

Research Article

Nickel Nanoparticles for Enhancing Carbon Capture

Gaurav Ashok Bhaduri, Mohammed A. H. Alamiry, and Lidija Šiller

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

Correspondence should be addressed to Gaurav Ashok Bhaduri; gabhaduri@gmail.com and Lidija Šiller; lidija.siller@newcastle.ac.uk

Received 28 May 2015; Revised 26 August 2015; Accepted 7 October 2015

Academic Editor: Yibing Cai

Copyright © 2015 Gaurav Ashok Bhaduri et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Hydration reaction of CO₂ is one of the rate limiting steps for CO₂ absorption (in aqueous solutions) and aqueous CO₂ mineralization. The catalytic activity of nickel nanoparticles (NiNPs) for CO₂ hydration is studied at different temperatures, pH, and low CO₂ partial pressures to mimic the true flue gas conditions. Results show that NiNPs can work as active catalyst for hydration of CO₂ in applications such as CO₂ separation and CO₂ mineralization. The NiNPs display optimum activity within 20–30°C and at pH value <8. NiNPs show catalytic activity even at low CO₂ partial pressures (12 vol%). In 50 wt% K₂CO₃ solution, an enhancement of 77% is observed in the rate of CO₂ absorption with NiNPs. Commercially, CO₂ saturated K₂CO₃ solutions are usually regenerated at 150°C; at these conditions, NiNPs show no considerable surface oxidation. They still exhibit catalytic activity for hydration reaction of CO₂. CO₂ absorption and mineralization (as CaCO₃) in DI water are three times higher in presence of NiNPs. Calcite (CaCO₃) particles precipitated in presence of NiNPs are spherical in morphology.

1. Introduction

Recently an increase has been observed in global atmospheric temperatures due to the greenhouse gas emissions resulting from human anthropogenic activities [1]. A major contributor to this global warming is CO₂ emitted from combustion of fossil fuels used for power generation and transportation. Consequently, there is a need for reduction of emitted CO₂ from the atmosphere and its safe storage. The process of separation, transportation, and storage of CO₂ is called carbon capture and storage (CCS) [2, 3].

Hydration of CO₂ is an important reaction in CO₂ absorption or wet chemical conversion of CO₂ to mineral carbonates. Amines and carbonates are widely used for CO₂ absorption separation [4–6]. Amine solutions have higher reaction rates with carbonic acid rather than CO_{2(aq)} [7]. Therefore, enhancing the rate of CO₂ hydration to carbonic acid can increase the rate of CO₂ separation and mineralization. The hydration of CO₂ is a pH dependent reaction with two different reaction mechanisms depending on the pH [8]. At pH values above 10, the reaction follows OH[−] reaction mechanism as shown by (1). At pH values below 8, it follows

a H₂O based reaction mechanism as shown in (2a) and (2b) [8]:



The reaction in (1) is faster than in (2a) having the kinetic rate constant of k_{OH} 8500 M^{−1} s^{−1} and k_{CO_2} 0.03 s^{−1}, respectively [8]. Bhaduri and Šiller [9, 10] observed that the hydration reaction of CO₂ with water is autocatalytic, due to the H⁺ ions generated by the dissociation of carbonic acid (2b) [11].

Carbonic anhydrase (CA) is one of the most studied and effective catalysts for hydration of CO₂ with rate constant of 10⁶ molecules per second [12]. Although CA is very efficient, its limitations include difficulty in recovery of catalyst, as it is a homogeneous catalyst [12], cost of immobilization [13–15], catalysing the reverse reaction at pH values below neutral (i.e., pH < 7) [16], and high extraction and processing costs [17, 18]. Therefore, other homogeneous organic [19, 20]

and inorganic catalysts [6, 21] have been investigated for the hydration of CO_2 . Although these catalysts are cheap, they can be lost during use. Therefore, immobilization of these catalysts becomes an important issue.

Recently, it was reported that nickel nanoparticles (NiNPs) can catalyze hydration of CO_2 [9, 11, 22]. Due to their magnetic properties, the NiNPs can be easily separated from the reaction mixture and recycled [9, 22]. Also, the NiNPs are more cost-effective to manufacture than CA [9]. Han et al. [23] immobilized NiNPs on silica aerogel support and tested the catalytic activity of supported catalyst for hydration of CO_2 . Bhaduri and Šiller [9] reported catalytic activity of NiNPs for CO_2 hydration reaction at pH of 5.5 and 6.5; activity was found to be pH independent. All previous studies [9, 11, 23] on the kinetics of CO_2 hydration in presence of NiNPs have been conducted at 1 atm partial pressure of CO_2 using a 100% CO_2 stream. The influence of CO_2 partial pressure, temperature, and alkaline pH on the activity of CO_2 hydration catalysed by NiNPs has not been investigated previously. Therefore, the purpose of this paper is to study the influence of low CO_2 partial pressure (12% CO_2 -air mix), temperature, and alkaline pH on the catalytic activity of NiNPs for hydration of CO_2 .

Flue gas generally contains 12% of CO_2 [24]; therefore, 12% CO_2 -air mixture is used to test the catalytic activity of NiNPs. At lower partial pressures, a reduction is observed in the rate of CO_2 hydration in the presence of NiNPs. The flue gas is emitted at a temperature of 60°C. Thus it is important to test the catalytic activity of NiNPs at a range of temperatures. Studies are carried out at temperatures between 10°C and 60°C using the methodology previously reported [9]. The NiNPs show optimum catalytic activity within 20–30°C.

Industrially, CO_2 capture is done using alkaline solutions such as amines and carbonates [25]. Therefore, the catalytic activity of NiNPs for hydration of CO_2 is evaluated for neutral and alkaline pH conditions. It is found at neutral pH values (i.e., <8) that the NiNPs are active catalysts for hydration of CO_2 but at higher pH values (i.e., >10) minimal catalytic activity is observed.

Potassium carbonate solutions (50 wt%) are commercially used for the separation of CO_2 [26] from flue gas stream [4, 26]. The K_2CO_3 solution has higher CO_2 loading capacity than amine solutions but is limited by low kinetic rates [26]. Therefore, the rate of CO_2 absorption in K_2CO_3 solutions has been studied using various homogeneous catalyst [5, 26–28]. The use of NiNPs for enhancing CO_2 absorption in K_2CO_3 solution has not been reported. Therefore, the rate of absorption of CO_2 in 50 wt% K_2CO_3 solution with NiNPs is studied. When carbonates are used for the separation of CO_2 from flue gases, the solvent is regenerated by heating the CO_2 saturated bicarbonate solution at 150°C to release the absorbed CO_2 [4, 26, 29]. Therefore, heat treatment of NiNPs was carried out to test the extent of oxidation of NiNP surface.

Bodor et al. [22] reported the use of NiNPs to enhance the mineralization of CO_2 as CaCO_3 and MgCO_3 using alkaline waste as Ca and Mg sources. They found that the rate of CaO and MgO carbonation in slurries can be reduced to half using NiNPs. But at higher solid-liquid ratio in the slurry the NiNPs

were ineffective. Therefore, we have tested the enhancement of the capture and mineralization of CO_2 in DI water as CaCO_3 in presence and absence of NiNPs. We observe that CaCO_3 crystals developed on the NiNPs to form spherical calcite precipitate, thus blocking the active sites of NiNPs and limiting their catalytic activity.

2. Experimental

The NiNPs are bought from NanoTechnology, Korea. Sodium hydroxide, calcium chloride, potassium carbonate, sodium carbonate, Bis-Tris buffer, and concentrated HCl (analytical grade) are purchased from Sigma Aldrich, UK. 99% CO_2 and 12% CO_2 -air synthetic gas were bought from BOC. 18.2 M Ω /cm resistivity water was used for all experiments obtained from Nanopure Barnstead UK.

The Bis-Tris-HCl buffer was prepared by mixing the Bis-Tris buffer in DI water (0.1 M). The pH of the buffer was adjusted by adding drop by drop of concentrated HCl. 0.1 M Na_2CO_3 solution was also prepared by mixing Na_2CO_3 in DI water. Saturated solution was made by bubbling CO_2 in DI water for 4 hours until it saturates. The procedure for qualitative kinetic analysis was carried out by the procedure described by Mirjafari et al. [30]. 20 mL of Bis-Tris-HCl buffer (or Na_2CO_3 solution 0.1 M) was taken in a 50 mL beaker. The pH of the solution was monitored using HI2500 pH meter (Hanna Instruments) in Log mode with data logging after every 5 sec. After 5 stable readings logged in the pH log, 20 mL of saturated CO_2 solution was added to the Bis-Tris-HCl buffer (or Na_2CO_3 solution 0.1 M). The pH was recorded until a stable reading was observed. For the NiNPs catalyst run, 30 ppm suspension of Bis-Tris-HCl buffer (or Na_2CO_3 solution) was prepared and the above process was repeated for this solution. The experiment was performed three times and the average of the results is presented.

The CO_2 hydration kinetics experiment was performed similar to the method used by Bhaduri and Šiller [9]. The CO_2 hydration rate was carried out in a 250 mL glass jar within a fixed volume (200 mL) of DI water (or 30 ppm NiNPs suspension). The CO_2 gas was sparged into the solution at a flow rate of 50 mL/min at 0.1 MPa pressure using a glass sinter (Pyrex 1, Sigma Aldrich, UK). The pH changes of the solution are monitored during the bubbling experiments using a HI2500 pH meter (Hanna Instruments). The readings were at an interval of 20 seconds. The temperature of the sample was maintained by immersing the glass jar in a water bath (BS5, Fisher Scientific) at different temperatures (i.e., 10°C, 20°C, 30°C, 40°C, 50°C, and 60°C, resp.). The same experiment with 12% CO_2 -air synthetic gas 20°C is repeated five times and its average results are presented.

