A High (Z)/(E) Ratio Obtained During the 3-Hexyne Hydrogenation with a Catalyst Based on a Rh(I) Complex Anchored on a Carbonaceous Support

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Abstract The (Z)/(E) ratio was analyzed for the 3-hexyne semi-hydrogenation at 275, 290 and 303 K. [RhCl(NH₂ (CH₂)₁₂CH₃)₃] pure and supported on a carbonaceous material were used as catalysts. The supported complex showed high values of conversion and selectivity, and its behaviour was much better than the Lindlar catalyst used as a reference.

Keywords (Z)/(E) Ratio \cdot 3-Hexyne partial hydrogenation \cdot Rhodium complex \cdot Carbonaceous support

1 Introduction

The synthesis and manufacture of food additives, flavors and fragrances, as well as pharmaceutical, agrochemical

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J. M. Badano · M. E. Quiroga INCAPE, Instituto de Investigaciones en Catálisis y Petroquímica, (FIQ-UNL, CONICET), Santiago del Estero 2654, S3000AOJ Santa Fe, Argentina e-mail: jbadano@fiq.unl.edu.ar and petrochemical substances, examples of fine and industrial chemicals, are closely related to selective alkyne hydrogenation [1, 2].

Regarding non-terminal alkyne semi-hydrogenation, the main goals are to avoid hydrogenation to single bond and to give priority to the highest possible conversion and selectivity to the (Z)-alkene [3-5]. The control over conversion and selectivity of a catalytic reaction can be exerted in different ways, e.g.: by varying (a) the active species or (b) the support, and/or by adding (c) a promoter/ a poison/a modifier, and finally, and not less important, modifying the reaction temperature. Examples of the factor (b) are: mesoporous [6] and siliceous [7] materials, a pumice [8], carbons [9], and hydrotalcite [3]. Cases of factor (c) are the typical Lindlar catalyst (palladium heterogenized on calcium carbonate poisoned by lead acetate or lead oxide, Pd-CaCO3-Pb) [10] and the presence of quinoline and triphenylphosphine [11, 12]. Research on the factors (a) and (c) include bi-elemental systems such as Ni-B, Pd-Cu, etc. [13-19]. An example of the effect of the reaction temperature is a paper by Choi and Yoon [20], who found that the selectivity to (Z)-alkene increases when the temperature decreases using a Ni catalyst.

On the other hand, transition metal complexes are a group of substances widely used as catalysts for homogeneous and heterogeneous hydrogenation reactions. In the context of the previous paragraph they could be considered as a new active species or as a metal conditioned by its ligands, a kind of "poison" or a modifier for the metal atom [21]. These catalysts have the advantages of higher activities and selectivities for this type of reaction, even under mild conditions of temperature and pressure [22–26]. An example of this kind of systems is the complex [PdCl₂(NH₂(CH₂)₁₂CH₃)₂] supported on γ -Al₂O₃ or on a micro-porous carbon [27, 28].

To our knowledge there are few publications that use transition metal complexes as catalysts for the partial hydrogenation of long chain non-terminal alkynes. Thus, the objective of this work was to study the (Z)/(E) product ratio for the partial hydrogenation of 3-hexyne, under different reaction temperatures (275, 290 and 303 K), using [RhCl(NH₂(CH₂)₁₂CH₃)₃], pure and supported on a commercial carbonaceous material (NORIT RX3) as catalysts. Activity and selectivity of the Rh(I) complex catalysts were evaluated and compared against those obtained with the conventional Lindlar catalyst.

2 Experimental

2.1 Synthesis of Pure [RhCl(NH₂(CH₂)₁₂CH₃)₃]

The [RhCl(NH₂(CH₂)₁₂CH₃)₃] complex (hereafter NH₂ (CH₂)₁₂CH₃ = TDA) was prepared by reaction of RhCl₃ (Aldrich, cat. 30786-6) and TDA (Fluka, cat 91950) following a method already reported [29].

2.2 Immobilization of [RhCl(NH₂(CH₂)₁₂CH₃)₃] on RX3

Immobilization of the complex was carried out on RX3 (hereafter $[RhCl(NH_2(CH_2)_{12}CH_3)_3]/RX3)$, a pelletized commercial carbon from NORIT[®], by means of the incipient wetness technique [30].

