A UNIFIED SYNTHETIC APPROACH TO POROUS HYBRID SINGLE-SITE METALLOSILICATES

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1. Introduction

Following on the excellent work of Ghosh,[1] Clark,[2] and Stýskalík et al.,[3] a highly flexible non-hydrolytic sol-gel procedure for the preparation of porous hybrid silicate matrices containing well-dispersed d-/p-block element oxide centers (sites) is presented. Firstly, a readily available spherosilicate building block $(Me_3Sn)_8Si_8O_{20}$ is reacted with a limited amount of a suitable site precursor. This leads to the formation of sparsely linked oligomers containing uniform sites, which are fully enveloped by the spherosilicate molecules. Secondly, a dose of a divalent inert linker is introduced in order to further cross-link the matrix to the point where it is rigid enough to retain porosity. The solvent as well as all condensation byproducts can be easily removed under vacuum to afford pure xerogels. The mild non-hydrolytic reaction conditions allow for the incorporation of sensitive moieties. All condensation reactions are intentionally irreversible to avoid any equilibria and site rearrangement, allowing for an approximately additive bottom-up approach. The networks are always inevitably amorphous and statistical in nature, however, a minimum site separation is enforced through the site envelopment by the bulky spherosilicate. The aim of this work is to unify the vast pool of knowledge that has been accumulated (with various goals) on this topic and to provide a „one size fits all" strategy for the synthesis of sites based on elements all across the periodic table, and with as much predictive power as possible for the reactivity-structure relationships.

2. Synthetic strategy

$(Me_3Sn)_8Si_8O_{20}$

= „molecular silica"

2-connected — 1.50 eq.
3-connected — 1.00 eq.
4-connected — 0.75 eq.
6-connected — 0.50 eq.

~ 0.9 nm

THF / toluene
−80 to 60 °C
− Me₃SnCl / Me₃SnR
1st STEP

homogeneous solution of oligomers

flexible or rigid

60 °C
− Me₃SnCl
2nd STEP

PRODUCT:
hybrid microporous single-site metallosilicate gel

SA_{BET} up to 400–800 m² g⁻¹
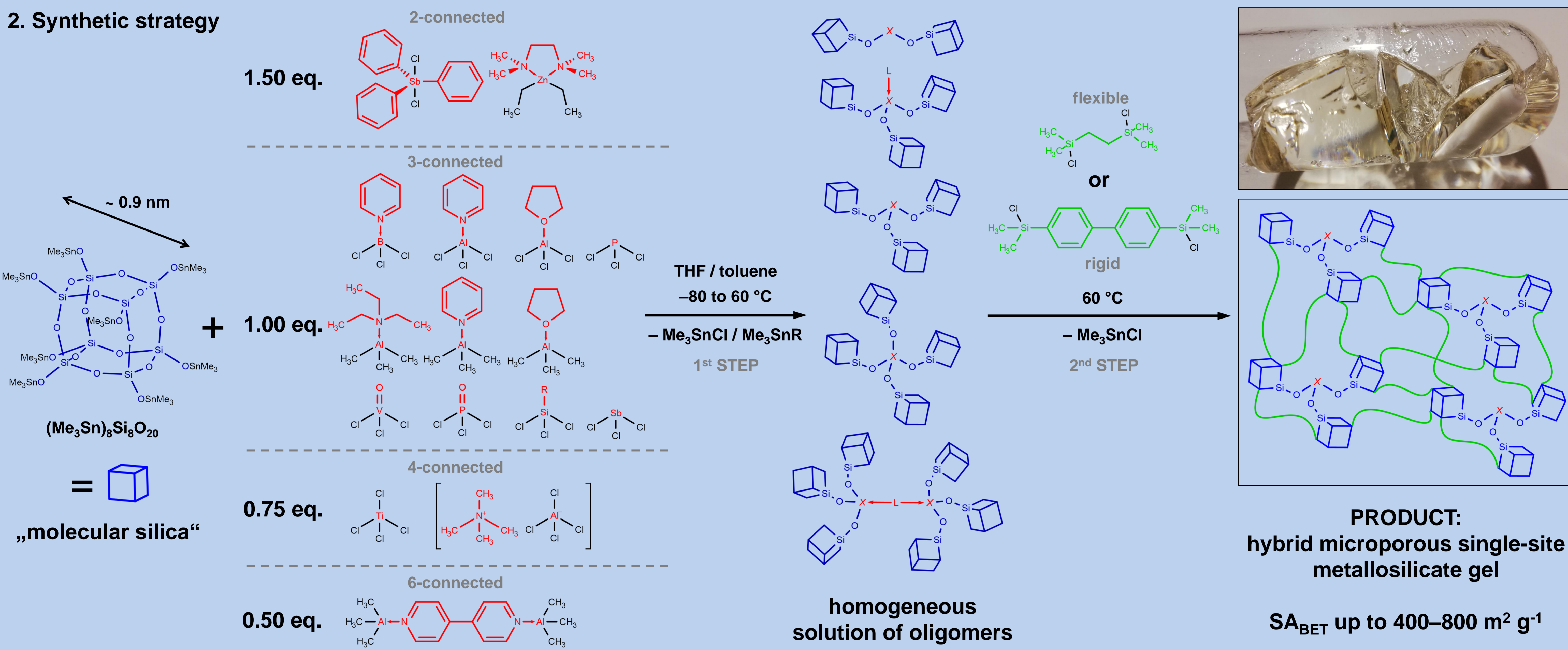
3. Suitable precursors

