Applied Organometallic Chemistry (1990) 4 157–162
0268-2605/90/020157-06 $05.00
© 1990 by John Wiley & Sons, Ltd.

Surface-bound organometallic rhodium precursors for 1-hexene hydrogenation

Juana Herrero,[a] Carmen Blanco,[a] Miguel A. Esteruelas[b] and Luis A. Oro[b]
[a]Departamento de Química, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain, and [b]Departamento de Química Inorgánica, Universidad de Zaragoza, Spain

Received 11 September 1989 Accepted 25 November 1989

Rhodium precursor catalysts supported on palygorskite, montmorillonite and silica were obtained from an organometallic cationic rhodium species and evacuated supports at different temperatures. Based on the different times which precursors took to be active in 1-hexene hydrogenation, in the liquid phase at atmospheric hydrogen pressure, it has been deduced that the supported rhodium species varies with the support and its dehydration temperature. Activity in this reaction also depended on the support, its dehydration temperature and storage in air. Precursors and catalysts were characterized by X-ray photoelectron and infrared spectroscopy. Very stable complexes are obtained under humid ambient conditions. With montmorillonite support, activity decreases if rhodium/1-hexene ratio decreases.

Keywords: Rhodium, palygorskite, montmorillonite, silica, 1-hexene hydrogenation, catalysts

INTRODUCTION

The preparation of heterogeneous catalysts from surface organometallic complexes, on oxide supports, is a method used to stabilize homogeneous catalysts and/or to obtain small metallic particles, which are nearly uniform in size and structure[1,2] and in some cases have resistance to sintering.[3]

Catalysts prepared by this method are more economical, as the minimum size means that all the metallic atoms are at the surface and thus they are all active centres. Another fundamental objective is to obtain uniform active species in order to be able to study the catalytic properties as a function of only one kind of active species.[4–6] In this way high selectivity can be obtained with heterogeneous catalysts. Another interest is to determine how a change in the ligand environment of a transition-metal complex affects the reactivity of a metal system bound to it,[7] i.e. to elucidate changes in molecular reactivity which occur when a soft ligand environment of a transition-metal complex is replaced by a hard, or rigid, oxygen-based one.

In general, the dehydration temperature influences the surface properties of a metal oxide because it determines the kind and concentration of surface hydroxyl groups.[8,9] With clays, in particular, important changes in catalytic activity can take place with small variations of this water content.[10]

In this paper, the preparation of catalysts from organometallic rhodium precursors on different supports, varying the outgassing temperature of the support, has been described. A preliminary communication on part of this work has already appeared.[11] The objective of this work is to study how the type of support and its water content influence the formation of rhodium species at the surface and their hydrogenation activity.

EXPERIMENTAL

Materials

Silica Aerosil 200 (Degussa) was used as support without any pretreatment and evacuated at 400 °C. Palygorskite was used as support without any pretreatment and evacuated at 150 °C and 400 °C. The temperature of 150 °C was chosen in order to obtain a reversible state of folded palygorskite with half of its coordinated water.[12] Both types of supports were evacuated at 10^{-5} torr (1 torr = 133.3 N m^{-2}) for 12 h after equilibrium was reached. After cooling in vacuum, 5 cm^3 of acetone was quickly added to the evacuated support and the cationic rhodium complex was added.

Catalyst preparation

[Rh(nbd)(Me$_2$CO)$_x$]ClO$_4$

This cationic rhodium complex was prepared by reacting 23 mg (0.05 mmol) of [Rh(nbd)Cl]$_2$ (nbd = norbornadiene) [prepared from RhCl$_3$.3H$_2$O (Strem) by the method described[13]], with 0.1 mmol of silver perchlorate (AgClO$_4$) in acetone (Merck p.a.). After stirring for 30 min in the absence of light, the precipitated silver chloride (AgCl) was filtered off on Kieselguhr and the filtrate, corresponding to 0.1 mmol of the cationic compound, was collected in a flask.

