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# Carbonylation of Naphtha by a Rhodium Complex Immobilized on Poly(4-vinylpyridine)

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**Abstract** This work describes the carbonylation of hex-1-ene, cyclohexene, 2,3-dimethyl-but-1-ene and 2-methyl-pent-2-ene, their quaternary mixture and a real Venezuelan naphtha, catalyzed by a rhodium(I) [Rh(cod)(4-picoline)$_2$](PF$_6$) (cod = 1,5-cyclooctadiene) complex immobilized on poly(4-vinylpiridine) (P(4-VP)) in contact with methanol under carbon monoxide atmosphere. The conversion (%) of olefins to carbonylated products for the individual olefins decreases in the order: hex-1-ene (63) > cyclohexene (58) > 2,3-dimethyl-but-1-ene (50) > 2-methyl-pent-2-ene (31), under the following conditions: 0.5 g of P(4-VP) for [Rh] = 2 wt.% ($1 \times 10^{-4}$ mol), 10 mL of $CH_3OH$, [olefin] = $1 \times 10^{-2}$ mol, S/C = 100, P(CO) = 33 atm at 110 °C for 24 h. Other products such as $H_2$ and $CO_2$ coming from the catalysis of the water–gas shift reaction are observed.

**Keywords** Rhodium · Poly(4-vinylpyridine) · Carbonylation · Catalysis · Naphtha

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## 1 Introduction

The practice of immobilizing catalytically active transition metal complexes on polymers has spawned a class of materials that incorporate the major advantages of both heterogeneous and homogeneous systems into a single system, e.g. the high activity, specificity and reproducibility typical of homogeneous catalysts can be paired with the ease of product separation and catalyst recovery characteristic of heterogeneous catalysts [1–3].

The synthesis of oxygenated organic products by reaction of an olefinic substrate with CO and water or alcohols (ROH, R = H or alquil group, Eq. 1) in the presence of transition metal complexes has been known as Reppe reaction [4]. This reaction has received considerable attention [5–9] and it is the subject of a recent review [10].

$$R'HC{=}CH_2 + CO + ROH \rightarrow R'H_2C{-}CH_2C({=}O){-}OR \qquad (1)$$

The products coming from the catalytic carbonylation reactions of C6–C8 olefins by soluble and immobilized transition metal complexes offer access to wide range of important oxygenated compounds which could be used in a though be future industrial catalytic process for gasoline improving based on in situ carbonylation reaction over olefins present in naphtha [11].

The naphtha, which constitutes a stream extracted from crude oil, is formed by combinations of $C_5$–$C_8$ saturated and unsaturated hydrocarbons. The light naphtha is used principally for the formulation of gasoline. The olefin content in the naphtha is ca. 43.5% and it must be less than 6% in volume, according to the standard regulation [12, 13]. Higher amounts of these compounds in the gasoline induces chemical reactions in the combustion motors of the vehicles at high working temperatures, giving solid particles, which can block the injector and the valve system of the motor, therefore diminishing its efficiency.

A heterogeneous catalytic hydrogenation process is employed to reduce the olefin content of the naphtha to saturated hydrocarbons. However, this process has some limitations, which are associated with the high consumption of the expensive $H_2$ and production of low octane content gasoline. Accordingly, the direct carbonylation of the olefin in naphtha via the Reppe process could, in principle increased the octane content by allowing in situ transformation of this olefins in oxygenated compounds likes esters, aldehydes and acetals, among others and avoiding the expensive catalytic hydrogenation.

Work in our laboratories have long been concerned with the use of rhodium compounds immobilized on poly(4-vinylpyridine) (P(4-VP)) as catalysts for the hydroesterification and hydroformylation-acetalization of hex-1-ene under CO/methanol or CO/ethanol [14–16]. Due to their facile preparation, good stability, and moderate to high catalytic activities we have been able to demonstrate the versatility of these rhodium containing organic polymers as active catalysts for the aforementioned system.

In the present study we extend the use of the $[Rh(cod)(4\text{-picoline})_2](PF_6)/P(4\text{-VP})$ compound as an attractive candidate to catalyze the carbonylation of some olefins and a real naphtha.

