

## Research article

# Selective ring opening of methylcyclohexane and decalin over Rh–Pd supported catalysts: Effect of the preparation method



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## ABSTRACT

Bimetallic Rh–Pd catalysts prepared by various impregnation methods were evaluated in the selective ring-opening of decalin and methylcyclohexane (MCH) used as model molecules of hydrogenated aromatics of the Light Cycle Oil fraction. Rh and Pt were deposited on Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> (S40) by coimpregnation (CI) or successive impregnations (SI) with different orders of metal addition. Catalysts were characterized by H<sub>2</sub> chemisorption, temperature-programmed reduction, temperature-programmed desorption of pyridine, and test reactions of cyclopentane hydrogenolysis and isomerization of 3,3-dimethyl-1-butene. Their catalytic behaviors for the ring-opening reaction were deeply influenced by the acidity of the support, and in a lesser extent by the metal deposition method. On both supports, the CI catalysts, displaying the highest dispersion values, exhibited the best ring opening performances. In the case of the SI catalysts, the addition order of both metals modified in a moderate way the properties of the catalyst. The yield to ring opening products obtained in MCH ring opening with CI catalysts supported on Al<sub>2</sub>O<sub>3</sub> was 39–69% higher than those prepared by SI (conversion = 55–60%) while for the catalysts supported on S40, the yield to ring opening products was 8–48% higher for the CI catalysts compared to SI catalysts (conversion = 72–77%). The conversion of decalin for the bimetallic catalysts supported on Al<sub>2</sub>O<sub>3</sub> was lower than 20% being dehydrogenated compounds the main reaction products regardless the preparation method. The catalyst supported on S40 showed decalin conversion values between 46–53% and yield to ring opening near to 30%. Moreover, the CI catalysts have yield to ring opening 10 to 20% higher than the catalysts prepared by SI. The catalyst prepared by coimpregnation supported on S40 was the most appropriate for opening the MCH and decalin due to an optimal balance between the metal and acid functions.

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## 1. Introduction

The selective ring opening (SRO) of naphthenic molecules is a way for the valorization of products resulting from various processes. The increase of the cetane number (CN) through aromatics hydrogenation is not sufficient to significantly increase the quality of the middle distillates, because the cetane numbers of cycloalkanes and decalin are low [1]. LCO (light cycle oil) is a residual stream of fluid catalytic cracking (FCC) unit, which is used for heating and is added to heavy fuel in order to adjust the viscosity [2]. Due to the increasing demand for diesel, a more interesting application would be to combine the LCO fraction to the diesel pool. The LCO product distribution mainly consists of two ring aromatic compounds; therefore, a molecule of two rings such as decalin can be considered as a model molecule. The opening of only one ring in molecules constituted of two rings does not lead to a substantial increase in CN. Therefore, the opening of the second ring is crucial. Moreover, a highly selective catalyst corresponds to a system

able to break C–C bonds to obtain linear paraffins and minimize branched paraffins which exhibit low CN [3].

SRO needs bifunctional catalysts operating at high pressure and high temperature in the presence of H<sub>2</sub>. Acid sites catalyze cracking, isomerization and dealkylation, while metallic sites promote hydrodehydrogenation and hydrogenolysis [4]. The combination of the acid function with the high hydrogenolytic activity of Ir produces more selective catalysts for the conversion of naphthenes to alkanes [5]. Using Ir/H,A-Beta zeolite catalysts for decalin ring opening, Santi et al. highlighted the importance of the metal function in the hydrogenolysis step and of the Brønsted acid sites in the isomerization step of six-membered into five-membered naphthenic rings [6]. Upare et al. [7] studied iridium catalyst supported on USY zeolite doped with potassium for hydrotreating of light cycle oil (LCO). They found that the elimination of strong acid sites by K reduces the formation of cracking products. In agreement with these results, it was reported that zeolites with a low density of Brønsted acid sites favor ring opening, but a strong Brønsted acidity produces excessive cracking, dealkylation and coke formation [8,9]. Platinum-modified zeolites (Beta, Y, Mordenite) were investigated in the ring opening of decalin by Kubicka et al. [10]. They found that the interaction between platinum and Brønsted acid sites

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decreases the amount of cracking products. Moreover, Santikunaporn et al. [11] reported that the production of ring-contraction and ring-opening products from tetralin is much more effective on Pt/HY catalysts as well as physical mixtures of HY and Pt than on HY catalysts. The metal dispersion and the acidity of the catalysts are key parameters influencing the performances of bifunctional catalysts. The MCP ring-opening mechanism depends on the metal dispersion for Rh-based catalysts [12]. For Pt–Rh bimetallic catalysts supported on alumina or silica tested in methylcyclohexane ring opening under pressure, it was concluded that the metal dispersion influences the selectivity to ring opening products [13]. On the other hand, when Pd–Pt catalysts supported on a mesoporous aluminosilicate were studied for naphthalene hydrogenation, the method of metal incorporation (by direct incorporation in the synthesis gel, impregnation or ion exchange) affected the accessibility of the metal surface [14]. Pd–Rh catalysts supported on mesoporous aluminosilicate were used in industrial processes aiming to improve diesel quality by hydrogenation and ring-opening of aromatic components by increasing the thioresistance [15].

In the open literature, there are numerous studies on bimetallic systems used for hydrogenolysis of naphthenic compounds, especially methylcyclopentane [16,17] and a few on methylcyclohexane and decalin at high pressure. The selective ring opening of C<sub>6</sub> rings may occur via the isomerization to C<sub>5</sub> rings [5,10,18–23]. Resasco et al. [24] reported that the decalin ring opening is catalyzed by both the acidic function through  $\beta$ -scission and the metal via dicarbene mechanism leading to highly isomerized products. Recently, Moraes et al. [25] proposed a mechanism for decalin and methylcyclohexane opening on Ir/WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts. The ring contraction reaction mainly occurs according to a bifunctional mechanism. Moreover, the formation of olefins by dehydrogenation of decalin on the metal sites is manifested by a rapid cis/trans-decalin isomerization. For ring-opening reactions, two pathways are considered: a direct one occurring on the metal sites, and an indirect one involving the formation and then, the opening of contraction products on the metallic sites or via a bifunctional mechanism. Until now the discussion on the role of acid and metal functions in each reaction step continues [26]. In a previous study [27], bimetallic Rh–Pd catalysts with various Rh/Pd ratios were deposited by coimpregnation on supports with various acidities, namely alumina, silica and silica–alumina in order to study the effect of the support and to optimize the metal composition for each type of support. Alumina was the best support for ring opening of methylcyclohexane, whereas the silica–alumina (SIRAL 40) led to the highest performances for the transformation of decalin, silica being inappropriate for both reactions. Also the best Rh/Pd ratio depended on the support, the optimum being Rh/Pd  $\approx$  0.5 on alumina and Rh/Pd  $\approx$  2 on SIRAL 40.

