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Final report

Research activity July 2007

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The research activity, carried out from 8th to 27th July 2007 in the framework of the CNR Short Term Mobility Programm, was mainly devoted to the use of hydrothermal and/or solvothermal synthesis for the preparation rare earth (RE)- based hybrid open networks and other molecular precursors.

In particular, the proposed activity can be subdivided in **6 different topics**:

1- preparation of metalorganic frameworks (MOF) based on mixed rare-earth metals

In this framework, two homologues series on Ln1-Ln2 were prepared, namely based on **La-Ln** (Ln =Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb) and **Er-Ln** (Ln =La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Tm, Yb) in order to investigate the feasibility of **MIL 103 homologues with mixed lanthanides** and with the aim to produce materials which can be interesting for luminescent properties.

The materials were characterised by XRD, EDAX and, on some selected specimens, by nitrogen sorption.

The main results as far as the **microstructure** is concerned, can be summarized as following:

a- all the prepared materials are crystalline

b- all the produced materials, except in the case of LaTm, display an XRD pattern which, although a shift of the reflexes which depends on the nature of the metal, is the same of MIL 103

c- the unit cell determination, carried out for selected samoples, evidences how there is not a clear correlation between unit cell volume and radius of the lanthanide Ln2, although the analysis is still in progress. It should moreover taken into account that the different mixed materials are characterised by different Ln1/Ln2 atomic ratios, which can affect the unit cell volume

As far as the **specific surface area** is concerned, a selection of the samples displaying the higher degree of crystallinity was analysed. All the specimen show a Langmuir specific surface in the interval 500-1300 m^2/g, depending on the activation time.

The **EDAX analyses** allowed to get the Ln1-Ln2 atomic ratios in the different materials.

It is interesting to evidence as the atomic ratios of the different lanthanides are quite different among the different specimens, but in each sample their atomic ratios are the same when mediated on three different points.

2- preparation of metalorganic frameworks (MOF) based on mixed lanthanum and transition metal atoms (M= Ni, Mn, Fe)

In this case, the aim of the work was to combine in a same MOF two different metals (one lanthanide and a transition metal) to exploit the **magnetic exchange interaction between 3d and 4f metal centres** connected by an organic linker. The synthesis were carried out in solvothermal conditions by using two different kind of organic linkers (trimesic acid and the tris acid {4-[3,5-Bis-(1-carbonylmethyl-1*H*-[1,2,3]triazol-4-yl)-phenyl]-[1,2,3]triazol-1-yl}-acetic acid, in the following "triazol tricarbossilic acid" [see below]) and different ligand/ (sum of metals) and transition metal/lanthanide molar ratios.

Four different sets of the experiments have carried out, and for each of them 11-12 batches were prepared.

1- La/Fe with trimesic acid
2- La/Ni with trimesic acid
3- La/Mn with trimesic acid
4- Eu/Co with triazol tricarbossilic acid
5- Pr/Co with triazol tricarbossilic acid

As far as Experiment set 1 is concerned, **LaFe**, no evidence of crystalline samples could be evidenced, and only broad reflexes were detected. Instead, for both Ni and Mn, some of the prepared specimens show a well defined crystallinity. In particular, in the case of **LaNi**, most of the samples show a common XRD pattern, and EDAX analyses evidence a Ni/La atomic ratio of about 7/1.

