

N°1069 / PC

TOPIC(s) : Homogenous, heterogenous and biocatalysis

HYBRID CATALYST BASED ON NITROXIDE SUPPORTED ON NANOMETRIC METAL OXIDES FOR SUGAR OXIDATION

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PURPOSE OF THE ABSTRACT

With the depletion of fossil resources, using renewable and abundant biomass to produce valuable chemicals and functional materials is becoming a very interesting area of research, within a context of sustainability. Carbohydrates represent the most abundant valuable raw material that can lead to many high added-value products such as detergents, pharmaceuticals, cosmetics or polymers after chemical modifications. As example, glucaric acid, a di-oxidized glucose, is one of the top 12 platform chemicals from biomass and can be a precursor of adipic acid, widely used in plastics and textile industries.¹⁻⁴ The challenge lies in the development of eco-efficient processes to ensure sustainability for the synthesis of such carbohydrate-based compounds.

Conventional oxidation conditions using chromium or manganese reagents exhibit several drawbacks such as high toxicity and/or limited selectivity, needing partial protection of carbohydrates. To overcome these issues, nitroxide radical such as TEMPO ([2,2,6,6-tetramethylpiperidin-1-yl] oxy) has been found to be the homogeneous catalyst of choice for selective oxidation of primary alcohols of sugars.⁵ A counterpart heterogeneous system has been recently studied for selective oxidation of primary alcohols. Supported-TEMPO catalyst not only allows recycling and easier separation between the product and the catalyst (filtration or centrifugation) but also a better catalytic activity compared to the homogeneous system.⁶

We recently described a new series of TEMPO-supported catalysts for selective sugar oxidation. This approach is based on the immobilization of a nitroxide derivative on nanometric metal oxides.⁷ The evaluation of the activity of the catalysts on methyl glucoside oxidation, used as model reaction, will be presented. TEMPO was linked either by carboxy or by phosphonic function to the metal oxide surface. First trends on the stability of such catalysts upon oxidation conditions will be discussed.

In all cases, higher catalytic activity was highlighted for supported-TEMPO catalysts, with up to 25 times less nitroxyl radical required for complete conversion than under homogeneous conditions.

FIGURES

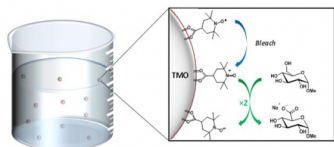


FIGURE 1

TEMPO-supported catalyst for selective sugar oxidation

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FIGURE 2

KEYWORDS

sugar oxidation | TEMPO-supported catalyst

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