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PhD Thesis Proposal

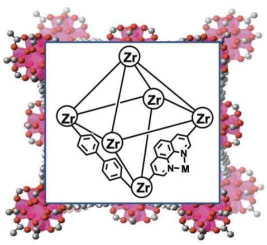
Porous materials based on metal complexes with 1,10-phenanthroline for catalysis

Chemical reactions catalysed by metal complexes have become one of the central tenets and instruments of modern organic synthesis. This was clearly demonstrated by awarding three Nobel prizes in this field during first ten years of XXI century. However, when used in industrial production of fine chemicals, these reactions have important drawbacks. The catalysts are expensive, difficult to separate from the products and cannot be reused in the next batch. Therefore, considerable attention has been devoted to the immobilization of homogeneous catalysts onto solid supports. These studies are aimed at the simplification of the products purification, recycling of catalysts and expected benefits of catalytic sites isolation such as increasing the catalyst stability and generation of the shape selectivity.[1] However, heterogenized catalysts are still rarely used in industry that shows a crucial importance of well-understood but ill-solved problems related to these materials such as a decrease in catalytic activity in comparison with homogeneous catalysts or leaching, to which heterogenized catalysts are prone.

One of the ways to approach these aging problems relies on the design of *porous* functional materials allowing to diminish the catalyst leaching and the influence of mass transfer processes on the rates of catalytic reactions. Moreover, such materials are useful to create efficient catalysts for tandem reactions because several catalytic centres can be anchored on the same support controlling their quantity, location and spacing.

We are developing strategies for immobilization of air-stable metal complexes with nitrogen ligands by using phosphonate and carboxylate anchoring groups. Among them, metal (Fe^{3+}, Pd^{2+}, Cu^{2+}, Ag^{+}, Ru^{2+}, Rh^{+}) complexes with 1,10-phenanthrolines are of particular interest because they are efficient catalysts for a broad spectrum of chemical reactions under homogeneous conditions (C–C and C–Het (Het = N, B, Si) bond forming reactions, rearrangements, carbonylation and oxidation reactions, activation of CO_2 and photocatalytic processes). Recently we have demonstrated that these complexes can be incorporated into metal-organic frameworks (Figure 1, A) or grafted on the surface of mesoporous titania (Figure 1, B) affording reusable multi-process catalysts.[2]

A



B

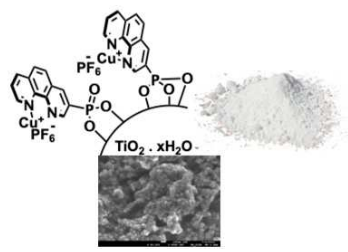


Figure. *Porous materials based on metal complexes with 1,10-phenantroline: MOF bearing metalloligands (A); 2) surface-modified titania (B).*

The goal of this PhD is to develop reusable catalytic systems for tandem catalytic reactions and solid catalysts for continuous-flow reactions by using these synthetic approaches. We will investigate 1) grafting of metal complexes with 1,10-phenanthrolines on the surface of titania aerogels; 2) preparation of stable and hierarchically porous composite materials combining the advantages of MOFs and silica or titania matrices; 3) synthesis of materials bearing two different catalytic sites into metal-organic frameworks or at the surfaces of mixed silica/titania materials.

This multidisciplinary project at the interface of organic synthesis, catalysis, coordination and material chemistry involves organic synthesis, sol-gel technology, solvothermal reactions, numerous methods for characterization of molecular compounds and material (IPC, NMR, UV, IR, ESI/MS, isotherms of gas adsorption, SEM, TEM). This project is an integral part of the French-Russian cooperation program and short stages in Lomonosov Moscow State University will be possible.

References

1. *Heterogeneous Catalysts for Clean Technology: Spectroscopy, Design, and Monitoring*. Wiley-VCH Verlag GmbH & Co.: Weinheim, Germany, 2014; p 478.

2. a) Mitrofanov A., Brandès S., Herbst F., Rigolet S., Bessmertnykh-Lemeune A., Beletskaya I., *J. Mater. Chem. A*, **2017**, *5*, 12216–12235; b) Abel A. S., Mitrofanov A. Yu., Yakushev A. A., Zenkov I. S., Morozkov G. V., Averin A. D., Beletskaya I. P., Michalak J., Brandes S., Bessmertnykh-Lemeune A., *Asian J. Org. Chem.* **2019**, *8*, 2128–2142.

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