[Rh]/support

The support, weighing 1 g, was suspended in 25 cm^3 of 4×10^{-3} mol dm^{-3} [Rh(nbd)(Me$_2$CO)$_x$]ClO$_4$ dissolved in acetone (the filtrate solution of the above paragraph). The suspension was stirred in the absence of light under argon. The colour of the solution changes from yellow to light yellow and that of the support from white or grey (paly-400) to beige, pink or grey upon interaction. After 24 h the resulting coloured solid, denominated as the [Rh]/support, was filtered off and washed with acetone. The [Rh]/paly precursor was pink until dried. The rhodium loading which was achieved in these conditions is shown in Table 1. This was determined by using UV–VIS spectroscopy to measure the concentration of [Rh(nbd)(Me$_2$CO)$_x$]ClO$_4$ species at its λ_{max} = 382 nm in filtrate solutions.

Rh$_x$/support

The precursor [Rh]/support, weighing 1 g, was suspended in acetone. The suspension was stirred under molecular hydrogen in the absence of light. The original solid became grey after the time shown in Table 1. Then, the grey solid formed, denominated as Rh$_x$/support, was filtered off and washed with acetone. The filtrate solutions of the Rh$_x$/support were colourless if the support was a phyllosilicate. However, some leaching of rhodium complex (*ca* 0.003 mmol) was observed with silica support in some cases.

The dehydration temperature (T_d) did not influence the rhodium content on silica, but it did have an influence on palygorskite.

Attempts to obtain a higher rhodium content on silica by concentrating the suspension were not successful, because the rhodium complex leached off the silica support during its reduction.

Catalytic activity

Hydrogenation of 1-hexene was carried out in a round-bottomed flask fitted with a side arm with a septum to allow injection and sampling for gas chromatography. The flask was connected to a gas burette that allowed pumping of the system and hydrogen dosing. The catalyst suspension, the quantity of which was equivalent to 0.02 mmol of rhodium catalyst in 10 cm^3 of acetone (Merck p.a.), was outgassed in the hydrogenation flask and then hydrogen at one atmosphere pressure was admitted. After 1 h of prehydrogenation time, 1-hexene (2 mmol) was admitted. Hydrogenation rates to n-hexane were followed with a Perkin–Elmer Sigma 3, using a 3.2 mm × 4 m column, packed with 15% β,β'-oxidipropionitrile Chromosorb W 80/100 mesh.

Table 1 Supports, precursors prepared, rhodium content (%Rh) achieved and time (*t*) which precursors took to be active in 1-hexene hydrogenation

Support	T_d (°C)	Precursor	Reaction time with hydrogen, *t*	%Rh	Catalyst
SiO$_2$	–	[Rh]/SiO$_2$	30 min	0.6	Rh$_x$/SiO$_2$
SiO$_2$	400	[Rh]/SiO$_2$-400	12 h	0.6	Rh$_x$/SiO$_2$-400
mont	–	[Rh]/mont	24 h	1	Rh$_x$/mont
paly	–	[Rh]/paly	3 days	0.8	Rh$_x$/paly
paly	150	[Rh]/paly-150	6 h	0.9	Rh$_x$/paly-150
paly	400	[Rh]/paly-400	4 h	0.9	Rh$_x$/SiO$_2$-400

Reaction conditions: Precursor, *ca* 1 g; volume of acetone solution, 30 cm^3; hydrogen pressure, 1 atm. The time (*t*) depends on the ageing in air when the support is a phyllosilicate. If [Rh]/paly precursor (pink), without drying, is put in acetone under a hydrogen atmosphere, Rh$_x$/paly is obtained, not in 3 days but after 1½ hours.

X-ray photoelectron spectroscopy (xps)

The XPS spectra were recorded on a LHS-10 spectrometer using AlKα radiation (1486.6 eV) for excitation and a pass energy of 50 eV. Binding energy (BE) was referenced to the C 1*s* level at 284.6 eV. The spectrometer was interfaced to an H-P 1000 E computer.

Infrared spectroscopy

Spectra were recorded using a Perkin–Elmer 577 spectrometer. Samples were formed into thin wafers weighing 10 mg cm^{-2} which were mounted in a quartz holder and placed in an infrared cell. The cell was designed so that the holder could be moved from a Pyrex section of the cell, where the sample could be heated, to a glass section where a pair of calcium fluoride windows were attached to allow collection of the spectra. The samples were subjected to a vacuum of 10^{-5} torr for 2 h.

X-ray diffraction

X-ray basal spacings of powder samples were determined with a PW 1710 Philips X-ray diffractometer and Cu Kα radiation. Diffraction patterns were also obtained for fully solvated and swelled samples when montmorillonite was the support. These were registered by placing a smooth paste made by mixing the sample with acetone on a sample holder with kapton windows held in place with cellophane tape.

