

Grafting of macroporous Si(HIPE) foams with acidic groups for heterogeneous catalysis of esterification

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Introduction

Liquid phase catalytic processes are often facing many scientific and practical challenges including diffusion limitations, mass transfer and separation of catalysts. Macroporous foams Si(HIPE) [1] show high potential for solving all these difficulties. The Si(HIPE) - the abbreviation stands for *silica-high internal phase emulsion* - is an organo-silica-based hybrid monolithic foam which has hierarchical texture (macro-, meso- and micropores) and high specific surface area. Besides these useful textural properties, Si(HIPE) has suitable surface chemistry (silanol -OH) which can be easily modified with different functionalities.

This work illustrates the direct silanization of Si(HIPE) by corresponding sulphonc-/phosphonic organosilanes for catalysis in esterification reaction.

Materials and Methods

Macrocellular foams Si(HIPE) have been used as support. These foams were synthesized via sol-gel process, direct emulsions and a lyotropic mesophase as a templating agent [1]. The grafting procedure was performed via direct silanization using *Chlorosulfonylphenylethyltrimethoxy-silane* (silane A) or *Diethylphosphatoethyltriethoxy-silane* (silane B) (schematically shown on the figure 2). The obtained materials were characterized and tested in the model reaction -

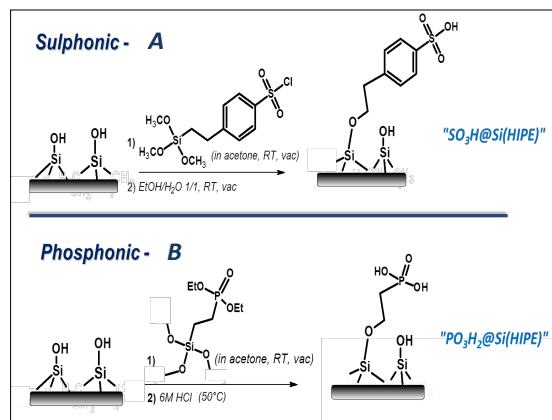


Figure 1. Schematic representation of Si(HIPE) grafting esterification of propionic acid (PA) with n-butanol (BuOH).

Results and Discussion

From the SAXS profile, the wall-to-wall distance of the mesopores is equal to 3.2 nm. However, from the N₂ adsorption/ desorption data, the materials are highly microporous.

The calculated surface area is 713 m²/g for SO₃H@Si(HIPE) and 0.27 m²/g for PO₃H₂@Si(HIPE). From the TGA analysis, the loss of organic phase is 5 and 13% for SO₃H@Si(HIPE) and PO₃H₂@Si(HIPE) correspondingly.

In the infrared spectra after the grafting of Si(HIPE) with the silane A two bands at 1354 and 691 cm⁻¹ appeared which can be referred to S=O and C-S vibrations. After the grafting with the silane B, the new bands at 1391, 1363 and 967 cm⁻¹ appeared which belongs to P=O and P-O vibrations. Additionally, the C-H vibrations were observed (~3000 cm⁻¹).

Catalytic studies showed that PO₃H₂@Si(HIPE) was slightly active (compared to the blank test, data are not shown). Low activity of the latter is referred to low accessibility of active species due to the low surface area of the material. Contrary, the first catalytic test with SO₃H@Si(HIPE) showed that the reaction goes faster in the presence of the catalyst (figure 2B). However, the leaching test showed partly homogeneous character (red curve on the figure, after the catalyst was removed). The recyclability tests (violet and green curves) showed that SO₃H@Si(HIPE) loses its activity but not completely. The obtained results may be referred to strong leaching of active phase and/or poisoning of the active species during the reaction.

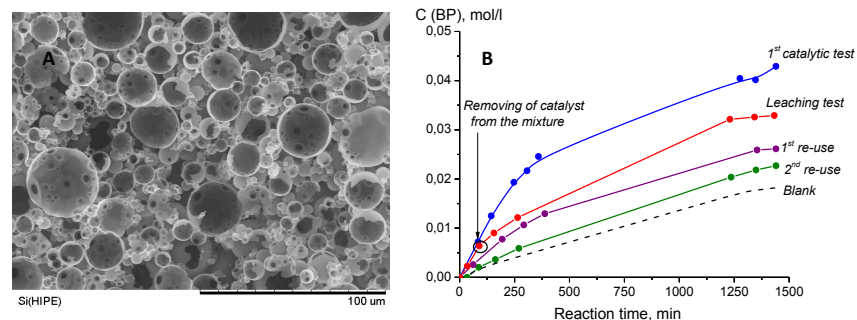


Figure 2. A- SEM image of Si(HIPE); B- Catalytic performance of SO₃H@Si(HIPE) in the esterification of PA with BuOH for the synthesis of butyl propionate (BP). Reaction conditions: PA:BuOH= 1:5 mol, 80°C, 0.1 g of catalyst. Leaching test (red curve on the figure B): after 90 min of the reaction the catalyst was removed and the test was continued. The blank test was without any catalyst (same conditions).

Significance

The applied method is the first attempt of the direct salinization by sulfonic-/phosphonic groups on the Si(HIPE). The first results suggest that by optimization of the synthesis parameters (such as amount of the silane, post-treatment) it would be possible to increase the stability and catalytic activity of the materials.

References

1. N.Brun, S.Ungureanu, H.Deleuze, R. Backov, Chem. Soc. reviews, 40(2) (2011) 771–88.