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## The CO<sub>2</sub> capturing ability of cellulose dissolved in NaOH(aq) at low temperature†

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Herein, we explore the intrinsic ability of cellulose dissolved in NaOH(aq) to reversibly capture CO<sub>2</sub>. The stability of cellulose solutions differed significantly when adding CO<sub>2</sub> prior to or after the dissolution of cellulose. ATR-IR spectroscopy on cellulose regenerated from the solutions, using ethanol, revealed the formation of a new carbonate species likely to be cellulose carbonate. To elucidate the interaction of cellulose with CO<sub>2</sub> at the molecular level, a <sup>13</sup>C NMR spectrum was recorded on methyl α-D-glucopyranoside (MeO-Glcp), a model compound, dissolved in NaOH(aq), which showed a difference in chemical shift when CO<sub>2</sub> was added prior to or after the dissolution of MeO-Glcp, without a change in pH. The uptake of CO<sub>2</sub> was found to be more than twice as high when CO<sub>2</sub> was added to a solution after the dissolution of MeO-Glcp. Altogether, a mechanism for the observed CO<sub>2</sub> capture is proposed, involving the formation of an intermediate cellulose carbonate upon the reaction of a cellulose alkoxide with CO<sub>2</sub>. The intermediate was observed as a captured carbonate structure only in regenerated samples, while its corresponding NMR peak in solution was absent. The reason for this is plausibly a rather fast hydrolysis of the carbonate intermediate by water, leading to the formation of CO<sub>3</sub><sup>2-</sup>, and thus increased capture of CO<sub>2</sub>. The potential of using carbohydrates as CO<sub>2</sub> capturing agents in NaOH(aq) is shown to be simple and resource-effective in terms of the capture and regeneration of CO<sub>2</sub>.

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## Introduction

Designing renewable materials for the capture of CO<sub>2</sub> is timely and of great importance for environmental challenges. Today, there are several materials capable of efficiently capturing CO<sub>2</sub> such as different types of amines and MOFs (metal-organic frameworks).<sup>1</sup> However, many of these systems suffer from being expensive or from being difficult to synthesise, and are to some extent not sustainable since a lot of energy is needed to regenerate CO<sub>2</sub> and to recycle the capturing agent. In this aspect, another interesting system for capturing CO<sub>2</sub> is NaOH (aq). Aqueous hydroxides are in general very efficient CO<sub>2</sub> capturing agents. In theory, to capture 1 ton of CO<sub>2</sub>, 0.9 tons of NaOH are needed in comparison with the 1.39 tons of the

commonly used amine, monoethanolamine (MEA). The capture of CO<sub>2</sub> in NaOH(aq) occurs through absorption and conversion of CO<sub>2</sub> by the reaction with hydroxide ions, resulting in different species depending on the pH of the solution. At a pH above 9, all CO<sub>2</sub> is converted to carbonate ions, CO<sub>3</sub><sup>2-</sup>, forming sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>, a reaction consuming two moles of NaOH for each mole of Na<sub>2</sub>CO<sub>3</sub> formed. However, in a recent study it was shown that the CO<sub>2</sub> capturing ability of NaOH(aq) was greatly increased by the addition of glycerol, suggesting the occurrence of two simultaneous reactions in the NaOH(aq)/glycerol-system.<sup>2</sup> Almost simultaneously, a similar study was published where it was found that the mass transfer coefficient for CO<sub>2</sub> in NaOH(aq) could be doubled if glycerol was added and thereby increase the chemical absorption of CO<sub>2</sub>, even though the viscosity increased with the addition of glycerol.<sup>3</sup> Furthermore, Song *et al.* implied, based on a series of studies performed in 1927 by Faurholt,<sup>4</sup> that glycerol is deprotonated in NaOH, and as glyceroxide, it is capable of competing with the hydroxide ions in the reaction with CO<sub>2</sub>. The final products would then be Na<sub>2</sub>CO<sub>3</sub> and glycerolcarbonate. Interestingly, it was found that the reaction kinetics between glyceroxide and CO<sub>2</sub> was 6–7 times faster than the reaction between the hydroxide ions and CO<sub>2</sub>, and hence a larger amount of CO<sub>2</sub> could be captured in a system containing both NaOH and glycerol.<sup>2</sup> On the other hand, this phenomenon has also been attributed to the ability of the indi-

