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**CATALYST CONCENTRATION EFFECT ON THE
HYDROESTERIFICATION AND HYDROFORMYLATION-
ACETALIZATION OF 1-HEXENE BY A Rh COMPLEX**

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Abstract

The complex, $[\text{Rh}(\text{COD})(4\text{-picoline})_2](\text{PF}_6)$ (COD = 1,5-cyclooctadiene), immobilized on poly(4-vinylpyridine) in contact with methanol catalyzes the hydroesterification and hydroformylation-acetalization of 1-hexene to methylheptanoate, heptanal and 1,1-dimethoxyheptane, respectively. The by-product, 1,1-dimethoxyheptane comes from the nucleophilic addition of methanol over the heptanal formed. Also, H_2 and CO_2 from the water gas shift reaction (WGS) are observed. The catalytic activity for the hydroformylation and the WGS proved to be non-linear in the rhodium total concentration range 0.9–5.0 wt.%.

Keywords: Hydroesterification, methyl-heptanoate, 1-hexene, rhodium

INTRODUCTION

The synthesis of oxygenated organic products by reaction of an olefin with CO and alcohols in the presence of transition metal complexes has been known [1, 2].

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The naphtha constituting a stream extracted from crude oil is formed by combinations of C₅ to C₈ saturated and unsaturated hydrocarbons. The light naphtha is used principally for the formulation of gasoline. The olefin content in the naphtha must be less than 6% in volume, according to the standard regulation. Higher amounts of these compounds in gasoline induce 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 naphtha. However, this process has some limitations associated with the high consumption of expensive H₂ and production of low octane content gasoline. Further, with the finality to increase the octane content in the gasoline and to improve the quality of the emissions, diverse oxygenated additives are added.

The Reppe reaction catalyzed by transition metal complexes could in principle be applied for improving the low stream refinery (LSR). That process could increase the octane content of the gasoline by allowing *in situ* transformation of the olefins already present in this type of oil in oxygenated compounds with high aggregated value, likes esters, aldehydes, acetals, among others. That kind of process could be carried out in one step avoiding the expensive catalytic hydrogenation.

In this work we performed the catalytic transformation of 1-hexene, which is present in about 33% among the olefins in the LSR, in oxygenate compounds by the [Rh(COD)(4-picoline)₂](PF₆) complex immobilized on poly(4-vinylpyridine) in contact with methanol at a range of rhodium contents.

EXPERIMENTAL

Materials

1-Hexene (Aldrich) and methanol (Aldrich) were simply distilled under nitrogen atmosphere. 4-picoline (4-pic) was obtained from Aldrich and was distilled over KOH. Poly(4-vinylpyridine), P(4-VP) 2% cross-linked was used as provided by Reilly Industries. All gas mixtures CO/CH₄ (94.2%/5.8%, v/v) and CO/CH₄/H₂/CO₂ (84.8%/5.1%/4.8%/5.3%, v/v) were purchased from BOC Gases and were used as received. The rhodium-immobilized complex prepared as reported [3] will be referred as to Rh(4-pic)₂/P(4-VP).

Catalyst testing

1-Hexene hydroesterification was performed as follows: a given amount of 1-hexene was added to a 150 mL magnetically stirred stainless steel Parr

autoclave (equipped with devices for collecting gas and liquid samples during the reaction) containing the catalytic mixture (0.5 g of P(4-VP)/a given wt.% content of Rh in contact with 10 mL of methanol (0.24 mol)). Afterwards, the reactor was charged with 20 atm of CO/CH₄ and placed in an electrically heated and mechanically stirred glycerol bath at $110 \pm 0.5^\circ\text{C}$ for 5 h. Gas and liquid samples were analyzed by GC at the end of the reaction time. Also liquid samples were analyzed by GC-MS, ¹H ¹³C-NMR.