RESULTS

Catalytic activity

All the catalysts prepared were active in 1-hexene hydrogenation. The hydrogen consumption, represented in Fig. 1, was in accordance with n-hexane analysis by gas chromatography (GC). For silica supports the activity decreased if the prehydrogenation time was increased; for phyllosilicates the activity remained constant.[11]

The times which precursors took to be active (Table 1) are for the fresh precursors. For aged precursors supported on palygorskite these times were longer, and the precursors were not reduced to metallic rhodium nor converted into active-species during the four-day observation period. When [Rh]/paly precursor that was not dried (pink, i.e. solvated in acetone) was put into acetone under a hydrogen atmosphere, the suspension

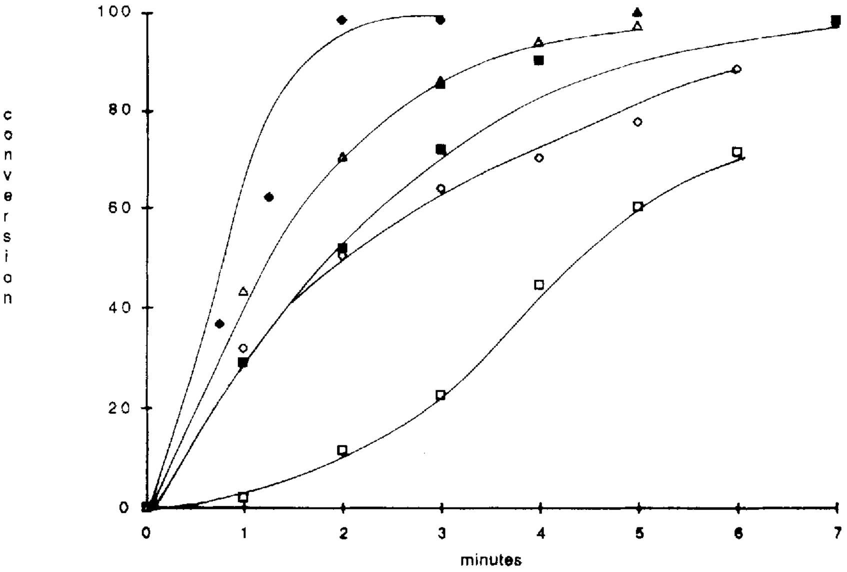

Figure 1 Hydrogenation of 1-hexene to n-hexane by Rh$_x$/support catalysts. Support: ◆, palygorskite evacuated at 400 °C; △, palygorskite evacuated at 150 °C, and natural palygorskite; ■, montmorillonite; ◇, silica; □, silica evacuated at 400 °C. With this latter support the result is not representative because activity decays quickly with prehydrogenation time.

took $1\frac{1}{2}$ hours to be active. The variation of this time with the ageing of the precursor has also been found for homogeneous rhodium catalysts.[14]

When the ratio 1-hexene/rhodium was varied from 100 to 1000, the activity remained of the same order for all the catalysts prepared, except for the catalyst named Rh_x/mont for which the activity decreased from 0.231 to 0.044 mmol $\text{H}_2\ \text{g}^{-1}(\text{Rh})\ \text{min}^{-1}$.

For the palygorskite supports, the addition of 1-hexene, during the reduction process, inhibits the formation of metallic rhodium; no more hydrogen consumption nor any change in the solution was observed.

Infrared spectra

The reactivity of the rhodium surface complex is in some way a measure of rhodium–support interaction. In this sense, the infrared spectra of precursors on silica supports show a decrease in the intensity of the band at 3740 cm^{-1}, compared with the silica infrared spectrum itself. However, the infrared spectra of the catalysts are similar to those of silica. In both catalysts, the band assigned to the hydroxyl groups appears.

