Nowadays, polyoxometalate (POM) compounds are growing importance multifunctional materials, mainly in the area of catalysis. Yet, their application as homogeneous catalysts induces drawbacks as difficult catalyst/product separation and catalyst reuse. Moreover, these species do not possess specific adsorption and shape-specificity properties.

Thanks to the heterogenization of POMs by electrostatic hybridization inside an organic matrix, this work aims at challenging these homogeneous catalyst disadvantages. The originality of the research comes from the selection of a homemade support: a polycationic self-assembled organic matrix.

The heterogeneous catalytic properties of the hybrid materials are screened via epoxidation reactions and are clearly demonstrated. The adjustable character of the matrix polarity has allowed to systematically investigate the importance of the matrix polarity in the epoxidation reaction mechanism. A hydrophobic catalyst surface is identified as required to favor alkene adsorption and to increase the catalytic activity. Also, this apolar surface enhances the polar epoxide desorption, allowing high epoxide selectivity. Further results indicate that these two effects are boosted by the use of polar solvents. Thereby, a Langmuir-Hinshelwood mechanism is put forward to justify the importance of the alkene adsorption step in the hybrid reactivity. Finally, first attempts allow to consider the presence of shape-specificity properties brought by the organic matrix, hindering bulky alkene diffusion to the active sites.

To conclude, this work highlights the new opportunities opened by the utilization of organic matrixes as support to control specifically the adsorption properties of heterogeneous catalysts.

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