

Schiff Base Functionalized Cellulose: Towards Strong Support-Cobalt Nanoparticles Interactions for high catalytic performances

* Correspondence: h.kaddami@uca.ma (H.K); nicolas.merle@univ-lille.fr (N.M)

Supporting Information

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1. Control of byproduct during periodate oxidation of cellulose

Periodate oxidation of cellulose can also lead to depolymerization of polysaccharides, which depends on the concentration of NaIO_4 , temperature, time, and pH. The literature describes the formation of several by-products during the oxidation of cellulose [1,2]. **Error! Reference source not found.** shows the structures of the by-products present in the mixture during the reaction.

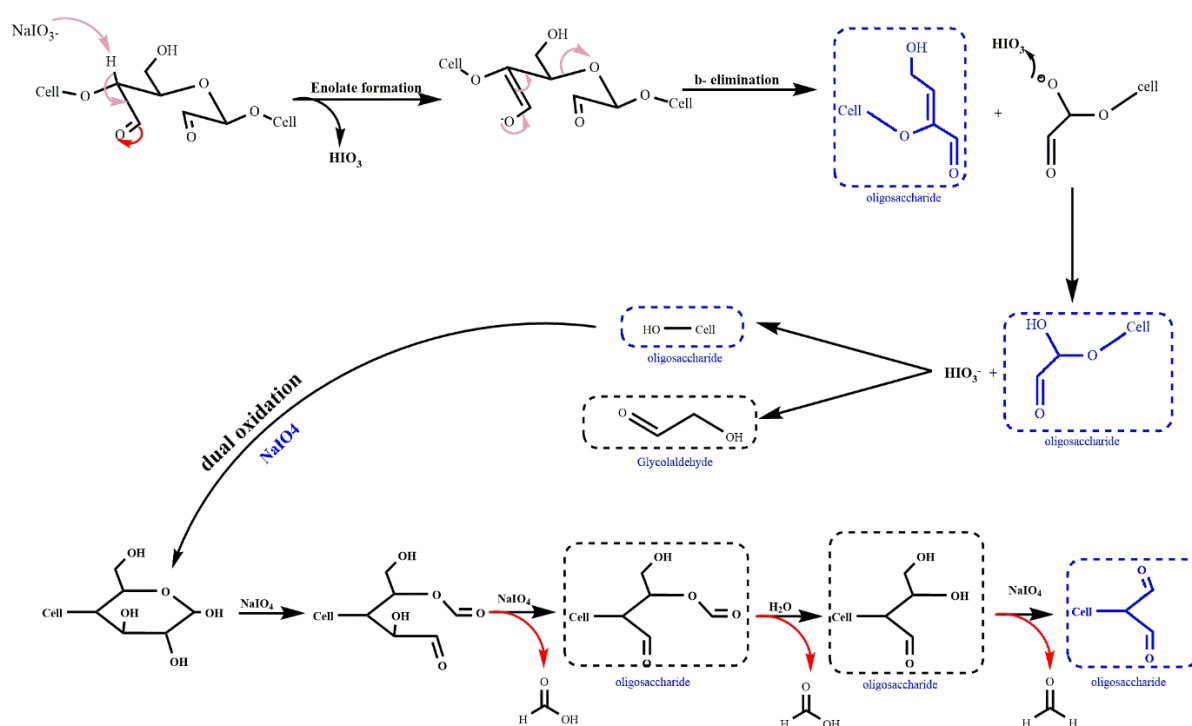
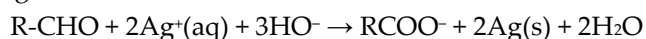


Figure S1. Structures of depolymerization products (oligosaccharides) possible during the periodate oxidation of cellulose.

