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Catalysis of CO₂ Absorption in Aqueous Solution by Inorganic Oxoanions and their Application to Post Combustion Capture

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KEYWORDS

Post Combustion Capture, CO₂ Capture, Catalysis, Inorganic Oxoanions

ABSTRACT

To reduce CO₂ emission into the atmosphere, particularly from coal-fired power stations, Post Combustion Capture (PCC) using amine-based solvents to chemically absorb CO₂ has been extensively developed. From an infrastructure viewpoint, the faster the absorption of CO₂, the smaller the absorber required. The use of catalysts for this process has been broadly studied. In this manuscript, a study of the catalytic efficiencies of inorganic oxoanions such as arsenite, arsenate, phosphite, phosphate and borate is described. The kinetics of the accelerated CO₂

absorption at 25°C was investigated using stopped-flow spectrophotometry. The catalytic rate constants of these anions for the reaction of CO₂ with H₂O were determined to be 137.7(3), 30.3(7), 69(2), 32.7(9) and 13.66(7) M⁻¹s⁻¹, respectively. A new mechanism for the catalytic reaction of oxoanions with CO₂ has also been proposed. The applicability of these catalysts to PCC was further studied by simulation of the absorption process under PCC conditions using their experimental catalytic rate constants. Arsenite and phosphite were confirmed to be the best catalysts for CO₂ capture. However, considering the toxicological effect of arsenic and the oxidative instability of phosphite, phosphate would be the most promising inorganic catalyst for PCC process from the series of inorganic oxoanions studied.

INTRODUCTION

The increasing emission of carbon dioxide (CO₂) into the atmosphere fosters the need for its removal from gas streams. There are many possible technologies available for CO₂ separation from a flue gas. CO₂ capture by chemical absorption using amine-based solvents in Post Combustion Capture (PCC) processes is currently seen as the most applicable and effective approach.¹ One of the important aspects for the optimisation of amine-based PCC is the rate of the interaction of CO₂ with aqueous amine solution. This needs to be fast to minimize the spatial requirements of the absorber column.

The hydration of CO₂ in aqueous solution follows two pathways.

The higher the concentration of OH⁻, that is the higher the pH, the faster the reaction of equation (2). Additionally, the hydroxide ions also absorb H⁺ in equation (1). To further accelerate CO₂ hydration, solutions of amines, particularly unhindered amines, can be used.

The reaction of CO₂ with amine to form carbamate (equation (3)) is fast. However, its associated disadvantage is the stoichiometry of requiring two moles of amine per mole of CO₂ absorbed. As a consequence, the use of catalysts to enhance the reaction between CO₂ and H₂O (equation (1)) is of interest to gain the molecular efficiency benefits of this pathway at practically useful rates of reaction. A wide range of catalysts such as borate, arsenite, metal ions, acetate and zinc complexes have been investigated.²⁻¹⁵

The catalytic effect of arsenite and arsenate on CO₂ absorption has been observed in an earlier work by Roughton and Booth in 1938.² Subsequent studies³⁻¹² also confirmed that arsenite played an important role in the acceleration of the reaction between CO₂ and water. Borate has also been claimed to have a catalytic effect on CO₂ absorption.^{2, 13-15} Despite extensive studies on these catalysts, the catalytic rate constants were only defined in some of the studies referenced above.

In view of the small range of the catalytic rate constants reported for the promoters for CO₂ hydration including arsenite and borate, further examination of these and other compounds is warranted. In this study, the catalysis of CO₂ absorption in aqueous solution by arsenite, arsenate, phosphate, phosphite and borate has been studied by stopped-flow spectrophotometry. Phosphite and phosphate were included in this project since phosphate has been commonly used as a buffer in the study of CO₂ hydration.^{2, 5} The primary aim of this study was to determine the

possible catalytic effects of these inorganic species on the absorption of CO₂ in aqueous solution and evaluate the rate constants associated with the reactions.