The employed condensation reactions resemble traditional proton-exchange chemistry with the difference that $Me_3Sn^+/Me_3SnCl/Me_3SnR$ interact only weakly and thus avoid the usual pitfalls of aqueous sol-gel chemistry. The byproducts of the condensations do not interfere with subsequent steps, they can be readily removed under vacuum, and gravimetric techniques can be used to monitor the degree of condensation. Quantum mechanical DFT calculations revealed that the preference of Me_3Sn^+ for O over Cl is negligible and the primary driving factor for the condensation is the oxophilicity of the site precursor. $Me_3SnOSiH_3$ was identified as a suitable model for the calculation of condensation thermodynamics as it was found to consistently over-estimate the reaction ΔG by 5–10 % compared to $Me_3SnOSi(OSiH_3)_3$ while providing an order of magnitude faster computation. A series of site precursors were computationally screened to determine if the condensation reaction is spontaneous and sufficiently irreversible (*Figure 1*). The reactivity was found to roughly correspond to the electronegativity of the central atom. The compound Ph_3SbCl_2 is a borderline example and while its full condensation was confirmed experimentally, the irreversibility of the reaction must be investigated further. The reactivity of $ZnEt_2/ZnCl_2$ was studied in depth in order to explain experimental observations. The data shows that while it is marginally possible to create $[ZnO_2]$ sites starting from $ZnEt_2$, the ultimate thermodynamic sink of the system is $ZnCl_2$, therefore once a source of Cl^- is introduced (inert linker), the structure is dissolved (*Figure 2*). Coordination of ligands stabilizes the preferred direction of the reaction in both cases.
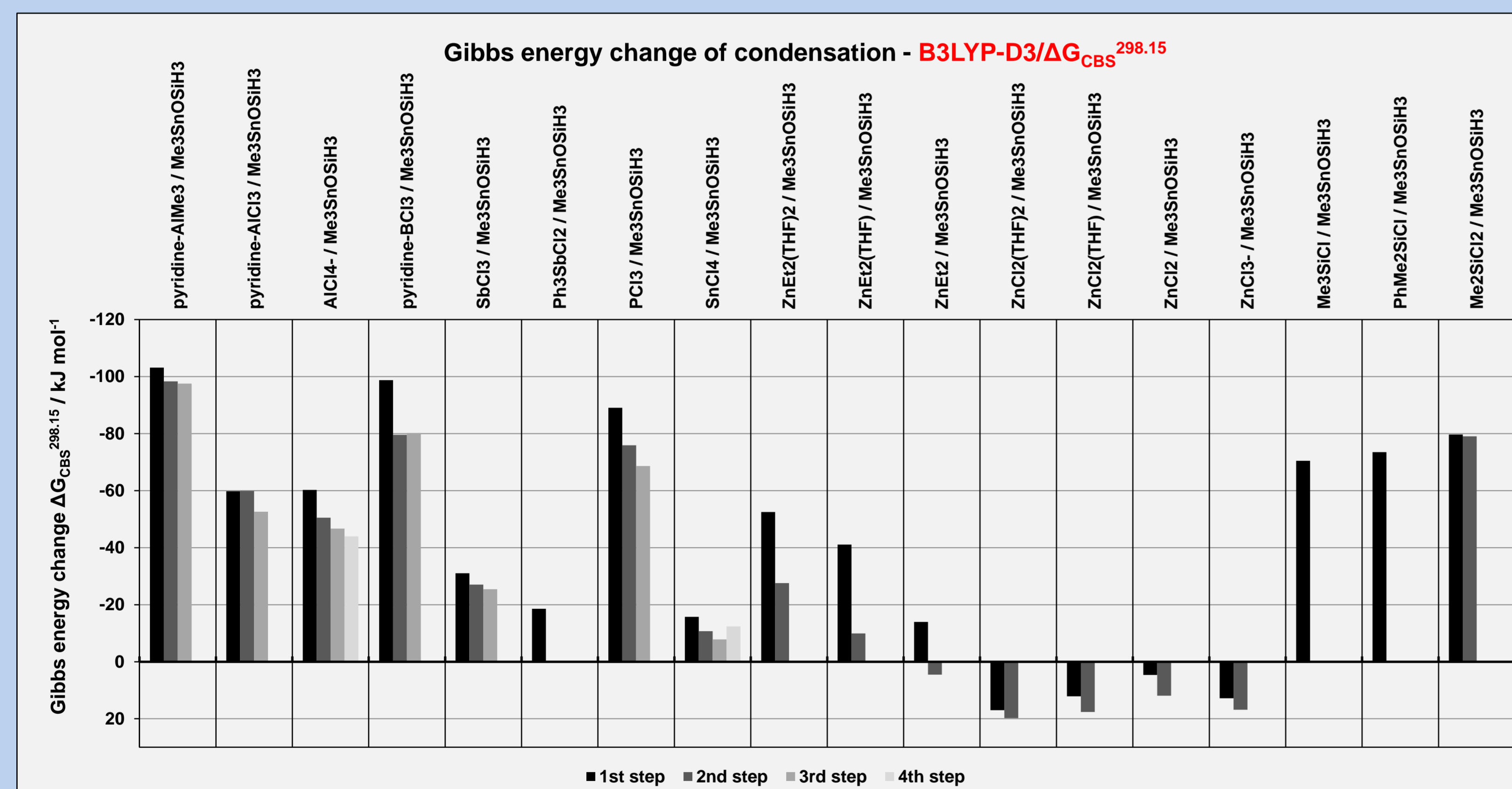