It is well known that the preparation method may affect the metal distribution at the support surface and consequently the metal function, the metal–support interaction and the acidity of the support. Nevertheless, to the best of our knowledge, no scientific paper deals with the influence of the preparation methods (coimpregnation or successive impregnation) on the catalytic properties related to methylcyclohexane and decalin ring opening using different supports (Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>). The objective of the present work is to study the influence of the incorporation method of Rh and Pd (coimpregnation and successive impregnation) used to prepare bimetallic catalysts with optimal metal loading on Al<sub>2</sub>O<sub>3</sub> (Rh/Pd  $\approx$  0.5) and SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> (SIRAL 40, Rh/Pd  $\approx$  2) (as determined in a previous paper [27]), on their performances for selective ring opening of methylcyclohexane and decalin.

## 2. Experimental

### 2.1. Preparation of the catalysts

Two supports were used in this study: a  $\gamma$ -alumina (Cyanamid Ketjen CK-300) and an alumina–silica (SIRAL 40 or S40 provided by

Sasol, 60.7 wt.% Al<sub>2</sub>O<sub>3</sub> and 39.3 wt.% SiO<sub>2</sub>), displaying a specific surface of 180 m<sup>2</sup> g<sup>-1</sup> and 514 m<sup>2</sup> g<sup>-1</sup>, and a pore volume of 0.5 cm<sup>3</sup> g<sup>-1</sup> and 0.9 cm<sup>3</sup> g<sup>-1</sup>, respectively. Prior to use, the two supports were treated by calcination under air at 450 °C for 4 h (10 °C min<sup>-1</sup>, 60 cm<sup>3</sup> min<sup>-1</sup>).

Rh–Pd bimetallic catalysts were prepared either by classical coimpregnation (CI) or by successive impregnations (SI). For the CI method, the support mixed with an aqueous solution of HCl (0.2 mol L<sup>-1</sup>) was left unstirred at room temperature for 1 h. Then, an aqueous solution containing both metallic precursors (RhCl<sub>3</sub> and PdCl<sub>2</sub> from Sigma-Aldrich) was added in order to respect a 1 wt.% total metal charge, and a specific Rh/Pd atomic ratio (R) i.e. R = 0.5 for Al<sub>2</sub>O<sub>3</sub> and R = 2 for S40, respectively. These atomic ratios are optimal for each support according to our previous studies dedicated to the SRO of decalin and MCH on Rh–Pd catalysts prepared by CI with various R ratios [27]. After 1 h under stirring at room temperature, the catalyst was dried in a thermostated bath at 70 °C then in a stove at 120 °C overnight, and finally calcined at 300 °C in flowing air (60 cm<sup>3</sup> min<sup>-1</sup>, 4 h) and reduced at 500 °C under flowing H<sub>2</sub> (60 cm<sup>3</sup> min<sup>-1</sup>, 4 h). The reduction temperature was chosen according to the catalytic test temperatures, especially regarding MCH conversion, which can reach 450 °C, and also to stabilize the metal function. The CI catalysts thus obtained (R0.5/Al<sub>2</sub>O<sub>3</sub> and R2/S40) are named CI/support.

For the SI catalysts, the atomic Rh/Pd ratios used for each support were the same than for CI samples. The incorporation of the first precursor solution (RhCl<sub>3</sub> or PdCl<sub>2</sub>) was performed as previously with the required metallic content. The sample was calcined and reduced in the same conditions as for CI catalysts. The second precursor was further introduced by the same procedure and the catalysts were again activated by calcination and reduction. These catalysts are designated SI Rh–Pd/support and SI Pd–Rh/support, according to the order in which the metals are added (Pd before Rh and Rh before Pd, respectively).

Moreover, 1 wt.% Pd and 1 wt.% Rh monometallic catalysts were prepared by impregnation and activated according to the same steps as described previously for the bimetallic catalysts. These catalysts are named Pd1/support and Rh1/support.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used to determine the final composition of the metal function. For that purpose, the solid sample was first treated by digestion in an acid solution.

### 2.2. Determination of the metallic accessibility by H<sub>2</sub> chemisorption

The metallic accessibility of the Pd, Rh and Rh–Pd particles on the surface of the catalyst was evaluated by hydrogen chemisorption after reduction for 1 h at 500 °C (10 °C min<sup>-1</sup>, H<sub>2</sub> 30 cm<sup>3</sup> min<sup>-1</sup>) of a 100 mg sample. Then, hydrogen adsorbed on the surface was eliminated by an argon flow (30 cm<sup>3</sup> min<sup>-1</sup>) for 2 h at 500 °C. After cooling down to 70 °C in argon, calibrated pulses of H<sub>2</sub> were injected into the reactor (HC1) until saturation of the sample. A second set of pulses was injected (HC2) after flushing the reactor with argon during 30 min. The metallic accessibility was determined by the difference HC1 – HC2 considering that one hydrogen atom chemisorbs on one accessible Pd or Rh atom (i.e. H/Pd and H/Rh = 1).

### 2.3. Temperature-programmed reduction (TPR)

Analyses by temperature-programmed reduction were performed in an Ohkura TP2002 apparatus equipped with a thermal conductivity detector. Prior to TPR, the catalyst samples were pretreated in situ in air at 400 °C for 1 h. The reduction was further programmed from 0 to 700 °C at 10 °C min<sup>-1</sup> in a gas stream of 5.0% hydrogen in argon (molar base).

## 2.4. Cyclopentane (CP) hydrogenolysis

The conditions of the cyclopentane hydrogenolysis were the following: catalyst mass = 150 mg, reaction temperature = 300 °C, pressure = 0.1 MPa, H<sub>2</sub> flow rate = 36 cm<sup>3</sup> min<sup>-1</sup>, CP flow rate = 0.483 cm<sup>3</sup> h<sup>-1</sup>. The catalysts were first pretreated by reduction for 1 h at 500 °C under hydrogen flow (60 cm<sup>3</sup> min<sup>-1</sup>). A Varian 3400 CX chromatograph equipped with a capillary column (Phenomenex ZB-1) and a flame ionization detector was used to analyze the products.

## 2.5. Temperature-programmed desorption (TPD) of pyridine

The amount and the strength of the acid sites were determined by TPD of pyridine. Samples (200 mg) impregnated with an excess of pyridine were rinsed and heated in a nitrogen stream at 110 °C for 1 h to eliminate the excess of physisorbed pyridine. Then the temperature was increased at 10 °C min<sup>-1</sup> to a final value of 700 °C. The amount of desorbed pyridine was measured by gas chromatography with a flame ionization detector. The estimated error in the position and area of the peaks is approximately 7% [28].

