Supporting information

Nanostarch functionalized ionic liquid containing imidazolium cation and cobalt chelate anion for the synthesis of carbamates from amines and dimethyl carbonate.

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$^1$H and $^{13}$C NMR spectra of 7a

$^1$H and $^{13}$C NMR spectra of 7c

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$^1$H and $^{13}$C NMR spectra of 7i

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$^1$H and $^{13}$C NMR spectra of 7k
Materials and Technique used

All amines and dimethyl carbonate were purchased from Across Organics and used as received. N-methyl imidazole, 3-chloropropyl trimethoxy silane and other reagents were purchased and used as obtained.

Vibrational spectra of the nanostarch and its supported catalyst were recorded using a Thermo Scientific Nicolet 8700 Research FT-IR spectrophotometer with a 4 cm\(^{-1}\) resolution using their KBr pellets. Thermal decomposition of nanostarch before and after functionalization were determined by using a Diamond TG-DTA analyzer (Perkin-Elmer). The morphology and structural features of the nanocrystalline starch and its functionalized catalyst 5 were characterized by field emission scanning electron microscopy (FESEM, FEI Quanta 200F). Loading of cobalt in the nanostarch-functionalized catalyst 5 was determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES, PS-3000 UV, Leeman Labs). 10 mg of each sample was dissolved in 1 mL of concentrated HNO\(_3\), heated and diluted to 10 mL. The resulting solutions were filtered and subjected to analysis for Co content by ICP-AES analysis. The \(^1\)H and \(^{13}\)C NMR spectra were recorded on a Bruker Avance 500 Spectrometer in CDCl\(_3\) with CHCl\(_3\) (7.27 ppm for \(^1\)H, 77 ppm for \(^{13}\)C) as a standard and the chemical shifts are expressed in \(\delta\) parts per million relative to tetramethylsilane (TMS) as the internal standard.

Synthesis of nanocrystalline starch 1: Starch nanocrystals from native corn starch granules were synthesized by following the literature procedure\(^1\). A suspension of native corn starch (1 g) in distilled water (20 mL) was heated at 90 °C for 1 h with continuous stirring which subsequently followed by the dropwise addition of ethanol (20 mL) under continuous stirring at room temperature for one h. The suspension was washed by successive centrifugations with ethanol to
remove the water. The resulting starch nanocrystalline material was dried at 50 °C and analyzed by SEM. The particle size of the corn starch nano crystals was under the range of 50 to 100 nm.

**Synthesis of 1-(3-trimethoxysilylpropyl)-3-methylimidazolium Chloride 2:** A mixture of N-methylimidazole (20 ml, 25 mmol) and (3-chloropropyl) trimethoxysilane (6 g, 25 mmol) was taken in a round bottom flask at 110 °C for 36 h without stirring. After cooling to room temperature, the resulting liquid was washed thoroughly with diethyl ether (10 x 3) to remove unreacted materials. The resulting liquid was dried under reduced pressure at room temperature, followed by heating under high vacuum, to yield a colorless ionic liquid 2. The finally obtained material was a viscous liquid with a little yellow color and was stored at room temperature. Yield 97 %. IR (KBr): 1636, 1571, 1192, 1078, 1052 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ: 0.15 (2H, t, -CH₂-Si), 1.82 (2H, m, CH₂), 3.37 (9H, s, (-OCH₃)), 3.86 (3H, s, NCH₃), 4.02 (2H, t, -N-CH₂), 7.30 (1H, d, pr-H), 7.43 (1H, d, pr-H), 9.02 (1H, pr-H). ¹³C NMR (CDCl₃): 11.9, 36.6, 125.3, 127.4, 139.3.; Anal. Calcd. for C₁₀H₂₁N₂O₃SiCl: C, 42.77; H, 7.54; N, 9.98. Found: C, 42.53; H, 7.96; N, 10.21.
Supporting Fig. 1: $^1$H NMR spectra of 2 in DMSO-D$_6$

Supporting Fig. 2: $^{13}$C NMR spectra of 2 in DMSO-D$_6$

*Synthesis of starch functionalized imidazolium chloride ionic liquid 3*: Starch nanocrystals 1 (1 g) and 3-propyltrimethoxysilyl imidazolium chloride 2 (0.28 g, 1 mmol) were added in acetonitrile and stirred at room temperature for 48 h under nitrogen atmosphere. The obtained solid was separated by filtration and washed thoroughly with ethanol, dried under vacuum for 12 h. The loading of imidazolium to the functionalized nanostarch support 3 was determined by
nitrogen content (1.43 % N; calc. 2.24 %) as analyzed by elemental analysis. The loading of imidazolium was found to be 0.51 mmol/g.

Supporting figure 3: TGA of functionalized nanostarch 3

*Synthesis of starch functionalized cobalt based ionic liquid 5:* CoCl$_2$ (1/3 eqv.) was added to [NH$_4$][F$_6$-acac] (1 eqv.) solution in acetonitrile and the mixture was vigorously stirred at room temperature for 12 h. After that halide ionic liquid 3 (1/3 eq) was added to the solution. Then, after stirring for 12h at room temperature, the starch functionalized ionic liquid 5 was filtered and washed thoroughly Et$_2$O. The obtained ILs was dried in high vacuum for 24 h and the cobalt content of 5 was found to be 3.2 % as determined by Atomic Absorption Spectroscopy (AAS).

*General experimental procedure for the reaction between amine and DMC:* In order to avoid the reaction between amines and carbon dioxide in air, all reactions were conducted in a stainless autoclave equipped with magnetic stirring. In each reaction, the amine (2 mmol), DMC (10 mmol) and catalyst 5 (5 mol%) were introduced successively without any additional organic solvents. The reaction proceeded at 60 °C for the time as mentioned in Table 1. After reaction, the autoclave was cooled to room temperature and catalyst was isolated by filtration. The excess DMC and methanol were recovered by distillation. After that 10 ml water was added into the
resulted reaction mixture. The desired resulted product was precipitated out and obtained after filtration, washing, and dryness. The recovered ionic liquid was resued for recycling experiments.
$^1$H & $^{13}$C NMR spectra of products

Table 1, entry 1 7a
Table 1, entry 3, 7c
Table 1, entry 4, 7d
Table 1, entry 5, 7e
Table 1, entry 8, 7h
Table 1, entry 9, 7i
Table 1, entry 10, 7j
Table 1, entry 11, 7k
References