RX3 presents a BET surface area of 1,411 m² g⁻¹, a total pore volume of 1.217 mL g⁻¹, with a distribution of pore volume and sizes as follows, micropores: 0.356 mL g⁻¹/<0.7 nm, supermicropores: 0.333 mL g⁻¹/0.7–2 nm, mesopores: 0.098 mL g⁻¹/2–7.5 nm and macropores: 0.430 mL g⁻¹/7.5–50 nm [31].

A solution of $[RhCl(NH_2(CH_2)_{12}CH_3)_3]$ in chloroform/ methanol (5/1, v/v), in a suitable concentration, was used for impregnation to obtain a 0.3 Rh wt% catalyst. The solvent was let evaporate in a desiccator at 298 K, until constant mass was verified.

2.3 Elemental Composition

After catalytic runs, [RhCl(NH₂(CH₂)₁₂CH₃)₃]/RX3 was analyzed by standard chemical techniques for the presence of rhodium, chlorine and nitrogen and their weight percent values, on a C- and H- free base [29].

2.4 X-Ray Photoelectron Spectroscopy (XPS)

Fresh $[RhCl(NH_2(CH_2)_{12}CH_3)_3]/RX3$ was analyzed by XPS to determine the presence of rhodium, nitrogen and chlorine, their electronic states and atomic ratios, according

to a procedure previously described [31]. Determinations were carried out on a Shimadzu ESCA 750 electron spectrometer coupled to a Shimadzu ESCAPAC 760 Data System. The superficial electronic states of rhodium, nitrogen and chlorine were studied following the maximum position of the Rh $3d_{5/2}$, N 1 s and Cl $2p_{3/2}$ peaks respectively; the C $1s_{1/2}$ line was taken as an internal standard at 285.0 eV [32].

2.5 Catalytic Runs

To evaluate the (Z)/(E) ratio for the 3-hexyne partial hydrogenation, a batch stainless-steel stirred tank reactor was used. The reaction tests were performed using the following catalysts: (1) commercial Lindlar catalyst (Aldrich cat. 20,573-7) $(4.5 \times 10^{-3} \text{ g})$, (2) [RhCl(NH₂ $(CH_2)_{12}CH_3)_3$] (1.6 × 10⁻³ g), and (3) [RhCl(NH₂) $(CH_2)_{12}CH_3)_3]/RX3 (7.5 \times 10^{-2} \text{ g}), \text{ at three temperatures:}$ $T_1 = 275$ K, $T_2 = 290$ K and $T_3 = 303$ K, with 150 kPa of hydrogen pressure. In all the cases, 100 mL of a 2% (v/v) solution of 3-hexyne (Aldrich cat. 30,689-4) in toluene was used, with a 3-hexyne/M (M = Rh or Pd) molar ratio ca. 8.05×10^3 . All of the catalytic tests were carried out at a stirring velocity of 600 rpm, during 120 min. To avoid the possible contamination of the reaction media with metal cations, the reactor and the stirrer were poly(tetrafluoroethylene) coated. To study the possibility of the existence of external and internal diffusional limitations in the catalytic tests performed, experiments at different stirring velocities and various particle sizes were mounted [33, 34]. On the one hand the stirring velocity was varied from 180 to 1,400 rpm, with a constancy of activity and selectivity above 500 rpm, ensuring that external diffusional limitations were absent at the rotary speed selected. On the other hand, the heterogenized complex catalyst was crushed up to 1/4 of the original size of the RX3 pellets used as support. In every case, the conversion and selectivity values obtained were the same than those corresponding to the non-crushed catalyst, concluding that internal diffusional limitations were absent at the operational conditions of this work. Additionally, the catalyst cylinders were properly treated and weighed after ending the reaction. The difference in the mass of catalyst cylinders, before and after the test reaction, was within the experimental error of the analytical balance method, meaning that there was no mass loss from the cylinders. Thus, it can be considered that the attrition effect is absent or is negligible enough to play a role in determining an additional mass transfer limitation.

Reactants and products were analyzed by gas chromatography, using a flame ionization detector and a CP WAX 52 CB capillary column. All runs were carried out in triplicate; the relative experimental error was about 3%.