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vidual C–O bonds in CO<sub>2</sub> being able to interact with the polar groups of the glycerol through hydrogen bonding.<sup>5,6</sup> Furthermore, glycerol and carbohydrates, with a larger number of hydroxyl groups, have been shown to have a higher affinity for CO<sub>2</sub> than, e.g. poly(ethylene glycol)(PEG),<sup>5</sup> which is claimed to be a CO<sub>2</sub> capturing polymer through a Lewis base–Lewis acid mechanism between the carbon in CO<sub>2</sub> and the ether oxygen in PEG. Clearly, there are different explanations for the CO<sub>2</sub> capturing ability of alcohols in general and of alcohols in NaOH(aq) in particular. From this point of view, it is interesting to note similarities to our recent work which reports on a previously overlooked feature of the NaOH(aq) system used for the dissolution and reshaping of cellulose into regenerated (precipitated) cellulose materials. Our study showed that CO<sub>2</sub>, readily dissolved in NaOH(aq), to a certain extent sorbs onto the dissolved cellulose.<sup>7</sup> The sorption of CO<sub>2</sub> onto dissolved cellulose was proven using ATR-IR (Attenuated Total Reflectance – Infrared) spectroscopy on samples regenerated in ethanol. Ethanol, as such, has been shown to preserve chemisorbed CO<sub>2</sub> in synthesised organic carbonates, whilst precipitation in water promotes the desorption of CO<sub>2</sub>,<sup>8</sup> which was also observed in our recent study. Both the preservation of sorbed CO<sub>2</sub> as well as the desorption, depending on the type of regenerating agent used, is promising for the application of using cellulose as a sustainable CO<sub>2</sub> capturing agent. As mentioned before, there is to our knowledge still no mechanistic understanding of the CO<sub>2</sub> capture in these systems, and that is why many questions remain. The focus of this work has therefore been set on investigating the molecular interactions that occur between CO<sub>2</sub> and cellulose in its dissolved state in NaOH(aq). Essential in this investigation is the molecular state of the CO<sub>2</sub> when interacting with cellulose dissolved in NaOH(aq) (*i.e.* CO<sub>2</sub>(aq) or CO<sub>3</sub><sup>2-</sup>). Particular emphasis has, thus, been placed on comparative studies exploring the consequences of adding CO<sub>2</sub> pre or post-dissolution of cellulose in a NaOH(aq) system. In the case of CO<sub>2</sub> added prior to the dissolution of cellulose, the high alkalinity of the system can be assumed to completely convert CO<sub>2</sub> into CO<sub>3</sub><sup>2-</sup>, before the cellulose is added to the NaOH(aq). On the other hand, when CO<sub>2</sub> is added to a system already containing dissolved cellulose (post-dissolution addition), CO<sub>2</sub> in its aqueous state could interact with the dissolved and, most likely, deprotonated cellulose (cellulose alkoxides) and possibly form cellulose carbonate. Microcrystalline cellulose (MCC) and a model compound, MeO-Glcp, were therefore employed in ATR-IR spectroscopy and NMR studies in order to elucidate the interactions occurring between CO<sub>2</sub> and cellulose dissolved in NaOH(aq). The model compound MeO-Glcp allows for an increased sensitivity and accuracy in the NMR measurements compared to cellulose. A recent study by Bialik *et al.*<sup>9</sup> reports on partial deprotonation of the hydroxyl groups in cellobiose in NaOH(aq), especially on the C2 carbon, which could provide a reaction site for CO<sub>2</sub>(g) forming a cellulose carbonate. The deprotonation or dissociation constants of different sugars were actually studied already in the 1950s<sup>10</sup> and are in line with the observed results in the more recent study by

Bialik *et al.* The effects of deprotonation were therefore studied in terms of comparing the addition of CO<sub>2</sub>(g) to MeO-Glcp dissolved in a NaCl(aq) or NaOH(aq) solution. Furthermore, CO<sub>2</sub>(g) was also added as a function of time (30, 60 or 120 seconds) before or after the addition of MeO-Glcp, to monitor the effects of various CO<sub>2</sub>-species as well as the uptake of CO<sub>2</sub>.

## Results and discussion

### Reversible sorption of CO<sub>2</sub> on MCC

Initially, ocular observations were made on the influence of CO<sub>2</sub> addition on the dissolved state of MCC in NaOH(aq), owing to the fact that NaOH(aq) itself is able to absorb CO<sub>2</sub>.<sup>11</sup> Roughly one litre of CO<sub>2</sub> was percolated into 10 ml of NaOH(aq) solution before or after the dissolution of 4 wt% MCC, denoted as NaOH + CO<sub>2</sub> + MCC and NaOH + MCC + CO<sub>2</sub>, respectively. The optimal dissolution conditions for cellulose in NaOH(aq) have been found to be –5 °C and 8 wt% NaOH,<sup>12</sup> and were thus employed here. The transparent solutions were then stored for two weeks at room temperature. After two weeks, the reference sample without added CO<sub>2</sub> still remained as a liquid solution while the NaOH + CO<sub>2</sub> + MCC had turned opaque but surprisingly the NaOH + MCC + CO<sub>2</sub> had formed a gelled structure (Fig. 1). Hence, percolating CO<sub>2</sub> disrupts the stability of the MCC solutions, and interestingly, the effect is even more significant when CO<sub>2</sub> is added after the dissolution of MCC in NaOH(aq), thus enabling a direct interaction between the dissolved MCC and the freshly added CO<sub>2</sub> as CO<sub>2</sub>(aq), before the conversion to CO<sub>3</sub><sup>2-</sup> takes place. On the other hand, pre-dissolution addition of CO<sub>2</sub>, leading to the conversion of CO<sub>2</sub> to CO<sub>3</sub><sup>2-</sup> prior to the interaction with MCC, seems to be of minor importance.

The visible difference in the dissolved state of MCC was further characterised by regenerating the solutions with

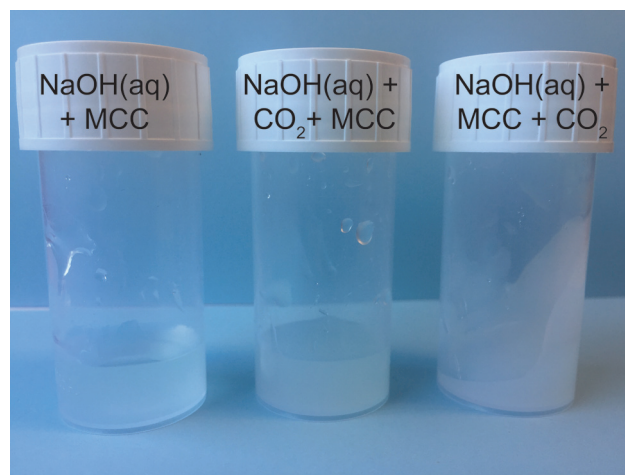


Fig. 1 MCC solutions after two weeks at room temperature. Reference sample NaOH(aq) + MCC (left), NaOH(aq) + CO<sub>2</sub> + MCC (middle), and NaOH(aq) + MCC + CO<sub>2</sub> (right).



