

Synthesis of transition metal carbides and nitrides using metal atom cluster precursors: applications in heterogeneous catalysis.

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Context. This proposal joins within the framework of an international collaboration between the Institute of the chemical Sciences of Rennes (ISCR-UMR 6226 CNRS-UR1), the ‘Laboratory of Innovative Materials and Key Structures’ located in Tsukuba in Japon (UMI CNRS-Saint-Gobain 3629) and the Ceramic Synthesis and Fonctionnalisation Laboratory (LSFC-UMR 3080 CNRS-Saint-Gobain) located in Cavaillon (France).

Goals. The proposal deals with the synthesis of ceramics within the family of transition metal carbides and nitrides for Saint-Gobain applications. One advantage of transition metal carbides and nitrides is that they can potentially replace noble metals as catalysts in low temperature fuel cells for vehicles. The proposal aims at (i) synthesizing particles of nitrides and carbides with controlled size and morphology thanks to the use of metal atom clusters as precursors and (ii) establishing the relationship between structural properties and catalytic performances. This work will need deep physical-chemical analysis and crystal chemistry characterizations such as: X-ray powder diffraction, XPS and if applicable *operando* XAFS.

Work plan. The PhD student will prepare cluster-based halides in the CSM-ISCR team using high temperature solid state synthesis and by combining solid state and solution chemistries. The carburization reactions will be performed at LSFC by controlled decomposition under inert atmosphere of a co-precipitate obtained from cluster precursors and organic bio-sourced precursors. Cluster nitridation will be performed by gas-solid reactions in the V&C-ISCR team. After optimization of the synthesis of nitride and carbide ceramics, first catalytic tests will be performed at LSFC. Studies of the compositions and structures of catalysts will be performed at National Institute for Materials Science at Tsukuba (NIMS) wherein unique characterizations facilities are available (HRTEM, XPS, SIMS, ...). For the best performing catalysts, *operando* analysis such as XPS or XAFS are foreseen to establish a structure-reactivity relationship. After optimization of synthesis of powdered ceramics and validation of catalytic performances, the last part of the work will consist to make deposition of catalysts onto catalytic supports.

The PhD will administratively belong to ‘Université de Rennes 1’. Several visits to the LSFC in Cavaillon are foreseen for catalyst preparation and catalytic testing. At least one visit at NIMS/Tsukuba is planned and will be carried out within the framework of student exchange program NIMS-UR1.

Skills and know-how :

- deep expertise in synthesis, physical-chemistry and crystal chemistry of inorganic materials,
- knowledge of usual structural characterization technics used in solid state chemistry.

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