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The CO_2 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_2. The stability of cellulose solutions differed significantly when adding CO_2 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_2 at the molecular level, a ^{13}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_2 was added prior to or after the dissolution of MeO-Glcp, without a change in pH. The uptake of CO_2 was found to be more than twice as high when CO_2 was added to a solution after the dissolution of MeO-Glcp. Altogether, a mechanism for the observed CO_2 capture is proposed, involving the formation of an intermediate cellulose carbonate upon the reaction of a cellulose alkoxide with CO_2. 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_3^{2-}, and thus increased capture of CO_2. The potential of using carbohydrates as CO_2 capturing agents in NaOH(aq) is shown to be simple and resource-effective in terms of the capture and regeneration of CO_2.

Introduction

Designing renewable materials for the capture of CO_2 is timely and of great importance for environmental challenges. Today, there are several materials capable of efficiently capturing CO_2 such as different types of amines and MOFs (metal–organic frameworks).[1] 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_2 and to recycle the capturing agent. In this aspect, another interesting system for capturing CO_2 is NaOH (aq). Aqueous hydroxides are in general very efficient CO_2 capturing agents. In theory, to capture 1 ton of CO_2, 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_2 in NaOH(aq) occurs through absorption and conversion of CO_2 by the reaction with hydroxide ions, resulting in different species depending on the pH of the solution. At a pH above 9, all CO_2 is converted to carbonate ions, CO_3^{2-}, forming sodium carbonate, Na_2CO_3, a reaction consuming two moles of NaOH for each mole of Na_2CO_3 formed. However, in a recent study it was shown that the CO_2 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.[2] Almost simultaneously, a similar study was published where it was found that the mass transfer coefficient for CO_2 in NaOH(aq) could be doubled if glycerol was added and thereby increase the chemical absorption of CO_2, even though the viscosity increased with the addition of glycerol.[3] Furthermore, Song *et al.* implied, based on a series of studies performed in 1927 by Faurholt,[4] that glycerol is deprotonated in NaOH, and as glyceroxide, it is capable of competing with the hydroxide ions in the reaction with CO_2. The final products would then be Na_2CO_3 and glycerolcarbonate. Interestingly, it was found that the reaction kinetics between glyceroxide and CO_2 was 6–7 times faster than the reaction between the hydroxide ions and CO_2, and hence a larger amount of CO_2 could be captured in a system containing both NaOH and glycerol.[2] 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_2 being able to interact with the polar groups of the glycerol through hydrogen bonding.[5,6] Furthermore, glycerol and carbohydrates, with a larger number of hydroxyl groups, have been shown to have a higher affinity for CO_2 than, e.g. poly(ethylene glycol)(PEG),[5] which is claimed to be a CO_2 capturing polymer through a Lewis base–Lewis acid mechanism between the carbon in CO_2 and the ether oxygen in PEG. Clearly, there are different explanations for the CO_2 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_2, readily dissolved in NaOH(aq), to a certain extent sorbs onto the dissolved cellulose.[7] The sorption of CO_2 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_2 in synthesised organic carbonates, whilst precipitation in water promotes the desorption of CO_2,[8] which was also observed in our recent study. Both the preservation of sorbed CO_2 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_2 capturing agent. As mentioned before, there is to our knowledge still no mechanistic understanding of the CO_2 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_2 and cellulose in its dissolved state in NaOH(aq). Essential in this investigation is the molecular state of the CO_2 when interacting with cellulose dissolved in NaOH(aq) (i.e. CO_2(aq) or CO_3^{2-}). Particular emphasis has, thus, been placed on comparative studies exploring the consequences of adding CO_2 pre or post-dissolution of cellulose in a NaOH(aq) system. In the case of CO_2 added prior to the dissolution of cellulose, the high alkalinity of the system can be assumed to completely convert CO_2 into CO_3^{2-}, before the cellulose is added to the NaOH(aq). On the other hand, when CO_2 is added to a system already containing dissolved cellulose (post-dissolution addition), CO_2 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_2 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.[9] 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_2(g) forming a cellulose carbonate. The deprotonation or dissociation constants of different sugars were actually studied already in the 1950s[10] 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_2(g) to MeO-Glcp dissolved in a NaCl(aq) or NaOH(aq) solution. Furthermore, CO_2(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_2-species as well as the uptake of CO_2.

