Title: Synthesis and Characterization of New Metal Carbonyl Clusters

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Object. The proposed project will focus on the synthesis and characterization of new metal clusters belonging to one of the following three categories: 1) homo- and hetero-metal carbonyl nanoclusters, 2) carbonyl clusters decorated by N-heterocyclic carbenes (NHCs), 3) water-soluble heteroleptic clusters. These compounds will be prepared under inert atmosphere using Schlenck techniques. Project 1 will focus on the synthesis of high nuclearity metal carbonyl clusters with reversible redox properties which may be viewed as models of ultra-small metal nanoparticles [1]. Possibly, bimetallic clusters will be used also as precursors of catalytic-active metal nanoparticles with controlled dimensions and composition [2]. The aim of project 2 will be the synthesis of carbonyl clusters containing NHC ligands. The approach for their synthesis will be the reaction of preformed anionic metal carbonyl clusters with M(NHC)Cl complexes (M = Au, Ag or Cu) on the attempt to isolate unprecedented high nuclearity or otherwise unstable carbonyl compounds [3]. Finally, project 3 will concern the synthesis of heteroleptic platinum clusters using water-soluble phosphines in order to test their potential antitumor activities.

Characterization. The compounds will be characterized via X-ray crystallography and by combined FT-IR, ESI-MS and NMR spectroscopy studies. Finally, preliminary electrochemical studies will be carried out in the case of clusters with multivalent behavior.


Keywords: cluster, multivalent behavior, carbonyl, N-heterocyclic carbene (NHCs)
Title: Synthesis, characterization and application of supported metal nanoparticles

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This Project case study deals with the synthesis and characterization of metal nanoparticles on different substrates. In recent years considerable attention has been drawn to the possibility of deposition of metal nanoparticles onto substrates (conducting or not conducting) due to its great importance in the fabrication of practical devices such as heterogeneous catalytic systems, electronic sensors, biosensors or biomaterials. Several methods have been reported to accomplish this purpose; among these chemical and electrochemical synthesis have been proved to be very striking because of the simple instrumentation needed and the capability to readily control the size and morphology of the as-deposited nanostructures through adjusting the experimental parameters. The aim is to provide the necessary tools for the preparation of non conductive (i.e. silica, hydroxyapatite, hydrotalcite) or conductive (i.e. Indium Tin Oxide (ITO), Glassy Carbon (GC)) surfaces modified with metal nanoparticles via polyelectrolyte mediated chemical synthesis or one step electrosynthesis, respectively. The effect of some variables as the choice of precursor used, the presence of additives, the kind of substrate, the electrolyte employed or the electrodeposition conditions on the nanoparticles size and distribution have been investigated. Catalytic tests will be performed both in batch and continuous-flow conditions. These studies could offer a new approach to cost-effective way to prepare supported metal nanoparticles. From an experimental point of view the student at the end of the training should have gained a valuable experience in the field of the synthesis and characterization of nanomaterials and their use in catalysis. Moreover a good knowledge of the following techniques and instruments will be acquired: FT-IR and ATR-IR, Atomic Absorption Spectroscopy, Cyclic voltammetry, Dynamic Light Scattering, Scanning Electrode Microscopy, UV-Vis spectroscopy and X-Ray Diffraction. In addition, the project is expected to improve the skills of the student in scientific communication, research work in a multidisciplinary environment and presentation of research results. Such experience will be a valuable contribution to the development of the research abilities of the young researcher and a help for their future job in a scientific career.

BIBLIOGRAPHY


Keywords: Metal nanoparticles, composite nanomaterials, electrosynthesis, catalysis, biomedical applications.
Title:
Materials for architectural and artistic applications: interaction with the environment and decay processes

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Part of the experimental activities could be carried out at the Electron Microscopy and Microstructural Analysis Lab (Dept. of Industrial Engineering) under the supervision of Dr. Carla Martini or at the Diagnostic Lab (Dept. of Cultural Heritage) under the supervision of Dr. Cristina Chiavari.

Topic

The work aims to study the decay of materials used for architectural and artistic applications in relation to their environmental exposure. Metals, such as bronze and steel, are mainly investigated, but further classes of materials can be also considered.

In order to study and follow the evolution of the decay processes, specimens of the considered material will be artificially aged by laboratory accelerated tests in conditions simulating different aggressive environments, the presence of different pollutants and different outdoor exposure geometries (e.g. unsheltered areas, exposed to rainwater runoff, or sheltered areas, exposed to PM accumulation, rain stagnation or moisture). At the same time, specimens could be also exposed to natural ageing in coupon racks (unsheltered/sheltered conditions) installed in an environmentally monitored site in Rimini (marine urban environment). During the exposure, at increasing time intervals, both the exposed surfaces and the ageing solutions (artificial or natural) will be characterized. The characterisation of the exposed surfaces is performed by microscopy and spectroscopic techniques such as SEM+EDS, micro-Raman, XRD, while the ageing solutions are analysed by wet chemical analysis, e.g. by AAS and IC. During natural ageing, monitoring and analysis of environmental conditions and pollutants could be performed.

