Scheme 4, 3-methylhexane (3MH) yields:

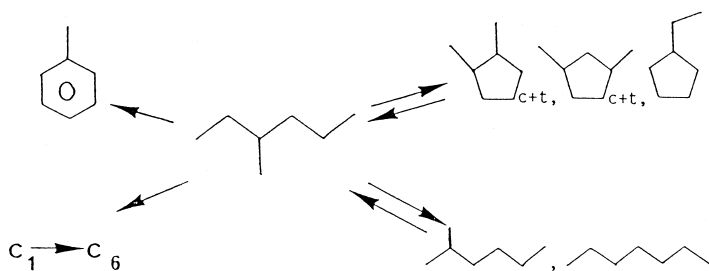
- Irreversible aromatization to toluene with selectivity S_A .
- Irreversible hydrocracking to C1–C6 hydrocarbons S_H .
- Reversible isomerization and 1–5 deshydrocyclization products S_I .

Some results have been obtained in 3MH conversion at 360°C. Activities in overall reaction A_T and in aromatization A_A are reported in Table 7 together with the respective selectivities in hydrocracking S_H , isomerization (and deshy-

Table 6

2 and 3MP isomerization at 300°C on Pd–Ce/Al₂O₃. Overall products distribution

Series no.	(RE/Pd)· 1000 (molar)	α_T (%)	S_{CM}	S_{BS}	S_H
Ref. [24]	0.0	13	35	7	58
Ref. [26]	0.0	9	35	3	62
I-6	140	5	45	7	48
I-8	1490	11	48	13	39
III-18	1250	17	53	7	40



Scheme 4. 3MH reactivity.

drocyclization) S_I and aromatization S_A . As for the MCP hydrogenolysis, overall and aromatization activities slightly increase at low cerium content and then decrease. The maximum in activity is reached for a Ce/Pd molar ratio of about 0.05. As far as the activities are concerned, no influence of the rare earth content could be detected, but both S_H and S_A are large on the lanthanum-promoted catalysts.

4. Discussion

The study of Pd-RE/ Al_2O_3 catalysts (RE = La, Ce) reveals a slight influence of nature of the rare earth but a strong influence of rare earth content in connection with the palladium precursor salt. Let us recall the main results which assess the increasing importance of the following factors.

The hydrocarbon conversion (hydrogenolysis, isomerization, aromatization) is larger by one to two orders of magnitude when palladium chloride is used as precursor salt (series I–IV) instead of palladium nitrate (series V). This trend increases with the rare earth content. Whatever the series, the activity drops with the rare earth content.

The 2MP selectivity in MCP hydrogenolysis is slightly increased with (i) the use of palladium chloride and (ii) the rare earth content.

The overall selectivity in 2MP isomerization is noticeably increased to the detriment of hydrocracking by rare earth addition. Isomerization products are predominantly formed through a cyclic mechanism.

In a set of preceding papers, many catalysts of this study were characterized by means of spectroscopic and microscopic investigations [20–22]. In the case of the Pd(chloride) cata-

Table 7
3MH reactivity at 360°C on Pd-RE/ Al_2O_3

Series no.	(RE/Pd) · 1000 (molar)	α_T (%)	A_T ($\mu\text{mol/s.g}_{Pd}$)	A_A ($\mu\text{mol/s.g}_{Pd}$)	S_H	S_I	S_A
I-1	0	11	2.3	0.10	38	57	5
I-3	37	19	4.5	0.35	38	53	9
I-5	85	13	3.8	0.26	40	53	7
I-7	350	10	2.7	0.18	39	54	7
I-8	1490	9	2.7	0.11	41	55	4
I-9	6650	–	0.6	0.05	30	62	8
II-12	(93)	15	2.8	0.20	50	43	7
II-13	(840)	11	2.3	0.18	55	37	8
II-14	(7829)	–	0.8	0.10	51	37	12

lysts, a model of interaction between the rare earth and transition metal was developed. A specific localization of chlorine anions was proposed at the interface between the transition metal and the rare earth. They can provide new catalytic sites. We now discuss how such sites infer modifications of the catalytic activity and selectivity of saturated hydrocarbons.