## 2 Experimental

### 2.1 Materials and Instrumentation

4-Picoline (4-pic) was obtained from Aldrich and distilled over KOH. Methanol, hex-1-ene, cyclohexene, 2,3-dimethyl-but-1-ene and 2-methyl-pent-2-ene (Aldrich) were distilled prior to use. Poly(4-vinylpyridine)/divinylbenzene(2%), was used as provided by Reilly Industries. All gas mixtures $He/H_2$ (91.4%/8.6%, v/v), $CO/CH_4$ (94.16%/5.84%, v/v) and $CO/CH_4/CO_2/H_2$ (84.8%/5.1%/5.3%/4.8%, v/v) were purchased from BOC Gases and were used as received. The rhodium-immobilized complex was synthesized as reported [17]. Analyses of Rh concentration in the filtered solution were performed on a Perkin-Elmer Lambda 10 UV–Visible spectrophotometer and on a GBC Avanta atomic absorption spectrophotometer operated in the flame mode. In all cases, the immobilization of the rhodium complexes on 0.5–1.5 g of P(4-VP) is greater than 99%. This complex will be referred hereafter as $Rh(4\text{-pic})_2/P(4\text{-VP})$.

Gas sample analyses from catalysis runs were performed as previously described in detail [18] on a Hewlett-Packard 5890 Series II programmable (ChemStation) gas chromatograph fitted with a thermal conductivity detector. The column employed was Carbosieve-B (80–100) mesh obtained from Hewlett-Packard and using the $He/H_2$ mixture as the carrier gas. Analyses of liquid phase were done on a Buck Scientific 910 programmable gas chromatograph fitted with a MXT-1 (30 m × 0.52 mm × 1.0 mm) column and flame ionization detector, and using He as the carrier gas. A Varian Chrompack 3800 programmable gas chromatograph fitted with a CP-Sil-8-CB (phenyldimethylpolysiloxane) (30 m × 0.250 mm) column and a Varian Chrompack, Saturn 2000 mass selective detector were used to confirm the identity of the organic reaction products at the end of each run. Also the organic products were separated by column chromatography and analyzed by $^{13}C$ and $^{1}H$ NMR in a Jeol Eclipse 270 NMR spectrometer.

### 2.2 Catalyst Testing

Catalytic runs were performed in a 30 mL mechanically stirred and electrically heated stainless steel Parr reactor. In a typical run, 0.5–1.5 g of the catalyst $Rh(4\text{-pic})_2/P(4\text{-VP})$ ([Rh] = 2 wt.%), $1 \times 10^{-2}$ mol of olefin and 10 mL of methanol were added to the reaction vessel. The system was then flushed with nitrogen to remove the air and subsequently flushed with carbon monoxide to remove all the nitrogen from the system. The reaction vessel was then charged with $CO/CH_4$ at the desired pressure (22–33 atm) and electrically heated to 80–130 °C for 6–24 h. After a given time the reaction was stopped, the reactor cooled to room temperature, excess pressure was vented and the products were analyzed by GC and GC–MS techniques.

## 3 Results and Discussion

### 3.1 General Aspects

The study of the catalytic carbonylation reaction was divided in three steps. In the first step the carbonylation of each of the following olefins: hex-1-ene, cyclohexene, 2,3-dimethyl-but-1-ene and 2-methyl-pent-2-ene was tasted separately. These olefins were used as a model because they are generally present in mayor proportion among other olefins in real naphtha [12]. The results for the carbonylation of this four olefin-model system show that 2-methyl-pent-2-ene is the less reactive (Table 1). For that reason, the studies for achieving optimal conditions (reaction time, pressure of CO and temperature) were the primary focus for this $\beta$-disubstituted olefin.