Some authors[15,16] have found analogous results. These observations can be rationalized in terms of the reactions described by Yermakov,[15] viz. Eqns [1] and [2].

$$\text{Si—O—H} + [\text{Rh(nbd)}(\text{Me}_2\text{CO})_x]\text{ClO}_4 \rightarrow \text{Si—O—Rh(nbd)} + \text{HClO}_4 + x\text{Me}_2\text{CO} \qquad [1]$$

$$\text{Si—O—Rh(nbd)} \xrightarrow[-\text{H}_4\text{nbd}]{\text{H}_2} \text{Si—O—H} + \text{Rh}_x \qquad [2]$$

There is a significant difference between the silica support without outgassing and the support outgassed at 400 °C. In the first case the rapid reduction suggests that there is less interaction. This difference is seen in the thermolysis of this sample. Its colour changes to grey at 200 °C, 100 °C before the sample with silica outgassed at 400 °C. With natural palygorskite as the support, the infrared spectrum of the precursor, at 150 °C in vacuum, does not show bands of coordinated water compared with that of the palygorskite;[12] instead, broad bands appear at 3420 and 3220 cm^{-1} assigned to hydrogen-bonded oxygen of the tetrahedral layer, due to polarization of the coordinated water[17] to cations (exchange or octahedral magnesium). However in the corresponding catalyst, Rh_x/paly, in the same conditions, the spectrum of palygorskite reappears in part; bands of coordinated water and bonded hydrogen appear. The anchorage of the rhodium compound on palygorskite may take place by two different processes (Eqns [3] and [4]).

$$[\text{paly—H}_2\text{O}]\text{M}^{n+} + [\text{Rh(nbd)}(\text{Me}_2\text{CO})_x]\text{ClO}_4 \rightarrow [\text{paly—}\overset{\text{H}}{\text{O}}\rightarrow[\text{Rh(nbd)}]]\text{M}^{n+} + \text{HClO}_4 + x\text{Me}_2\text{CO} \qquad [3]$$

$$[\text{paly—H}_2\text{O}]\text{M}^{n+} + [\text{Rh(nbd)}(\text{Me}_2\text{CO})_x]\text{ClO}_4 \rightarrow [\text{paly—H}_2\text{O}][\text{Rh(nbd)}]^+ + \text{M}(\text{ClO}_4)_n + x\text{Me}_2\text{CO} \qquad [4]$$

If the support is palygorskite evacuated at 150 °C, the same infrared spectrum is recorded for precursor and catalyst. If the support is palygorskite evacuated at 400 °C, a lower intensity of a broad and poorly defined band of hydroxyl groups is recorded for the catalyst in comparison with the precursor.

X-ray photoelectron spectroscopy (xps)

Table 2 shows the binding energy and the assigned oxidation state for some of the precursors and catalysts prepared. There is no signal in the rhodium 3*d* energy level for catalysts on the silica support. The other catalysts, called Rh_x/support, have their rhodium 3*d* binding energy at about 307 eV, which is assigned to metallic rhodium.[18–20] However, the precursors [Rh]/support show rhodium 3*d* binding energy at 309.2 and 308.6 eV which have been assigned to rhodium(III) and rhodium(I) respectively on the basis of previous

Table 2 Oxidation state and binding energy for various rhodium catalysts

Oxidation state	Binding energy (eV)	Catalyst	Reference
Rh^0	307	Rh/TiO_2	20
	307	$\text{Rh/Al}_2\text{O}_3$	19
	307	Rh_x/paly	
	307.2	Rh_x/paly-400	
Rh^I	308.0 (Si2*p*)	$\text{Rh}^\text{I}/\text{SiO}_2$	7
	308.6	$\text{Rh}^\text{I}/\text{Al}_2\text{O}_3$	21
	308.6	[Rh]/paly-400	
Rh^III	308.6	LaRhO_3	18
	309.2	Rh^I/polymer	22
	309.2	[Rh]/paly	
	309.2	[Rh]/paly-150	

works.[7,21,22] Catalysts and precursors do not contain anions coming from the complex.

X-ray diffraction

In order to determine whether the decrease in activity in 1-hexene hydrogenation by the Rh_x/mont catalyst is due to some collapse of the layers, diffraction patterns have been taken. Basal spacings are at the same distance, 14.7 Å (1.47 nm), for montmorillonite, [Rh]/mont and Rh_x/mont powder. However the intensity for this last sample is very low (30% of the intensity of the other samples), in the same conditions. On swollen samples, in acetone suspension, the three samples do not show basal spacings as expected, only a peak at 11.7 Å, due to the layer structure solvated by acetone,[23] and several joint peaks, 7–7.9 Å, probably due to complexes of cationic exchange and acetone, were observed. The intensity of the peak at 11.7 Å (equal to 9.6 Å, layer, +2.1 Å, acetone) is less in the Rh_x/mont sample, probably due to some collapse of the layers.