ethanol followed by solid state analysis using ATR-IR spectroscopy. The gelled state of MCC observed upon post-dissolution addition of  $\text{CO}_2$  suggests specific interactions between deprotonated MCC and  $\text{CO}_2$ , possibly through the formation of an organic carbonate which in turn can give rise to carbonate bridges.<sup>13</sup> Moreover, it is well known that synthesised organic carbonates are preserved during work-up in ethanol but decompose if instead water is used.<sup>8</sup> If an organic carbonate is formed through the reaction of deprotonated MCC and  $\text{CO}_2$ , it is expected to be observed as a new waveband around  $1590\text{ cm}^{-1}$  in the ATR-IR spectrum, similar to the structure found for carboxymethylated cellulose, corresponding to the out-of-phase stretching in the ionic state.<sup>14</sup> In addition to this, it is important to remember that all the studied solutions, including those where no  $\text{CO}_2$  was added purposely, contained a certain amount of post-dissolution introduced  $\text{CO}_2$  due to the diffusion of  $\text{CO}_2$  present in the surrounding air. From the ATR-IR spectroscopy analysis it could indeed be concluded that a new structure was introduced on MCC through the addition of  $\text{CO}_2$  as a new waveband at  $1590\text{ cm}^{-1}$  appeared, both for the samples only in contact with air  $\text{CO}_2$  as well as those subjected to  $\text{CO}_2$  percolation (Fig. 2). Moreover, compared to the reference MCC, the addition of  $\text{CO}_2$  to the MCC solutions (both pre and post-dissolution)

resulted in a decrease in the OH-stretching around  $3300\text{ cm}^{-1}$  as well as a change in the waveband around  $1000\text{ cm}^{-1}$  in the ATR-IR spectra, corresponding to the primary alcohol absorption band of the MCC.<sup>15</sup> These changes are attributed to a difference in interactions between the hydroxyl groups in MCC and indicate a change in the crystalline structure, probably due to the interruption of the hydrogen bonding pattern.<sup>16</sup> Additionally, the spectra reveal that solutions subjected to pre or post-dissolution addition of  $\text{CO}_2$  to a different extent show the formation of  $\text{Na}_2\text{CO}_3$ , giving rise to new wavebands at  $1427\text{ cm}^{-1}$  and  $880\text{ cm}^{-1}$  (see the ESI† for comparison with the ATR-IR spectrum for  $\text{Na}_2\text{CO}_3$ ). Nonetheless, the new waveband at  $1590\text{ cm}^{-1}$  observed for the ethanol regenerated cellulose samples is not present in the spectrum for  $\text{Na}_2\text{CO}_3$ , indeed proving the formation of a new species of  $\text{CO}_2$  ( $\text{CO}_2$  out-of-phase stretching) associated with the presence of MCC when dissolved in  $\text{NaOH}(\text{aq})$ . Interestingly, the formation of this new species seems to be competing with the formation of  $\text{Na}_2\text{CO}_3$  as the increased percolation time of  $\text{CO}_2$  does not lead to an increase in the intensity of the  $\text{CO}_2$  out-of-phase stretching but rather the opposite: the highest intensity of this signal is observed for the MCC subjected to the post-dissolution addition of  $\text{CO}_2$  for 60 s or the one only subjected to  $\text{CO}_2$  from the surrounding air. The reason for this could possibly be an