To ensure that undesirable by-products were significantly removed from the reaction mixture, a control by Tollens' reagent was performed (3). This reagent was used to check for the presence of soluble aldehyde functions in the supernatants during centrifugal washing. For this purpose, 5 drops of Tollens' reagent were added to 2 ml of supernatant liquid from each wash in a test tube and then the tube is placed in a water bath. During the reaction; the silver ion oxidizes the aldehyde to give a carboxylate ion according to the following redox reaction:



In this process, R-CHO can react with Tollen's reagent to form a silver mirror (**Error! Reference source not found.**). The positive result indicates the presence of aldehyde (4).

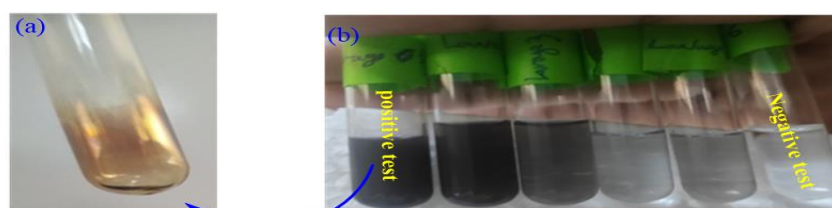


Figure S2. (a)- silver mirror on the test tube of the positive tollens test (b)- tests of the tollens of each wash.

2. Reaction scheme of the Co@DAC-OAP catalyst preparation

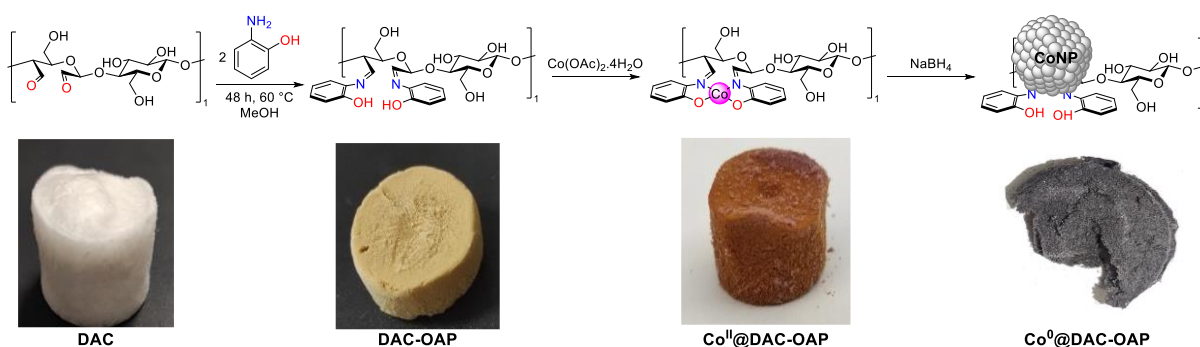


Figure S3. reaction scheme of the Co@DAC-OAP catalyst preparation. .