Results and discussion

Reversible sorption of CO_2 on MCC

Initially, ocular observations were made on the influence of CO_2 addition on the dissolved state of MCC in NaOH(aq), owing to the fact that NaOH(aq) itself is able to absorb CO_2.[11] Roughly one litre of CO_2 was percolated into 10 ml of NaOH(aq) solution before or after the dissolution of 4 wt% MCC, denoted as NaOH + CO_2 + MCC and NaOH + MCC + CO_2, respectively. The optimal dissolution conditions for cellulose in NaOH(aq) have been found to be −5 °C and 8 wt% NaOH,[12] 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_2 still remained as a liquid solution while the NaOH + CO_2 + MCC had turned opaque but surprisingly the NaOH + MCC + CO_2 had formed a gelled structure (Fig. 1). Hence, percolating CO_2 disrupts the stability of the MCC solutions, and interestingly, the effect is even more significant when CO_2 is added after the dissolution of MCC in NaOH(aq), thus enabling a direct interaction between the dissolved MCC and the freshly added CO_2 as CO_2(aq), before the conversion to CO_3^{2-} takes place. On the other hand, pre-dissolution addition of CO_2, leading to the conversion of CO_2 to CO_3^{2-} 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
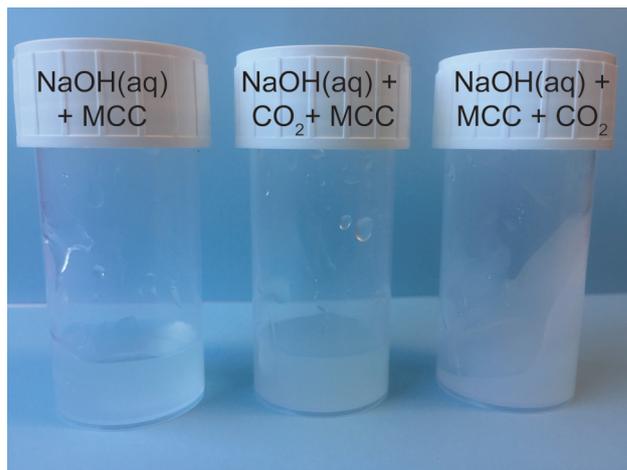

Fig. 1 MCC solutions after two weeks at room temperature. Reference sample NaOH(aq) + MCC (left), NaOH(aq) + CO_2 + MCC (middle), and NaOH(aq) + MCC + CO_2 (right).

ethanol followed by solid state analysis using ATR-IR spectroscopy. The gelled state of MCC observed upon post-dissolution addition of CO_2 suggests specific interactions between deprotonated MCC and CO_2, possibly through the formation of an organic carbonate which in turn can give rise to carbonate bridges.[13] Moreover, it is well known that synthesised organic carbonates are preserved during work-up in ethanol but decompose if instead water is used.[8] If an organic carbonate is formed through the reaction of deprotonated MCC and CO_2, it is expected to be observed as a new waveband around 1590 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.[14] In addition to this, it is important to remember that all the studied solutions, including those where no CO_2 was added purposely, contained a certain amount of post-dissolution introduced CO_2 due to the diffusion of 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 CO_2 as a new waveband at 1590 cm^{-1} appeared, both for the samples only in contact with air CO_2 as well as those subjected to CO_2 percolation (Fig. 2). Moreover, compared to the reference MCC, the addition of CO_2 to the MCC solutions (both pre and post-dissolution)

