

Inorganic and Organometallic Chemistry

Joaquim Marçalo

The activities of the Group comprise the synthesis, characterisation and chemical reactivity studies of inorganic, organometallic and intermetallic compounds of actinides and lanthanides with the aim of understanding the influence of the electronic structure in the chemical properties of their compounds. Chemical reactivity is assessed by stoichiometric reactions and by homogeneous and heterogeneous catalytic studies, which are also carried out in an effort to find new applications for lanthanide and actinide compounds. Gas-phase ion chemistry studies with the same elements and studies of the energetics of their compounds, using advanced mass spectrometric and calorimetric techniques, are also undertaken with the same objective.

Relevant facilities maintained by the Group are a laboratory for handling highly radioactive actinides, a laboratory for catalytic studies, a laboratory for calorimetric studies and thermal analysis, and two select mass spectrometers, a FTICR with EI and LDI sources, and a QIT with ESI and APCI sources. The QIT mass spectrometer was acquired with the support of the "National Program for Scientific Hardware Renewal" of FCT and is part of the National Mass Spectrometry Network.

Pursuing previous work on environmental issues, we continue to apply our knowledge to the activation and valorisation of methane and carbon dioxide as valuable C1 feedstocks, namely through the catalytic partial oxidation of CH₄ (POM reaction) and electrochemical treatment of CO₂. Of interest to the latter activity is the ongoing collaboration with OMNIDEA, Lda., a start-up company dedicated to R&D of aerospace technology and energy systems (ITN-OMNIDEA cooperation protocol).

We have studied the POM reaction on catalysts obtained by two routes: i) an intermetallic route, using LnCu₂ and LnNi₂ (Ln = from La to Yb) or AnNi₂ and ThCu₂ and ii) a sol-gel route (urea or citric acid methods) to obtain nanoparticles of heterobimetallic oxides. The electrochemical study of CO₂ activation

was also undertaken, this time using a pilot scale reactor. Both approaches allowed the production of syngas with high conversion of methane, high electric efficiency and the appropriate H₂/CO mol ratio of 2, especially for the nickel based catalysts that are cheaper and depicted an activity and selectivity comparable to that of one of the best catalysts reported so far in the literature (5 wt. % Rh/Al₂O₃).

New alkyl derivatives of yttrium bis(phenolate)-diamine complexes were synthesised. The tris(pyrazolyl)methane ligands started to be explored in the preparation of U(III) and U(IV) complexes. The photochemical properties of different complexes lanthanide complexes with tris(pyrazolyl)borate ligands started to be evaluated.

FTICR/MS was used to probe new ligations for the actinides, namely U-N, U-P and U-S. ESI-QIT/MS was employed in the speciation of U in basic solutions of ammonium and tetrabutylammonium uranates and in preliminary studies of the complexation of lanthanide nitrates by several N-donor ligands.

Studies with ionic liquids were pursued and the kinetics of some of their reactions were studied using FTICR/MS. Also, the thermal properties of some ionic liquids were studied using DSC techniques and the correspondent reactivity was explored using ESI-QIT/MS.

The collaboration with the Radiation Technologies: Processes and Products Group (UFA) was continued with studies of gamma radiation effects on gallic acid. Joint projects with the Research Unit "Glass and Ceramics for the Arts" (a collaboration between ITN, FBAUL and FCT/UNL) on new lanthanide based fluorescent glasses, on ruby glass and on provenance studies of Portuguese glasses continued.

An important part of the activity of the Group is the training of research students. Some of the group members are involved in undergraduate and MSc university courses. The work is financially supported by FCT and other sources, via research projects and PhD and Post-doc grants.

Research Team

Researchers

J. MARÇALO, Princ., Group Leader
A. PIRES DE MATOS, Coord. (Retired Sep.)
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Technical Personnel

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Students

M. H. CASIMIRO, Ph.D. student (Jan.-Sep.)
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R. MELO, Ph.D. student, FCT grant
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F-Block Element Intermetallic Compounds as Catalysts

J. B. Branco, A. C. Ferreira, T. A. Gasche, M. R. Correia¹, A. P. Gonçalves

Objectives

The main objective of this research is: (i) to study the f-block elements behaviour as catalysts or catalytic precursors, (ii) to develop new methods for the preparation of 4f and 5f nanostructured materials for catalytic purposes and (iii) to contribute for the resolution of key environmental issues.

