

Hydroformylation of 1-octene using Rh catalysts supported on P-containing activated carbon materials

*C. M. Giménez-Eiras, J. Torres-Liñán, M. García-Rollán, M. J. Valero-Romero,
J. Rodríguez-Mirasol, T. Cordero*

*Departamento de Ingeniería Química, Andalucía Tech, Universidad de Málaga,
Campus de Teatinos s/n, 29010 Málaga, España.*

Introduction

Hydroformylation is a relevant industrial homogeneously catalyzed reaction, largely applied in industry for production of aldehydes and other bulk chemical platforms. The most common catalysts used at industrial scale are homogeneous cobalt and rhodium complexes, especially those with phosphorus ligands, which further require severe separation processes [1]. Therefore, the heterogenization of these catalysts leads to a cost-efficient and environmentally friendly process, even more convenient when biomass residues are used as renewable carbon-based catalyst supports.

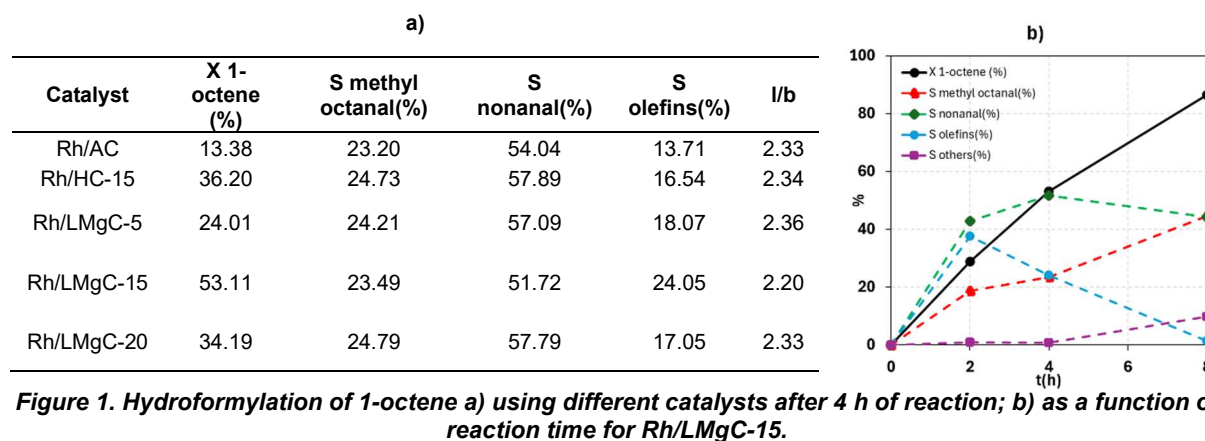
The objective of the present work is to use P-containing activated carbon materials prepared from lignin, a co-product from the paper-making industry, as the catalysts support for Rh catalysts for the hydroformylation of 1-octene. The influence of different P/Rh molar ratios, as well as the presence of Mg on the carbon precursor and the catalyst recyclability was studied.

Experimental

The activated carbons were prepared by physical activation of olive stone with H₂O at 800 °C (AC, without P and Mg) and by chemical activation of two residual lignins (Hansa, HNa, and Lignex, LMg) with H₃PO₄ (H₃PO₄:lignin ratio of 3) at 800 °C under N₂. Rh₂(OOCCH₃)₄ was deposited on the carbon supports by incipient wetness impregnation, using different P/Rh molar ratios (5, 10, 15 and 20). For AC, 1 wt% of Rh was added. All samples were submitted to a reduction step under 10% H₂ at 250 °C. The hydroformylation experiments were carried out in a batch setup under constant syngas pressure (semi-batch conditions), with a H₂/CO molar ratio of 1, a 1-octene/Rh molar ratio of 9800, at 70 °C, 40 bar and up to 8 h. LMgC-x and HC-x correspond to the activated carbons prepared from LMg and H lignins, respectively, where x is the P/Rh molar ratio.

Results and discussion

LMgC and HC activated carbons exhibit relatively high BET surface areas of 305 and 1490 m²/g, respectively, along with mesopore volumes of 0.29 m³/g for LMgC and 1.33 cm³/g for HC. XPS analysis reveals that the surface concentrations of P and Mg in LMgC are 5.9 and 0.6 wt%, respectively, while in HC, they are 2.5 and 0.0 wt%.



1-Octene conversion and selectivities towards major reaction products are presented in Figure 1. The major reaction products are nonanal, methyl octanal and olefinic C8 isomers. The presence of P and Mg on the activated carbon support leads to higher conversions of 1-octene, whereas the linear-to-branch (I/b) aldehydes ratio remains constant. The I/b aldehyde ratio shows a value of 2.2-2.3 for all the catalysts after 4 h of reaction, which is similar to that obtained for the homogeneous phase catalyst RhH(CO)(PPh₃)₃ at iso-conversion conditions [1].

The highest conversion of 1-octene is obtained for Rh/LMgC-15 at any reaction time, with a maximum value of 86 % after 8 h of reaction and a yield to nonanal of 35 %. On the other hand, the I/b aldehyde ratio decreases with long reaction times (Figure 1b), since olefinic C8 isomers are converted into branched aldehydes.

In summary, the use of renewable carbon-based supports has been studied for the hydroformylation of 1-octene. The presence P and Mg on the activated carbons produces higher conversions, while maintaining a high selectivity to aldehydes.

References

[1] Sartipi, S. et al., "Dynamic release-immobilization of a homogeneous Rhodium hydroformylation catalyst by a polyoxometalate metal-organic framework composite", *ChemCatChem* **7**, (2015) 3243-3247

Acknowledgements

The authors express their gratitude to MICIU/AEI/10.13039/501100011033 and the European Union's "Next Generation EU" for funding the project CNS2022-135418.