

MS20-03 Interaction of water with (silico)aluminophosphate zeotypes: A comparative investigation using dispersion-corrected DFT

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Porous aluminophosphates (AIPOs) and silicoaluminophosphates (SAPOs) with zeolite-like structures have received considerable attention as potential adsorbents for heat transformation applications using water adsorption/desorption cycles.^(1,2) While experimental investigations have been reported for some materials like AIPO-18 (AEI topology) and SAPO-34 (CHA topology), more systematic insights into the relationships between structure and water adsorption properties are lacking. In this contribution, dispersion-corrected density-functional theory (DFT-D) calculations are employed to study the interaction of water with a variety of AIPOs and SAPOs, allowing for an identification of the structural features that tend to enhance the affinity towards water.

In the first part, the results of DFT-D calculations for six topologically different AIPOs and their SAPO analogues are presented. Structurally, the systems differ in the pore size and in the shape of the main pores (elongated vs. nearly spherical). For the AIPOs, the calculations predict rather similar adsorbent-water interaction energies for all systems, indicating a minuscule influence of pore size and topology on the affinity towards water. However, considerable differences are observed in the response of the framework to the adsorbed water molecules. In the SAPO materials, the structural environment of the framework proton strongly influences the interaction strength at low water loadings (one H₂O per proton), whereas the interaction energies at high water loadings (near saturation) depend primarily on the silicon content.

In the second part of the contribution, the influence of structural heterogeneities (e.g. silicon islands) and defects on the affinity of SAPO-34 towards water is assessed on the basis of DFT-D calculations. A rather pronounced effect is found at low water loadings: Here, heterogeneities in the silicon distribution tend to create particularly strong adsorption sites, whereas the interaction with water is reduced considerably in defective models. At high water loadings, however, the average interaction strength is affected only slightly when compared to the defect-free reference system which contains isolated silicon atoms.⁽³⁾

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Keywords: thermal energy storage, zeolites, density-functional theory, computational chemistry

MS20-04 TiO₂ nanocontainers and nanospheres as photocatalysts for CO₂ reduction and photoelectrochemical water splitting: Structural modification.

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CO₂ gas is one of the major factors of the climate imbalance. The reduction of CO₂ by photocatalysis is proposed to convert CO₂ gas into more valuable molecules (such as CH₄, CH₃OH etc.)¹ because solar energy, being an alternative, cheap and environmentally friendly source of energy, can be used as power supply¹. For this process, titanium dioxide-based materials with various structures are commonly used as photocatalysts^{2,3}. Furthermore, the photocatalytic water splitting using the TiO₂-based materials could be a great option for hydrogen production to obtain clean and renewable energy sources⁴.

In this project, the TiO₂ nanocontainers and nanospheres (Figure 1 (A), (B)) with different crystalline structures are investigated because the crystalline phase, the size and the shape of TiO₂ may have an influence on its band gap energy and consequently on its photocatalytic properties⁵. Moreover the embedment of silver nanoparticles into the TiO₂ material is explored. Indeed, the presence of silver islands may enhance its photoactivity⁶.

The objective of this study (Figure 1 (C)) is the correlation between the morphology of the TiO₂-based materials and their photocatalytic properties for the CO₂ reduction and the photoelectrochemical water splitting.

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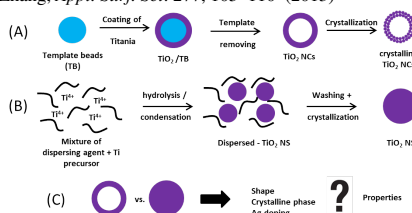


Figure 1. Synthesis of (A) TiO₂ nanocontainers, (B) TiO₂ nanospheres and (C) the study objectives

Keywords: TiO₂ nanocontainers, TiO₂ nanospheres, photoreduction of CO₂, photoelectrochemical water splitting

MS20-05 The influence of mobile monovalent ions on structures and properties of multinary thermoelectric tellurides

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Crystal structures and thermoelectric properties in the system (GeTe)_{1-x}Sb_xTe₃ (GST materials) are dominated by high concentrations of vacancies associated with diffusion-controlled phase transitions.[1] Partially replacing Ge by twice the amount of monovalent cations M⁺ reduces the number of vacancies and yields stable compounds without reconstructive phase transitions. In the case of Li, the lattice thermal conductivity is as low as that of compounds with high vacancy concentrations, indicating that Li acts as a "pseudo vacancy".[2] Such materials reach thermoelectric figures of merit ZT up to ca. 1. Varying the ratio of M⁺, Ge²⁺ and Sb³⁺ enables the adjustment of the vacancy concentration and consequently the Li mobility. Thus, LiGe_{3.5}Sb_{0.5}Te₃ or LiGe_{11.5}Sb_{5.5}Te₁₅ exhibit lower thermal conductivities (0.4 and 1.6 Wm⁻¹K⁻¹, respectively) than the vacancy-free variants Li₂Ge₂Sb₂Te₆ and Li₂Ge₁₁Sb_{5.5}Te₁₅ (1.3 and 2.5 Wm⁻¹K⁻¹).² As corroborated² by superionic Li-ion conductivity in Li₂Te, the mobility of Li may lead to PLEC (phonon liquid/electron crystal) behavior at elevated temperature.⁷ Li solid-state NMR spectra clearly indicate Li mobility. Motional narrowing of the NMR signal sets in at temperatures slightly above room temperature. Compounds with vacancies exhibit higher Li mobilities, correlation times are in the order of magnitude of 10⁻³ s at ca. 300 K and less at higher temperatures.

Using Na instead of Li is also possible whereas samples with Cu contain precipitates of copper tellurides. The interplay of doping GST and nanoscale heterostructures leads to ZT values of 1.5 and higher.

Since SnSe emerged as a promising and cheap thermoelectric material,[3] related substitution strategies in the system Sn/Sb/Se seem intriguing. SnSb₂Se₄ with a chain-like "sulfosal" structure [4] is an n-type semiconductor with a high Seebeck coefficient; however, the ZT value is limited by the low electrical conductivity, similar to that of comparable sulfosalts. Formally adding Na₂Se leads to p-type Na₂SnSb₂Se₄ which crystallizes in a NaCl-type structure and is surprisingly stable against air and moisture.

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