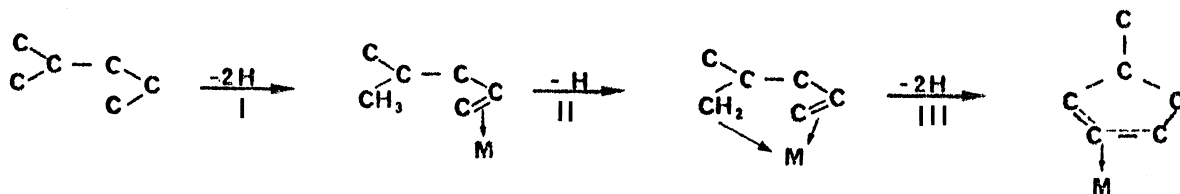
For catalytic activity, the most important result is the large difference of activity between the chloride and the nitrate precursor palladium salts. Even on the unpromoted catalysts, the ratio of activity of chloride precursor salt versus nitrate catalyst is ca. 7. This ratio increases with the rare earth content up to about 100. The origin of such a strong effect of the palladium precursor salt can be multiple.

A first explanation accounts for modifications of the dispersion (mean particle size) or changes in the morphology of the metallic particle induced by the rare earth or chlorine addition. There is an increase of the mean crystallite size with increasing rare earth content, in connection with the loss of surface area [20]. However, the large mean particle size determined on these catalysts, whatever the palladium precursor salt, may induce only little changes in the catalytic activity, taking the assumption of a constant turnover frequency per palladium site. This assumption is reported in the hydrogenolysis of cyclopentane [33]. In the same way, a modification in the morphology of the particles by rare earth addition which changes the basal surface plans could not be excluded as an epitaxial orientation of rhodium particles on ceria had been observed by Bernal et al. [34,35]. In spite of the lack of data in literature on palla-

dium, but taking into account the results obtained on platinum [31], we may expect however small differences in reforming activity on different surface planes of palladium. Thus we believe that neither a dispersion effect nor a morphological effect can explain the large difference of activities observed between the two series of rare earth-promoted palladium catalysts.

Modification of the kinetics parameters induced by the chloride ions of the palladium precursor salt. Once the activity, the selectivities (reaction pathways) and the activation energies are concerned.

First, let us recall the main mechanistic pathways of hydrocarbon reforming on unpromoted palladium [24,26,31]. It is now widely admitted that the MCP hydrogenolysis as well as the 2MP isomerization occur through the so-called cyclic mechanism. It involves common intermediates which are 1,2,5 triadsorbed π -olefin σ -alkyl species (Scheme 5) [26,31]. The stability of such intermediates on palladium explains the high selectivity towards 1–5 deshydrocyclization of adsorbed hexanes and further ring opening. The occurrence of such intermediates is clearly identified by the use of adequate ^{13}C hydrocarbon reagents. Whatever the rare earth content, no change occurs in the isotopic distribution of labelled hexanes products. This means that the cyclic mechanism of isomerization also predominates whatever the rare earth content. However if the ^{13}C isotopic labelling yields useful information on the main isomerization mechanism of hexanes, we need to consider the overall product distribution to get an overview of the real mechanistic balance, especially con-

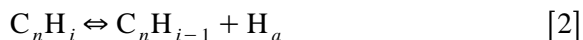
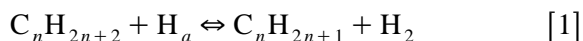


Scheme 5. Sequence of intermediates in MCP deshydrocyclisation and 2MP isomerization displaying π -adsorbed 2MP (I); 1,2,5 σ -alkyl π -olefin 2MP (II) and σ -alkyl MCP (III).

