

# Influence of the Brønsted acidity, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio and Rh–Pd content on the ring opening. Part II. Selective ring opening of methylcyclohexane

Silvana A. D'Ippolito<sup>a</sup>, Catherine Especel<sup>b</sup>, Laurence Vivier<sup>b</sup>, Florence Epron<sup>b</sup>, Carlos L. Pieck<sup>a,\*</sup>

<sup>a</sup> Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE) (FIQ-UNL, CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina

<sup>b</sup> Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), UMR 7285, CNRS - Université de Poitiers, 4 rue Michel Brunet, 86022 Poitiers Cedex, France

## ARTICLE INFO

### Article history:

Received 25 February 2013

Received in revised form 24 May 2013

Accepted 2 June 2013

Available online 19 June 2013

### Keywords:

Ring opening

Brønsted acidity

Bimetallic catalysts

Rh–Pd

Bifunctional catalysts

Methylcyclohexane

Decalin

## ABSTRACT

Monometallic and bimetallic Pd–Rh catalysts with various Rh/Pd atomic ratios (=0.5, 1 and 2) and a total metal charge of 1 wt% supported on SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> (SIRAL 40, 20, 5) were studied for the ring opening of methylcyclohexane (MCH). The results were compared with those obtained previously for ring opening of decalin. It was found that the total acidity and the Brønsted acidity of the support have a higher influence on the activity for ring opening of naphthenic bicycles than on the activity for opening single rings. The influence of the metal charge is more important on the reaction of MCH. All the catalysts display a high MCH conversion, which increases with the reaction temperature. The bimetallic catalyst with the Rh/Pd ratio equal to 2 and supported on SIRAL 40 has the highest yield to ring opening products.

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## 1. Introduction

In the last years, there has been a large interest for developing catalysts to remove polynuclear aromatics from diesel fuel due to the stringent environmental legislation associated with clean fuels. Besides their negative environmental impact, polynuclear aromatics decrease the cetane number and diminish the overall quality of the diesel. The selective ring opening (SRO) of naphthenic molecules is an alternative route for their valorization.

RO occurs by hydrogenolysis over some noble metals [1], but bifunctional catalysts seem to be more suitable for this process [2–13] because a C<sub>6</sub> to C<sub>5</sub> ring contraction occurs over the acid function which facilitates the opening of C<sub>5</sub> rings over the metal function [6,11,12]. It has been found that alumina supported metals such as Pt, Pd, Ir, Ru and Rh are active and selective for ring opening of methylcyclopentane to C<sub>6</sub> paraffins [1,14]. Some researchers [6,15] have taken an interest in Rh-based catalysts for the RO reaction due to the Rh high hydrogenolytic activity. The use of acidic catalysts is required for the ring opening of multicyclic naphthenes such as decalin. On the contrary, monocyclic naphthenes such as

cyclohexane can be open on some monofunctional metallic catalysts, such as those based on iridium [16].

On acid catalysts, it is believed that the opening of C<sub>6</sub> and C<sub>7</sub> naphthenic rings occurs on Brønsted acid sites, being initiated by protolytic cracking and followed by chain reactions involving formed carbenium ions [17–19]. The mechanisms of cracking and isomerization of alkanes on acid catalysts have been widely studied [20–24], and it may also be applied to naphthenes with saturated C–C bonds. Results from experimental works and predictions from theoretical calculations allow inferring that either protolytic cracking or dehydrogenation, hydride transfer, skeletal isomerization, and the β-scission and alkylation of adsorbed ions are involved [25,26]. It was confirmed that the first step for methylcyclohexane conversion is ring contraction to C<sub>5</sub> naphthenes [5,27,28]. In the literature, numerous bimetallic systems were tested for the hydrogenolysis of naphthenic compounds, notably methylcyclopentane [29–34], but few deals with the selective opening of methylcyclohexane and even less under high pressure conditions [35,36].

In this work, the influence of the Brønsted acidity brought by the support on the selective ring opening of naphthenes was studied. Monometallic and bimetallic Pd–Rh catalysts supported on SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> with different SiO<sub>2</sub> contents (SiO<sub>2</sub> = 5, 20 and 40 wt%) and different atomic Rh/Pd ratios were used. Methylcyclohexane

\* Corresponding author. Tel.: +54 342 4533858; fax: +54 342 4531068.

E-mail address: [pieck@fiq.unl.edu.ar](mailto:pieck@fiq.unl.edu.ar) (C.L. Pieck).

(MCH) was taken as model molecule. The studied samples are those prepared in the first part of this paper [37], characterized by measurement of the Pd and Rh contents, X-ray diffraction, H<sub>2</sub> chemisorption, temperature-programmed desorption of pyridine, isomerization of 3,3-dimethyl-1-butene (33DM1B), and evaluated for the selective ring opening of decalin.

## 2. Experimental

### 2.1. Catalysts preparation

Three commercial SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> supports provided by Sasol (SIRAL 5, SIRAL 20 and SIRAL 40) were used as support. Previously, they were calcined at 450 °C for 4 h (10 °C min<sup>-1</sup>, air, 60 cm<sup>3</sup> min<sup>-1</sup>). Rh and/or Pd were added by a common impregnation method. An aqueous solution of HCl (0.2 mol L<sup>-1</sup>) was added to the support and the system was left unstirred at room temperature for 1 h. Then an aqueous solution of RhCl<sub>3</sub> and/or PdCl<sub>2</sub> (Sigma–Aldrich) was added in order to have a 1 wt% of total metal charge. For the bimetallic catalyst, the Rh/Pd atomic ratio was  $x = 0.5, 1$  and  $2$ . The slurry was gently stirred for 1 h at room temperature and then it was put in a thermostated bath at 70 °C until a dry solid was obtained. The drying was completed in a stove at 120 °C overnight. Finally, the samples were calcined in flowing air (60 cm<sup>3</sup> min<sup>-1</sup>) at 300 °C for 4 h and reduced under flowing H<sub>2</sub> (60 cm<sup>3</sup> min<sup>-1</sup>, 500 °C, 4 h). The monometallic catalysts are named Pd1/Sy or Rh1/Sy, while the bimetallic are named Rx/Sy, where Sy is the support (SIRAL) and y is the weight percentage of SiO<sub>2</sub>. In the case of the bimetallic catalysts, R corresponds to the Rh/Pd atomic ratio and x is the value of this ratio.