Figure 1:
Calculated ΔG for the condensation of selected site precursors with the spherosilicate building block at 298.15 K
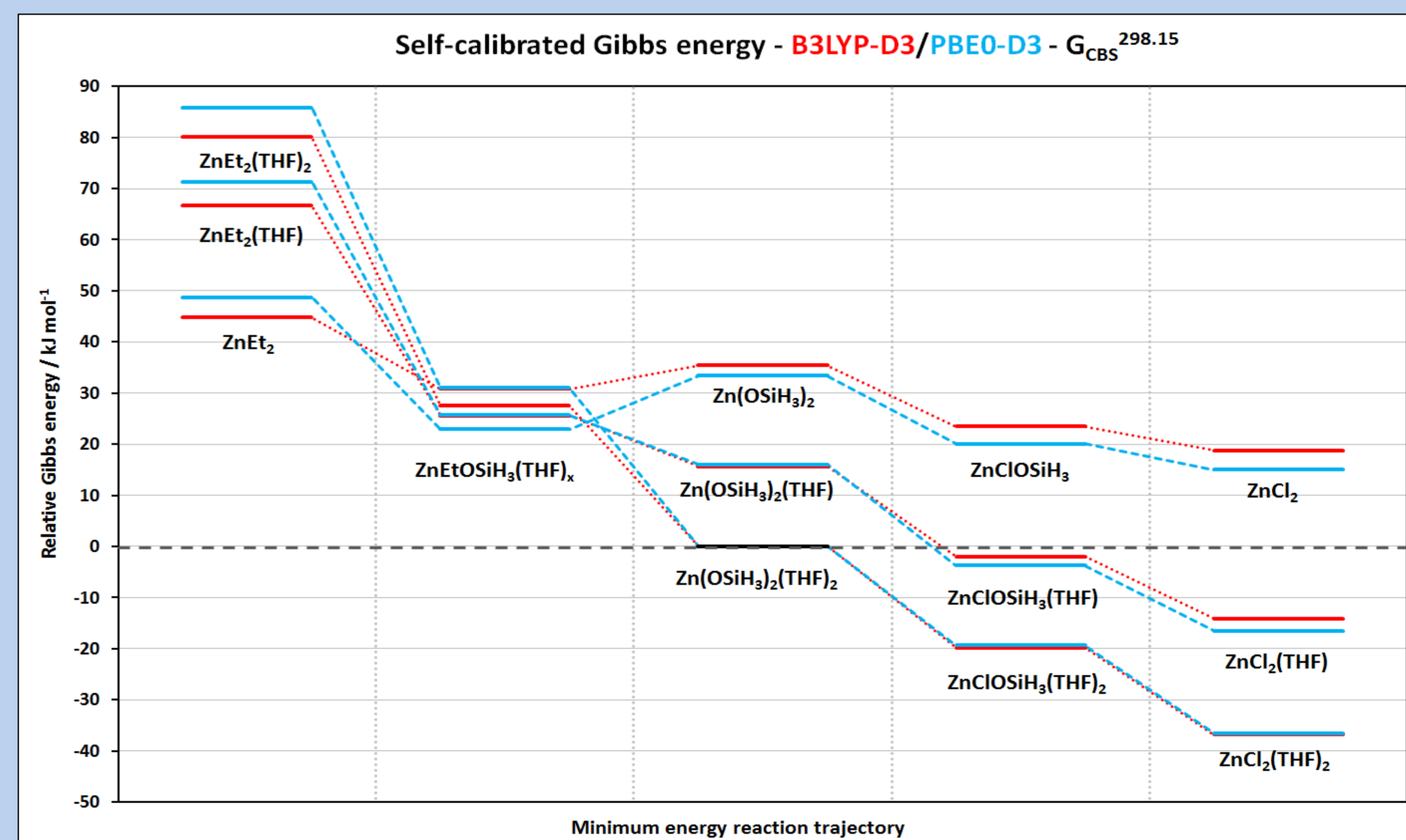*Method: B3LYP-D3/cc-pVTZ+aug-cc-pVTZ-PP(Sn,Sb)//CBS*

