From Molecules to Materials

Professur Koordinationschemie

Prof. Dr. Michael Mehring

e-mail: michael.mehring@chemie.tu-chemnitz.de

Technische Universität Chemnitz, Institut für Chemie,
Professur Koordinationschemie,
Straße der Nationen 62, D-09111 Chemnitz

TECHNISCHE UNIVERSITÄT CHEMNITZ
1836-2011 175 Jahre

Investigations on Self-Organization and Nucleation: Towards Metastable Bismuth Oxides:

M. Mehring, *Coord. Chem. Rev.* **2007**, *521*, 974,
D. Mansfeld et al., *Angew. Chem.* **2005**, *117*, 250,
M. Mehring et al., *Chem. Eur. J.* **2006**, *12*, 1767.

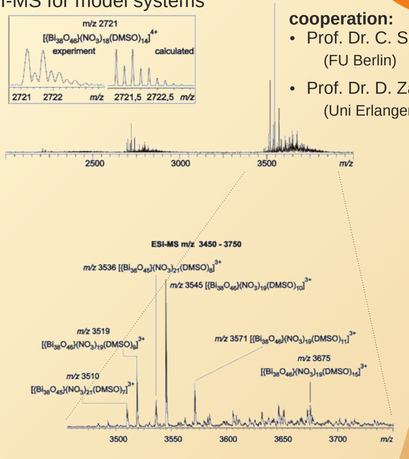
SPP 1415

TECHNISCHE UNIVERSITÄT CHEMNITZ

synthesis and characterization
(AK Mehring)

cooperation:
- Prof. Dr. C. Schalley (FU Berlin)
- Prof. Dr. D. Zahn (Uni Erlangen-Nürnberg)

ESI-MS for model systems



nucleation in solution

ion $[Bi(H_2O)_x]^{3+}$

cluster

e.g. $[Bi_{12}O_{16}(OSiMe_2{}^tBu)_{12}]$

bulk

Bi_2O_3,
6 polymorphs
known until now

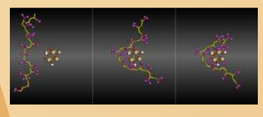
number of octaeders A

- 1: $[Bi_4O_2(OSiEt_3)_8]$
- 1: $[Bi_6O_{4+y}(OH)_{4-y}]^{(6+)}X_{(6-y)}$ (X = NO_3, OTf, ClO_4)
- 1: $[Bi_6O_7(L)_{13}]$ (L = $OSiMe_3$, hfac, Hsal)
- 1: $[Bi_{10}O_8(HSal)_{14}]$
- 4: $[Bi_{16}O_{16}(OSiMe_3)_{16}]$
- 4: $[Bi_{20}O_{16}(OSiMe_3)_{24}]$
- 8: $[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}]$
- 10: $[Bi_{33}NaO_{36}(OSiMe_3)_{24}]$
- 13: $[Bi_{38}O_{45}(L)_{24}]$ (L = hfac, OTf)
- 13: $[Bi_{38}O_{44}(HSal)_{26}]$, $[Bi_{38}O_{45}(OH)_2(HSal)_{22}]$
- 20: $[Bi_{60}Na_2O_{64}(OH)(OSiMe_3)_{22}]$
- ∞: Bi_2O_3

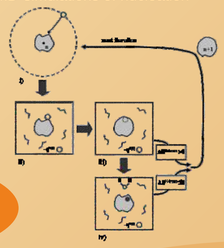
building unit A

- hydrolysis and pyrolysis results in the formation of different bismuth oxides or silicates

- MD-simulations of the interaction between a bismuth-oxido cluster and a polyacrylate which acts as inhibitor for the crystallization process



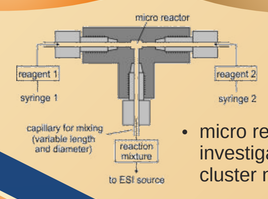
Kawska-Zahn method:
MD-simulations of nucleation



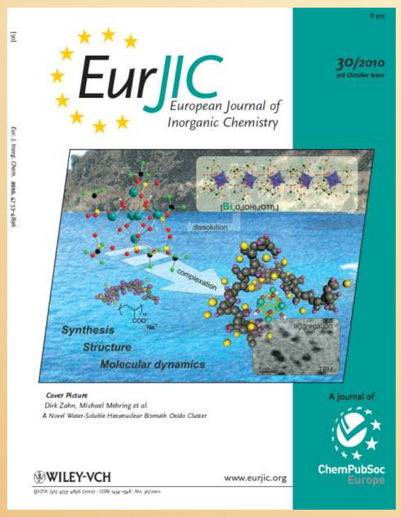
***in-situ* investigations using ESI-MS**
(AK Schalley)

mechanisms of formation, controlled synthesis of bismuth oxide polymorphs

molecular dynamics simulations
(AK Zahn)

