# High yield direct synthesis of liquid organics from CO<sub>2</sub> and CH<sub>4</sub> in a plasmacatalysis packed bed reactor

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**Abstract**: In this paper, a vertical tubular DBD reactor was developed with its analytical apparatus. Co catalysts supported by  $SiO_2$  aerogel were synthesized by different methods and then characterized. The plasma experiments of  $CO_2$  discharge with  $CH_4$  were conducted at ambient condition without external heating, and the performance of the catalysts was evaluated. The gas and liquid products were analysed.

Keywords: hydrocarbon synthesis, plasma catalysis, liquid products

#### **1.Introduction**

Due to the growing energy demand and the concern of atmospheric green-house gas concentration, the clean and renewable energy, such as biomass, solar and wind, now has drawn a great interest [1]. In this context, the conversion of carbon dioxide and methane, which as two major green gases are the main by-products in oil industry and main compounds of biogas, can offer environmental benefits and promising solution to the storage of renewable energy [2, 3].

Previously, researchers have made great effort in the study of conventional thermo-chemical method including dry reforming to syngas and direct conversion to liquid organics. However, high temperature is essential, and the deactivation of catalysts is also another critical issue [4]. To overcome these problems, plasma approach, which offers a unique pathway to induce chemical reactions, unlike thermo-chemical pathway due to its high concentration of energetic and chemically active species [5], has been exploited for decades. Non-thermal plasma associated with catalysts has been figured out as a feasible approach with the advantage of absence of external heating. Nevertheless, the low conversion rate of feeing gases, occasional reported liquid products, and the complex plasma-catalysts interaction don't make the approach always very promising to some extends. Tu et al. [6, 7] has reported that the full packing of catalysts with supports in the discharge volume could modify the discharge behaviour from a typical filamentary discharge to a combination of surface discharges and spatially limited microdischarges, leading to the decreasing of power in discharge and conversion of reactants.

This paper aims to develop a promising catalysts support and explore the possibility of direct liquid organic synthesis via plasma-catalytic pathway at ambient condition. The plasma experiments were firstly conducted in a tubular dielectric barrier discharge reactor at ambient pressure and temperature, and the influence of different variables were investigated. The hydrophobic SiO<sub>2</sub> aerogel was chosen as the support for Co catalyst due to its hydrophobicity and high porosity, which can avoid the extreme reduction of discharge volume. The Co loaded hydrophobic  $SiO_2$  aerogel catalysts) obtained by different methods were designed, synthesized, dried at ambient condition after surface modification, and then characterized. Finally, the catalysts were placed into the reactor, and the catalytic performance of the catalysts was investigated and presented.

#### 2. Experimental setup

The schematic diagram of the experimental setup for plasma experiments is shown in Fig. 1. Our system consists mainly of three parts: a power supply system, a reaction system, and a products collection and analysis system. The power supply system, applied to the reactor, is composed of a signal function generator (HP 33120A), an audio amplifier (IMG Stageline STA-1400) and a transformer. The schematic diagram of the DBD reactor is presented in Fig. 2. The reactor mainly consists of a borosilicate dielectric tube with a length of 300 mm, the inner and outer diameter of 10 and 12 mm, an inner high voltage electrode (D = 6mm), an outer grounded electrode  $(L = 200 \text{ mm}, \text{ discharge volume} \sim 10 \text{ cm}^3)$ , and two movable caps (D = 10 mm). The two movable Teflon caps were coupled with the aluminum rod to ensure the concentricity of electrode and borosilicate tube.12 pores (semi-circle) with a diameter of 1 mm evenly distributed around the caps. Before the reactor, the flow rate of the inlet gas is controlled by two flowmeters. The two gases flowed into the discharge area via the pores of the bottom cap and then flowed out through the pores of the top cap. The gas products after discharge were analysed online by a gas chromatography (Micro GC Fusion) and the liquid products after condensation were analysed offline by a GCMS (GCMS-QP2010, Shimadzu).

To determine the discharge power, a capacitor  $C_s$  (3.9 nF) is connected in series after the DBD reactor. Instead of accurately recording the microdischarge current spikes

which needs a high sensibility of apparatus and not easy to process the data, the current through the reactor is accumulated in the capacitor and thus can be determined by measuring the voltage on the capacitor  $V_c$ .



Fig. 1. Schematic diagram of the experimental setup.



Fig. 2. Schematic diagram of the DBD reactor.