The work could include also tests to evaluate the effectiveness of new protective products in order to reduce material decay.

Keywords: environment, pollutants, decay, corrosion, cultural heritage, conservation
The replacement of traditional materials with renewable substrates, solvents and catalysts is occupying a prominent role in the development of sustainable synthetic methodologies. In this respect, the exploitation of polysaccharides of marine origin, such as chitosan (deacetylated chitin) and alginate appears highly attractive as it would not compete with food production. As a collaborative effort with the laboratory directed by Dr Françoise Quignard and Nathalie Tanchoux (CNRS Montpellier, France), specialized in the treatment and the manipulation of these biopolymers to render highly porous materials (aerogels), this project will test the recovery of commonly employed chiral organocatalysts from reaction mixtures, exploiting non-covalent interactions between the basic catalyst and the highly disperse, slightly acidic alginic acid aerogel beads. Subsequent release of the catalyst species in a second catalytic batch, by addition of an additive, results in a straightforward and trivial procedure for catalyst recovery and reuse (see Figure). In fact, whereas the employment of small organic molecules as catalysts (organocatalysis) has recently emerged as a very powerful approach for performing enantioselective transformations, a considerable flaw of this approach is represented by the usually low turnover numbers and frequencies displayed by these small molecule catalysts, thus making catalyst recovery and reuse essential from an economic standpoint. Such approach combines the advantages of homogeneous catalysis (high and predictable activity and selectivity) with the benefits of heterogeneous catalysis (easy separation of the catalyst from the product, catalyst reuse).

**keywords:** Organocatalysis, Alginic acid gel, Homogeneous catalysis
Title: Research Practical Course in X-Ray Spectrometry in Analytical Chemistry

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Topic

The use of the X-rays in the field of analytical chemistry will be the subject of this experimental course. The student will acquire competencies for the primary analysis of the x-ray absorption spectroscopy measurements (XAS) data and its significance in the various technological topics such as materials chemistry, solution chemistry and electrode materials.

A secondary part of the PCS will be devoted to practical session using the XRF technique (Panalytical AXIOS Advanced wavelength dispersive Spectrometer). In this case the student will be involved in the chemical analysis by XRF of a specific test material. Other analytical spectroscopic techniques may be involved (AAS, FAAS).

After completing this unit the student will have gained competencies in the methodologies required to complete a project in experimental research involving x-ray analysis by absorption and emission. In addition, the course provides educational experiences which challenge students to gain transferable skills like “project management”, bibliographical research, academic presentations and writing, working in an international team.

keywords: EXAFS, XANES, XRF, AAS
Title:

University: Dipartimento di Chimica Industriale, University of Bologna. Italy.
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Topic

The main goal of our research is the study of high-resolution infrared spectra of molecules of atmospheric and astrophysical importance. The spectra are recorded in our laboratory with a Fourier Transform Infrared (FTIR) spectrometer at a maximum resolution of 0.004 cm$^{-1}$.

The investigated species are generally stable but also transient molecules, such as ions or radicals, can be studied. This type of research is carried out in collaboration with the Chemistry Department of Bologna, where a millimetre-wave spectrometer suitable for the production of unstable species is available. In this case, only pure rotational spectra are studied.

The combination of infrared and submillimetre laboratory spectroscopy provides an extremely accurate background for undertaking astronomical searches, which are not confined to the investigation of molecules in our galaxy and in the interstellar medium, but also in the atmospheres of exoplanets and even in distant galaxies.

The species chosen for this investigation are usually less abundant isotopomers of fundamental molecules. Examples are doubly deuterated diacetylene C$_4$D$_2$, $^{14}$ND$_3$ and $^{15}$ND$_3$. The experimental study of the rare $^{15}$ND$_3$ isotopologue, although of less astrophysical relevance, provides very useful spectroscopic parameters that can be used by theoreticians to test their quantum chemical calculations.

