

MS35-P10

Exploring the catalytic performances of a series of bimetallic MIL-100(Fe-Ni) MOFs

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The development of multifunctional solid catalysts is currently of foremost relevance in the field of heterogeneous catalysis. The reason is that it is expected that bi/multi-functionalization achieve specific reactions in one single step thus noticeably reducing processing costs. In this context, Metal-Organic Frameworks (MOFs) can play a crucial role given their chemically modulable nature and their already proved suitable performance as solid heterogeneous catalysts for specific liquid phase chemical transformations. The synthesis of stable mixed-metal MOFs however, is not always obvious and requires a control of the metal stoichiometry based on cations with different oxidation states and therefore very distinct chemical reactivities.

In this work we present a series of mixed-metal Fe^{III}/Ni^{II} MOFs of the MIL-100 type material containing different metal ratios. The resulting heterometallic MIL-100(FeNi) materials maintain thermal, chemical and structural stability with respect to the parent MIL-100(Fe) MOF as can be deduced from XRPD, N₂ adsorption, FTIR and thermal analysis. The nature and the oxidation state of the accessible cations have been evaluated by *in situ* infrared spectroscopy analysis. The obtained mixed-metal MIL-100(FeNi) MOFs and the parent MIL-100(Fe) material have been evaluated as heterogeneous catalysts in a model acid-catalyzed reaction such is the Prins reaction. It is found that the catalytic activity improves more than one order of magnitude for a certain metal substitution, with a complete selectivity for the formation of Nopol. The proposed mechanism will be discussed.

Keywords: MOFs, heterogeneous catalysis

MS35-P11

Sulfur polyconjugated organic ligands as building block in photoactive metal-organic frameworks

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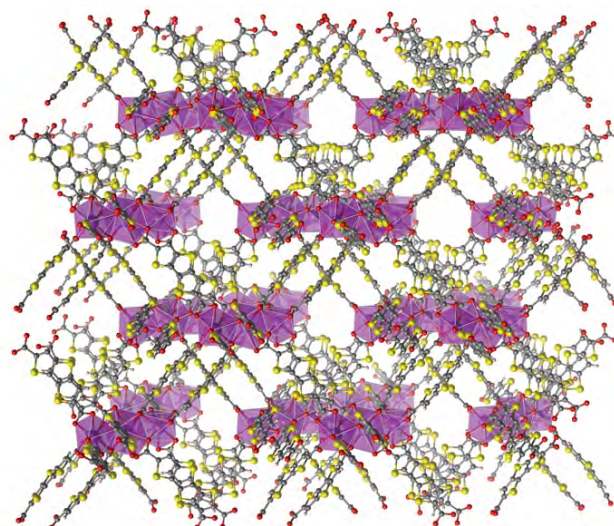
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Metal-organic frameworks or MOFs, are relative recent hybrid structures form by the joint between metal clusters and organic ligands. These networks have raised notable research interest because of their components are responsible for the structure properties resulting in a wide range of applications. Therefore, the appropriate choice of these building blocks could improve its features and direct the properties towards different applications like catalysis, gas separation and storage, magnetism, sensors, drug delivery [1].

Here we report the synthesis of photoactive MOFs with the combination of hole transport sulfur-conjugated ligands and different metals such as bismuth and indium. The use of electroactive organic ligands can provide charge transfer phenomena in these tridimensional networks and can leads to significant electronic interactions with the metal center-coordinated metal ions under light irradiation leading to an improvement of the optoelectronic and photo-catalytic properties [2]. In addition, a metal-node with relative large ionic radius with possibility of act with high oxidation state and empty orbitals to accept electron transfer is desired.

The opto-electronic and conductive properties of these networks have been determined by several characterization tools. Transient absorption spectroscopy reveals different electron-hole recombination rates compared with the corresponding metal oxides. Moreover, photocurrent measurements reveals changes in the conductivity in function of the used metal node.

In this way we have study the expected potential properties of these specifically tailored structures to their application into photocatalytic reactions.



References:

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- [1] Furukawa, H.; Cordova, K. E.; O'Keeffe, M. & Yaghi, O. M. (2013) *Science*, 341, 6149, 1230444
- [2] Diercks, C. S.; Liu, Y.; Cordova, K. E. & Yaghi, O.M. (2018) *Nature Materials* 17, 301-301.
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Keywords: Metal-organic frameworks, conjugated ligands, charge transfer

MS35-P12**Structural flexibility in the solid state**

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In order to understand solid-gas inclusion processes at the molecular level it is important to correlate physico-chemical data (e.g. sorption isotherms and calorimetric analysis) with structural data. It is therefore desirable to carry out structural elucidation and calorimetric analysis under conditions that closely mimic those of the sorption/desorption experiments. However, the crystallographic analysis of samples under controlled gas environments poses significant technical challenges, particularly given the limited space associated with the sample compartment of standard commercial diffractometer. In this regard, an environmental gas cell has been developed in parallel with a pressure-programmed differential scanning calorimeter. Use of these complementary techniques has provided new insight into features such as pressure-induced phase transformations that give rise to inflections and hysteresis in sorption isotherms. The influence of guest molecules on aspects such as structural flexibility and changes in network interpenetration will be discussed.

Keywords: porosity, structure-property relationships, in situ analysis