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Catalysis of CO_2 absorption in aqueous solution by vanadate and sulfate and their application to post combustion capture

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ABSTRACT

A promising option to improve post combustion capture (PCC) is to use inorganic catalysts to accelerate the absorption process of CO_2, in particular the reaction between CO_2 and water to form carbonic acid. In this study, the efficiency of sulfate and vanadate on enhancing the hydration reaction of CO_2 to form H_2CO_3 for PCC has been studied at 25 °C by stopped-flow spectrophotometry. The catalytic rate constants were determined to be 14.2(2) and 277(6) $M^{-1}\,s^{-1}$ for sulfate and vanadate, respectively. Their application to PCC was further investigated by simulating the effect of these catalysts on the absorption process under PCC operating conditions. Vanadate was confirmed to have a greater efficiency toward CO_2 hydration than sulfate and also a series of other inorganic catalysts reported earlier.

1. Introduction

Post combustion capture (PCC) is currently the most advanced technology for reduction of emissions of carbon dioxide (CO_2) into the atmosphere from fossil fuel combustion. An obvious aim of PCC research is to investigate the use of catalysts for the acceleration of the hydration reaction of CO_2 and thus reduce the size of the absorber column. In particular, the use of inorganic catalysts to accelerate the absorption of CO_2 in aqueous solution in the PCC processes has been the subject of many studies (Alper, 1981; Astarita et al., 1981; Augugliaro and Rizzuti, 1987; Bandyopadhyay et al., 1980; Danckwerts, 1981; Eickmeyer, 1985; Ghosh et al., 2009; Guo et al., 2011; Nicholas et al., 2014; Roberts and Danckwerts, 1962; Roughton, 1943; Roughton and Booth, 1938; Sharma and Danckwerts, 1963a,b; Vázquez et al., 1997).

Following on from the study of the catalysis of CO_2 hydration by inorganic oxoanions including arsenite, arsenate, phosphite, phosphate and borate (Phan et al., 2014), this investigation extends the study of the catalytic effects of inorganic anions to sulfate and vanadate at 25 °C by stopped-flow spectrophotometry. Both sulfate and vanadate feature similar structures compared with the other oxoanions. The outcomes of the study of these two inorganic species not only reveal their catalytic effect on the absorption of CO_2 in aqueous solution but also supports the mechanism previously proposed (Scheme 1) (Phan et al., 2014) for the interaction of CO_2 with oxoanions.

The efficiency of these two inorganic oxoanions to PCC was subsequently investigated. This numerical investigation was performed firstly by simulating the kinetics of the absorption of $CO_{2(aq)}$ into an equilibrated solution containing a tertiary amine as a base, catalyst and various amount of already absorbed CO_2. Further numerical analyses allowed the determination of the proportions of CO_2 reacting along different possible reaction pathways in aqueous solution, the direct reactions with H_2O and with OH^- as well as the catalysed reaction, as defined by the following equations:

$$CO_2\,(+H_2O) \underset{k_{-1}}{\overset{\text{slow},k_1}{\rightleftarrows}} H_2CO_3 \tag{1}$$

$$CO_2 + OH^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} HCO_3^- \tag{2}$$

$$CO_2\,(+H_2O) + \text{Cat} \underset{k_{-cat}}{\overset{k_{cat}}{\rightleftarrows}} H_2CO_3 + \text{Cat} \tag{3}$$

where Cat is either sulfate or vanadate. The hydration reaction (1) is defined as a pseudo-first order reaction as the concentration of

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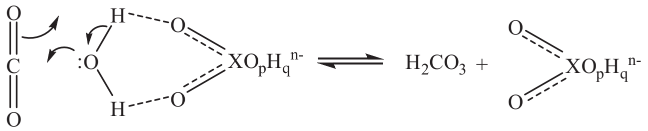

Scheme 1. Proposed mechanism for the catalytic reaction of hydrated oxoanions (Phan et al., 2014).

water is in large excess and thus essentially constant. Similarly, the catalytic forward reaction is defined as a pseudo-second order reaction. This is indicated by the brackets for the water reagent.

2. Materials and methods

2.1. Materials

High purity CO_2 gas (BOC), analytical grade thymol blue sodium salt (Sigma-Aldrich, ACS reagent), 3-dimethylamino-1-propanol (3-DMAP) (Sigma-Aldrich), sodium hydrogen sulfate ($NaHSO_4$, >99%, AnalaR) and sodium orthovanadate (Na_3VO_4, 99.98%, Sigma-Aldrich) were used without further purification. Ultrahigh purity Milli-*Q* water which was boiled in advance to remove CO_2 gas was used to prepare the solutions. The experimental solutions were freshly prepared on the same day as the measurements were conducted.

