

Heterogeneous catalysis inside a microreactor containing acid-functionalized polymer brushes

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Microreactor technology represents a new and promising approach to carry out analytical and organic chemistry.¹ This is mainly due to the numerous advantages, especially in terms of increased surface-to-volume ratio as a result of the downsizing of the dimensions (order of microns). This allows a better and faster mixing between the components of a reaction. The small dimensions created within the channeling system increase the heat and mass transfer and facilitate the handling of exothermic and runaway reactions.² The large surface available within a microreactor can be exploited in catalysis, offering the possibility to increase the rate and the yield of a reaction. The use of polymer brushes anchored on the inner walls of glass microreactors offers the possibility to perform heterogeneous catalysis inside the chip (Figure 1).

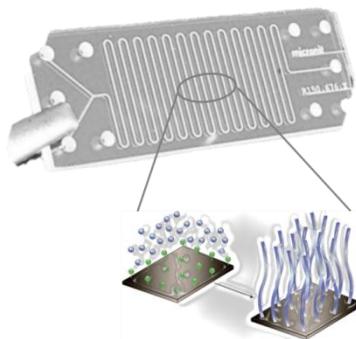
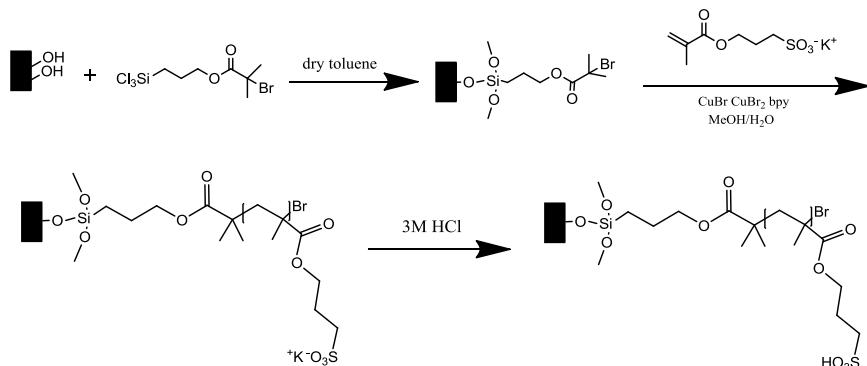


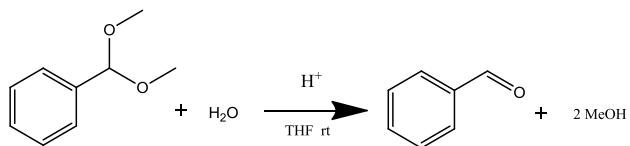
Figure 1. Glass microreactor functionalized with polymer brushes.

Polymer brushes are polymer coatings consisting of polymer chains which are tethered to a surface.³ The growth of such polymers via Surface Initiated-Atom Transfer Radical Polymerization (SI-ATRP) enables the control over the thickness and the type of monomer incorporated (homo-, copolymers). Many functionalities can be incorporated in the polymeric structure either in terms of functional monomers or after-polymerization modification. The number and the density of these functionalities can be tuned which is of use for heterogeneous catalysis.⁴ Here we present the fabrication and application of acid-functionalized polymer brushes grown at the inner walls of a glass microreactor (Scheme 1).



Scheme 1. General scheme for the growth of poly(3-sulfopropyl methacrylate) polymer brushes.

The acid-functionalized microreactor was then used for a test reaction, i.e. the acid-catalyzed hydrolysis of benzaldehyde dimethyl acetal (Scheme 2).



Scheme 2. Hydrolysis of benzaldehyde dimethyl acetal.

Preliminary results showed a good activity of the polymeric structure. The reaction reaches high conversions within 10 minutes when 0.1M solutions of both reactants in acetonitrile were flowed through the microreactor at room temperature (Figure 1). The expected thickness of the brushes is around 150 nm (as measured on a flat silicon oxide surface functionalized in the same way with poly(3-sulfopropyl methacrylate)).

Studies were carried out to prove whether the catalytic activity is due to the sulfonic acid groups at the polymer brushes. When the protons were replaced by Na^+ flowing an aqueous solution of NaCl through the microreactor, the activity disappeared. Upon reactivation with a 3M HCl solution the pristine activity was resumed (Figure 2). The same reaction carried out in a bare microreactor did not show any conversion.

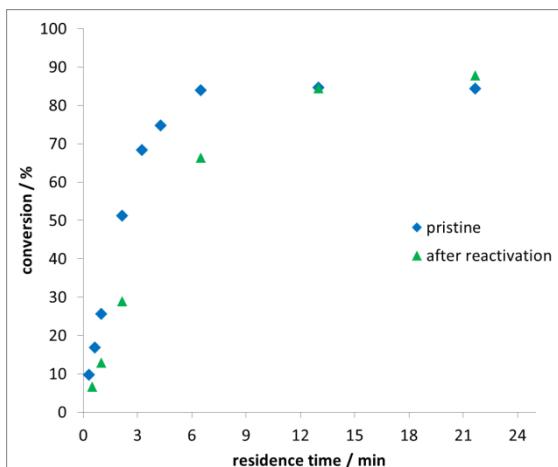


Figure 2. Conversion versus residence time for the acid-catalyzed hydrolysis of benzaldehyde dimethyl acetal.

Different types of acid-catalyzed reactions are being investigated using the sulfonic acid-functionalized microreactor.

References

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