The generally agreed mechanism for the catalysis of the hydration of CO₂ by oxoanions like arsenite and borate is shown in Scheme 1.²

Scheme 1. Catalytic reaction process of oxoanions of the type OX[−].

According to Astarita *et al.*⁹ and Danckwerts,¹⁰ all species that feature O[−] or OH groups, or that act as Lewis bases with CO₂ being the Lewis acid, or that have a pyramidal or tetrahedral structure to facilitate CO₂ molecular approach to the basic site, can potentially act as a catalyst. As shown in the proposed scheme, in aqueous solution, these species first react with CO₂. This reaction is followed by hydration in which H₂CO₃ is produced and the catalyst is regenerated.

Following on from the above studies, the applicability of the catalysts was subsequently investigated by modeling their effects in the PCC process. The simulation was performed by modeling the reactions of CO_{2(aq)} in an equilibrated solution containing a tertiary amine as a base, using various catalysts and different amounts of already absorbed CO₂. These solutions mimic the processes at different levels of a PCC absorber column. From this we were able to determine which inorganic oxoanion(s) is the best catalyst for PCC.

MATERIALS AND METHODS

Materials

Inorganic catalysts studied in this project included sodium arsenite (NaAsO_2 , >98 %), sodium arsenate (Na_2HAsO_4), boric acid (H_3BO_3 , 99.5 %) (all BDH, General Purpose Reagent), sodium hydrogen phosphite (Na_2HPO_3) (Pfaltz & Bauer, Inc.) and potassium hydrogen phosphate (K_2HPO_4 , >99.5 %) (Mallinckrodt Analytical Reagent). High purity CO_2 gas (BOC), 3-dimethylamino-1-propanol (3-DMAP) (Sigma-Aldrich), analytical grade thymol blue sodium salt, bromothymol blue sodium salt and bromocresol green (all Sigma-Aldrich, ACS reagents) were used without further purification. Ultrahigh purity Milli-Q water boiled in advance to remove CO_2 gas was used to prepare solutions. The experimental solutions for stopped-flow spectrophotometry were freshly prepared on the same day as the measurements were conducted.

Experimental Methods

The accelerated kinetics of the hydration of CO_2 with different amounts of inorganic materials including NaAsO_2 , Na_2HAsO_4 , Na_2HPO_3 , K_2HPO_4 and H_3BO_3 were performed on an Applied Photophysics DX-17 stopped-flow spectrophotometer equipped with a J&M Tidas MCS 500-3 diode-array detector. The reactions were initiated by mixing a solution containing various amounts of catalyst (0.0, 1.7, 3.4 and 5.1 mM), the tertiary amine 3-DMAP (25 mM) and the indicator thymol blue with a solution of water saturated with CO_2 (17.25 mM) at 25°C. The concentrations shown are the values after mixing unless stated otherwise.

The pH changes of the solutions were followed via coupling to the protonation of the acid-base indicator over the wavelength range of 400-700 nm.

97 **Data analysis**

98 The experimental data obtained by stopped-flow spectrophotometry were analysed using in-
99 house developed software in MatLab. Algorithms that take into account process-induced pH
100 changes and subsequent adjustment of the protonation equilibria were employed to model the
101 kinetic data.¹⁶

102 Standard Newton-Gauss-Levenberg/Marquardt algorithms were used for non-linear least-squares
103 fitting of the relevant parameters and the rate or equilibrium constants.¹⁷⁻¹⁹

104 All possible reactions of CO₂ species in aqueous solution were included in the model for data
105 analyses, more details of which are presented below. In order to determine the catalytic effect of
106 the inorganic oxoanions on CO₂ hydration, the measurements at four different concentrations of
107 each catalyst were globally analysed. The statistically averaged catalytic efficiency values
108 calculated from the analyses of a triplicate of four measurements and the associated errors are
109 reported for each catalyst.