2.6 Possibility of Complex Leaching

The possibility of complex leaching from the supported catalyst during the hydrogenation tests was checked, after each catalytic run, determining the presence of rhodium in the remaining solutions by Atomic Absorption Spectrophotometry.

3 Results and Discussion

3.1 Supported Complex Structure

3.1.1 Rhodium Coordination Sphere and Complex Minimum Formula

According to previously published results [25] of elemental composition and XPS (Table 1) for the pure complex, it was suggested that the rhodium coordination sphere is formed by chloro and TDA ligands; and that the complex empirical formula could be $[RhCl(NH_2(CH_2)_{12}CH_3)_3]$ [29].

Elemental composition weight % values of the supported complex after catalytic evaluations, for Rh, Cl and N on a C- and H- free base were 57.0, 19.8 and 23.0, respectively. According to these results, the Rh, Cl and N molar stoichiometry can be expressed as ca. 1:1:3, in total accordance with the corresponding values for the pure complex [29].

Additionally, XPS results of binding energies and atomic ratios, for the anchored and pure complex are shown on Table 1. From this information, it can be observed that: (a) the atomic ratios Cl/Rh and N/Rh are in total accordance with the results obtained from elemental composition for the pure complex; and (b) there was a constancy of the Rh 3d_{5/2}, N 1 s and Cl 2p_{3/2} XPS BE, meaning that their electronic state remain unchanged. Item (a) indicates that the supported complex may be considered as tetra-coordinated, maintaining its chemical identity when it is anchored, and item (b) suggests that Rh is not in contact with the carbon surface, and in this way the heterogenization of the complex took place via a physicochemical interaction between the last part of the TDA hydrocarbon chains and the carbon basal planes, i.e. an anchoring showing a kind of "table" arrangement.

3.1.2 Rhodium Local Site Symmetry, HOMO-LUMO Electron Configuration and Complex Geometry

Knowing that tetra-coordinated rhodium(I) complexes have a square-planar geometry [35] and that the complex formula is [RhCl($NH_2(CH_2)_{12}CH_3$)₃], two facts can be considered:

- (I) A C_{2v} local site symmetry for the closest rhodium atom environment; in this site symmetry, with tridecylamine as an electron-donating σ ligand and chloride as an electron-withdrawing σ/π ligand and the two-fold rotation axis along the z cartesian axis, the Angular Overlap Model (AOM) [36] was used to predict the HOMO-LUMO frontier orbitals. Applying this model, with Rh(I) as a d⁸ central atom, we determined the following orbital distribution in an increasing order of energy: non-bonding (\mathbf{d}_{xy}) , antibonding double-degenerate e_{π}^* ((d_{xz}, d_{vz})*), 7/4 e_{σ}^* $((d_{z2})^*)$ and 9/4 e^*_{σ} $((d_{x2-y2})^*)$. Assigning the eight electrons to this scheme, it turns out that $(\mathbf{d}_{z2})^*$ (z direction) is the HOMO and $(\mathbf{d}_{x2-\mathbf{v2}})^*$ (x and y directions) is the LUMO frontier orbitals, with a relatively high energy due to the low oxidation number of the rhodium atom. The former is useful to produce the cleavage of the H-H bonding, generating hydrogen atoms and the latter is available to receive electron density from the substrate molecule, weakening the C-C triple bond; both of them are key factors in the catalytic cycle leading to the hydrogenation of the substrate.
- (II) The approximate molecular size of the metal complex was estimated in order to study structural aspects related to its location on the support porosity. We did this taking into account the square planar geometry, typical covalent radii, a 109.5° C–C–C angle and basic trigonometry, determining the longest dimensions, the TDA–Rh–TDA and the Cl–Rh–TDA lengths, as ca. 4 and 2.3 nm, respectively. On the other hand, according to the distribution of pore sizes given in the "Experimental" section it can be concluded that the complex can be located only in the meso and macropores (2–7.5 and 7.5–50 nm respectively), thus occupying ca 43% of the support total pore volume available.