In the second step a quaternary mixture (hex-1-ene, 45%; cyclohexene, 20%; 2,3-dimethyl-but-1-ene, 20%; and 2-methyl-pent-2-ene, 15%) of these model olefins was prepared and its catalytic carbonylation was carried out under the optical conditions previously determined in the

**Table 1** WGSR and carbonylation of olefins by [Rh(4-pic)$_2$]/P(4-VP) catalyst[a]

| Olefin | TF[b] | | Overall yield (%)[c] | Selectivity (%) |
|---|---|---|---|---|
| | $H_2$ | $CO_2$ | | |
| Hex-1-ene | 22 | 38 | 34 | Isomerization (4) |
| | | | | Carbonylation (95) |
| 2,3-Dimethyl-but-1-ene | 26 | 43 | 28 | Isomerization (8) |
| | | | | Carbonylation (91) |
| Cyclohexene | 25 | 41 | 26 | Isomerization (0) |
| | | | | Carbonylation (100) |
| 2-Methyl-pent-2-ene | 39 | 49 | 3 | Isomerization (8) |
| | | | | Carbonylation (91) |

[a] [Rh] = 2 wt.% ($1 \times 10^{-4}$ mol), 0.5 g of P(4-VP), 10 mL of $CH_3OH$, [olefin] = $1 \times 10^{-2}$ mol, S/C = 100, P(CO) = 22 atm at 110 °C for 6 h

[b] TF(gas) = [((mol of gas)/(mol of Rh)) × (rt)] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty < 10%

[c] Overall yield = % of olefin conversion to carbonylated products

first step. In the third step the catalytic carbonylation of real Venezuelan naphtha was studied under the optimal reaction conditions ([Rh] = 2 wt.% ($1 \times 10^{-4}$ moles), 0.5 g of P(4-VP), 10 mL of methanol, [olefin] = $1 \times 10^{-2}$ mol, S/C = 100, P(CO) = 33 atm at 110 °C for 24 h).

Control experiments reveal that the activity toward the carbonylation of the above listed olefins under CO was not observed when the mixtures of methanol with the individual or the quaternary olefins system were tested under similar experimental conditions in the absence of the Rh(4-pic)$_2$/P(4-VP) catalyst.

## 3.2 Carbonylation Catalysis of the Four Olefin-Model System

In order to determine the reactivity order for the four olefin-model systems, the overall yield (%) to oxygenated organic products for each individual olefin were obtained under identical reaction conditions. The CO pressure and temperature used were chosen based upon previously reported systems [14]. The results for the catalytic carbonylation of the four olefin-model system are given in Table 1.

The following order of reactivity (%) is observed: hex-1-ene (34) > 2,3-dimethyl-but-1-ene (28) ≥ cyclohexene (26) ≥ 2-methyl-pent-2-ene (3) under the reactions conditions described in Table 1. This order of reactivity concords with the reported by Ercoli [19], whom points that the mayor observed reactivity corresponds to α-olefins, followed by cyclic and by β-disubstituted olefins. The catalytic carbonylation of hex-1-ene gives methyl-heptanoate, heptanal, 2-methyl-hexanal, and 1,1-dimethoxy-heptane as the main reaction products. The catalytic carbonylation of cyclohexene gives methyl-cyclohexylmethanoate and cyclohexanecarbaldehyde. The catalytic carbonylation of 2-methyl-pent-2-ene and 2,3-dimethyl-but-1-ene give many oxygenated compounds among them esters (methyl-2,2-dimethylpentanoate and methyl-3,4-dimethyl-pentanoate) aldehydes (3,4-dimethyl-pentanal and 2,2-dimethylpentanal) and acetals (1,1 dimethoxy-3,4-dimethyl-pentane and 1,1-dimethoxy-2,2-dimethylpentane). The methyl-heptanoate and methyl-cyclohexylmethanoate coming from the hex-1-ene and cyclohexene hydroesterification in methanol, respectively (Eq. 2, R = alkyl or phenyl); the heptanal, 2-methyl-hexanal and cyclohexanecarbaldehyde come from the hex-1-ene and cyclohexene hydroformylation (Eq. 3) and the 1,1-dimethoxy-heptane come from the nucleophilic addition between methanol and the formed heptanal, Eq. 6, respectively [20] (Eq. 4). Acetal formation under carbonylation conditions in the presence of alcohols has also been reported [21, 22].

$$\text{Olefin} + CO + CH_3OH \xrightarrow{Rh/P(4-VP)} R-C(O)OCH_3 \tag{2}$$

$$\text{Olefin} + 2CO + H_2O \xrightarrow{Rh/P(4-VP)} R-C(O)H + CO_2 \tag{3}$$

$$CH_3-(CH_2)_5-C(O)H + 2CH_3OH \xrightarrow{R-C(O)H+CO_2} CH_3-(CH_2)_5-CH(OCH_3)_2 + H_2O \tag{4}$$