#### 3. Materials and methods

A series of Co/SiO<sub>2</sub> aerogel catalysts with a various targeted mass ratio of Co to SiO<sub>2</sub> aerogel were firstly prepared via the sol-gel method. The aiming amount of CoCl<sub>2</sub>·6H<sub>2</sub>O (Acros Organics, ≥99%) was dissolved in ethanol (Fisher Scientific, Absolute) in a polyethylene vial while stirring. Simultaneously, polyethoxydisiloxane (P75W20, PCAS, <30%) was added to the ethanolic solution of CoCl<sub>2</sub>·6H<sub>2</sub>O and stirred for 5 mins. After that, distilled water was added to the mixed solution as the hydrolysis agent, and (3-Aminopropyl) triethoxysilane (APTES, Thermo Fisher, 98%) solution (APTES: Ethanol = 1:50) was added to adjust the pH value for gelation. The final mixture solution was covered and allowed to gel and age at 60 °C for 48 h. Hexamethyldisilazane (HMDZ, Acros Organics, 98%) was added to the Co loaded silica gels and remained covered and kept for 3 nights at ambient conditions to remove the hydroxyl groups. Following hydrophobizing, the hydrophobic silica gels were washed in ethanol for 5 times (in 2 days) to remove excessive HMDZ. The gels were transferred into an oven and dried for 2h at 140 °C for drying. The final gels were calcinated in air at 400 °C for 5h. Before the experiments, the catalysts samples were reduced in  $H_2/N_2$  (5%/95%) flow at 600  $^\circ C$  for 10 h.

Another series of Co/SiO<sub>2</sub> aerogel catalysts with the same targeted mass ratio as which were prepared via the sol-gel method were prepared by the wetness impregnation method. The targeted ethanolic solution of  $Co(NO_3)_2 \cdot 6H_2O$  (Acros Organics,  $\geq 99\%$ ) were introduced into the same volume of 0 wt% SiO<sub>2</sub> aerogels prepared by the sol-gel method and impregnated for one night. Following the impregnation procedure, the samples were dried, calcinated, and reduced as the same procedures as those prepared by the sol-gel method.

All the catalysts were characterized via N2 ad/desorption, XRD, XPS, SEM, and TEM methods before tests, and observed via XPS after tests. According to the measurements of GC before and during each experiment, the conversion rate (x) of H<sub>2</sub> and CO is calculated as:

$$\kappa_{CH_4} = \frac{\text{moles of } CH_4 \text{ comsumed}}{\text{moles of } CH_4 \text{ inlet}} \%$$
(1)

$$x_{CO_2} = \frac{\text{moles of } CO_2 \text{ comsumed}}{\text{moles of } CO_2 \text{ inlet}} \%$$
(2)

The selectivity of products can be calculated as

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$$S_{H_2} = \frac{\text{moles of } H_2 \text{ produced}}{2 \times \text{moles of } CH_4 \text{ consumed}} \%$$
(3)  
moles of C0 produced

$$S_{CO} = \frac{\text{moles of CO produced}}{\text{moles of } CO_2 \text{ consumed} + \text{moles of } CH_4 \text{ consumed}} \% (4)$$

$$S_{CO} = \frac{x \times \text{moles of } C_x H_y \text{ produced}}{x \times \text{moles of } C_x H_y \text{ produced}} \% (5)$$

 $S_{C_XH_y} = \frac{1}{moles \ of \ CO_2 \ consumed + moles \ of \ CH_4 \ consumed}} \%(5)$ The carbon balance can be calculated as

$$B_{C} = \frac{[CH_{4}]_{out} + [CO_{2}]_{out} + [CO]_{out} + x \times [C_{x}H_{y}]_{out}}{[CH_{4}]_{in} + [CO_{2}]_{in}} \%$$
(6)

The specific input energy (SIE) is defined as the formula lfollowing:

$$SIE = \frac{Plasma \ power(kW)}{Flow \ rate(\frac{L}{min})} * 60(\frac{s}{min})$$
(7)

The GCMS was calibrated using a standard liquid sample (20 vol% of methanol, ethanol, acetic acid, acetone and water) to quantify the main products, and the results were normalized by abstracting water. Then the selectivity towards liquid organics can be calculated due to:

$$S_{liquid} = 100\% - S_{CO} - S_{C_x H_y}$$
(8)

$$S_{C_xH_yO_z} = x * mole\% of C_xH_yO_z * S_{liquid}$$
(9)