Table 1 Rh $3d_{5/2}$, N 1 s, and Cl $2p_{3/2}$ peaks binding energies (BE) and the atomic ratios N/Rh and Cl/Rh for [RhCl(TDA)₃] and [RhCl(TDA)₃]/RX3

Sample	Rh 3d _{5/2} (eV)	N 1 s (eV)	Cl 2p _{3/2} (eV)	N/Rh (at./at.)	Cl/Rh (at./at.)
[RhCl(TDA) ₃] (from Ref. [29])	307.1	402.1	198.1	3.00	1.01
[RhCl(TDA) ₃]/RX3	307.1	401.9	198.0	3.00	1.02

3.2 Possibility of Complex Leaching

Results from Atomic Absorption Spectrophotometry revealed that no rhodium was present in the remaining solution from all the heterogeneous catalytic runs, meaning that the complex was not leached under the reaction conditions, and kept anchored on the carbonaceous support.

3.3 Catalytic Evaluation

3.3.1 Chemical Considerations

(Z)-3-hexene, (E)-3-hexene and *n*-hexane were the only products detected by GC during the catalytic runs using the catalytic systems: (1) commercial Lindlar catalyst (2) [RhCl(NH₂(CH₂)₁₂CH₃)₃], and (3) [RhCl(NH₂(CH₂)₁₂CH₃)₃]/ RX3. In Fig. 1 the conversions to (Z)-3-hexene and (E)-3-hexene are shown as a function of the 3-hexyne total conversion for the Lindlar catalyst and for Rh(I) homogeneous and heterogeneous complex. It can be noted the predominant formation of the (Z)-alkene stereo-isomer, the desired product. In this respect, it can be seen, from Fig. 1, that all of the catalytic systems show an initial part with an almost linear slope, which takes a value of 45° for the [RhCl(NH₂(CH₂)₁₂CH₃)₃]/RX3 catalyst. After that initial part, all of the systems have a similar shape with an increasing 3-hexyne total conversion, showing a maximum value of conversion to (Z)-3-hexene. There was also a relatively low amount of the side products: (E)-3-hexene formed either as initial product or via $Z \rightarrow E$ isomerization, and n-hexane (not plotted in Fig. 1 because of the low values obtained and for the sake of clarity) produced either



Fig. 1 Conversion to (*Z*)-3-hexene and to (*E*)-3-hexene versus 3-hexyne total conversion for: Lindlar catalyst (*I*), $[RhCl(TDA)_3]$ (2), $[RhCl(TDA)_3]/RX3$ (3); *filled square/open square 275* K, *filled triangle/open triangle 290* K, *filled diamond/open diamond 303* K. Open symbols: (*E*)-3-hexene, solid symbols (*Z*)-3-hexene

by hydrogenation of the alkyne or the alkene isomers [7, 37]. Last but not least, $[RhCl(NH_2(CH_2)_{12}CH_3)_3]/RX3$ showed the lowest conversion values to the (*E*) isomer and to the alkane.

In Fig. 2, a detail from Fig. 1, it can be observed that, for a given catalytic system, the variation of conversion to (Z)-3-hexene versus 3-hexyne total conversion follows an increasing tendency as the temperature is raised. However, it can be noted that the performance of Rh(I) complex heterogeneous system is slightly sensitive to temperature changes while the homogeneous system and the Lindlar catalyst are considerably sensitive to temperature changes.

For a given temperature, the $[RhCl(NH_2(CH_2)_{12}CH_3)_3]/RX3$ system shows the highest conversions to (*Z*)-3-hexene at the highest 3-hexyne total conversions (maximum value: $X_{(Z)} = 95.0\%$ at $X_T = 99.8\%$), followed by $[RhCl(NH_2 (CH_2)_{12}CH_3)_3]$ and then by the Lindlar catalyst.

In Fig. 3 the selectivity to (*Z*)-3-hexene versus the 3-hexyne total conversion values are presented. The selectivity plots show an initial plateau-shaped behaviour followed by a marked decreasing tendency for the increasing 3-hexyne total conversion. The [RhCl(NH₂(CH₂)₁₂CH₃)₃]/RX3 system allows to obtain a practically constant value of a very high selectivity (not lower than 98.5%) up to a very high 3-hexyne total conversion (ca. 85%); after that, the selectivity decays in a very slight way. Meanwhile, in the case of [RhCl(NH₂(CH₂)₁₂CH₃)₃] and the Lindlar catalyst, high values of selectivities (ca. 89.4 and ca. 94.2 respectively) were obtained for a lower 3-hexyne total conversion (ca. 44%); then both systems show a monotonously decreasing profile shape, which is more pronounced in the case of the Lindlar catalyst.