## 2.6. Isomerization of 3,3-dimethyl-1-butene (33DM1B)

The catalyst (50 mg) was pretreated in situ by reduction at 450 °C (H<sub>2</sub> 60 cm<sup>3</sup> min<sup>-1</sup>, 1 h), and then cooled under N<sub>2</sub> (30 cm<sup>3</sup> min<sup>-1</sup>) to reach the reaction temperature. This temperature was adjusted in order to obtain low conversions and to avoid secondary reactions. The partial pressure of the reagent (injected from the saturator) and the flow rate were 20.9 kPa and 15.2 mmol h<sup>-1</sup>, respectively. For the conversion, a 6.5% variance was determined in a set of seven experiments conducted to estimate the error associated to this measurement [29].

## 2.7. Ring opening of methylcyclohexane (MCH)

MCH hydrogenolysis was performed in a fixed-bed continuous reactor in gas phase, in the following reaction conditions: catalyst mass = 1.5 g, total pressure = 3.9 MPa, molar ratio H<sub>2</sub>/MCH = 8, WHSV = 2 h<sup>-1</sup> and temperature = 250–450 °C. Under these experimental conditions, intra- and extra-granular diffusion limitations were absent, as previously checked [30]. Before reaction, the catalysts were reduced in situ under 3.9 MPa of H<sub>2</sub> (60 cm<sup>3</sup> min<sup>-1</sup>) at 500 °C for 1 h. During the MCH hydrogenolysis, the conversion was measured at various temperatures programmed in 25 °C steps, starting from an initial reaction temperature chosen according to the nature of each sample (metal loading, support). When a conversion near 100% was reached, the temperature was no longer increased. In average, four measurements were performed at each temperature, leading to a maximum estimated error of 5%.

## 2.8. Ring opening of decalin

The ring opening of decalin was performed in a stainless steel autoclave reactor, according to the following reaction conditions: catalyst mass = 1 g, volume of decalin = 25 cm<sup>3</sup>, hydrogen pressure = 3 MPa, temperature = 350 °C, and stirring rate = 1360 rpm. The decalin used for this study contained 37.5% of the cis isomer, with a trans/cis ratio equal to 1.63. Previously, it was checked that diffusional limitations due to mass transfer were negligible [29].

## 3. Results and discussion

### 3.1. Characterization of the metal function of the catalysts

Table 1 shows that the Rh/Pd atomic ratio determined by ICP practically agrees with the theoretical values (i.e. 0.5 and 2.0 for the Al<sub>2</sub>O<sub>3</sub> and S40 supports, respectively). On both supports, the catalysts prepared by coimpregnation (CI) exhibit higher H<sub>2</sub> chemisorption values than those

**Table 1**

Rh and Pd contents and Rh/Pd atomic ratio determined by ICP, hydrogen chemisorption, particle size (d) and conversion during cyclopentane hydrogenolysis obtained on the monometallic and bimetallic catalysts prepared by coimpregnation (CI) or successive impregnations (SI).

| Catalyst                                | Rh (wt.%) | Pd (wt.%) | Rh/Pd | Hydrogen chemisorption <sup>a</sup> | d <sup>b</sup> (nm) | CP <sup>c</sup> |
|---|-----------|-----------|-------|-------------------------------------|---------------------|-----------------|
| Pd1/Al <sub>2</sub> O <sub>3</sub>      |           | 0.83      | –     | 16                                  | 5.4                 | 7.3             |
| CI/Al <sub>2</sub> O <sub>3</sub>       | 0.31      | 0.61      | 0.53  | 39                                  | 2.3                 | 33.7            |
| SI Rh–Pd/Al <sub>2</sub> O <sub>3</sub> | 0.32      | 0.65      | 0.51  | 33                                  | 2.6                 | 31.0            |
| SI Pd–Rh/Al <sub>2</sub> O <sub>3</sub> | 0.32      | 0.67      | 0.49  | 36                                  | 2.4                 | 19.6            |
| Rh1/Al <sub>2</sub> O <sub>3</sub>      | 0.81      |           | –     | 43                                  | 1.9                 | 98.1            |
| Pd1/S40                                 |           | 0.78      | –     | 37                                  | 2.5                 | 14.6            |
| CI/S40                                  | 0.52      | 0.28      | 1.92  | 34                                  | 2.6                 | 38.2            |
| SI Rh–Pd/S40                            | 0.51      | 0.29      | 1.82  | 28                                  | 3.1                 | 28.7            |
| SI Pd–Rh/S40                            | 0.53      | 0.28      | 1.96  | 28                                  | 3.1                 | 34.2            |
| Rh1/S40                                 | 0.79      |           | –     | 36                                  | 2.3                 | 72.0            |

<sup>a</sup> H/(Pd + Rh) \* 100.

<sup>b</sup> Deduced from H<sub>2</sub> chemisorption.

<sup>c</sup> Cyclopentane conversion (%).

prepared by successive impregnations (SI) and smaller metal particle sizes. This difference could be due to the formation of metal alloys in the catalysts prepared by successive impregnation compared to random deposition of the second metal on the support by coimpregnation as reported by Del Angel et al. [31]. The blocking of the acid sites caused by the deposition of the second metal on the support would be consistent with the lower total acidity of the catalysts prepared by SI in SIRAL 40. In both preparation methods a strong interaction between the metal particles was found, so it is difficult to determine whether the second metal is located over the first metal or directly adjacent to the support.

No difference in the hydrogen chemisorption values was observed on the SI catalysts deposited on S40 regarding the order of metal addition, while the Rh incorporation in a second step leads to an increase in the metal dispersion on the catalysts supported on Al<sub>2</sub>O<sub>3</sub>.

Hydrogenolysis of cyclopentane (CP) is a structure sensitive reaction, which requires a number of metal atoms with a given configuration. Large metallic crystals are more likely to display specific ensembles for the cyclopentane hydrogenolysis, therefore they are more active. On the other hand, well dispersed metal crystals have low CP hydrogenolysis activity [32,33]. This effect could be due to geometric or electronic factors operating on active metallic particles. The geometric factor involves the blocking of active sites ensembles by added promoter atoms. The electronic factor corresponds to the modification of the electronic density of a metallic atom due to an interaction with the other metal or neighboring atoms. Such electronic modification would in turn change the energy of adsorption of the chemical species participating in the catalytic reaction. Table 1 shows the conversion values obtained for the cyclopentane hydrogenolysis reaction. Monometallic Rh catalysts present hydrogenolytic activity remarkably higher than the Pd ones. As the catalysts supported on S40 contain more Rh than the ones supported on Al<sub>2</sub>O<sub>3</sub> (higher Rh/Pd ratio), a higher hydrogenolytic activity of the bimetallic S40 series is expected. However, no great difference in conversion values is observed between both series. This can be attributed to the support influence: indeed, the monometallic Rh1/S40 catalyst displays a conversion notably lower than Rh1/Al<sub>2</sub>O<sub>3</sub>, despite comparable Rh contents and larger Rh particles on S40 supported sample.

