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ABSTRACT BOOK

L-PO-28 **NITRATE- AND NITRITE- ASSISTED CONVERSION OF AN ACETONITRILE LIGAND INTO AN AMIDATO BRIDGE AT AN {MO2(CP)2(SME)3} CORE.** Christine Le Roy, François Yves Petillon, Philippe Schollhammer, Jean Talarmin, *UMR 6521, Chimie, Electrochimie Moléculaires et Chimie Analytique, UFR Sciences et Techniques, Université de Bretagne Occidentale -Brest- FRANCE, christine.leroy@univ-brest.fr*

Keywords: amidato bridge; electrochemistry; dimolybdenum sulfur complexes

The search for a "biologically-inspired" process to reduce NOx- (x = 2, 3) ions to dinitrogen has led us to study the reactivity of dinuclear thiolato-bridged molybdenum compounds with NOx- (x = 2, 3).

We therefore examined the reaction of the bis(acetonitrile) complex [Mo2(Cp)2(SMe)3(MeCN)2]+ 1+ with nitrate and nitrite. However, these reactions did not produce NO3 or NO2 derivatives, but a amidato complex.

This communication will focus on the reactions of 1+ with NO3- and NO2- as well as the electrochemical behaviour of the reaction product, the amidato complex (20/+)[1].

Reference

[1] Le Henanf M., Le Roy C., Petillon F.Y., Schollhammer P., Talarmin J.,. : Eur. J. Inorg. Chem., 19, 3875-3883, 2005.

L-PO-29 **ENZYMATIC RESOLUTION OF INDINAVIR PRECURSORS IN IONIC LIQUIDS AND REUSE OF REACTION MEDIUM BY PRODUCT SUBLIMATION.** Nuno M. T. Lourenço, Carlos A. M. Afonso, *REQUIMTE/CQFB, Departamento de Química, Faculdade de Ciencias e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal, nuno.lourenco@dq.fct.unl.pt*

Keywords: enzymatic resolution; ionic liquid; reuse

The development of green and efficient routes to achieve enantiomeric pure compounds is subject of considerable interest due to their use as precursors of many drugs with physiological activity such as Indinavir, a HIV protease inhibitor. In the past few years several enzymatic and non-enzymatic procedures have been described for the preparation of chiral cis-1-amino-indan-2-ol.[1]

The use of ionic liquids (ILs) in enzymatic resolutions is a well established methodology. ILs provide a stable and friendly environment for the enzymes where they retain their catalytic activity even after several cycles. The efficient reuse and purification of ILs makes them a powerful toll to be used in bio-catalyse.[2]

Herein we presented our studies on the use and reuse of ILs for the efficient enzymatic resolution of (+/-)-cis-Benzyl N-(1-hydroxyindan-2-yl)carbamate were the products are simply recovered from IL by sublimation.

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[1] Ghosh, A. K.; Fidanze, S.; Senanayake, C. H. Synthesis 1998, 937-961.

[2] Jain, N.; Kumar, A.; Chauhan, S.; Chauhan, S. M. S. Tetrahedron 2005, 61, 1015-1060.

L-PO-30 **SUPPORTED NOBLE METAL CATALYSTS PREPARED BY PHOTOCHEMICAL DEPOSITION.** Bruno F. Machado, Helder T. Gomes, Joaquim L. Faria, *Laboratório de Catálise e Materiais, Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal, bmachado@fe.up.pt*

Keywords: heterogeneous catalysis; selective hydrogenation; fine chemistry

Photochemical deposition of noble metals in different supports is gaining importance because of its simplicity and advantages. Its main advantage is the ability of spreading very effectively the metal throughout the support, thus leading to very high dispersions. The materials prepared in such way can be used as catalysts resulting in higher molecular control, with a positive effect on both activity and selectivity.

The selective catalytic hydrogenation of organic substrates containing unsaturated functional groups, like steroids or alpha,beta-unsaturated aldehydes, is a common synthetic route for industrial preparation of fine chemicals. The quest for efficient catalysts for this process is very active domain of research.

Different catalysts (Pt and Ir supported on TiO2) were prepared by liquid phase photodeposition and used in the model reaction of cinnamaldehyde selective hydrogenation to test their activity and selectivity. The photodeposition method was able to produce materials with an outstanding performance for selective hydrogenation of cinnamaldehyde leading to selectivities as high as 64% towards cinnamyl alcohol at 79% conversion under mild operating conditions.