The CaCO_3 precipitation experiments were carried out using the following methodology. 100 mL of DI water (or 30 ppm NiNPs suspension) was taken in a 150 mL glass jar and was bubbled with CO_2 with a flow rate of 1.96 mL/min, at 0.1 MPa pressure different time intervals (i.e., 0.5 hr, 1 hr, 2 hrs, and 4 hrs, resp.). To the respective CO_2 saturated samples were added 10 mL of 1 M NaOH solution and 10 mL of 1 M CaCl_2 solution. The samples were stirred and the calcium carbonate was allowed to precipitate in the glass jar.

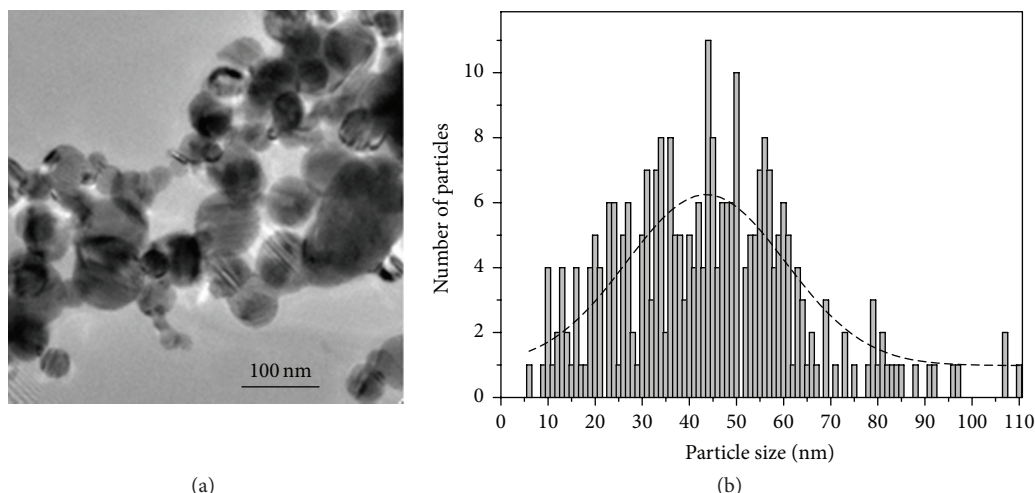


FIGURE 1: (a) HRTEM image of the NiNPs and (b) particle size distribution of nickel NiNPs determined by HRTEM.

The precipitates are filtered using a vacuum filter using a Watman 54, air dried at 60°C for 1 hour, and then weighted. The CaCO₃ precipitated in the presence of NiNPs were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD) for shape and structural determination. All experiments have been repeated three times and average data is presented.

To study the influence of NiNPs on the absorption rate of CO₂ in K₂CO₃ solutions, the 50% (by weight) K₂CO₃ solution was prepared in 50 mL DI water. For the NiNPs suspension-K₂CO₃ solution, 1.5 mg of NiNPs was added into 50% K₂CO₃ solution and sonicated in the ultrasonic bath at constant temperature to make a 30 ppm solution. The concentration of 30 ppm was selected based on our previous studies [9]. The CO₂ absorption experiments are performed in a 180 mL glass jar (Wheaton Industries, UK). The solution with the glass bubbler (Pyrex 1) was assembled and weighed before the introduction of CO₂. The CO₂ gas was bubbled at a flow rate of 1.69 mM/min at a pressure of 0.1 MPa. The final weight was obtained when there was no further possibility of gas flow through the bubbler. The gas bubbler was blocked by the formation of potassium bicarbonate crystals on the glass bubbler. The entire absorption experiment was carried out at 20°C using a water bath (BS5, Fisher Scientific). All the above experiments were carried out in triplets and average data is presented.

For the heat treatment, the NiNPs were placed in a silica crucible and heated in an oven at 150°C for 8 hours. The NiNPs was kept in an air tight container with ample desiccator beads to absorb any moisture present until further use. X-ray photoelectron spectroscopy (XPS) of the NiNPs before and after heat treatment was carried out using (Kratos Axis Ultra) equipped with a monochromatic Al K α X-ray source, with a pass energy of 20 eV. The spectra were fitted with Shirley background [31] and mixed singlet peaks [32]. The spectra were calibrated by assigning the C 1s peak at 284.4 eV to adventitious carbon [33, 34]. All binding energy values reported are within an error of ± 0.1 eV. The CO₂ hydration catalysis using the heat treated NiNPs was carried

out using the same methodology used for temperature dependent kinetics mentioned above. CO₂ catalysis was carried out for the heat treated NiNPs using same methodology as Bhaduri and Šiller [9] at room temperature and atmospheric pressure. The kinetic analysis of the heat treated NiNPs and DI water was carried out in triplet and average data is presented.

3. Results and Discussions

3.1. HRTEM and Particle Size Distribution of Nickel Nanoparticles. Figure 1(a) shows the high resolution transmission electron microscope images of the commercially purchased NiNPs to determine their size distribution. The particle size distribution of the nanoparticles based on statistical analysis is presented in Figure 1(b). The average particle size of the NiNPs was determined by fitting the distribution curve with a Gaussian function and was ~ 43 nm. The majority of the particles smaller than the prescribed manufacture size of 100 nm.

3.2. Kinetics of CO₂ Hydration Reaction with NiNPs at Low Partial Pressure of CO₂. It is known that the rate of CO₂ hydration is dependent on the concentration of CO_{2(aq)} [4, 9, 35]. CO_{2(aq)} concentration depends on the partial pressure of CO₂ in the gas phase. As the partial pressure decreases in the gas phase, the concentration of CO₂ molecules decreases at the interface and thus the reaction kinetics should decrease [35].

Figure 2(a) shows the change in pH of DI water and NiNPs suspension when 100% CO₂ gas is bubble in them, respectively. Figure 2(b) shows that the pH change is still more rapid in the presence of NiNPs in suspension as compared to DI water when 12% CO₂-air gas mixture is bubbled through them, respectively. This result is similar to the results observed previously [9]. The results in Figure 2(c) show that the catalytic hydration rate of CO₂ (in presence of NiNPs) slightly decreases when the partial pressure of the CO₂ in the gas phase is decreased. However, it can be

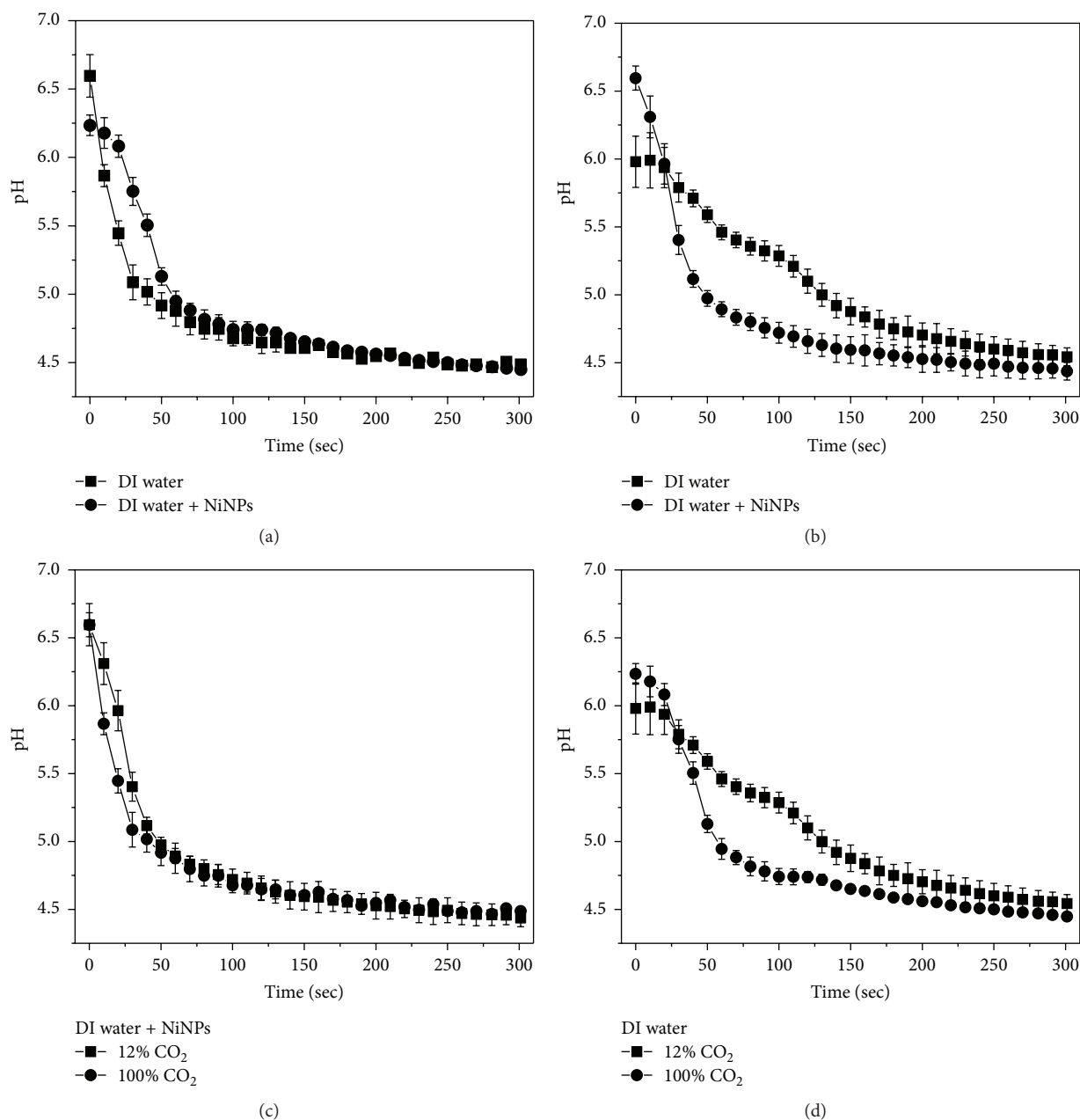


FIGURE 2: (a) pH changes when 100% CO₂-air mixture is bubbled in DI water and 30 ppm NiNPs suspension, (b) pH changes when 12% CO₂-air mixture is bubbled in DI water and 30 ppm NiNPs suspension, (c) pH change when 12% and 100% CO₂ is bubbled in 30 ppm NiNPs suspension, and (d) pH change when 12% and 100% CO₂ is bubbled in DI water.