The profiles of temperature-programmed reduction (TPR) shown in Fig. 1 allow the appreciation of the degree of metal–metal and metal–support interactions. By comparison of the monometallic catalysts supported on Al<sub>2</sub>O<sub>3</sub> and S40, it can be observed that Pd oxides are reduced at a lower temperature than the Rh oxides on both supports. It can be seen that Pd1/Al<sub>2</sub>O<sub>3</sub> was reduced at 75 °C while Pd1/S40 shows a reduction peak centered at about 111 °C. This shows a higher Pd-support interaction on S40 than on Al<sub>2</sub>O<sub>3</sub>. In the case of monometallic Rh catalysts, the reduction peak of Rh oxides was centered at a similar temperature in both supports but the Rh1/S40 catalyst showed a

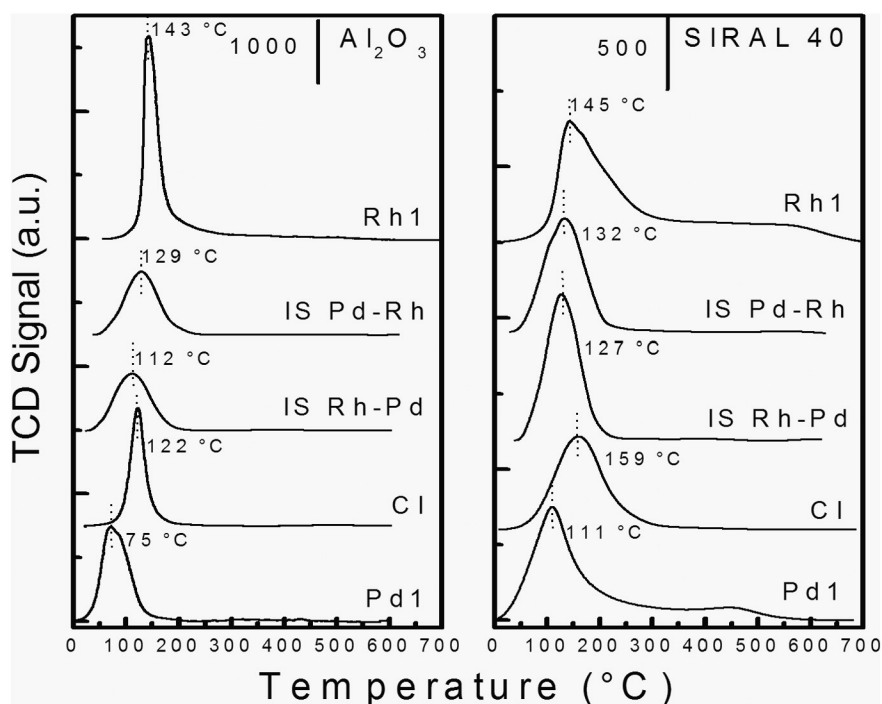


Fig. 1. TPR of the monometallic, CI and SI bimetallic catalysts supported on  $\text{Al}_2\text{O}_3$  and S40. The values of the curves correspond to the maximum peak temperatures.

reduction peak extended until 250 °C, which can be ascribed to the presence of small metal particles in strong interaction with the support [27]. This behavior is not observed on the catalysts supported on  $\text{Al}_2\text{O}_3$ . All the CI and SI bimetallic catalysts exhibit a single reduction peak at an intermediate temperature, attributed to a simultaneous reduction of Pd and Rh oxides, indicating a strong Pd–Rh interaction whatever the preparation method. According to the observed reduction temperatures for all the bimetallic catalysts (>100 °C), there is no large isolated monometallic Pd particles on these samples, since the reduction of large crystalline  $\text{PdO}$  to  $\text{Pd}^0$  was shown to occur at room temperature [34,35]. Moreover, the reduction temperatures of the bimetallic catalysts supported on S40 are higher than those supported on  $\text{Al}_2\text{O}_3$ . It must be also considered that the reduction peak practically does not change with the Rh/Pd ratio on S40 [27]. Therefore, the metal–support interaction must be higher on S40 than on  $\text{Al}_2\text{O}_3$ . The larger profiles of reduction peaks for the S40 series could be attributed to a more heterogeneous distribution of the metals species on the support surface. The CI/S40 catalyst exhibits a reduction peak centered at 159 °C, whereas for the SI/S40 catalysts the peak is placed around 130 °C. This difference may be due to the presence of smaller particles in stronger interaction with the support in the first case, in agreement with the hydrogen chemisorption results (Table 1). The differences in the metal dispersion of  $\text{Al}_2\text{O}_3$  series are not revealed by TPR results.

On the TPR profiles, the reduction peak attributed to the decomposition of the  $\beta\text{-PdH}_x$  phase was not detected due to its overlapping with the peak at ~120 °C [27,29].

### 3.2. Characterization of the acid function

It was shown in a previous paper that the addition of Pd and Rh on the  $\text{Al}_2\text{O}_3$  and S40 supports increases their acidity, which is due to the introduction of chlorine species during the impregnation process [27]. Thus, on the monometallic and bimetallic CI catalysts, the chlorine content is ~0.9% on  $\text{Al}_2\text{O}_3$  and ~1.4% on S40.

Pyridine desorption experiments provide information on the distribution of the strength of the acid sites, and the area under the curve (given in Table 2) indicates the total acidity of the catalysts. Also, the desorption temperatures of pyridine allow to classify the acid sites

in three categories: weak (110–250 °C), moderate (250–450 °C) and strong (450–600 °C). Catalysts supported on S40 present higher total acidity than the catalysts supported on  $\text{Al}_2\text{O}_3$ . Even if S40 is clearly more acidic than alumina, this difference is also due in part to the fact that the Brønsted acid sites of alumina are too weak to form pyridinium ions. In addition, on this support, pyridine is only bound to Lewis acid sites, whereas on the S40 support pyridine is bound on both types of acid sites. For all SI catalysts, no substantial difference in acidity was found according to the order of metal addition. In the case of the S40 series, the total acidity of the SI catalysts is almost 40% lower than that obtained on the CI sample, whereas the preparation method displays no influence on the total acidity of the catalysts supported on  $\text{Al}_2\text{O}_3$ . In order to explain the differences it must be taken into account that alumina and silica can interact with the impregnation solution, notably by partial dissolution [36,37]. As a consequence, during metal impregnation a certain quantity of Al and Si is dissolved and later precipitate during water elimination. It could be argued that in the case of alumina, this phenomenon is very slow and has little influence on the support (i.e., two impregnations have the same influence that only one impregnation step) while in the case of S40, this dissolution and

Table 2

Total pyridine TPD area (relative to CI/ $\text{Al}_2\text{O}_3$  catalyst), and acid sites distribution determined from the surface of the desorption peak in the 110–250 °C range (weak acid sites), 250–450 °C range (medium acid sites) and 450–600 °C range (strong acid sites).

