Functionalization of the Internal Surface to the Ultra Stable Zirconium Metal Organic Framework, UiO-66.

Søren Jakobsen[1], Merete h. Nilsen[1], Cherif Larab[2]i, Unni Olsbye[1], Mats Tilset[1], Carlo Lamberti[3], Silvia Bordiga[3] and Karl Petter Lillerud[1]*

[1]*Department of Chemistry, University of Oslo, Oslo, Norway*

[2]*Laboratoire de Chimie Organométallique de Surface CNRS Villurbanne, France*

[3]*Department of Chemistry IFM & NIS Centre of Excellence, University of Torino, Torino, Italy.*

*kpl@kjemi.uio.no

Introduction

Porous crystals are strategic materials with industrial applications within petro-chemistry, catalysis and selective separation. Their unique property is based on the molecular scale porous character. However, a principal limitation of zeolites and similar oxide based materials are the relatively small size of the pores, typically in the range of medium sized molecules and the limited possibility to chemically modify the large internal surface. Metal Organic Frameworks (MOFs) provided a breakthrough both in respect surface area and its chemical diversity.

Materials and Methods

Synthesis: All chemicals were obtained commercially (Aldrich) and used without further purification. Standard synthesis of Zr-BDC MOF was performed by dissolving $ZrCl_4$ (0.227 mmol) and 1,4-benzene-dicarboxylic acid (H_2BDC) (0.227 mmol) in N,N`-dimethylformamide (DMF) (340 mmol) and H_2O (0.227 mmol) at room temperature. The thus obtained mixture was sealed and placed in a pre-heated oven at 120 ˚C for 24 hours. Crystallization was carried out under static conditions. The Zr- MOFs with boron and functionalized linkers are synthesized by replacing BDC with equivalent amounts of the modified linkers.

Characterization: Powder XRD, TGA-MS, EXAFS, SEM, IR and adsorption.

Results and Discussion

Here we present the synthesis of very high surface area MOFs with unprecedented stability. The high stability is based on the combination of strong Zr-O bonds and the ability of the inner Zr_6-cluster to rearrange reversibly upon removal or addition of μ_3-OH groups, without any changes in the connecting carboxylates. This MOF material show the stability required for applications in industrial processes, thermal stability (400 ºC under oxidizing conditions) chemical resistance to most solvents including steam and resistance to high mechanical pressure (10 tonn/cm^2) This structure has been made with a large number of linkers, both by our group[1] and by C. Serre et.al[2]. In this work is the structures extended to linkers containing functional groups, like amines and born groups. The interaction of the modified surface and probe molecules are followed by IR-spectroscopy.

Significance

Metal Organic Frameworks (MOFs) is a promising fast growing new class of nanoporous materials. The new Zr-MOFs are the most stable MOF materials reported so far, here do we report a first step towards functionalization of these materials, as a first step towards introducing catalytic properties.

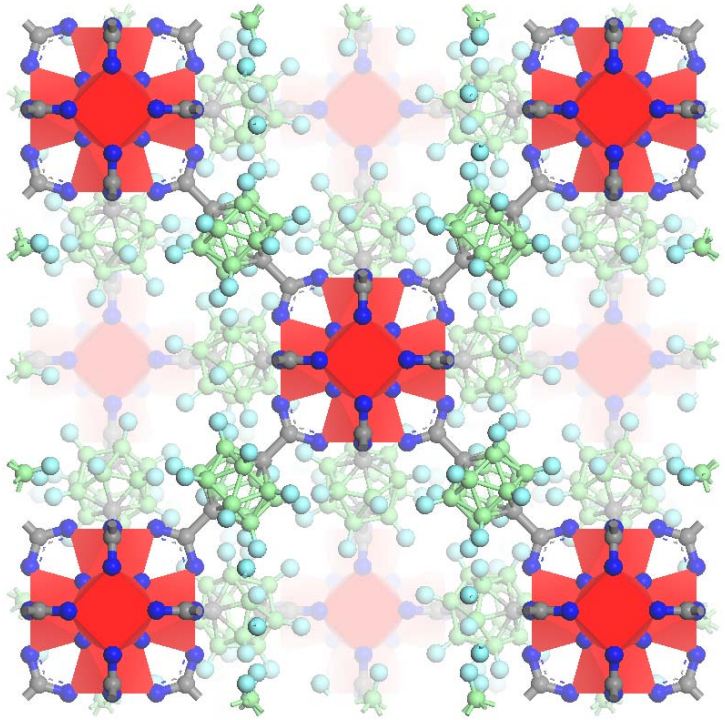

Figure 1. Zr-borane-MOF, UiO-66-B1. Crystallizes as a cubic structure with a_o = 21.3 Å

References

1. Hafizovic Cavka, Jasmina; Jakobsen, Soren; Olsbye, Unni; Guillou, Nathalie; Lamberti, Carlo; Bordiga, Silvia; Lillerud, Karl Petter. A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. JACS (2008), 130(42), 13850.
2. C. Serre et al. MOF-08. Augsburg, Germany. 8-10 October 2008.