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Gunnarsson, M., Bernin, D., Östlund, Å. et al (2018). The CO₂ capturing ability of cellulose dissolved in NaOH(aq) at low temperature. *Green Chemistry*, 20(14): 3279-3286.
<http://dx.doi.org/10.1039/C8GC01092G>

N.B. When citing this work, cite the original published paper.



Cite this: *Green Chem.*, 2018, 20, 3279

The CO₂ 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 CO₂. The stability of cellulose solutions differed significantly when adding CO₂ 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 CO₂ at the molecular level, a ¹³C 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 CO₂ was added prior to or after the dissolution of MeO-Glcp, without a change in pH. The uptake of CO₂ was found to be more than twice as high when CO₂ was added to a solution after the dissolution of MeO-Glcp. Altogether, a mechanism for the observed CO₂ capture is proposed, involving the formation of an intermediate cellulose carbonate upon the reaction of a cellulose alkoxide with CO₂. 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 CO₃²⁻, and thus increased capture of CO₂. The potential of using carbohydrates as CO₂ capturing agents in NaOH(aq) is shown to be simple and resource-effective in terms of the capture and regeneration of CO₂.

Received 6th April 2018,
Accepted 13th June 2018

DOI: 10.1039/c8gc01092g
rsc.li/greenchem

Introduction

Designing renewable materials for the capture of CO₂ is timely and of great importance for environmental challenges. Today, there are several materials capable of efficiently capturing CO₂ 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 CO₂ and to recycle the capturing agent. In this aspect, another interesting system for capturing CO₂ is NaOH (aq). Aqueous hydroxides are in general very efficient CO₂ capturing agents. In theory, to capture 1 ton of CO₂, 0.9 tons of NaOH are needed in comparison with the 1.39 tons of the

commonly used amine, monoethanolamine (MEA). The capture of CO₂ in NaOH(aq) occurs through absorption and conversion of CO₂ by the reaction with hydroxide ions, resulting in different species depending on the pH of the solution. At a pH above 9, all CO₂ is converted to carbonate ions, CO₃²⁻, forming sodium carbonate, Na₂CO₃, a reaction consuming two moles of NaOH for each mole of Na₂CO₃ formed. However, in a recent study it was shown that the CO₂ 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 CO₂ in NaOH(aq) could be doubled if glycerol was added and thereby increase the chemical absorption of CO₂, 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 CO₂. The final products would then be Na₂CO₃ and glycerolcarbonate. Interestingly, it was found that the reaction kinetics between glyceroxide and CO₂ was 6–7 times faster than the reaction between the hydroxide ions and CO₂, and hence a larger amount of CO₂ 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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†Electronic supplementary information (ESI) available. See DOI: 10.1039/c8gc01092g



vidual C–O bonds in CO₂ 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 CO₂ than, *e.g.* poly(ethylene glycol)(PEG),⁵ which is claimed to be a CO₂ capturing polymer through a Lewis base–Lewis acid mechanism between the carbon in CO₂ and the ether oxygen in PEG. Clearly, there are different explanations for the CO₂ 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 CO₂, readily dissolved in NaOH(aq), to a certain extent sorbs onto the dissolved cellulose.⁷ The sorption of CO₂ 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 CO₂ in synthesised organic carbonates, whilst precipitation in water promotes the desorption of CO₂,⁸ which was also observed in our recent study. Both the preservation of sorbed CO₂ as well as the desorption, depending on the type of regenerating agent used, is promising for the application of using cellulose as a sustainable CO₂ capturing agent. As mentioned before, there is to our knowledge still no mechanistic understanding of the CO₂ 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 CO₂ and cellulose in its dissolved state in NaOH(aq). Essential in this investigation is the molecular state of the CO₂ when interacting with cellulose dissolved in NaOH(aq) (*i.e.* CO₂(aq) or CO₃²⁻). Particular emphasis has, thus, been placed on comparative studies exploring the consequences of adding CO₂ pre or post-dissolution of cellulose in a NaOH(aq) system. In the case of CO₂ added prior to the dissolution of cellulose, the high alkalinity of the system can be assumed to completely convert CO₂ into CO₃²⁻, before the cellulose is added to the NaOH(aq). On the other hand, when CO₂ is added to a system already containing dissolved cellulose (post-dissolution addition), CO₂ 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 CO₂ 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 CO₂(g) forming a cellulose carbonate. The deprotonation or dissociation constants of different sugars were actually studied already in the 1950s¹⁰ 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 CO₂(g) to MeO-Glcp dissolved in a NaCl(aq) or NaOH(aq) solution. Furthermore, CO₂(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 CO₂-species as well as the uptake of CO₂.