### 2.2. Ring opening of methylcyclohexane

MCH hydrogenolysis was performed in a fixed-bed continuous reactor (stainless steel tube of 1.3 cm inner diameter) with 1.5 g of catalyst, under a total pressure of 39 atm, with a molar ratio H<sub>2</sub>/MCH = 8 (weighted hourly space velocity WHSV = 2 h<sup>-1</sup>) and in a temperature range from 250 to 425 °C. Previously, the catalysts were reduced in situ at the reaction pressure at 500 °C for 1 h using 60 cm<sup>3</sup> min<sup>-1</sup> of H<sub>2</sub>. The methylcyclohexane flow was controlled using a HPLC pump (Gilson). Effluent products were analyzed by an on-line chromatograph (Varian 3900) using a FID and equipped with a PONA capillary column. The conversion was varied by changing the reaction temperature, by steps of 25 °C. The initial reaction temperature was chosen according to the metal loading and the support of each catalyst. After reaching a conversion near 100%, the temperature was not increased more. Four measurements were performed at each temperature; the values given in the results correspond to the average of these four measurements. The error associated with the data is at maximum of 5%. It was checked on some catalysts that the deactivation occurring during the reaction is negligible. For that purpose, after having reached the highest reaction temperature and then the maximum of conversion, the temperature was decreased by steps of 25 °C to the lowest temperature. The MCH conversion as well as the products distribution obtained was considered as similar. The absence of intra and extragranular diffusion limitations in these experimental conditions was checked by varying independently the particle size (in the 0.1–0.6 mm range), the amount of catalyst (from 500 mg to 2 g) and the reactant flow rates (from 0.0325 to 0.1300 mL min<sup>-1</sup>).

## 3. Results and discussion

The MCH conversion was determined as a function of temperature. The reaction products are classified in: (i) cracking products,

i.e., C<sub>1</sub>–C<sub>6</sub> products resulting from either deep hydrogenolysis or cracking; (ii) isomerization products, i.e., saturated cyclic alkanes containing the same number of carbon atoms as MCH but with C<sub>5</sub> ring; (iii) ring opening products, i.e., C<sub>7</sub> alkanes resulting from the opening of MCH and its isomers; (iv) dehydrogenation product, i.e., toluene. The yield in each kind of products was defined as the percentage of MCH converted into the given products. The selectivities were calculated by dividing the yield in each kind of products by the amount of MCH converted as reported previously [36].

Fig. 1 shows the conversion as a function of reaction temperature for all the studied catalysts supported either on SIRAL 5, SIRAL 20 or SIRAL 40. All the catalysts display a high MCH conversion which increases as the temperature increases. For the three series, the Rh1 monometallic catalysts are more active than Pd1 monometallic ones, putting in evidence the higher activity of Rh than Pd. For this reason, bimetallic catalysts with higher Rh content are more active. The activity follows the order: Rh1 > R2 > R1  $\cong$  R0.5  $\cong$  Pd1. So, the addition of Rh to Pd allows working at lower temperatures to obtain high conversion.

Fig. 2 shows the yield and the selectivity to RO products as a function of the reaction temperature. All the catalysts have a maximum of yield to RO products with the reaction temperature, with the sole exception of the Pd1 catalysts that do not yield RO products at all. It can be seen that the temperature of maximum yield is shifted to lower temperatures when the Rh content increases in the catalysts. Moreover, as the Rh content in the bimetallic catalysts is increased, higher yields to RO products are obtained, the optimum being obtained for the R2 bimetallic samples, which also present higher yield in RO products than the monometallic Rh catalyst. Likewise, at higher conversions (>70%), the R2 bimetallic catalysts are more selective to RO than Rh1 catalysts. The effect of Rh addition to the Pd metal function is stronger in the case of the SIRAL5 catalyst; only with this support the bimetallic R0.5 catalyst was more selective to RO than the Pd1 catalyst. On the S20 and S40 series, the increase in selectivity to RO is noticeable especially for R2 catalysts. The maximum yield to RO on the S5 series increases in the following order: R2 > R1 > Rh1 > R0.5  $\gg$  Pd1, while for the S20 series the order is: R2 > Rh1  $\gg$  R1 > R0.5 > Pd1, and for the R40 series: R2 > Rh1  $\gg$  R0.5 > R1 > Pd1. At conversions higher than 80%, the selectivity to RO products decreases dramatically because the catalysts produce cracking and dehydrogenated products, which are thermodynamically favored at higher reaction temperature as it can be seen in Figs. 3 and 6. Again, the higher hydrogenolytic character of Rh compared to Pd leads to an increase of the RO reaction. However, the maximum yields to RO products (Fig. 2) are obtained on the bimetallic R2 catalyst. Both catalysts (R2 and Rh1) supported on SIRAL 40 have similar metallic dispersion [37], but the Rh1 catalyst presents the highest activity, which could be attributed to a higher accessibility of rhodium in the monometallic catalyst than in the bimetallic R2 catalyst. The lower yield in RO product obtained with the Rh1 catalysts compared to the R2 ones can be explained by the higher yields in cracking products obtained with these catalysts as shown in Fig. 3. Thus, the presence of rhodium at the bimetallic particle surface favors the activity in hydrogenolysis but the presence of Pd limits deep hydrogenolysis thus favoring the formation of RO products.

In fact, as shown in Fig. 3, the yield and selectivity to cracking products increase with the reaction temperature, however with quite different behaviors according to the nature of the catalyst and the support. For the catalysts supported on SIRAL 5, all the systems containing Rh lead to cracking products, Rh1 and R2 being the most selective ones. On the other hand, on SIRAL 20 and SIRAL 40, the R0.5 and R1 catalysts (besides Pd1 systems) have little selectivities to cracking products (lower than 15%). The hydrogenolytic character of Rh is more evident on the S5 (Table 1). The differences in the behavior of catalysts supported on SIRAL 5 and those

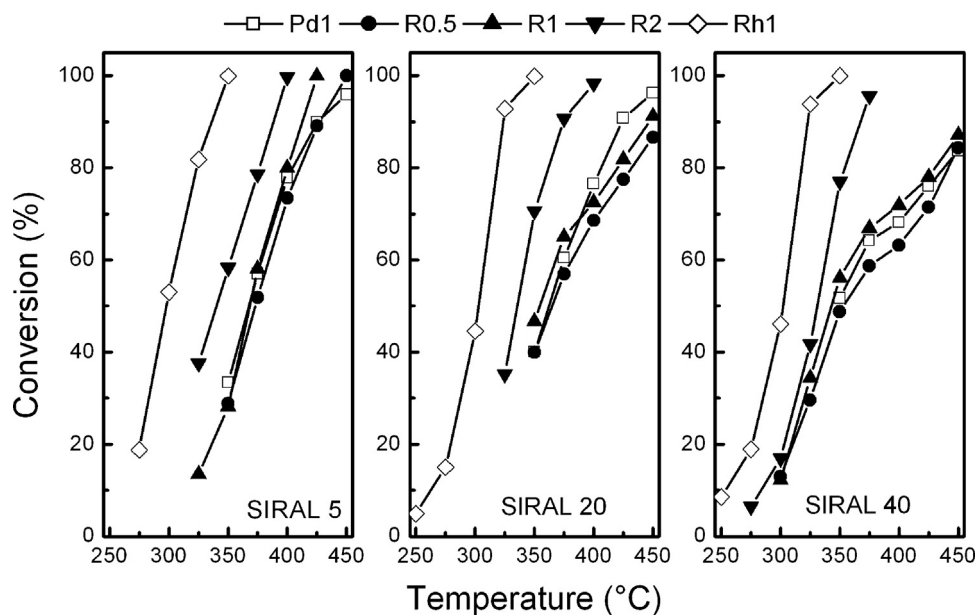


Fig. 1. MCH conversion as a function of the reaction temperature for the three series of catalysts.