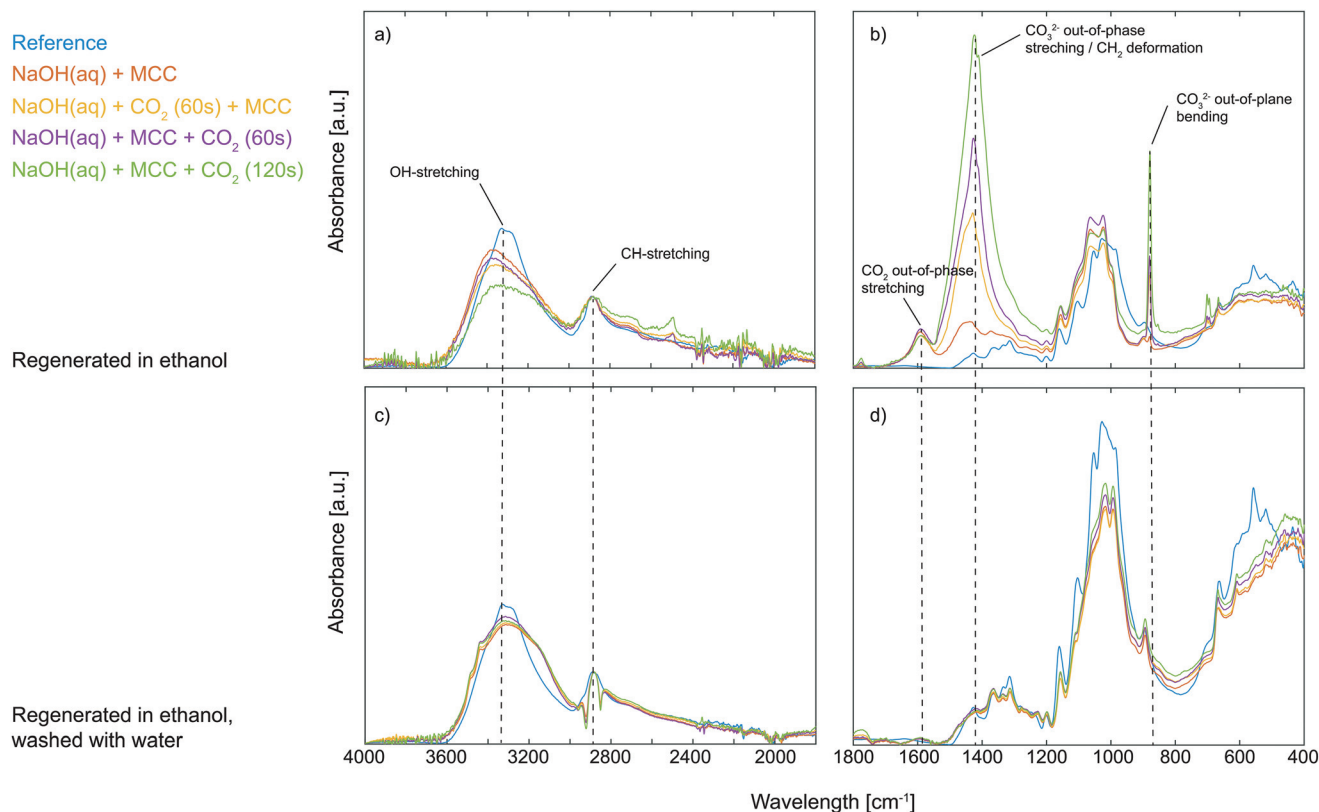


Fig. 2 ATR-IR spectra from  $4000\text{--}1800\text{ cm}^{-1}$  and  $1800\text{--}400\text{ cm}^{-1}$  of untreated reference MCC (blue), MCC dissolved in  $\text{NaOH}(\text{aq})$  (red), MCC dissolved in  $\text{NaOH}(\text{aq})$  with 60 s pre-dissolution addition of  $\text{CO}_2$  (yellow), MCC dissolved in  $\text{NaOH}(\text{aq})$  with 60 s post-dissolution addition of  $\text{CO}_2$  (purple) and MCC dissolved in  $\text{NaOH}(\text{aq})$  with 120 s post-dissolution addition of  $\text{CO}_2$  (green). All solutions were regenerated in ethanol and dried (a and b) and subsequently washed with water and dried (c and d).



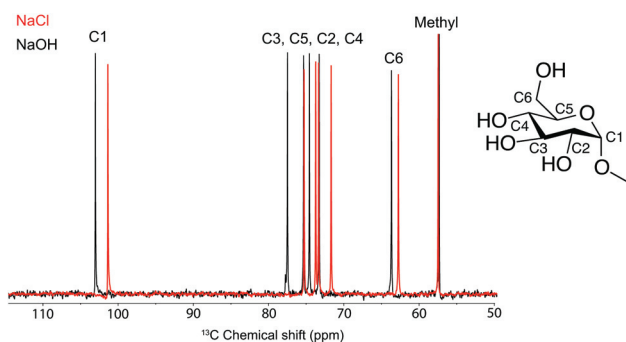
effect of deterioration of the dissolved state of the MCC, which is the result of consuming  $\text{OH}^-$  ions due to the extensive  $\text{CO}_2$  addition and the formation of  $\text{Na}_2\text{CO}_3$ . As already mentioned, a change in the structure of the primary alcohol on MCC could be observed in the spectra, this is why the corresponding change for the  $\text{CH}_2$ -group on MCC carrying the primary alcohol should be observable as well. Unfortunately, the waveband for  $\text{CH}_2$  deformation on MCC is overlapping with the  $\text{CO}_3^{2-}$  out-of-phase stretching (originating from the  $\text{Na}_2\text{CO}_3$ ) and with that said, it is not possible to declare whether this band carries information on the interactions between MCC and  $\text{CO}_2$  added pre- or post-dissolution. However, sorption of  $\text{CO}_2$  on MCC is evidently taking place when dissolved in  $\text{NaOH}$  (aq),<sup>7</sup> which explains why the stability of the sorbed  $\text{CO}_2$  was evaluated. The regenerated MCC was hence washed with water, filtered and dried before analysis once again using ATR-IR spectroscopy (Fig. 2). From this it was confirmed that the sorption of  $\text{CO}_2$  on MCC indeed is reversible as almost no traces of the waveband for the  $\text{CO}_2$  out-of-phase stretching could be detected after washing with water. This indicates that the sorption of  $\text{CO}_2$  on MCC in  $\text{NaOH}$ (aq) is both simple and sustainable in terms of capturing  $\text{CO}_2$  as well as the subsequent regeneration by the use of a water-based system.

### Impact of $\text{CO}_2$ on a model system

Although ATR-IR spectroscopy provides structural information, many questions are still unresolved such as in which state  $\text{CO}_2$  interacts with MCC in a  $\text{NaOH}$ (aq) solution when the sorption occurs. Characterisation using solution NMR (nuclear magnetic resonance) has been shown to be a promising method to study similar systems,<sup>17</sup> but for polymers such as MCC, the observed peaks are unfortunately broad and featureless. The model compound methyl  $\alpha$ -D-glucopyranoside (MeO-Glcp) was therefore instead used, which unlike unprotected glucose or cellobiose does not ring open. The MeO-Glcp was dissolved in either  $\text{NaCl}$  or  $\text{NaOH}$  to elucidate the role of the solvent in the sorption of  $\text{CO}_2$  in the MCC/ $\text{NaOH}$ -system. The  $^{13}\text{C}$  NMR spectra of MeO-Glcp dissolved in  $\text{NaCl}$ (aq) and  $\text{NaOH}$ (aq) (Fig. 3) showed that all carbon peaks in the MeO-Glcp were shifted to higher chemical shift values upon dissolution in

