

# Carboxylation of Aromatics by CO<sub>2</sub> under “Si/Al Based Frustrated Lewis Pairs” Catalytic System

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## Abstract

Carboxylation of aromatics by CO<sub>2</sub> to generate corresponding carboxylic acids is recently providing a novel approach to utilize the green gas CO<sub>2</sub>, in which the activation of CO<sub>2</sub> is the key procedure. Among the many catalytic systems employed in the carboxylation, the concept of “Frustrated Lewis Pairs” (FLPs) was scarcely mentioned, which perform excellently in activating small molecules like CO<sub>2</sub>. The FLPs are combinations of Lewis acids and Lewis bases which failed to form adducts due to their bulky steric congestion. In this paper, we first attempted various Si/Al Based FLPs to catalyze the carboxylation of aromatics through the activation of CO<sub>2</sub>, and a good yield of 62% - 97% was obtained. The reaction mechanism was proposed, involving the activation of CO<sub>2</sub> mainly contributed by AlCl<sub>3</sub> in cooperation with organosilane, forming an intermediate consisting of CO<sub>2</sub>, AlCl<sub>3</sub>, and R<sub>4</sub>Si, as well as the subsequent electrophilic attack to aromatics, thus to promote the carboxylation reaction.

## Keywords

Carboxylation, Frustrated Lewis Pairs, Carbon Dioxide, Aromatic, Catalytic System

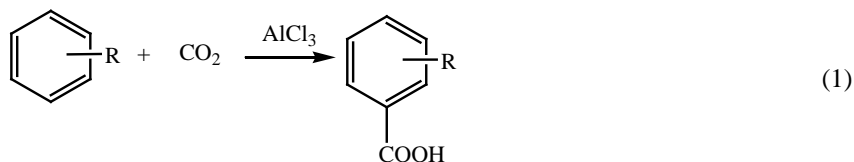
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## 1. Introduction

Carboxylation of aromatics by CO<sub>2</sub> is a competitive alternative to generate corresponding carboxylic acids, in view of its narrow spectra of by-products, effective utilization of greenhouse gas CO<sub>2</sub>, as well as the mild reacting conditions [1]. Olah *et al.* [2] first discovered that mixing of benzene with CO<sub>2</sub> at 5.7 MPa and 70°C in the presence of Al/AlCl<sub>3</sub> led to benzoic acid as the sole product with 88% in yield, and the pathway of the reaction was studied using DFT calculation, only to find that the carboxylation was proceeded through the formation of “CO<sub>2</sub>-(AlCl<sub>3</sub>)<sub>n</sub>” complexes via activation of CO<sub>2</sub>, which was then reacting with the aromatics in a typical electrophilic substitution. Various Lewis acids were proved to be catalytic for the carboxylation, among which AlCl<sub>3</sub> performs the best (Equation (1)).

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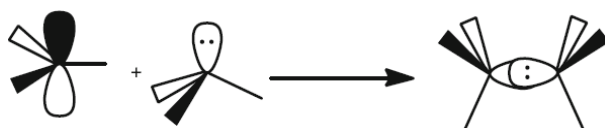
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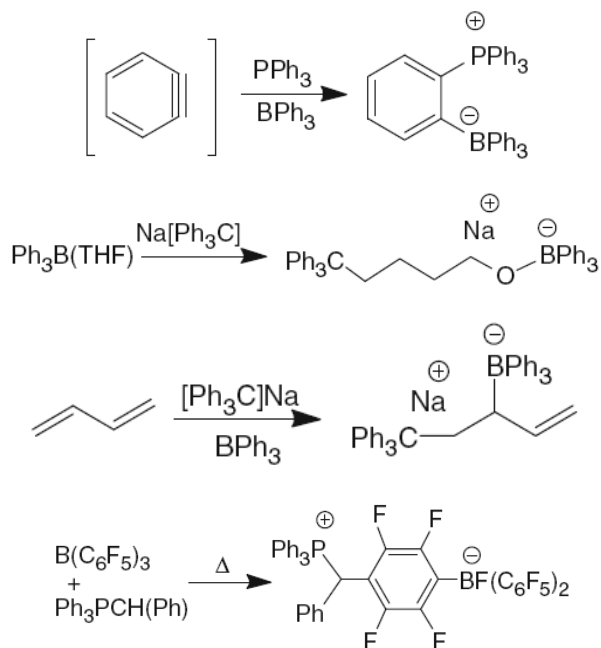
More recently, Munshi *et al.* [3] [4] found that the activation of  $\text{CO}_2$  by  $\text{AlCl}_3$  before mixing with toluene could promote the carboxylation remarkably, while Nemoto *et al.* [5] [6] found the Lewis acid-mediated carboxylation of aromatic compounds with  $\text{CO}_2$  could be greatly promoted by the addition of a large excess of silyl chlorides, and a good to excellent yield of arylcarboxylic acids was obtained. However, we found that the utilization of FLPs, a novel catalytic system, could significantly accelerate the reaction, and also improve the isolated yield of carboxylic acids.