110 An activity coefficient correction was applied to all charged species for the kinetic studies. The
111 extended Debye-Hückel equation, equation (4), was used to estimate the activity coefficients.²⁰

112
$$\log \gamma_i = \frac{-Az_i^2 \sqrt{\mu}}{1 + \sqrt{\mu}} \quad (4)$$

113 where γ_i is the activity coefficient, μ ionic strength and z_i the charge of i^{th} component.

114 The activity coefficient γ_i is a function of the ionic strength μ . The parameter A is defined by
115 the dielectric constant of the solvent and the temperature which in water at 25°C equals 0.51. The

116 ionic strength correction at high species concentrations is not perfect, but it is better than
117 ignoring it when fitting data.²¹

118 **RESULTS**

119 **Reaction model for data analyses**

120 In order to analyse the data, a model that includes all species existing in the system and all
121 possible interactions had to be developed. The species present in the solutions consist of all
122 species of the carbon dioxide/carbonate-amine system, tertiary amine and the indicator in both
123 deprotonated and protonated forms. The tertiary amine 3-dimethylamino-1-propanol (3-DMAP,
124 $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{OH}$) was used as a buffer and base for all experiments. This amine acts as a
125 proton accepting base such that the experimental pH range allows us to investigate the reaction
126 of CO_2 with water and hydroxide in detail. Additionally, the use of a tertiary amine simplifies the
127 analytical system as the possibility of carbamate formation that exists for primary and secondary
128 amines is eliminated. The possible reactions in the system include instantaneous protonation
129 equilibria that are quantitatively defined by equilibrium constants and kinetically observable
130 reactions which are defined by rate and equilibrium constants (equations (5)-(10)).

In the above equations, A is 3-DMAP, Ind²⁻ is thymol blue, Cat_{tot} is (As(OH)₃, AsO(OH)₂⁻), (HAsO₄²⁻), (HPO₃²⁻), (HPO₄²⁻), or (B(OH)₃, B(OH)₄⁻). The inclusion of two forms for arsenite and borate are required as both forms exist in the studied pH range. All equilibrium constants for protonation of carbonate species and the indicators at 25°C and 0 ionic strength are well defined in the literature.^{20, 22-25} The protonation equilibrium constant of the tertiary amine 3-DMAP was experimentally determined by potentiometric titration using the method reported by Fernandes *et al.*²⁶

Before investigating the catalytic effects of the inorganic species, a series of stopped-flow spectrophotometric experiments was conducted to examine whether 3-DMAP had any effect on the hydration of CO₂. The presence of 3-DMAP was found not to have any influence on CO₂ absorption in aqueous solution (see Supporting Information).

For each catalyst, four measurements which contained 3-DMAP (25 mM), indicator (25 μM) and different concentrations of the catalyst (0.0, 1.7, 3.4 and 5.1 mM) were globally analysed to verify whether the reversible reaction of CO₂ with H₂O or OH⁻ was catalysed and if so to determine the rate constant for the accelerated reaction.

Catalysis of CO₂ absorption by inorganic catalysts

Figure 1 shows an example of the experimental and fitted traces for the absorption of CO₂ in aqueous solution containing the tertiary amine 3-DMAP and AsO₂⁻ (see Figure S4, Supporting Information for other catalysts).

Figure 1. Experimental (dash lines) and fitted (solid lines) data for the catalytic study of AsO_2^- at 25°C . [Catalyst] = 0.0, 1.7, 3.4 and 5.1 mM, [3-DMAP] = 25 mM, $[\text{CO}_2]$ = 17.25 mM, [thymol blue] = 25 μM .