Figure 2:
Calculated relative ΔG for the condensation/coordination of the $ZnEt_2/ZnCl_2/THF$ system at 298.15 K
Method: B3LYP-D3/PBE0-D3/cc-pVTZ+aug-cc-pVTZ-PP(Sn)//CBS

4. Site homogeneity

In addition to the routine spectroscopic (IR, MAS NMR) characterization of products, the uniformity of the spatial distribution of sites at the nanometer scale was for the first time directly confirmed by STEM-EDS. The sample images (*Figure 3*) illustrate the typical texture exhibited by the whole family of materials, with no apparent difference among the studied precursors. Statistical methods are currently being applied in order to characterize the level of chaos/correlation from the EDS data.

Figure 3 (right):
STEM-HAADF/STEM-EDS images of a single-site matrix containing [pyridine-AlO₃] moieties.
Instrument: FEI Titan Themis 60-300
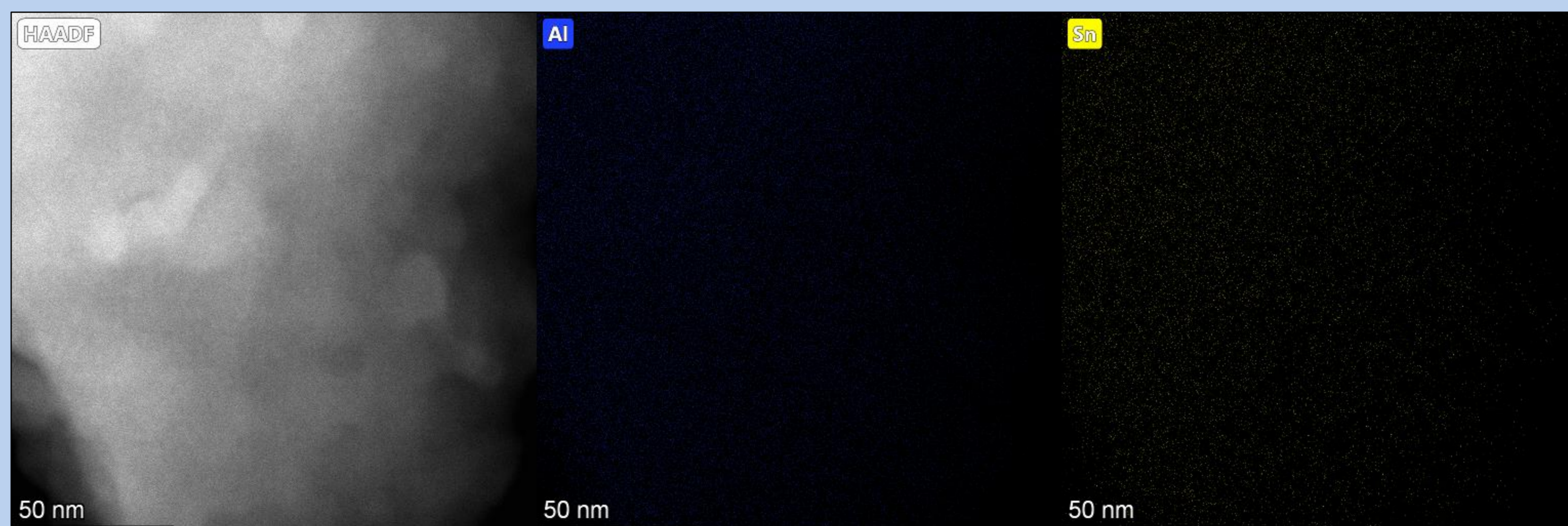
5. References

1. Ghosh, N. N.; Clark, J. C.; Eldridge, G. T.; Barnes, C. E.; *Chem. Commun.*, 2004, 856–857
2. Clark, J. C.; Barnes, C. E.; *Chem. Mater.*, 2007, 19, 3212–3218
3. Styskalik, A.; Abbott, J. G.; Orick, M. C.; Debeckere, D. P.; Barnes, C. E.; *Catalysis Today*, 2019, 334, 131–139

6. Acknowledgment