supported on SIRAL 20 and SIRAL 40, especially for R1 and R0.5, are mainly due to the low acidity of the former. The SIRAL 5 series shows clearly that predominates the metal function and thus provides increased performance in hydrocracking products (mainly  $C_1$  and  $C_6$ ,) by incorporating small amounts of rhodium. Comparing the results obtained for Pd1/S5, R1/S5, R0.5/S5 and Rh1/S5 (Table 1) is remarkable the higher hydrogenolytic character of the Rh respect to palladium, even in the bimetallic catalysts. In the case of catalysts supported on SIRAL 5 the cracking products are mainly attributed to the hydrogenolysis on rhodium. In the first part of this work [37], we determined that Pd and Rh decrease the total acidity of the support, the monometallic Pd1 catalysts having the lowest total

acidity associated with the strongest acid sites. On bimetallic catalysts the total acidity increases as the Rh content is increased, but the acid strength is lower since desorption peak of pyridine was observed to shift to lower temperatures. If only a monofunctional acid cracking mechanism is considered, the obtained results mean that the cracking selectivity is more influenced by the amount of acid sites than the strength of these last. But, it is necessary also to take into account the metallic mechanism. Indeed, among the cracking products, the major part is constituted of  $C_1$  and  $C_6$  products, mainly produced on the metallic function by hydrogenolysis, as it can be seen in Fig. 4. An acidic cracking would yield to  $C_3$  and  $C_4$  products. Then, it can be inferred, in particular for Pd1, R0.5 and

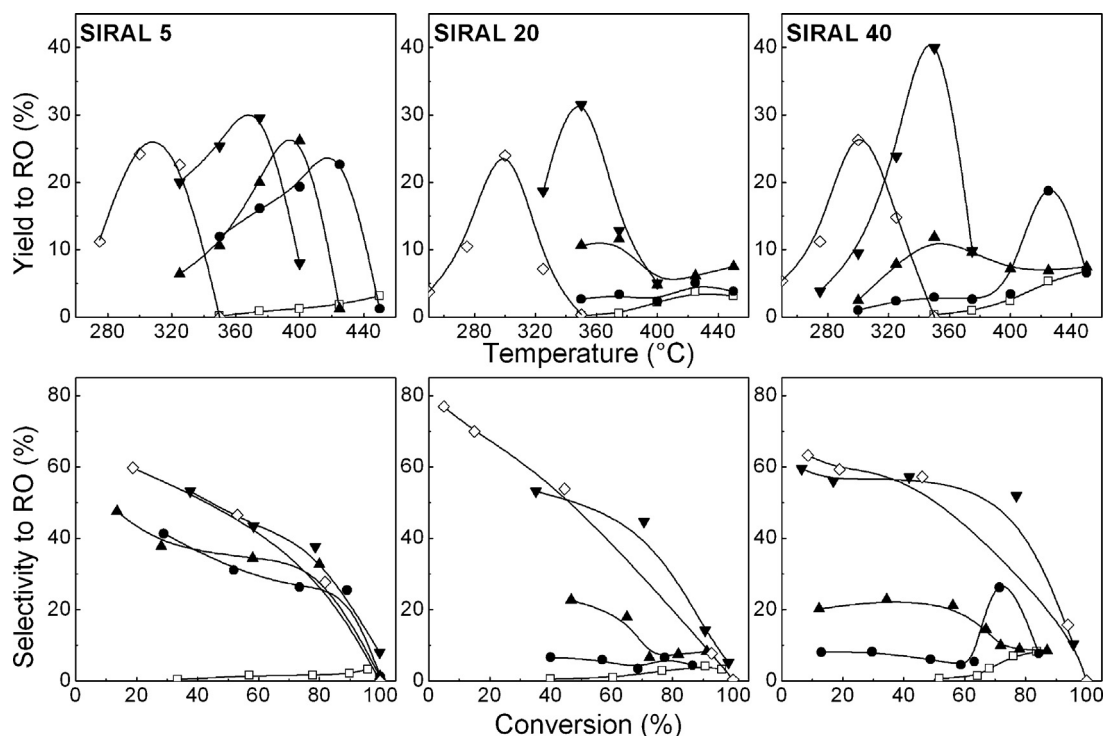


Fig. 2. Yield and selectivity to ring opening (RO) products at different reaction temperatures. Symbols as in Fig. 1.