Diffraction patterns for Rh_x/paly-150 are the same as for palygorskite, indicating that the palygorskite structure is recovered during sample preparation. For the Rh_x/paly-400 sample, a straight line is registered, i.e. the structure is broken.

DISCUSSION

The reducibility of the supported rhodium species varies if the support or its T_d is changed, suggesting the formation of different species or different interactions between rhodium and support.

A different behaviour has been found for the [Rh]/paly precursor. The stability of the rhodium species formed may be due to steric hindrance of these species. Formation of a complex or water polarization may be induced by rhodium, a process in some way analagous to hydrolysis of cation exchange previously described.[24] A possible species formed may be related to the synthesis of a rhodium(I) complex $[Rh(OH)(nbd)]_2$,[25] the oxygen being one from the palygorskite. In this case, in the suspension, there are 200 mg of water, which is 20% of the weight of palygorskite, so this complex formation may take place during the drying process when the acetone/water ratio is inverted. An analogous complex formation should explain the infrared bands observed in the precursor and the lack of reactivity with hydrogen. The capability of palygorskite to stabilize high oxidation states of rhodium may be due to the fact that this support is easily reduced or to an isomerization reaction of the type studied by Weiss.[26]

Ward and Schwartz[27] have described the formation of rhodium hydride species during the reduction at the solid–gas interface of an allylic rhodium complex supported on silica and on titanium dioxide.[28] It is suggested that in the absence of chemical anchoring to the oxide, hydrogenation of the allyl–rhodium complex will give rhodium particles. Rhodium hydride species are also formed from the same complex on titanium dioxide at 70 torr hydrogen pressure.[29] In our work, rhodium–support interaction must take place in catalysts as the re-use of catalysts indicates,[11] and in precursors as infrared spectra show. It is possible that the formation of metallic particles is due to the fact that the reduction is performed in acetone medium. The difference in behaviour of palygorskite and silica supports suggests that in palygorskite the interaction takes place through tetrahedral oxygen as cation exchange and not on the very few silanol groups of silica.

With palygorskite support, the addition of 1-hexene during the prehydrogenation time blocks hydrogen consumption and, thereby, the reduction of the precursor to active metallic rhodium. This inhibition suggests a stable olefin adsorption which prevents further rhodium reduction. Tennakoon *et al.*[30] have found 1-hexene adsorption for an aluminium(III) laponite sample by aluminium(III) cation exchange. The 1-hexene adsorbed at tetrahedral-layer aluminium sites could block hydrogen adsorption by rhodium, which is probably located as an exchange cation.

The different rate of hydrogen consumption shown in Fig. 1 may be due only to a smaller metal particle size (i.e. a higher percentage of rhodium atoms exposed) or to an electronic deficiency of these small aggregates as a result of a partial electron transfer to the clay, as has been postulated for rhodium/zeolites.[1] The highest activity found is for the catalyst designated Rh_x/paly-400. Rhodium 3*d* binding energy is slightly higher than in the rest of catalysts. This indicates a lower electron density, which could be the cause of higher activity.

The behaviour of the Rh_x/mont sample, where the activity decreases if the ratio 1-hexene/rhodium changes from 100 to 1000, may be due to the fact that reaction takes place on the accessible surface. Rhodium is located on both internal surfaces, that are in some extent collapsed as the diffraction patterns show, and external surfaces. So the 1-hexene/accessible rhodium ratio is not 1000, but higher. In this context, Schoonheydt *et al.*[31] have found a related result: the layers do not swell after an organometallic rhodium complex is intercalated in hectorite, so other dissolvent molecules cannot be intercalated.

The 1-hexene double-bond migration found is in accordance with results of pyridine adsorption by infrared spectroscopy.[32]

In summary, the rhodium organometallic cationic complex reacts with clays. Rather different rhodium species are obtained depending on the water content. Very stable species are formed if the support is natural palygorskite. All species formed are precursors for 1-hexene hydrogenation after a time which depends on the species formed and, therefore, on the support. Molecular reactivity changes when a soft ligand of a transition-metal complex is replaced by a hard one. Supplementary material is available, namely RX diffraction patterns, IR and XP spectra. This can be obtained by contacting one of the authors (JH).