Instrumentation

Gas sample analyses from catalytic runs were performed on a Hewlett-Packard 5890 Series II programmable gas chromatograph fitted with Carbosieve-B (mesh 80-100) column and thermal conductivity detector. The oven was programmed from 60 to 175°C (11.5°C/min) using the He/H₂ as carrier-gas at a flow rate of 50 mL/min. Analyses of liquid phase reaction products were done on a Hewlett-Packard 5890 Series II programmable gas chromatograph fitted with HP-1 (methyl silicone gum) capillary column (50 m x 0.53 mm x 2.65 μm) and flame ionization detector, and identified by co-injection on a HP-Mass Selective Detector Varian Chrompack, Saturn 2000 fitted with a CP-Sil-8-CB column (30 m x 250 μm x 0.25 μm). The temperature of the column was programmed from 60 to 290°C (30°C/min) using helium as a carrier gas (1 mL/min). ¹³C and ¹H-NMR spectra were recorded in a Jeol Eclipse 270 spectrometer.

Methane was used as internal standard, to allow calculation of absolute quantities of CO consumed and H₂ and CO₂ produced. The amount of organic products was determined by using the response factor method for gas chromatographic analyses [4].

RESULTS AND DISCUSSION

Runs were carried out for a series of different [Rh] over the range of 0.9-5.0 wt.%. The amount of 1-hexene was varied from 1.86 mL (1.5×10^{-2} mol) at [Rh] = 0.9 wt.% to 5.58 mL (4.5×10^{-2} mol) at [Rh] = 5.0 wt.% in order to keep the ratio [1-hexene]/[Rh] = 300 in all runs (Table 1).

A typical kinetic run involved determining the reaction rate defined as turnover frequency TF(product) as a function of [Rh] under P(CO) = 20 atm at 110°C in 10 mL of methanol (0.24 mol). Under these reaction conditions the oxygenated organic product observed were methyl-heptanoate, heptanal and 1,1-dimethoxyheptane, coming from 1-hexene hydroesterification in methanol, eq. (1), hydroformylation eq. (2), and nucleophilic addition between methanol

Table 1
Rhodium content effects on WGSR, hydroesterification and hydroformylation-acetalization of 1-hexene in methanol, catalyzed by Rh(4-pic)₂/P(4-VP) complex^a

[Rh] wt.% (mol x 10 ⁻⁴)	[CO ₂] mol x 10 ⁻⁴	TF(CO ₂) ^b Total	[H ₂] mol x 10 ⁻⁴	TF(H ₂) ^b	[MH] ^c mol x 10 ⁻⁴ (Yield %)	TF(MH) ^{b,c}	[Heptanal] mol x 10 ⁻⁴ (Yield %)	[DMH] ^d mol x 10 ⁻⁴ (Yield %)
0.9 (0.5)	23.5	113	18.8	90	33.1	59	1.0	3.4
1.4 (0.8)	23.1	111	14.0	67	25.5	122	0.7	8.1
1.9 (1.1)	20.4	98	11.0	53	19.7	95	0.5	8.9
2.7 (1.5)	35.6	171	8.3	40	16.4	79	0.6	26.1
3.5 (1.9)	34.2	164	6.5	31	14.2	68	0.6	27.5
4.0 (2.2)	34.6	166	5.8	28	11.5	55	0.4	29.0
5.0 (2.8)	35.4	170	4.2	20	9.0	43	0.3	30.2

^a 0.5 g of P(4-VP), [1-hexene] = 1.86 – 5.58 mL (1.5 x 10⁻² – 4.5 x 10⁻² mol), 1-hexene/Rh = 300, 10 mL (0.24 mol) of methanol, P(CO) = 20 atm at 110 °C for 5 h. ^bTF(product) = [(mol of product)/(mol of Rh) x (rt)] x 24 h, where (rt) = reaction time in hours. Experimental uncertainty < 10%. ^cMH = Methyl heptanoate. ^dDMH = 1,1-Dimethoxyheptane

and the heptanal formed, eq. (3), respectively. A recent, example of acetal formation under hydroformylation catalysis condition by rhodium complexes in presence of alcohols has been reported [5]. Also, formation of molecular H₂ coming from the WGSR, eq. (4) was observed. Even though the reagents and solvents used were predried, formation of water occurred *via* acetal formation, eq. (3) [1].