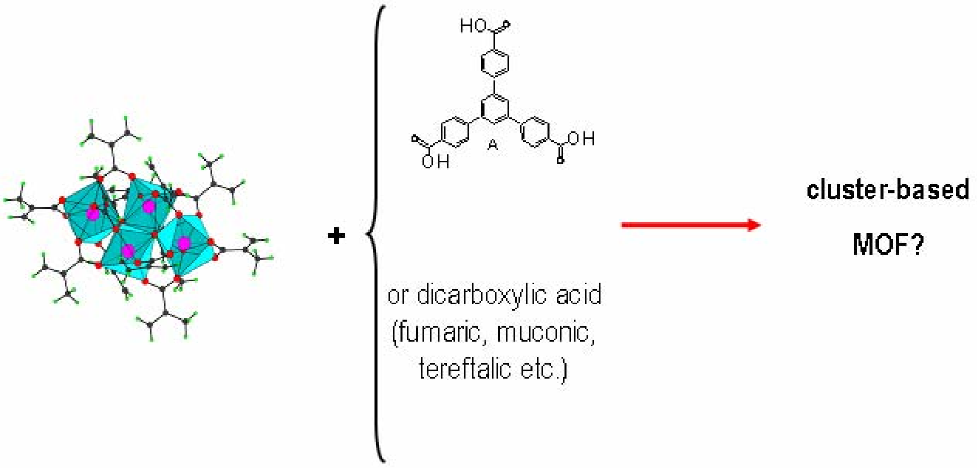
In the case of **LaMn**, most of the samples present a polycrystalline pattern, which are more or less intense but basically the same. One of the most crystalline samples, displaying a needle-shaped morphology (SEM micrograph) has a La:Mn 1:1 molar ratio.

In the case of triazole ligand, the samples **EuCo**, some of the samples show the pattern of the homologue compound with the same ligand (td574), whereas the EuCo_12 sample, prepared in DMF instead of the EtOH/H_2O mixture, show a diffractogramm with very sharp and intense peak, which however is completely different from Eu-MIL 112.

As far as the **PrCo** samples are concerned, the analyses are still in progress, but the preliminary XRD results evidence quite crystalline samples and the formation of a **new phase** which is neither the one presented by the Pr-MIL 112 nor an alreday known phase. Most of the samples are pink, indicating the presence of cobalt. EXD analyses should be performed on these samples to ascrtain the actual presence of both metals.

3- experiments concerning the use of the transition oxocluster $Zr_4O_2(OMc)_{12}$ (Zr4) as polytopic ligand for the synthesis of new MOF

As already described in the proposal, the aim of this part of the experimental work to use the **polyfunctional zirconium oxocluster Zr4 as inorganic polytopic secondary building unit** (SBU). In this case, the presence of the 12 methacrylate groups on the surface of the cluster could be exploited to exchange them with di- or tricarboxylic ligands (although for steric hindance and topological requirements the former have to be preferred) and to build new MOF in which the SBU, differently from the already known MOF based on trimeric (Cr, Fe) or tetrameric (Zn) SBU's, would be characterised by a higher functionality. The explored strategy is schematically reported in Figure 1.



In this framework, the Zr4 cluster was reacted with fumaric, tereftalic and muconic acids, by using different Zr4/ligand molar ratios (ranging from understoichiometric, i.e. Zr4:L 1:0.5 to an excess of bicarboxylic acid (12 equivalents). Different temperatures (90-130°C) and treatment times (6-24 h) were applied.

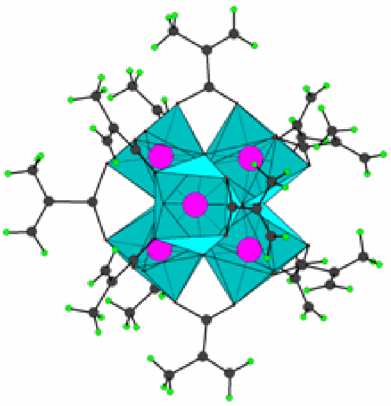
Although no single crystal could be isolated, and in some case gels were instead obtained, the X-ray diffractogramms of the dried products reveal the presence of a common pattern characterised by a main reflex at $2\theta = 7.49$ and 7.86 and smaller reflexes, hinting at the formation of a polycristalline materials. The XRD pattern is different from that of the cluster itself as well as that of tetragonal zirconia, or oxo-hydroxo species, which could be expected to form upon hydrolysis of the oxocluster.

