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Hydrothermal synthesis of imidazole functionalized carbon spheres and their application in catalysis

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ABSTRACT

We describe the production and catalytic application of highly functionalized mesoporous carbonaceous materials, obtained *via* a one step green and cheap process relying on the hydrothermal carbonization of carbohydrates (*e.g.* glucose) in the presence of functional organic monomers (*e.g.* vinyl imidazole). The resulting materials could be further functionalized to feature imidazolium bromides on their surface and be used for various transesterification, Knoevenagel and Aldol reactions.

1. Introduction

Functional porous carbon materials touch many aspects of our daily lives being used as sorbents [1], filters [2], electrodes [3], catalysts [4] or sensors [5]. Carbon materials are particularly attractive due to their remarkable properties such as light-weight, high thermal resistance, and tuneable porosity as well as exciting electronic properties. Among their many important applications, catalysis has major importance. They are commonly used as a supportive material due to their stability at high temperature and chemical inertness against solvents, reactants or by-products.

The synthesis of nanostructured carbon materials generally relies on very harsh conditions which are by far beyond the sustainability values. In stark contrast to these high cost and energy consuming technologies, hydrothermal carbonization (HTC) was described as a sustainable one-step methodology for the synthesis of monodisperse hard carbonaceous particles [6–8]. This route involves the hydrothermal decomposition of various aqueous carbohydrates solutions (herein glucose) in closed autoclaves into carbonaceous material under mild hydrothermal synthesis conditions (<200 °C, <20 h).

This approach has the advantage of being very cheap and mild following some important rules of green chemistry since it does not involve organic solvents, catalysts or surfactants. The resulting carbon is spherically shaped and its surface is decorated with oxygenated functional groups. A simplified reaction mechanism for the formation of the carbon spheres involves the dehydration of the carbohydrate into a furan-like molecule (mainly 5-(hydroxymethyl)-2-furaldehyde) as the first step and subsequent polymerization and carbonization as a second step [7].

Moreover HTC is also a nice way to produce functionalized carbons. Indeed, different water soluble vinylic monomers can be added to the HTC mixture thus yielding materials that combine the surface properties of the polymers with the structural, mechanical, thermal, and electric properties of the carbon framework. Recently, we reported HTC in the presence of acrylic acid as a functional monomer leading to materials rich in carboxylate groups which are successfully employed as adsorbents for Pb^{2+} and Cd^{2+} removal from water [9].

Here, we report on a straightforward methodology for the production of carbonaceous materials containing imidazole groups residing at their surface. This procedure is based on the hydrothermal carbonization of glucose in the presence of small amounts of functional organic monomer (vinyl imidazole), inside a porous network of a silica template, followed by subsequent removal of the sacrificial template [10]. The resulting grafted imidazole moieties were, in a second step, converted into the corresponding alkyl imidazoliums and successfully employed as catalysts for various reactions including transesterification, Diels–Alder or Knoevenagel condensations.

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2. Experimental

2.1. Incorporation of water soluble monomers

In this strategy, the main precursor is a cheap water soluble carbohydrate (glucose), while the organic monomer (vinyl imidazole) is required in very small amounts in order to provide the functionality. 1, 2, 5 and 10 wt.% of vinyl imidazole with respect to the total glucose concentration (10 wt.%) have been employed. In order to obtain porous functional carbonaceous materials, a mesoporous silica template (Si-100, supplied by Merck) was used as a sacrificial template. Thus, according to the pore volume (1 mL/g), 1 g of silica was filled with 1 mL of the glucose containing imidazole solution, and the filled particles were hydrothermally treated at 190 °C for 16 h. After the hydrothermal carbonization the silica template was removed using a 4 M aq. solution of NH_4HF_2. The resulting samples were named according to the monomer concentration added into the reaction mixture, 1%, 2%, 5% and 10 wt.% vinyl imidazole; HC-1Im, HC-2Im, HC-5Im and HC-10Im, respectively. The carbon material obtained from 10% pure glucose solution without any monomer was quoted HC.

2.2. Formation of the imidazoliums

In order to test the availability of these grafted functions for other applications, we decided to test the catalytic activity of the solids we obtained (as other functional hydrothermal carbons have already proved to be good catalysts [11]). Unfortunately, imidazoles themselves are neither strongly basic nor strongly nucleophilic and thus have found only limited catalytic applications [12]. On the opposite, imidazoliums (especially imidazolium based ionic liquids) have found numerous catalytic applications, on their own [13–16] or as stable carbenes [17–19]. We thus alkylated HC-10Im by refluxing it over night in toluene in the presence of one mass equivalent of butyl bromide. The resulting powder was collected by filtration, washed twice with toluene and will be labelled HC-$10Bu_2$ImBr.