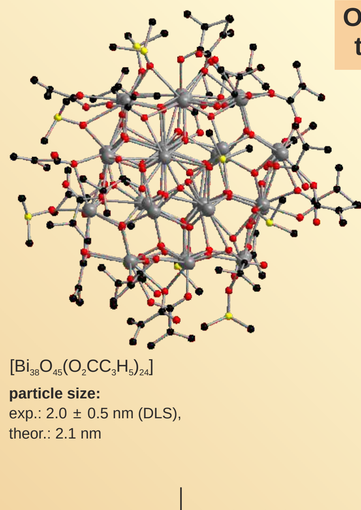


- micro reactor for in-situ investigations on cluster nucleations



L. Miersch et al., *Eur. J. Inorg. Chem.* **2010**, 4763.

- picture shows the novel hexanuclear bismuth oxido cluster $[Bi_6O_4(OH)_4(OTf)_6]$
- compound forms a 1D coordination polymer in the solid state
- highly soluble in water and polar organic solvents
- reaction with sodium polyacrylate gave a nano-sized hybrid material
- snapshot of the molecular dynamics simulation shows the apparent complexation of $[Bi_6O_4(OH)_4]_6$ by polyacrylate in water
- polyacrylate effectively prevents further aggregation of bismuth oxido clusters

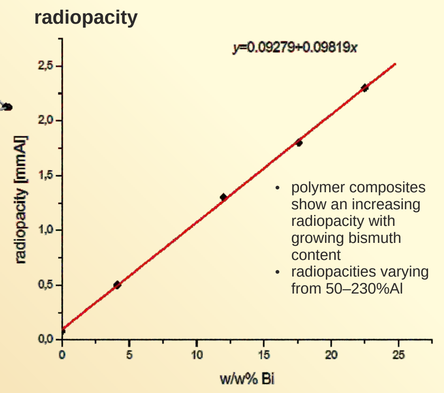


$[Bi_{38}O_{45}(O_2CC_3H_5)_{24}]$

particle size:
exp.: 2.0 ± 0.5 nm (DLS),
theor.: 2.1 nm

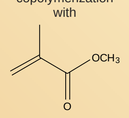
Organic-Inorganic Hybrid Materials on the Basis of Bismuth-Oxido Clusters:

radiopacity



- polymer composites show an increasing radiopacity with growing bismuth content
- radiopacities varying from 50–230%Al

copolymerization with



AIBN, DMF, 60 °C, 6h

vacuum, drying, 100 °C

- polymerizations carried out with varying bismuth content (5–30% w/w)
- transparent glassy materials after removal of solvent

Thermal behavior:
- DSC thermograms show three distinct peaks (167 °C, 286 °C, 377 °C) ? endothermic degradation processes for radically polymerized PMMA
- additional point of decomposition at 401 °C
- hardly altering of PMMA by addition of $[Bi_{38}O_{45}(O_2CC_3H_5)_{24}]$ as inorganic building block

Summary:
- accessibility of organic-inorganic hybrid materials by radical copolymerization of $[Bi_{38}O_{45}(O_2CC_3H_5)_{24}]$ with methyl methacrylate
- these glassy composites are transparent, show no phase separation and do not alter the thermal properties of PMMA
- Furthermore we have demonstrated its radiopaque properties with regard to the application of $[Bi_{38}O_{45}(O_2CC_3H_5)_{24}]$ as promising X-ray contrast agent, for example in dental and bone cements.