The influence of increasing concentration of the catalyst on the acceleration of the kinetics of CO_2 hydration is apparent for AsO_2^- (Figure 1). The kinetic data were analysed using an analytical model that included the complete suite of possible reactions in solution as outlined above. The analytical model including a different catalytic reaction,

was also considered. However, this model did not give as good data fitting as that given by the model including the catalysis of CO_2 with H_2O for all catalysts investigated. The rate constants of CO_2 absorption catalysed by the oxoanions were determined by data fitting while the rate constants for the back reaction were calculated based on

the known equilibrium constant $K_1 \left(= \frac{k_1}{k_{-1}} \right)$ (equation (5)) which is not affected by the catalyst.

It is noticeable that, despite the large apparent rate constants, the back reaction is not relevant at the pH range of interest for PCC as the concentration of H_2CO_3 is very low. Table 1 summarises

the rate constant values obtained from the averages of three sets of experimental data for each of the catalysts studied.

Table 1. Experimental rate constants of catalysed reversible CO₂ hydration.

Catalyst	pK _a ²⁵	pH range	Cat + CO ₂ (+H ₂ O) $\xrightleftharpoons[k_{-cat}]{k_{cat}}$ Cat + H ₂ CO ₃	
			$k_{cat} (M^{-1}s^{-1})$	$k_{-cat} (M^{-1}s^{-1})$
As(OH) ₃ , AsO(OH) ₂ ⁻	pK _a = 9.29	10.86–9.07	137.7(3)	92.99(3) × 10 ³
HPO ₃ ²⁻	pK _{a1} = 6.78(5) pK _{a2} = 1.5(1)	10.86–9.02	69(2)	46.47(7) × 10 ³
HPO ₄ ²⁻	pK _{a1} = 12.375(10) pK _{a2} = 7.198(2) pK _{a3} = 2.148(10)	10.86–9.00	32.7(9)	22.08(4) × 10 ³
HAsO ₄ ²⁻	pK _{a1} = 11.5 pK _{a2} = 6.96(2) pK _{a3} = 2.24(6)	10.86–9.20	30.3(7)	20.49(4) × 10 ³
B(OH) ₃ , B(OH) ₄ ⁻	pK _a = 9.236	10.86–8.94	13.66(7)	9.22(1) × 10 ³

Based on the catalytic rate constants alone, arsenite is the best catalyst for accelerating CO₂ absorption, followed by phosphite, phosphate and arsenate, while borate was the least effective for this purpose. Noticeably, phosphate and arsenate have similar catalytic efficiencies toward the hydration of CO₂.

Application to Post Combustion Capture

In order to investigate the efficiency of these catalysts in the PCC process, we simulated the kinetics of CO₂ absorption in amine solutions of variable pre-loading of CO₂. The simulation was conducted by modeling the reactions of CO_{2(aq)} in an equilibrated solution containing 5 M of 3-DMAP as a base, 0.01 M of the different catalysts and various amounts of already absorbed CO₂. These reactions mimic the processes at different levels of a PCC absorber column, with the lowest level of already absorbed CO₂ at the top of the column (Figure 2). The conditions of the simulation in terms of the involved species concentrations and pH were similar to those of a real facility for PCC, except that the temperature used was 25°C.

Figure 2. Scheme of simulated CO₂ absorption in the absorber column using inorganic catalysts.

There are three pathways for the hydration of CO₂ in aqueous solution (equations (5), (6) and (10)). In order to evaluate the efficiency of the catalysts in enhancing CO₂ hydration, the kinetics of the absorption process has been analysed in terms of the proportions of CO₂ following these three pathways. Figure 3 shows the simulated absorption of 0.1 M CO₂ into solutions that already contain 1.00, 2.50 and 3.50 M CO₂ (a loading of 0.2, 0.5 and 0.7 moles CO₂/moles amine

at the top, middle and bottom sections of the column, respectively) for arsenite and borate. The black solid line represents the concentration of free CO_2 . The proportions of CO_2 following the H_2O , OH^- and catalyst (Cat) routes are highlighted in blue, red and green, respectively.

Figure 3. Kinetics of simulated CO_2 absorption of the added 0.1 M along the absorber for AsO_2^- and B(OH)_4^- .