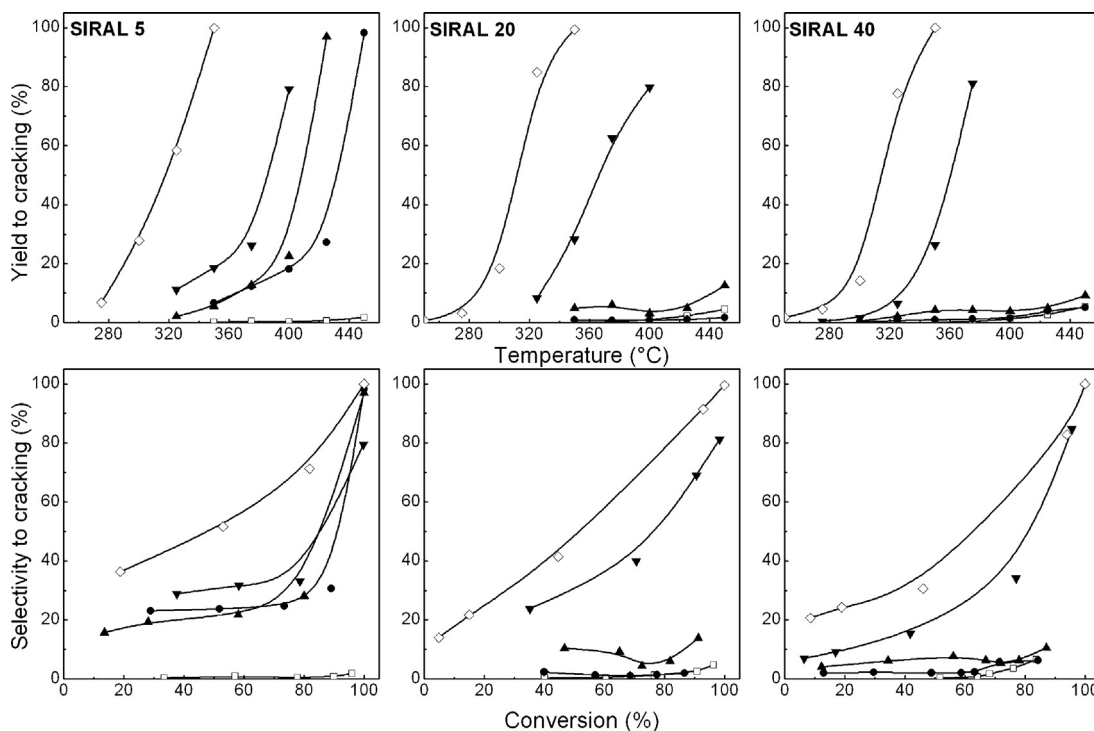


Fig. 3. Yield and selectivity to cracking (CR) products at different reaction temperatures. Symbols as in Fig. 1.

R1 catalysts of the S20 and S40 series, that the acidity is not strong enough to favor the cracking, but must be sufficient to isomerize methylcyclohexane, as demonstrated for the alumina support [36].

Table 1 shows the percentage of C<sub>1</sub> and C<sub>6</sub> in the cracking products at the reaction temperature for which the yield to cracking products is maximum. It can be seen that for all the Rh1 catalysts the C<sub>1</sub> and C<sub>6</sub> compounds correspond practically to 100% of the cracking products. It is also noted that the catalysts supported on SIRAL 5 have higher amounts of C<sub>1</sub> and C<sub>6</sub> products than those supported on SIRAL 20 that themselves have had more than those supported on SIRAL 40. Then, as the acidity of the support is increased, the metal function of the catalyst has less effect on to the formation of light

products, and a more important production of C<sub>3</sub> and C<sub>4</sub> products is observed. This phenomenon can be explained considering that C<sub>3</sub> and C<sub>4</sub> are produced on the strong acid sites by cracking reaction and C<sub>1</sub> and C<sub>6</sub> are produced on metallic function by hydrogenolysis.

It can be seen in Fig. 5 that almost all the catalysts show a maximum of yield to isomerization products as a function of the reaction temperature. The exception is Rh1/S5 catalyst which has almost near zero yields to isomerization products. On this support, the yield to isomerization slightly increases with the Pd content in the bimetallic catalysts, and the Pd1/S5 leads to the highest yield. For S20 and S50 supports, the yields to isomers are nearly similar for R0.5, R2 and Pd1, with maximum yield between 50%

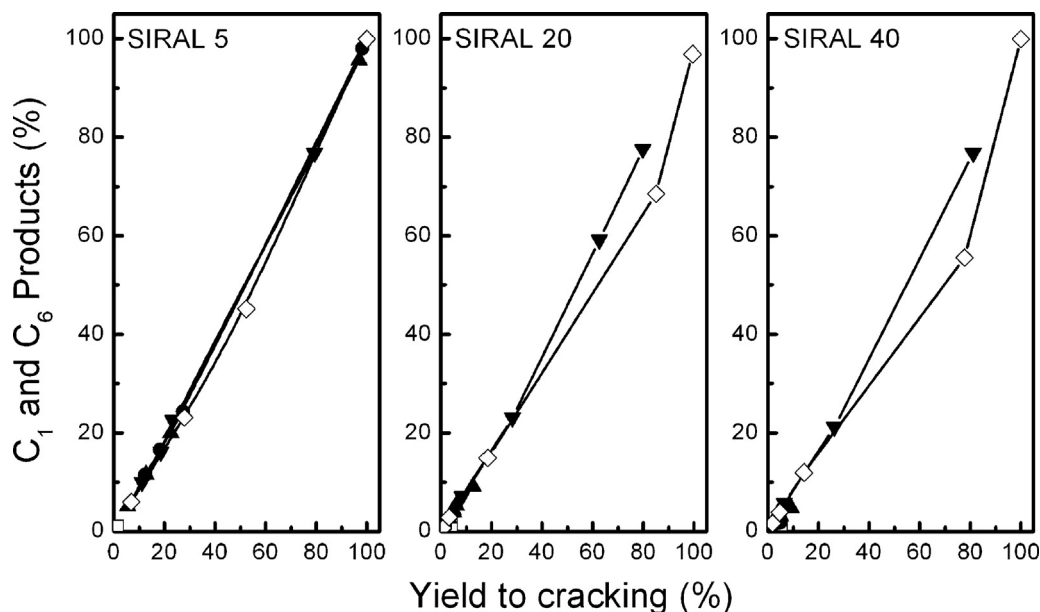


Fig. 4. C<sub>1</sub> and C<sub>6</sub> products as a function of yield to cracking for the three series of catalyst. Symbols as in Fig. 1.

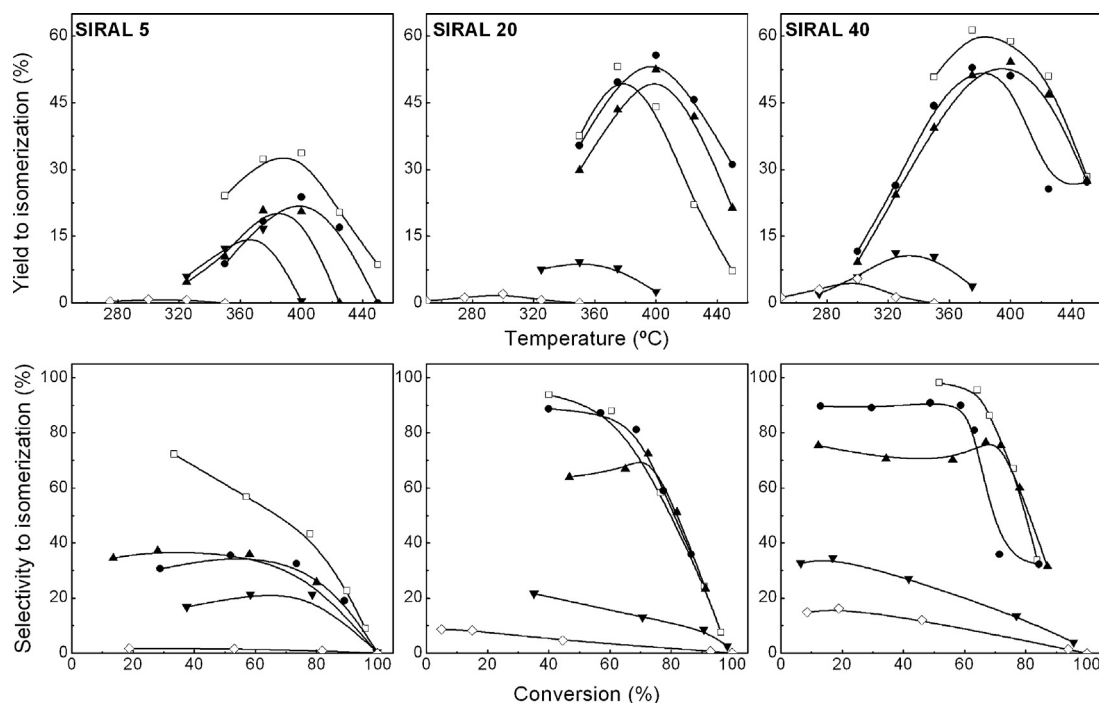


Fig. 5. Yield and selectivity to isomerization (Isom) products at different reaction temperature. Symbols as in Fig. 1.