resulted in a decrease in the OH-stretching around 3300 cm^{-1} as well as a change in the waveband around 1000 cm^{-1} in the ATR-IR spectra, corresponding to the primary alcohol absorption band of the MCC.[15] 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.[16] Additionally, the spectra reveal that solutions subjected to pre or post-dissolution addition of CO_2 to a different extent show the formation of Na_2CO_3, giving rise to new wavebands at 1427 cm^{-1} and 880 cm^{-1} (see the ESI† for comparison with the ATR-IR spectrum for Na_2CO_3). Nonetheless, the new waveband at 1590 cm^{-1} observed for the ethanol regenerated cellulose samples is not present in the spectrum for Na_2CO_3, indeed proving the formation of a new species of CO_2 (CO_2 out-of-phase stretching) associated with the presence of MCC when dissolved in NaOH(aq). Interestingly, the formation of this new species seems to be competing with the formation of Na_2CO_3 as the increased percolation time of CO_2 does not lead to an increase in the intensity of the 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 CO_2 for 60 s or the one only subjected to CO_2 from the surrounding air. The reason for this could possibly be an
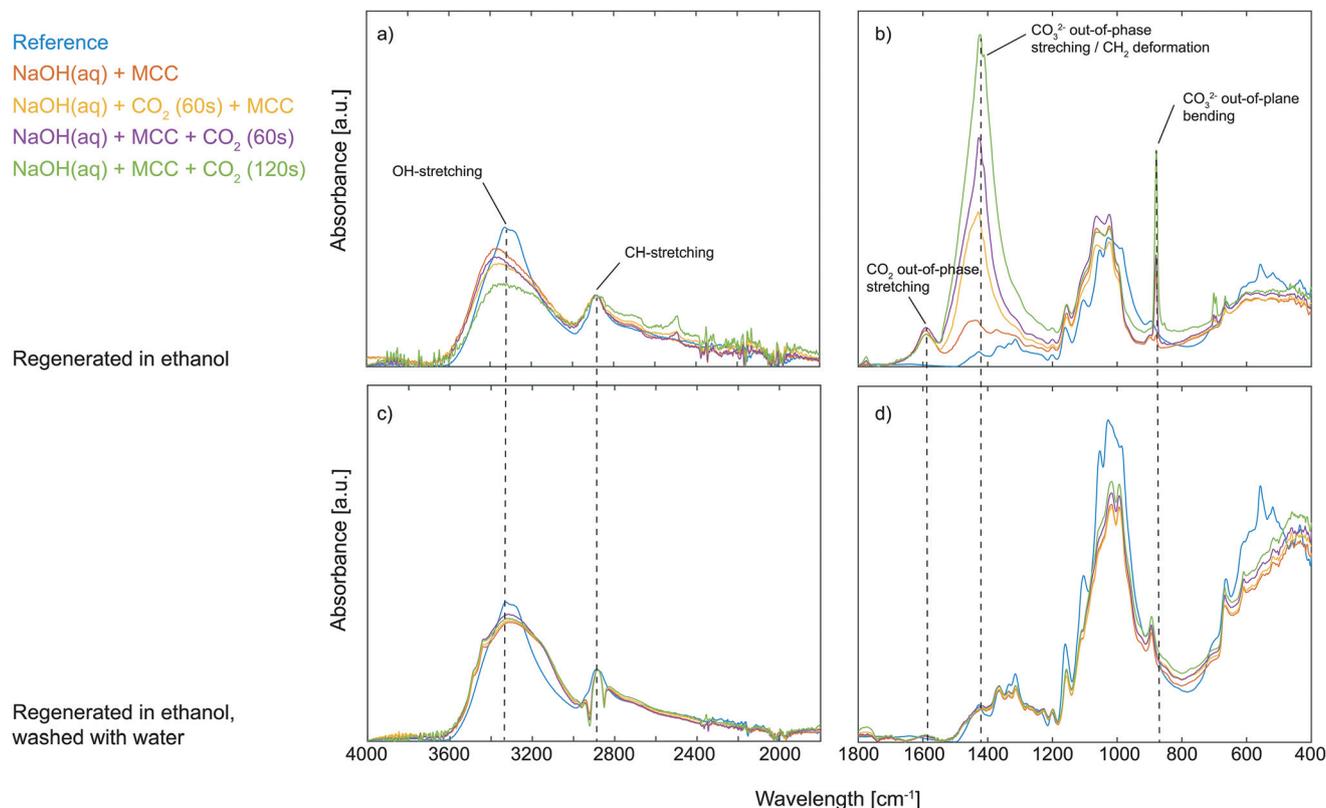