Results and discussion

Reversible sorption of CO₂ on MCC

Initially, ocular observations were made on the influence of CO₂ addition on the dissolved state of MCC in NaOH(aq), owing to the fact that NaOH(aq) itself is able to absorb CO₂.¹¹ Roughly one litre of CO₂ was percolated into 10 ml of NaOH(aq) solution before or after the dissolution of 4 wt% MCC, denoted as NaOH + CO₂ + MCC and NaOH + MCC + CO₂, 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 CO₂ still remained as a liquid solution while the NaOH + CO₂ + MCC had turned opaque but surprisingly the NaOH + MCC + CO₂ had formed a gelled structure (Fig. 1). Hence, percolating CO₂ disrupts the stability of the MCC solutions, and interestingly, the effect is even more significant when CO₂ is added after the dissolution of MCC in NaOH(aq), thus enabling a direct interaction between the dissolved MCC and the freshly added CO₂ as CO₂(aq), before the conversion to CO₃²⁻ takes place. On the other hand, pre-dissolution addition of CO₂, leading to the conversion of CO₂ to CO₃²⁻ 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

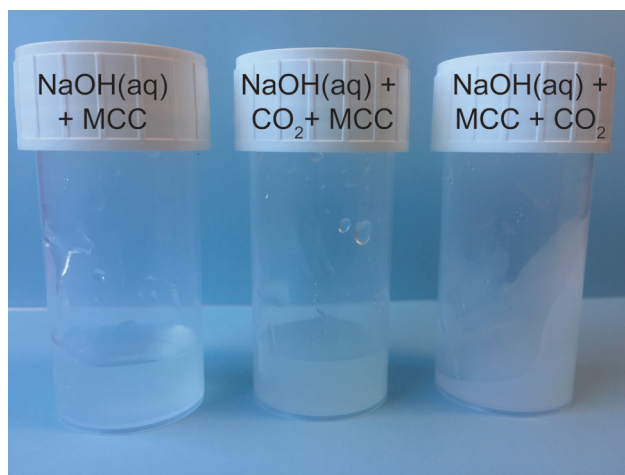


Fig. 1 MCC solutions after two weeks at room temperature. Reference sample NaOH(aq) + MCC (left), NaOH(aq) + CO₂ + MCC (middle), and NaOH(aq) + MCC + CO₂ (right).



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 $\text{NaOH}(\text{aq})$. 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