Fig. 2 Conversion to (Z)-3-hexene versus 3-hexyne total conversion for: Lindlar catalyst (1), [RhCl(TDA)₃] (2), [RhCl(TDA)₃]/RX3 (3) (a detail of Fig. 1 in the zone where the three systems present the most remarkable differences)



Fig. 3 Selectivity to (Z)-3-hexene versus 3-hexyne total conversion for: Lindlar catalyst (1), [RhCl(TDA)₃] (2), [RhCl(TDA)₃]/RX3 (3); *filled square* 275 K, *filled triangle* 290 K, *filled diamond* 303 K

To reinforce the conclusions given in the previous paragraphs, some relevant values of conversion and selectivity for different reaction conditions are summarized in Table 2.

The different activity and selectivity behaviour between the complex species supported and unsupported could be explained considering a higher concentration of the substrate around the supported complex catalyst than that in the bulk solution as alkynes are adsorbed more strongly than alkenes due to a physicochemical adsorption process.

Finally, for each system the higher the temperature the higher the selectivity and the higher the conversion to the (*Z*) isomer, although the $[RhCl(NH_2(CH_2)_{12}CH_3)_3]/RX3$ system behaves as the less sensitive catalyst to that variable.

From now on, the attention will be focused on the best complex system at the optimum temperature (303 K) and

Table 2 3-hexyne total conversion (X_T), conversions to (*Z*)-3-hexene ($X_{(Z)}$) and selectivities to (*Z*)-3-hexene, (*E*)-3-hexene and *n*-hexane ($S_{(Z)}$, $S_{(E)}$ and S_n , respectively) for the following catalysts: Lindlar, [RhCl(TDA)₃] complex unsupported and anchored on RX3

Reaction time (min)	Catalyst	T (K)	X _T (%)	$X_{(Z)}$ (%)	$S_{(Z)}$ (%)	$\mathbf{S}_{(E)}$ (%)	S _n (%)
50	Lindlar	275	48	44	92	3	5
		290	53	49	93	3	4
		303	57	53	93	4	3
	[RhCl(TDA) ₃]	275	76	61	79	13	8
		290	81	64	80	13	7
		303	82	69	84	13	3
	[RhCl(TDA)3]/RX3	275	87	85	98.6	2	0.3
		290	89	87	98.6	2	0.3
		303	92	90	98.6	1.5	0.5
75	Lindlar	275	55	48	87	4	9
		290	60	50	82	6	12
		303	66	52	79	7	14
	[RhCl(TDA) ₃]	275	88	64	72	16	11
		290	92	68	73	16	11
		303	93	72	78	16	6
	[RhCl(TDA) ₃]/RX3	275	98	92	94	3	3
		290	99	93	94	3	3
		303	99.8	95	95	2	3
120	Lindlar	275	60	46	77	6	17
		290	66	45	68	9	23
		303	73	44	61	11	28
	[RhCl(TDA) ₃]	275	94	55	58	21	21
		290	98	58	59	20	21
		303	98	62	64	20	16
	[RhCl(TDA) ₃]/RX3	275	99.9	82	82	9	9
		290	99.9	81	81	8	11
		303	99.9	82	82	8	10

Reaction conditions: hydrogen pressure 150 kPa, and different reaction temperatures (275, 290 and 303 K) at 50, 75 or 120 min of reaction

its performance will be compared with that of the Lindlar catalyst, which is typically considered as a reference system, at the same temperature.

In Fig. 4 the differences between the desired and side products ((E)-3-hexene plus *n*-hexane) versus 3-hexyne total conversion, for the Lindlar catalyst and for [RhCl(TDA)₃]/RX3, are plotted. It can be seen that the highest difference between the conversion to the desired product and to the side products ((E)-3-hexene + hexane), for the [RhCl(NH₂(CH₂)₁₂CH₃)₃]/RX3 system was obtained for a 3-hexyne total conversion equal to 96.4% (at 60 min). Meanwhile, the corresponding value for the Lindlar catalyst was achieved for a 3-hexyne total conversion of 57.5% (at 50 min). For these optimum 3-hexyne total conversions, the conversion to (Z)-3-hexene with $[RhCl(NH_2(CH_2)_{12}CH_3)_3]/RX3$ was 94%, 1.76 times higher than that corresponding to the Lindlar catalyst (53.5%). On the other hand, the selectivities to (Z)-3-hexene are 97 and 93, respectively.

