

A UNIFIED SYNTHETIC APPROACH TO POROUS HYBRID SINGLE-SITE METALLOSILICATES

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ABSTRACT:

A generalized low-temperature non-hydrolytic sol-gel strategy to produce uniformly dispersed metallosilicate sites in highly porous hybrid silicate matrices is reported (Figure 1). The materials can be used either directly as catalysts or as well-defined model systems in the research and development of heterogeneous catalysis. In the procedure, the readily available^{1,2} spherosilicate molecular building block $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ is cross-linked in two steps by irreversible condensation reactions with high-valence d- and p-block chlorides and alkyl-metals in toluene or THF to form statistically connected rigid amorphous networks. Initially, a limited amount of the metal site precursor (e.g., pyridine- AlCl_3 ,³ $\text{Et}_3\text{N-AIME}_3$, $[\text{Me}_4\text{N}^+][\text{AlCl}_4^-]$,³ ZnEt_2 , SbCl_3 , Ph_3SbCl_2 , PCl_3 , TiCl_4 ,² VOCl_3 ,^{1,4}) is introduced to an excess of the building block to achieve full condensation and uniformity. A minimum site separation of ≈ 1 nm is ensured by the bulky building block. In the second step, a limited amount of a ditopic hybrid linker – $\text{ClMe}_2\text{SiCH}_2\text{CH}_2\text{SiMe}_2\text{Cl}$ or $\text{ClMe}_2\text{Si}(\text{C}_6\text{H}_4)_2\text{SiMe}_2\text{Cl}$ – is added to produce extensively cross-linked gels while maximizing the probability of full condensation. The byproducts of the condensations (Me_3SnCl or Me_3SnR) are inert and volatile and they do not interfere with subsequent steps. Removal of all volatiles under vacuum affords pure xerogels. Since a kinetically-driven approach and mild conditions are used, a variety of complex sites can be produced, incorporating organic ligands and sensitive moieties (pyridine- $\text{Al}(\text{OSi}\equiv)_3$, $\text{Sb}(\text{OSi}\equiv)_3$, $\text{Ph}_3\text{Sb}(\text{OSi}\equiv)_2$). The prepared xerogels were characterized by IR and MAS NMR spectroscopies, N_2 gas adsorption, gravimetry, STEM/EDS, ICP-OES, and TG/DSC. The fundamental limits of the system and the interplay of parameters, such as site loading, linker flexibility, stoichiometry, and solvent effects, were explored and correlated with structure, condensation, and porosity. Observed precursor reactivity was supported by quantum chemistry DFT calculations on model compounds.

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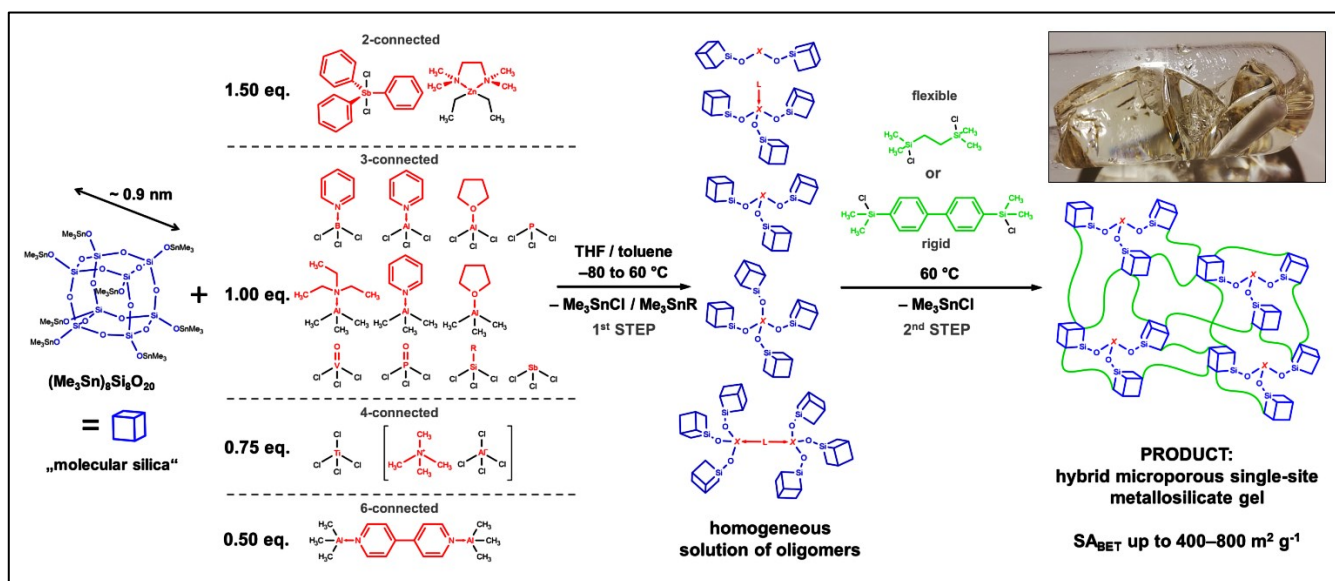


Figure 1: Generalized reaction scheme

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