Synthesis of Metal(IV)-Alkoxides which are Suitable for Twin-Polymerization:

organic-inorganic hybrid materials are obtained by **Twin Polymerization**:

$M(O^tBu)_4$ + R-OH

↓

$M(OR)_4$
1 monomer

↓ initiator

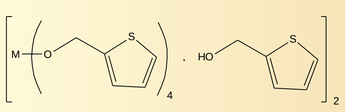
polymer / MO_2
polymer / metal oxide composite

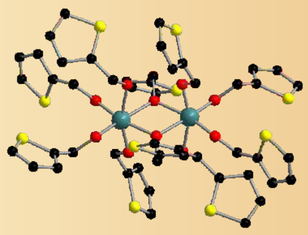
oxidation → **MO_2**

reduction → **C / M**

BASF The Chemical Company

example of a precursor:





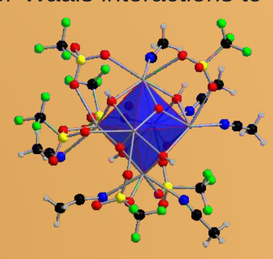
synthesis of:
- metal oxide / polymer hybrid materials
- metal oxide nanoparticles
- metal / C nanocomposites

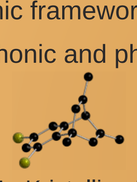
potential applications:
- catalysts
- sensors
- lithium-ion-batteries

„Nanoscale Tungsten Trioxide Synthesized by In Situ Twin Polymerization“
F. Böttger-Hiller, R. Lungwitz, A. Seifert, M. Hietschold, M. Schlesinger, M. Mehring, S. Spange,
Angew. Chem. Int. Ed. **2009**, *48*, 8878.

Research Interests

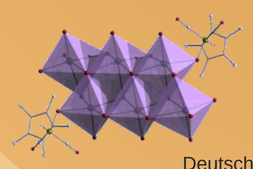
- synthesis and structural characterization of polynuclear metal-oxido clusters - preliminary stage of nucleation of metal oxides
- inorganic and metal-organic molecular compounds of group 14 and 15 - syntheses, structures and properties of materials
- organic-inorganic hybrid materials and metal oxides starting from twin polymerization and non-aqueous synthetic routes
- weak interactions in compounds of main group elements - from Van-der-Waals interactions to hydrogen bonds
- new *diene*-ligands in (asymmetric) catalysis
- metal-organic frameworks and coordination polymers
- chiral phosphonic and phophinic acids as potential organocatalysts

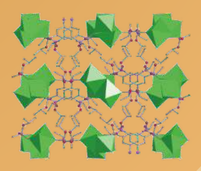




Selected Projects

- DFG-SPP 1415: „Kristalline Nichtgleichgewichtsphasen - Charakterisierung und in-situ-Untersuchungen der Bildungsmechanismen“ - formation and nucleation of metastable bismuth oxides via bismuth oxido clusters
- investigations on the structure and functionalization of nanoscaled clusters, like $[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}]$ or $[Bi_{38}O_{45}(OH)_2(L)_{22}]$ (L = Hsal, O-Val-Boc)
- organometallic compounds as precursors for the synthesis of (heterometallic) oxides like multiferroic $BiFeO_3$
- porous organic-inorganic nanocomposites by „Twin Polymerization“ starting from metal alkoxides with cationic polymerizable ligands (cooperation with BASF)
- organic-inorganic hybrid nanocomposites containing bismuth oxido clusters
- benzobarrelene derivatives as ligands in catalysis



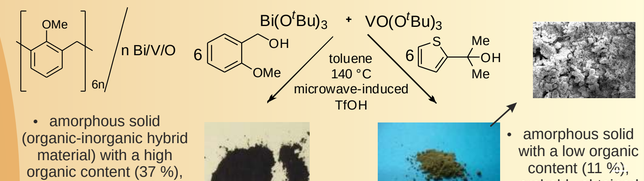


Acknowledgements / Funding

BASF
Deutsche Forschungs-gemeinschaft
Fonds der chemischen Industrie
Technische Universität Chemnitz
Ivoclar-Vivadent GmbH

Synthesis and Photocatalytic Activity of $BiVO_4$

synthesis by simultaneous „in-situ“ Twin Polymerization



- amorphous solid (organic-inorganic hybrid material) with a high organic content (37 %), probably obtained by simultaneous Twin Polymerization
- amorphous solid with a low organic content (11 %), probably obtained by non-hydrolytic process