Acknowledgements We wish to express our gratitude to Dr Agustin R González-Elipe and D Juan P Espinós for XP spectra and helpful discussions, and the XPS Laboratory at Universidad de Sevilla.

REFERENCES

1. Pajares, J A, Reyes, P, Oro, L A and Sariego, R *J. Mol. Catal.*, 1981, 11:181
2. Foley, H C, DeCanio, S J, Tau, K D, Chao, K J, Onuferko, J H, Dybowski, C and Gates, B C *J. Am. Chem. Soc.*, 1983, 105:3074
3. Yermakov, Yu I and Kuznetsov, B N *J. Mol. Catal.*, 1980, 9:13
4. Yermakov, Yu I *Pure Appl. Chem.*, 1980, 52:2075
5. Basset, J M and Choplin, A *J. Mol. Catal.*, 1983, 21:95
6. Gates, B C and Lamb, H H *J. Mol. Catal.*, 1989, 52:1
7. Schwartz, J *Acc. Chem. Res.*, 1985, 18:302
8. Zakharov, V A and Yermakov, Yu I *Catal. Rev. – Sci. Eng.*, 1979, 19:67
9. Lamb, H H, Gates, B C and Knözinger, H *Angew. Chem. Int. Ed. Engl.*, 1988, 27:1127
10. Adams, J M, Clapp, T V and Clement, D E *Clay Minerals*, 1983, 18:411
11. Herrero, J. Blanco, C and Oro, L A *Appl. Organomet. Chem.*, 1989, 3:553
12. van Scoyoc, G E, Serna, C J and Ahlrichs, J L *Am. Mineral.*, 1979, 64:215
13. Abel, E W, Bennet, M A and Wilkinson, G *J. Chem. Soc.*, 1959, 3178
14. Pinilla, E, Oro, L A and Sariego, R *J. Less Common Met.*, 1980, 72:P31
15. Yermakov, Yu I *Catal. Rev.* – Sci. Eng., 1976, 13:77
16. Keyes, M P and Watters, K L *J. Catal.*, 1986, 100:477
17. Blanco, C, Herrero, J, Mendioroz, S and Pajares, J A *Clays and Clay Minerals*, 1988, 36:364
18. Gysling, H J, Monnier, J R and Apai, G *J. Catal.*, 1987, 103:407
19. Huizinga, T, van't Blik, H F J, Vis, J C and Prins, R *Surf. Sci.*, 1983, 135:580
20. Munuera, G, González-Elipe, A R, Espinós, J P, Muñoz, A, Conesa, J C, Soria, J and Sanz, J *Catal. Today*, 1988, 2:663
21. van't Blik, H F J, van Zon, J B A, Huizinga, D T, Vis, J C, Koningsberger, D C and Prins, R *J. Am. Chem. Soc.*, 1985, 107:3139
22. Furlani, C, Mattogno, G, Polzonetti, G, Sbrana, G and Valentini, G *J. Catal.*, 1985, 94:335
23. Gutiérrez Ríos, E and Rodríguez, A *Anales de la RSEFyQ SerieB – Química*, 1961, 57B:117
24. Raythata, R and Pinnavaia, T J *J. Catal.*, 1983, 80:47
25. Usón, R, Oro, L A and Cabeza, J A *Inorg. Synth.*, 1985, 23:126
26. Weiss, A *Angew. Chem. Int. Ed. Engl.*, 1981, 20:850
27. Ward, M D and Schwartz, J *J. Mol. Catal.*, 1981, 11:397
28. Chang, T, Bernasek, S L and Schwartz, J *J. Am. Chem. Soc.*, 1989, 111:758
29. Asakura, K, Iwasawa, Y and Kuroda, H *J. Chem. Soc., Faraday Trans I*, 1988 , 84:1329
30. Tennakoon, D T B, Thomas, J M, Jones, W, Carpenter, T A and Ramdas, S *J. Chem. Soc., Faraday Trans. 1*, 1986, 82:545
31. Schoonheydt, R A, Pelgrims, J, Hendrikx, P and Luts, J *Clays and Clay Minerals*, 1984, 32:185
32. Herrero, J and Blanco, C to be published