Experimental work is based on heterogeneous catalytic reactions followed by gas chromatography. The f-block elements (lanthanides and actinides (Th, U)) catalysts synthesis was accomplished by either high temperature solid state reactions (intermetallic route) or liquid phase bench-top techniques (Sol-Gel route).

Results

F-block element binary intermetallic compounds have been found to be active in a variety of reactions. Recent years studies in our laboratories have shown that $AnNi_2$ ($An=Th, U$) and $LnCu_2$ ($Ln=La-Tm$), as Ln-Cu-O bimetallic oxides catalytic precursors, were active and selective in catalysis [1-3]. Such bimetallic oxide catalysts, Ln-Ni-O ($Ln=Pr, Gd, Tm$), An-Ni-O ($An=Th, U$) and Th-Cu-O were active and selective for the catalytic partial oxidation of methane (POM). The highest activity and stability (over a period of 24 h of time on stream) was obtained on the nickel-actinide or lanthanide oxide catalysts (Fig. 1). H_2 and CO selectivities were also very high (> 95%).

Therefore, the good catalytic behaviour of this nickel based catalysts and its high stability is a major achievement since the known and widely studied noble metal based catalysts are limited by their high cost, whereas the deactivation of others catalysts is the major drawback of this reaction that limit a widespread industrial application.

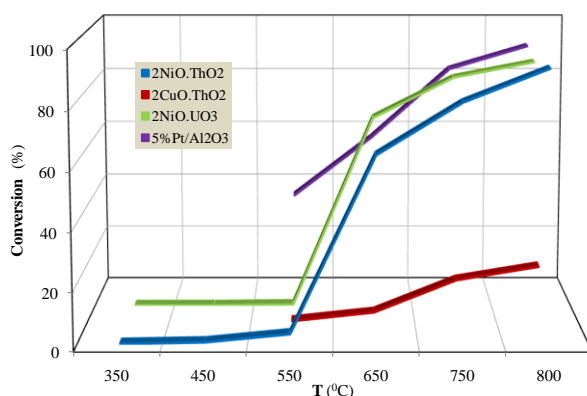


Figure 1. Activity and stability (shown for 2NiO.UO₃ at 800 °C) over the An-Ni-O bimetallic oxide catalysts

On the experimental side, the Sol-Gel technique was used as an alternative preparation route to obtain cheaper and nanostructured bimetallic oxide catalysts with high specific areas, which is a disadvantage of the intermetallic route. Preliminary results confirm that the catalysts morphology is very different (Fig. 2) but, the catalytic behaviour is very similar, mainly, in the case of the lanthanide and actinide-nickel catalysts. Our results seem also to confirm that the f-block elements have a direct role in the catalytic process. RAMAN studies provided direct evidences that the d metal incorporate in the f-block element oxide lattice, instead of dispersing on the surface. XRD confirm that the MO ($M=Cu, Ni$) phase is at least partial reduced at the end of reaction, pointing for a major catalytic role of such species on the synergetic relationship between d and f metal.

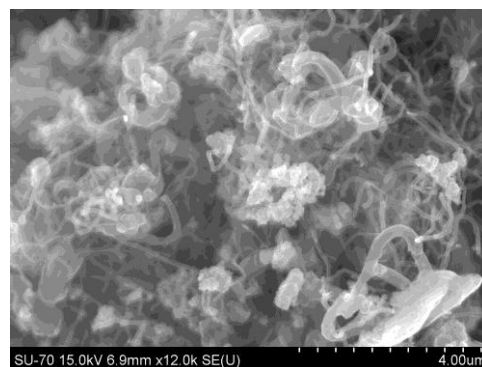


Figure 2. SEM pictures obtained after POM reaction for the Ce-Cu-O bimetallic oxide catalysts: formation of ceria oxide nanotubes and CuO platelets with an average size of ≈ 50 nm instead of a solid state solution in the case the samples obtained via intermetallics.

Published work

J.B. Branco, A.P. Gonçalves and A. Pires de Matos, *Isoprene gas phase hydrogenation catalyzed by ThNi₂ and UNi₂*, J. Alloys Compd., 465 (2008) 361-366.

J.B. Branco, D. Ballivet-Tkatchenko and A. Pires de Matos, *Reduction and catalytic behaviour of heterobimetallic copper-lanthanide oxides*, J. Alloys Compd., 464 (2008) 399-406.

