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A novel clean catalytic method for waste-free modification of polysaccharides by oxidation†

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A practical, clean, single step oxidative modification of polysaccharides by H_2O_2 catalysed by water soluble iron phthalocyanine, exemplified with starch, allows quantitative preparation of a range of tailor made materials without producing any waste.

Polysaccharides are abundant, non-toxic, biodegradable natural polymers already possessing a high degree of functionalization.[1] These inexpensive renewables are widely used as raw materials. However, to fulfil demand for tailored application profiles native biopolymers often need to be modified. For example, tailor made oxidation may provide industrially viable products for different technological applications to replace those derived from fossil feedstock.

Conventional oxidation of polysaccharides involves mainly stoichiometric oxidants. These oxidations are efficient but lead to large amounts of waste (for the NaOCl method the E-factor = 1–3) and, in the case of NaOCl, to toxic chlorinated by-products. Several catalytic approaches have been proposed to improve the starch oxidation, emphasizing synthetic interest in this transformation. Thus, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was applied in combination with NaOCl/NaBr[2] or with peroxides[3] to selectively oxidize primary hydroxyl groups in polysaccharides. However, this method can be applied only to soluble polysaccharides and does not solve the problems associated with the use of NaOCl. Several iron,[4] copper[4,5] and tungsten salts[4,6] have been proposed to activate H_2O_2 but the serious drawback is the need for a significant metal ion content (0.01–0.1% on a dry starch basis)[4,5] to achieve efficient oxidation.

Therefore, the quest for an efficient and clean method of oxidation of polysaccharides remains an important challenge. The oxidation should involve a green oxidant like H_2O_2 and/or O_2 in combination with accessible and inexpensive catalyst. The objective is the optimal utilization of renewables, avoiding the production of harmful side products and contamination of final products as well as limiting purification procedures.

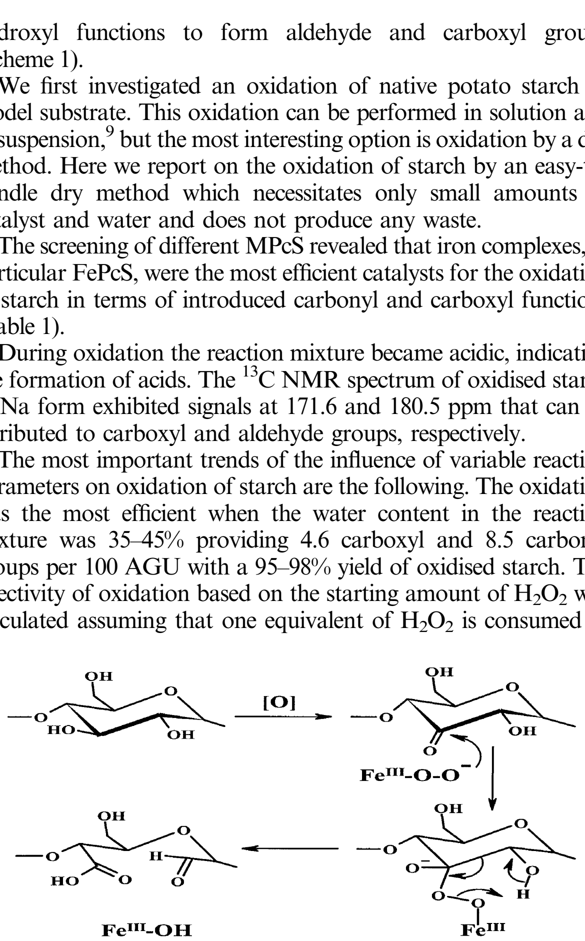
To tackle this challenging target we decided to use water-soluble tetrasulfonatophthalocyanine metal complexes (MPcS) that have been successfully applied by us[7] and others[8] for oxidative degradation of the recalcitrant chlorinated phenols. The macrocyclic structure of MPcS resembles that of porphyrin complexes widely used by Nature in the active sites of enzymes responsible for biological oxidation. In contrast to the porphyrin complexes, phthalocyanine counterparts are cheap and readily accessible on an industrial scale: their worldwide production is about 80 000 t/year, making them very attractive as potential industrial catalysts. The key step in the oxidation of chlorinated phenols was proposed to be a cleavage of the C–C bond bearing hydroxyl groups by the nucleophilic iron(III) peroxo complex $PcSFe^{III}OO^-$ to form acids *via* Grob type fragmentation.[8] We hypothesized that this active species could be competent to cleave the C_2–C_3 bond of an anhydroglucose unit of carbohydrate (AGU) having adjacent hydroxyl functions to form aldehyde and carboxyl groups (Scheme 1).