observed from Figure 2(d) that the autocatalytic activity of CO₂ hydration in DI water is highly reduced when the partial pressure of CO₂ is reduced. This proves the assumption made previously about partial of CO₂ affecting the rate of CO₂ hydration.

All the above data suggest that in the presence of the NiNPs the rate limiting step is the transfer of CO_{2(g)} to CO_{2(aq)} rather than the hydration of reaction of CO₂. The reduction in rate of CO₂ hydration (observed as the rate of pH change in Figure 2(c)) is due to the slow gas-liquid mass transfer due to the low partial pressure of CO₂.

3.3. pH Dependence of Catalytic Activity of NiNPs for CO₂ Hydration Reaction. A qualitative method was used to test the pH dependence of the NiNPs' activity for CO₂ hydration. The methodology was adapted from kinetic study of CA hydration as described by Mirjafari et al. [30] on recommendation of Britt [36]. Bis-Tris-HCl buffer has terminal OH groups for regulation of pH. As the NiNPs also have OH groups on their surface when dispersed in water [9], the adsorption of buffer would thus be limited. Figure 3 shows the pH changes in Bis-Tris-HCl buffer (Figure 3(a)) and sodium carbonate solutions (Figure 3(b)) when a CO₂

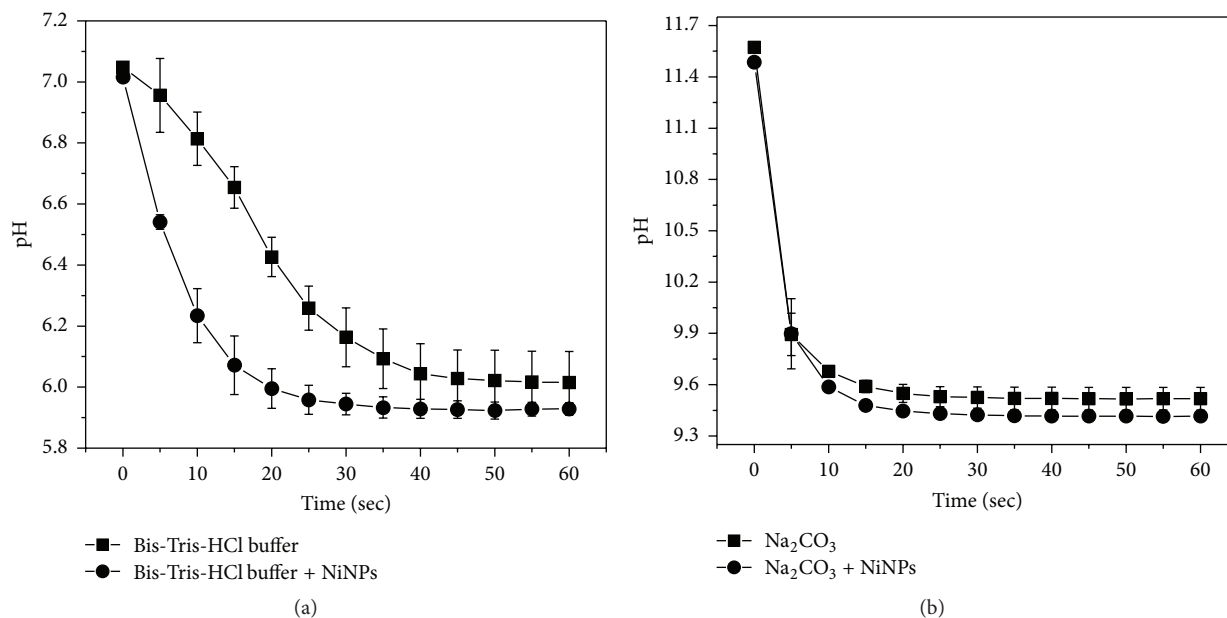


FIGURE 3: pH dependent hydration of CO₂ in presence of NiNPs at different pH (a) at pH 7 using Bis-Tris-HCl buffer and (b) at pH 11.5 using sodium carbonate solution.

saturated solution was added. Figure 3(a) shows a faster pH drop in Bis-Tris-HCl buffer solution with addition of NiNPs. This indicates an increase in catalytic activity due to the presence of NiNPs at pH values below 8 with CO₂ hydration following the reaction mechanism described by (2a) (see Section 1) [8]. Figure 3(b) shows the pH changes at alkaline pH values (i.e., pH > 10) in Na₂CO₃ solution. The NiNPs catalysis is minimal at alkaline pH (i.e., pH > 10) but can be observed when the pH drops below 10 (Figure 3(b)). Above pH 10, CO₂ hydration can be described by (1) (see Section 1) whilst it operates via a mixed mechanism ((1) and (2a)) at pH values between 10 and 8 [8]. Therefore, NiNPs catalysis cannot be observed at alkaline pH values above 10 but can be observed at pH values below 10.

3.4. Temperature Dependent Kinetics of Catalytic Hydration Reaction of CO₂ with NiNPs. NiNPs catalysis is analysed by observing the rate of change of pH when CO₂ is bubbled in DI water or NiNPs suspension. The change in pH is due to the formation of carbonic acid in solution. The results show (Figures 4(a)–4(f)) that in the presence of NiNPs the pH drop is more rapid than in its absence, but in the DI water system, there is an initial slow decrease in pH followed by a rapid decrease in pH. This is an autocatalytic behaviour of CO₂ hydration first observed by Bhaduri and Šiller [9] and is explained to be caused by the presence of H⁺ ions (see Supplementary Information of [11] in Supplementary Material available online at <http://dx.doi.org/10.1155/2015/581785>). Similar behaviour is observed in the current study. Due to the autocatalytic activity of hydration of CO₂ in DI water, the interpretation of the catalytic activity of NiNPs is done by observing the proximity of the catalysed and uncatalysed curves to one another. If the catalysed and uncatalysed curves

are close to one another, the catalytic activity of NiNPs is low but if they are further apart from one another the catalytic activity of the NiNPs is high.

Figures 4(a)–4(f) show the catalytic activity of NiNPs at all the tested temperatures. As the temperature changes, the proximity between the two curves (catalysed which is indicated with filled circles and uncatalysed which is indicated with filled squares) also changes mainly due to a change in the reaction kinetics of the uncatalysed hydration of CO₂. A higher catalytic activity was observed for the NiNPs to catalyse the hydration of CO₂ at ambient temperatures (20–30°C) than that at lower (10–20°C) or higher (40–60°C) temperatures, respectively. For all the profiles for the pH change for noncatalytic reaction (the filled squares in Figures 4(a)–4(f)) of CO₂ hydration in DI water there is an initial slow change in pH followed by a rapid change in pH; these results are similar to the observations made by Bhaduri and Šiller [9]. It is evident from Figure 4(c) that the reaction rate of CO₂ hydration in DI water is slower at 30°C than at other temperatures. The NiNPs suspension shows similar pH change profile at all tested temperatures. The observed changes in kinetic rates are likely due to the adsorption/desorption of water or CO₂ on the NiNPs surface which is affected with temperature [37, 38] along with the solubility of CO₂.