3. UV-Vis monitoring of the DAC-OAP washing after the reaction

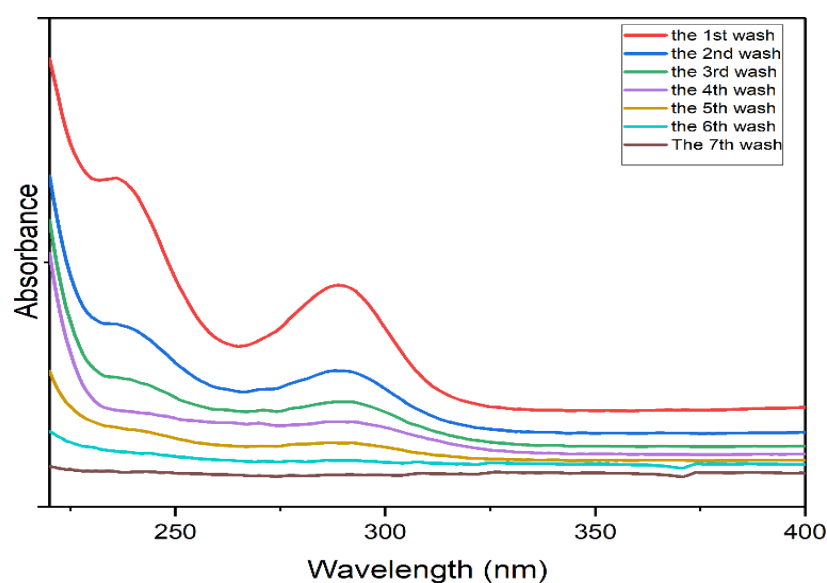


Figure S4. The UV-vis spectra obtained from the sequential washes of the DAC-OAP after the reaction occurred in the supernatant.

4. FTIR ANALYSIS: Cobalt supported on unmodified DAC (Co@DAC)

The stability and cycling performance of the catalyst prepared by using the aldehydes group of dialdehyde cellulose to immobilize cobalt nanoparticles (Co@DAC) can be studied under the same conditions for reducing nitrophenol to aminophenol. It can be observed from the Fig. 4 that the Co@salen (Co@DAC-OAP) has no significant decrease in performance after eight cycles of use. In comparison, after being recycled once, the catalytic performance of Co@DAC drops dramatically from 90% to 78 % over an 8 min reaction period (**Error! Reference source not found.**), which may attribute to the leaching of metal from DAC surface and the fact that the aldehyde can be converted to the corresponding primary alcohol during the reduction process of the cobalt ions under standard conditions (**Error! Reference source not found.**).

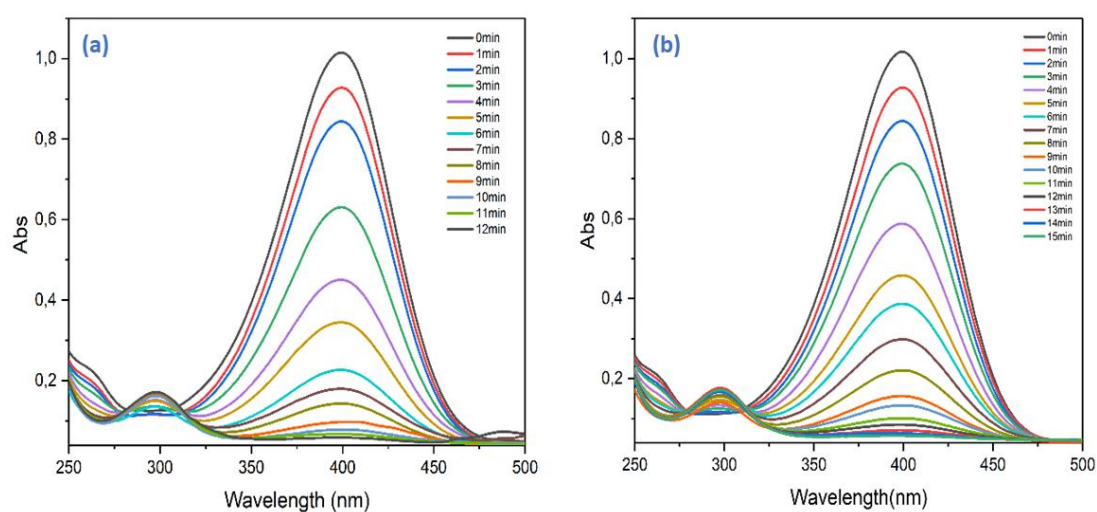


Figure S5. UV-Vis spectra for the reduction of 4-NP with NaBH₄ using Co@DAC: (a) 1st use of catalyst, (b) 2nd use of catalyst.

