Phosphonic acids as selective functionalizing agents: a study on halloysite surface modification based on model oxides

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Phosphonic acids are hetero-organic compounds bearing a C-$PO(OH)_2$ group, which are known for adsorbing covalently on oxide substrates and can be used to create self-assembled monolayers. Their selectivity towards certain oxides [1] can be exploited for the selective functionalization of inherently dual systems, such as halloysite nanotubes. Halloysite is a polymorph of kaolinite which naturally wraps itself to form nanotubes. Its numerous fields of application range from polymeric nanocomposites with superior mechanical and thermal properties, to catalysis and drug delivery [2]. Halloysite is one of the few nanotubular systems presenting an inner lumen and an outer surface characterized by different surface charge and structural composition: the inner lumen exposes aluminum hydroxyl groups, while their outermost layer is silica. This characteristic structural ambivalence holds potential for the separate modification of the two surfaces, which can thus be assigned different tasks. However, precisely defining the nature and location of molecule adsorption is a complex matter and the selective functionalization of halloysite inner and outer surfaces has been scarcely investigated in the literature [3].

In this work, the surface modification of halloysite with octylphosphonic acid (OPA) was investigated together with the functionalization of purposely prepared model oxides mimicking the inner and outer nanotube surfaces. Evidence of the preferential location of the OPA molecules in the halloysite inner lumen was gathered by both comparative studies on the model oxides as well as direct measurements on the functionalized nanotubes. Furthermore, the effect of the surface charge of the oxide on the functionalization efficiency and reversibility was investigated in detail. The isoelectric point of the oxide plays a major role in determining a stable OPA adsorption, as proved by functionalization isotherms on the model oxides measured at different pH values. An amphiphilic oxide (TiO_2) was also investigated as a reference [4]. The pH-triggered selective release of the adsorbed OPA molecules could be obtained and release conditions were determined for both the halloysite nanotubes and the model oxides.

The combination of the inner location of the functionalizing agents and the pH-dependent reversibility of their adsorption make of the phosphonic acid-functionalized halloysite nanotubes promising candidates in numerous fields.

REFERENCES

[1] S.P. Pujari, L. Scheres, A.T.M. Marcelis, H. Zuilhof, *Angew. Chem. Int. Ed.* 2014, 53, 6322.
[2] Y. Lvov, W. Wang, L. Zhang, R. Fakhrullin, *Adv. Mater.* 2016, 28, 1227.
[3] H. Zhang, T. Ren, Y. Ji, L. Han, Y. Wu, H. Song, L. Bai, X. Ba, *ACS Appl. Mater. Interfaces* 2015, *7*, 23805.
[4] G. Soliveri, R. Annunziata, S. Ardizzone, G. Cappelletti, D. Meroni, *J. Phys. Chem. C* 2012, 116, 26405.