International Journal of Greenhouse Gas Control 63 (2017) 249–259

Contents lists available at ScienceDirect

International Journal of Greenhouse Gas Control

journal homepage: www.elsevier.com/locate/ijggc

Enhancements in mass transfer for carbon capture solvents part I: Homogeneous catalyst

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ARTICLE INFO

Keywords:
Post-combustion
CO_2 capture
Mass transfer
Amine
Catalyst
Additives

ABSTRACT

The novel small molecule carbonic anhydrase (CA) mimic $[Co^{III}(Salphen\text{-}COO^{-})Cl]HNEt_3$ (**1**), was synthesized as an additive for increasing CO_2 absorption rates in amine-based post-combustion carbon capture processes (CCS), and its efficacy was verified. **1** was designed for use in a kinetically slow but thermally stable blended solvent, containing the primary amines 1-amino-2-propanol (A2P) and 2-amino-2-methyl-1-propanol (AMP). Together, the A2P/AMP solvent and **1** reduce the overall energy penalty associated with CO_2 capture from coal-derived flue gas, relative to the baseline solvent MEA. **1** is also effective at increasing absorption kinetics of kinetically fast solvents, such as MEA, which can reduce capital costs by requiring a smaller absorber tower. The transition from catalyst testing under idealized laboratory conditions, to process relevant lab- and bench-scale testing adds many additional variables that are not well understood and rarely discussed. The stepwise testing of both **1** and the novel A2P/AMP solvent blend is described through a transition process that identifies many of these process and evaluation challenges not often addressed when designing a chemical or catalytic additive for industrial CCS systems, where consideration of solvent chemistry is typically the primary goal.

1. Introduction

Increasing concern over global CO_2 emissions has led to new regulations from the US Environmental Protection Agency (EPA) for coal-fired power generation, which is responsible for the emission of billions of tons annually. As of January 2014, new coal burning units require carbon capture and storage (CCS) processes to reduce CO_2 emissions to 1100 lb/MW (Environmental Protection Agency, 2014a,b). Amine-based carbon capture is the most widely studied, and most likely to be implemented commercially, method for CO_2 purification from flue gas (Liang et al., 2015). However, the cost of these systems is still prohibitive, and reduction in both capital and operational costs, relative to the Department of Energy (DOE) reference case 12, 30 wt.% monoethanolamine (MEA), is necessary (Cost and Performance, 2010). In general, capital costs arise on the absorption side of the process, while operational costs arise on the CO_2 stripping/solvent regeneration side. Construction of the absorption tower (absorber) alone accounts for approximately 30% of the initial capital investment for construction of a carbon capture system; therefore significant effort has focused on understanding and increasing absorption kinetics of the amine solvent in the absorption tower (Liang et al., 2015; Lu et al., 2011; Vinoba et al., 2013; Penders-van Elk et al., 2013, 2015).

Research toward increasing CO_2 absorption in solvent-based CCS processes has focused on three main strategies: (1) solvent development/amine blends (Li et al., 2013; Voice et al., 2013; Sherman et al., 2013; Lin and Wong, 2014; Shi et al., 2014; Adeosun and Abu-Zahra, 2013; Aroonwilas and Veawab, 2007), (2) modification of the packing material to increase wetted surface area (Tsai et al., 2008, 2011), and (3) the addition of catalysts, such as small-molecule carbonic anhydrase (CA) mimics (Floyd et al., 2013; Koziol et al., 2012; Zhang et al., 1993; Zhang and Vaneldik, 1995), to increase the chemical kinetics of absorption and desorption (Liang et al., 2016) reactions. The development of new amines and solvent blends has been delivering incremental gains, as there is always a tradeoff between reactivity and stability, where increased absorption kinetics is generally associated with higher regeneration energy and reboiler duty (Evans and Polanyi, 1936; Nwaoha et al., 2017). In addition, the emission of amine degradation products (Huang et al., 2013; Wang and Jens, 2013), particularly carcinogenic nitrosamines from secondary amine solvents (Voice et al., 2015), raises concerns over the use of some potentially effective absorption solvents. Absorption catalyst development has also been plagued with process difficulties, and the most widely studied (1) carbonic