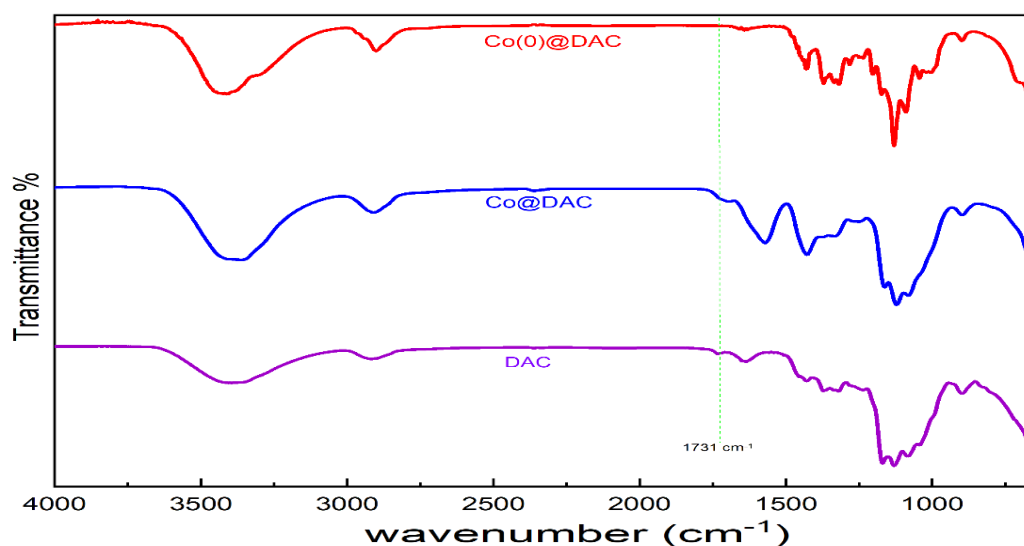


Figure S6. IR Spectrum of dialdehyde cellulose, its cobalt complexation and reduction.

5. FTIR ANALYSIS: Cobalt supported on modified DAC (Co@DAC-OAP)

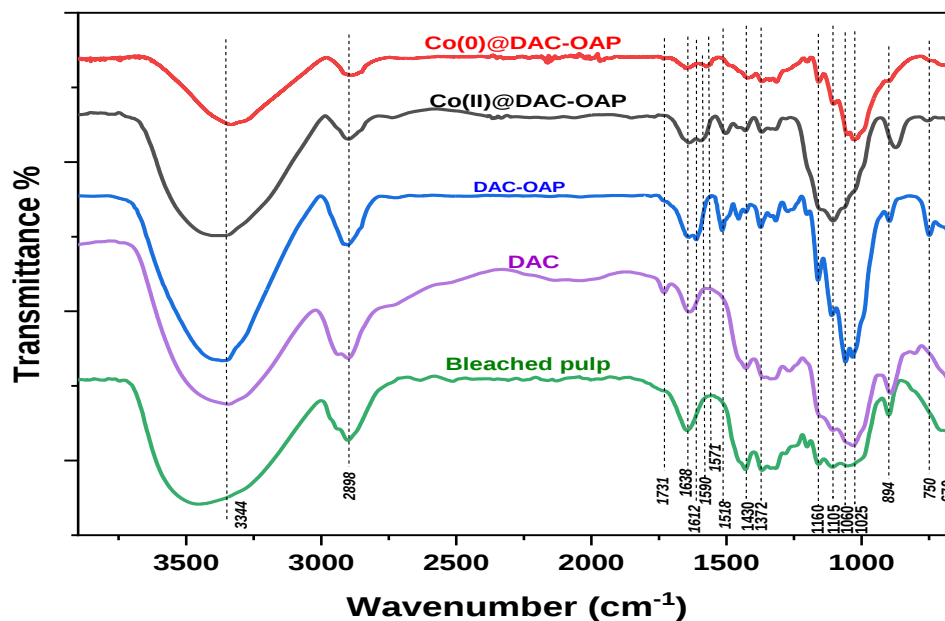


Figure S7. IR spectrums of cellulose and its derivative during the oxidation, modification, complexation.

Table S1. FTIR band assignments of cellulose and its derivative during the oxidation, modification, complexation.