L-PO-31 **HIGHLY EFFECTIVE "GREEN" TECHNOLOGY OF HIGHER A-OLEFINES PROCESSING**. Ildar M. Magdeev, Yulia H. Budnikova, Damir I. Tazeev, Oleg G. Sinyashin, Ilgizar A. Jakushev, Rafinat S. Yarullin, *Institute of Organic and Physical Chemistry of Russian Academy of Sciences, Kazan, Russia, magdeev@iopc.knc.ru*

Keywords: highest alpha – olefins; halogenoparaffins; technology

High-tech ecologically safety procedure of halogenated, first of all, chlorinated highest a-olefines, as alternate to industrial method founded on the use of chlorine gas, was designed. The offered process allows to obtain chloroparaffins with a controlled amount of chlorine (up to 50 %) in the mild conditions. Process consists in electrochemical generating radical chlorine (bromine) from chlorides or bromide in a water solution at the presence of the higher a-olefines and results in formation of halogenoparaffin with the contents of chlorine of 20-50 % (weight.). The yield of a product is about 100 %. Synthesis is not connected with formation of the by-products. Areas of application: petrochemical processing, preparation of halogenoparaffins C16-28 which applied as secondary softeners of polymeric materials, flame retardants, modified additives to polyolefines and to synthetic rubbers with the purpose of essential increase of mechanical and operational properties of compositions, increase in frost resistance, strength at break, decrease in combustibility.

L-PO-32 **TI(IV)-AND V(V) AMINE TRI(PHENOLATE) COMPLEXES AS 'WATERPROOF' CATALYSTS FOR OXYGEN TRANSFER PROCESSES.** Giulia Licini, Myriam Mba, Leonard J. Prins, Marta Pontini, *University of Padova, Italy, giulia.licini@unipd.it*

Keywords: sulfoxidations; peroxo complexes; C3 ligands

Supported noble metal catalysts prepared by photochemical deposition

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Photochemical deposition of noble metals in different supports is gaining importance because of its simplicity and advantages. Its main advantage is the ability of spreading very effectively the metal throughout the support, thus leading to very high dispersions. The materials prepared in such way can be used as catalysts resulting in higher molecular control, with a positive effect on both activity and selectivity.

The selective catalytic hydrogenation of organic substrates containing unsaturated functional groups, like steroids or alpha,beta-unsaturated aldehydes, is a common synthetic route for industrial preparation of fine chemicals. The quest for efficient catalysts for this process is a very active domain of research [1].

In the present study, hydrogenation catalysts prepared by photochemical deposition are compared against the usual incipient wetness catalysts and other commercial available catalysts. Different supports were tested (MWCNT and titania) in order to establish potential metal to support interactions. Catalyst loads were also varied in order to achieve the desired conversion and selectivity.

Noble metal catalysts supported on titania (1 and 5%wt) were prepared by the photochemical deposition method. The metals were dispersed on the surface by liquid phase photodeposition of the appropriate precursors. The procedure employed for the deposition was adapted from that described in the literature [2].

A set of TiO_2 supported Pt catalysts submitted to different thermal treatments was used for cinnamaldehyde selective hydrogenation, in order to test activity and selectivity. The reaction mixture contained heptane (solvent), cinnamaldehyde, decane (as an internal standard for gas chromatography) and the catalyst. The reaction temperature was 363K and the reaction started by feeding the reactor with hydrogen to a 10 bar pressure. Small aliquots of the reaction mixture were taken throughout the reaction to perform quantitative analysis (conversion and product selectivity). The analysis was performed in a GC DANI 1000, equipped with a WCOT Fused Silica column.

The catalysts produced by the photodeposition method revealed an outstanding activity and selectivity for hydrogenation of cinnamaldehyde into the cinnamyl alcohol.

The catalysts were fully characterized using different methods. The metal dispersion was determined by hydrogen chemisorption. Since catalysts were reduced at high temperatures (773K) there is the possibility that an interaction between metal and support reduces the H_2 chemisorption capacity leading to underestimated metallic area. More accurate measurements are currently underway (XRD) to determine the metal crystallite size and establish more specific relations between the preparation method and the performance of the catalysts.

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