2.3. Catalytic tests

The substrates for the catalysis as well as the solvents were used as purchased. All catalytic reactions were run in SCHOTT screw capped glass tubes (160 mm length, about 10 mm inside diameter) with stirring or in PAAR autoclaves without stirring. The solutions were heated at the expected reaction temperature for 12–72 h. GC–MS analyses were run on a Agilent Technologies, GC 6890N, MS 5975 instrument.

2.3.1. Diels–Alder reaction

In order to test the usefulness of HC10ImBr in Diels–Alder reaction, 25 mg of catalyst were weighted and added to a solution of 2 mmol of substrates together with 2 mL of acetonitrile. The solutions were then stirred and were heated at 90 °C for 48 h and then analysed by GC–MS.

2.3.2. Knoevenagel condensations

In order to test the versatility of our material as a catalyst for Knoevenagel condensations, 2 mmol of aldehyde or ketone and 2 mmol of nucleophile were mixed in 5 mL of acetonitrile in the presence of 25 mg of HC10ImBr. The reaction tubes were then heated to reaction temperature for 12–20 h. The reaction products were analysed by GC–MS. The conversion rates were determined on the basis of the nucleophile consumption.

Table 1
Elemental analysis of the imidazole functionalized carbon.

Sample	C %	H %	N %	O %
HC	66.70	4.51	–	29.79
HC-1Im	68.22	4.81	2.41	24.56
HC-2Im	68.84	5.26	3.41	22.49
HC-5Im	69.70	5.83	5.81	18.66
HC-10Im	69.58	6.24	8.22	15.96

2.3.3. Transesterification

For this catalytic test, 25 mg of HC10ImBr and 2 mmol of substrate were added to 5 mL of benzyl alcohol in a 50 mL Teflon lined PAAR autoclave. The autoclave was heated in an oven at 150 °C for 72 h. The reaction products were analysed by GC–MS. The conversion rates were determined on the basis of the initial ester consumption.

3. Results and discussion

3.1. Incorporation of water soluble monomers into hydrothermal carbon

The successful incorporation of imidazole groups into the resulting materials was firstly confirmed by elemental analysis in which the nitrogen contents increase with increasing the amount of added monomer; that is 2.41% for HC-1Im and reached up to 8.22% in HC-10Im (Table 1). Furthermore, a clear difference between the spectrum of the HC from pure glucose and the imidazole containing samples are depicted according to FT-IR spectrum (Fig. 1). Thus, besides the adsorption bands characteristic to hydrothermal carbon (C–OH, C=O, C=C, C–O–C, etc.), two new peaks are distinguished at 1458 cm^{-1} and 3100 cm^{-1} which are attributed to C=N and N–H vibrations, respectively. It can be noticed that the intensity of the C=N and N–H bands becomes more pronounced the more monomer is added into the system. Also the peak of C–N is present in the imidazole containing materials around 1000–1300 cm^{-1}.

Zeta potential measurements also confirm the presence of the imidazole ring anchored to our carbon materials (Fig. 2). Thus, the HC has a negative zeta potential over all the pH range while the imidazole containing materials show positive values at an acidic pH due to the protonation of the nitrogen atom linked to the carbon. The isoelectric point (IEP) increases from pH 2 in HC-1Im up to 6 in HC-10Im clearly demonstrating the basic character of the materials.

Fig. 3 shows SEM and TEM micrographs of the HC-10Im functional materials. The morphology and the particle size of the

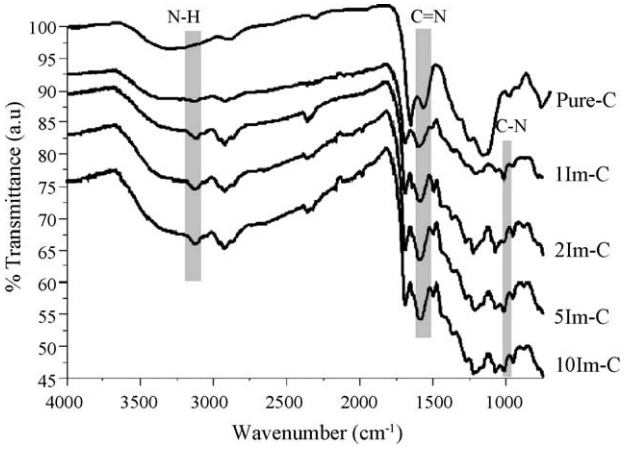

Fig. 1. FT-IR spectra of the pure and imidazole modified hydrothermal carbons.