It is apparent from Figure 3 that the catalytic path gains in importance with higher levels of CO_2 preloading, and thus at a lower pH. The simulation shows that CO_2 is absorbed most quickly by arsenite, followed by phosphite, phosphate and arsenate. The absorption of CO_2 in aqueous solutions containing arsenite, phosphite, phosphate and arsenate reached equilibrium in approximately 3.5, 6, 10 and 10 s, respectively, at the bottom of the absorber. In comparison, borate is the least efficient catalyst studied (Figure S5, Supporting Information).

A more detailed analysis of the simulated CO_2 hydration process in the absorber column for arsenite and borate is shown in Figure 4.

Figure 4. Distribution of CO₂ among the three pathways for AsO₂⁻ and B(OH)₄⁻ at different preloading in the absorber column.

In Figure 4, the proportions of CO₂ following three pathways are presented for incremental amounts of preloaded CO₂ from 1.00 M to 3.50 M in steps of 0.25 M. Taking the top of the absorber column (1.00 M CO₂ preloaded) as an example, for arsenite, approximately 58 % of total CO₂ was absorbed through the catalytic pathway while the contributions from water and hydroxide pathways were 1.7 and 40.3 %, respectively. In comparison, with borate only around 12 % of CO₂ amount was absorbed through the catalytic pathway and the hydroxide route dominated with 84.5 %. For all catalysts, the relative amount of the OH⁻ path decreases substantially due to the lower pH with increased loading. The H₂O path as well as the catalytic path increase but the catalytic path is clearly dominant for all catalysts (Figure S6, Supporting Information).

The simulation results showed that arsenite and phosphite were the best catalysts with most $\text{CO}_{2(\text{aq})}$ being absorbed following the catalytic pathway. Phosphate and arsenate were comparatively good catalysts for CO_2 capture in the absorber as well.

DISCUSSION

Catalysis of CO_2 absorption by inorganic oxoanions

We have shown that the reaction of CO_2 with H_2O was significantly enhanced with the presence of inorganic oxoanions, particularly arsenite and phosphite. The catalytic efficiencies of arsenite, phosphite, phosphate, arsenate and borate for the reaction of CO_2 with H_2O at 25°C and an ionic strength of 0 M were determined to be 137.7(3), 69(2), 32.7(9), 30.3(7) and 13.66(7) $\text{M}^{-1}\text{s}^{-1}$, respectively. The catalytic rate constants for arsenite and borate compare well with literature values. In the study conducted by Roberts and Danckwerts⁴ employing a wetted-wall column, the addition of arsenite was found to increase CO_2 absorption in alkaline solutions at 25°C and an ionic strength of 1 g ion/L with the rate constant of $160 \text{ M}^{-1}\text{s}^{-1}$. In another study in which the rate of CO_2 absorption in veronal buffer was measured by a manometric method over the pH range of 8.5–8.8, a temperature range of $0\text{--}15^\circ\text{C}$ and an ionic strength of 0.09 M, the catalytic rate constant of arsenite was calculated to be $226 \text{ M}^{-1}\text{s}^{-1}$ at 25°C .⁵ With respect to borate, the study on the kinetics of boron-catalysed CO_2 hydration using stopped-flow UV/visible spectrophotometry within $25\text{--}40^\circ\text{C}$ by Guo *et al.*¹⁵ gave the catalytic rate constant of $35.3 \pm 2.0 \text{ M}^{-1}\text{s}^{-1}$ at 25°C .

Interesting results came from the investigation of phosphite and phosphate. In this study, both were found to enhance the reaction of CO_2 and H_2O . However, in the study by Roughton and Booth,² phosphite and phosphate were found to have low catalytic coefficients on the rate of CO_2

uptake measured by a manometric boat method. Furthermore, according to Pocker and Bjorkquist,²² who used a stopped-flow indicator technique to study the hydration of CO₂ with different buffers including phosphate, the contribution of phosphate to the rate was negligible as long as the buffer concentration was maintained below 0.05 M. In comparison, the concentration range of phosphate used in this study was 0.0-5.1 mM and an acceleration of CO₂ hydration was observed.