In addition, GC analyses of the gas phase of the catalytic runs allowed the identification of $H_2$ and $CO_2$ as sole gaseous products. The $H_2$ and certain amount of $CO_2$ come from the water gas shift reaction (WGSR, Eq. 5). Another portion of the $CO_2$ produced comes from catalytic hydroformylation of hex-1-ene or cyclohexene under $CO/H_2O$ (Eq. 3) and the total $CO_2$ mass balances both (Eqs. 3 and 5).

$$CO + H_2O \xrightleftharpoons{Rh/P(4-VP)} CO_2 + H_2 \tag{5}$$

Catalytic WGSR is a known side reaction in olefin hydroesterification [23–26]. Even though reagents and solvents used were pre-dried, formation of water occurred via acetal production (Eq. 4). Further, a control experiment shows no WGSR activity in the absence of the Rh(4-pic)$_2$/P(4-VP) catalysts under similar reaction conditions. On the other hand, the Rh(4-pic)$_2$/P(4-VP) in contact with an aqueous solution of 2-ethoxyethanol under CO has been reported to be an efficient catalysts for the WGSR [17].

As a competitive reaction to the catalytic carbonylation of the olefins for the Rh(4-pic)2/P(4-VP) system, we can see that WGSR is favorable in the opposite direction. Namely, the catalytic production of $H_2$ defined as TF($H_2$)/24 h in the olefin/methanol medium follows the order: 2-methyl-pent-2-ene (39) > 2,3-dimethyl-but-1-ene(26) ≥ cyclohexene (25) > hex-1-ene (22).

### 3.3 Catalysis Activity in Response to Variation of Reaction Time, P(CO) and Temperature for the 2-Methyl-pent-2-ene/Rh(4-Pic)$_2$/P(4-Vp) System

The studies of the variation of some reaction parameters were made with the goal to increase the conversion of the less reactive 2-methyl-pent-2-ene olefin. We thought that the optimal conditions to be found for this olefin could be in principle the same for the rest of the individual olefins, for the quaternary system and for real naphtha.

The effect of varying the reaction time for the 2-methyl-pent-2-ene/Rh(4-pic)$_2$/P(4-VP) system in methanol is summarized in Table 2.

The results show a negative and a positive effect on the WGSR and the carbonylation of the olefin catalytic activities, respectively, with the increases of the reaction time in the 6–24 h range, keeping constant the other reaction parameters. Further optimization studies for the catalytic carbonylation of the olefins will set the optimal value to 24 h.

The effect of varying the CO pressure in the 22–33 atm range for the Rh(4-pic)$_2$/P(4-VP)/olefin system in methanol is summarized in Table 3. An increase in the P(CO) from 22 to 33 atm further increased both, the carbonylation overall yield (%) value from 26 to 31% and the catalysis of the WGSR (based on $H_2$ production) from 17 to 36 $(24\ h)^{-1}$. These findings indicate that catalyst activity for both reactions follows a linear dependence on [CO] in the range 22–33 atm and suggest the formation of polymer immobilized carbonyl-rhodium species followed by slower step to give organic products, $H_2$ and $CO_2$ (Eq. 6).

Further optimization studies for the catalytic carbonylation of the olefins will set the optimal value to P(CO) = 33 atm for 24 h.

The effect of varying the temperature in the 80–130 °C range for the Rh(4-pic)$_2$/P(4-VP)/olefin system in methanol under P(CO) = 33 atm for 24 h is summarized in Table 4.