Frustrated Lewis Pairs (FLPs) is now widely used for activation of  $\text{CO}_2$ . The so-called “frustrated Lewis pairs” is a kind of combination consisted of a Lewis acid and a Lewis base which failed to form an adduct due to their bulky steric congestion, or because of the weak attractions between Lewis acid and base, illustrated as **Figure 1** and **Figure 2**.

In 2006, Stephan *et al.* first observed the activation of  $\text{H}_2$  using bifunctional phosphinoborane species  $\text{R}_2\text{P}(\text{C}_6\text{F}_4)\text{B}(\text{C}_6\text{F}_5)_2$  ( $\text{R} = t\text{Bu}, \text{Mes}$ ), to yield a zwitterionic-phosphonium hydroborate salt  $\text{R}_2\text{PH}(\text{C}_6\text{F}_4)\text{BH}(\text{C}_6\text{F}_5)_2$  [8]. Afterwards, many achievements were reported in activation of small molecules such as olefins, alkenes, THF,  $\text{N}_2\text{O}$ ,  $\text{NO}$  and  $\text{CO}_2$  [9]-[11]. What worth mentioned is the activation of  $\text{CO}_2$  that can be efficiently accomplished by numerous phosphine-borane FLPs [12]-[15], where FLPs offer both nucleophilic and electrophilic synergy to enable the breaking of the strong  $\text{C}=\text{O}$   $\pi$ -bond in  $\text{CO}_2$ , concomitant with the formation of new nucleophile-C and electrophile-O bonds, which can increase the likelihood of further  $\text{CO}_2$  reactions [16] [17].



**Figure 1.** Classical formation of a Lewis acid-base adduct: Lewis acid + Lewis base  $\rightarrow$  Lewis acid-base adduct [7].



**Figure 2.** Non-conventional combinations of Lewis acids and bases: FLPs [7].

To the best of our knowledge, there is no research about the CO<sub>2</sub> activation in carboxylation of aromatics using FLPs consisted of AlCl<sub>3</sub>. In this paper, Si/Al Based FLPs were attempted to catalyze the carboxylation of aromatics, such as toluene, ethylbenzene, *m*-xylene, *etc.*, and a feasible mechanism of carboxylation under Si/Al Based FLPs catalytic system was proposed, involving the activation of CO<sub>2</sub> mainly contributed by AlCl<sub>3</sub> in cooperation with organosilane, as well as the subsequent electrophilic attack to aromatics, thus to promote the carboxylation reaction.

## 2. Experimental

### 2.1. Materials and Instruments.

Toluene (99.5%), ethylbenzene (99.5%), *m*-xylene (99%), mesitylene (97%), benzene (99.5%), CO<sub>2</sub> (99.99%), and anhydrous AlCl<sub>3</sub> were used for carboxylation, which were commercially purchased and used as received. The anhydrous AlCl<sub>3</sub> was handled under inert atmosphere to avoid decomposing by water. Organosilanes R<sub>4</sub>Si such as Me<sub>3</sub>SiCl, Me<sub>2</sub>PhSiCl, MePh<sub>2</sub>SiCl, Ph<sub>3</sub>SiCl were also used in carboxylation. HCl (36% - 38%), anhydrous diethyl ether (99.5%) and NaOH (96%) were used for separation of product carboxylic acids.

