

## 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.<sup>(1,2)</sup> 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 H<sub>2</sub>O 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.<sup>(3)</sup>

### References:

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## MS20-04 TiO<sub>2</sub> nanocontainers and nanospheres as photocatalysts for CO<sub>2</sub> reduction and photoelectrochemical water splitting: Structural modification.

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CO<sub>2</sub> gas is one of the major factors of the climate imbalance. The reduction of CO<sub>2</sub> by photocatalysis is proposed to convert CO<sub>2</sub> gas into more valuable molecules (such as CH<sub>4</sub>, CH<sub>3</sub>OH etc.)<sup>1</sup> because solar energy, being an alternative, cheap and environmentally friendly source of energy, can be used as power supply<sup>1</sup>. For this process, titanium dioxide-based materials with various structures are commonly used as photocatalysts<sup>2,3</sup>. Furthermore, the photocatalytic water splitting using the TiO<sub>2</sub>-based materials could be a great option for hydrogen production to obtain clean and renewable energy sources<sup>4</sup>.

In this project, the TiO<sub>2</sub> nanocontainers and nanospheres (Figure 1 (A), (B)) with different crystalline structures are investigated because the crystalline phase, the size and the shape of TiO<sub>2</sub> may have an influence on its band gap energy and consequently on its photocatalytic properties<sup>5</sup>. Moreover the embedment of silver nanoparticles into the TiO<sub>2</sub> material is explored. Indeed, the presence of silver islands may enhance its photoactivity<sup>6</sup>.

The objective of this study (Figure 1 (C)) is the correlation between the morphology of the TiO<sub>2</sub>-based materials and their photocatalytic properties for the CO<sub>2</sub> reduction and the photoelectrochemical water splitting.

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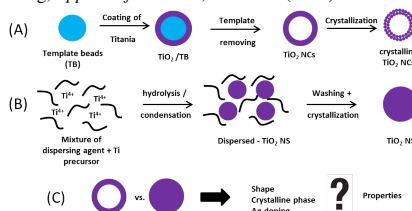
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**Figure 1.** Synthesis of (A) TiO<sub>2</sub> nanocontainers, (B) TiO<sub>2</sub> nanospheres and (C) the study objectives