Fig. 2 ATR-IR spectra from 4000–1800 cm^{-1} and 1800–400 cm^{-1} of untreated reference MCC (blue), MCC dissolved in NaOH(aq) (red), MCC dissolved in NaOH(aq) with 60 s pre-dissolution addition of CO_2 (yellow), MCC dissolved in NaOH(aq) with 60 s post-dissolution addition of CO_2 (purple) and MCC dissolved in NaOH(aq) with 120 s post-dissolution addition of 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 OH^- ions due to the extensive CO_2 addition and the formation of Na_2CO_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 CH_2-group on MCC carrying the primary alcohol should be observable as well. Unfortunately, the waveband for CH_2 deformation on MCC is overlapping with the CO_3^{2-} out-of-phase stretching (originating from the Na_2CO_3) and with that said, it is not possible to declare whether this band carries information on the interactions between MCC and CO_2 added pre- or post-dissolution. However, sorption of CO_2 on MCC is evidently taking place when dissolved in NaOH (aq),[7] which explains why the stability of the sorbed 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 CO_2 on MCC indeed is reversible as almost no traces of the waveband for the CO_2 out-of-phase stretching could be detected after washing with water. This indicates that the sorption of CO_2 on MCC in NaOH(aq) is both simple and sustainable in terms of capturing CO_2 as well as the subsequent regeneration by the use of a water-based system.

Impact of CO_2 on a model system

Although ATR-IR spectroscopy provides structural information, many questions are still unresolved such as in which state CO_2 interacts with MCC in a 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,[17] but for polymers such as MCC, the observed peaks are unfortunately broad and featureless. The model compound methyl α-D-glucopyranoside (MeO-Gclp) was therefore instead used, which unlike unprotected glucose or cellobiose does not ring open. The MeO-Glcp was dissolved in either NaCl or NaOH to elucidate the role of the solvent in the sorption of CO_2 in the MCC/NaOH-system. The ^{13}C NMR spectra of MeO-Glcp dissolved in NaCl(aq) and NaOH(aq) (Fig. 3) showed that all carbon peaks in the MeO-Glcp were shifted to higher chemical shift values upon dissolution in

NaOH(aq) compared to 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.[9] 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 NaOH(aq) resulting in an electron-deshielding effect on the carbon atoms.[18] 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 NaOH(aq) compared to NaCl(aq). Having established the deprotonation of the MeO-Glcp in NaOH(aq), the effect of adding CO_2 pre or post-dissolution of MeO-Glcp was evaluated by percolating CO_2 for 30, 60 and 120 s into the solutions. Notably, no precipitation of Na_2CO_3 was observed. In general, the addition of $CO_2(g)$ to NaOH(aq) causes a change in pH due to the consumption of OH^- ions. Thus, as expected, all the carbon peaks in MeO-Glcp were shifted to lower chemical shifts upon the addition of $CO_2(g)$, disregarding pre or post-dissolution addition (Fig. 4a).

Interestingly though, it was observed that the pre or post-dissolution addition of $CO_2(g)$ did not result in an identical change of the chemical shifts of the carbon peaks (Fig. 4b). Namely, the post-dissolution addition of 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 $CO_2(g)$, as well as a combination of both. As the interaction between the available OH^- ions in the solvent and the added 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 ^1H 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 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 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 NaOH(aq) solution at 10 °C (Fig. 4c). The initial pH of the 0.5 M 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 NaOH(aq). From the pH decrement, a degree of deprotonation could be estimated to be around 15% which further suggests the pK_a for the majority of the MeO-Glcp hydroxyls to be higher than 13.8. On the other hand, the pK_a is probably
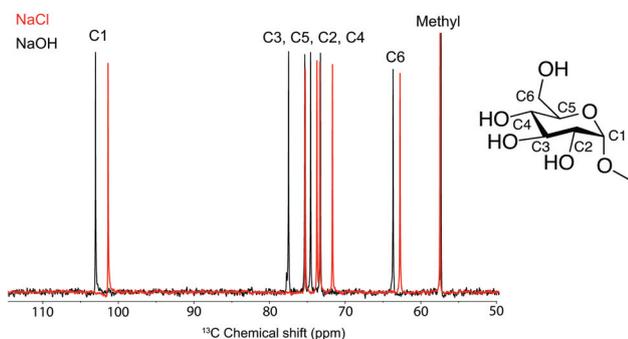

