Reply to comment on nickel nanoparticles catalyse reversible hydration of carbon dioxide for mineralization carbon capture and storage

Gaurav A. Bhaduri¹, Richard A. Henderson⁵, Lidija Šiller¹*

1. School of Chemical Engineering and Advanced Materials, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK
2. School of Chemistry, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK

SUPPLEMENTARY INFORMATION

Introduction:

The literature related to the kinetics of non-catalytic hydration of CO₂ has been based on the changes in the equilibrium coefficient of the saturated solution of CO₂¹. (The details of the related theory are given elsewhere²) The methodology of this process of kinetic rate determination consists of mixing a saturated carbonic acid solution (known as CO₂(aq) in papers related to CA) with a buffer or basic solution (preferably Na₂CO₃) and studying the pH change of the mixture. As CA is responsible for the rapid equilibrium of CO₂ in the body³, this change in equilibrium can be utilized to study its reaction kinetics.

The reactions associated with the hydration of CO₂ are stated as:

\[
\begin{align*}
\text{CO}_2(\text{g}) & \rightleftharpoons \text{CO}_2(\text{aq}) \quad 1 \\
\text{CO}_2(\text{aq}) + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{CO}_3 \quad 2 \\
\text{H}_2\text{CO}_3 & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \quad 3 \\
\text{CO}_2(\text{aq}) + \text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \quad 4
\end{align*}
\]

In the saturated solution of CO₂ all the above reactions have been completed and only H⁺ and HCO₃⁻ ions co-exist with dissolved CO₂. As the H₂CO₃ species has a very short life time before they dissociate (eq 3) thus the effective reaction (eqs 2 & 3) can be written as follows⁴

\[
\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-
\]

When the saturated solution of carbonic acid (in equilibrium) is mixed instantaneously with a high pH solution (basic or buffer), the equilibrium (eq 4) is suddenly shifted forward towards the right as the acid is quenched by the base (Na₂CO₃ solution that is commonly used for CO₂ kinetics⁵) or the buffer. This shift towards the new equilibrium depends on the concentration and pH of the base or buffer⁴. If the concentration of the base or buffer is high, this rate of hydration will reduce and can be easily traced by the change in pH of the solution using a pH meter. If the concentration of base or buffer is low the hydration rate is too fast to monitor with pH meter⁶,⁷ so there have been use of spectroscopic methods (like stopped-flow spectrophotometry) which use the an indicator dye⁴,⁵,⁸ to monitor the changes in the pH (for details see Kern⁶ and Palmer and van Eldik⁴ and see references there in). Thus knowing the equilibrium constants (by stopped flow) of the hydration and dehydration reaction, the rate of the forward and backward reaction can be determined. Wang et al⁵ have accurately determined the rate of the hydration and dehydration (non-catalytic) reaction of
CO₂ using stopped-flow spectrophotometry. The rate constants for the reversible hydration of CO₂ have been thus calculated by considering the shift in the equilibrium of the reaction 4. So all above mentioned is valid for liquid-liquid reactions.

Study by Bhaduri and Šiller⁹ is for capture of gaseous CO₂ in DI water (gas-liquid reaction) and the kinetic analysis of the reaction presented by them is for a non-equilibrium based system. Similarly Kim et al¹⁰. bubbled CO₂ in absence and presence of CA in buffer solutions and noted the change in pH and compared the pH profile (gas –liquid reaction) to study their catalytic activity for hydration of CO₂. As pH is the measure of the H⁺ ions; the rate of formation of the acid is measured by studying the pH changes¹⁰.

In the experiments by Bhaduri and Šiller⁹ the pH changes in DI water (or NiNPs suspension) with respect to time was measured when CO₂ gas is bubbled. pH is a function of H⁺ ions concentration due to the acid formation (figure 5 a and 5 c)⁹. In addition the conductivity of the solution was also measured and the leaching of Ni²⁺ ions is minimal as seen from figure 6 (in paper⁹), therefore the changes in conductivity must be related to the formation of carbonic acid alone. In the literature it has been reported that the H⁺ ions catalyse the formation of carbonic acid¹¹,¹² at low pH values, pH range ~ 4.9-4.6 (the alkalinity of the CO₂-H₂O solution is zero and only the acid is present)¹². There is also consensus in literature that the hydration reaction of CO₂ is faster in the presence of hydroxyl groups in solution on pH values above 8¹³. In Figure 5 b, at ~ 80 sec in both DI water with and without NiNPs the conductivity slope is changed, and from Figure 5 a we can read out that the pH at that time is ~4.9 and ~ 4.5, respectively, which is close to the suggested range from ref 16 when H⁺ I on catalysis would exist. This is also observed in Fig 5 d at 120 sec with the similar pH values. Bhaduri and Šiller⁹ reported from XPS results the surface of the nickel have -OH groups, so from the initial value until the pH of 4.5 the gas – liquid hydration reaction is catalysed by OH groups present on the Ni surface. We believe this explains the difference in behaviour of pH profiles in this non-equilibrium reaction.