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http://dx.doi.org/10.1016/j.ijggc.2017.05.019
Received 16 December 2016; Received in revised form 7 April 2017; Accepted 26 May 2017
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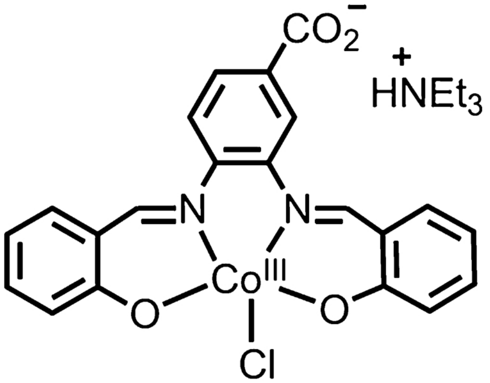

Fig. 1. Proposed structure of **1**.

anhydrase (CA), and (2) the CA mimic, [Zn(cyclen)(H_2O)](ClO_4)$_2$, are ineffective under CCS conditions (Kelsey et al., 2016; Evans and Polanyi, 1936).

Recent work has led to the first reported examples of homogenous CO_2 hydration catalysts that allowed for mass transfer enhancement in kinetically-fast primary amine solvents (Kelsey et al., 2016; Lippert et al., 2014a,b). These catalysts incorporate electron donating ligand environments and ionic secondary coordination sphere groups to increase solubility in aqueous solutions, promote CO_2 hydration, and facilitate bicarbonate dissociation away from the metal center. Previous reports have detailed the synthesis, characterization, and preliminary laboratory testing of these catalysts under conditions conducive to carbon capture processes, i.e. low CO_2 concentration (0.14 atm), and high amine concentration (5 M). These previously reported complexes were shown to be stable toward the high temperatures (up to 145 °C) and oxidizing flue gas contaminants (SO_x and NO_x) associated with industrial CCS processes. Herein we report the testing and analysis of the novel catalyst [Co^{III}(Salphen-COO^-)Cl]$HNEt_3$ (1, Fig. 1), and describe the difficulties associated with integrating the new additive into a bench scale, heat-integrated absorber-stripper process.

2. Experimental

2.1. General

Reagents for solvent mixtures, catalyst synthesis, and kinetics studies were purchased from Sigma Aldrich, monoethanolamine was purchased from Univar. Solutions of monoethanolamine (MEA, 5 M) and the A2P/AMP blended solvent (0–30 wt.% of each component) were prepared by weight% and adjusted to an alkalinity of 5.0 mol N/Kg. Experimental methods for pH drop (Kelsey et al., 2016; Bond et al., 2001), total inorganic carbon loading (Liu et al., 2013), and alkalinity (Liu et al., 2013) measurements were conducted according to reported procedures. The surface tension and the surface elasticity data were acquired at 22 °C on a Biolin Scientific Optical Tensiometer, using Oneattension software. The viscosity of the solutions were determined by using the Brookfield DVI viscometer. Catalyst loading of 2.3 g/L is used based on previously reported studies (Lippert et al., 2014a,b). Foaming volume measurements were conducted in a 100 mL graduated cylinder, with 10 mL of solvent, under study. Simulated flue gas (14% CO_2 with balance N_2) gas was purged through a gas impinger at a constant flow rate (0.6 L/min). The volume of the foam formed with continuous purging of CO_2 was then recorded as a function of time.