J.B. Branco, C.J. Dias and A.P. Gonçalves, *Thermal Studies on Oxidation-Reduction of LnCu₂ Intermetallic Compounds and their Catalytic Behavior for 2-Propanol Decomposition*, J. Alloys Compd., doi:10.1016/j.jallcom.2008.11.113. (in press)

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f-Element Chemistry with Multidentate Nitrogen and Oxygen Donor Ligands

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In order to investigate the catalytic activity of lanthanide complexes supported by the bis(phenolate)diamine ligand (${}^{\text{tBu}_2}\text{O}_2\text{NN}'=[\text{Me}_2\text{N}(\text{CH}_2)_2\text{N}\{\text{CH}_2-(2-\text{OC}_6\text{H}_2-\text{Bu}^1_{2-3,5})_2\}]$) in the polymerization of cyclic esters, the search for yttrium derivatives continued during 2008. Formation of the alkyl derivatives $[\text{Y}({}^{\text{tBu}_2}\text{O}_2\text{NN}')(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)]$ and $[\text{Y}({}^{\text{tBu}_2}\text{O}_2\text{NN}')(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2)]$ was observed when $[\text{YCl}({}^{\text{tBu}_2}\text{O}_2\text{NN}')(\text{DME})]$ reacted with the lithium salts of the corresponding alkyls. The latter also reacted with $\text{LiCH}_2\text{SiMe}_3$ to yield the ate complex $[\text{Y}({}^{\text{tBu}_2}\text{O}_2\text{NN}')(\text{CH}_2\text{SiMe}_3)_2\text{LiCl}(\text{THF})]$. Recrystallization of this compound from THF gave crystals of the unusual $[\{\text{Y}({}^{\text{tBu}_2}\text{O}_2\text{NN}')(\text{CH}_2\text{SiMe}_3)_2\}_2(\mu\text{-O})(\mu\text{-Li})_2]$. The reactivity of the alkyl derivatives was checked in the reactions with acetonitrile. Acetonitrile inserts into the Y-C bond of $[\text{Y}({}^{\text{tBu}_2}\text{O}_2\text{NN}')(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)]$ to yield a product resulting from migratory insertion, $[\text{Y}({}^{\text{tBu}_2}\text{O}_2\text{NN}')\{\text{HNC}(\text{Me})\text{C}(\text{H})\text{C}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)\text{NH}\}]$. Excess of acetonitrile led to the formation of the six-membered heterocycle complex $[\text{Y}({}^{\text{tBu}_2}\text{O}_2\text{NN}')\{\text{k}^2\text{-}(\text{HNC}(\text{Me})\text{C}(\text{H})\text{C}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)\text{NH})\}]$.

The anionic tris(pyrazolyl)borate (Tp) ligands have been successfully used as ancillaries for the f elements. The neutral analogues of Tp ligands, the tris(pyrazolyl)methanes (Tpm), have not received the same attention as the borates. Preliminary reactions of $\text{UI}_3(\text{THF})_{2.5}$ and UCl_4 with Tpm^* (tris(3,5-dimethylpyrazolyl)methane) in THF gave $\text{UI}_3(\text{Tpm}^*)(\text{THF})$ and $\text{UCl}_4(\text{Tpm}^*)$, respectively, and the x-ray crystal structures of these two complexes were determined.

New organic ligands (sensitizer) with potential 'antenna effect' are expected to be synthesised and anchored in several lanthanides mainly in their +3 oxidation state. Different complexes Tp_2LnCl and $\text{Tp}'_2\text{LnL}$ have been synthesised according with the literature and their photochemical properties evaluated. Preliminary results show that functionalization of the C3 of the pyrazole ring with 4-fluorophenyl in the tris(pyrazolyl)borate ligand corresponds to modifications of the emission spectra, going from a visible to ultraviolet emitter.

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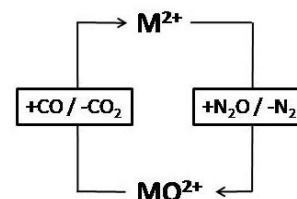
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Gas-Phase Ion Chemistry of Actinides and Lanthanides

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Fundamental aspects of the chemistry of atomic and molecular actinide and lanthanide ions and neutrals continued to be examined by advanced mass-spectrometry techniques, namely, Laser Desorption/Ionization Fourier Transform Ion Cyclotron Resonance MS (LDI-FTICR/MS) and Electrospray Ionization Quadrupole Ion Trap MS (ESI-QIT/MS). Parallel theoretical studies of selected actinide molecular ions were also carried out via collaborations to validate the interpretation of the experimental observations.

