Novel porous Metal@SiCN ceramics via molecular approach

Günter Motz[a)], Germund Glatz[b)], Thomas Schmalz[a)], Rhett Kempe[b)]

[a)]Lehrstuhl Keramische Werkstoffe, Universität Bayreuth, Ludwig-Thoma-Str. 36b, 95440 Bayreuth, Germany,
e-mail: guenter.motz@uni-bayreuth.de

[b)]Lehrstuhl für Anorganische Chemie II, Universität Bayreuth, Universitätsstr. 30, 95440 Bayreuth, Germany

Main applications for preceramic polymers (precursors) are ceramic fibres, ceramic matrices and coatings. Especially SiCN precursor ceramics have been investigated intensively due to very interesting properties like high temperature stability, corrosion resistance long term durability or special functional properties. A further extension of the property profiles like improved electrical and thermal conductivity or regarding catalytic activity can be expected by the introduction of different transition metals in the ceramic material. Usually metal-ceramic composites are produced by using porous ceramics, ceramic particles or ceramic fibers in combination with a molten metal (e.g. Al, Cu). This leads to a relatively coarse microstructure.
To provide for a homogeneous distribution of the metals a general molecular approach basing on metal (e.g. Cu, Fe, Au, Pt, Sc) aminopyrodinates and polycarbosilazanes was developed. The aminopyridinato metal complexes react with the precursors forming a covalent bonding between the metal atom and the precursor backbone as could be shown for the commercially available product HTT 1800. Cross-linking of the metal modified polycarbosilazane and subsequent pyrolysis leads to the M@SiCN ceramic. This molecular approach not only allowed the variation of the metal and the metal content in a wide range it is also possible to synthesize porous ceramics by mixing the metal modified precursor with a pore forming agent like fine polyethylene powder before cross-linking. SEM investigations of the ceramic material in addition with EDS-mappings revealed the presence of particles consisting of elemental metals. The in-situ formation of metallic particles from the metal compound during the pyrolysis process is due to the reducing atmosphere generated by the gaseous pyrolysis products methane and hydrogen.
To cite Cu@SiCN ceramics as an example a high metal content up to 14% is reachable. The number and the size of the formed Cu particles depend on the Cu content. The higher the Cu concentration in the starting precursor the bigger (from nanometer scale up to microns) and more are the Cu particles.
All Cu@SiCN ceramics show good catalytical activity towards selective oxidation of cycloalkanes. The selectivity of the reaction raises clearly with increasing copper content, whereas the turnover numbers decrease. The catalysts are recyclable and show only minor catalyst leaching. These results confirm the applicability of this new class of metal containing ceramics in heterogeneous catalysis and show great promise for further applications.