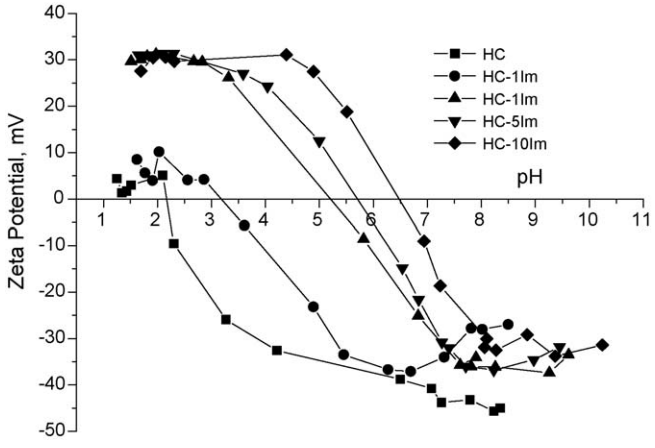

Fig. 2. Zeta potential of the pure and imidazole modified hydrothermal carbons.

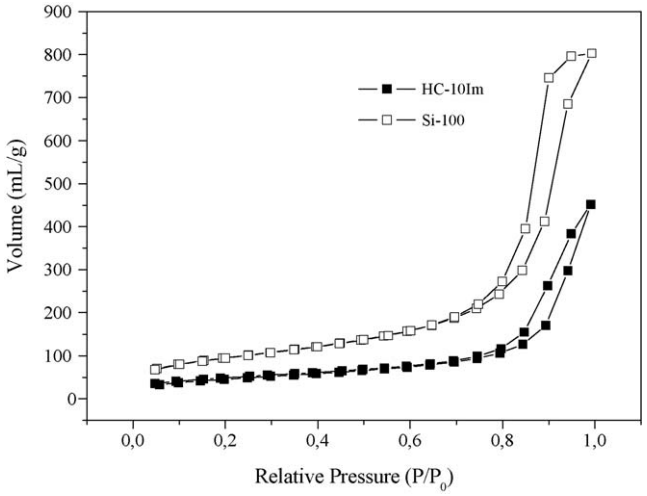

Fig. 4. Nitrogen adsorption isotherms of the template (Si-100) and vinyl imidazole functionalized hydrothermal carbon material (HC-10Im).

initial silica template are successfully maintained through the replication process. The TEM micrographs show that the mesopore system of the silica template was also successfully reproduced and this is also confirmed by N_2 adsorption measurements (Fig. 4). The isotherms of Si-100 and HC-10Im show a sharp condensation in the range of 0.7–0.8 relative pressure, corresponding to the existence of mesopores. According to nitrogen adsorption, surface area of the HC-10Im slightly decreased from 338 m^2/g to 170 m^2/g showing a hysteresis loop with type IV isotherm.

3.2. Imidazolium synthesis and catalytic tests

The successful alkylation of the surface imidazol moieties could be evidenced by EDX showing the presence of bromine in our solids (up to 1.5 at.%) (data not shown).

The catalytic activity of HC-10Bu_2ImBr was tested on three reactions, which were recently reported to be promoted by imidazolium halides: (i) the aromatisation of unsaturated six rings (especially Diels–Alder condensation products) [20], (ii) Knoevenagel and Aldol condensations [21] and (iii) transesterifications. The obtained results are summarised in Fig. 5.

As can be seen, when the Diels–Alder condensation of naphthquinone and cyclohexadiene is run in the presence of HC-10Bu_2ImBr (Fig. 5A), a nearly complete conversion of the reactants is obtained and anthraquinone (the re-aromatisation product) represents around 25 mol% of the products. This confirms that bromide ions are present in the catalyst and that they feature a strong nucleophilicity. Similarly both the Knoevenagel condensation of benzaldehyde with malononitrile and the Aldol condensation of benzaldehyde with acetophenone are achieved by HC-10Bu_2ImBr in high yields under relatively mild conditions (Fig. 5B). Finally, HC-10Bu_2ImBr was deprotonated with a 2 mol% solution of BenzONa in benzylalcohol and tested as N heterocyclic carbene in a standard transesterification reaction, namely the reaction of phenyl acetate with benzyl alcohol. Here, again the expected benzyl acetate is obtained in a moderate yield (Fig. 5C).