3.5. Enhancing CO₂ Uptake in Potassium Carbonate Solution with NiNPs. In the current study, gravimetric method was used to study the enhancement of CO₂ in carbonate solutions. Figure 5 shows the results of gravimetric uptake of CO₂ in 50 wt% K₂CO₃ solution in the absence and presence of NiNPs. The experiment was run until no additional change in the weight of the reaction vessel was observed. The reaction

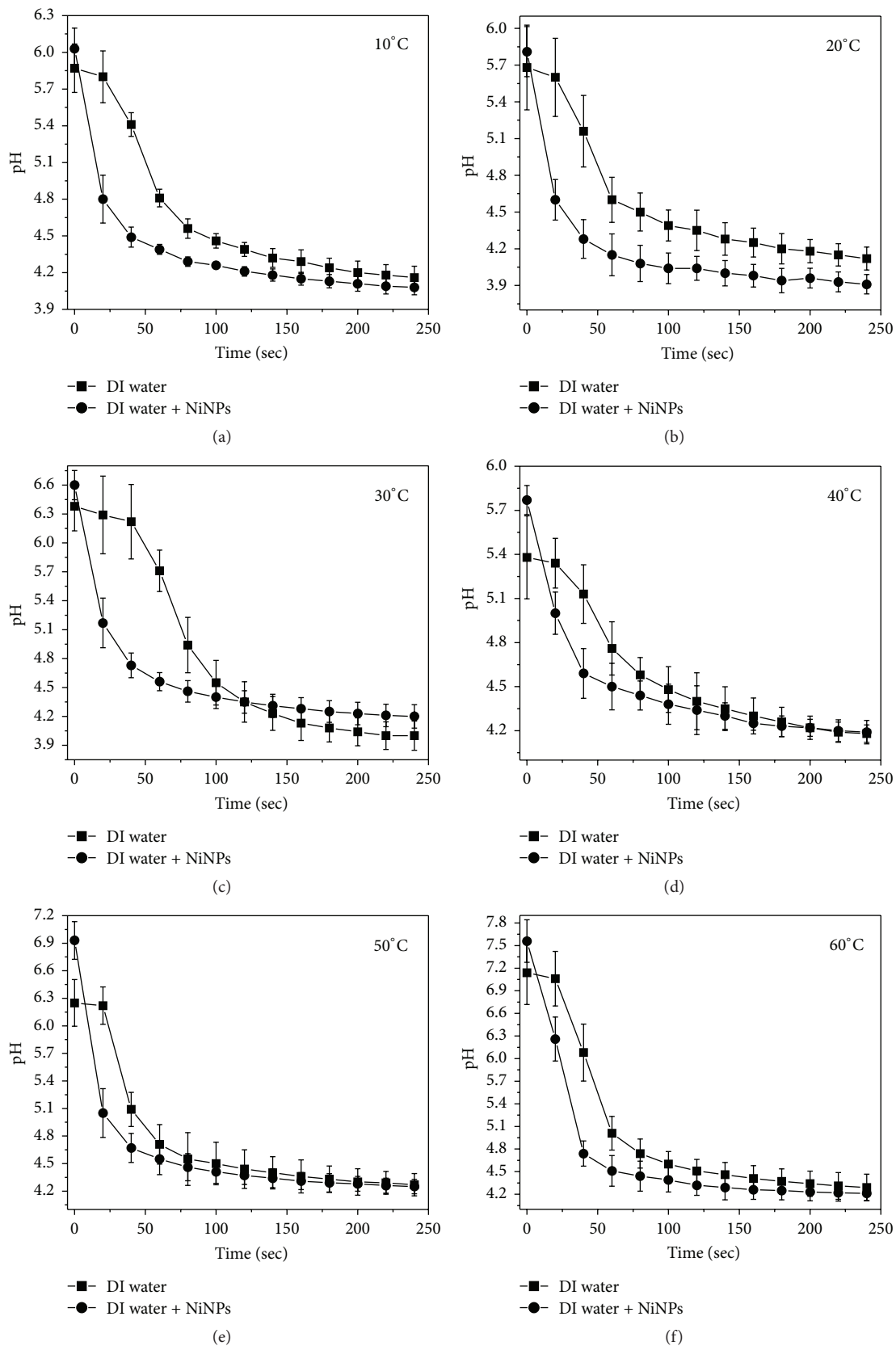


FIGURE 4: Change in pH of DI water (square) or NiNPs suspension (circle) when CO_2 is bubbled through liquid maintained at temperatures (a) 10°C, (b) 20°C, (c) 30°C, (d) 40°C, (e) 50°C, and (f) 60°C.

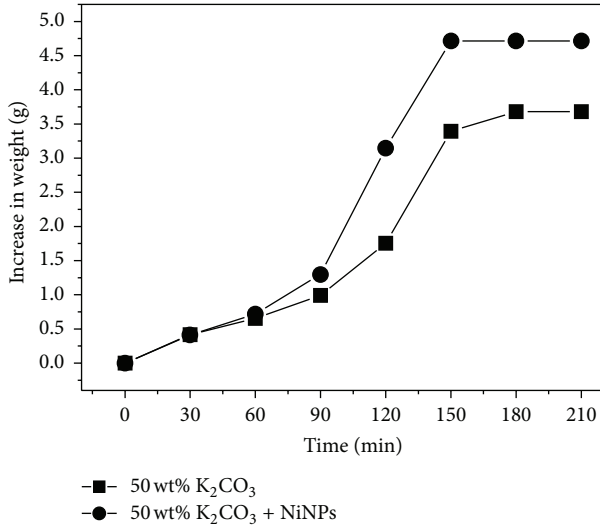


FIGURE 5: Increase in weight of 50 wt% K₂CO₃ solution with and without NiNPs when CO₂ is bubbled in it.

in the reactor can be represented by the following reaction equations:



Carbonate solutions (K₂CO₃ and Na₂CO₃) have a high pH (i.e., >11) and as CO₂ is bubbled into the carbonate solution its pH drops [11]. The reaction 3a takes place when the K₂CO₃ is instantaneously dissolved in DI water and CO₂ hydration reaction takes place via reaction (3b) till the pH reaches 10 [8]. Reaction mechanisms (3b) and (3c) simultaneously occur between pH 10 and 8 with reaction (3c) being the slowest step [8]. Reactions (3d) and (3e) like (3a) are instantaneous [39]. Thus, CO₂ hydration is the most important step in the CO₂ capture when using potassium carbonate solutions. Therefore, in summary, as the CO₂ and carbonic acid start reacting with the carbonate solution, the pH of the solution changes and the reaction mechanisms of CO₂ hydration changes [11] from (3b) to (3c) depending on the pH of the solution [8]. From Figure 5, it can be observed that initial rate of CO₂ absorption is similar for 50 wt% K₂CO₃ solution both with and without NiNPs catalyst but after 60 minutes the rate of reaction is faster in presence of the NiNPs. This kind of enhancement in CO₂ absorption is a result of the carbonate-bicarbonate buffering ability of carbonate solutions. Pinsent and Roughton [40] report that the rate of CO₂ hydration increases as the bicarbonate/carbonate ($[\text{HCO}_3^-]/[\text{CO}_3^{2-}]$) ratio increases. Therefore, as CO₂ reacts with the carbonate solution, the bicarbonate ions are formed (following reaction (3b)) (the value of the numerator increases while that of

TABLE 1: Rate of CO₂ absorption in K₂CO₃ solutions with and without NiNPs.

System	Rate (moles/min)	Regression (R^2)
Potassium carbonate	0.0048	0.963
Potassium carbonate + NiNPs	0.00852	0.971

the denominator decreases), leading to the observed autocatalytic enhancement absorption of CO₂.

Figure 5 shows that in the presence of NiNPs there is the increase in weight of the carbonate solution (after saturation) due to enhanced kinetic rate of CO₂ hydration (but lower than the full capacity of the carbonate solution, which is 15.92 g, if there is 100% conversion of K₂CO₃ to KHCO₃). There is an increase in CO₂ loading (mol of CO₂ per mol of K₂CO₃) by ~27%.

In Figure 5, the rapid increase in CO₂ absorption after 60 min until saturation is used to estimate the enhancement in absorption rate of CO₂ in carbonate solutions in presence of NiNPs. The data points between 60 min and saturation are linearly fitted (see Supplementary Figure S1) and the data is shown in Table 1. It can be observed that the data showed a good linear fit ($R^2 > 0.96$) and the slope can be used to compare the enhancement in rate. There is ~77% increase in the absorption rate of CO₂ in carbonate solution in the presence of NiNPs under the same operating conditions.

3.6. Heat Treatment of NiNPs. Carbonate solutions are generally regenerated at a temperature of 150°C [4, 26, 29]; therefore, in order to use NiNPs as enhancers in carbonate separation technology a set of experiments were performed to test the effect of heating on the catalytic activity of NiNPs. The NiNPs were heated at 150°C for 8 hours to study the changes in surface chemistry and its catalytic activity for CO₂ hydration. XPS analysis was done before and after heat treatment in order to check any surface chemistry changes due to heating.