Wavenumber (cm ⁻¹)	Band assignment*
3340	O-H stretching vibration
2898	stretching vibration of C-H
1731	C=O aldehyde
1638	absorbed water (hydrogen-bonded)
1612	C=N stretch
1590	C=N after complexation with cobalt
1571	bending vibrations of the-NH- after reduction of C=N
1518	C=C stretches in the aromatic ring
1430	deformation or asymmetric C-O stretch of C-O stretching
1372	deformation vibrations of C-H
1160	C-O-C at glycosidic linkage
1106	ring in plane stretching
1060	C-O of secondary alcohols
894	COC at glycosidic linkage; amorphous region
750	C-H Aromatic bending
670	C-OH out-of-plane bending mode

*(5) (6) (7)(8).

6. Performance comparisons of our catalyst with catalysts reported in the literature

Table S2. Comparison of the reducing ability of Co@DAC-OAP in reduction of nitrophenol with other reported Co systems.

Catalyst systems	Concentration (M)		% molar or Catalyst amount	Co NPs size (nm)	K (min ⁻¹)	cycle number	Reference
	4-NP (M)	NaBH ₄					
TBAB stabilized Co NPs	2×10 ⁻⁵	2 × 10 ⁻⁵	3mg	90–95	0.21 (29°C)	5	(9)
Co@N-Doped carbon	0,2×10 ⁻³	0,0263	23.8%	8	0,96	--	(10)
LDO-supported cobalt	0,2×10 ⁻³	16×10 ⁻³	15%	6.8–11.1	1	8	(11)
Co/RGO	0.096 ×10 ⁻³	0,1	1.2 g/L	8	0.03	6	(12)
Co _{0.85} Se	0. 5 ×10 ⁻³	0.02	0.1g/l	-	0.331	5	(13)
Co-CC	0.16 ×10 ⁻³	0.2	0.27 g/l	15–30	0,42	5	(14)
p(AMPS)–Co	1.44 × 10 ⁻²	2.88 × 10 ⁻¹	15%	100	0.1184 (30 °C)	5	(15)
Co@SiO ₂	0.6×10 ⁻³	0,3×10 ⁻³	13,2%	20	0,8	4	(16)
Cobalt Microflowlers	6.15×10 ⁻⁵	1.96×10 ⁻¹	40%	3–15	0,243	3	(17)
Unsupported Co	3.5×10 ⁻³	35×10 ⁻³	5%	-	0.13	-	This work
Co@BP	3.5×10 ⁻³	35×10 ⁻³	5%	-	0,21	3	This work
Co@DAC	3.5×10 ⁻³	35×10 ⁻³	5%	-	0,22	3	This work
Co@DAC-OAP	3.6×10 ⁻³	36×10 ⁻³	5%	2–7	0.522	8	This work

Table S3. Catalytic performance of various Co catalysts in the selective hydrogenation of CAL to COL.

Catalysts	Co content (%)	T(°C)	P (MPa)	t (h)	Conv. (%)	Sel. (%)	Reference
Co/ZSM-5	16.7	100	2.0	6	99.10	34.90	(18)
Co/TiO ₂	15	120	1.0	1	27.10	58.00	(19)
Co@CN-900	38.7	80	n-hexanol as a proton donor	48	> 99	99.00	(20)
CoRe/TiO ₂	1.98	160	Formic acid as a proton donor	12	96	82.00	(21)
Co/SiO ₂	15	120	1.0	1	20.00	38.00	(19)
Co/Al ₂ O ₃	15	120	1.0	1	10.00	17.00	(19)
CoxSi@C-N	31.9	90	1	4	82.5	75.1	(22)
Co/p-BN-500	7.98	120	0.4	4	51.98	73.1	(23)
Co/p-BN-500	7.98	140	0.4	2	77.40	67.80	(23)
Co@DAC-OAP	5,7	120	0.5	7	98.2	86.3	This work

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