**[E.47]**

**Bio-generated metal-binding polysaccharide as catalyst for synthetic applications and organic pollutant transformations**

Franco Baldi*[1], Davide Marchetto[1], Stefano Paganelli[1], Oreste Piccolo[2]
*[1]Cà Foscari University, Italy, [2]SCSOP, Italy*

Bio-generated metal-binding polysaccharides may be novel potential sustainable catalysts for numerous synthetic applications and environment remediation. Depending on the nature of the metal bound to carbohydrates it is possible to perform hydrogenation, oxidation and C-C bond formation reactions. In this context we are currently investigating the properties of different metals, such as Fe(III) and Pd (II), bound to exopolysaccharides (EPS) produced by a *Klebsiella oxytoca* BAS-10 isolated from pyrite mines in the Southern Tuscany (Italy). This strain, under anaerobic conditions, during Fe(III)–citrate fermentation produces in the late stationary phase a large amount of colloidal material. EPS production was approximately 6.65 $g.l^{-1}$ and contains 36% of total iron bound to polysaccharide. EPS can be also prepared without Fe(III) using sodium citrate during the fermentation; by adding an aqueous or organic solution of some suitable metal salts, it is possible to produce Me-EPS by cation exchange. Gel or semi-crystalline products may be easily recovered and characterized. An eptameric unit with 4 $\alpha$-rhamnose, 2 $\beta$–glucuronic acids and 1 $\beta$–galactose is repeated to form long polysaccharide molecules of several million Dalton; metals should be located mostly in the proximity of the two glucuronic acids molecules.

In some experiment tests Fe(III)-EPS catalyzed the oxidation of phenol with 35% $H_2O_2$ in water or in a mixture of acetonitrile/water nearly 1/1 in the presence or absence of catalytic amount of acetic acid, to afford a mixture of catechol and hydroquinone. In the best reaction conditions, using phenol/ $H_2O_2$ in 1.6-2.6 molar ratio, a conversion of 25-18% of phenol was observed with a selectivity ranged 94-96% in dihydroxylated products (cathecol/hydroquinone molar ratio was nearly 2). The selectivity based on $H_2O_2$, i.e. mol of dihydroxylated derivatives produced × 100/mol of used hydrogen peroxide. was satisfactory and equal to 48-58%.

Pd(II)-EPS was also prepared and its application as potential catalyst in reductive dehalogenation of halo arenes in a bi-phase water/organic solvent mixture and in a Heck-type reaction between bromo-benzene and unsaturated esters in DMA is currently under investigation.

This new approach for preparation and application of catalysts seems to be promising with some economic and environment friendly advantages and the number of potential application might be broad.

Keywords: Metal, exopolysaccharide, organic compunds, transformation