and 60%, whereas the R1 catalysts show a singular behavior, with a maximum yield around 8%, not very different from the yields obtained with Rh1 catalysts on the same support. The high selectivity to isomerization products at low MCH conversion obtained for Pd1 catalysts could be attributed to the fact that the RO of MCH occurs preferentially via a bifunctional mechanism on this metal, following two steps, the first one consisting in the isomerization of the C<sub>6</sub> ring to alkylcyclopentanes which are further opened to paraffins. The Rh1 catalysts have a very low yield and selectivity

to isomerization products, i.e., in this case, a direct MCH conversion occurs preferentially on the metal function. For the three series of catalysts, the increase in Pd content leads to an increase in the yield and selectivity to isomerization products. The selectivity to isomerization products increases in the following order: Pd1 > R0.5 ≫ R1 > R2 > Rh1. The highest selectivities are obtained on the catalysts supported on SIRAL 40 and SIRAL 20 due to their higher acidity. In a previous work [37] we reported that the incorporation of Rh and Pd decreases the strength of the acid sites, this decrease

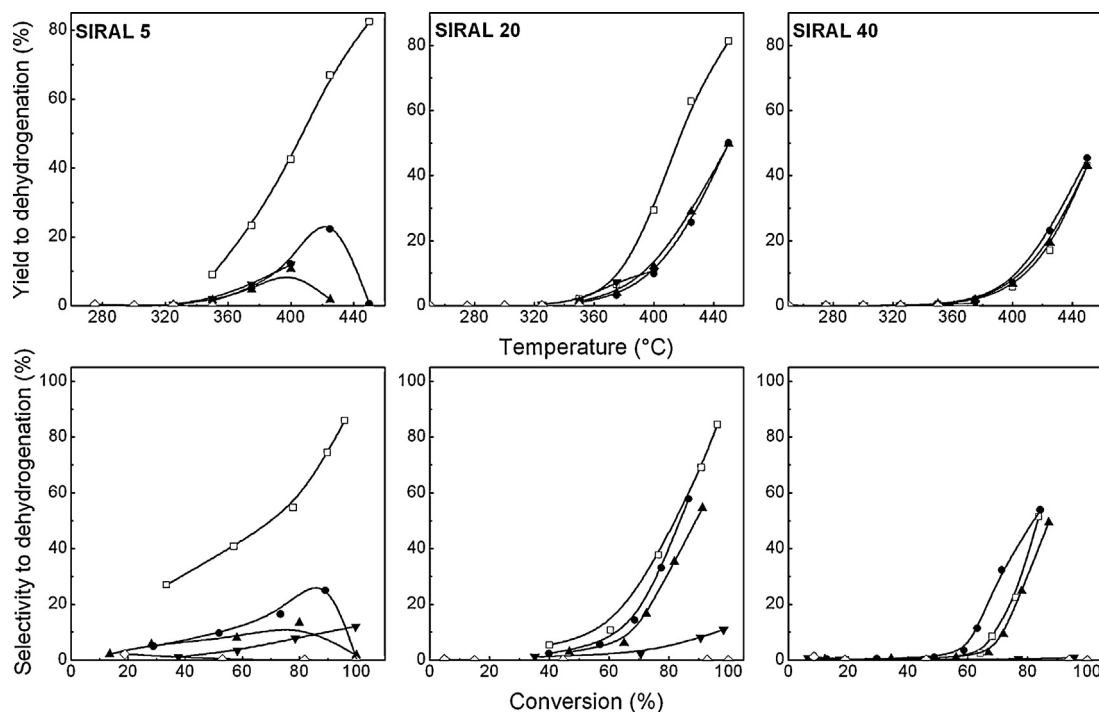


Fig. 6. Yield and selectivity of dehydrogenation products at different reaction temperature. Symbols as in Fig. 1.



**Table 1**  
Percentage of C<sub>1</sub> and C<sub>6</sub> in the cracking products at the temperature for which the yield to cracking is maximum.

Catalyst	T (°C)	Yield to cracking products (%)	Yield to C <sub>1</sub> and C <sub>6</sub> (%)	C <sub>1</sub> and C <sub>6</sub> in the cracking product (%)
Pd1/S5	450	1.7	1.1	60.3
Pd1/S20	450	4.6	1.1	24.4
Pd1/S40	450	5.5	1.1	20.9
R0.5/S5	450	98.2	98.1	99.8
R0.5/S20	450	1.7	0.9	51.8
R0.5/S40	450	5.2	1.9	36.6
R1/S5	425	96.9	95.7	98.7
R1/S20	450	12.6	9.1	72.0
R1/S40	450	9.2	4.7	51.1
R2/S5	400	79.2	76.8	96.9
R2/S20	400	79.8	77.5	97.1
R2/S40	375	81.1	74.8	92.2
Rh1/S5	350	99.9	99.9	100.0
Rh1/S20	350	99.4	96.9	97.4
Rh1/S40	350	99.9	99.9	100.0

being more important as the Rh increased. So, according to the results it can be concluded that the isomerization reaction needs strong acid sites.

Fig. 6 shows the yield and selectivity to the dehydrogenation product, toluene, at different reaction temperatures. The formation of toluene decreases the yield in ring opening products and this reaction must remain limited. The increase in conversion (i.e., reaction temperature) leads to an increase in the formation of dehydrogenated products, the dehydrogenation reaction being favored at high temperatures. Clearly, the Pd1 catalysts supported on S5 and S20 favors the formation of dehydrogenated compounds. On the other hand, the increase in Rh content decreases the aromatic formation for the three series of catalysts. The Rh1 catalysts have almost a null activity to dehydrogenated products. The higher selectivity to dehydrogenated products of Pd compared to Rh is in agreement with the superior hydrogenation/dehydrogenation activity of Pd. Each catalyst of the S40 series has lower selectivity to aromatic than the respective S20 catalysts which in turn are greater than those supported on SIRAL 5, except for the R0.5 catalyst.

