

coordinate, from which one can get the structural change and reaction speed as a function of time. Forces on atoms can be related to $\rho(\mathbf{r}, t)$ via Hellmann-Feynman forces. Indeed it is also necessary to relate the behaviour of an isolated set of molecules to the real situation occurring in a chemical process. We feel essential to focus attention onto the key properties of $\rho(\mathbf{r}, t)$, that is the leading link between most aspects of a non stationary system, from microscopic or macroscopic experimental side, or from a theoretical viewpoint. The acquired experience concerning diversified systems in a steady state should help in finding original and simple models for time evolving systems, a fascinating challenge for the near future.

KN07

Porous Nanomaterials, João Rocha, *Department of Chemistry, CICECO, University of Aveiro, Portugal*
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Zeolites, the archetype of microporous materials, are well known as excellent molecular sieves, heterogeneous catalysts and ion exchangers. Although these 'conventional' areas of application will remain important in the nanotechnology era, microporous solids will find uses in new fields, such as optoelectronics and magnetism. In the early nineties of the last century, zeolite-type silicates built up of transition-metals (mostly Ti) heteropolyhedra, were developed [1]. By the turn of the century, the constituent elements of heteropolyhedral silicates were extended to lanthanides (Ln) and, thus, photoluminescence (PL) properties became available [1-3]. The work in the field of 'bright zeolites' culminated with the report of the intriguing chiral system $\text{Na}_3[(\text{Y}, \text{Ln})\text{Si}_3\text{O}_9] \cdot 3\text{H}_2\text{O}$: it was shown that Eu^{3+} PL spectroscopy with excitation by unpolarised light in the absence of an external magnetic field is able to identify enantiomeric domains in chiral frameworks [4].

With the turn of the century there was a surge of activity on inorganic-organic hybrid solids known as coordination polymers or metal-organic frameworks (MOFs). These materials are of considerable interest because the combination of inorganic and organic fragments produces a large number of new crystal architectures and allows the design of solids with specific functions [5]. Interesting properties which may lead to industrial applications include gas storage and separation, catalysis, guest-exchange and sensors based on optical and magnetic properties. So far, only 10% or so of MOFs are effectively microporous and exhibit zeolite-type behaviour and much work remains to be done. Outstanding examples include the MIL-88 family [6].

In this talk I wish to review the recent developments in the field of microporous heteropolyhedral silicates. I shall also show the kaleidoscopic opportunities provided by inorganic-organic hybrid systems to engineer new nanoporous materials [7]. Finally, I shall pay attention to an often overlooked feature of nanoporous materials: the assembling of water molecules into small clusters, chains, layers [7] and 3D structures, in the voids of silicates and MOFs.

[1] Rocha, J., Lin, Z., in *Micro- and Mesoporous Mineral Phases, Reviews in Mineralogy and Geochemistry*, Ferraris G. and Merlino S. (eds.), Mineralogical Society of America, Geochemical Society, 2005, Vol 57, Chapter 6, 173.

- [2] Ferreira, A., Ananias, D., Carlos, D., Morais, C. M., Rocha, J., *J. Am. Chem. Soc.*, 2003, 125: 14573.
 [3] Ananias, D., Ferreira, A., Rocha, J., Ferreira, P., Rainho, J.P., Morais, C., Carlos, L.D., *J. Am. Chem. Soc.*, 2001, 123, 5735.
 [4] Ananias, A., Paz, F.A.A., Carlos, L.D., Geraldes, F.G.C., Rocha, J., *Angew. Chem. Int. Ed.*, 2006, 45, 7938.
 [5] Yaghi, O.M., O'Keefe, M., Ockwig, N.W., Chae, H.K., Eddaoudi, M., Kim, J., *Nature*, 2003, 423, 705.
 [6] Serre, C., Mellot-Draznieks, C., Surble, S., Audebrand, N., Filinchuk, Y., Ferey, G., *Science*, 2007, 315, 1828.
 [7] Shi, F.-N., Cunha-Silva, L., Sá Ferreira, R.A., Mafra, L., Trindade, T., Carlos, L.D., Almeida Paz, F.A., Rocha, J., submitted.

KN08

Structural aspects of chiral-at-metal complexes: On the origin of stereoselectivity Fernando J. Lahoz, Daniel Carmona, M. Pilar Lamata, Fernando Viguri, Joaquina Ferrer, Luis A. Oro *Departamento de Química Inorgánica, IUCH, ICMA, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, 50009 Zaragoza, Spain.*
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Asymmetric catalysis is an efficient method for synthesizing optically active organic compounds and the use of chiral metal complexes as homogeneous molecular catalysts is one of the most powerful strategies. Half-sandwich complexes of the three-legged piano-stool type have been extensively used as catalyst precursors in organic transformations often with a high degree of asymmetric induction and, in addition, their four-coordinate, pseudo-octahedral geometry facilitates the investigation of the stereochemistry of reactions at the metal centre.

Starting from some classical related contributions relating weak interactions and stereoselectivity, we will review the different half-sandwich chiral-at-metal complexes prepared and essayed in catalysis from our group. Complexes are of the general type $[(\eta^5\text{-arene})\text{M}(\text{A-B}^*)\text{L}]^{\text{n}+}$ with $\text{M} = \text{Ru}, \text{Os}, \text{Ir},$ or Rh , A-B^* being different bidentate ligands (diphosphines, amino-acidates, pyridylamines or imines, etc) containing, at least, one previously controlled chiral centre [1]. We will discuss the different strategies for the synthesis of these complexes, the characterization of diastereomers equilibria and their behaviour as catalyst precursors in different reactions (hydrogen transfer or diverse Diels-Alder processes).

We will focus on the structural characterization of the different species that have been suggested to be involved in the catalytic cycles, and especially in the description of feeble non-bonding interactions that seem to be at the origin of stereoselectivity [2].

[1] See Carmona, D.; Medrano, R.; Dobrinovich, I.T.; Lahoz, F.J.; Ferrer, J.; Oro, L.A. *J. Organomet Chem.* 2006, 691, 5560 and references therein.

[2] Carmona, D.; Vega, C.; García, N.; Lahoz, F.J.; Elipse, S.; Oro, L.A.; Lamata, M.P.; Viguri, F.; Borao R. *Organometallics* 2006, 25, 1592; Carmona, D.; Lamata, M.P.; Viguri, F.; Rodríguez, R.; Oro, L.A.; Lahoz, F.J.; Balana, A.I.; Tejero T.; Merino P. *J. Am. Chem. Soc.* 2005, 127, 13386