These preliminary results indicate that the substitution of the methacrylic ligands by the bicarboxylic ones to give a network is feasible, and that the careful optimisation of the experimental paramters could lead to more ordered and more crystalline materials.

To address this aim, further experiments will be carried out in Padova working at room temperature and under inert atmosphere by using the same molar ratios and reagents used in Versailles.

Furthermore, the samples prepared in Versailles will be analysed by EXAFS to investigate whether the core structure of the Zr4 cluster has been retained after the reaction with bicarboxylic acid, or either the Zr4 cluster decomposed.

At this regard, also **the replacement of the more symmetric and “spheric-shaped” Zr6 oxocluster** drawn in figure XX, and presenting less hindered methacrylic ligands could allow an easier exchange and the formation of a high interconnected framework, in which the Zr6 acts as “crosslinker” for the forming metalorganic framework.



$M_6(OH)_4O_4(OMc)_{12}$

This would be in turn interesting consequences on the properties of the so obatined materials, mainly an expected higher specific surface area due to the more open structure obtained by replacing the tri- or tetrafunctional SBU generally employed with the 12-fold functional.

4- preparation of Fe_3O modified with acrylate ligands

This part of the work was devoted to the synthesis and purification of sodium acrylate which was then used for the **synthesis of the Fe(III) trimer with acylate groups** on its surface, which is the homolog of the acetate Fe(III) trimer $Fe_3O(OAC)_6$. Needle-shaped red crystal was separated from the dark red the solution, using heptane or acetonitrile as cosolvent, which were characterised by single-crystal. Although the refinement is still in progress, the crystal structure is expected to be the same published by Cronin et al. in 2006, although the synthesis route is completely different.

This precursor will be used as inorganic building block for the synthesis of inorganic-organic hybrid materials, by exploiting the presence of the six acrylate bonds on the trimer surface.

5- preparation of Fe-MIL88 modified with acrylate ligands

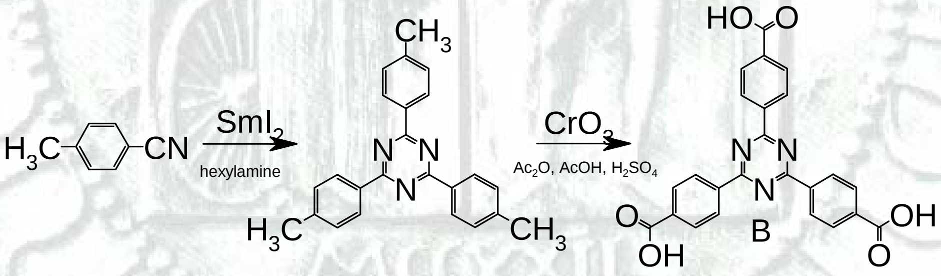
The aim of these experiments was to prepare a MIL88 of Fe(III) functionalised with acrylate ligands, by reacting iron chloride with a mixture of tereftalic and acrylic acid, by using different tereftalic/acrylic acid molar ratios.

In several case, a diffractogramm consisting of sharp reflexes was obtained, which strongly resembles that of MIL88 obtained in DMF (see file MIL88_FeAcr- in the folder MIL88 FeAcr). The most striking difference at this regard concerns the shift of all the Bragg peaks at lower angles, although a careful analysis has not yet been carried out.

6- Synthesis of tritopic funtionalised ligands

Part of the work was also devoted to the synthesis of **two tritopic ligands** to be used for the synthesis of new MOFs. In particular, two different tricarboxylic triazole and triazine-derivatives were prepared and characterised by H^1- NMR.

4, 4’, 4’’-s-triazine, 2,4,6 triyltribenzoic acid



Tris acid {4-[3,5-Bis-(1-carbonylmethyl-1*H*-[1,2,3]triazol-4-yl)-phenyl]-[1,2,3]triazol-1-yl}-acetic acid

Figura

The compounds were obtained pure and in high yield (80-90%, depending on the batch)