**Supplementary Materials (A)**

**The development of Elementary reaction steps from Eley-Rideal models**

# **The Eley – Rideal model was developed based on the reactions of CO2 + MeOH.**



Fig. S1. Elementary mechanistic steps proposed for the formation of dimethyl carbonate (DMC) from CO2 and methanol by an Eley–Rideal mechanism

Ref 25: V. Eta, P. Maki-Arvela, J. Warna, T. Salmi, J.P. Mikkola, D.Y. Murzin, Appl. Catal. A 404 (2011) 39–46.

This research developed Elementary reaction steps based on similar reactions, with CO2 and Eley-Rideal models. The other chemicals (b) adsorbed onto solid surface, and CO2 react with it directly.



**The Elementary steps based on Figure 1**

|  |  |  |  |
| --- | --- | --- | --- |
| **B1** |

|  |
| --- |
| RNH2 + (\*) RNH2(\*)  |

 | *k1, k-1* |
| **B2** |

|  |
| --- |
| CO2 (g) + RNH2(\*)  RNH2+-COO-(\*) (Zwitterion)  |

 | *k2, k-2* |
| **B3** | H2O + RNH2+-COO- (\*)RNH-COO- (\*)(Carbamate) + H3O+ | *k3, k-3* |
| **B4** |

|  |
| --- |
| RNH-COO- (\*) RNH-COO- (Carbamate) + (\*) |

 | *k4, k-4* |

**The Elementary steps for Eley - Rideal model with Apparent Rate Law Derivation**

# **The Catalytic carbamate formation from Eley - Rideal model:**



**The derivation of Apparent rate law was similar from Ref.[26]**

**The Elementary steps based on Figure 1**

|  |  |  |  |
| --- | --- | --- | --- |
| **B1** |

|  |
| --- |
| RNH2 + (\*) RNH2(\*)  |

 | *k1, k-1* |
| **B2** |

|  |
| --- |
| CO2 (g) + RNH2(\*)  RNH2+-COO-(\*) (Zwitterion)  |

 | *k2, k-2* |
| **B3** | H2O + RNH2+-COO- (\*)RNH-COO- (\*) (Carbamate) + H3O+ | *k3, k-3* |
| **B4** |

|  |
| --- |
| RNH-COO- (\*) RNH-COO- (Carbamate) + (\*) |

 | *k4, k-4* |

Abbreviations: A = Amine, C = Carbamate, B = CO2, Z = Zwitterion, H+ = H3O+, W = H2O;

Some foundations should be laid here:

B5 if r1 = 0.

B6 if r2 = 0.

B7 if r3 = 0.

B8 if r4 = 0.

The overall active sites on surface area:

B9

## 2.1 Rate equations development: B1 to B4

**CASE I:** **B1** is the rate-determine-step (RDS), where the rest equations reached equilibrium:

r = ; B1 r2 = r3 = r4 = 0 where B1 is RDS.

Some variables: B10 from eqn B8 where r4 = 0.

 B11 from eqn B7\*B8 where r3 = r4 = 0.

 B12 from eqn B6\*B7\*B8 where r2=r3 = r4 = 0.

B9

 =

 =

 B9 for the case where B1 as RDS

Replace B12 into B1

 where

Input B9 into B1

 set

 B13

Under absorption conditions, , [H+] is negligible, the equation can be simplified as

 B13’ simplifed format of B13

**CASE II:** **B2** is the rate-determine-step (RDS), the rest equations reached equilibrium:

r = ; B2 r1 = r3 = r4 = 0 where B2 is RDS.

Some variables: B10 from eqn B8, where r4 = 0.

 B11 from eqn B7\*B8, where r3 = r4 = 0.

 B14 from eqn B5, where r1 = 0.

B9

 =

 =

 B9 for the case where B2 as RDS

Replace B14, B11 into B2

Imput B9 into B2

 where ,

= B15.

Under absorption conditions, , H+ is negligible, the equation can be simplified as

 B15’ simplifed format of B15

**CASE III:** **B3** is the rate-determine-step (RDS), where the rest equations reached equilibrium:

r = ; B3 r1 = r2 = r4 = 0 where B3 is RDS.

Some variables: B10 from eqn B8, where r4 = 0.

 B16 from eqn B5\*B6, where r1 = r2 = 0.

 B14 from eqn B5, where r1 = 0.

B9

 =

 =

 B9 for the case where B3 as RDS

Replace B16, B10 into B3

 [W] is constant move to a new *k3*,

Imput B9 into B3

 where ,

 = B17.

Under absorption conditions, , H+ is negligible, the equation can be simplified as

 B17’ simplifed format of B17

**CASE IV:** **B4** is the rate-determine-step (RDS), where the rest equations reached equilibrium:

r = ; B4 r1 = r2 = r3 = 0 where B4 is RDS.

Some variables: B18 from eqn B5\*B6\*B7, where r1 = r2 = r3 = 0.

 B16 from eqn B5\*B6, where r1 = r2 = 0.

 B14 from eqn B5, where r1 = 0.

B9

 =

 =

 B9 for the case where B4 as RDS

Replace B16, B10 into B4

Input B9 into B4:

 where ,

 = B19.

Under absorption conditions, , H+ is negligible, the equation can be simplified as

 B19’ simplifed format of B19, pseudo 0th order

## 2.2 Rate model Validation with experimental datasets of (XA, t):

**Case I: The RDS = B1**

**The rate is controlled by amine adsorption onto solid surface**:

**Sub Case: K4[C] << 1:**

**Sub Case: K4[C] >> 1:**

**CASE II: The RDS = B2, the rate is controlled by N-C bond formation of carbamate formation**:

***ka* = 0.5 K1 K4 ;**

 **Sub Case: *ka* = 0.05; *ka* = 0.01; *ka* = 0.005;**

 **Special: *ka* = 0;**