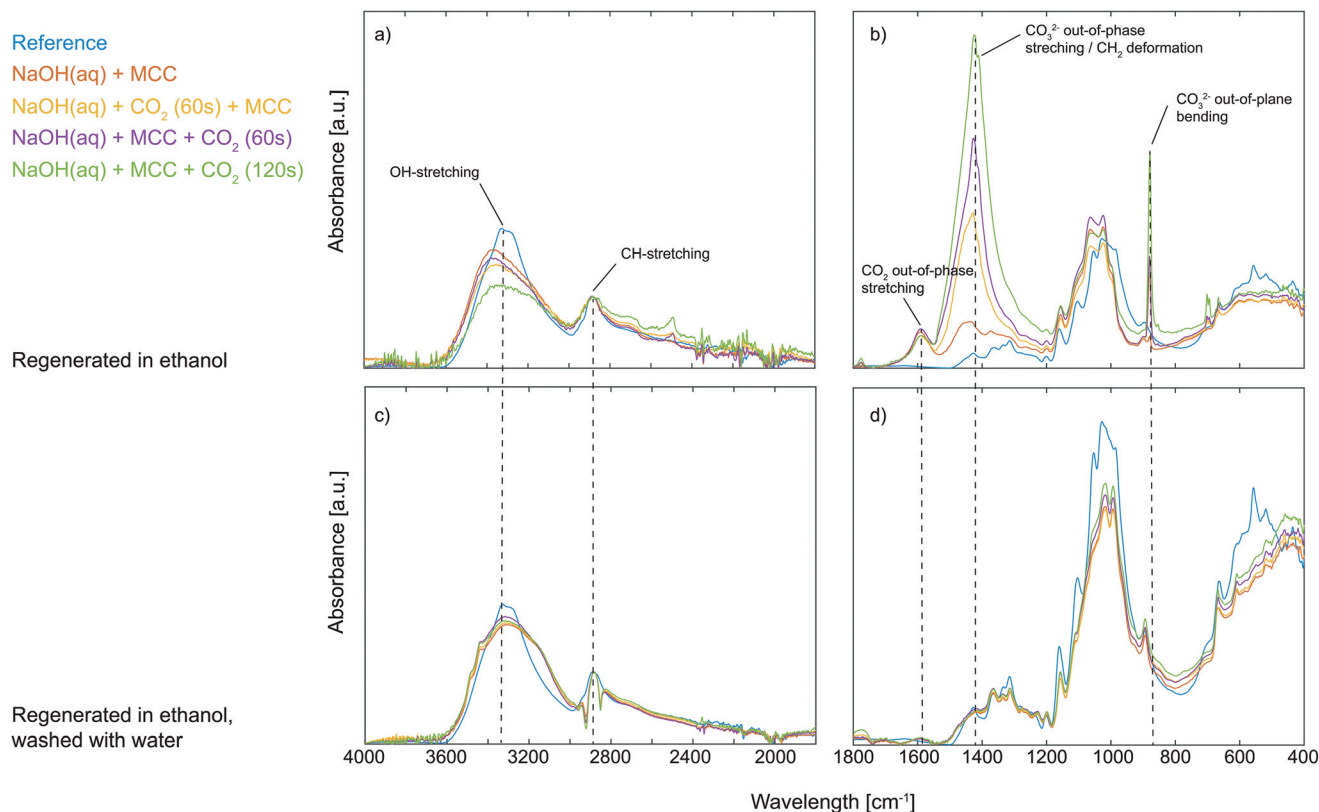


Fig. 2 ATR-IR spectra from $4000\text{--}1800\text{ cm}^{-1}$ and $1800\text{--}400\text{ cm}^{-1}$ of untreated reference MCC (blue), MCC dissolved in $\text{NaOH}(\text{aq})$ (red), MCC dissolved in $\text{NaOH}(\text{aq})$ with 60 s pre-dissolution addition of CO_2 (yellow), MCC dissolved in $\text{NaOH}(\text{aq})$ with 60 s post-dissolution addition of CO_2 (purple) and MCC dissolved in $\text{NaOH}(\text{aq})$ 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-Glcp) 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 $\text{p}K_a$ for the majority of the MeO-Glcp hydroxyls to be higher than 13.8. On the other hand, the $\text{p}K_a$ is probably

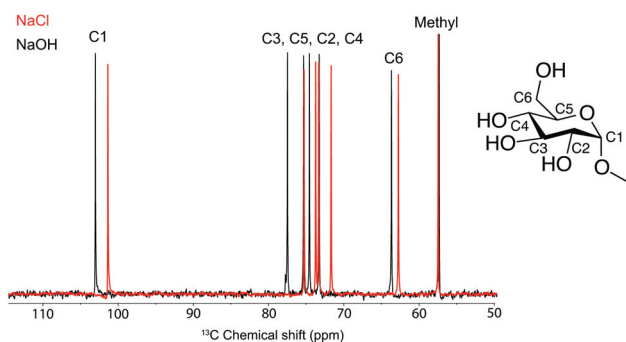


Fig. 3 ^{13}C NMR spectra of MeO-Glcp dissolved in NaCl (aq) and NaOH (aq). All measurements were recorded at +5 °C in D_2O . Inset shows the chemical structure of MeO-Glcp.



