**Twin Polymerization using metal alkoxides -  a nonaqueous synthetic route for metal oxide-based hybrid materials**

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**Abstract**

Organic-inorganic hybrid materials with high porosity, well defined and nanoscaled pore geometry, and monodisperse domain size distribution are currently an active field of research. Materials with domain sizes in the range between 3 to 100 nm are accessible by several synthetic concepts, whereas smaller domain sizes are difficult to address. A novel concept, the so-called *Twin Polymerization* (TP), is based on nonaqueous synthetic processes and gives access to domain sizes below 3 nm for metal oxide based organic-inorganic composites. For example, *Twin Polymerization* of 2,2’-Spirobi[4*H*-1,3,2-benzodioxasiline] provides a composite material composed of interpenetrating SiO2/Phenol resin networks with defined nanostructured domains of 0.5 to 3 nm. Oxidation of this composite material provides highly porous SiO2, while carbonization and consecutive removal of SiO2 gives microporous carbon. This modular approach also gives access to metal oxide nanoparticles. Here, the synthesis and reaction behavior of diverse novel monomers including main group elements such as Si, Ge, Sn, Bi, In etc. is presented and their use with regard to *Twin Polymerization* and the related *Simultaneous Twin Polymerization* will be focused on. The as-prepared organic-inorganic composite materials and metal oxide nanoparticles were characterized with focus on structure and properties such as porosity, pore size distribution and particle size. In order to support our hypothesis of a reactivity scale of the monomers DFT calculations accompany the experiments in order to obtain a more detailed insight into the first reaction steps of this novel type of synthetic route for organic-inorganic hybrid materials.

 [1] selected examples: a) S. Spange, P. Kempe, A. Seifert, A. A. Auer, P. Ecorchard, H. Lang, M. Falke, M. Hietschold, A. Pohlers, W. Hoyer, G. Cox, E. Kockrick and S. Kaskel, *Angew. Chem., Int. Ed.* **2009**, *48*, 8254–8258; b) T. Löschner, A. Mehner, S. Grund, A. Seifert, A. Pohlers, A. Lange, G. Cox, H.-J. Hähnle, S. Spange, *Angew. Chem. Int. Ed.* **2012**, *51*, 3258–3261;c) F. Böttger-Hiller, R. Lungwitz, A. Seifert, M. Hietschold, M. Schlesinger, M. Mehring, S. Spange, *Angew. Chem. Int. Ed.* **2009**, *48*, 8878–8881; g) C. Leonhardt, S. Brumm, A. Seifert, G. Cox, A. Lange, T. Rüffer, D. Schaarschmidt, H. Lang, N. Jöhrmann, M. Hietschold, F. Simon, M. Mehring, ChemPlusChem 2013, DOI: 10.1002/cplu.201200242