

Inorganic and Organometallic Chemistry

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The activities of the group comprise the **synthesis, characterisation and chemical reactivity studies of inorganic, organometallic and intermetallic compounds of actinides and lanthanides** in order to understand the influence of the electronic configuration and of the size of these elements in the chemical behaviour of their compounds. Chemical reactivity is assessed by **stoichiometric reactions and by homogeneous and heterogeneous catalytic studies. Gas-phase ion chemistry studies** with the same elements and the study of the **energetics of f-element compounds** are also made with the same objective.

Relevant facilities maintained in the group are the Fourier transform ion cyclotron resonance mass spectrometer (FT/ICR), a laboratory for catalytic studies including work with CO, a laboratory for calorimetric studies and a laboratory for handling macroscopic quantities of the most toxic actinides. We are starting to apply our knowledge to environmental studies, particularly concerning radioactive waste containing actinides. Of interest to this activity was the collaboration project with Plastval/Sociedade Ponto Verde dealing with non-radioactive waste which finished this year. A collaboration is also given to the Radiation Technologies: Processes and Products Group (Physics Sector) in a study of the gamma radiation effect on several waste water sources.

The work made during 2004 is summarized as follows:

We pursued reactivity studies of two uranium(III) systems, $U(Tp^{Me_2})_2I$ and $[U\{(SiMe_2NPh)_3-tacn\}]$. The reactivity of $[U\{(SiMe_2NPh)_3-tacn\}]$ may be illustrated by their mediation of the following selected reactions: 1) the formation of complex heterocycles from the reduction of various organic substrates, 2) reductive cleavage of S-S and S-P bonds, 3) oxidation by silver halides or Tl salts of cyclopentadienyls or phosphoryls.

Pursuing previous work on binary actinide intermetallic compounds as catalyst precursors, $ThCu_2$ and $AnNi_2$ ($An=Th, U$), leading to $2MO.ThO_2$ ($M=Cu, Ni$) and $2CuO.UO_3$, proved to be active for the oxidative coupling of methane with carbon dioxide. The activity is comparable to that of the best catalyst reported on the literature. The C2 selectivity is higher.

The heterometallic lanthanide oxide, $Eu-Ca-O$, was tested on the oxidative coupling of methane (OCM),

using CO_2 as oxidant agent. The C2 yield (70%) and the C_2H_4/C_2H_6 selectivities (30:70%) are the best results so far reported for this reaction.

Gas-phase ion chemistry studies of the actinides (An) by FTICR/MS were pursued and the work was now extended to Pa. The focuses continued to be the thermochemistry of An oxides and the comparative reactivity of An cations with hydrocarbons. The thermochemical studies permitted us to derive hydration enthalpies for the actinyls (AnO_2^{2+} ; $An = U, Np, Pu, Am$). Another result of interest was the first observation of "bare" protactinyl, PaO_2^{2+} , formally a Pa(VI) species. Experiments involving An^+ and An^{2+} ions ($An = Th, Pa, U, Np, Pu, Am$) and alkanes and alkenes were completed. The addition of Pa allowed us to draw more definitive conclusions on the relative reactivity of An cations in the first half of the series.

During 2004 the energetics of lanthanide (organometallic), alkaline and alkaline-earth compounds (alkoxides, phenoxides, thiolates) and hydrocarbons were studied. It should be stressed that a critically accessed compilation of existing enthalpies of formation for hydrocarbons was made and used to obtain a new parameterization of an extended Laidler method of additive contributions. This new parameterization allows to estimate the enthalpy of formation (gas and condensed phase) for virtually any hydrocarbon. For the first time, physical meaning was associated to the parameters leading to a deeper understanding of bond energetics on these compounds

Know how in glass science projects started to be developed very recently in ITN to contribute to the research on radioactive waste vitrification processes. Synthesis and characterization of glasses has been the main task during 2004.

An important part of the output of the Group has been the training of young research students. Some of the group members have been involved in undergraduate and post-graduate university courses. Joint projects with the Faculty of Fine Arts of the University of Lisbon on new lanthanide based fluorescent glasses continued.

The work made was financially supported by four projects of FCT, one project supported by an industrial association, SPV, two BIIC FCT grants and three FCT PhD grants. Three new projects were approved by FCT, one involving the acquisition of an ESI/MS equipment.

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Research Team

Researchers

- A. PIRES DE MATOS, Coord. Researcher, Group Leader
- N. MARQUES, Princ. Researcher
- J. MARÇALO, Aux. Researcher
- J. BRANCO, Aux. Researcher
- J.P. LEAL, Aux. Researcher
- T.A. GASCHÉ, Aux. Researcher
- J.M. CARRETAS, Aux.. Researcher
- A. DOMINGOS, Princ. Researcher, retired in August 2003, continued to collaborate with the Group on X-ray diffraction

Students

- C. HIPÓLITO, PhD student, FCT grant
- C. DIAS, BIIC grantee, POCTI
- M. A. ANTUNES, PhD student, FCT grant
- M. SANTOS, PhD student, FCT grant
- M. DIAS, BIIC grantee, POCTI
- A.S. CORREIA, graduate student

Technical Personnel

- A. CARVALHO, Laboratory assistant
- A.J. SOARES, Analyst

Funding (€)

Research Projects:	11.772,00
Services:	0
Total:	11.772,00

Publications

Journals:	8 and 5 in press
Proceedings:	1
Conf. Communications:	13
Other publications:	2