cerning the competitive desorption and the ring opening of the adsorbed methylcyclopentane (Scheme 2 or in more details Scheme 5 of Ref. [26]). We thereby clearly put into evidence an increase in the cyclic mechanism with rare earth content from ca. 35 to 55% of the overall products, including both isomerization and deshydrocyclization (Table 6). Furthermore, the selectivity in isomerization increases with rare earth content with the noteworthy exception of the nitrate precursor series (Fig. 6). This increase in cyclic mechanism is due to an enhanced desorption of MCP rather than a ring opening of the adsorbed MCP. The evolution of the ratio of the 2MP isomerization rate versus MCP hydrogenolysis rate with the rare earth content (Fig. 5) also supports the assumption that the MCP adsorption is inhibited. It is interesting to note that the same trends in the catalytic selectivity and activity of 2MP and MCP were observed on highly-dispersed Pd/Al₂O₃ catalysts [26]. Let us recall however that these considerations about selectivities must be handled with care, as the rates of isomerization according to a cyclic mechanism vs. deshydro-

cyclization are in strong correlation with conversion [31].

It is possible to more quantitatively ascertain this interpretation in the framework of the competitive hydrogen–hydrocarbon multisite adsorption model of Frennet et al. [36]. In this model, the per site rates of hexanes isomerization and MCP deshydrocyclization had been calculated [37]. Hydrogenolysis of methylcyclopentane and isomerization of 2-methylpentane according to a cyclic mechanism have been described according to a common scheme [26,37], including successive adsorption–desorption [1], deshydrogenation–hydrogenation [2] and isomerization [3] steps according to the equilibria:



where the index *a* states for an adsorbed intermediate; *i* < 2*n* + 2 and *j* = *k* < 2*n* + 2. Let us recall briefly the basic assumptions of this model.

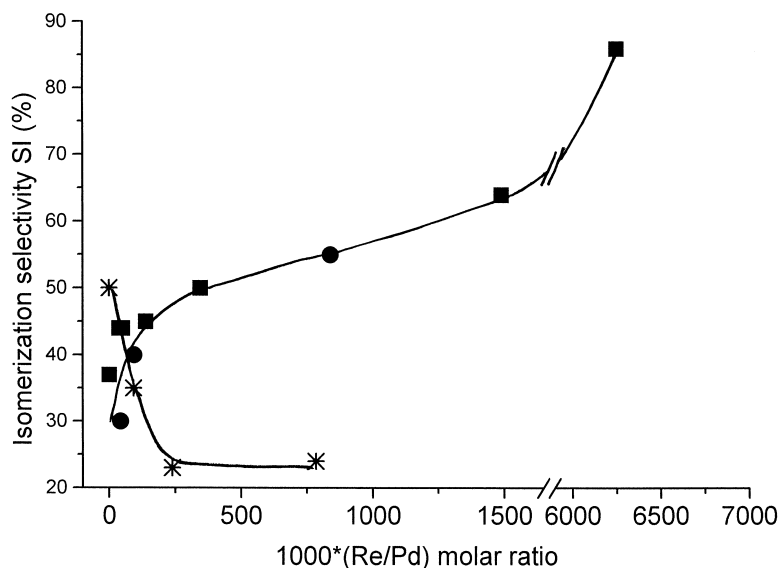


Fig. 6. Isomerization selectivity in 2MP reactivity as a function of the molar ratio RE/Pd. (Square) Series I; (Circle) series II; (Star) series V. The conversion level is kept below 5%.

(1) The adsorption steps [1] occur according to a bimolecular mechanism whereas the deshydrogenation steps [2] occur according to a unimolecular one. Such difference in the mechanisms of consecutive reactions of adsorption and deshydrogenation had been shown for the deuteration of methane on rhodium [38]. A modification of these mechanistic assumptions does not change however the general conclusions of this work, provided that the same mechanism was applied to the two reagents. This is ascertained by the use of the ^{13}C label.

(2) The ultimate degree j of deshydrogenation is identical, whatever the hydrocarbon is.

(3) The adsorption and deshydrogenation of cyclic and acyclic hexanes require the same number of contiguous sites z . Luck [39] have shown that the difference in size of the active sites required for the adsorption of these hydrocarbons on platinum does not exceed 0.5.