The detection of molecules containing less abundant isotopes, for example deuterium, $^{13}$C or $^{15}$N, is crucial to estimate the values of the D/H, $^{13}$C/$^{12}$C and $^{15}$N/$^{14}$N isotopic ratios in various space environments. In the case of deuterium, the interstellar processes that lead to the formation of molecules highly enriched in D are the same that lead to complex organic species. Therefore, deuterium is a special tracer for studying the cosmic evolution of organics. It has also a cosmological significance, as it can be a test for the cosmic microwave background results. In the case of nitrogen, the measurements of its $^{15}$N/$^{14}$N isotopic ratio shows great variations in different astrophysical environments. Its evaluation can therefore provide very useful information about the evolutionary processes in the regions involved.

Molecules of atmospheric importance, mainly halogen substituted organic species, have also been investigated by FTIR spectroscopy. The laboratory analysis of their spectra is very useful for the identification of such species in the atmosphere.

Some recent publications.

1) Fine and hyperfine structure of the $N = 1\leftarrow 0$ transition of ND($X^3\Sigma^{-}$) in vibrational excited states. L. Dore, L. Bizzocchi, C. Degli Esposti, F. Tamassia. Mol. Phys., 109, 2191 (2011).


keywords:
Title: Catalysis for the transformation of renewables to bio-chemicals, practical examples

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Topic

Project cases include the preliminary characterization and reactivity study of chemo-catalysts for the gas-phase or liquid-phase transformation of renewables into bio-chemicals. Examples include:

a. the oxidehydration of 1,2-propanediol to aldehydes and C3 carboxylic acids, catalyzed by bi-functional mixed oxides catalysts.
b. the liquid-phase oxidation of platform molecules (glucose) into dicarboxylic acids, catalyzed by supported metallic nanoparticles and alloys.
c. the oxidation or bio-alcohols into chemicals, catalyzed by either metal nanoparticles or mixed oxide catalysts

keywords: heterogeneous catalysts; renewable raw materials; catalysts characterization; bio-chemicals
keywords:
Title: ATR-IR study of intermediates for Aqueous Phase Reforming heterogeneous process

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Laboratory: Catalysis
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Topic

The project is focused on the synthesis and study of nanocrystalline catalysts as TiO$_2$, MgO, Mg/Al mixed oxides and mixed oxides loaded with different metals (Pt, Ru, Ni...). These catalysts are applied in the research group for the polyols transformation, such as Aqueous Phase Reforming reaction, for the production of hydrogen and chemicals from sugars and alcohols. The reactions involved in liquid phase are still under study due to the complexity of the mechanism and the high number of possible products.

The aim of the project is thus to investigate the formation of products and intermediates by an operando techniques as ATR-IR on the heterogeneous system. Reactions will be performed on a heated ZnSe crystal loaded with a thin catalyst film and reagent solution to simulate the reaction environment. The obtainable results are exemplified in Figure 1, reporting the formation of products and intermediates for a reaction performed at 70°C.

![Figure 1. In-situ ATR-IR of glycerol solution reaction catalyzed by Pt/TiO$_2$](image)

The study will be coupled with batch system reactions over supposed intermediates and with in-depth characterization of the oxides. In particular, this will concern pre and post analysis of the surface by TEM, surface porosity, XRD, XPS and probe gas spectroscopy analyses to follow the transformations of catalyst surface and of the active metal distribution. Moreover, catalyst obtained by microemulsion technique will be prepared and studied to enhance nanocrystallinity and surface properties.

keywords: IR in operando spectroscopy, heterogeneous catalysis, XRD, XPS, TEM characterisation
Title: IR and NMR mechanistic investigations for homogeneous catalysis

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Topic

The project deals with the synthesis, characterization and study of the reactivity and catalytic activity of ruthenium complexes bearing ligands such as carbonyls, cyclopentadienones and N-substituted N-heterocyclic carbene (an example in Figure 1).

![Figure 1. Ruthenium based catalyst for hydrogen transfer reactions](image1)

The main program will regard the use of IR and NMR spectroscopy, assisted by DFT calculations, in order to shed light on the activation and mechanism of, for example, hydrogen transfer reaction catalyzed by the ruthenium complex prepared. In situ ATR-IR and NMR spectroscopy allow to follow the transformation of functional groups of both substrate and catalyst giving back information on active catalyst and intermediates.

![Figure 2. In-situ ATR-IR of hydrogen transfer reactions catalyzed by Ruthenium based complexes](image2)

The present project is integrated in a collaboration between the laboratory of inorganic chemistry (Prof. Valerio Zanotti, Dr. Rita Mazzoni) and the laboratory of catalysis (Prof. Francesco Basile). Furthermore within a collaboration with the University of Insubria (Dr. Carlo Lucarelli, Prof. Massimo Mella) DFT calculations will be exploited to predict IR spectra. The DFT feedback will be also useful in order to design novel experiments.

*keywords: IR spectroscopy, NMR spectroscopy, homogeneous catalysis, DFT calculations.*