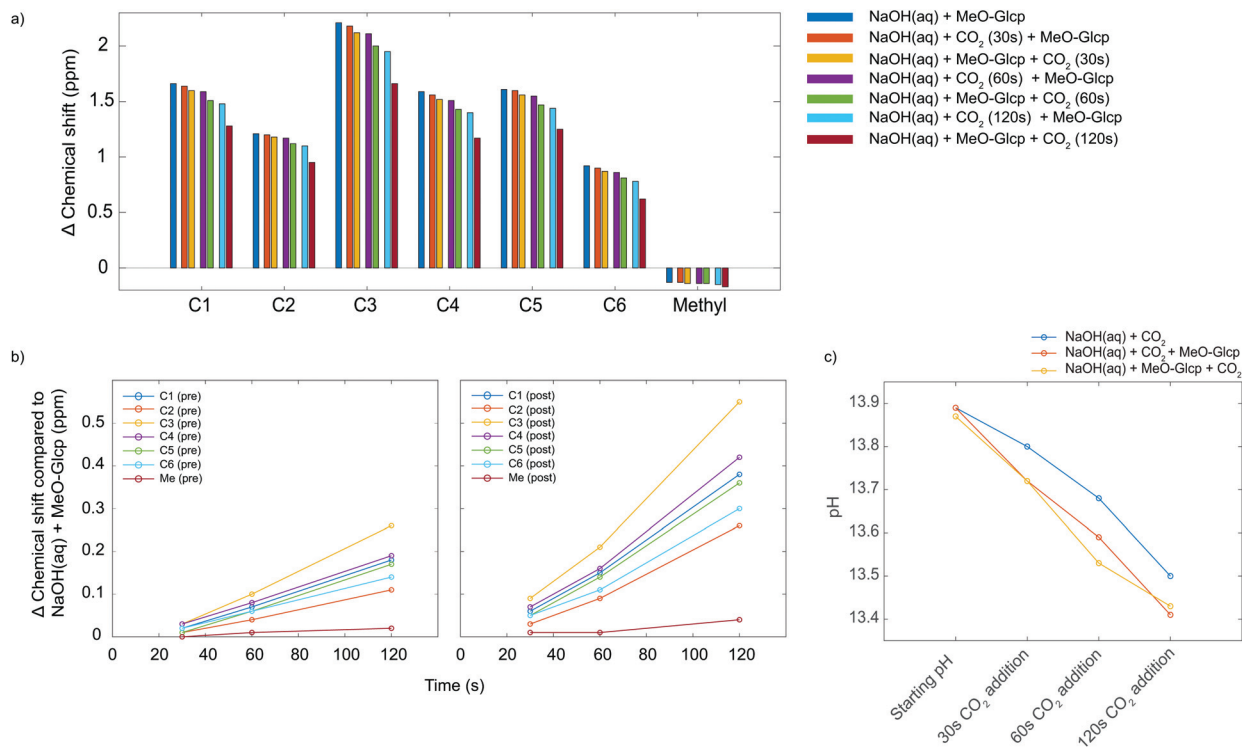
$\text{NaOH}$ (aq) compared to  $\text{NaCl}$ (aq), except for the methyl group bonded to C1, which was shifted from 57.8 to 57.6 ppm. The observed change in the chemical shifts agrees well with the chemical shift changes reported previously by Bialik *et al.*<sup>9</sup> for cellobiose, which was explained as a consequence of the deprotonation of one or several of the hydroxyl groups on the glucose ring. This phenomenon has also been discussed earlier by Isogai, who ascribed it to a dissociation of the hydroxyl groups in  $\text{NaOH}$ (aq) resulting in an electron-deshielding effect on the carbon atoms.<sup>18</sup> The largest change in the chemical shift was observed for the carbons at the C1 and C3 positions, indicating that the hydroxyl group in position C2 is deprotonated to the highest extent. In contrast to this, the position C6 in MeO-Glcp was observed as being the least affected when dissolved in  $\text{NaOH}$ (aq) compared to  $\text{NaCl}$ (aq). Having established the deprotonation of the MeO-Glcp in  $\text{NaOH}$ (aq), the effect of adding  $\text{CO}_2$  pre or post-dissolution of MeO-Glcp was evaluated by percolating  $\text{CO}_2$  for 30, 60 and 120 s into the solutions. Notably, no precipitation of  $\text{Na}_2\text{CO}_3$  was observed. In general, the addition of  $\text{CO}_2$ (g) to  $\text{NaOH}$ (aq) causes a change in pH due to the consumption of  $\text{OH}^-$  ions. Thus, as expected, all the carbon peaks in MeO-Glcp were shifted to lower chemical shifts upon the addition of  $\text{CO}_2$ (g), disregarding pre or post-dissolution addition (Fig. 4a).

Interestingly though, it was observed that the pre or post-dissolution addition of  $\text{CO}_2$ (g) did not result in an identical change of the chemical shifts of the carbon peaks (Fig. 4b). Namely, the post-dissolution addition of  $\text{CO}_2$  resulted in a larger chemical shift change of the carbon peaks. An explanation for this could partly be due to a difference in change of pH or due to an interaction between the deprotonated MeO-Glcp and the added  $\text{CO}_2$ (g), as well as a combination of both. As the interaction between the available  $\text{OH}^-$  ions in the solvent and the added  $\text{CO}_2$  is assumed to be identical both in the case of pre and post-dissolution addition it should thus give rise to the same change in chemical shift as a result of the pH change. The same effect could additionally be observed in the corresponding  $^1\text{H}$  spectra, with the difference that the protons were shifted in the opposite direction as they become shielded, instead, during deprotonation and by the addition of  $\text{CO}_2$ . Furthermore, the pH of the solutions was measured in order to investigate if a variation in pH was the cause for the differences in chemical shifts for the MeO-Glcp with pre or post-dissolution addition of  $\text{CO}_2$ . When measuring pH, a limiting factor is the accuracy of the electrode, especially at high pH. In addition to this, temperature has a large influence on the accuracy of the measurement and becomes even more important at low temperature. The pH was therefore measured for a 0.5 M  $\text{NaOH}$ (aq) solution at 10 °C (Fig. 4c). The initial pH of the 0.5 M  $\text{NaOH}$ (aq) was found to be 13.87 and decreased to 13.79 when MeO-Glcp was added, which supports the results discussed above pointing out the deprotonation of MeO-Glcp in  $\text{NaOH}$ (aq). From the pH decrement, a degree of deprotonation could be estimated to be around 15% which further suggests the  $\text{pK}_a$  for the majority of the MeO-Glcp hydroxyls to be higher than 13.8. On the other hand, the  $\text{pK}_a$  is probably



