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

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SUPPLEMENTARY INFORMATION

Introduction:

The literature related to the kinetics of non-catalytic hydration of CO_2 has been based on the changes in the equilibrium coefficient of the saturated solution of CO_2[1]. (The details of the related theory are given elsewhere[2]) The methodology of this process of kinetic rate determination consists of mixing a saturated carbonic acid solution (known as $CO_{2(aq)}$ in papers related to CA) with a buffer or basic solution (preferably Na_2CO_3) and studying the pH change of the mixture. As CA is responsible for the rapid equilibrium of CO_2 in the body[3], this change in equilibrium can be utilized to study its reaction kinetics.

The reactions associated with the hydration of CO_2 are stated as:

$$CO_{2(g)} \Longleftrightarrow CO_{2(aq)} \qquad 1$$

$$CO_{2(aq)} + H_2O \Longleftrightarrow H_2CO_3 \qquad 2$$

$$H_2CO_3 \Longleftrightarrow H^+ + HCO_3^- \qquad 3$$

In the saturated solution of CO_2 all the above reactions have been completed and only H^+ and HCO_3^- ions co-exist with dissolved CO_2. As the H_2CO_3 species has a very short life time before they dissociate (eq 3) thus the effective reaction (eqs 2 & 3) can be written as follows[4]

$$CO_{2(aq)} + H_2O \Longleftrightarrow H^+ + HCO_3^- \qquad 4$$

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 (Na_2CO_3 solution that is commonly used for CO_2 kinetics[5]) or the buffer. This shift towards the new equilibrium depends on the concentration and pH of the base or buffer[5]. 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 meter[6, 7], so there have been use of spectroscopic methods (like stopped-flow spectrophotometry) which use the an indicator dye[4, 5, 8] to monitor the changes in the pH (for details see Kern[8] and Palmer and van Eldik[4] 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 al[5] have accurately determined the rate of the hydration and dehydration (non-catalytic) reaction of

CO_2 using stopped-flow spectrophotometry. The rate constants for the reversible hydration of CO_2 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 Šiller[9] is for capture of gaseous CO_2 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 al[10]. bubbled CO_2 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 CO_2. As pH is the measure of the H^+ ions; the rate of formation of the acid is measured by studying the pH changes[10].

In the experiments by Bhaduri and Šiller[9] the pH changes in DI water (or NiNPs suspension) with respect to time was measured when CO_2 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 Ni^{2+} ions is minimal as seen from figure 6 (in paper[9]), 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 acid[1, 11] at low pH values, pH range ~ 4.9-4.6 (the alkalinity of the CO_2-H_2O solution is zero and only the acid is present)[12]. There is also consensus in literature that the hydration reaction of CO_2 is faster in the presence of hydroxyl groups in solution on pH values above 8[13]. 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 Šiller[9] 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 CO_2 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 Fe_2O_3 nanoparticles were bought from Nanostructured and Amorphous Materials Inc. USA.

As requested by the comment the methodology by Mirjafari et al[6] 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 al[5] was followed with a few modifications. Na_2CO_3 solutions of 8mM, 16mM, 24mM, 32mM, and 36 mM were prepared with and without 60 ppm of NiNPs. Saturated CO_2 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 CO_2 saturated water with Na_2CO_3 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 Orgin 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_2CO_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:

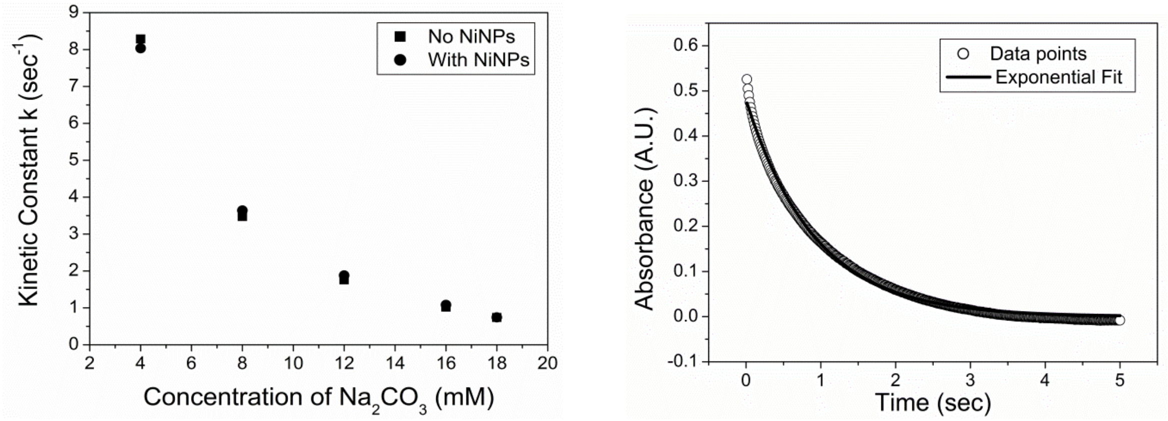

Figure 1: Kinetic constant as a function of sodium carbonate concentration and an example of the exponential fit of the data.

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_2CO_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.

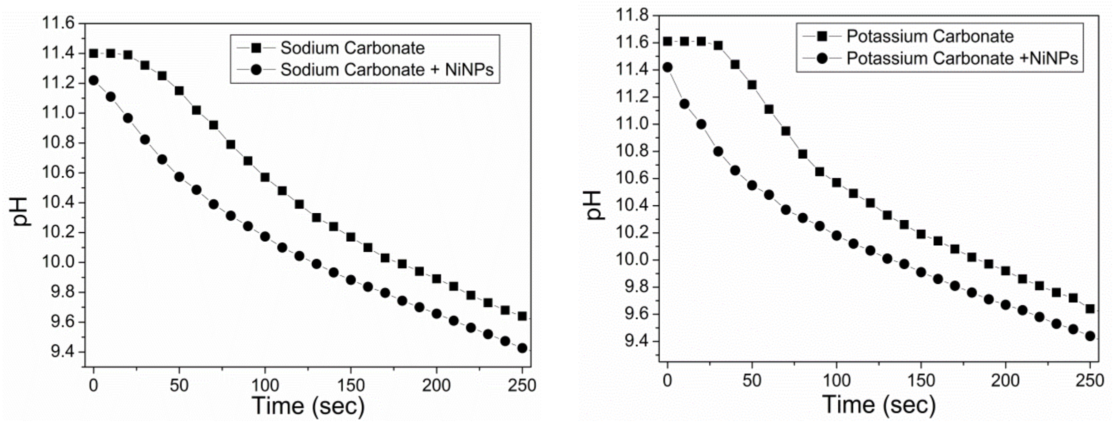

Figure 2: pH profile during bubbling of CO_2 in sodium and potassium carbonate solution with and without NiNPs.

Bhaduri and Šiller[9] had reported an enhancement in the rate of reaction for gaseous CO_2 and liquid H_2O, where as in stopped-flow spectrophotometry there is liquid-liquid reaction. Therefore an additional experiment was carried out with bubbling CO_2 in sodium carbonate solution (0.1 M) and the pH changes monitored. It was observed that when gaseous CO_2 bubbled through an aqueous solution of Na_2CO_3 the initial rate of absorption is faster with the NiNPs than without the NiNPs (Figure 2). The hydration reaction of CO_2 is the most important step in the absorption of CO_2 by different absorbers[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[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_2O_3 nanoparticles and bubbled in water (results not shown). Fe_2O_3 nanoparticle were chosen because it was observed that Fe_2O_3 nanoparticles also have similar hydroxyl (-OH) groups on their surface when treated with water[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_2O_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.

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