**Table 2** Reaction time effects on WGSR and carbonylation of 2-methyl-pent-2-ene by [Rh(4-pic)$_2$]/P(4-VP) catalyst[a]

| Reaction time (h) | TF[b] | | Overall yield (%)[c] |
|---|---|---|---|
| | $H_2$ | $CO_2$ | |
| 6 | 39 | 49 | 3 |
| 12 | 31 | 39 | 8 |
| 18 | 22 | 32 | 19 |
| 24 | 17 | 26 | 26 |

[a] [Rh] = 2 wt.% ($1 \times 10^{-4}$ mol), 0.5 g of P(4-VP), 10 mL of $CH_3OH$, [2-methyl-pent-2-ene] = $1 \times 10^{-2}$ mol, S/C = 100, P(CO) = 22 atm at 110 °C for a given reaction time

[b] TF(gas) = [((mol of gas)/(mol of Rh)) × (rt)] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty < 10%

[c] Overall yield = % of olefin conversion to carbonylated products

**Table 3** Carbon monoxide effects on WGSR and carbonylation of 2-methyl-pent-2-ene by [Rh(4-pic)$_2$]/P(4-VP) catalyst[a]

| CO (atm) | TF[b] | | Overall yield (%)[c] |
|---|---|---|---|
| | $H_2$ | $CO_2$ | |
| 22 | 17 | 26 | 26 |
| 27 | 26 | 34 | 28 |
| 33 | 36 | 43 | 31 |

[a] [Rh] = 2 wt.% ($1 \times 10^{-4}$ mol), 0.5 g of P(4-VP), 10 mL of $CH_3OH$, [2-methyl-pent-2-ene] = $1 \times 10^{-2}$ mol, S/C = 100, a given P(CO) at 110 °C for 24 h

[b] TF(gas) = [((mol of gas)/(mol of Rh)) × (rt)] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty < 10%

[c] Overall yield = % of olefin conversion to carbonylated products

**Table 4** Temperature effects on WGSR and carbonylation of 2-methyl-pent-2-ene by [Rh(4-pic)$_2$]/P(4-VP) catalyst[a]

| Temperature (°C) | TF[b] | | Overall yield (%)[c] |
|---|---|---|---|
| | $H_2$ | $CO_2$ | |
| 80 | 18 | 23 | 8 |
| 90 | 22 | 27 | 15 |
| 100 | 27 | 33 | 25 |
| 110 | 33 | 40 | 31 |
| 120 | 41 | 51 | 22 |
| 130 | 59 | 64 | 4 |

[a] [Rh] = 2 wt.% ($1 \times 10^{-4}$ mol), 0.5 g of P(4-VP), 10 mL of $CH_3OH$, [2-methyl-pent-2-ene] = $1 \times 10^{-2}$ mol, S/C = 100, at P(CO) = 33 atm at a given temperature for 24 h

[b] TF(gas) = [((mol of gas)/(mol of Rh)) × (rt)] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty <110%

[c] Overall yield = % of olefin conversion to carbonylated products

Figure 1 shows the plot of overall yield (%) values vs. T (°C) for the carbonylation process. An increase in temperature from 80 °C further increased the overall yield (%) value, reaching a maximum at 110 °C. The activity towards oxygenated compounds production starts decreasing at $T \geq 120$ °C. These results show that the carbonylation rate is very sensitive to reaction temperature and it does not follow a linear dependence on 80–130 °C range, suggesting the intervention of less-active catalytic species for the carbonylation process at $T \geq 110$ °C. Previous DTA–TGA analyses show that the immobilized catalyst is stable until 250 °C [17] and these results rule out the possible degradation of the catalyst at the working temperatures (80–130 °C).

However, the catalysis of the WGSR increases almost linearly in this range. Figure 2 displays a plot of Ln TF($H_2$) vs. 1/T for [Rh] = 2 wt.% at P(CO) = 33 atm. The resulting Arrhenius-type plot is linear on the 100–130 °C range and an activation energy ($E_a$ = 31.1 kJ/mol K) was calculated.

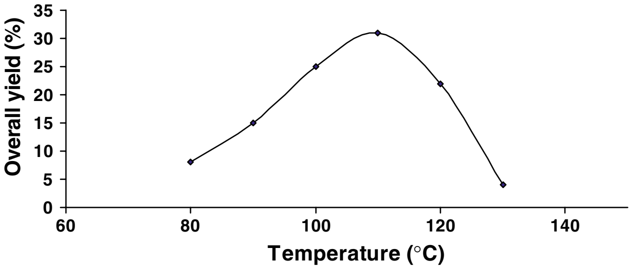


**Fig. 1** Overall yield (%) vs. T (°C): [Rh] = 2 wt.% ($1 \times 10^{-4}$ mol), 0.5 g of P(4-VP), 10 mL of methanol, [2-methyl-pent-2-ene] = $1 \times 10^{-2}$ mol, S/C = 100, at P(CO) = 33 atm for 24 h. Lines drawn for illustrative purpose only

