**Support Information of manuscript**

Catalytic CO2-MEA absorptions with the aid of CaCO3, MgCO3 and BaCO3 in the batch and semi-batch processes

**Theory:**

1. **The proposed mechanism of heterogeneous catalysis on solid surface:**

 We completed the Figure of proposed mechanism of heterogeneous catalysis of CO2-MEA with 4 elementary steps. The mechanism is similar to the **Eley-Rideal model** of Gas-Solid absorption. The mechanism study will be conducted in the near future.

 Fig. S1 Proposed mechanism of catalytic carbamate formation for MEA: **Eley-Rideal Model**.

Table 1 (manuscript) listed the proposed elementary steps (E1 to E4) of the catalytic CO2 – amine absorption with aid of catalysts, where (\*) represents the active sites on the surface.

**Table 1.** The elementary steps of catalytic CO2 absorption

|  |  |  |
| --- | --- | --- |
| Elementary Steps | Reaction Scheme | Description |
| **E1** | RNH2 + (\*) 🡪 RNH2(\*)  | Amine adsorption |
| **E2** | RNH2(\*) + CO2 🡪 RNH2+-COO-(\*)  | Zwitterion formation |
| **E3** | RNH2+-COO-(\*) + RNH2 🡪 RNH2+-COO-(\*) + RNH3+  | Carbamate formation |
| **E4** | RNH2+-COO-(\*) 🡪 RNH2+-COO- + (\*)  | Carbamate desorption |

**The brief reaction mechanism of catalytic absorption from Table 1: 4 steps**

The MEA molecules were pre-adsorbed onto the solid surface via amine adsorption (E1). Then, when CO2 was approaching the solid surface, it reacts with MEA (RNH2) via N-C bond formation and generate Zwitterion (E2). Later on, the Zwitterion transfer a proton to other MEA or water to generate Carbamate (E3) and release heat. The released reaction heat facilitated the desorption of Carbamate apart from the solid surface (E4).

**Experiments:**

1. **The AAD% analysis of Chittick analysis:**

 The value of 2.5% is a typical AAD% of the Chittck apparatus. The CO2 was released out of the loaded amine solutions by titration, and then collected and measured properly.

Typically, the CO2 loading (α) was calculated with the equation below:

 α = $\frac{VCO2}{24.45 C V} \frac{10^{-3} ml gas}{\frac{L}{mol gas} 10^{-3} mol Amine }$ (24.45 is L/mol for ideal gas at 298K)

 The titration method is highly accurate, with an AAD% of 0.2%, which is negligible.

Then, the calculation of CO2 loading was based on the CO2 gas collected in the apparatus. The gas for each test is around 10~50 ±0.5 ml. The minimum measurement of gas volume is 1 ml, the deviation is around ±0.5 ml. Under experiments, we pipette many 2 ml samples for analysis, the volume of CO2 is within 20-50 ml. We considered 20 ml CO2 was collected in the apparatus as maximum error.

The AAD% is calculated below:

AAD% = 0.5 / 20.0 \* 100% = 2.5 %.

1. **The picture of semi-batch process of CO2 absorber with catalytic packing.**

This is the real process, corresponding to Fig 1 B.

  

1. **The size of pelletized solid and balls of catalysts:**

From the photos below, these solids **were pelletized at size on 2-3mm first**, and then wrapped into several balls with similar sizes, and then they are suspended onto the gas-liquid interface. The intersection area of two solid balls are about 9.05 cm2 (2.4 cm diameter each). The uncertainty is estimated to be around 0.1 cm (~ 4%).



The solid chemicals were also paved into one layer of two structured packing materials in the absorber of Semi-Batch Process. **The size was also 2-3 mm, same as that in batch process**.



**Results: Summary of CO2 absorption profiles in a batch process.**

1. **The summarized Table S1 of absorption profiles Fig 3-5.**

Table S1. The overall time period of CO2 absorption with different catalysts.

|  |  |
| --- | --- |
| **1M MEA** | Reaction time period (min) |
|  | Types of Catalyst |
| **Mass of Catalyst (g)** | **MgCO3** | **CaCO3** | **BaCO3** |
| 0 | 14.0 | 14.0 | 14.0 |
| 5 | 9.0 | 12.0 | 13.0 |
| 10 | 8.5 | 9.0 | 12.0 |
| 15 | **7.0** | 8.0 | 11.0 |
| 20 | 8.0 | **7.0** | 10.0 |
| 25 |  |  | **8.0** |
| Overall reduction of time % | **50.0%** | **50.0%** | **42.9%** |
|  |  |  |  |
| **3M MEA** | Reaction time period (min) |
|  | Types of Catalyst |
| **Mass of Catalyst (g)** | **MgCO3** | **CaCO3** | **BaCO3** |
| 0 | 38.0 | 38.0 | 38.0 |
| 5 | 32.0 | 32.0 | 32.0 |
| 10 | 29.0 | 29.0 | 30.0 |
| 15 | 24.5 | 25.0 | 29.0 |
| 20 | **24.0** | **23.0** | 26.0 |
| 25 |  | 26.0 | **24.0** |
| Overall reduction of time % | **36.8%** | **39.5%** | **36.8%** |
|  |  |  |  |
| **5M MEA** | Reaction time period (min) |
|  | Types of Catalyst |
| **Mass of Catalyst (g)** | **MgCO3** | **CaCO3** | **BaCO3** |
| 0 | 47.0 | 47.0 | 47.0 |
| 5 | 42.0 | 40.0 | 40.0 |
| 10 | 40.0 | 37.0 | 38.0 |
| 15 | **38.0** | 35.0 | 37.0 |
| 20 | 39.0 | **31.9** | 35.0 |
| 25 |  | 35.0 | **34.5** |
| Overall reduction of time % | **19.1%** | **31.9%** | **26.6%** |