The characterization of the gas-phase thermodynamics of neutral and ionized CmO by FTICR/MS was completed; of note in these studies was also the observation that CmO^{2+} catalyzes the O-atom transport from N_2O to CO. LDI-FTICR/MS was used to probe new ligations for the actinides, namely U-N, U-P and U-S, with samples prepared by high-temperature synthesis; preliminary studies of the oxidation reactions of US^+ (and ThS^+) were also carried out. The formation of molecular uranates continued to be examined and the high-yield production of these species from anhydrous and hydrated UO_3 by LDI-FTICR/MS was achieved. In a related study, ESI-QIT/MS was used in the speciation of U in solutions of ammonium and tetrabutylammonium uranates. ESI-QIT/MS was also employed in preliminary studies of the complexation of lanthanide nitrates by several N-donor ligands; competitive CID experiments were performed with systems involving two different ligands.



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Molecular Energetics of Organic, Inorganic and Organometallic Compounds

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The main objective of this research line is to collect data and rationalize it in a systematic way that enables a deeper knowledge of energetics of molecules (both inorganic and organic compounds). Special importance is given to f-element compounds (both on solid state and in solution). To achieve this goal, lanthanide and actinide (organometallic and intermetallic), alkaline and alkaline-earth compounds, hydrocarbons and ionic liquids were studied.

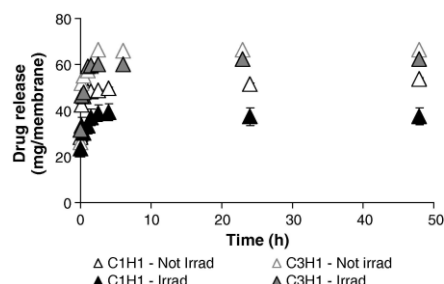
During 2008, enthalpies of formation published for CH, CHO and CHN compounds were critically revised and used to improve an extended Laidler method of additive contributions. The nature of ionic liquids in the gas phase was studied and the kinetics of some of the reactions where they are involved began to be studied using FTICR/MS. Also, the thermal properties of some ionic liquids were studied using DSC techniques and the correspondent reactivity was explored using ESI-QIT/MS. The degradation/decomposition of gallic acid and its derivatives, either gamma-irradiated or not, was also studied using ESI-QIT/MS. Using FTICR/MS, the measurement of the gas-phase acidity of methoxy di-substituted phenols was undertaken.

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Gamma Irradiated Chitosan/pHEMA Membranes for Drug Release Systems

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To obtain biocompatible and sterilized matrices for controlled drug release to be used in direct contact with skin, films with different contents in chitosan and hydroxyethyl methacrylate (HEMA) have been prepared by γ irradiation from a ⁶⁰Co source. Those films naturally exhibit antimicrobial properties with good mechanical behavior. The loading with amoxicillin lead to active membranes that show an insignificant level of hemolysis and present a fast rate of amoxicillin release. Also, membranes using polyethylene as backbone polymer and HEMA as grafting molecule, produced through irradiation on a ⁶⁰Co source, were synthesized and the corresponding properties extensively studied.



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Glass Science with Applications in Archaeometry and Art Studies

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A. Pires de Matos is coordinating the research unit VICARTE - “Glass and Ceramics for the Arts”, supported by FCT, with participants from ITN, FBAUL and FCT/UNL. Expertise on glass science is being developed, particularly in the synthesis of glasses with new properties and in chemical characterisation of glasses for provenance studies.

In 2008 the archaeometric studies of portuguese glasses using several techniques continued. In the analytical characterization of Coina glasses from an archeological excavation four types of glass were identified. For comparison with glass from Marinha Grande, glass objects of the Museu Nacional de Soares dos Reis, Porto,



Museu Nacional de Machado Castro, Coimbra, and Museu do Vidro, Marinha Grande, were characterized using micro-X ray fluorescence. Comparisons with formulations in an Arcano of 1793 of Guilherme Stephens were made.

Another research area is related with the development of glasses for artistic applications. Studies on luminescent glasses with rare earths have continued, as well as the quenching of luminescence by d-transition elements. Gold and copper ruby glass were synthesized

using gamma radiation for reduction of the metal ions and to improve nucleation of the metal nano-particles.

The first experiments to characterize glass by LIBS (Laser Induced Breakdown Spectroscopy) were made using a Nd:YAG laser (ITN) and a fiber optics UV-Vis optical absorption spectrometer.

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