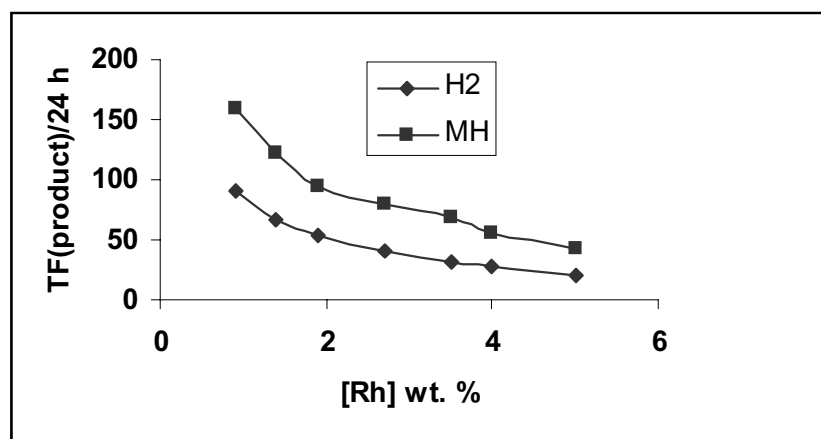
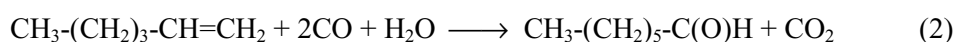
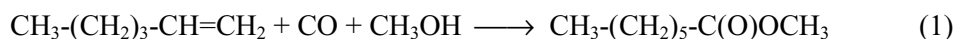


Fig. 1. Plots of TF(product)/24 h vs. [Rh] (wt.%): \blacklozenge H₂; \blacksquare methyl-heptanoate. The reaction conditions are given in Table 1. (Lines drawn for illustrative purposes only)

An increase in [Rh] from 0.9 to 3.5 wt.% resulted in a decrease in both TF(MH)/24 h and TF(H₂)/24 h, followed by nearly constant values at higher [Rh] (Fig. 1). The results indicate that the reaction rate is not first order for both reactions in the [Rh] 0.9-5.0 wt.% range, and suggest that the active species may be present in several forms having different nuclearity (mononuclear and polynuclear). This suggestion is strongly supported by the FT-IR and XPS data reported for the immobilized Rh(4-pic)₂/P(4-VP) WGSR catalysts, which show the presence of rhodium species with different nuclearities (mononuclear and

polynuclear) and oxidation state (I) or (-I). The oxidation state of the mononuclear and the polynuclear species are (I) and (-I), respectively [3]. Further, mechanistic studies for WGS catalyzed by this Rh(4-pic)₂/P(4-VP) complex suggests a nucleophilic attack by water on the coordinated CO, assisted by free P(4-VP) yielding a hydroxycarbonyl Rh species and a protonated polymer as a fundamental step [6]. The negative charge of the anionic polynuclear complex (-I) increases the energy of this step and diminishes the catalytic activity.

In summary, it has been demonstrated the catalytic transformation of 1-hexene, in oxygenated compounds (esters and acetals) under CO atmosphere by the Rh(4-pic)₂/P(4VP) system and this approximation constitutes a promising work for a future industrial catalytic process for gasoline improvement based on Reppe-type reactions.

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REFERENCES

1. P. Pino, F. Piacenti, M. Bianchi: in I. Wender, P. Pino, *Organic Synthesis via Metal Carbonyls*, Vol. 2. Wiley, New York 1968.
2. G. Kiss: *Chem. Rev.*, **101**, 3435 (2001).
3. A.J. Pardey, M. Fernández, J. Alvarez, C. Urbina, D. Moronta, V. Leon, M. Haukka, T.A. Pakkanen: *Appl. Catal. A*, **199**, 275 (2000).
4. H.M. McNair, J.M. Miller: *Basic Gas Chromatography*, Ch. 8. Wiley-Interscience, New York 1997.
5. B. El Ali, J. Tijani, M. Fettouhi: *J. Mol. Catal. A*, **230**, 9 (2005).
6. A.J. Pardey, M. Fernández, J. Alvarez, M.C. Ortega, M. Canestrari, C. Longo, P. Aguirre, S.A. Moya, E. Lujano, P.J. Baricelli: *Bol. Soc. Chil. Quím.*, **45**, 347 (2000).