So, in the case of the bimetallic systems, the high selectivities to RO products can be due to both an exaltation of the MCH direct opening activity (via Rh contribution) and the higher capacity for opening C<sub>5</sub> isomer rings. Nevertheless, at the highest temperatures, the cracking as well dehydrogenation reactions are favored, and as a consequence the formation of isomers and then of RO products is decreased.

Table 2 shows a summary of the temperatures and values of the maximum yields to cracking (CR), isomerization (Isom), ring opening (RO) and dehydrogenation (DH) products, respectively. At 450 °C (i.e., the highest temperature in the studied range), the Pd1 catalysts have low yields to cracking products and high yields to dehydrogenated products. On the contrary, the Rh1 catalysts at 350 °C (i.e., the highest work temperature for these systems) have high yields to cracking and negligible yields to dehydrogenated product. The R2 bimetallic catalysts present the highest yields to RO products, the maximum value (40%) being reached for the sample supported on SIRAL 40. It can be concluded that monometallic Pd catalysts favor dehydrogenation reaction while monometallic Rh catalysts favor cracking reactions. In an intermediate way, the bimetallic catalysts are more suitable to RO reactions. The high difference in cracking products found between Pd1 and Rh1 catalysts cannot be explained by differences in acidity of the catalysts. It must be taken into account that in the named cracking products are also considered hydrogenolysis products (like C<sub>1</sub> and C<sub>6</sub>).

Table 3 shows the selectivity to cracking, isomerization, ring opening and dehydrogenated products obtained at isoconversion for a given metallic charge. It can be seen that on monometallic Pd1 catalysts the selectivity to cracking, isomerization and ring opening products increases with the support acidity whereas the dehydrogenated products are decreased. For the bimetallic catalysts, the increase in Rh content leads to an increase in the selectivity to RO products. As previously pointed out, the R2 catalyst supported on SIRAL 40 presents the highest selectivity to RO (52%). For the three catalysts series, as the Rh content is increased the selectivity to isomerized products is decreased.

Among the various ring opening products obtained from methylcyclohexane, two categories can be distinguished [5,38]: (i) direct ring opening products corresponding to a monofunctional metal mechanism: *n*-heptane (*n*-C<sub>7</sub>), 2-methylhexane (2MH) and 3-methylhexane (3MH); (ii) indirect ring opening products corresponding to a bifunctional metal-acid mechanism: 3-ethylpentane (3EP), 2,3-dimethylpentane (2,3DMP), 2,4-dimethylpentane (2,4DMP), 3,3-dimethylpentane (3,3DMP) and 2,2-dimethylpentane (2,2DMP), as well as once again *n*-C<sub>7</sub>, 2MH and 3MH. According to bifunctional mechanism, MCH is first isomerized toward C<sub>5</sub> rings (three dimethylcyclopentanes

**Table 2**  
Temperature and values of the maximum yields to cracking (CR), isomerization (Isom), ring opening (RO) and dehydrogenation (DH) products.

Catalyst	Temperature (T, °C) associated with the maximum yield (%)							
	T	CR	T	Isom.	T	RO	T	DH
Pd1/S5	450	1.7	400	33.7	450	3.2	450	82.4
Pd1/S20	450	4.6	375	53.2	425	3.7	450	81.8
Pd1/S40	450	5.5	375	61.3	450	6.9	450	43.0
R0.5/S5	450	98.2	400	23.8	425	22.6	425	22.2
R0.5/S20	450	1.7	400	55.7	425	5.1	450	50.0
R0.5/S40	450	5.2	400	51.1	425	18.7	450	45.4
R1/S5	425	96.9	375	20.8	400	26.2	400	10.7
R1/S20	450	12.6	400	52.5	375	11.6	450	49.7
R1/S40	450	9.2	400	54.2	350	11.9	450	43.0
R2/S5	400	79.7	375	16.7	375	29.5	400	12.0
R2/S20	400	79.8	350	9.3	350	31.5	400	10.8
R2/S40	375	81.1	325	11.3	350	40.0	375	0.8
Rh1/S5	350	99.9	300	0.8	300	24.2	275	0.4
Rh1/S20	350	99.4	300	2.1	300	24.0	300	0.0
Rh1/S40	350	99.9	300	5.5	300	26.3	250	0.1

**Table 3**

Selectivity to cracking (CR), isomerization (Isom), ring opening (RO) and dehydrogenated (DH) products at isoconversion.

Catalyst	T (°C)	Conversion (%)	Selectivity (%)			
			CR	Isom	RO	DH
Pd1/S5	400	77.8	0.4	43.3	1.6	54.7
Pd1/S20	400	76.6	1.2	58.3	2.8	37.7
Pd1/S40	425	76.0	3.5	67.0	7.0	22.5
R0.5/S5	400	73.4	24.7	32.5	26.3	16.5
R0.5/S20	400	68.6	1.1	81.1	3.4	14.4
R0.5/S40	425	71.4	5.7	35.8	26.2	32.3
R1/S5	400	80.0	28.1	25.7	32.8	13.4
R1/S20	425	81.8	6.0	51.2	7.5	35.3
R1/S40	425	78.0	6.3	60.0	8.9	24.8
R2/S5	375	78.6	33.2	21.4	37.6	7.8
R2/S20	350	70.6	39.9	13.1	44.7	2.3
R2/S40	350	76.9	34.1	13.6	51.9	0.4
Rh1/S5	325	81.8	71.3	0.9	27.7	0.1
Rh1/S20	325	92.8	91.5	0.7	7.7	0.1
Rh1/S40	325	93.8	82.8	1.4	15.7	<0.1

DMCP, or ethylcyclopentane ECP) on the acidic function, and then the obtained C<sub>5</sub> rings are opened on the metal function.

Fig. 7 presents the distribution of the various RO products obtained when the maximum RO yield is reached for each catalyst. They are grouped in “direct” ring opening products (2MH, 3MH and *n*-C<sub>7</sub>) knowing as previously indicated that these compounds can also be obtained from indirect opening, i.e. products (2,2DMP + 3,3DMP), 2,3DMP, 2,4DMP, 3EP and “other” products (2,2,3-trimethylbutane). As previously described, the ring opening is not favored on the Pd1 catalysts. All the bimetallic catalysts supported on SIRAL 5 have a maximum yield to RO products largely higher than that of the monometallic Pd1/S5 sample, and even higher than that of the Rh1/S5 catalyst for the R1 and R2 ratios. On the other hand, on the two other supports, only the R2/20 and R2/S40 samples have higher RO yield than the corresponding Rh1 catalysts, the best performances being obtained on R2/S40 catalyst. On Rh samples, the RO products are produced mainly by a direct ring opening, since isomerization is not favored. Indeed, with the Rh monometallic catalysts, the major part of the RO products is constituted of the “direct” compounds. On the bimetallic catalysts, a direct ring opening mechanism can be suspected as still majority, given the great part of the “direct” compounds obtained in the RO products distribution. These results show that on R2 bimetallic catalysts an alloy or ensembles of Rh–Pd are formed because the sites are more selective to RO products than pure Pd and Rh.