(4) In the case of 2MP isomerization, the parallel and competitive reactions of hydrocracking and bond shift isomerization are neglected as they require different intermediate species [31].

(5) In the methylcyclopentane hydrogenolysis, the rate limiting step is assumed to be the ring opening of σ -alkyl methylcyclopentane towards the 1,2-5 σ -alkyl π -olefin hydrocarbon (inverse of reaction III in Scheme 5). The adsorption rate of cyclic hydrocarbons is known to be fast.

(6) In 2MP cyclic isomerization, the rate limiting step is supposed to be the deshydrocyclization of the 1,2-5 triadsorbed complex towards the σ -alkyl cycle formation (reaction III of Scheme 5). This hypothesis can be supported for two reasons: first, if adsorption–desorption or deshydrogenation–hydrogenation were rate limiting steps, we must then yield a randomization of the ^{13}C label in the isomers that we did not observe at all. Second, the ratio of selectivity 3MP/nH is quite the same in 2MP isomerization and in MCP hydrogenolysis. This is a strong argument for a reaction limited by the ring formation. Furthermore we assume that no

change of the rate limiting step occurs while increasing the rare earth content. This is partly supported by the absence of any randomization of the ^{13}C label.

Within the limits of these assumptions, we can now express the rates of reaction. The rate of 2MP isomerization A_I can thus be written as follows:

$$A_I = (1 - \theta_C - \theta_H)^{z+2} \cdot P_{\text{HC}} \cdot k_i \cdot K^I / \theta_H \cdot P_H \quad (2)$$

and the rate of MCP hydrogenolysis A_H as:

$$A_H = P_{\text{HC}} \cdot k_H \cdot K^D \cdot (1 - \theta_C - \theta_H)^z \cdot \theta_H / P_H \quad (3)$$

where k_I and k_H are the rate constants per site for the limiting steps of isomerization and hydrogenolysis, respectively. K^I and K^D are the equilibrium constants for hydrocarbon adsorption and deshydrogenation, respectively. P_{HC} and P_H are the hydrocarbon and hydrogen pressures, respectively. θ_C and θ_H are the hydrocarbon and hydrogen coverages, respectively, and z is the number of free adjacent atoms which define a reactive site for a hydrocarbon reaction, in the sense of Frennet [36].

From Eqs. (2) and (3), we foresee that a change in θ_H and θ_C will result in a net change in the rates of isomerization A_I and hydrogenolysis A_H by a factor including the terms $f = [(1 - \theta_C - \theta_H)^{z+2} / \theta_H]$ and $g = [(1 - \theta_C - \theta_H)^z \cdot \theta_H]$, respectively. The number of contiguous sites z is about 10 for hexanes [40]. The hydrogen coverage θ_H is expected around 0.7 in our conditions [41]. Therefore small changes in θ_H can induce large changes in the reaction rates A_I and A_H due to the high value of the number of contiguous sites z . For example, a decrease of 0.1 for θ_H with the following set of parameters ($\theta_H \approx 0.7$, $\theta_C \approx 0.1$ and $z = 10$) increases the rates of isomerization and hydrogenolysis by about 150 and 50, respectively, leading to a three-fold increase of the ratio A_I/A_H . In a paper previously devoted to the characterization of these catalysts, two types of

sites were identified on Pd(chloride) catalysts [20]. Type I sites are classical palladium surface sites, whereas type II sites are settled at the interface of the transition metal and the rare earth or the alumina support with a chlorine bridge. Chlorine at the interface was detected both by X-ray photoelectron spectroscopy (XPS) and Extended X-ray absorption fine structure (EXAFS) [22]. Only type I sites do exist on the Pd(nitrate) catalysts. On type II sites the strong basicity of chloride anion could help to the adsorption of hydrogen. Hydrogen is easily decomposed through chemisorption on the metallic sites I, and then may diffuse to the interface sites II full of chloride anions. Hence in the steady conditions the hydrogen coverage decreases on type I sites and more free sites are available on palladium for the chemisorption of hydrocarbons (Scheme 6). The rates A_I and A_H both increase according to Eqs. (2) and (3), respectively, owing to $\delta\theta_C \ll \delta\theta_H$. This depletion of the hydrogen surface concentration on the metal does not occur when nitrate is the precursor salt. There are some studies in the literature by thermo-programmed-desorption

(TPD) or thermo-programmed-oxidation (TPO) that reported the enhanced strength of the chemisorbed hydrogen on transition metal/ceria catalysts when chloride anions are present [42–44].