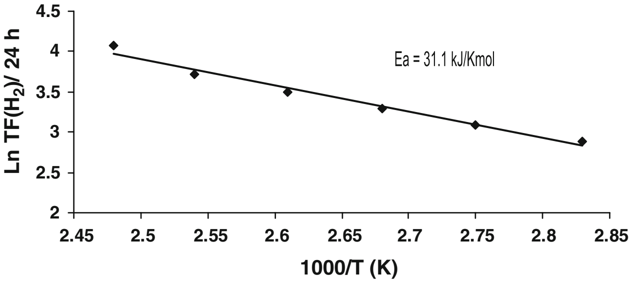


**Fig. 2** The Arrhenius plot for the catalytic hydrogen production. [Rh] = 2 wt.% ($1 \times 10^{-4}$ mol), 0.5 g of P(4-VP), 10 mL of methanol, [2-methyl-pent-2-ene] = $1 \times 10^{-2}$ mol, S/C = 100, at P(CO) = 33 atm for 24 h

The activation energy for the WGSR catalyzed by Rh(4-pic)/P(4-VP) catalyst in contact with aqueous 2-ethoxyethanol in the absence of any olefins and the same catalyst in contact with hex-1-ene/methanol are 50.9 kJ/mol K (at the temperature range 100–120 °C) [14] and 143.7 kJ/mol K (at the temperature range 110–130 °C) [14], respectively. As can be seen the activation energy for the WGSR for the Rh(4-pic)//P(4-VP)/methanol/2-methyl-pent-2-ene is lower the two above catalyst systems, thus favoring the WGSR for the less reactive olefin.

Quantitative analyses indicate that optimal conditions for the catalytic carbonylation of 2-methyl-pent-2-ene by the Rh(4-pic)$_2$/P(4-VP) system are: [Rh] = 2 wt.% ($1 \times 10^{-4}$ mol), 0.5 g of P(4-VP), 10 mL of $CH_3OH$, [olefin] = $1 \times 10^{-2}$ mol, S/C = 100, P(CO) = 33 atm at 110 °C for 24 h. Accordingly, these optimal values will be used to examine the catalytic conversion for the rest of the individual olefins. These results are shown in Table 5.

These results shown an expected increment of the olefin conversion (% of overall yield) of 1.9 (hex-1-ene), 2.1 (2,3-dimethyl-but-1-ene), 2.2 (cyclohexene) and 10.3-fold (2-methyl-pent-2-ene) when the P(CO) and the reaction time changes at 110 °C from 22 to 33 atm and from 6 to 24 h, respectively.

**Table 5** WGSR and carbonylation of olefins by [Rh(4-pic)$_2$]/P(4-VP) catalyst under optimal conditions[a]

| Olefin | TF[b] | | Overall yield (%)[c] |
|---|---|---|---|
| | $H_2$ | $CO_2$ | |
| Hex-1-ene | 23 | 38 | 63 |
| 2,3-Dimethyl-but-1-ene | 25 | 39 | 50 |
| Cyclohexene | 26 | 40 | 58 |
| 2-Methyl-pent-2-ene | 36 | 43 | 31 |

[a] [Rh] = 2 wt.% ($1 \times 10^{-4}$ mol), 0.5 g of P(4-VP), 10 mL of $CH_3OH$, [olefin] = $1 \times 10^{-2}$ mol, S/C = 100, P(CO) = 33 atm at 110 °C for 24 h

[b] TF(gas) = [((mol of gas)/(mol of Rh)) × (rt)] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty < 10%

[c] Overall yield = % of olefin conversion to carbonylated products

## 3.4 Recycling of the Immobilized Catalyst

The recycling efficiency of the Rh/P(4-VP) catalyst was studied in the carbonylation of 2-methyl-pent-2-ene. The catalyst was filtered from the supernatant solution (in nitrogen atmosphere) and returned to the autoclave with fresh reactants. The results are presented in Table 6. A dramatic change of the catalytic activity was observed. A drop of ca. 65 and 94% was observed for the catalytic activity toward carbonylation after a third and a fourth use, respectively. Some changes of the color of the solid were observed after repetitive use. Namely, the fresh catalyst has a light-yellow color and it changes to an intermediate dark-yellow to a final brown color after the repetitive use. Studies of the nature of these intermediates and final species are in progress. The catalytic results show that the polymer-anchored catalyst has not a high stability during the recycling process due to the formation of less catalytic species.