2.2. Experimental methods

The kinetic study of the acceleration of CO_2 hydration with different amounts of inorganic materials including $NaHSO_4$ and Na_3VO_4 were performed on an Applied Photophysics DX-17 stopped-flow spectrophotometer equipped with a J&M Tidas MCS 500-3 diode-array detector. The reaction was initiated by mixing equal volumes of a solution containing various amounts of catalyst, the tertiary amine 3-DMAP and the indicator thymol blue with a solution of water saturated with CO_2, all thermostatted at 25 °C. The resulting initial concentrations were: catalyst (0.0, 1.7, 3.4 and 5.1 mM), 3-DMAP (25 mM), thymol blue (25 μM) and CO_2 (17.25 mM). The reactions involved aqueous solutions with homogenous mixing. Therefore, there was no gas–liquid phase transfer, hence no mass transfer problem. Under these conditions, CO_2 reacts in parallel reactions, directly with water, hydroxide and on the catalytic path (Eqs. (1)–(3)). Under the prevalent pH, the initial formation of carbonic acid is immediately followed by its deprotonation to form the bicarbonate ion. This reaction results in the lowering of the pH which in turn is observed by the change in the colour of the indicator. This method has been developed (Penny and Ritter, 1983) and is well established for CO_2 research (Conway et al., 2011; McCann et al., 2009). Tertiary amines do not react with CO_2. They only react as proton acceptors driving the reactions towards the products. Their only relevant property is the protonation constant. 3-DMAP was chosen because its protonation constant perfectly matches that of the indicator. Moreover, due to the low solubility of CO_2 in aqueous solution, the stopped-flow experiments have to be performed at low total concentration of all reactants. The extrapolation to industrially more relevant conditions is facilitated by using activity coefficients for all ionic species (see Section 3.2).

2.3. Data analysis

Data analysis for the catalysis of CO_2 hydration by sulfate and vanadate was performed using the same method previously reported by Phan et al. (2014).

Table 1
Experimental rate constant of catalysed reversible CO_2 hydration.

Catalyst	pH range	$Cat + CO_2\ (+H_2O) \underset{k_{-cat}}{\overset{k_{cat}}{\rightleftarrows}} Cat + H_2CO_3$	
		k_{cat} ($M^{-1}\ s^{-1}$)	k_{-cat} ($M^{-1}\ s^{-1}$)
SO_4^{2-}	10.03–8.76	14.2(2)	9.6(1) × 10^3
HVO_4^{2-}	11.54–9.32	277(6)	187(4) × 10^3

The experimental data obtained by stopped-flow spectrophotometry were analysed using in-house developed software in MatLab and the simulations were performed using ReactLab (King and Maeder, 2014). Algorithms that take into account process-induced pH changes and subsequent adjustment of the protonation equilibria were employed to model the kinetic data (Maeder et al., 2003).

Standard Newton–Gauss–Levenberg/Marquardt algorithms were used for non-linear least-squares fitting of the relevant parameters and the rate or equilibrium constants (Bevington, 1969; Maeder and King, 2012; Maeder and Neuhold, 2007).

All reactions of CO_2 species in aqueous solution were included in the model for data analyses, more details of which have been previously presented by Phan et al. (2014). In order to determine the catalytic rate constants of the inorganic oxoanions on CO_2 hydration, the measurements at four different concentrations of each catalyst were globally analysed. The statistically averaged rate constant values calculated from the analyses of a triplicate of four measurements and the associated errors are reported for each catalyst.

An activity coefficient correction was applied to all charged species for the kinetic studies. The extended Debye–Hückel equation, Eq. (4), was used to estimate the activity coefficients (Stumm and Morgan, 1996).

$$\log\ \gamma_i = \frac{-Az_i^2\sqrt{\mu}}{1+\sqrt{\mu}} \tag{4}$$

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

The activity coefficient γ_i is a function of the ionic strength μ. The parameter A is defined by the dielectric constant of the solvent and the temperature which in water at 25 °C equals 0.51. The ionic strength corrections are not perfect, but adequate for the concentrations and ionic strengths used in this study (Haubrock et al., 2007).

3. Results

3.1. Catalysis of CO_2 absorption by inorganic oxoanions

The chemical model used for the study of the catalysis of CO_2 absorption in aqueous solution using sulfate and vanadate is similar to that applied for the system using arsenite, arsenate, phosphite, phosphate and borate (Phan et al., 2014). As not all protonation constants for vanadate at 25 °C and an ionic strength of 0 M were readily available, their values at an ionic strength of 0.5 M were extrapolated to 0 M for data analysis (pK_{a1} = 12.96, pK_{a2} = 7.76 and pK_{a3} = 3.76) (Dyrssen and Sekine, 1964; Ingri and Brito, 1959; Newman et al., 1958; NIST, 2001; Pope, 1983). Under our experimental conditions, sulfate and vanadate exist in the forms of SO_4^{2-} and HVO_4^{2-}, respectively. The relevant pH ranges are listed in Table 1.

The experimental and fitted data together with the concentration profile of CO_2 over time for the acceleration of CO_2 hydration by sulfate are shown in Fig. 1.