Fig. 8 shows the distributions of the RO products yields determined for the best catalyst of each series at different temperatures near to the maximum RO yield. It can be seen that the RO products distribution is related to the reaction temperature. Whatever the temperature the “direct” products comprise the biggest fraction. If we recall that the products can be produced by a bifunctional (metal–acid) or a monofunctional (metal) mechanism, the results could indicate that the monofunctional metallic mechanism is more important than the bifunctional one, even for the most acidic S40 support.

However, it is clear that on the R2 catalysts the ring opening can also occur via a bifunctional mechanism due to the non negligible fraction of DMP (2,2-, 3,3-, 2,3- and 2,4-) and 3EP products. The presence of both metal and acid sites in close or medium-range vicinity would enable the ring opening of MCH by a bifunctional mechanism with an intermediate isomerization step.

**Table 4**

Conversion and selectivity to cracking (CR), isomerization (Isom), ring opening (RO) and dehydrogenated (DH) products in MCH reaction at 350 °C.

Catalyst	Conversion (%)	Selectivity (%)			
		CR	Isom	RO	DH
Pd1/S5	33.4	0.3	72.3	0.4	27.0
R0.5/S5	28.9	23.1	30.7	41.3	4.9
R1/S5	28.1	19.4	37.2	37.8	5.6
R2/S5	58.3	31.8	21.3	43.5	3.4
Rh1/S5	99.9	>99.9	<0.1	<0.1	<0.1
Pd1/S20	40.0	0.2	93.8	0.6	5.4
R0.5/S20	39.9	3.3	88.7	6.6	2.4
R1/S20	46.7	10.4	64.0	22.7	2.9
R2/S20	70.6	39.9	13.1	44.7	2.3
Rh1/S20	99.9	99.6	<0.1	0.4	<0.1
Pd1/S40	51.7	0.3	98.2	0.7	0.8
R0.5/S40	48.8	2.0	90.9	6.0	1.1
R1/S40	56.1	7.6	70.2	21.2	1.0
R2/S40	76.9	34.1	13.6	51.9	0.4
Rh1/S40	>99.9	99.9	<0.1	<0.1	<0.1

**Table 5**

Conversion and selectivity to cracking (CR), ring contraction (RC), ring opening (RO) and dehydrogenated (DH, including naphthalene) products in decalin reaction at 350 °C.

Catalyst	Conversion (%)	Selectivity (%)			
		CR	RC	RO	DH
S5	0.8	13.8	12.3	30.5	43.4
Pd1/S5	6.4	0.9	1.7	2.1	95.3
R0.5/S5	14.5	0.3	4.1	3.2	92.4
R1/S5	23.2	0.4	3.5	4.7	91.4
R2/S5	32.5	<0.1	3.6	4.9	91.5
Rh1/S5	29.9	0.4	4.6	5.2	89.8
S20	19.5	12.6	17.4	56.6	13.4
Pd1/S20	25.1	0.9	18.2	38.6	42.3
R0.5/S20	28.6	2.5	14.6	46.8	36.1
R1/S20	30.6	2.6	15.9	51.2	30.3
R2/S20	42.7	1.2	13.2	46.1	39.5
Rh1/S20	38.3	1.0	17.0	47.8	34.2
S40	34.5	15.4	13.6	61.0	10.0
Pd1/S40	39.8	6.8	14.3	57.7	21.2
R0.5/S40	43.3	3.4	15.2	55.4	26.0
R1/S40	42.2	4.0	17.5	57.2	21.3
R2/S40	52.8	9.0	15.5	60.5	15.0
Rh1/S40	65.4	7.0	10.1	57.1	25.8

### 3.1. Comparison between MCH and decalin reaction

McVicker et al. [6] reported that MCH has higher reactivity compared to decalin. The thermodynamic equilibrium between cis/trans decalin is rapidly reached, resulting in the enrichment of the reactant mixture in trans-decalin. Santikunaporn et al. [9] and Sousa-Aguiar [39] found that trans-decalin is less reactive due to the acid-catalyzed reaction. In the trans-decalin a tertiary C–H bond is hindered, making protonation and formation of adsorbed carbocations more difficult than in the case of cis-decalin. The higher reactivity of cis-decalin can be explained taking into account the ring strain values reported by Wiberg [40]:  $-7.9 \text{ kJ mol}^{-1}$  for cis-decalin, against  $5.0 \text{ kJ mol}^{-1}$  for trans-decalin. Moreover, trans-decalin exhibits higher ring strain than that of MCH (ca.  $4.2 \text{ kJ mol}^{-1}$  [6]). Thus, the transformation of decalin is more difficult when compared to that of MCH due to the higher stability of trans-decalin.

In order to compare the catalytic performances in the ring opening reactions of one and two naphthenic rings, Tables 4 and 5 show results of conversion, selectivity to cracking, isomerization, ring opening and dehydrogenated products of MCH and decalin

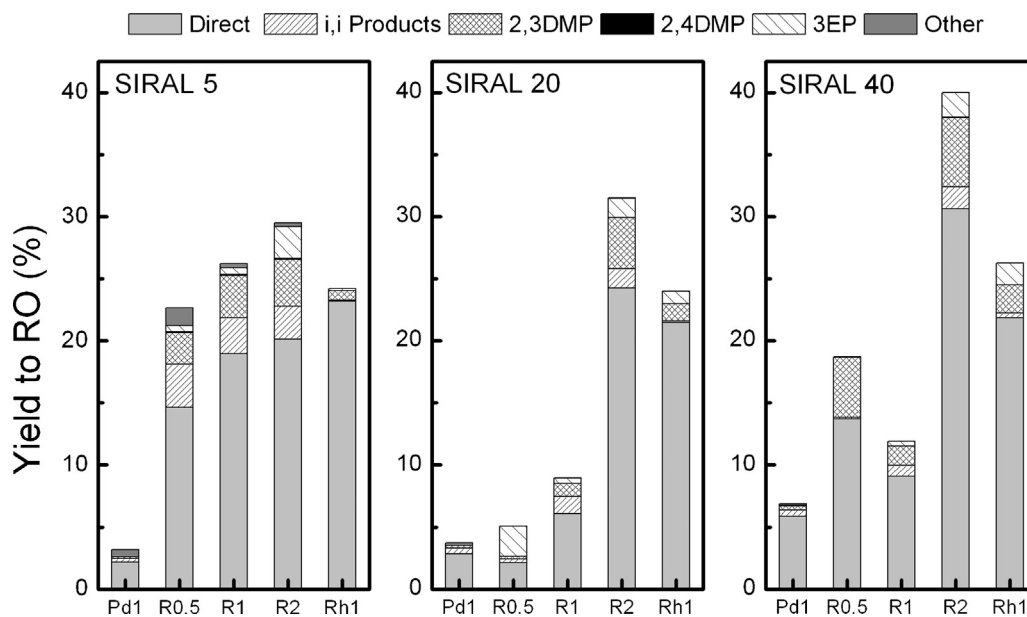


Fig. 7. Yield to different RO products at the maximum RO.