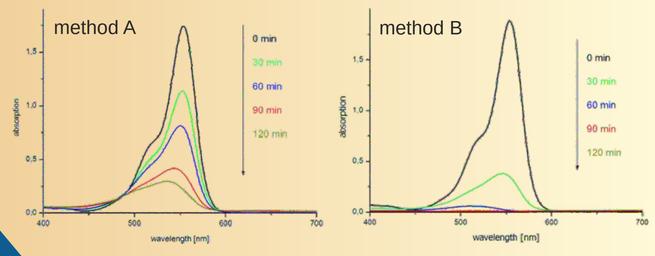
pyrolysis at 400 °C

$BiVO_4$ $BiVO_4$

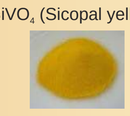
BET-A_O 11 m²/g BET-A_O 5 m²/g

XRPD is indicative for the formation of monoclinic $BiVO_4$ as single phase

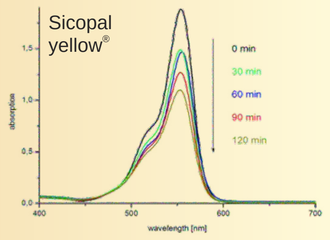
photocatalysis with $BiVO_4$ - decomposition of rhodamine B



$BiVO_4$ (Sicopal yellow®)

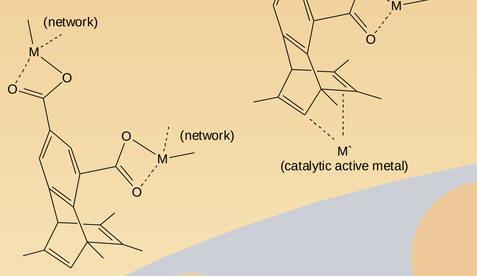


BET-A_O 10 m²/g



Conclusion:
- $BiVO_4$ with high photocatalytic activity was obtained by „in-situ“ simultaneous Twin-Polymerization and non-hydrolytic decomposition follwed by pyrolysis in comparison with Sicopal yellow®.

concept:

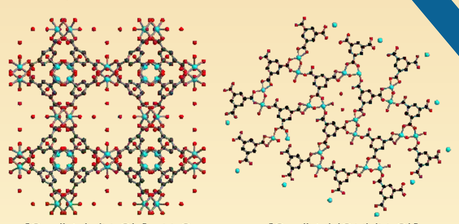


New Diene Ligands as Precursors with Potential for Asymmetric Heterogeneous Catalysis:

future prospect

asymmetric heterogeneous catalysis in MOF / MOP systems

„Evaluation of synthetic methods for microporous metal–organic frameworks exemplified by the competitive formation of $[Cu_3(btc)_2(H_2O)_3]$ and $[Cu_2(btc)(OH)(H_2O)]$“
M. Schlesinger et al., *Microporous Mesoporous Mater.* **2010**, *132*, 121.



$[Cu_3(btc)_2(H_2O)_3]\cdot xH_2O$ $[Cu_2(btc)(OH)(H_2O)]$

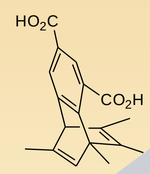
synthetic methods for MOF / MOP systems:
- electrochemical synthesis
- synthesis under atmospheric pressure and reflux
- ultrasonic synthesis
- mechanochemical synthesis
- solvothermal synthesis
- microwave assisted solvothermal synthesis

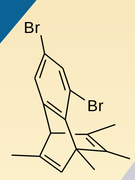
C Cl Br Rh Cu O

MOF - metal-organic framework
MOP - metal-organic polyhedron

chiral MOFs / MOPs

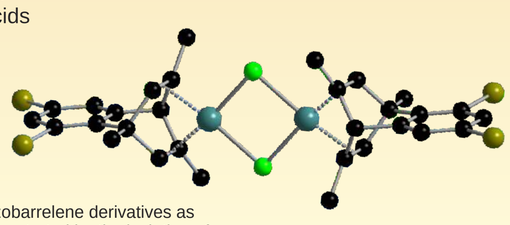
immobilization of catalytic active metals at the diene system



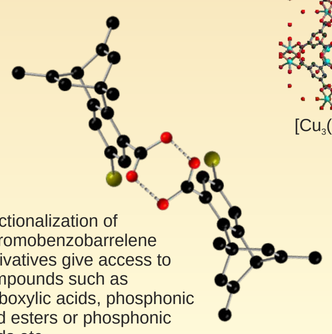


chiral benzobarrelene dicarboxylic or diphosphonic acids

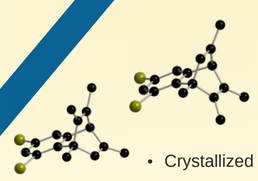
chiral dibromobenzobarrelene derivatives



- The potential of benzobarrelene derivatives as *diene ligands* is demonstrated by the isolation of a rhodium complex.



- functionalization of dibromobenzobarrelene derivatives give access to compounds such as carboxylic acids, phosphonic acid esters or phosphonic acids etc.



- Crystallized as racemat.