2.2. Synthesis of [Co^{III}(Salphen-COO^-)Cl]$HNEt_3$ (1)

N,N′-disalicylidene-4-carboxy-1,2-phenylenediamine (Salphen-COOH) (Delaney et al., 1990) was synthesized by stirring salicylaldehyde (1.80 mL, 16.9 mmol) and 3,4-diamino benzoic acid (1.01 g, 6.5 mmol) in ethanol (40 mL) overnight, then collecting the orange solid (2.05 g, 86% yield) by filtration and washing with ethanol and diethyl ether. The Salphen-COOH ligand was suspended in ethanol (30 mL), followed by addition of triethylamine (2.80 mL, 20.1 mmol). An ethanolic (30 mL) solution of $CoCl_2{\cdot}6H_2O$ (1.49 g, 6.2 mmol) was added to the reaction mixture dropwise over 15 min to give dark brown solution, and the reaction mixture was stirred overnight at room temperature. Diethyl ether (50 mL) was added, and the resulting brown precipitate was collected by vacuum filtration. The solid product was washed with methanol (30 mL), diethyl ether (30 mL), and allowed to air dry, giving **1** (3.07 g, 93%) as a brown powder. FTIR-ATR (cm^{-1}): 3369 (s), 2979 (m), 1601 (s, C = N), 1539 (s), 1442 (s), 1369(s), 1304(s), 1151(s). ESI-ToF (*m/z*): 417.02777 [**1** − Et_3N − Cl]$^+$. Elemental analysis [**1**·$2H_2O$]. Anal. Calc. for $C_{27}H_{33}ClCoN_3O_6$: C, 54.97; H, 5.64; N, 7.12. Found: C, 55.43; H, 5.64; N, 6.82 (Fig. 1).

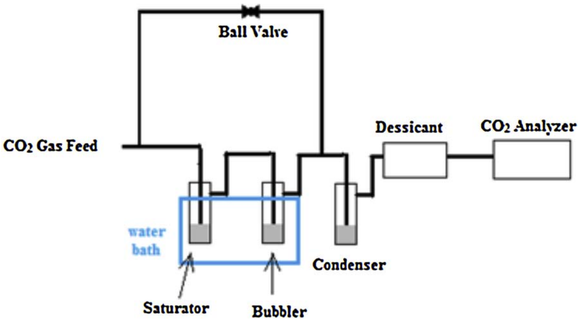

Fig. 2. Schematic of breakthrough apparatus.

2.3. Breakthrough solvent evaluation apparatus

Breakthrough experiments were conducted as previously reported (Kelsey et al., 2016; Lippert et al., 2014b). In a representative procedure, the breakthrough solvent evaluation apparatus (Fig. 2) consists of a 30 mL gas saturator, a 30 mL bubbler, a condenser, and a CO_2 analyzer. Both the saturator and the bubbler are made of Pyrex®, and are immersed in a water bath maintained at 40 °C. A CO_2 feed gas stream (12%–14%) balanced with N_2 is saturated with water in the saturator and bubbled through a 30 wt% MEA solution in the bubbler (1 L/min). The gas effluent is dried over drierite and analyzed for CO_2 concentration (vol%) using a CO_2 analyzer (VIA-510, HORIBA, 0.5% precision). Data of CO_2 outlet concentration with respect to time is continuously recorded with 1 s interval using an in-house Labview program.

The difference of inlet and outlet CO_2 concentration represents the absorbed amount of CO_2 at a particular time. The integration of the concentration difference represents the CO_2 loading, as expressed in Eq. (1),

$$\text{CO}_2\ \text{Loading (mol CO}_2\text{/ kg solution)} = \frac{\int_0^t (C_{in} - C_{out}(t))dt}{m_{sol}} \tag{1}$$

where C_{in} is the CO_2 feed gas rate in mol/s, C_{out} is the CO_2 effluent rate in mol/s, t is time in second, and m_{sol} is the mass of solution in kg.

In addition, the absorption rate can be described by the derivate of CO_2 loading with respect to time is given by Eq. (2),

$$\text{Abosorption rate (mol CO}_2\text{/kg solution/s)}=\frac{dCO_2\ Loading}{dt} \tag{2}$$

2.4. Determination of mass transfer coefficient by wetted wall column (WWC)

Wetted wall column experiments were conducted as previously reported (Liu et al., 2013). A schematic of the WWC used in this test is shown in Fig. 3. In a representative procedure, 30 wt% aqueous MEA is

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