Figure 6 shows the surface species present on the NiNPs surface before and after heat treatment. Three different species were observed in Ni 2p_{3/2} spectra for NiNPs before and after heat treatment, respectively. In Figure 6(a), the peaks at 852.5 eV, 854.1 eV, and 855.7 eV can be assigned to Ni⁰, NiO, and Ni(OH)_x, respectively [41–44], and in Figure 6(b) the peaks at 852.4 eV, 854.0 eV, and 855.7 eV can be assigned to Ni⁰, NiO, and Ni(OH)_x, respectively [42–44]. The peak at 861.0 eV in Figure 6(a) (or 860.9 eV in Figure 6(b)) is assigned the value for a collective plasmon peak of Ni [9, 33, 34]. No change in the peak positions of the Ni and NiO is observed (peaks are within the experimental error limit of ±0.1 eV) after heat treatment, although after heat treatment there is a 27% increase of oxide on the surface. The presence of the two peaks in the O 1s spectra shows the presence of oxygen in two oxidation states. In Figure 6(c), the peak at 529.3 eV corresponds to NiO [41] whereas the peak at 531.0 eV corresponds to NiOH_x [45]. The existence of the NiOH_x is due to the dissociative adsorption of water from the atmosphere. It is known that the OH bond on the surface has a binding energy difference of 1.8 eV higher than that of

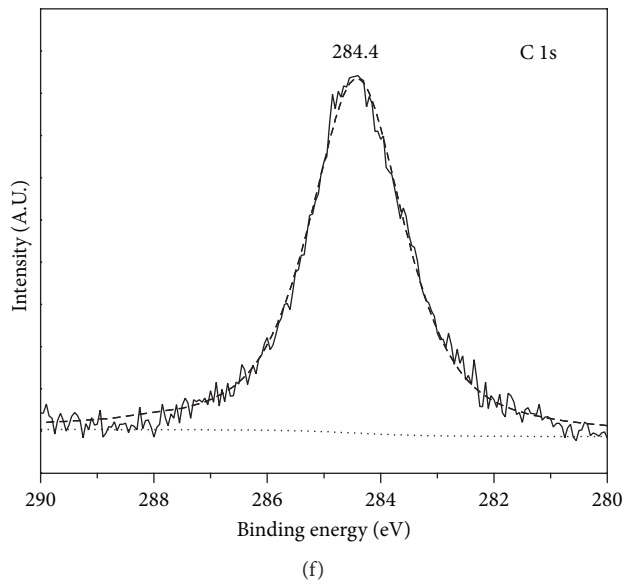
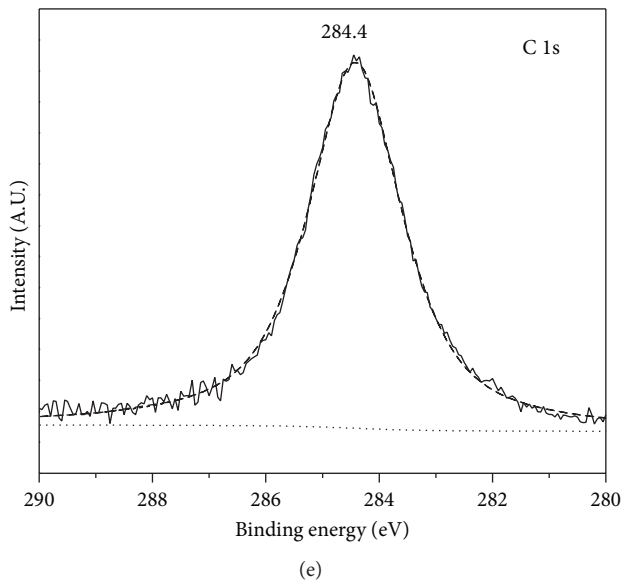
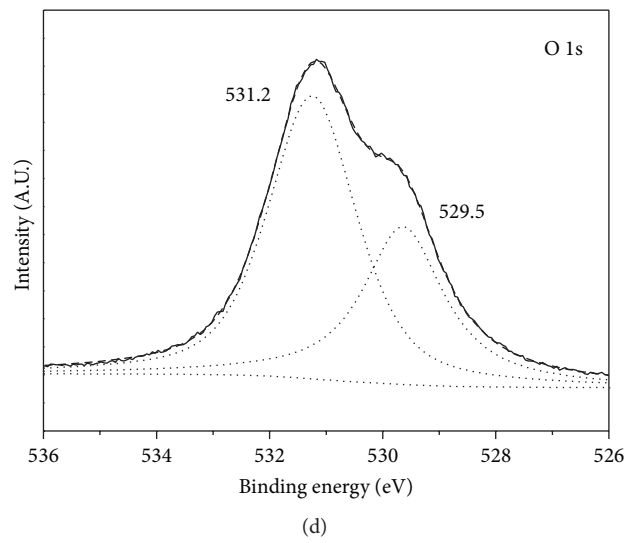
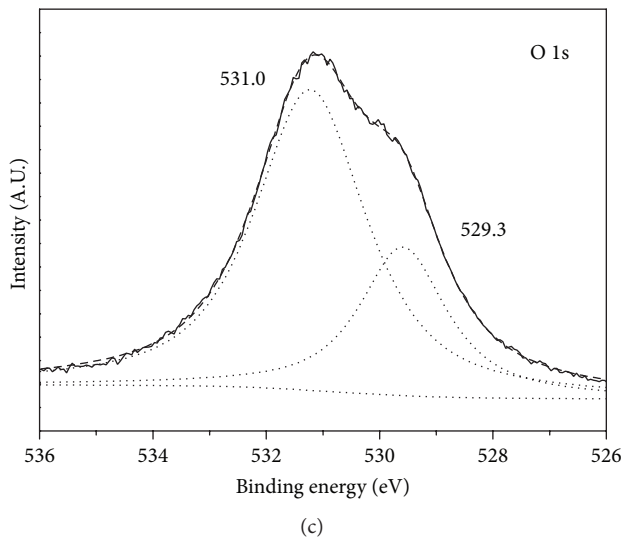
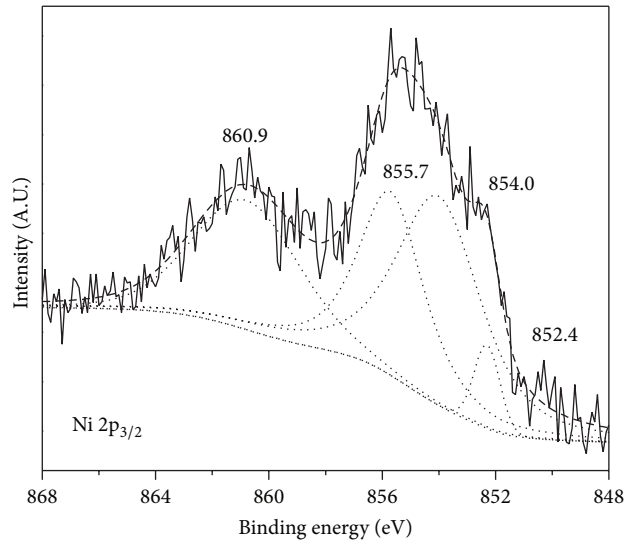
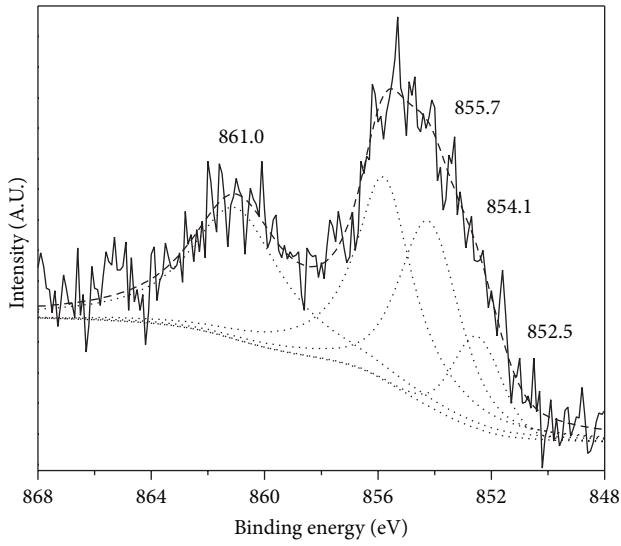


FIGURE 6: Continued.

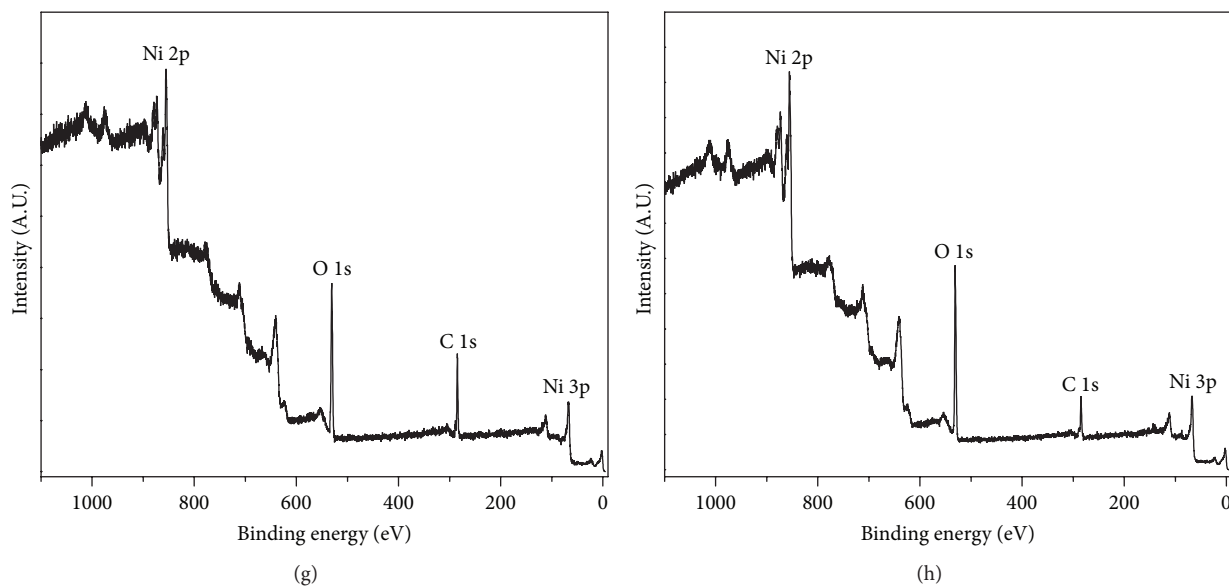


FIGURE 6: XPS results of the NiNPs before ((a) Ni $2p_{3/2}$, (c) O 1s, (e) C 1s, and (g) survey) heat treatment and after ((b) Ni $2p_{3/2}$, (d) O 1s, (f) C 1s, and (h) survey) heat treatment at 150°C for 8 hours in air.

