

Application of mesoporous phenolic resins in various liquid phase reactions

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Mesoporous phenolic resins are highly versatile towards functionalization and application in catalysis. They are built from cheap raw materials and commercial templates, but the main argument for using phenolic resins compared to e.g. silica supports is their unprecedented high hydrothermal and mechanical stability and the possibility to create a strong covalent bond between the resin and the functional group or immobilizing complex [1].

Here, we present the synthesis of three different types of functionalized mesoporous phenolic catalyst systems, each applied and demonstrated in a different liquid phase reaction.

At first, the mesoporous phenolic resins were sulphonated via the aromatic ring or through silylation of the phenolic hydroxyl groups using various synthetic functionalization approaches. The solid acid catalysts were tested in the Fischer esterification of n-propanol with acetic acid, re-used and the leaching resistance in aqueous medium was evaluated.

Secondly, the $-\text{SO}_3\text{H}$ containing resins acted themselves as novel supports for the non-covalent immobilization of chiral primary amino acid-derived diamines through acid-base pair interaction and were tested in the asymmetric aldol condensation reaction of 2-butanone with 4-(trifluoromethyl)benzaldehyde [2]. The catalysts showed about 90% ee of the syn-isomer.

For the above catalyst systems, we systematically studied how the functionalization method impacts the performance of the resin for the esterification and aldol reactions.

In a third mesoporous phenolic catalyst system, a covalent immobilization of the Jacobsen catalyst was established onto the mesoporous resin. The anchoring consists of a simple and direct reflux procedure resulting in a direct axial coordination of the complex on the surface phenol groups. The catalyst is active in the asymmetric epoxidation of diline and was recovered and re-used.

[1] Muylaert, I., Verberckmoes, A., De Decker, J., Van Der Voort, P., *Adv. Colloid Interface Sci.* 175 (2012) 39-51.

[2] Demuynek, A.L.W., Peng, L., de Clippel, F., Vanderleyden, J., Jacobs, P.A., Sels, B.F., *Adv. Synth. Catal.* 353 (2011) 725-732.

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