We first investigated an oxidation of native potato starch as model substrate. This oxidation can be performed in solution and in suspension,[9] but the most interesting option is oxidation by a dry method. Here we report on the oxidation of starch by an easy-to-handle dry method which necessitates only small amounts of catalyst and water and does not produce any waste.

The screening of different MPcS revealed that iron complexes, in particular FePcS, were the most efficient catalysts for the oxidation of starch in terms of introduced carbonyl and carboxyl functions (Table 1).

During oxidation the reaction mixture became acidic, indicating the formation of acids. The ^{13}C NMR spectrum of oxidised starch in Na form exhibited signals at 171.6 and 180.5 ppm that can be attributed to carboxyl and aldehyde groups, respectively.

The most important trends of the influence of variable reaction parameters on oxidation of starch are the following. The oxidation was the most efficient when the water content in the reaction mixture was 35–45% providing 4.6 carboxyl and 8.5 carbonyl groups per 100 AGU with a 95–98% yield of oxidised starch. The selectivity of oxidation based on the starting amount of H_2O_2 was calculated assuming that one equivalent of H_2O_2 is consumed to



Scheme 1

Table 1 Oxidation of starch by H_2O_2 by dry method catalysed by metal phthalocyanine complexes[a]

Catalyst	DS_{COOH}[b]	DS_{CO}[b]	Yield[c], %
FePcS	4.0	8.0	95
CoPcS	0.3	1.3	95
MnPcS	< 0.1	< 0.1	95
VOPcS	< 0.1	< 0.1	97
$FePc(COOH)_4$	2.2	4.6	95

[a] Typical procedure: aqueous solution containing 0.04 mmol of catalyst was mixed with starch (50 g, dry basis: 42 g, 260 mmol AGU) and 5 mL of 35% H_2O_2 (57 mmol) were added. Resulting solid mixture was mixed and allowed to react at 60 °C during 14 h. After complete H_2O_2 consumption determined by iodometric method colourless product was washed with 100 mL water and dried. [b] Degrees of substitution in carboxyl (DS_{COOH}) and carbonyl (DS_{CO}) expressed as the number of carboxyl and carbonyl groups per 100 AGU were determined by Smith's methods as described in ref. 4. [c] Weight of isolated oxidised starch/weight of starting material, based on dry basis.

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† Electronic supplementary information (ESI) available: experimental, FePcS structure, SEM pictures of native and oxidised starches. See http://www.rsc.org/suppdata/cc/b4/b411694a/

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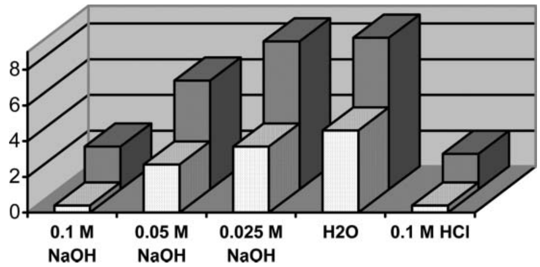

Fig. 1 Dependence of DS_{CHO} (back row) and DS_{COOH} (front row) on the base and acid additives.

form an aldehyde group and two equivalents of H_2O_2 are necessary to obtain a carboxyl function. The efficiency of utilisation of H_2O_2 to form carbonyl and carboxyl groups reached 70–80%.

Taking into account the formation of acids we checked the influence of the base by adding the catalyst to starch in aqueous solution; in 0.025, 0.05 and 0.1 M NaOH solution; and in 0.1 M HCl solution. Notably, the highest DS_{COOH} and DS_{CO} were obtained when the catalyst was added in pure water (Fig. 1).

This finding is an important advantage, allowing the oxidation of starch without using the base, acid or buffer solutions that are used in all current methods.