Within the pH range examined in the current study, the forms of the catalysts, that is the protonation state, responsible for the acceleration of CO₂ hydration could not be defined despite investigating multiple analytical models to define the reaction. Within the pH range of 9.00-10.86, phosphite mostly exists in the deprotonated form, HPO₃²⁻ and phosphate and arsenate in the monoprotinated forms, HPO₄²⁻ and HAsO₄²⁻, respectively. Therefore, HPO₃²⁻, HPO₄²⁻ and HAsO₄²⁻ are most likely the catalytic forms for the acceleration of CO₂. With borate and arsenite, the compounds exist in both protonated and deprotonated forms within the experimental pH range. As a result, it is impossible to confirm which form of these catalysts was responsible for the increase in CO₂ hydration rate. Further studies which cover a broader pH range in which the catalysts exist in defined protonation states would be required in order to elucidate the catalytically active species.

Based on the mechanism shown in Scheme 1, it was speculated that the efficiencies of these catalysts were correlated to the charge of the oxygen atom in the oxoanion. In order to verify this assumption, the electrostatic charges on the oxygen atoms of all possible forms of the catalysts with the lowest-strain-energy geometries present in the aqueous solution within the pH range studied were obtained, using Spartan'04 (Wavefunction Inc., Irvine, CA, USA) with the B3LYP functional and a 6-311++G (d,p) basis set. Electrostatic charges were used rather than natural

charges as they provide a greater range of values for similar compounds. Mulliken charges were not used because they are more basis-set-dependent than electrostatic charges and natural charges. The calculation of the charge on the oxygen atoms in HPO_3^{2-} , B(OH)_3 and B(OH)_4^- resulted in single values. For both HPO_4^{2-} and HAsO_4^{2-} , the oxygen atom charges were averaged from individual values for all atoms in each species as the proton is mobile in both cases and can move from oxygen to oxygen.

Further insights were obtained for borate and arsenite. As discussed above, data analyses for stopped-flow spectrophotometric measurements alone could not conclude which forms of borate and arsenite were catalytically active. However, quantum chemical calculations could potentially elucidate this matter. For borate, the resulting charges on the oxygen atoms for B(OH)_3 and B(OH)_4^- indicated that B(OH)_4^- was likely a better catalyst for CO_2 hydration than B(OH)_3 because of the higher oxygen charge (-0.98 and -0.76, respectively). This is in agreement with the study conducted by Guo *et al.*¹⁵ With respect to arsenite, the charges on the oxygen atoms for As(OH)_3 and AsO(OH)_2^- (-0.52 and -0.71, respectively) did not explain why arsenite had higher catalytic effect on the hydration of CO_2 than other catalysts examined. However, it is known by $^1\text{H-NMR}$ spectroscopy that the hydrogens in As(OH)_3 and all of its sequentially deprotonated species exchange rapidly with water.²⁷ A possible mechanism likely involves an attack of OH^- on an As(III)-oxo species with the formation of H_2O and deprotonated $-\text{OH}$ group. One such species is formed by the addition of OH^- to AsO(OH)_2^- to give $\text{As(OH)O}_2(\text{H}_2\text{O})^{2-}$. The charge on the water oxygen is now -1.20, which is consistent with arsenite being the most effective catalyst. The proposed species is only an intermediate in this exchange mechanism, but could act as the catalytically active species for CO_2 hydration if it has some reasonable lifetime. Following on from this, it is likely that all other species could have water molecules bi-coordinated to oxo

groups of the anions by hydrogen bonding. This leads to an assessment of the oxygen charges on the hydrated forms of these anions. It is interesting that the resulting charges on the water oxygen atoms are quite similar to those of the anion oxygens (highlighted in blue and pink, respectively, in the chemical formulas below). Table 2 summarises the electrostatic charges on the oxygen atoms in the species that are more likely to be catalytically active for all of the inorganic oxoanions studied, both with and without the added water molecules. Also included is the analogous data for hydroxide and water itself. Their chemical structures are shown in Table S2 in Supporting Information.