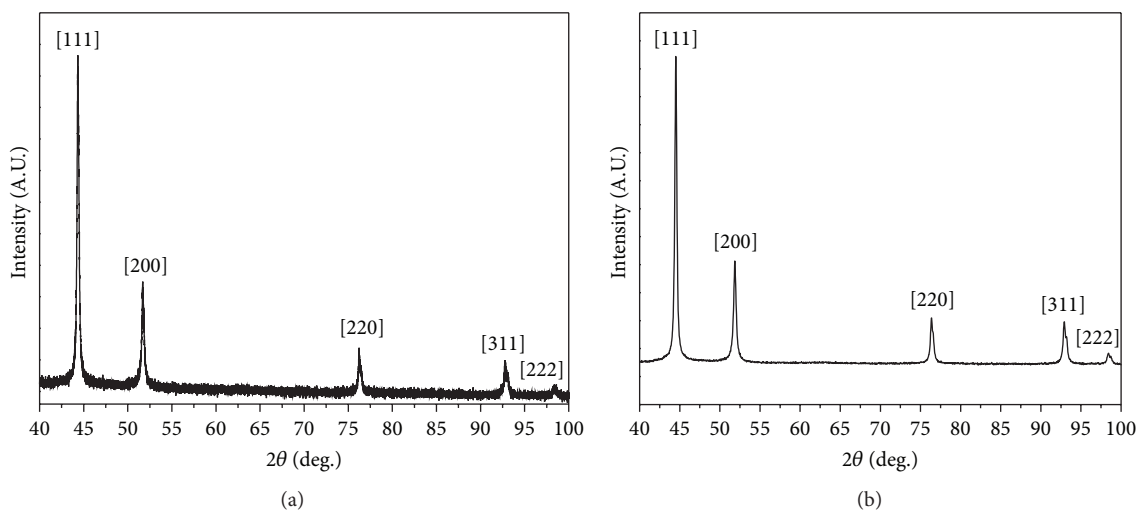


FIGURE 7: X-ray diffraction pattern of the NiNPs (a) before and (b) after heat treatment at 150°C for 8 hours.

NiO [45]. Thus, the peak at 531.0 eV is assigned to NiOH_x . The peaks in O 1s at 529.5 eV and 531.2 eV after heat treatment observed in Figure 6(d) also correspond to NiO [41] and NiOH_x [45, 46]. The C 1s peak in Figures 6(e) and 6(f) at 284.4 eV can be attributed to adventitious carbon [33, 34]. The survey spectrum shows presence of Ni 3p, Ni 2p, C 1s, and O 1s peaks for NiNPs before (Figure 6(g)) and after (Figure 6(b)) heat treatment.

Figure 7 shows the X-ray diffraction pattern of the NiNPs before and after heat treatment at 150°C for 8 hours. The XRD pattern detects the bulk changes taking place in the NiNPs due to heat treatment. The crystal planes observed as peaks can be associated with the [111], [200], [220], [311], and [222] planes associated with $2\theta = 44.43^\circ$, 51.78° , 76.26° , 92.77° ,

and 98.27° , respectively, of cubic nickel lattice with space group of Fm- $m3$ [47, 48]. The absence of NiO peaks ($2\theta = 43.20^\circ$ (most intensive), 62.87° , 75.20° , and 79.38°) from the XRD diffraction patterns shows that no any significant bulk oxidation of the NiNPs occurred during the heat treatment.

Based on the results of the XPS analysis, the catalytic activity of the heat treated NiNPs was studied. Figure 8 shows the pH change profile when CO_2 is bubbled in NiNPs suspension compared to DI water. The pH change profiles of heat treated (Figure 8(a)) and untreated (Figure 8(b)) NiNPs compared to DI water are similar. The catalytic activity of NiNPs was observed even after heat treatment (150°C for 8 hours in air) thus making the NiNPs a suitable candidate to be used as enhancers in carbonate absorber systems.

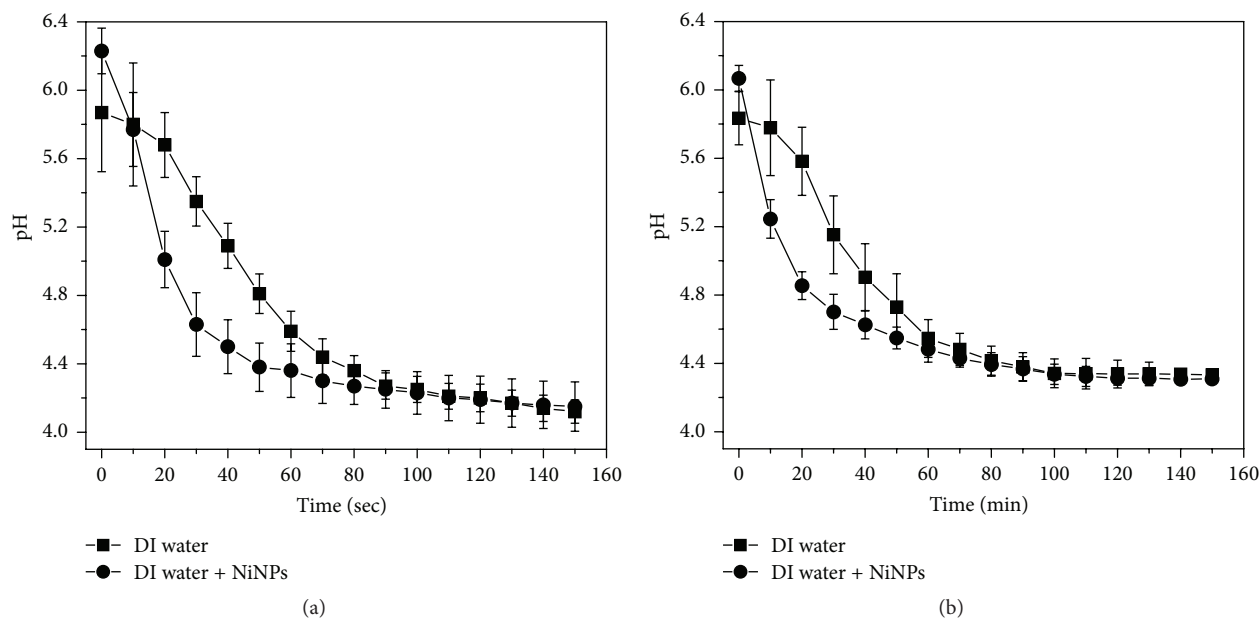


FIGURE 8: pH changes during bubbling of CO₂ through DI water (a) heat treated NiNPs (at 150°C for 8 hours in air) suspension and (b) without heat treatment.

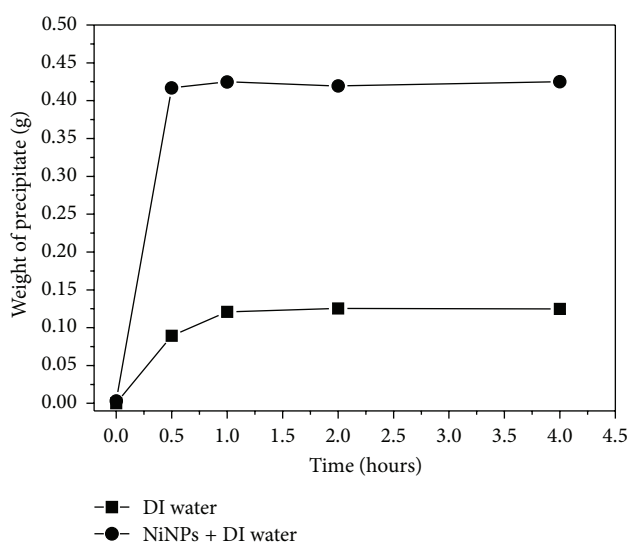


FIGURE 9: CaCO₃ precipitate obtained in DI water and NiNPs suspension after CO₂ bubbling at different time intervals.

3.7. Increase in CaCO₃ Precipitation with NiNPs. Figure 9 shows the amount of CaCO₃ precipitated in presence and absence of NiNPs in DI water. The CaCO₃ precipitate yield in the presence of the NiNPs was higher than that of DI water alone; therefore, the NiNPs increase the CO₂ uptake and hydration constant rate even under the presaturation conditions. The CaCO₃ precipitate yield in the presence of the NiNPs was three times higher than that of DI water, similar to the results observed by Bhaduri and Šiller [9].

Figure 10 shows the SEM images of the CaCO₃ precipitate in presence of NiNPs. Micron sized (2–10 μm) spherical

precipitates are observed. XRD of the precipitate is shown in Figure 11, which confirms the presence of the calcite phase of CaCO₃ [49]. The diffraction plane of Ni [111] is also present [50] which indicates also the presence of NiNPs in the precipitates. Therefore, the NiNPs could act as nucleation sites for the crystals to grow, since the NiNPs are spherical in shape (reported previously [9]), and the carbonate precipitates are also spherical (instead of normal cubic shape [51, 52]). Bodor et al. [22] studied the application of NiNPs for mineralization of CO₂ using alkaline wastes slurries containing MgO or CaO. They suggested that the activity of NiNPs is dependent on the solid to liquid ratio of the slurry based on the observation of low enhancement at high solid to liquid ratio. They did not provide a reason for the decrease in the activity of NiNPs. We suggest, based on our mineralization results, that at higher solid to liquid ratio the in situ mineral precipitation of carbonates (MgCO₃ or CaCO₃) would have blocked the NiNPs active sites. The carbonate (MgCO₃ or CaCO₃) would have precipitated on the NiNPs covering the particles. Thus, this would have lowered the activity of NiNPs.