| Catalyst                          | Pyridine TPD | Acid sites distribution (%) |                     |                     |
|-----------------------------------|--------------|-----------------------------|---------------------|---------------------|
|                                   |              | Weak (110–250 °C)           | Medium (250–450 °C) | Strong (450–600 °C) |
| Pd1/ $\text{Al}_2\text{O}_3$      | 0.9          | 2                           | 66                  | 32                  |
| CI/ $\text{Al}_2\text{O}_3$       | 1.0          | 3                           | 95                  | 2                   |
| SI Rh–Pd/ $\text{Al}_2\text{O}_3$ | 1.1          | 4                           | 86                  | 10                  |
| SI Pd–Rh/ $\text{Al}_2\text{O}_3$ | 1.2          | 3                           | 90                  | 7                   |
| Rh1/ $\text{Al}_2\text{O}_3$      | 0.9          | 4                           | 95                  | 1                   |
| Pd1/S40                           | 2.9          | –                           | 51                  | 49                  |
| CI/S40                            | 3.1          | 4                           | 76                  | 20                  |
| SI Rh–Pd/S40                      | 1.9          | 1                           | 81                  | 18                  |
| SI Pd–Rh/S40                      | 1.8          | 1                           | 82                  | 17                  |
| Rh1/S40                           | 3.1          | 3                           | 79                  | 18                  |

reprecipitation phenomenon has more influence on the total acidity because the acid sites are created by the interaction between Al and Si. Another factor that may play a role is the fact that Siral 40 has a specific surface area three times higher than alumina. It can be seen in Table 2 that all the catalysts exhibit mainly moderate acidity sites. However, the catalysts supported on S40 possess more strong acid sites than the catalysts supported on  $\text{Al}_2\text{O}_3$ . Monometallic Pd catalysts proportionately exhibit more strong acid sites than the other catalysts.

The reaction of 33DM1B isomerization was used to estimate the concentration of Brønsted acid sites. Kemball et al. [35,38] demonstrated that the Lewis acid sites are not involved in this reaction. In the experimental conditions used (reaction temperature < 300 °C) only two isomers are formed: 2,3-dimethyl-2-butene (23DM2B) and 2,3-dimethyl-1-butene (23DM1B) [39]. Table 3 shows the 33DM1B conversion and the selectivity to 23DM2B and 23DM1B at different reaction temperatures for the catalysts supported on  $\text{Al}_2\text{O}_3$  and S40. The reaction was performed at different temperatures according to the support acidity in order to obtain low reaction rates avoiding diffusion and deactivation problems. Additional experiments performed at different reaction temperatures with the same catalyst showed that the conversion increased with the reaction temperature (results not shown). Then, it can be inferred that the amount of Brønsted acid sites on S40 supported catalysts significantly exceeds that of  $\text{Al}_2\text{O}_3$  supported ones (even at 250 °C on  $\text{Al}_2\text{O}_3$ , conversions are lower than those obtained at 150 °C on S40). Regarding the preparation method, the observed differences between catalysts of a given series are less than 5%, inferior to the 6.5% experimental error estimated for this experiment [29]. The values of selectivities in 23DM1B and 23DM2B at 150 °C for S40 and 250 °C for  $\text{Al}_2\text{O}_3$  are similar to the theoretical ones calculated at the thermodynamic equilibrium at both temperatures.

### 3.3. Catalytic evaluation

#### 3.3.1. Ring opening of MCH

The evolution of methylcyclohexane (MCH) conversions as a function of reaction temperature (Fig. 2) shows that the S40 supported catalysts are more active than those supported on  $\text{Al}_2\text{O}_3$ . Concerning the preparation method, the Cl/ $\text{Al}_2\text{O}_3$  catalyst displays higher conversion from 375 °C than those prepared by SI. In the case of the  $\text{Al}_2\text{O}_3$  series, there is no difference between the activities of the two SI catalysts, whereas on S40, the SI Pd–Rh sample exhibits higher conversion compared to the SI Rh–Pd, without exceeding the conversion of the Cl/S40 catalyst.

The selectivities to cracking ( $\text{C}_1$  to  $\text{C}_6$  alkanes), isomerization (saturated  $\text{C}_5$  cyclic alkanes with 7 carbon atoms), ring opening (RO) and dehydrogenated (toluene) products as a function of conversion are shown in Figs. 3 and 4 for the  $\text{Al}_2\text{O}_3$  and S40 series, respectively. The isomerization reaction, which needs an acid function, converts the  $\text{C}_6$  ring of MCH into  $\text{C}_5$  alkylcyclopentanes, which are more easily opened to paraffins. In general, for each series, higher reaction temperatures, inducing higher conversions, promote cracking reactions due to the

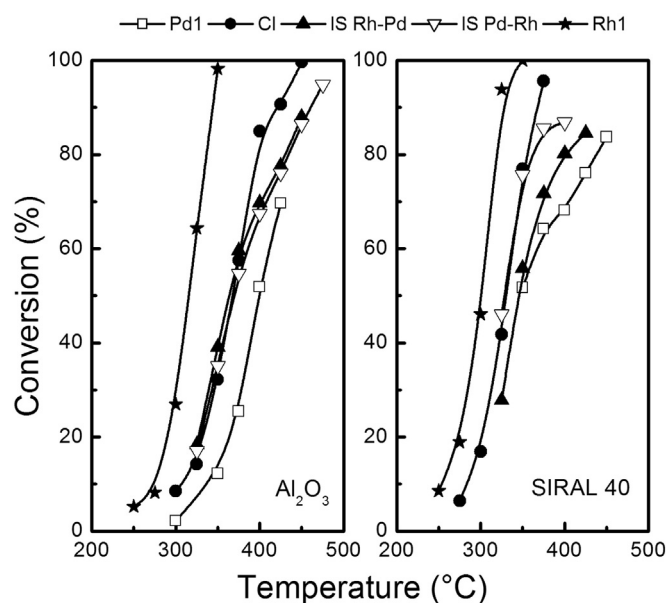


Fig. 2. Methylcyclohexane (MCH) conversion as a function of reaction temperature for the monometallic, Cl and SI bimetallic catalysts supported on  $\text{Al}_2\text{O}_3$  and S40 in a fixed-bed continuous flow reactor.  $\text{H}_2/\text{MCH} = 8$ , total pressure = 3.9 MPa, mass of catalyst = 1.5 g, and WHSV = 2  $\text{h}^{-1}$ .

high activation energy of cracking reaction [40]. In a previous work, it was found that the major part (>70%) of cracking products are constituted of  $\text{C}_1$  and  $\text{C}_6$  products, mainly produced by hydrogenolysis on the metallic function of the catalysts [27]. For this reason, monometallic Rh catalysts, which exhibit high hydrogenolytic activity, produce more cracking products than monometallic Pd catalyst. The catalysts prepared by coimpregnation on both supports display a higher selectivity to cracking products than the corresponding bimetallic catalysts prepared by SI. These results are in agreement with the values of cyclopentane conversion reported in Table 1 highlighting the great influence of the metallic function on the formation of cracking products. However, an acid-catalyzed cracking reaction involving strong acid sites can also occur, and produce  $\text{C}_3$  and  $\text{C}_4$  products [40]. This explains the higher selectivity to cracking products of S40 supported catalysts compared to  $\text{Al}_2\text{O}_3$  supported ones, the S40 series containing more total acid sites and Brønsted acid sites than the  $\text{Al}_2\text{O}_3$  series.