The instruments used in this work were Nuclear Magnetic Resonance (NMR, Bruker 500), and Infrared Imaging Spectrometer (Nicolet 6700). The carboxylation was carried out in a 100 ml 316 L stainless steel autoclave coated with a heating jacket and a magnetic stirrer.

### 2.2. Carboxylation of Aromatics to Generate Corresponding Arylcarboxylic Acids

All materials including Al<sub>2</sub>Cl<sub>6</sub> (2.25 mmol, 0.6 g), toluene (20 ml), and Me<sub>3</sub>SiCl (0.25 g, 2.25 mmol) were added to the autoclave. After pressurization of CO<sub>2</sub>, the temperature was raised to 80 °C, where the carboxylation was conducted for 12 h until the reaction reached equilibrium. Afterwards, the reaction was stopped by cooling down to room temperature. Water was added to the reacted mixture and the products were extracted with diethyl ether and 10% NaOH. The extracted aqueous phase was adjusted to pH = 1 by adding hydrochloric acid. Precipitated white crystals were obtained after the ice bath cooling.

The toluic acid obtained was qualitatively identified by IR. The ratio of the acid isomers was evaluated by relative integration ratio of <sup>1</sup>H NMR signals, δH (500MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 2.56 (H, s, *o*-Me), 2.39 (H, s, *m*-Me), 2.31 (H, s, *p*-Me). The ratio of *ortho*, *meta*, and *para* was found to be 9:4:87.

Other experiments with different Si/Al Based FLPs were conducted in a similar manner as detailed above, and the contrast experiment employing only AlCl<sub>3</sub> as catalyst was also conducted.

## 3. Results and Discussion

### 3.1. Carboxylation of Toluene by CO<sub>2</sub> under Si/Al Based FLPs

Several combinations of Si/Al Based FLPs were selected to carry out the carboxylation of toluene by CO<sub>2</sub>, to generate corresponding *p*-toluic acid (*p*-TA). The results were listed in **Table 1**. Since the aluminium chloride tends to dimerize in most organic solvents like toluene, benzene, xylene, *etc.*, here we calculate the isolated yield based on dimer Al<sub>2</sub>Cl<sub>6</sub>.

**Table 1.** Carboxylation of toluene through CO<sub>2</sub> activation under Si/Al Based FLPs.

Entry	Si/Al pairs <sup>a</sup>	Temp./°C	CO <sub>2</sub> pressure/Mpa	Isolated yield <sup>b</sup> /%
1	Me <sub>3</sub> SiCl/AlCl <sub>3</sub>	70	5.5	62
2	Me <sub>2</sub> PhSiCl/AlCl <sub>3</sub>	70	5.5	83
3	MePh <sub>2</sub> SiCl/AlCl <sub>3</sub>	70	5.5	92
4	Ph <sub>3</sub> SiCl/AlCl <sub>3</sub>	70	5.5	95
5	--/AlCl <sub>3</sub>	70	5.5	78

a: Molar ratio R<sub>3</sub>SiCl/AlCl<sub>3</sub> = 1:1. b: Isolated yield is calculated based on Al<sub>2</sub>Cl<sub>6</sub> : *p*-TA = 1:1. Products obtained by extraction with diethyl ether and NaOH, followed by precipitation in ice bath after adjusted to pH = 1.