4. Summary

In the current study, the temperature, pH dependence, and CO₂ partial pressure dependence of NiNPs catalysis for hydration of CO₂ are studied. As compared to other homogenous catalysts used for CO₂ hydration, NiNPs are cost-effective and have ease of separation for repeatable use. The NiNPs catalysis was optimum within 20–30°C for hydration of CO₂ and at pH below 8. NiNPs catalysis for hydration of CO₂ is observed at lower partial pressure of CO₂. NiNPs show an enhancement in CO₂ uptake of 50 wt% K₂CO₃ solution. An enhancement of CO₂ absorption rate of

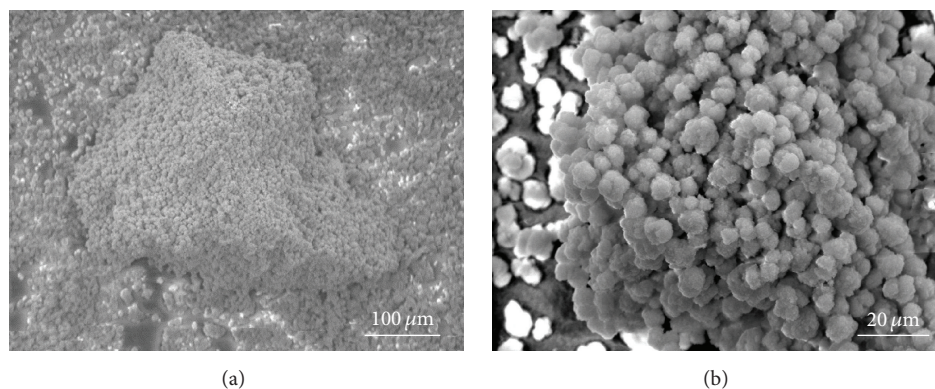


FIGURE 10: SEM images of the precipitate of CaCO_3 obtained in presence of NiNPs catalysed hydration of CO_2 using NaOH and CaCl_2 .

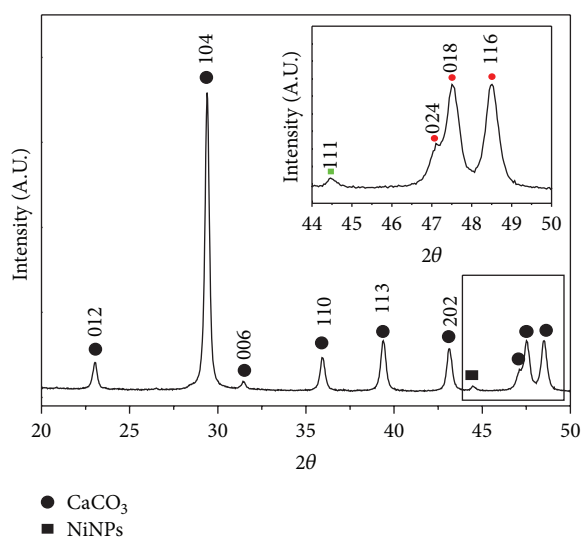


FIGURE 11: XRD of the precipitate of CaCO_3 obtained in presence of NiNPs catalysed hydration of CO_2 using NaOH and CaCl_2 . Insert is the magnification of the later end of the XRD pattern to show the Ni peak.

~77% was observed in the presence of NiNPs more than in its absence. This suggests that NiNPs can be used as enhancers for CO_2 separation using carbonate solutions and could work for other alkaline absorbing solutions as well. It was observed the heat treatment does not have major changes on the surface of NiNPs and the catalytic activity of NiNPs is retained after heat treatment. As compared to other homogeneous catalysts, the NiNPs have an advantage to be used at high temperature CO_2 separation with low loss in activity. The NiNPs also increase the precipitation of CO_2 as CaCO_3 in DI water by up to three times as compared to in its absence. The NiNPs act as nucleates for CaCO_3 growth and thus the calcite precipitates are spherical in shape. This suggests that the NiNPs need to be separated from the solution before carbonate formation during aqueous mineralization carbon capture and storage. Alternatively, the NiNPs can be immobilised on supports for easy separation and reuse during aqueous mineralization of CO_2 as it has been recently demonstrated by Han et al. [23].

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

Gaurav Ashok Bhaduri thanks Newcastle University for Teaching Scholarship. All authors thank the EPSRC for the grant (EP/K004689/1) and EPSRC Impact Acceleration Account for financial support. The authors thank ACMA, Newcastle University, for SEM and XRD analysis and Dr. Alan Harvey for the HRTEM analysis. This work has been supported by Newcastle University and Patent PCT/GB2013/051243 (WO2013171480 A3) has been awarded. Data supporting this publication is openly available under an “Open Data Commons Open Database License”. Additional metadata are available at 10.17634/135315-1. Please contact Newcastle Research Data Services at rdm@ncl.ac.uk for access instructions.

References

- [1] IPCC, *Renewable Energy Sources and Climate Change Mitigation*, edited by: O. Edenhofer, R. P. Madruga, Y. Sokona, Intergovernmental Panel on Climate Change, New York, NY, USA, 2012.
- [2] IEA, *Redrawing the Energy-Climate Map World Energy Outlook Special Report*, International Energy Agency, Lyon, France, 2013.
- [3] IEA and Global CCS Institute, *Tracking Progress in Carbon Capture and Storage: International Energy Agency/Global CCS Institute Report to the Third Clean Energy Ministerial*, International Energy Agency and Global CCS Institute, Lyon, France, 2012.
- [4] P. V. Danckwerts, *Gas Liquid Reactions*, McGraw-Hill, New York, NY, USA, 1970.
- [5] D. Roberts and P. V. Danckwerts, “Kinetics of CO_2 absorption in alkaline solutions—I Transient absorption rates and catalysis by arsenite,” *Chemical Engineering Science*, vol. 17, no. 12, pp. 961–969, 1962.
- [6] M. M. Sharma and P. V. Danckwerts, “Catalysis by Brønsted bases of the reaction between CO_2 and water,” *Transactions of the Faraday Society*, vol. 59, pp. 386–395, 1963.