Fig. 3 ^{13}C NMR spectra of MeO-Glcp dissolved in NaCl(aq) and NaOH (aq). All measurements were recorded at +5 °C in D_2O. Inset shows the chemical structure of MeO-Glcp.
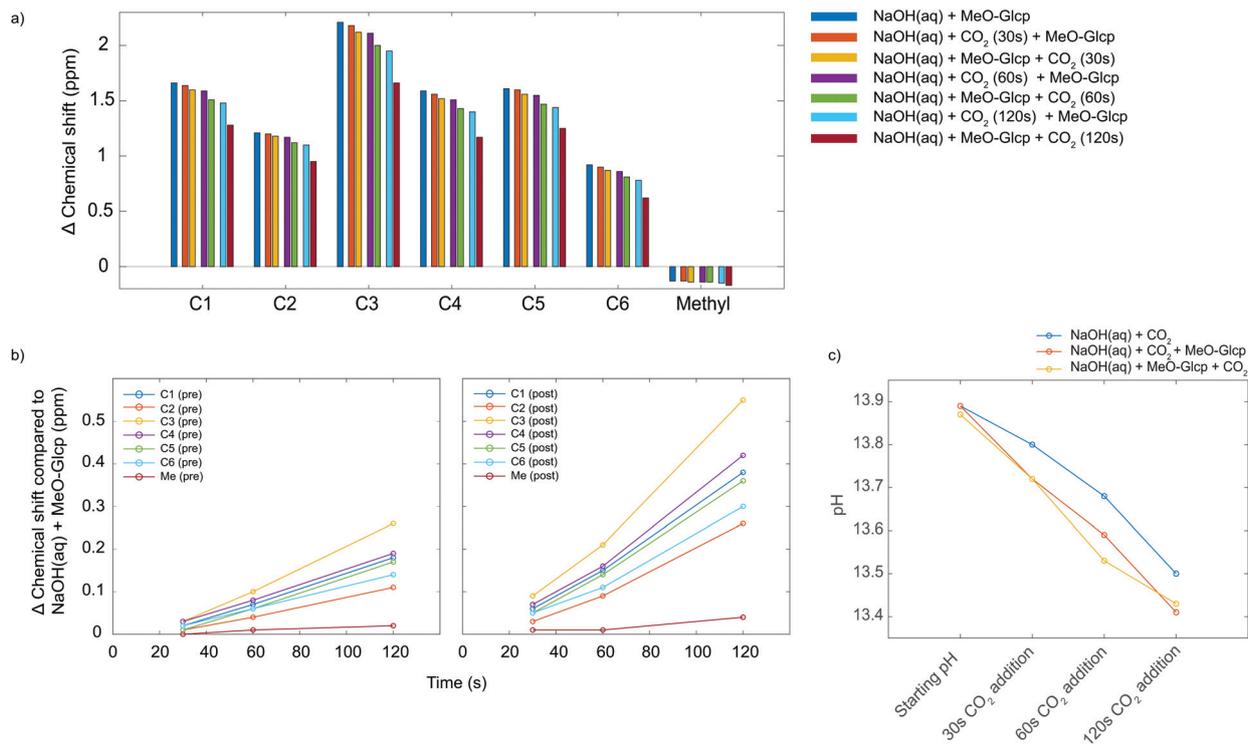
Fig. 4 (a) The difference in chemical shift for MeO-Glcp in NaOH(aq) with pre or post-dissolution addition of CO_2 in comparison with MeO-Glcp in NaCl(aq). All measurements were recorded at +5 °C in D_2O. (b) An extension of the difference in chemical shift for MeO-Glcp in NaOH(aq) with pre or post-dissolution addition of CO_2 in comparison with MeO-Glcp in NaOH(aq). (c) The change in pH for 0.5 M NaOH(aq) with MeO-Glcp and pre or post-dissolution addition of CO_2.

quite close to 13.8 since the pH scale is logarithmic. Moreover, when CO_2 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_2, which means that an equal amount of OH^- ions is consumed in both cases. Therefore, the observed increase in chemical shift change for the solution with post-dissolution addition of CO_2 could not be due to a larger change in pH but rather a difference in interaction with the added CO_2.