**Fig. 3**  $^{13}\text{C}$  NMR spectra of MeO-Glcp dissolved in  $\text{NaCl}$ (aq) and  $\text{NaOH}$ (aq). All measurements were recorded at +5 °C in  $\text{D}_2\text{O}$ . Inset shows the chemical structure of MeO-Glcp.





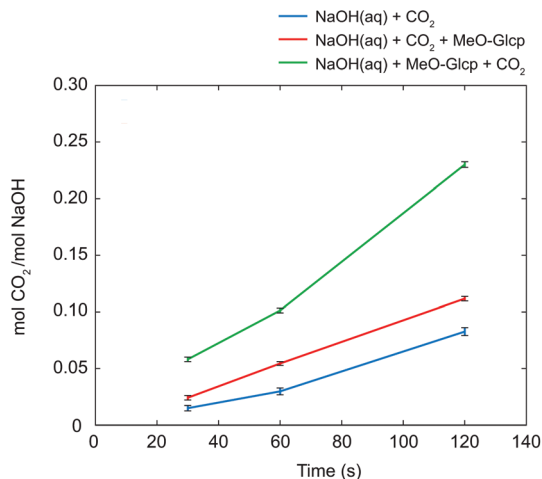
**Fig. 4** (a) The difference in chemical shift for MeO-Glep in NaOH(aq) with pre or post-dissolution addition of CO<sub>2</sub> in comparison with MeO-Glep in NaCl(aq). All measurements were recorded at +5 °C in D<sub>2</sub>O. (b) An extension of the difference in chemical shift for MeO-Glep in NaOH(aq) with pre or post-dissolution addition of CO<sub>2</sub> in comparison with MeO-Glep in NaOH(aq). (c) The change in pH for 0.5 M NaOH(aq) with MeO-Glep and pre or post-dissolution addition of CO<sub>2</sub>.

quite close to 13.8 since the pH scale is logarithmic. Moreover, when CO<sub>2</sub> was added to the solutions the pH decreased as expected but interestingly enough the decrement was equal for the solutions with pre or post-dissolution addition of CO<sub>2</sub>, which means that an equal amount of OH<sup>-</sup> ions is consumed in both cases. Therefore, the observed increase in chemical shift change for the solution with post-dissolution addition of CO<sub>2</sub> could not be due to a larger change in pH but rather a difference in interaction with the added CO<sub>2</sub>.

As discussed in the Introduction section, several studies on the increased capture of CO<sub>2</sub> in NaOH(aq) have been based on the hypothesis that a deprotonated alcohol reacts with CO<sub>2</sub> in the formation of an organic carbonate<sup>19,20</sup> which in <sup>13</sup>C NMR should result in a new peak around 150 ppm. No such peak could be observed in the present study, this is why complementary NMR measurements were made on both glycerol and PEG in NaOH(aq) in order to elucidate the origin of the CO<sub>2</sub> sorption mechanism of alcohols and ethers. As previously reported, both the presence of glycerol and PEG increases the CO<sub>2</sub> capturing ability of NaOH(aq) and several explanations have been presented on this phenomenon, *e.g.* the formation of glycerol carbonate<sup>2</sup> or as an interaction between CO<sub>2</sub> and terminal hydroxyl groups<sup>5,6</sup> or the ether bridge.<sup>21</sup> Surprisingly, no such interactions could be observed in the complementary NMR measurements (see the ESI†), thereby suggesting another mechanism for the increased CO<sub>2</sub> capture in NaOH(aq). On