- [7] G. Zhang, X. Wang, W. Conway, M. Maeder, Q. Sun, and H. Yu, "Kinetics of $\text{CO}_2(\text{aq}), \text{HCO}_3^-$ with primary and secondary amines in aqueous solution," *CIESC Journal*, vol. 64, no. 8, pp. 2883–2890, 2013.
- [8] D. M. Kern, "The hydration of carbon dioxide," *Journal of Chemical Education*, vol. 37, no. 1, p. 14, 1960.
- [9] G. A. Bhaduri and L. Šiller, "Nickel nanoparticles catalyse reversible hydration of carbon dioxide for mineralization carbon capture and storage," *Catalysis Science & Technology*, vol. 3, no. 5, pp. 1234–1239, 2013.
- [10] L. Šiller and G. A. Bhaduri, "Carbon capture," World patent WO2013171480 A3, 2013.
- [11] G. A. Bhaduri, R. A. Henderson, and L. Šiller, "Reply to the 'Comment on "nickel nanoparticles catalyse reversible hydration of carbon dioxide for mineralization carbon capture and storage"' by D. Britt, Catal. Sci. Technol., 2013, 3, DOI: 10.1039/C3CY00142C," *Catalysis Science and Technology*, vol. 3, no. 9, pp. 2197–2198, 2013.
- [12] G.-M. Bong, J. Stringer, D. K. Brandvold, F. A. Simsek, M.-G. Medina, and G. Egeland, "Development of integrated system for biomimetic CO_2 sequestration using the enzyme carbonic anhydrase," *Energy & Fuels*, vol. 15, no. 2, pp. 309–316, 2001.
- [13] M. Vinoba, M. Bhagiyalakshmi, S. K. Jeong, S. C. Nam, and Y. Yoon, "Carbonic anhydrase immobilized on encapsulated magnetic nanoparticles for CO_2 sequestration," *Chemistry—A European Journal*, vol. 18, no. 38, pp. 12028–12034, 2012.
- [14] M. Vinoba, M. Bhagiyalakshmi, S. K. Jeong, Y. I. Yoon, and S. C. Nam, "Immobilization of carbonic anhydrase on spherical SBA-15 for hydration and sequestration of CO_2 ," *Colloids and Surfaces B: Biointerfaces*, vol. 90, no. 1, pp. 91–96, 2012.
- [15] M. Vinoba, K. S. Lim, S. K. Lee, S. K. Jeong, and M. Alagar, "Immobilization of human carbonic anhydrase on gold nanoparticles assembled onto amine/thiol-functionalized mesoporous SBA-15 for biomimetic sequestration of CO_2 ," *Langmuir*, vol. 27, no. 10, pp. 6227–6234, 2011.
- [16] J. C. Kernohan, "The pH-activity curve of bovine carbonic anhydrase and its relationship to the inhibition of the enzyme by anions," *Biochimica et Biophysica Acta—Nucleic Acids and Protein Synthesis*, vol. 96, no. 2, pp. 304–317, 1965.
- [17] A. C. Pierre, "Enzymatic carbon dioxide capture," *ISRN Chemical Engineering*, vol. 2012, Article ID 753687, 22 pages, 2012.
- [18] C. D. Boone, S. Gill, A. Habibzadegan, and R. McKenna, "Carbonic anhydrase: an efficient enzyme with possible global implications," *International Journal of Chemical Engineering*, vol. 2013, Article ID 813931, 6 pages, 2013.
- [19] P. C. Sahoo, Y.-N. Jang, and S.-W. Lee, "Immobilization of carbonic anhydrase and an artificial Zn(II) complex on a magnetic support for biomimetic carbon dioxide sequestration," *Journal of Molecular Catalysis B: Enzymatic*, vol. 82, pp. 37–45, 2012.
- [20] M. Bräuer, J. L. Pérez-Lustres, J. Weston, and E. Anders, "Quantitative reactivity model for the hydration of carbon dioxide by biomimetic zinc complexes," *Inorganic Chemistry*, vol. 41, no. 6, pp. 1454–1463, 2002.
- [21] A. E. Dennard and R. J. P. Williams, "The catalysis of the reaction between carbon dioxide and water," *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*, pp. 812–816, 1966.
- [22] M. Bodor, R. M. Santos, Y. W. Chiang, M. Vlad, and T. Van Gerven, "Impacts of nickel nanoparticles on mineral carbonation," *The Scientific World Journal*, vol. 2014, Article ID 921974, 10 pages, 2014.
- [23] X. Han, F. Williamson, G. A. Bhaduri, A. Harvey, and L. Šiller, "Synthesis and characterisation of ambient pressure dried composites of silica aerogel matrix and embedded nickel nanoparticles," *The Journal of Supercritical Fluids*, 2015.
- [24] D.-H. Kim, M. Vinoba, W.-S. Shin, K.-S. Lim, S.-K. Jeong, and S.-H. Kim, "Biomimetic sequestration of carbon dioxide using an enzyme extracted from oyster shell," *Korean Journal of Chemical Engineering*, vol. 28, no. 10, pp. 2081–2085, 2011.
- [25] M. Zaman and J. H. Lee, "Carbon capture from stationary power generation sources: a review of the current status of the technologies," *Korean Journal of Chemical Engineering*, vol. 30, no. 8, pp. 1497–1526, 2013.
- [26] P. V. Danckwerts, "Promotion of CO_2 mass-transfer in carbonate solutions," *Chemical Engineering Science*, vol. 36, no. 10, pp. 1741–1742, 1981.
- [27] M. M. Sharma and P. V. Danckwerts, "Fast reactions of CO_2 in alkaline solutions—(a) Carbonate buffers with arsenite, formaldehyde and hypochlorite as catalysts (b) Aqueous monoisopropanolamine (1-amino-2-propanol) solutions," *Chemical Engineering Science*, vol. 18, no. 12, pp. 729–735, 1963.
- [28] X. Ye and Y. Lu, " CO_2 absorption into catalyzed potassium carbonate-bicarbonate solutions: kinetics and stability of the enzyme carbonic anhydrase as a biocatalyst," *Chemical Engineering Science*, vol. 116, pp. 567–575, 2014.
- [29] I. Jayaweera, P. Jayaweera, R. Elmore, J. Bao, and S. Bhamidi, "Update on mixed-salt technology development for CO_2 capture from post-combustion power stations," *Energy Procedia*, vol. 63, pp. 640–650, 2014.
- [30] P. Mirjafari, K. Asghari, and N. Mahinpey, "Investigating the application of enzyme carbonic anhydrase for CO_2 sequestration purposes," *Industrial & Engineering Chemistry Research*, vol. 46, no. 3, pp. 921–926, 2007.
- [31] D. A. Shirley, "High-resolution x-ray photoemission spectrum of the valence bands of gold," *Physical Review B*, vol. 5, no. 12, article 4709, 1972.
- [32] J. Yu, Q. Xiang, and M. Zhou, "Preparation, characterization and visible-light-driven photocatalytic activity of Fe-doped titania nanorods and first-principles study for electronic structures," *Applied Catalysis B: Environmental*, vol. 90, no. 3-4, pp. 595–602, 2009.
- [33] M. C. Biesinger, B. P. Payne, L. W. M. Lau, A. Gerson, and R. S. C. Smart, "X-ray photoelectron spectroscopic chemical state quantification of mixed nickel metal, oxide and hydroxide systems," *Surface and Interface Analysis*, vol. 41, no. 4, pp. 324–332, 2009.
- [34] B. P. Payne, M. C. Biesinger, and N. S. McIntyre, "The study of polycrystalline nickel metal oxidation by water vapour," *Journal of Electron Spectroscopy and Related Phenomena*, vol. 175, no. 1–3, pp. 55–65, 2009.
- [35] L. K. Doraiswami and M. M. Sharma, *Heterogeneous Reactions: Analysis, Examples and Reactor Design*, vol. 2, John Wiley & Sons, New York, NY, USA, 1984.
- [36] D. Britt, "Comment on 'nickel nanoparticles catalyse reversible hydration of carbon dioxide for mineralization carbon capture and storage' by G. Bhaduri and L. Šiller, Catal. Sci. Technol., 2013, 3, 1234," *Catalysis Science & Technology*, vol. 3, no. 9, pp. 2195–2196, 2013.
- [37] H.-J. Freund and M. W. Roberts, "Surface chemistry of carbon dioxide," *Surface Science Reports*, vol. 25, no. 8, pp. 225–273, 1996.

- [38] A. F. Carley, S. Rassias, and M. W. Roberts, "The specificity of surface oxygen in the activation of adsorbed water at metal surfaces," *Surface Science*, vol. 135, no. 1–3, pp. 35–51, 1983.
- [39] V. L. Snoeyink and D. Jenkins, *Water Chemistry*, John Wiley & Sons, New York, NY, USA, 1980.
- [40] B. R. W. Pinsent and F. J. W. Roughton, "The kinetics of combination of carbon dioxide with water and hydroxide ions," *Transactions of the Faraday Society*, vol. 47, pp. 263–269, 1951.
- [41] K. S. Kim and N. Winograd, "X-ray photoelectron spectroscopic studies of nickel-oxygen surfaces using oxygen and argon ion-bombardment," *Surface Science*, vol. 43, no. 2, pp. 625–643, 1974.
- [42] P. Lorenz, J. Finster, G. Wendt, J. V. Salyn, E. K. Žumadilov, and V. I. Nefedov, "Esca investigations of some NiO/SiO₂ and NiO-Al₂O₃/SiO₂ catalysts," *Journal of Electron Spectroscopy and Related Phenomena*, vol. 16, no. 3, pp. 267–276, 1979.
- [43] N. S. McIntyre and M. G. Cook, "X-ray photoelectron studies on some oxides and hydroxides of cobalt, nickel, and copper," *Analytical Chemistry*, vol. 47, no. 13, pp. 2208–2213, 1975.
- [44] A. Roustila, C. Severac, J. Chêne, and A. Percheron-Guégan, "Hydrogen effects on the electronic and microstructural properties of Ce, Ni, and CeNi₂ intermetallic compound," *Surface Science*, vol. 311, no. 1–2, pp. 33–44, 1994.
- [45] J. Ciston, A. Subramanian, D. M. Kienzle, and L. D. Marks, "Why the case for clean surfaces does not hold water: structure and morphology of hydroxylated nickel oxide (1 1 1)," *Surface Science*, vol. 604, no. 2, pp. 155–164, 2010.
- [46] L. Salvati Jr., L. E. Makovsky, J. M. Stencel, F. R. Brown, and D. M. Hercules, "Surface spectroscopic study of tungsten-alumina catalysts using X-ray photoelectron, ion scattering, and Raman spectroscopies," *The Journal of Physical Chemistry*, vol. 85, no. 24, pp. 3700–3707, 1981.
- [47] S. Dellis, A. Christoulaki, N. Spiliopoulos, D. L. Anastasopoulos, and A. A. Vradis, "Electrochemical synthesis of large diameter monocrystalline nickel nanowires in porous alumina membranes," *Journal of Applied Physics*, vol. 114, no. 16, Article ID 164308, 2013.
- [48] H. T. Takeshita, T. Oishi, and N. Kuriyama, "Disproportionation of CaNi₃ hydride: formation of new hydride, CaNiH₃," *Journal of Alloys and Compounds*, vol. 333, no. 1–2, pp. 266–273, 2002.
- [49] H. E. Swanson and R. K. Fuyat, National Bureau of Standards (U.S.) Circular II (1953) 51.
- [50] D. E. Zhang, X. M. Ni, H. G. Zheng, Y. Li, X. J. Zhang, and Z. P. Yang, "Synthesis of needle-like nickel nanoparticles in water-in-oil microemulsion," *Materials Letters*, vol. 59, no. 16, pp. 2011–2014, 2005.
- [51] R. Yadav, M. Joshi, S. Wanjari et al., "Immobilization of carbonic anhydrase on chitosan stabilized Iron nanoparticles for the carbonation reaction," *Water, Air, and Soil Pollution*, vol. 223, no. 8, pp. 5345–5356, 2012.
- [52] S. Wanjari, C. Prabhu, R. Yadav, T. Satyanarayana, N. Labhsetwar, and S. Rayalu, "Immobilization of carbonic anhydrase on chitosan beads for enhanced carbonation reaction," *Process Biochemistry*, vol. 46, no. 4, pp. 1010–1018, 2011.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