As discussed in the Introduction section, several studies on the increased capture of CO_2 in NaOH(aq) have been based on the hypothesis that a deprotonated alcohol reacts with CO_2 in the formation of an organic carbonate[19,20] which in ^{13}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_2 sorption mechanism of alcohols and ethers. As previously reported, both the presence of glycerol and PEG increases the CO_2 capturing ability of NaOH(aq) and several explanations have been presented on this phenomenon, *e.g.* the formation of glycerol carbonate[2] or as an interaction between CO_2 and terminal hydroxyl groups[5,6] or the ether brigde.[21] Surprisingly, no such interactions could be observed in the complementary NMR measurements (see the ESI†), thereby suggesting another mechanism for the increased CO_2 capture in NaOH(aq). On

the other hand, the occurrence of a CO_3^{2-} peak at 171.0 ppm in NaOH(aq) could clearly be observed in ^{13}C NMR, showing that CO_2(g) dissolves and converts, as expected, into CO_3^{2-} 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_2 to NaOH(aq) of different durations (30, 60 or 120 s) correlated well with the integral of the CO_3^{2-} peak. From the peak integral of CO_3^{2-}, the amount of absorbed CO_2 could be calculated which is shown as mol CO_2/mol NaOH in Fig. 5. Comparing the amount of absorbed CO_2 in the system MeO-Glcp/NaOH(aq) with the pre-dissolution addition of CO_2 to pure NaOH(aq) with the same amount of CO_2 added, the amount was observed to be larger, indicating either a stabilising effect of MeO-Glcp on CO_2 (hypothetical coordination through hydrogen bonding) dissolved in NaOH or/and an additional post-dissolution addition of CO_2 from the surrounding air facilitated by the presence of MeO-Glcp in the solution. Interestingly, in the case of MeO-Glcp with the post-dissolution addition of CO_2, the amount of absorbed CO_2 increased even more profoundly and was shown to be more than twice as large as the amount of absorbed CO_2 in pure NaOH(aq). If this would be the result of CO_2 (aq) and OH^- ions converting to CO_3^{2-} in the presence of MeO-Glcp, 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_3^{2-} in the presence of
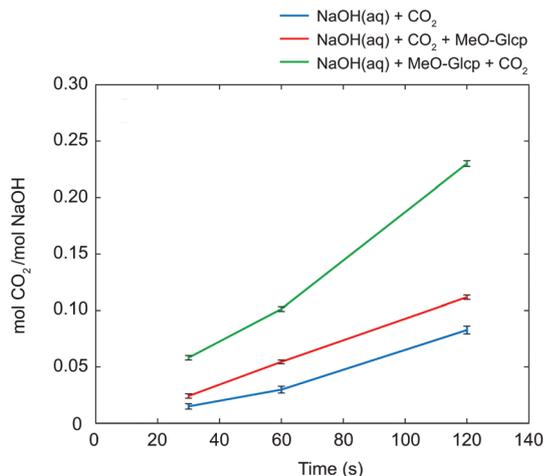
Fig. 5 Amount of CO_2 captured calculated from the integral of CO_3^{2-} at 171 ppm and reported as mol CO_2/mol NaOH with errorbars for NaOH(aq) with the addition of CO_2 (blue), NaOH(aq) with pre-dissolution addition of CO_2 (red) and NaOH(aq) with post-dissolution addition of CO_2 (green). All NMR measurements were recorded at +5 °C in D_2O.

Fig. 6 Possible mechanism for conversion of CO_2 to CO_3^{2-} mediated by MeO-Glcp as the catalyst.