The selectivities to isomerization products evolve inversely compared to the selectivities to cracking products, i.e. the catalyst with the highest selectivity to cracking products leads to the lowest selectivity to isomerization on both supports. Pd1 and the bimetallic catalysts prepared by SI exhibit the higher selectivity to isomers in both series. Moreover, these catalysts supported on  $\text{Al}_2\text{O}_3$  are more selective to isomers than the catalysts supported on S40. The isomerization reactions are catalyzed by the acid function of the catalyst. Therefore, higher selectivity to isomers is expected on the S40 series. The poor selectivity to isomers of the S40 series compared to  $\text{Al}_2\text{O}_3$  series could result from the higher formation of cracking products on the catalysts supported on S40.

The selectivities to dehydrogenated products increase in both series with the conversion (i.e. with the reaction temperature), since the dehydrogenation is an endothermic and reversible reaction [40]. The fact that the dehydrogenation reaction is more noticeable on the catalysts supported on  $\text{Al}_2\text{O}_3$  compared to the ones supported on S40 can be linked to the hydrogen chemisorption values reported in Table 1.

In both series the selectivity to RO products is higher on the catalysts prepared by coimpregnation compared to those prepared by successive impregnations. The different behaviors can be attributed to the greater metal dispersion on Cl catalysts and in a less extent to the different acidity. On both series, SI catalysts are more selective to isomerized products than the catalyst prepared by Cl (and even more selective to dehydrogenation

Table 3

Results of 33DM1B isomerization (conversion and selectivity to 23DM1B and 23DM2B) used as model reaction for characterizing the Brønsted acidity.

| Catalyst                          | T (°C) | Conversion (%) | Selectivity (%) |        |
|-----------------------------------|--------|----------------|-----------------|--------|
|                                   |        |                | 23DM1B          | 23DM2B |
| Pd1/ $\text{Al}_2\text{O}_3$      | 250    | 8.2            | 31.1            | 68.9   |
| Cl/ $\text{Al}_2\text{O}_3$       | 250    | 8.3            | 37.9            | 62.1   |
| SI Rh–Pd/ $\text{Al}_2\text{O}_3$ | 250    | 7.4            | 37.3            | 62.7   |
| SI Pd–Rh/ $\text{Al}_2\text{O}_3$ | 250    | 7.2            | 38.3            | 61.7   |
| Rh1/ $\text{Al}_2\text{O}_3$      | 250    | 20.1           | 31.3            | 68.7   |
| Pd1/S40                           | 150    | 24.7           | 18.1            | 81.9   |
| Cl/S40                            | 150    | 27.9           | 22.5            | 77.5   |
| SI Rh–Pd/S40                      | 150    | 25.9           | 22.5            | 77.5   |
| SI Pd–Rh/S40                      | 150    | 23.3           | 23.4            | 76.6   |
| Rh1/S40                           | 150    | 22.2           | 18.2            | 81.8   |

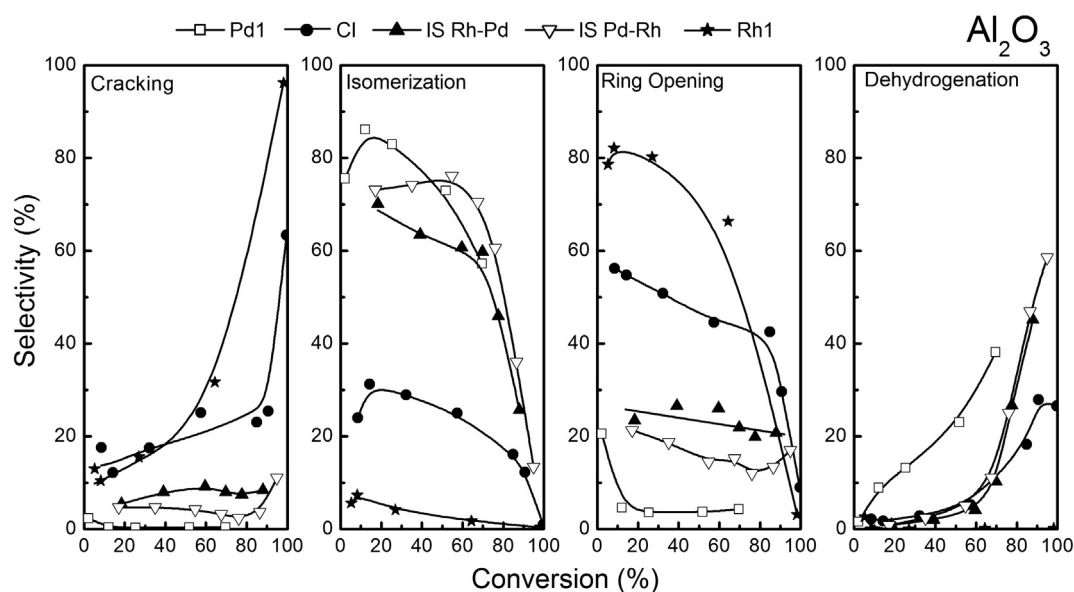


Fig. 3. Selectivity to cracking, isomerization, ring opening and dehydrogenation products as a function of MCH conversion for the monometallic, CI and SI bimetallic catalysts supported on  $\text{Al}_2\text{O}_3$ .

on the  $\text{Al}_2\text{O}_3$  support). As a consequence the selectivity to RO products decreases.

### 3.3.2. Ring opening of decalin

The reaction products of decalin transformation were classified using the same criterion reported in a previous work [41], i.e. in: Cr: cracking products ( $\text{C}_1$ – $\text{C}_9$ ); RO: ring opening products ( $\text{C}_{10}$ ); RC: ring contraction products; DH: naphthalene and others including heavy dehydrogenated products. Fig. 5 shows percentages of trans and cis-decalin and yields to Cr, RC, RO, and DH after 6 h of reaction at 350 °C. The catalysts with higher total and Brønsted acidities (i.e. supported on S40) are more active, whereas the ones supported on  $\text{Al}_2\text{O}_3$  convert less than 20% of decalin after 6 h. Moreover, catalysts supported on  $\text{Al}_2\text{O}_3$  produce mainly dehydrogenated products. On the S40 series, RO products are predominant and for the CI catalyst, which is the most acidic of the series, a noticeable amount of cracking products and a low yield to dehydrogenation products (naphthalene) are also

observed. Consequently, the acidity of the catalysts is a key factor for the ring opening of decalin.