Such explanation also supports the enhanced selectivity towards deshydrocyclization of 2MP, the evolution of the ratio A_I/A_H and the increasing apparent activation energy E_a in MCP hydrogenolysis. The loss of hydrogen coverage enhances the desorption of the less-hydrogenated intermediates like adsorbed σ -alkyl methylcyclopentane instead of ring opening and further hydrogenation of the isomers.

From Eqs. (2) and (3), the ratio A_I/A_H can be expressed as:

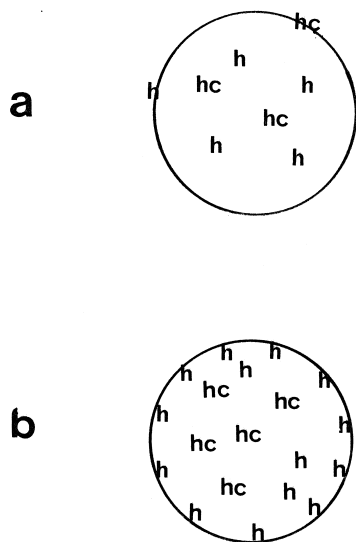
$$A_I/A_H = (1 - \theta_C - \theta_H)^2 \cdot k_i \cdot K^I / \theta_H^2 \cdot k_H \cdot K^D \\ = k \cdot [(1 - \theta_C - \theta_H) / \theta_H]^2 \quad (4)$$

Some decrease in hydrogen coverage may result in an increase in the ratio A_I/A_H , which is clearly observed at high rare earth content, whatever the nature of the rare earth. On the other hand, on the Pd(nitrate) catalysts no modification of the hydrogen coverage occurs as no special interaction does exist between palladium and the promoted support (Scheme 6). Even more, the adsorption of hydrocarbons through carbene intermediates enhances the highly-dehydrogenated and irreversibly adsorbed hydrocarbons. Hence the overall activity and the ratio A_I/A_H steeply drop whereas the selectivity towards hydrogenolysis highly increases. Possibly also large areas of the palladium surface are poisoned.

Finally, according to Eq. (3), the apparent activation energy E_a in MCP hydrogenolysis can be written according to Eq. (5):

$$E_a = E_0 + a \cdot H_h + b \cdot H_c + \delta \text{Log}H / \delta(1/T) \quad (5)$$

where E_0 is the true activation energy, H_h and H_c are the variations in enthalpy for the adsorption of hydrogen and hydrocarbons with coeffi-



Scheme 6. Top view of a palladium particles with hydrocarbon (hc) and hydrogen (h) in the cases (a) no interaction with the support; (b) interaction with rare earth promoter (chloride precursor salt of palladium).

cients a and b , respectively and H is a surface function which depends from hydrogen and hydrocarbon coverages according to Eq. (6):

$$H = (1 - \theta_C - \theta_H)^z. \quad (6)$$

A change in the hydrogen coverage with temperature leads to $\delta \log H / \delta (1/T) < 0$. Consequently, the apparent activation energy can be modified up to about 20 kcal/mol [41]. However the hydrogen desorption from sites II is expected to be highly activated. Both TPD and TPO had reported such high temperature hydrogen desorption on transition metal/ceria catalysts containing chloride anions [42,45]. We effectively find that in the presence of rare earth the apparent activation energy decreases by about 10 kcal/mol, relatively to the unpromoted catalyst.