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_2, both pre and post-dissolution. The result showed no effect on either the ^{1}H nor ^{13}C chemical shifts, nor on the integral intensities. A tiny ^{13}C peak of bicarbonate was however observed, indicating that a small amount of CO_2 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_2 or CO_3^{2-} dissolved in NaOH(aq) and, thus increases the amount of CO_2 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_2(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_2(aq), yielding a MeO-Glcp-carbonate intermediate. The MeO-Glcp-carbonate intermediate, which probably is in equilibrium with the free CO_3^{2-} ions in solution, is further readily hydrolysed by water and thereby converted to CO_3^{2-} (Fig. 6). The observed increased tendency of gelation of MCC solutions upon post-dissolution addition of CO_2 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_2 to CO_3^{2-}
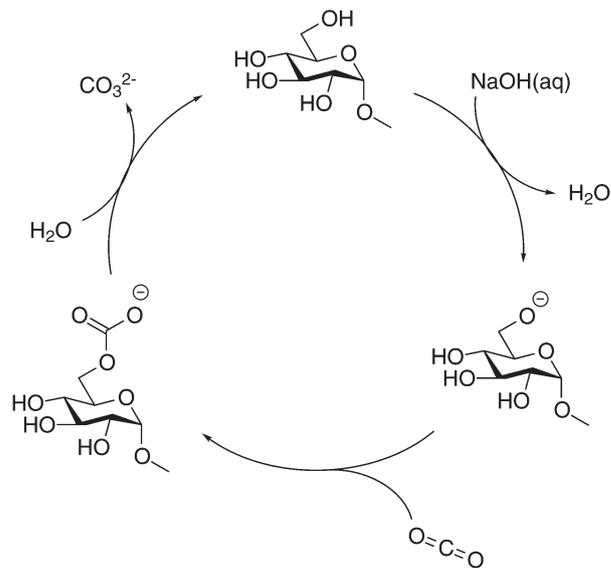
going via the MeO-Glcp-carbonate intermediate with water as the hydrolysing agent (instead of OH^-) leaving the pH of the system largely unaffected. Consequentially, more CO_2 can be captured in the presence of MeO-Glcp or similar alcohols due to their catalytic role in the conversion of CO_2 to CO_3^{2-}. This hypothesis is in line with the results previously reported and concluded by both Faurholt in 1927 and Song in 2017,[2,4] where alcohols such as methanol and glycerol were observed to increase the amount of CO_2 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_2 capture.

Conclusions

In summary, this work elucidates the sorption of CO_2 in NaOH(aq) in the presence of the model compound MeO-Glcp or MCC. The CO_2 capturing capacity of NaOH(aq) was evaluated in terms of pre or post-dissolution addition of CO_2 and was shown, using NMR spectroscopy, to increase drastically when MeO-Glcp was dissolved in NaOH(aq) prior to the addition of CO_2. As a consequence, a significant capture of CO_2 in the system could be observed as CO_3^{2-} in NMR and ATR-IR measurements, while retaining rather constant pH. The potential of using MCC as a CO_2 capturing agent was further evaluated in terms of regeneration of the captured CO_2 and proved to be efficient through just washing the regenerated MCC samples with water. The increased CO_2 capturing ability is explained according to the present findings on the specific interaction of a deprotonated carbohydrate and freshly added CO_2, likely leading to the formation of an organic carbonate intermediate, which was observable on regenerated MCC as CO_2 out-of-phase stretching (1590 cm^{-1}) 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 CO_2 to CO_3^{2-} in terms of the amount of OH^- consumed. Simultaneously, a deprotonated carbohydrate is regenerated upon the release of CO_3^{2-}, and is able to continue into the conversion of CO_2 to 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 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 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 α-D-glucopyranoside (<99%), NaOH (<98%), NaCl and D_2O (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% $MCC : NaOH : H_2O$. 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 D_2O at +5 °C. The MeO-Glcp solution was then added to either NaOH or NaCl in D_2O, maintaining a temperature of −5 °C. The final concentrations of the MeO-Glcp and the NaOH or NaCl in D_2O were 0.4 M and 3.0 M, respectively. 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 CO_2, mounted with a flow regulator set to approximately 1 l 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 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 cm^{-1} and 32 scans. All spectra were corrected against air, baseline corrected and normalised against the CH-band around 2890 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}C NMR spectra were recorded with a low angle radio frequency pulse to minimize relaxation-weighting using a single pulse experiment with ^1H 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 CO_2 while a repetition delay of 5 s was used for the observation of chemical shift differences. A capillary containing D_2O with 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS) was placed inside the tube as the internal reference. The amount of CO_2 captured was converted from the 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.

Acknowledgements

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