Santikunaporn et al. [11] and Sousa-Aguier et al. [42] found that trans-decalin is less reactive than cis-decalin due to the acid-catalyzed reaction. For 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 also be explained taking into account the ring strain values reported by Wiberg [43]:  $-7.9 \text{ kJ mol}^{-1}$  for cis-decalin, against  $5.0 \text{ kJ mol}^{-1}$  for trans-decalin. Consequently, trans-decalin is thermodynamically more stable and much less reactive than cis-decalin towards ring-opening. The trans/cis-decalin ratios after 6 h of reaction reported on Fig. 5 are higher than the initial one (1.63), probably due to the higher reactivity of the cis isomer and also to the catalytic cis/trans isomerization reaction [44]. It is known that cis-decalin is more selectively converted to RO products than trans-decalin, which is converted mainly into cracking products [11]. The higher yield to RO products obtained

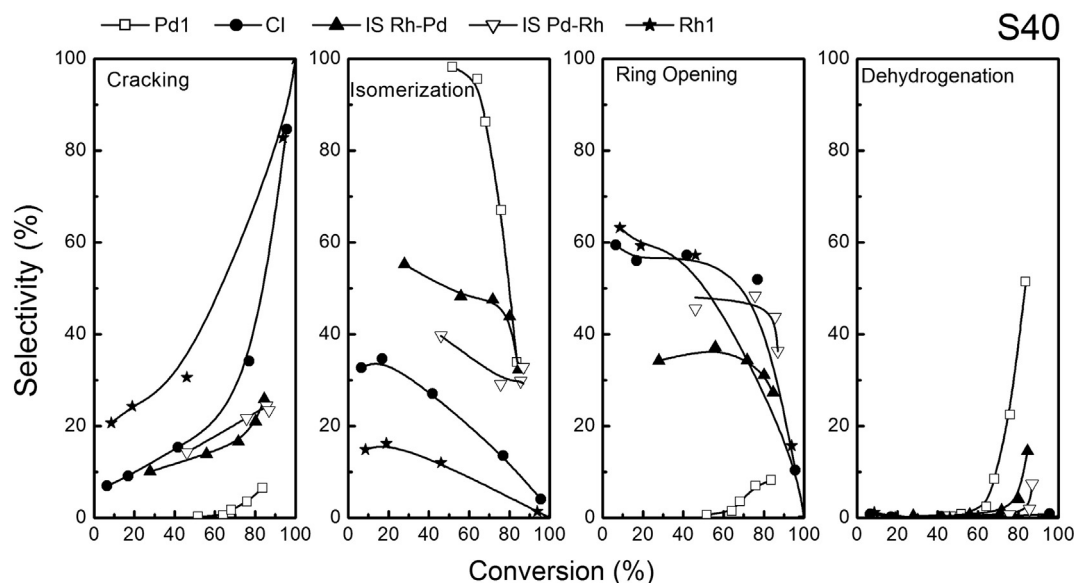
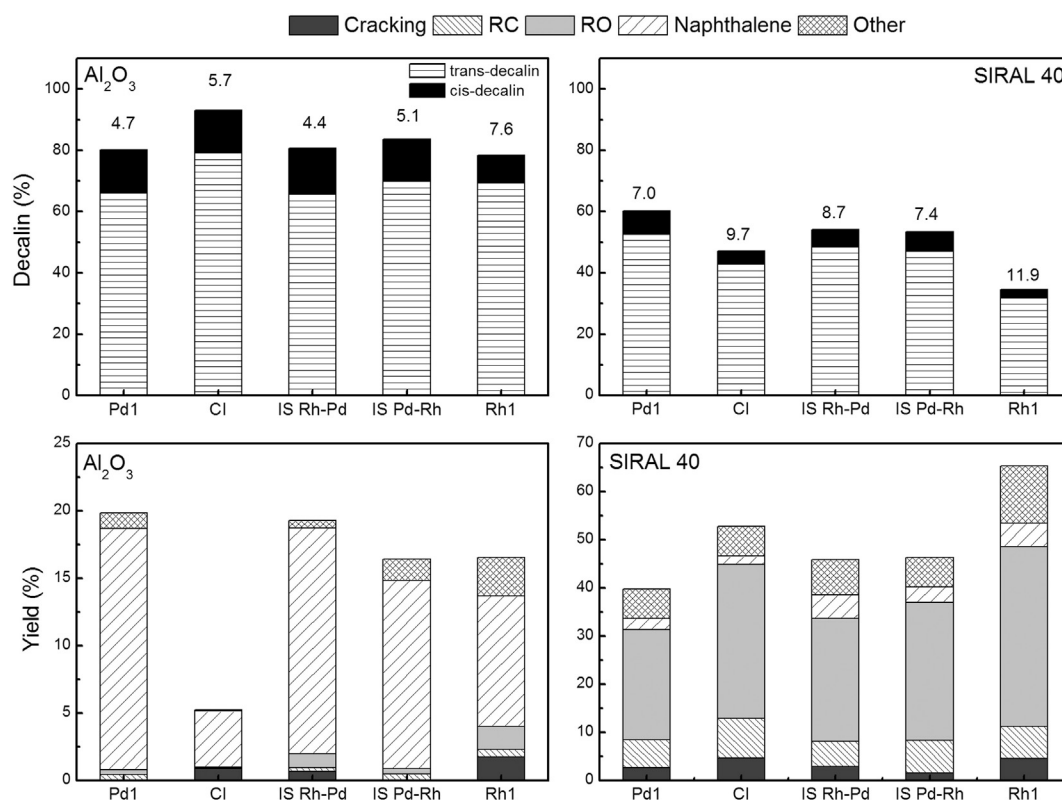


Fig. 4. Selectivity to cracking, isomerization, ring opening and dehydrogenation products as a function of MCH conversion for the monometallic, CI and SI bimetallic catalysts supported on S40.



**Fig. 5.** Trans and cis-decalin and yield to cracking, ring contraction (RC), ring opening (RO), naphthalene and other dehydrogenated products after 6 h reaction time of decalin transformation in a batch reactor.  $T = 350\text{ }^{\circ}\text{C}$ ,  $\text{H}_2$  pressure = 3 MPa, mass of catalyst = 1 g, volume of decalin = 25 cm<sup>3</sup>, stirring rate = 1360 rpm. (Numbers at the top of the bars indicate the trans/cis ratios).

with the catalysts supported on S40 is related to the lower amount of cis-decalin in the final reaction mixture. In this series, the CI/S40 catalyst, which displays the highest acidity and metal dispersion, favors the ring opening of decalin and limits the dehydrogenation reactions. For the SI/S40 catalysts, changing the metal addition order has no consequence on the catalytic behavior, in agreement with the similar dispersion and acidity of both samples. Finally, it can be concluded that the support acidity has more influence than the hydrogenolytic character of Rh in decalin conversion.