Table 2. Correlation between catalytic efficiency and electrostatic charge on the oxygen atom in oxoanion O-X and on water oxygen.

Catalyst	Catalytic rate constant ($\text{M}^{-1}\text{s}^{-1}$)	Water oxygen charge (O)	Oxoanion oxygen charge (O) (without water)
OH^-	$12.1(4) \times 10^3$	-	-1.23
$\text{As}(\text{OH})(\text{O})_2(\text{H}_2\text{O})^{2-}$	137.7(3)	-1.20	-0.71
$\text{HPO}_3(\text{H}_2\text{O})^{2-}$	69(2)	-1.10	-1.10
$\text{HPO}_4(\text{H}_2\text{O})^{2-}$	32.7(9)	-1.07	-1.04
$\text{HAsO}_4(\text{H}_2\text{O})^{2-}$	30.3(7)	-1.06	-0.99
$\text{B}(\text{OH})_4(\text{H}_2\text{O})^-$	13.66(7)	-0.94	-0.98
H_2O	$6.6(4) \times 10^{-4}$	-0.77	-

It is apparent from Table 2 that there is a correlation of the charge on the oxygen atom with the catalytic rate constant toward the hydration of CO_2 . Additionally, a new mechanism for the interaction of CO_2 and oxoanions can now be proposed, in which there is a nucleophilic attack of

the oxygen atom of the hydrogen-bonded water molecule on the carbon atom of CO₂, giving H₂CO₃ and the oxoanion, after breaking the hydrogen bonds to the oxoanion (Scheme 2). This model is simpler than the process described in Scheme 1.

Scheme 2. Proposed mechanism for the catalytic reaction of hydrated oxoanions.

Although arsenite was found to be the best catalyst for CO₂ hydration, arsenic is known to negatively affect human health, causing melanosis, gangrene, cancer and eventually death as a result of the consumption of As-polluted water.²⁹ It was estimated in 2004 that globally about 200 million people from more than 70 countries faced the risk of drinking groundwater contaminated with As.³⁰ Taking this into account, phosphite and phosphate would be better choices for the CO₂ capture purpose. However, phosphite is easily oxidised to form phosphate.³¹ As a result, phosphate appears to be the best candidate for the acceleration of CO₂ absorption.³²

Application of inorganic catalysts to PCC

The simulations for the application of the oxoanion catalysts to PCC show that arsenite, phosphite, phosphate and arsenate are promising candidates for reducing CO₂ emissions into the atmosphere. The fast kinetics of CO₂ hydration using these catalysts would help to reduce the size of the absorber column, and hence the operation costs. However, in the present study, the kinetics parameters were, nevertheless, examined at 25°C only. Therefore, further investigation

of these catalysts under PCC operational temperatures of 40–60°C in the absorber should be undertaken. It would be expected that the catalytic efficiencies of these species will increase with higher temperatures. As such, temperature dependence of these catalysts would also be worth investigating. Such results would help to elucidate the energy requirements for the desorption process, thus optimising the overall PCC procedure.

ASSOCIATED CONTENT

Supporting Information.

Supporting Information includes the experimental and analytical results of the possible effect of 3-DMAP on the hydration of CO₂; the experimental and fitted data for the catalytic study of all oxoanions; kinetics of simulated CO₂ absorption along the absorber for all catalysts; the distribution of CO₂ among the three pathways at different preloading in the absorber column for all catalysts and the correlation between the catalytic efficiency and electrostatic charges on the oxygen atom. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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