#### 4. Results and discussion

The plasma experiments of different  $CO_2$  to  $CH_4$  ratio were firstly conducted without catalysts and with only silica aerogels. The total flow rate was 30 mL<sub>n</sub>/min, the frequency and the voltage of the DBD reactor were set at 3000 Hz and 5.5 kV. The results are shown in Fig. 5 and Fig. 6. A period of voltage data recording of the reactor and capacitor during plasma experiments were shown Fig. 7. The introduction of silica aerogels into the discharge zone didn't significantly alter the  $CO_2/CH_4$  discharge behaviour. Moreover, when using only pure  $CH_4$  or  $CO_2$ plasma, the introduction of silica aerogels appeared only limited effects on the conversion of the two gases. While introducing silica aerogels promoted the conversion of the CO<sub>2</sub> and CH<sub>4</sub> and slightly promoted the formation of liquid products when using the CO<sub>2</sub>/CH<sub>4</sub> plasma. The explanation can be the introduction of silica aerogels on the one hand didn't significantly reduce the discharge volume as many other supports, on the other hand the The reason could be the strong adsorption capacity of SiO<sub>2</sub> aerogel, which caused the adsorption of reactive species, such as CH<sub>x</sub>O, into the mesoporous structure of silica aerogel (Table S1 of supporting materials), where plasma was hardly formed. As a result, the decomposition of CH<sub>x</sub>O into CO could be inhibited and the residence time could also increase. The CO<sub>2</sub> to CH<sub>4</sub> ratio of 2: 1 favoured the conversions of both gases.



Fig.5. Conversion rate of CO<sub>2</sub> and CH<sub>4</sub>.



Fig. 6. Power of the DBD plasma.





Fig. 7. The voltage data recording of the reactor and capacitor of the CO<sub>2</sub>/CH<sub>4</sub> DBD: a. without packing, b. with aerogels, c. with Co-NO-I

To evaluate the performance of the catalysts, the  $CO_2/CH_4$  ratio of 2 was chosen for the further plasma experiments according to the previous tests. The DBD was kept running for 90 mins after the discharge was stable and the liquid products were condensed for the offline analysis via GC-MS. Fig. 8 demonstrates the conversion rate of  $CO_2$ ,  $CH_4$  and the selectivity of  $H_2$ , CO, and  $C_{2+}$ . Fig. 9 shows the specific input energy during the experiments with these catalyst samples. Fig. 10 demonstrates the analysis of the main liquid products via GC-MS.

It is fascinating that introducing the Co catalysts with its SiO<sub>2</sub> aerogel support greatly promote the formation of liquid organics comparing to SiO2 aerogel only or no packing. Meanwhile, the conversion rates of CO2 and CH4 increased with an apparent decrease in the selectivity towards gaseous products. We also found the Co catalyst exhibited the effects on discharge behaviour due to abatement of discharge volume and the modification of conductivity, resulting in the slight increase of discharge power. In addition to the mesoporous structure of the SiO<sub>2</sub> aerogel, the well-dispersed Co in the supports significantly affected the selectivity of the products and shifted the products towards liquid organics (methanol up to 20.1%, acetic acid up to 17.9%). The synergistic effect and mechanism between catalysts and plasma were quite complicated and debated. The possible explanations could be: 1) the introducing of the catalysts altered the discharge behavior, which made discharge more stable and slightly increased the discharge power; 2) the strong adsorption behavior of mesoporous structure in the support as mentioned above would inhibit the decomposition of CH<sub>x</sub>O species; 3) the well-dispersed Co, as conventional catalysts used for the direct synthesis of long chain products in conventional FTS and reforming process, remarkably enhanced the conversion of CO<sub>2</sub> and the formation of methanol and acetic acid. We also noted that Co-NO-I favoured the formation of acetic acid with a higher conversion rate of CH<sub>4</sub> and more long chain organics (propanol, methyl acetate) were detected in the liquid products via GC-MS. The results were significant that value-added liquid organics were directly synthesized as well as syngas with considerable selectivity and conversion rates using the catalysts at ambient conditions.



Fig.8. The conversion rate of CO<sub>2</sub>, CH<sub>4</sub> and the selectivity of the products derived from online GC as a function of the different catalysts.



Fig.9. The specific energy input as a function of the different catalysts.



Fig.10. Selectivity towards main liquid products.

## 5. Conclusion

This work aimed to explore the direct production of liquid organics from  $CO_2$  and  $CH_4$  via a DBD plasma with catalysts at ambient condition. The introduction of

aerogel supports avoided the decrease of discharge power due to the reduction of discharge volume. The cobalt catalysts sufficiently promoted the formation of the liquid organics, particularly acetic acid. Besides, a remarkable concentration of CO and H<sub>2</sub> were detected in the gas product, the conversion rate of reactants also increased. This work provides an approach for non-thermal plasma conversion of CO<sub>2</sub> and CH<sub>4</sub> into value-added products.

### 6. References

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