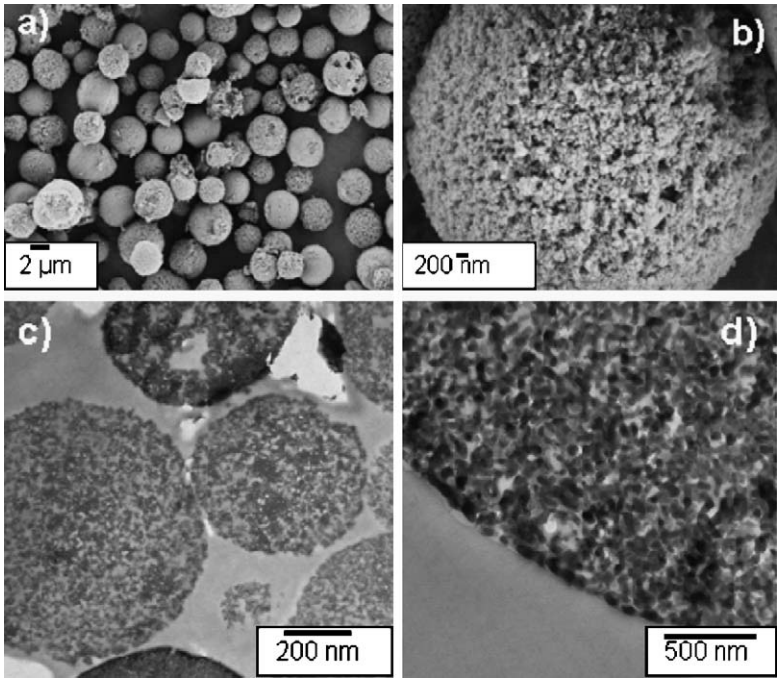

Fig. 3. Electron micrographs of the HC-10Im sample: (a and b) SEM; (c and d) TEM.

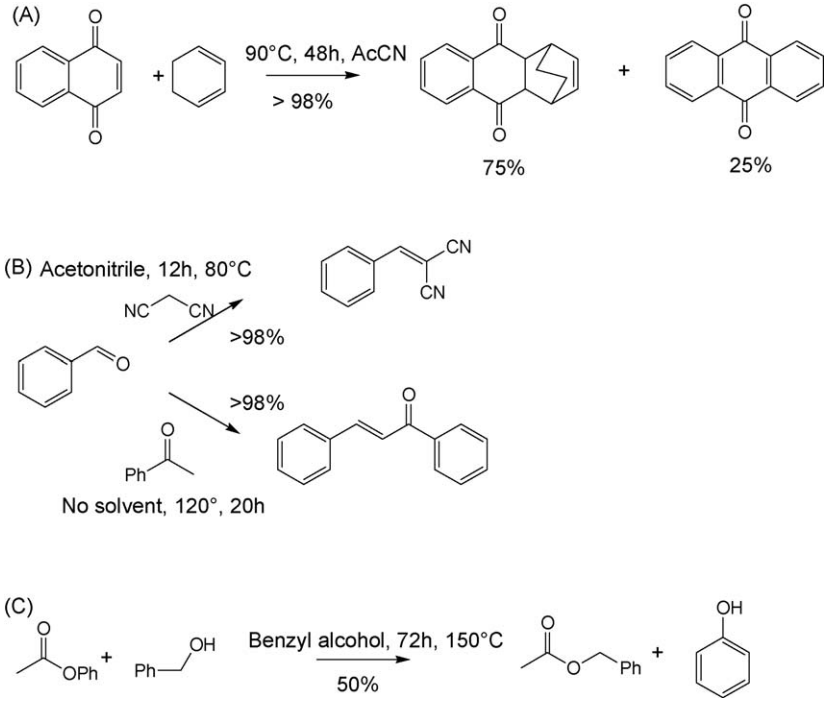

Fig. 5. Some reactions catalyzed by HC-10Bu_2ImBr: (A) the aromatisation of Diels–Alder condensates; (B) Knoevenagel and Aldol condensations; (C) transesterifications.

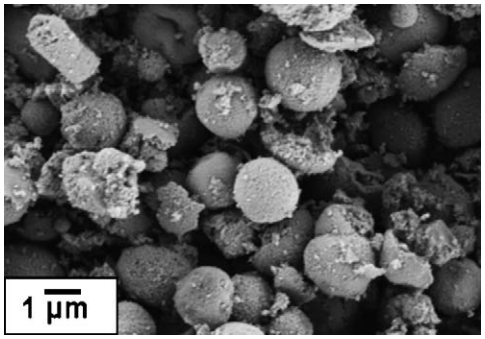

Fig. 6. SEM images of HC-10Im after use as catalyst for transesterification reaction.

The catalytic stability and reusability are important phenomena in catalyzed reactions for a practical industrial application. Here, the SEM morphology of the catalyst after transesterification reaction (Fig. 6) seems to be similar with the one before catalysis (Fig. 3) which clearly suggesting that the heating and stirring did not induce any structural change in the catalysts.

4. Conclusions

In conclusion we have successfully synthesized mesoporous carbonaceous materials containing imidazole group by simple hydrothermal carbonization of glucose in the presence of vinylimidazole. Once alkylated, these materials proved to be successful catalysts for organo-catalysis. We, however, feel that the range of applications of such materials can also be extended towards adsorption and electrochemistry. Furthermore, this method provides a versatile, green and cheap strategy towards carbon materials with a high degree of functional groups, which are determined by the choice of organic monomer.

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