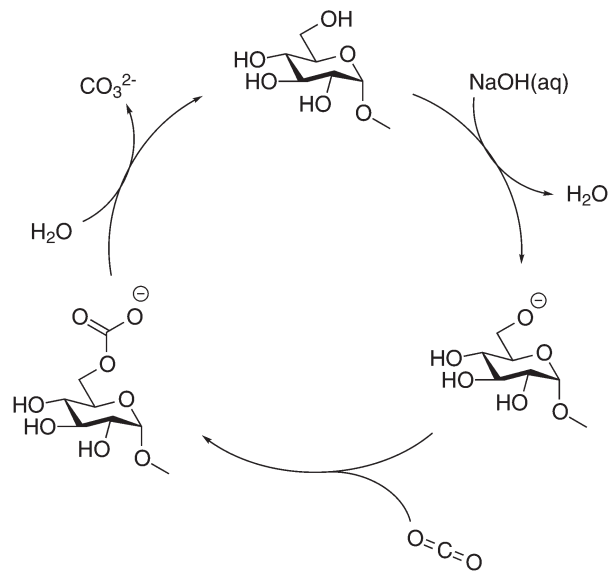
the other hand, the occurrence of a CO<sub>3</sub><sup>2-</sup> peak at 171.0 ppm in NaOH(aq) could clearly be observed in <sup>13</sup>C NMR, showing that CO<sub>2</sub>(g) dissolves and converts, as expected, into CO<sub>3</sub><sup>2-</sup> in the NaOH(aq) at this high pH (which was also true for the complementary measurements on glycerol and PEG in NaOH(aq)). Moreover, the addition of CO<sub>2</sub> to NaOH(aq) of different durations (30, 60 or 120 s) correlated well with the integral of the CO<sub>3</sub><sup>2-</sup> peak. From the peak integral of CO<sub>3</sub><sup>2-</sup>, the amount of absorbed CO<sub>2</sub> could be calculated which is shown as mol CO<sub>2</sub>/mol NaOH in Fig. 5. Comparing the amount of absorbed CO<sub>2</sub> in the system MeO-Glep/NaOH(aq) with the pre-dissolution addition of CO<sub>2</sub> to pure NaOH(aq) with the same amount of CO<sub>2</sub> added, the amount was observed to be larger, indicating either a stabilising effect of MeO-Glep on CO<sub>2</sub> (hypothetical coordination through hydrogen bonding) dissolved in NaOH or/and an additional post-dissolution addition of CO<sub>2</sub> from the surrounding air facilitated by the presence of MeO-Glep in the solution. Interestingly, in the case of MeO-Glep with the post-dissolution addition of CO<sub>2</sub>, the amount of absorbed CO<sub>2</sub> increased even more profoundly and was shown to be more than twice as large as the amount of absorbed CO<sub>2</sub> in pure NaOH(aq). If this would be the result of CO<sub>2</sub> (aq) and OH<sup>-</sup> ions converting to CO<sub>3</sub><sup>2-</sup> in the presence of MeO-Glep, it would have been visible as a larger decrease in pH which was not the case according to the pH measurements. Instead, the increased formation of CO<sub>3</sub><sup>2-</sup> in the presence of





**Fig. 5** Amount of CO<sub>2</sub> captured calculated from the integral of CO<sub>3</sub><sup>2-</sup> at 171 ppm and reported as mol CO<sub>2</sub>/mol NaOH with errorbars for NaOH(aq) with the addition of CO<sub>2</sub> (blue), NaOH(aq) with pre-dissolution addition of CO<sub>2</sub> (red) and NaOH(aq) with post-dissolution addition of CO<sub>2</sub> (green). All NMR measurements were recorded at +5 °C in D<sub>2</sub>O.

deprotonated MeO-Glcp at rather constant pH indicates a decisive role of deprotonated glucose (working as a catalyst) in this conversion. Lastly, a concluding reference measurement was made on the MeO-Glcp dissolved in NaCl(aq) with the addition of CO<sub>2</sub>, both pre and post-dissolution. The result showed no effect on either the <sup>1</sup>H nor <sup>13</sup>C chemical shifts, nor on the integral intensities. A tiny <sup>13</sup>C peak of bicarbonate was however observed, indicating that a small amount of CO<sub>2</sub> dissolves in NaCl(aq) but without influencing the chemical shifts of MeO-Glcp. From the results obtained with NMR spectroscopy in combination with the pH measurement, it is evident that the dissolution, and most probably the deprotonation, of MeO-Glcp in NaOH(aq) give rise to specific interactions with CO<sub>2</sub> or CO<sub>3</sub><sup>2-</sup> dissolved in NaOH(aq) and, thus increases the amount of CO<sub>2</sub> that can be sorbed in NaOH(aq). Even though the anticipated MeO-Glcp-carbonate peak was lacking in the NMR spectroscopy measurements, the ATR-IR analysis of precipitated samples clearly showed the introduction of an organic carbonate on MCC when dissolved in NaOH(aq) and subjected to CO<sub>2</sub>(g). An explanation for this is most likely the capture, during precipitation in ethanol, of the intermediate state of the reaction between a deprotonated hydroxyl on MeO-Glcp and CO<sub>2</sub>(aq), yielding a MeO-Glcp-carbonate intermediate. The MeO-Glcp-carbonate intermediate, which probably is in equilibrium with the free CO<sub>3</sub><sup>2-</sup> ions in solution, is further readily hydrolysed by water and thereby converted to CO<sub>3</sub><sup>2-</sup> (Fig. 6). The observed increased tendency of gelation of MCC solutions upon post-dissolution addition of CO<sub>2</sub> observed in the ocular investigation could thus be the result of an interaction between the cellulose chains *via* the intermediate (carbonate bridges) or a re-protonation of the cellulose hydroxyl groups when the intermediate is hydrolysed. Overall, this process is thus a more lean conversion of CO<sub>2</sub> to CO<sub>3</sub><sup>2-</sup>



**Fig. 6** Possible mechanism for conversion of CO<sub>2</sub> to CO<sub>3</sub><sup>2-</sup> mediated by MeO-Glcp as the catalyst.

going *via* the MeO-Glcp-carbonate intermediate with water as the hydrolysing agent (instead of OH<sup>-</sup>) leaving the pH of the system largely unaffected. Consequentially, more CO<sub>2</sub> can be captured in the presence of MeO-Glcp or similar alcohols due to their catalytic role in the conversion of CO<sub>2</sub> to CO<sub>3</sub><sup>2-</sup>. This hypothesis is in line with the results previously reported and concluded by both Faurholt in 1927 and Song in 2017,<sup>2,4</sup> where alcohols such as methanol and glycerol were observed to increase the amount of CO<sub>2</sub> captured in an aqueous hydroxide to a larger extent compared to a system without alcohol. Altogether, these results prove the potential of using cellulose as a mediator in water-based systems for CO<sub>2</sub> capture.