Methodology:

Sodium carbonate (99%), potassium carbonate (99%) and phenolphthalein (50% alcohol) was bought from Sigma Aldrich and was used without further purification. The CO₂ gas (99%) was bought from BOC, UK. DI water was used for all experiments and had a conductivity of <0.1 μScm⁻¹. The NiNPs were bought from Nano Technologies Inc. Korea and Fe₂O₃ nanoparticles were bought from Nanostructured and Amorphous Materials Inc. USA.

As requested by the comment the methodology by Mirjafari et al⁶ was tried, but were unsuccessful as the reaction was too fast to be monitored by our pH meter (HI2550, Hanna Instruments). Thus stopped-flow spectrophotometry was used to evaluate the kinetic rate as explained above.

For the stopped-flow spectrophotometry the procedure by Wang et al⁵ was followed with a few modifications. Na₂CO₃ solutions of 8mM, 16mM, 24mM, 32mM, and 36 mM were prepared with and without 60 ppm of NiNPs. Saturated CO₂ solution was prepared by adding dry ice in 200 ml of DI water at 15 °C (40mM). The kinetics study was performed using the Applied Photophysics SX18MV stopped-flow spectrophotometer. The kinetics of hydration reaction was studied by mixing CO₂ saturated water with Na₂CO₃ solution (8-36 mM) in a 1:1 v/v ratio. Phenolphthalein was used as an
indicator to monitor the reaction over the wavelength of 553 nm. The data of the reaction was fit using Origin 6.1 software with an exponential fit.

The CO$_2$ bubbling experiment similar to that reported by Bhaduri and Šiller$^9$ was performed by bubbling CO$_2$ at 1 atm pressure (gas flow rate of 1.69 mM/min) in (200 ml) of 0.1 M Na$_2$CO$_3$ solution in a 250 ml glass reactor with a sinter. The temperature of the glass reactor was maintained at 20 °C using a BS5 water bath (Fisher Scientific). The pH was monitored using HI2550 pH meter (Hanna Instruments) and the data was logged to a computer.

Results and Discussion:

![Graph showing kinetic constant as a function of sodium carbonate concentration and an example of the exponential fit of the data.]

Figure 1: Kinetic constant as a function of sodium carbonate concentration and an example of the exponential fit of the data.

The results (figure 1) of the stopped-flow spectrophotometry to determine the rate of NiNPs on the hydration of CO$_2$ was carried out following a similar methodology as Wang et al$^5$. The kinetic constant of the reaction was calculated by fitting the data with an exponential function using Origin 6.1 software (an example of the curve fitting is provided in figure 1). In the stopped flow experiments the concentration of CO$_2$ solution was kept constant and the concentration of carbonate solution was changed. The resultant kinetic constants at different Na$_2$CO$_3$ concentrations are plotted in figure 1. It can be observed that there was no appreciable change in the rate constant of the reaction in the presence of NiNPs. This indicates that the NiNPs did not affect the equilibrium coefficient of the hydration reaction that is reflected by this method of rate determination.
Bhaduri and Šiller\textsuperscript{9} had reported an enhancement in the rate of reaction for gaseous CO\textsubscript{2} and liquid H\textsubscript{2}O\textsubscript{2}, where as in stopped-flow spectrophotometry there is liquid-liquid reaction. Therefore an additional experiment was carried out with bubbling CO\textsubscript{2} in sodium carbonate solution (0.1 M) and the pH changes monitored. It was observed that when gaseous CO\textsubscript{2} bubbled through an aqueous solution of Na\textsubscript{2}CO\textsubscript{3} the initial rate of absorption is faster with the NiNPs than without the NiNPs (Figure 2). The hydration reaction of CO\textsubscript{2} is the most important step in the absorption of CO\textsubscript{2} by different absorbers\textsuperscript{14} that are used industrially. Thus the absorber solution was changed to potassium carbonate and similar results were obtained (figure 2). As seen from the equilibrium studies that the reaction rate of reaction of carbonic acid and sodium carbonate is not catalysed by the NiNPs, but when the same reaction is done in the non-equilibrium based system the enhancement in rate is observed. Thus it was thought that the enhancement that was reported by Bhaduri and Šiller\textsuperscript{9} could be just due to a mass transfer enhancement.

In order to validate whether that the enhancement is caused due to enhancement of mass transfer alone; another experiment was done by replacing the NiNPs with Fe\textsubscript{2}O\textsubscript{3} nanoparticles and bubbled in water (results not shown). Fe\textsubscript{2}O\textsubscript{3} nanoparticle were chosen because it was observed that Fe\textsubscript{2}O\textsubscript{3} nanoparticles also have similar hydroxyl (-OH) groups on their surface when treated with water\textsuperscript{15-18}. It was found that there was no observable change in the pH profile, compared to that of DI water, in the presence of Fe\textsubscript{2}O\textsubscript{3} nanoparticles as is observed with NiNPs. It is thus evident that the enhancement that is being observed is not just related to mass transfer alone.

References