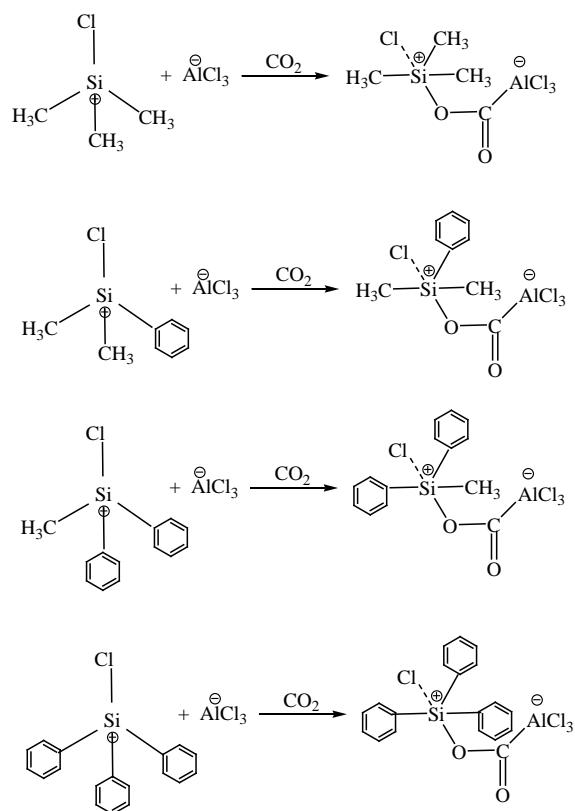
According to **Table 1**, all the Si/Al Pairs were capable to catalyze the carboxylation of toluene by CO<sub>2</sub>, giving satisfying yields of 62% - 95%. When Ph<sub>3</sub>SiCl was added accompanied with AlCl<sub>3</sub>, the *p*-TA yield reached 95% (entry 4), which exceeded a lot compared to that of only AlCl<sub>3</sub> used (78%, entry 5). However, the yield dropped to 62% when employed Me<sub>3</sub>SiCl/AlCl<sub>3</sub> pairs instead (entry 1), suggesting that the catalytic effect is influenced by the steric hindrance of organosilane molecules. This supposition was further demonstrated by the phenomenon of introducing Me<sub>2</sub>PhSiCl and MePh<sub>2</sub>SiCl that the *p*-TA yield is ranked as Ph<sub>3</sub>SiCl > MePh<sub>2</sub>SiCl > Me<sub>2</sub>PhSiCl > Me<sub>3</sub>SiCl, just corresponds to their size of substituent groups, *i.e.*, the steric hindrance.

As advocate above, the key procedure in carboxylation of aromatics is the activation of CO<sub>2</sub>, which means the catalytic performance is depended on the activation effect. According to the formation mechanism of FLPs, it is combined by the weak electronic attractions owing to the bulky structure, thus the organosilane which possessed larger substituent group is favorable to form the FLPs with AlCl<sub>3</sub>, leading to a high efficiency in activation of CO<sub>2</sub>. The activation process is shown in **Figure 3**.

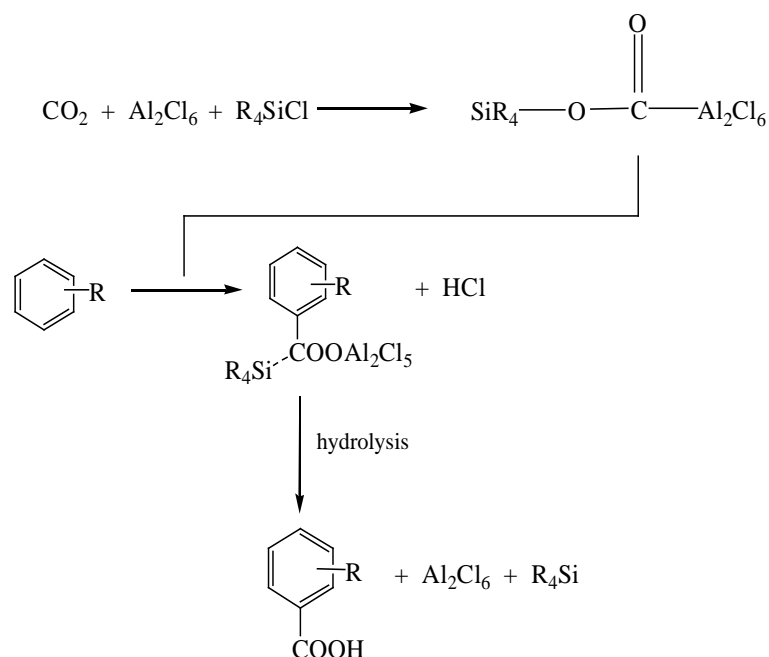
### 3.2. Activation of CO<sub>2</sub> in Carboxylation of Aromatics