## 3.5 Carbonylation Catalysis of the Quaternary Mixture (Synthetic Naphtha)

The oxygenated reaction products coming from the catalytic carbonylation of a quaternary olefin mixture

**Table 6** Recycling efficiency for the carbonylation of 2-methyl-pent-2-ene catalyzed by [Rh(4-pic)$_2$]/P(4-VP) catalyst[a]

| Used time | Overall yield (%)[b] |
|---|---|
| 1st | 31 |
| 2nd | 30 |
| 3th | 11 |
| 4th | 2 |

[a] Rh] = 2 wt.% p/p ($1 \times 10^{-4}$ mol), 0.5 of P(4-VP), 10 mL of $CH_3OH$, [olefin] = $1 \times 10^{-2}$ mol, S/C = 100, P(CO) = 33 atm at 110 °C for 24 h

[b] Overall yield = % of olefin conversion to carbonylated products

(composed by 45% of hex-1-ene, 20% of cyclohexene, 20% of 2,3-dimethyl-but-1-ene, and 15% of 2-methyl-pent-2-ene) under the optimal conditions reported above are given in Table 7. The reaction products for the synthetic naphtha show a similar pattern of product formation as the separated substrates. In addition, formation of $H_2$ ($TF(H_2) = 30$ $(24\ h)^{-1}$) and $CO_2$ ($TF(CO_2) = 40$ $(24\ h)^{-1}$) were also observed.

A separated GC quantitative analysis for the products formed in the catalytic carbonylation of hex-1-ene taken as a model system (under the conditions described in Table 7) revealed the following results ($1 \times 10^{-5}$ mol): Methyl-heptanoate (352), heptanal and 2-methyl-hexanal (31) and 1,1-dimethoxy-heptane (183). Resulting the following selectivity (%): methyl-heptanoate (62), heptanal and 2-methyl-hexanal (6) and 1,1-dimethoxy-heptane (32).

### 3.5.1 *Effect of the Amount of Complex Rh(4-Pic)$_2$/P(4-Vp) on the Catalytic Carbonylation of Synthetic Naphtha and WGSR*

Three kinds of catalysts, on which the amount of the immobilized complex Rh(4-pic)$_2$/P(4-VP) are 0.5, 1.0 and 1.5 g ([Rh] = 2 wt.%) were used in the carbonylation of the synthetic naphtha. Table 8 summarizes the experimental results. Evidently, the greater the amount of complex Rh(4-pic)$_2$/P(4-VP), the higher the catalytic activity for both carbonylation and WGS reactions.

**Table 8** Amounts of the [Rh(4-pic)$_2$]/P(4-VP) catalyst effects on WGSR and carbonylation of synthetic naphtha[a]

| Amounts of the catalyst (g) | TF[b] | | Overall yield (%)[c] |
|---|---|---|---|
| | $H_2$ | $CO_2$ | |
| 0.5 | 30 | 40 | 51 |
| 1.0 | 45 | 61 | 58 |
| 1.5 | 55 | 72 | 69 |

[a] [Rh] = 2 wt.% ($1 \times 10^{-4}$ mol), 10 mL of methanol, 1 mL of synthetic naphtha (hex-1-ene 45% v/v ($3.6 \times 10^{-3}$ mol), cyclohexene 20% v/v ($2.0 \times 10^{-3}$ mol), 2,3-dimethyl-but-1-ene ($1.6 \times 10^{-3}$ mol) 20% v/v, 2-methyl-pent-2-ene 15% v/v ($1.2 \times 10^{-3}$ mol), P(CO) = 33 atm at 110 °C for 24 h

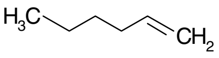
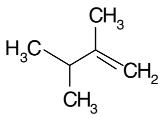
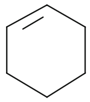
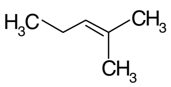
[b] TF(gas) = [((mol of gas)/(mol of Rh)) × (rt)] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty < 10%

