

Designing Pickering Emulsions for Catalysis: Influence of Nanoscale Particle Properties on Microscale Droplets

Sebastian Stock¹, Annika Schlander², Dmitrij Stehl¹, Ariane Weber³, Reinhard Schomäcker³, Markus Gallei², Regine von Klitzing¹

¹*Department of Condensed Matter Physics, TU Darmstadt, Germany*

²*Ernst Berl-Institute for Technical and Macromolecular Chemistry, TU Darmstadt, Germany*

³*Institute for Chemistry, TU Berlin, Germany*

Introduction

Pickering Emulsions (PEs) were first studied in detail in the beginning of the last century and describe emulsions stabilized by particles that adsorb at the oil/water interface and prevent coalescence of the droplets.^[1] The aim of the work was to design PEs as a reaction environment for catalytic reactions. As a model reaction the hydroformylation of 1-dodecene was investigated.^{[2][3]} Due to the PEs high stability separation methods with outstanding energy efficiency are applicable e. g. the separation of the oil phase by nanofiltration. One of the main intentions is the retention of the expensive and water-soluble Rh-catalyst in the water phase. The oil phase can then be separated after the reaction or even integrated in a continuous flow.^[4]

One of the most important goals when investigating and designing PEs is the determination of their limiting factors for the reaction performance. Current research often focusses on maximizing the internal droplet surface in order to increase the catalyst substrate contact. The influence of other factors like for example the particle coverage on the droplet surface or the catalyst particle interaction is often neglected. The present data implies that these factors have a larger impact than initially assumed. Many macroscopic properties in the PEs structure result from the characteristics of the nanosized and interface active particles such as hydrophobicity, charge, size and shape. In order to distinguish the impact of particle surface charge both positively and negatively charged silica spheres were produced. This was achieved by adequate surface modification.

Transmission Electron Microscopy (TEM), ζ -potential and sessile drop measurements show that the particles have a similar size, hydrophobicity and similar values of surface potential but of opposite sign. Obviously, the negatively charged catalyst only adsorb onto the positively charged nanoparticles (Figure 1). The effect of different sign of surface potential of the nanoparticles on the PEs structure was investigated in detail and the PEs behavior in the reaction and filtration was tested.

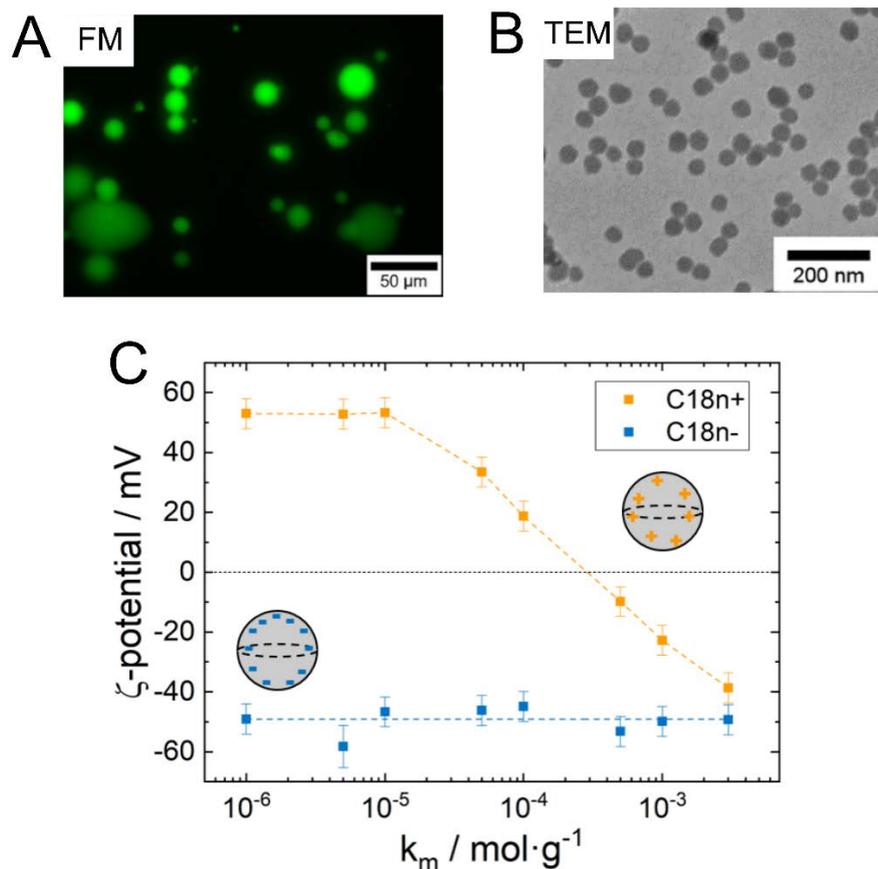


Figure 1: **A** TEM image of the modified silica nanospheres (SNS), **B** Fluorescence microscopy image of SNS stabilized PE (water phase dyed with fluorescein), **C** ζ -potential curve for oppositely charged SNS with increasing catalyst concentration shows catalyst particle interaction

References

- [1] S. U. Pickering: *CXCVI.—Emulsions*, J. Chem. Soc., Trans. 91 **1907**, p. 2001–2021
- [2] R. von Klitzing, D. Stehl et al., *Halloysites Stabilized Emulsions for Hydroformylation of Long Chain Olefins*, Adv. Mater. Interfaces 4 (1) **2017**, 1600435
- [3] D. Stehl., N. Milojević, S. Stock, Schomäcker, R. von Klitzing, *Synergistic Effects of a Rhodium Catalyst on Particle-Stabilized Pickering Emulsions for the Hydroformylation of a Long-Chain Olefin* Ind. Eng. Chem. Res. 58 (7) **2018**, p. 2524–2536
- [4] D. Stehl, L. Hohl, M. Kraume et al., *Characteristics of Stable Pickering Emulsions under Process Conditions*, Chemie Ingenieur Technik 88 (11) **2016**, p. 1806–1814