## Conclusions

In summary, this work elucidates the sorption of CO<sub>2</sub> in NaOH(aq) in the presence of the model compound MeO-Glcp or MCC. The CO<sub>2</sub> capturing capacity of NaOH(aq) was evaluated in terms of pre or post-dissolution addition of CO<sub>2</sub> and was shown, using NMR spectroscopy, to increase drastically when MeO-Glcp was dissolved in NaOH(aq) prior to the addition of CO<sub>2</sub>. As a consequence, a significant capture of CO<sub>2</sub> in the system could be observed as CO<sub>3</sub><sup>2-</sup> in NMR and ATR-IR measurements, while retaining rather constant pH. The potential of using MCC as a CO<sub>2</sub> capturing agent was further evaluated in terms of regeneration of the captured CO<sub>2</sub> and proved to be efficient through just washing the regenerated MCC samples with water. The increased CO<sub>2</sub> capturing ability is explained according to the present findings on the specific interaction of a deprotonated carbohydrate and freshly added CO<sub>2</sub>, likely leading to the formation of an organic carbonate intermediate, which was observable on regenerated MCC as CO<sub>2</sub> out-of-phase stretching (1590 cm<sup>-1</sup>) using ATR-IR



spectroscopy. The corresponding carbonate peak in the NMR measurements was absent, which indicates a rather fast hydrolysis of the intermediate by water, leading to a lean conversion of  $\text{CO}_2$  to  $\text{CO}_3^{2-}$  in terms of the amount of  $\text{OH}^-$  consumed. Simultaneously, a deprotonated carbohydrate is regenerated upon the release of  $\text{CO}_3^{2-}$ , and is able to continue into the conversion of  $\text{CO}_2$  to  $\text{CO}_3^{2-}$  and thus works as a catalyst. In contrast to this, the possibility of a re-protonation of the carbohydrate also exists, which instead would quench the catalytic cycle. From this point of view, it is plausible to suggest that the formation of an intermediate state could be the reason for the observed tendency of MCC to form a gel upon the post-dissolution addition of  $\text{CO}_2$ . On one hand, an intermediate could cause an interaction with a neighbouring cellulose chain in solution through a so-called carbonate bridge hence causing the system to gel. While on the other hand, a re-protonation of the MCC would disrupt the dissolved state, leading to the precipitation of the MCC and phase separation into a gel. These findings could play an important role not only in the development of sustainable and efficient  $\text{CO}_2$  capturing agents but also in the innovation of functional bio-based materials.

## Experimental

### Materials and methods

Microcrystalline cellulose (MCC) Avicel PH-101, with a degree of polymerisation of 260, was purchased from FMC BioPolymer and used without further treatment. Methyl  $\alpha$ -D-glucopyranoside (<99%), NaOH (<98%), NaCl and  $\text{D}_2\text{O}$  (99.9%) were purchased from Sigma Aldrich and used as received. Dissolution of MCC was carried out by dispersing MCC in deionised water and pre-cooling it to +5 °C. The dispersed MCC was then added to a NaOH aqueous solution with a temperature of -5 °C, and stirred for 1 h. The solutions had a transparent appearance at the end of this procedure; the final concentrations were 4 : 8 : 88 wt% MCC : NaOH :  $\text{H}_2\text{O}$ . The MCC solutions were regenerated using ethanol. The regenerated materials were washed with ethanol until neutral and dried *in vacuo*, and were later washed with water, filtered and dried in an oven at 105 °C. Solutions were prepared by dissolving MeO-Glcp in  $\text{D}_2\text{O}$  at +5 °C. The MeO-Glcp solution was then added to either NaOH or NaCl in  $\text{D}_2\text{O}$ , maintaining a temperature of -5 °C. The final concentrations of the MeO-Glcp and the NaOH or NaCl in  $\text{D}_2\text{O}$  were 0.4 M and 3.0 M, respectively.  $\text{CO}_2$  was added for 30, 60 or 120 s to the solutions pre or post-dissolution of MCC or MeO-Glcp by immersing a syringe into the solutions. The syringe was connected to a tube containing  $\text{CO}_2$ , mounted with a flow regulator set to approximately 1 l  $\text{min}^{-1}$ . pH measurements were carried out by pre-cooling NaOH(aq) with a concentration of 0.5 M at +10 °C. The pH was then measured pre or post-dissolution of MeO-Glcp (4 wt%) in combination with the addition of  $\text{CO}_2$  for 30, 60 and 120 s pre or post-dissolution of the MeO-Glcp according to method above.

### Characterisation

Fourier Transform Infrared (FT-IR) spectra were obtained on a PerkinElmer Frontier equipped with an Attenuated Total Reflectance (ATR) sampling accessory (PIKE Technologies GladiATR). Samples were placed on top of the ATR crystal and secured using a metal clamp to ensure consistent pressure; they were measured with a resolution of 4  $\text{cm}^{-1}$  and 32 scans. All spectra were corrected against air, baseline corrected and normalised against the CH-band around 2890  $\text{cm}^{-1}$  which was shown not to be affected by the different treatments in the experiments. All spectra are shown without an absorbance scale. All NMR experiments were run on an 800 MHz magnet equipped with a Bruker Avance HDIII console and a TXO cryoprobe.  $^{13}\text{C}$  NMR spectra were recorded with a low angle radio frequency pulse to minimize relaxation-weighting using a single pulse experiment with  $^1\text{H}$  decoupling during acquisition. Hence, the repetition delay and number of scans were set to 33.0 s and 128, respectively, for monitoring the amount of dissolved  $\text{CO}_2$  while a repetition delay of 5 s was used for the observation of chemical shift differences. A capillary containing  $\text{D}_2\text{O}$  with 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS) was placed inside the tube as the internal reference. The amount of  $\text{CO}_2$  captured was converted from the  $\text{CO}_3^{2-}$  peak integral using the peak integrals of MeO-Glcp or DSS. The pH was measured using a HACH HQ430D Multimeter with an Intellical PHC705A1 pH probe.

### Conflicts of interest

There are no conflicts to declare.

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