METAL-FREE SYSTEM FOR THE CELLULOSE OXIDATION

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The most abundant natural polymer on Earth, i.e. cellulose, has been already implemented as a key source for a wide variety of products.[1] Obviously, from extraction to the end-product, cellulose suffers a long chain of processes including delignification, extraction, purification, often derivatization (functionalization). The most common processes involving chemical modification of cellulose includes oxidation reaction.[2-5] *N*-hydroxyphthalimide (NHPI) as one of the best and modern catalysts, having great performances in oxidation reaction, when through a homolytic scission of the >N-O-H bond, the active species, phthalimide-*N*-oxyl radical (PINO) is formed, has been extensively used for the selective oxidation of cellulose, Fig. 1.[6-8]

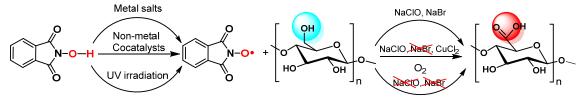


Fig. 1 Cellulose oxidation performed by N-hydroxyphthalimide under various reaction conditions

In this presentation, we propose a new, innovative protocol for the cellulose oxidation using NHPI in a metal-free system. The generation of the active radical species PINO is possible due to the presence of sodium hypochlorite and sodium bromide, as actual oxidants. The hypohalides presents into system, take over the role of metal cocatalyst, oxidizing the NHPI into PINO, which starts the catalytic cycle of oxidation.

[5] S. Coseri, Cellulose: To depolymerize... or not to?. Biotechnol. Adv., 2017, 35, 251-266.

[6] S. Coseri, A New and Efficient Heterogeneous System for the Phthalimide-N-oxyl Radical (PINO) Generation. Eur. J. Org. Chem., 2007, 1725-1729.

[6] S. Coseri, S., N-Hydroxyphthalimide (NHPI)/lead tetraacetate reactions with cyclic and acyclic alkenes. J. Phys. Org. Chem., 2009, 22, 397-402.

[7] S. Coseri, S., Phthalimide-N-oxyl (PINO) Radical, a Powerful Catalytic Agent; Its Generation and Versatility Towards Various Organic Substrates. Catal. Rev. 2009, 51, 218-292.

^[1] J. Credou, T. Berthelot, Cellulose: from biocompatible to bioactive material. J. Mater. Chem. B., 2014, 2, 4767-4788.

^[2] S. Coseri, G. Nistor, L. Fras, S. Strnad, V. Harabagiu, B. C. Simionescu, Mild and Selective Oxidation of Cellulose Fibers in the Presence of N-Hydroxyphthalimide. Biomacromolecules 2009, 10, 2294-2299.

^[3] S. Coseri, G. Biliuta, Bromide-free oxidizing system for carboxylic moiety formation in cellulose chain. Carbohyd. Polym. 2012, 90, 1415-1419.

^[4] S. Coseri, G. Biliuta, L. Fras-Zemljic, J. Stevanic Srndovic, T. Larsson, S. Strnad, T. Kreze, A. Naderi, T. Lindstrom, One-shot carboxylation of microcrystalline cellulose in the presence of nitroxyl radicals and sodium periodate. RSC Adv. 2015, 5, 85889-85897.