Other alkylbenzenes were carboxylated with the acid of different Si/Al Based FLPs, and we proposed a feasible mechanism of carboxylation under Si/Al Based FLPs catalytic systems, involving the activation of CO<sub>2</sub> mainly contributed by AlCl<sub>3</sub> in cooperation with organosilane, as well as the subsequent electrophilic attack to aromatics, which is illustrated as **Figure 4**.

The reaction is believed to be an electrophilic aromatic substitution (S<sub>E</sub>AR) by an attack to the aromatics nucleus of the activated "CO<sub>2</sub>-AlCl<sub>3</sub>-R<sub>4</sub>Si". It is known that a trialkylsilyl group on the aromatics nucleus promotes the S<sub>E</sub>AR reaction, as the silyl group stabilizes the transition state, leading to the (p-σ)<sub>π</sub> conjugation between the Si-C bond and the formation of a benzenonium intermediate. Suspension of AlBr<sub>3</sub> and Ph<sub>3</sub>SiCl in cyclohexane to CO<sub>2</sub> reveals a C=O stretching vibration, assigned to a species consisting of CO<sub>2</sub>, AlBr<sub>3</sub>, and Ph<sub>3</sub>SiCl [6]. This suggests that organosilane could activate CO<sub>2</sub> in cooperation with AlX<sub>3</sub>, which also indicated that the mechanism proposed in **Figure 4** is convinced.



**Figure 3.** Activation of CO<sub>2</sub> using different Si/Al Based FLPs.



**Figure 4.** Feasible mechanism of carboxylation of aromatics through activation of  $\text{CO}_2$ .

**Table 2.** Activation of  $\text{CO}_2$  in carboxylation of aromatics.

Aromatics	Si/Al pairs <sup>a</sup>	Product	Isolated yield <sup>b</sup> /%
ethylbenzene	$\text{Ph}_3\text{SiCl}$	ethylbenzoic acid	81
<i>m</i> -xylene	$\text{Me}_3\text{SiCl}$	dimethylbenzoic acid	87
<i>m</i> -xylene	$\text{Ph}_3\text{SiCl}$	dimethylbenzoic acid	73
mesitylene	$\text{Me}_3\text{SiCl}$	2,4,6-trimethylbenzoic acid	89
mesitylene	$\text{Ph}_3\text{SiCl}$	2,4,6-trimethylbenzoic acid	97
benzene	$\text{Ph}_3\text{SiCl}$	benzoic acid	20

a: Molar ratio  $\text{R}_3\text{SiCl}/\text{AlCl}_3 = 1:1$ . b: Isolated yield is calculated based on  $\text{Al}_2\text{Cl}_6 : p\text{-TA} = 1:1$ . Products obtained by extraction with diethyl ether and NaOH, followed by precipitation in ice bath after adjusted to pH = 1.

## 4. Conclusion

Various combinations of Si/Al Based FLPs were employed to catalyze the carboxylation of aromatics, such as toluene, ethylbenzene, *m*-xylene, etc., and the results indicated that all of the catalytic systems could activate  $\text{CO}_2$  with a satisfying carboxylic acid yield. A feasible mechanism was proposed, involving the activation of  $\text{CO}_2$  mainly contributed by  $\text{AlCl}_3$  in cooperation with organosilane, as well as the subsequent electrophilic attack to aromatics, thus to promote the carboxylation reaction.

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