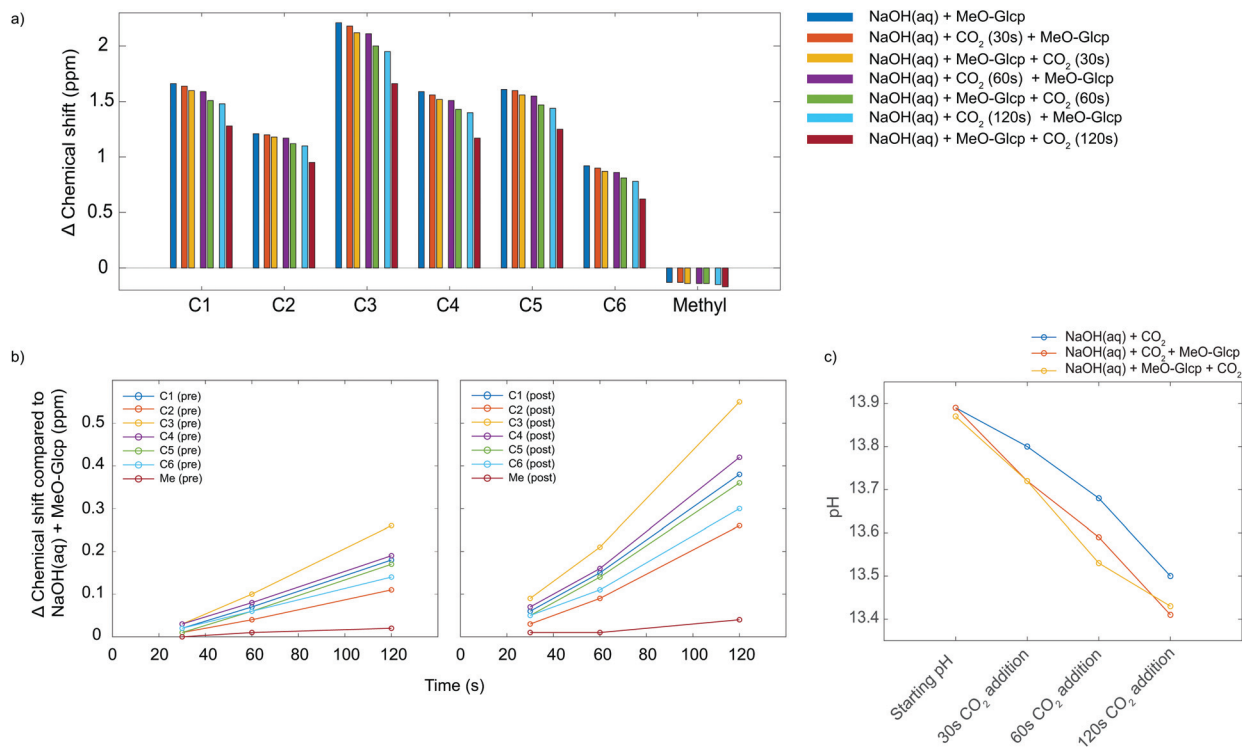


Fig. 4 (a) The difference in chemical shift for MeO-Glep in NaOH(aq) with pre or post-dissolution addition of CO₂ in comparison with MeO-Glep in NaCl(aq). All measurements were recorded at +5 °C in D₂O. (b) An extension of the difference in chemical shift for MeO-Glep in NaOH(aq) with pre or post-dissolution addition of CO₂ 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 CO₂.

quite close to 13.8 since the pH scale is logarithmic. Moreover, when CO₂ 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 CO₂, 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 CO₂ could not be due to a larger change in pH but rather a difference in interaction with the added CO₂.

As discussed in the Introduction section, several studies on the increased capture of CO₂ in NaOH(aq) have been based on the hypothesis that a deprotonated alcohol reacts with CO₂ in the formation of an organic carbonate^{19,20} which in ¹³C 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 CO₂ sorption mechanism of alcohols and ethers. As previously reported, both the presence of glycerol and PEG increases the CO₂ capturing ability of NaOH(aq) and several explanations have been presented on this phenomenon, *e.g.* the formation of glycerol carbonate² or as an interaction between CO₂ and terminal hydroxyl groups^{5,6} or the ether bridge.²¹ Surprisingly, no such interactions could be observed in the complementary NMR measurements (see the ESI†), thereby suggesting another mechanism for the increased CO₂ capture in NaOH(aq). On

the other hand, the occurrence of a CO₃²⁻ peak at 171.0 ppm in NaOH(aq) could clearly be observed in ¹³C NMR, showing that CO₂(g) dissolves and converts, as expected, into CO₃²⁻ 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 CO₂ to NaOH(aq) of different durations (30, 60 or 120 s) correlated well with the integral of the CO₃²⁻ peak. From the peak integral of CO₃²⁻, the amount of absorbed CO₂ could be calculated which is shown as mol CO₂/mol NaOH in Fig. 5. Comparing the amount of absorbed CO₂ in the system MeO-Glep/NaOH(aq) with the pre-dissolution addition of CO₂ to pure NaOH(aq) with the same amount of CO₂ added, the amount was observed to be larger, indicating either a stabilising effect of MeO-Glep on CO₂ (hypothetical coordination through hydrogen bonding) dissolved in NaOH or/and an additional post-dissolution addition of CO₂ 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 CO₂, the amount of absorbed CO₂ increased even more profoundly and was shown to be more than twice as large as the amount of absorbed CO₂ in pure NaOH(aq). If this would be the result of CO₂ (aq) and OH⁻ ions converting to CO₃²⁻ 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 CO₃²⁻ in the presence of



