11th International School of Organometallic Chemistry

SUMMER SCHOOL

San Benedetto del Tronto, Italy

02-06 September 2017

http://d7.unicam.it/isoc/

University of Camerino

School of Pharmacy

School of Science and Technology

Interdivisional Group of Organometallic Chemistry

Organometallic chemistry: from theory to applications

Poster 61

Nitrogen-enriched graphene metal and metal oxide nanoparticles as innovative catalysts: new uses

Abhijnan Sarkar, Dario Formenti, Fabio Ragaini

Università degli Studi di Milano, Dipartimento di Chimica, via C. Golgi 19, 20133 Milano, Italy

A new class of catalysts has recently brought the attention of researchers, which is generated by pyrolyzing first transition row metal complexes with nitrogen ligands adsorbed on an inert support, such as carbon, silica. The catalysts have a metal/metal oxide core, surrounded by a few nitrogen-enriched graphene layers (NGr). These materials, which only contain cheap and abundant metals such as iron and cobalt, catalyze reactions for which noble metals are usually required; thus representing a cheaper and more sustainable alternative of the costly noble metals. Until now, such catalysts have been employed mainly in the context of hydrogenation reactions. The objective of this work is to expand the field of applicability of this new class of catalysts. We have used Fe_2O_3/NGr@C to catalyze olefin cyclopropanation, a reaction for which the use of these catalysts has not previously been investigated. The activity of Fe_2O_3/NGr@C has been studied by using ethyl diazoacetate and α-methylstyrene as substrates. Various parameters such as solvents, temperature and time were changed. Fe_2O_3/NGr@C-catalysts showed best activity in dimethoxyethane at 60 ^{o}C, affording high yields of the desired cyclopropanes (mixture of *cis* and *trans* isomers) and only 1-2 % of ethyl maleate and fumarate.

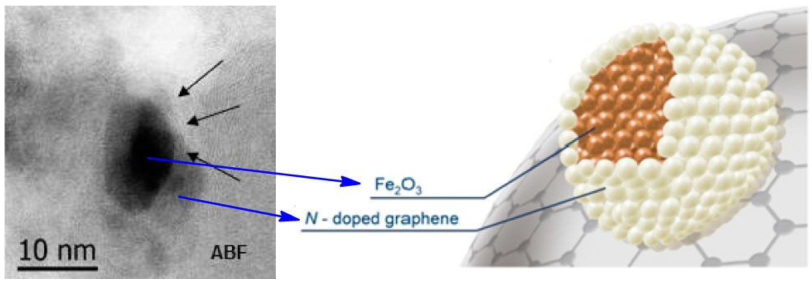


Figure 1 Nanoscaled Fe_2O_3 particles surrounded by nitrogen-doped graphene layers.

References

[1]Li, M.; Xu, F.; Li, H. ; Wang, Y. *Catal. Sci. Technol.* **2016**, *6*, 3670-3693.

[2] Pisiewicz, S.; Stemmler, T.; Surkus, A.-E.; Junge, K.; Beller, M. *ChemCatChem* **2015**, *7*, 62-64.

[3] Jagadeesh, R. V.; Stemmler, T.; Surkus, A. E.; Junge, H.; Junge, K.; Beller, M. *Nat. Protoc.* **2015**, *10*, 548-557.

[4] Formenti, D.; Ferretti, F.; Topf, C.; Surkus, A.-E.; Pohl, M.-M.; Radnik, J.; Schneider, M.; Junge, K.; Beller, M.; Ragaini, F. *J. Catal.* **2017**, *351*, 79-89.

[5] Formenti, D.; Topf, C.; Junge, K.; Ragaini, F.; Beller, M. *Catal. Sci. Technol.* **2016**, *6*, 4473-4477.

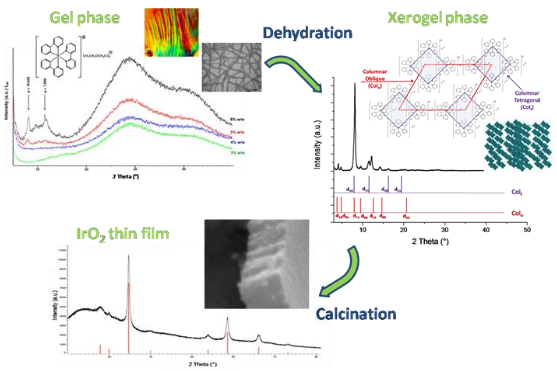
Poster 62

Nanostructured IrO_2 thin films obtained from Ir(III) metallogels

Francesca Scarpelli,*Andreea Ionescu, Iolinda Aiello, Massimo La Deda, Alessandra Crispini, Mauro Ghedini, Nicolas Godbert

Laboratorio MAT-INLAB, Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, I-87036 Arcavacata di Rende (CS), Italy, *francesca.scarpelli@unical.it

Ir(III) metallogels were prepared starting from the luminescent hydrogelator Ir(III) complex $[(ppy)_2Ir(bpy)](CH_3CH_2OCH_2CO_2)$.[1] The gel phases and the corresponding xerogel phases were examined through POM, PXRD and TEM. TEM micrographs show a network of entangled fibers, characteristic of many gel phases. Furthermore, POM analysis of the gel phases reveals an intense and homogeneous birefringent texture, which is retained in the xerogel phases, suggesting the presence of an ordered anisotropic arrangements of molecules. PXRD studies allowed to elucidate the supramolecular architecture: the gel phase consists of tetragonal columnar strands of self-assembled Ir(III) cations, surrounded by counterions. These strands are, in turn, organized in a columnar oblique system. The gel phases at different concentrations were deposited onto quartz substrates through spin-coating and after several days xerogels thin films were obtained. The calcinations of the xerogels led to the formation of highly crystalline IrO_2 thin films. Moreover, SEM micrographs of the obtained IrO_2 films showed an interesting inner nanostructuration made up of ordered vertical IrO_2 arrays, a reminiscence of the ordered self-assembled columnar features of the starting xerogels. The procedure here described could be the starting point for the development of a new method to prepare ordered IrO_2 thin films and, in a more general perspective, other inorganic nanostructures taking advantage of a well-organized organometallic gel precursor.



References

[1] Scarpelli, F.; Ionescu, A.; Ricciardi, L.; Plastina. P.; Aiello, I.; La Deda, M.; Crispini, A.; Ghedini, M.; Godbert, N. *Dalton Trans.* **2016**, 45, 17264–17273.