The influence of the precursor salt of the transition metal promoted by ceria on the catalytic has been studied in Refs. [42–48]. Some of these studies report the formation of an intermetallic [12,13,46,47], but it should be emphasized that the catalysts were then not preliminary calcined. The behaviour of such catalysts is quite different if they are preliminary calcined or not [49]. Moreover, the catalytic activity of such intermetallics become very weak [50], which is not the case of this study. A so-called bifunctional mechanism can also be excluded [51,52]. Hence, the creation of acidic sites on the support due to the high content and the basicity of chloride ion in the presence of rare earth can be expected. However the isotopic ^{13}C distribution in the 2MP isomerization clearly indicates that these reactions occur on the metallic sites instead of the support [53]. This point is further supported by the low aromatization selectivity at 360°C. Another explanation involves an electronic charge transfer from the rare earth to the palladium to explain modifications of the selective hydrogenation of butadiene [48]. Such a transfer cannot be fully excluded, although by XPS we fail to clearly put into evidence such transfer on the reduced catalysts as well as the large size of the particles precludes a sharp

modification of the electron density [20,27]. Nevertheless the occurrence of some electronic transfer could explain some results that remain unexplained by the model above developed. First a small but different behaviour occurs between lanthana and ceria-promoted catalysts at low rare earth content in MCP hydrogenolysis activity (Fig. 1). Second, the decrease of hydrogen coverage cannot explain the smaller hydrocracking activity of 2MP when promoted by ceria or lanthana (Table 4). Finally we observe a slight initial decrease of the ratio r of the 2MP isomerisation vs. MCP hydrogenolysis (Fig. 5). It is well-known that the hydrocracking of hydrocarbons requires more deeply deshydrogenated intermediates [31,54], and thus we expect an increase of the hydrocracking selectivity which is not observed. This apparent discrepancy can be relied to a size effect and to a different nature of the interfacial type II sites. We showed extensively in previous papers that the ceria is strongly reduced in such catalysts, whereas lanthana is not [22,23,27]. The strong oxophile character of reduced ceria on sites II helps to the dissociation of hydrocarbons as well as CO. Therefore, we believe sites II provide enhanced per site activity on the ceria-promoted catalysts but not on lanthana-promoted catalysts. On catalysts of large surface area like those with a low rare earth content, the relative amount of interfacial sites II is not negligible and the overall activity increases. On catalysts of low surface area like those with a high rare earth content, the mean particle size increases and the relative amount of interfacial sites becomes negligible. Hence the overall activity drops and this difference of behaviour between ceria and lanthana promotion cancels. Not only these sites enhance the activity, but they also modify the selectivity. The high hydrogen concentration near sites II prevents the hydrocracking activity. This can also explain the small decrease in $r = A_I/A_H$ observed at lower rare earth content on Pd (chloride) catalysts.

Finally, it is quite interesting to note that a similar study performed on a Pt–Ce/Al₂O₃

catalyst also points out a maximum of *n*-heptane conversion at similar Ce/Pt molar ratio ($0.35 < \text{Ce/Pt} < 0.14$) [42]. This maximum is interpreted by both an electronic (increasing) and structural (decreasing) effects. These effects can be accounted in our study by the enhanced selectivity on sites II and the drop of the density of sites I due to the size increase, respectively. Another study underlines the better isomerization selectivity of nH, to the detriment of hydrocracking and aromatization selectivities [55].

5. Conclusions

The main conclusions of this study can be summarized as follows.

For catalysts with palladium particles of large size, there is a large difference in reforming activity in strong relationship with the palladium precursor salt. Starting from a chloride as palladium precursor salt, the catalytic activity is from one to two orders of magnitude more active than a nitrate precursor salt. This effect is independent of the rare earth nature (Ce or La) and increases with the rare earth content.

Modifications of activity and selectivity in reforming reactions are explained by kinetic effects (decrease of the hydrogen coverage on metallic sites induced by preferential diffusion of hydrogen at the metal-support interface, creation of new active sites at the interface by interaction between the metallic particle and the promoted support) and dispersion effects (loss of surface area of the support).

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