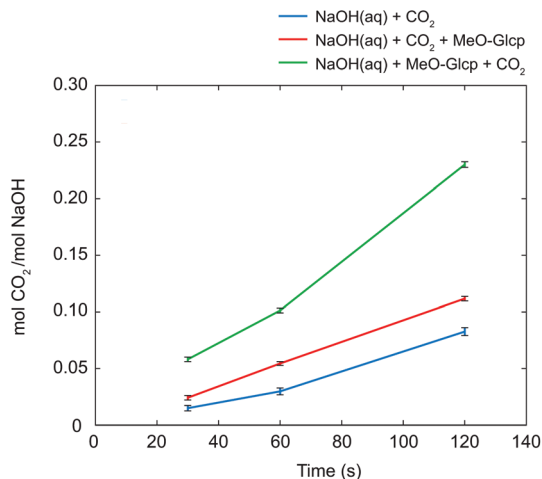


Fig. 5 Amount of CO₂ captured calculated from the integral of CO₃²⁻ at 171 ppm and reported as mol CO₂/mol NaOH with errorbars for NaOH(aq) with the addition of CO₂ (blue), NaOH(aq) with pre-dissolution addition of CO₂ (red) and NaOH(aq) with post-dissolution addition of CO₂ (green). All NMR measurements were recorded at +5 °C in D₂O.

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 CO₂, both pre and post-dissolution. The result showed no effect on either the ¹H nor ¹³C chemical shifts, nor on the integral intensities. A tiny ¹³C peak of bicarbonate was however observed, indicating that a small amount of CO₂ 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 CO₂ or CO₃²⁻ dissolved in NaOH(aq) and, thus increases the amount of CO₂ 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 CO₂(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 CO₂(aq), yielding a MeO-Glcp-carbonate intermediate. The MeO-Glcp-carbonate intermediate, which probably is in equilibrium with the free CO₃²⁻ ions in solution, is further readily hydrolysed by water and thereby converted to CO₃²⁻ (Fig. 6). The observed increased tendency of gelation of MCC solutions upon post-dissolution addition of CO₂ 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 CO₂ to CO₃²⁻

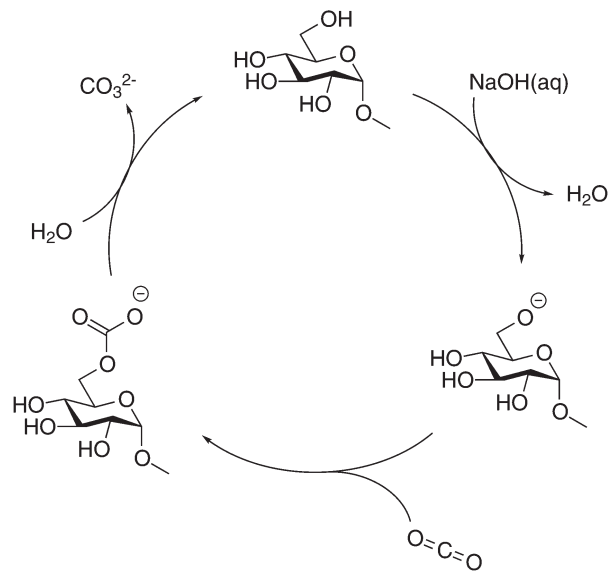


Fig. 6 Possible mechanism for conversion of CO₂ to CO₃²⁻ mediated by MeO-Glcp as the catalyst.

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 CO₂ can be captured in the presence of MeO-Glcp or similar alcohols due to their catalytic role in the conversion of CO₂ to CO₃²⁻. 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 CO₂ 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 CO₂ capture.

Conclusions

In summary, this work elucidates the sorption of CO₂ in NaOH(aq) in the presence of the model compound MeO-Glcp or MCC. The CO₂ capturing capacity of NaOH(aq) was evaluated in terms of pre or post-dissolution addition of CO₂ and was shown, using NMR spectroscopy, to increase drastically when MeO-Glcp was dissolved in NaOH(aq) prior to the addition of CO₂. As a consequence, a significant capture of CO₂ in the system could be observed as CO₃²⁻ in NMR and ATR-IR measurements, while retaining rather constant pH. The potential of using MCC as a CO₂ capturing agent was further evaluated in terms of regeneration of the captured CO₂ and proved to be efficient through just washing the regenerated MCC samples with water. The increased CO₂ capturing ability is explained according to the present findings on the specific interaction of a deprotonated carbohydrate and freshly added CO₂, likely leading to the formation of an organic carbonate intermediate, which was observable on regenerated MCC as CO₂ 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

This work is part of the framework of Avancell – Center for Fiber Engineering, which is a research collaboration between Södra Innovation and Chalmers University of Technology. The authors are grateful to the Södra Skogsägarna Foundation for Research, Development and Education for their financial support.

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