reaction at 350 °C (from ref. [37]), respectively. It can be seen that in both catalytic reactions the presence of Rh leads to an increase of the conversion. Moreover, the catalysts supported on S40 are more active than their counterparts supported on S20 and S5. It has been previously reported [37] that the increase in Rh content produces a slight decrease in the dispersion of the entire metal phase. Higher Rh contents however produce a surface enrichment of Rh atoms and an increase of the catalytic conversion.

During MCH transformation (Table 4), whatever the nature of the support, the increase in the Rh content increases the selectivity to cracking products and decreases that of isomerization and dehydrogenated products. For a given metal function, the acidity of the support moderately affects the conversion. Finally, on the bimetallic samples, the addition of more Rh leads to the increase

in the RO products selectivity, the R2/S40 sample being the most efficient among all the studied catalysts.

During decalin transformation (Table 5), the Rh content has a lower influence on the selectivity to ring opening products but the acidity of the support has a strong influence on the conversion. The best performances are obtained with catalysts supported on SIRAL 40 followed by the series supported on SIRAL 20. These results are in agreement with the higher total acidity and the higher Brønsted acidity of the S40 series. However, the selectivities to ring contraction products are similar between S40 and S20 series. On the other hand, the important acidity of the S40 support unfortunately leads also to some cracking products higher than those obtained on the two other SIRAL supports. Finally, the best performances in term of selectivity to RO products are obtained for the

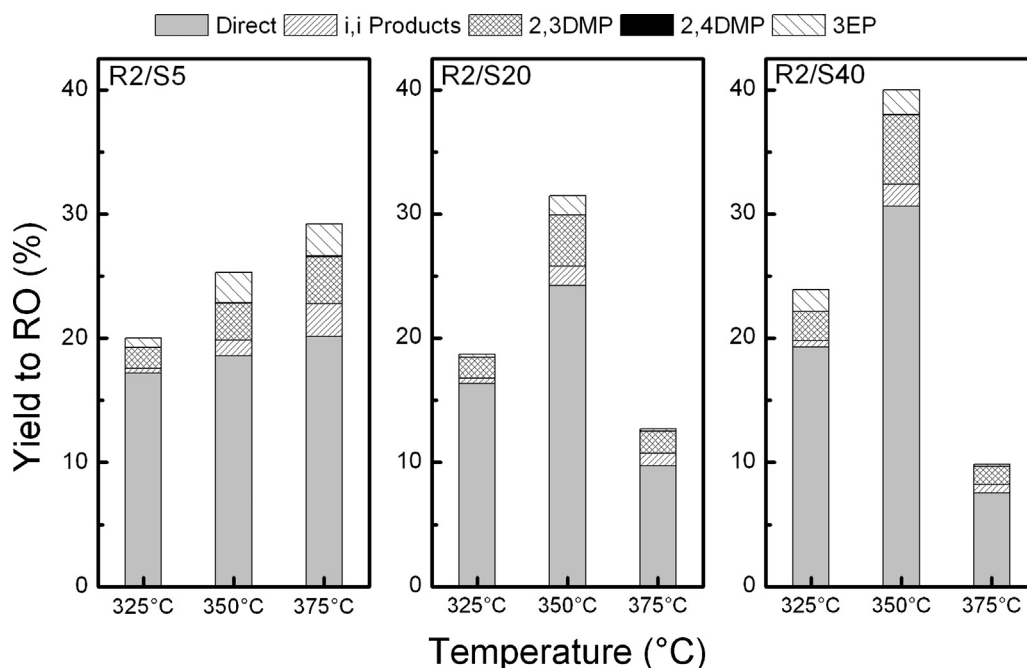


Fig. 8. Yield to different RO products at 325, 350 and 375 °C of the best catalysts.



bimetallic R2 supported on SIRAL 40, due to a better metal-acid functions balance.

Thus, for the two reactions of decalin and MCH transformation, the best catalyst in terms of selectivity to RO products is the R2/S40 one. On this catalyst, in the case of MCH transformation, the major products, after the RO products (selectivity of 51.9%) are cracking products (selectivity of 34.1%), which are formed on the metal function, and more precisely on Rh. For decalin conversion, the other major products after RO products (selectivity of 60.5%) are both ring contraction products (selectivity of 15.5%) and dehydrogenation products (selectivity of 15%), which are formed on Brønsted acid sites and the metallic sites, i.e., Pd. In conclusion, for both reactions, the best balance between the two metal functions, Pd and Rh, and the acidity, which leads to the best selectivity to RO, is obtained with the most acidic support, S40, and Rh/Pd molar ratio of 2. However, the effect of the acidity is more important on decalin transformation.

#### 4. Conclusions

This paper follows a first part of the work devoted to the study of mono and bimetallic Pd–Rh catalysts supported on various SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> (SIRAL 5, 20 and 40) supports, and of the influence of the Brønsted acidity of these oxides on the selective ring opening of decalin. In the present paper, the catalyst behavior was evaluated for the ring opening of a single ring naphthene, i.e., methylcyclohexane, and compared with the previous results obtained with the bicycle (decalin). On the one hand, it was found that the total acidity of the support and the Brønsted acidity have a higher incidence on the catalytic performances during decalin transformation than during the MCH one. The influence of the metal charge (Rh/Pd atomic ratio comprised between 0 and 1) is more important on the reaction of MCH. Finally, the bimetallic catalyst with the Rh/Pd ratio equal to 2 and supported on SIRAL 40 has the highest yield to ring opening products. However, the increase in the reaction temperature leads systematically to an increase in cracking and dehydrogenation products.

#### Acknowledgements

The authors gratefully acknowledge the “Bernardo Houssay” program for the financial support of this work through a 6 month research Grant (Silvana A. D'Ippolito), as well as the SECYT-ECOS program n°A12E02 (2013–2015) which allows continuing the collaboration between the two research teams.

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