### 3.3.3. Comparison of the two ring opening reactions

In order to compare the catalytic performances obtained for ring opening of MCH and decalin, Tables 4 and 5 show results of conversion and selectivity to cracking, isomerization, ring opening and dehydrogenated products at 350 °C during decalin and MCH transformations, respectively. The conversion values are in agreement

with the thermodynamic predictions, with systematically higher conversions of MCH compared to decalin for a given catalyst. However, the comparison of MCH and decalin conversion remains a difficult task because the decalin reaction was performed in a batch reactor and the MCH one in a continuous flow reactor. For both reactions, the best catalyst in terms of conversion and RO selectivity is the CI/S40 sample. On this catalyst, a RO selectivity of 52% is reached with 77% conversion during MCH reaction, cracking products being also formed in noticeable amount (34% of selectivity). During decalin conversion, the CI/S40 catalyst is less active (conversion = 53%) but leads to higher RO selectivity (near 61%), the other major products being both ring contraction and dehydrogenation products (selectivities about 15%).

In conclusion, for both reactions, the best balance between the metal and acid functions which leads to the best RO yields is obtained by using the S40 support and the CI preparation method. The acidity of the support is crucial for the transformation of the naphthenic rings, more notably in the case of decalin compared to MCH. The deposition method

**Table 4**

Decalin conversion and selectivity to cracking (Cr), ring contraction (RC), ring opening (RO) and dehydrogenated products (DH) in a batch reactor after 6 h of reaction.  $T = 350\text{ }^{\circ}\text{C}$ ,  $\text{H}_2$  pressure = 3 MPa, mass of catalyst = 1 g, volume of decalin = 25 cm<sup>3</sup>, and stirring rate = 1360 rpm.

| Catalyst                                | Conversion (%) | Selectivity (%) |      |      |      |
|---|----------------|-----------------|------|------|------|
|   |                | Cr              | RC   | RO   | DH   |
| Pd1/Al <sub>2</sub> O <sub>3</sub>      | 19.9           | 0.3             | 2.0  | 1.7  | 96.0 |
| CI/Al <sub>2</sub> O <sub>3</sub>       | 7.0            | 16.6            | 0.8  | 1.7  | 80.9 |
| SI Rh–Pd/Al <sub>2</sub> O <sub>3</sub> | 19.3           | 3.5             | 1.5  | 5.4  | 89.6 |
| SI Pd–Rh/Al <sub>2</sub> O <sub>3</sub> | 16.4           | 0.4             | 2.7  | 2.2  | 94.7 |
| Rh1/Al <sub>2</sub> O <sub>3</sub>      | 16.6           | 10.5            | 3.5  | 10.3 | 75.7 |
| Pd1/S40                                 | 39.8           | 6.8             | 14.3 | 57.7 | 21.2 |
| CI/S40                                  | 52.8           | 8.9             | 15.5 | 60.5 | 15.1 |
| SI Rh–Pd/S40                            | 45.9           | 6.3             | 11.5 | 55.8 | 26.4 |
| SI Pd–Rh/S40                            | 46.5           | 3.3             | 14.7 | 61.7 | 20.3 |
| Rh1/S40                                 | 65.4           | 7.1             | 10.1 | 57.1 | 25.7 |

**Table 5**

MCH conversion and selectivity to cracking (Cr), isomerization (ISO), ring opening (RO) and dehydrogenated products (DH) in a fixed-bed continuous flow reactor.  $T = 350\text{ }^{\circ}\text{C}$ ,  $\text{H}_2/\text{MCH} = 8$ , total pressure = 3.9 MPa, mass of catalyst = 1.5 g, and WHSV = 2 h<sup>-1</sup>.

| Catalyst                                | Conversion (%) | Selectivity (%) |      |      |     |
|---|----------------|-----------------|------|------|-----|
|   |                | Cr              | ISO  | RO   | DH  |
| Pd1/Al <sub>2</sub> O <sub>3</sub>      | 12.2           | 0.4             | 86.1 | 4.6  | 8.9 |
| CI/Al <sub>2</sub> O <sub>3</sub>       | 32.2           | 17.4            | 28.9 | 50.8 | 2.9 |
| SI Rh–Pd/Al <sub>2</sub> O <sub>3</sub> | 39.1           | 8.0             | 63.5 | 26.5 | 2.0 |
| SI Pd–Rh/Al <sub>2</sub> O <sub>3</sub> | 35.0           | 4.7             | 74.2 | 18.7 | 2.4 |
| Rh1/Al <sub>2</sub> O <sub>3</sub>      | 98.2           | 96.2            | 0.4  | 3.2  | 0.2 |
| Pd1/S40                                 | 51.7           | 0.3             | 98.2 | 0.7  | 0.8 |
| CI/S40                                  | 76.9           | 34.1            | 13.6 | 51.9 | 0.4 |
| SI Rh–Pd/S40                            | 55.8           | 13.9            | 48.3 | 37.1 | 0.7 |
| SI Pd–Rh/S40                            | 75.7           | 21.7            | 29.2 | 48.4 | 0.7 |
| Rh1/S40                                 | 99.9           | 99.9            | 0.0  | 0.1  | 0.0 |

of the metallic functions constituted of Pd and Rh (CI or SI) seems to be less crucial. However, on S40 support, the higher dispersion of the metallic active sites of the CI sample can explain the best performances of this catalyst.

#### 4. Conclusion

Rh–Pd catalysts prepared by successive impregnations (SI) and coimpregnation (CI) supported on  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3\text{--SiO}_2$  (S40) were evaluated in methylcyclohexane and decalin ring opening reaction at high pressure. For a given support, the metallic functions were found quite comparable between the different preparation methods. However, slightly higher hydrogen chemisorption values were found for the CI samples compared to the SI ones. The total and Brønsted acidities of the S40 supported catalysts were significantly higher than that of those deposited on  $\text{Al}_2\text{O}_3$ . It was found that the preparation method affects the acidity of the catalysts, which depends on the support used. In S40, which has higher acidity than  $\text{Al}_2\text{O}_3$ , the total acidity of the catalysts prepared by successive impregnation is lower than the one of the catalysts prepared by coimpregnation. On the contrary, no major variation in acidity was found as a function of the preparation method when using  $\text{Al}_2\text{O}_3$  as support.

The best performances in MCH and decalin opening were obtained with the catalyst prepared by coimpregnation supported on S40, the most acidic support. The acidity is then decisive, notably to open the rings of decalin. Concerning the catalysts prepared by successive impregnations, changing the order of metal addition has little influence on the catalytic performances, in agreement with the comparable metal and acid functions observed. Consequently, the CI/S40 catalyst appears as the most appropriate formulation due to an optimal balance between the metal and acid functions which favors the opening of molecules with one and two naphthenic rings.

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