The relative differences to the (*Z*)-3-hexene product obtained with [RhCl(NH₂(CH₂)₁₂CH₃)₃]/RX3 (S_{Zcomplex}) and with the Lindlar catalyst (S_{ZLindlar}) were calculated as follows: $\Delta S(\%) = [(S_{Zcomplex} - S_{Z/Lindlar})/S_{ZLindlar}] \times 100$. This ΔS is plotted in Fig. 5 as a function of 3-hexyne total conversion. For a 3-hexyne total conversion of 57.5%, although it is not the optimum for [RhCl(NH₂(CH₂)₁₂ CH₃)₃]/RX3 but the best value for the Lindlar catalyst, the relative difference in selectivity (ΔS) for the Z species favors the former in 7.23%.

On the other hand, considering that after catalytic evaluation the elemental composition of the run supported complex is equal to that of the pure complex, and that there is no leaching at all, it can be suggested that: (a) the coordination compound maintains its identity after being



Fig. 4 Difference in conversion, versus 3-hexyne total conversion at 303 K, for: Lindlar catalyst (1), [RhCl(TDA)₃],/RX3 (3). Note: ΔX (%) = [X_(Z)-(X_(E) + X_{hexane})]



Fig. 5 Relative difference in selectivity to the Z species (ΔS) versus 3-hexyne total conversion (X_T), at 303 K. Note: ΔS (%) = [(S_{ZComplex}-S_{ZLindlar})/S_{Z Lindlar}] × 100

used in the hydrogenation reaction, remaining adsorbed as a whole on the support surface and (b) it is the catalytically active species.

At this point, gathering information from some of the previous paragraphs, the best catalytic behaviour shown by [RhCl(TDA)₃]/RX3 for the 3-hexyne partial hydrogenation can be explained by:

- (a) A [RhCl(TDA)₃] "table" type anchoring on RX3 without loosing its coordination sphere structure associated to a C_{2v} local site-symmetry, what in turns means to have available, on the one hand, a high electron density (the HOMO frontier orbital) along the z axis ready to overlap with the hydrogen σ antibonding orbital, thus favouring H–H bond breaking; and on the other hand, an empty orbital extended on the xy plane (the LUMO frontier orbital) available to interact with the electron density from the 3-hexyne triple bond, thus weakening one of its π bonds.
- (b) A [RhCl(TDA)₃] major distribution into the RX3 meso and macropores, sites where the 3-hexyne can be easily adsorbed, augmenting its concentration around the complex, via a physicochemical interaction.

3.3.2 Practical considerations

As the best catalyst system was $[RhCl(NH_2(CH_2)_{12}CH_3)_3]/RX3$, that presents high conversion and selectivity values with a low sensitivity to the variation of temperature, some practical-economical benefits could be mentioned: (a) the easy and cheap way in which the catalyst is removed from the remaining solution after ending the hydrogenation reaction; (b) the main product does not need further purification due to a possible contamination with a heavy metal

compound because no complex leaching was detected; and lastly, (c) there is no need for a costly temperature control system.

4 Conclusions

It is possible to hydrogenate 3-hexyne to obtain (Z)-3-hexene, under mild conditions using [RhCl(TDA)₃] as catalyst in homogeneous/heterogeneous systems with a very good general performance, and better than that of the Lindlar catalyst. [RhCl(TDA)₃]/RX3 shows the highest 3-hexyne total conversion and selectivity to (Z) 3-hexene, the desired product. This behaviour may be understood by considering electronic and structural effects, which can be explained by concepts of complex dimensions, local site symmetry, frontier orbitals and physicochemical interactions.

Additionally, the performance of [RhCl(TDA)₃]/RX3 as a catalyst exhibits a low sensitivity to the variation of temperature, a factor that is useful for technological applications, when: (a) deciding investment on temperature control system, (b) removing the catalyst from the reactor and (c) purifying the desired product.

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