A small amount of catalyst was sufficient to achieve oxidation (Table 2). The best results were obtained with a molar ratio substrate (expressed in AGU)/catalyst 12900/1 (0.0078 mol% catalyst). Any further increase of catalyst charge did not improve the degree of oxidation of starch. Oxidation was still efficient with only 0.0039 mol% of catalyst (run 3). Under the conditions of runs 2 and 3 of Table 2 turnovers of more than 2000 have been attained. This finding coupled with a high product yield based on H_2O_2 demonstrates the efficiency of the catalytic system. The very small amount of FePcS used for oxidation of starch represents another important advantage of this catalytic system compared to conventional methods based on metal salts that need at least 0.2 mol% of catalyst.[4] In addition, this small charge of catalyst yielded a purer oxidised starch. To further demonstrate the benefits of FePcS we have compared the oxidation of starch in suspension in the presence of FePcS and conventional $FeSO_4$ catalyst. No detectable oxidation of starch was observed with $FeSO_4$ in the same molar amount as FePcS. To obtain a similar substitution degree with $FeSO_4$ we had to increase the amount of catalyst by a factor of 20 as compared to that used in the case of FePcS catalyst. Importantly, oxidised starches obtained with FePcS had practically the same residual Fe content as the native starch (6–20 ppm) whereas oxidised starch prepared using iron salt had a significant content of iron left (190–480 ppm).

The scanning electron microscopy (SEM) images indicate that the starch oxidized by the dry method retains its granular structure with the same distribution of particle size, 5–50 μm (ESI). The granule surface of native starch is smooth, practically with no defects (Fig. 2A). As oxidation of starch progresses the surface defects appear, developing with increased degree of substitution (Fig. 2B,C). Highly oxidised materials along with surface defects contain holes, indicating that the oxidation takes place in the interior of the granule as well as at the surface.

Table 2 Influence of catalyst amount on dry oxidation of starch at 60 °C

AGU/FePcS mmol/mmol	DS_{COOH}	DS_{CO}	Yield, %	Selectivity[a] on H_2O_2, %	Turnover[b]
6500 : 1	4.0	8.0	91	73	1040
12900 : 1	3.7	8.0	90	70	2002
25800 : 1	1.5	5.6	93	39	2236

[a] H_2O_2 consumed for product formation/starting amount of H_2O_2. [b] mmol of CO + mmol of COOH × 2/mmol of catalyst.

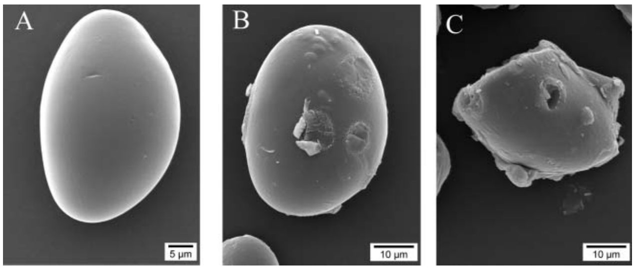

Fig. 2 SEM pictures of individual granules of native potato starch (A); oxidised starch with $DS_{CO} = 2.84$, $DS_{COOH} = 0.27$ (B); and oxidised starch with $DS_{CO} = 8.50$, $DS_{COOH} = 4.60$ (C).

The scope of the method has been extended to the oxidation of starches from different sources having different properties (amylose/amylopectin ratio, granule size, temperature of gelatinization). All these starches have been successfully modified (ESI). Preliminary experiments showed that other polysaccharides can also be oxidised by this catalytic system.

In conclusion, this practical oxidation of polysaccharides corresponds to criteria of green chemistry and sustainable development. Indeed, only small amounts of water, clean H_2O_2 oxidant and cheap iron phthalocyanine are needed for single step modification of renewables. The product can be recovered without additional treatment with almost quantitative yields. No waste is formed because no acids, bases or buffers are used. This green chemistry approach offers an evident advantage over traditional oxidation methods involving NaOCl, $NaIO_4$ as terminal oxidants. Due to the flexibility of this procedure hydrophilic tailor made materials can be obtained just by changing the reaction conditions to provide the products with *desired content of carboxyl and carbonyl groups*. The presence of carboxyl functions provides a better solubility in water that is very important for numerous technological applications. In turn, the presence of active carbonyl groups allows us to obtain modified materials having special properties. We believe that this catalytic method, which is easy to handle, might have a real future in sustainable development using starting renewable materials, clean oxidant and accessible catalyst.

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