[c] Overall yield = % of olefin conversion to carbonylated products

## 3.6 Carbonylation Catalysis of Natural Naphtha

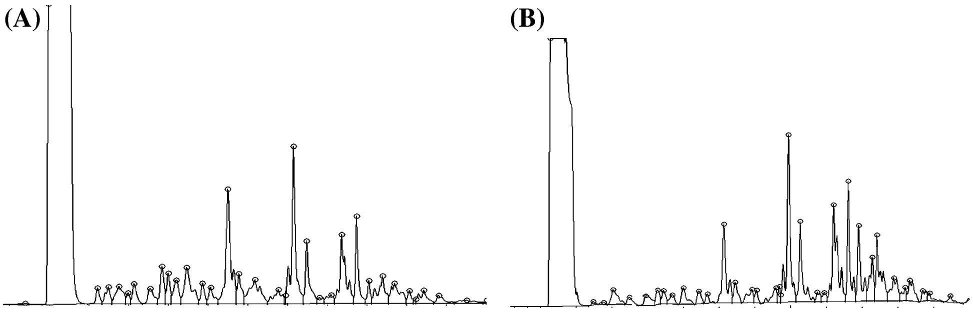
One of the objectives of this study is to examine the possibility to carry out the catalytic carbonylation of real naphtha using this immobilized Rh complex with the aim of reduce olefin content and produce in situ oxygenated

**Table 7** Carbonylation of quaternary olefin mixture by [Rh(4-pic)$_2$]/P(4-VP) catalyst[a]

| Total conversion of the mixture (%) | Individual components[b] | Products |
|---|---|---|
| 51 | <br>(hex-1-ene) | Methyl-heptanoate<br>Heptanal<br>2-Methyl-hexanal<br>1,1-Dimethoxy-heptane |
| | <br>(2,3-dimethyl-but-1-ene) | 3,4-Dimethyl-pentanal<br>Methyl-3,4-dimethyl-pentanoate<br>1,1-Dimethoxy-3,4-dimethyl-pentane |
| | <br>(cyclohexene) | Cyclohexanecarbaldehyde<br>Methyl-cyclohexylmetanoate<br>Dimethoxy-cyclohexylmetane |
| | <br>(2-methyl-pent-2-ene) | 2,2-Dimethylpentanal<br>Methyl-2,2-dimethylpentanoate<br>1,1-Dimethoxy-2,2-dimethylpentane |

[a] [Rh] = 2 wt.% ($1 \times 10^{-4}$ mol), 0.5 g of P(4-VP), 10 mL of $CH_3OH$, [olefin] = $8.4 \times 10^{-3}$ mol, S/C = 84, P(CO) = 33 atm at 110 °C for 24 h

**Fig. 3** Chromatogram obtained for the hydroformylation of real naphtha before (**a**) and (**b**) after carbonylation



compounds at the same time, in order to get better gasoline formulations.

The GC chromatograms (Fig. 3) obtained from the liquid phase before and after catalytic reaction of real Venezuelan naphtha are complexes. However, the areas of peaks associates to the olefins present on the naphtha before carbonylation are higher than those of the carbonylated naphtha. Also, it is observed in the chromatogram of the carbonylated naphtha the appearance of new peaks and the growing of other peaks. These results indicated that the amount of olefins of the real naphtha diminishes and the amount of oxygenated products increases after the carbonylation process. Additionally, formation of $H_2$ ($TF(H_2) = 69\ (24\ h)^{-1}$) and $CO_2$ ($TF(CO_2) = 78\ (24\ h)^{-1}$) were also observed.

## 4 Conclusions

The rhodium immobilized complex shows catalytic carbonylation activity for hex-1-ene, cyclohexene, 2-methyl-pent-2-ene and 2,3-dimethyl-but-2-ene, also for the quaternary mixtures of these substrates and for natural naphtha in methanol under the condition studied. The principal carbonylated products obtained include ester, aldehyde and acetal. The carbonylation with the real naphtha shows promising results for improving the quality of gasoline through a Reppe type process.

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