Experimental study on plasma promoted catalytic synthesis of hydrocarbons from syngas

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Abstract: In this paper, a vertical tubular DBD reactor containing packed catalysts was realized with its analytical apparatus. Different Co/SiO2 aerogel catalysts were synthesized by ambient drying method and then characterized via N2 ad/desorption, XRD, XPS, SEM, and TEM methods. The plasma experiments with different variables were conducted at ambient condition, and the performance of the catalysts was evaluated. The results indicate that a considerable concentration of hydrocarbons was synthesized via our reactor at the ambient condition with a very low specific input energy.

Keywords: hydrocarbon synthesis, plasma catalysis, Fisher-Tropsch

1. Introduction

Nowadays global warming due to the continuous accumulation of greenhouse gases in the atmosphere has been one of the most critical issues in human society. Meanwhile, the demand for fossil fuels, especially petroleum, continues to increase. Within this context, Fischer-Tropsch synthesis (FTS), which was first proposed and published by two German chemists [1], has drawn great interests for researchers in recent years [2].

The catalyst has significant effects on the distribution of the final product, so a proper catalyst is necessary for FTS. All metals of Group VIII and some other alkali metals have a noticeable catalytic activity for F-T synthesis reactions [3]. Among them, Co is more active in the view of site basis according to chemisorption analysis [4] and shows high resistance to oxidation by water [5, 6] and low activity to Water Gas Shift Reaction [7]. Another crucial aspect of the research concerning of the FTS catalyst is the supports. Silica-supported cobalt catalysts exhibit a high catalytic activity and liquid hydrocarbon selectivity in FTS due to the physical and chemical properties of silica: 1) high surface area which makes moderately high Co dispersion at relatively high loadings of Co [8]; 2) controllable wide range of pore size which ensures a uniform diffusion of gas components; and 3) adjustable surface chemistry property which enables a high reducibility of metal [9].

Plasma, which offers a unique pathway to induce chemical reactions, unlike thermo-chemical pathway due to its high concentration of energetic and chemically active species [10], could be an interesting technique to overcome the energy barrier for FTS with a lower energy consumption and moderate condition. Our group [11, 12] has conducted some experiments on FTS via very highpressure plasma without catalysts; the results indicated that even at very high pressure (~2 MP) with high specific input energy (varying from 1000 to 10000 KJ/mol), light hydrocarbons are dominant among all the products. Meanwhile, Al-Harrasi et al. [13] have studied plasma promoted FTS with external heating and operating pressure and catalysts. The results have shown the existence of C_{5+} at a low H₂/Co ratio (~0.5) with a specific input energy of 2500 KJ/mol. Until now, no research on non-thermal plasma promoted FTS at ambient condition is found.

This paper aims to explore the possibility of hydrocarbons synthesis from syngas via plasma-catalytic promoted FTS at ambient condition. The hydrophobic SiO_2 aerogel was chosen as the support for Co catalyst due to its hydrophobicity and high porosity, which may avoid the extreme reduction of discharge volume. The Co loaded hydrophobic SiO_2 aerogel catalysts (Co/SiO₂) obtained by different methods, and Co precursors 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 mm, discharge volume ~ 10 cm³), 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/SiO₂ aerogel catalysts with a various targeted mass ratio of Co to SiO₂ aerogel were firstly prepared via the sol-gel method. The aiming amount of CoCl₂·6H₂O (Acros Organics, \geq 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 CoCl₂·6H₂O 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 various temperatures for 5h. Before the experiments, the catalysts samples were reduced in H₂/N₂ (5%/95%) flow at 600 °C for 10 h.

Another series of Co/SiO₂ 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 CoCl₂· 6H₂O and Co(NO₃)₂· 6H₂O (Acros Organics, \geq 99%) were introduced into the same volume of 0 wt% SiO₂ 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 N_2 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 H₂ and CO is calculated as:

$$x_{H_2} = \frac{\text{moles of } H_2 \text{ comsumed}}{\text{moles of } H_2 \text{ inlet}} \%$$
(1)

$$x_{CO} = \frac{moles of CO consumed}{moles of CO inlet} \%$$
(2)

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

$$SIE = \frac{Plasma \ power(kW)}{Flow \ rate(\frac{L}{min})} * 60(\frac{s}{min})$$
(3)

4. Results and discussion

The characterization results of N_2 ad/desorption, XRD, XPS, SEM, and TEM are shown in the figures and tables below.

Compared with the samples prepared by the sol-gel method, the surface area of the samples prepared by the impregnation method is lower, while the average pore diameter is higher. This is because as widely known the incipient wetness impregnation method cannot guarantee a uniform dispersion of catalysts into the supports as the solution is drawn into pores by capillary action. When the samples were calcinated, they are easier to aggregate thus blocking some of the small pores.

 Table 1. Surface area, pore volume and average pore size of the samples.

Catalysts	surface	pore	average pore	t-plot
	area	volume	diameter	micropore area
Aerogel (blank)	736	1.72	8.2	20.79

CoCl ₂ /SiO ₂ - solgel-10%	719	1.31	6.0	26.87
CoCl ₂ /SiO ₂ - solgel-20%	708	1.27	7.9	28.96
CoCl ₂ /SiO ₂ -im- 20%	624	1.19	7.9	/
Co(NO ₃) ₂ /SiO ₂ - im-10%	655	1.22	8.1	/

Fig. 3 shows the XRD patterns of Co/SiO₂-20% catalysts prepared by different methods and different cobalt sources. Only a few obscure peaks were detected in XRD patterns. The reason can be explained that the cobalt phase was well dispersed on the supports and the crystallite sizes were nanometer scale. As the calcination temperature increased, cobalt seems to interact with silica supports, resulting in the loss of Co peaks thus providing a smaller crystallite size. As the catalysts prepared from the cobalt nitrate precursors are known less stable at high temperature than cobalt chloride, it could facilitate a strong Co–support interaction, leading to a less apparent crystalline peak and smaller crystallite size.

Catalysts	Crystallite size
CoCl ₂ /SiO ₂ -solgel-20%	13.5
CoCl ₂ /SiO ₂ -im-20%	30.3
Co(NO ₃) ₂ /SiO ₂ -im-20%	6.5



Fig. 3. The XRD patterns of Co/SiO₂-20% catalysts prepared by different methods, different cobalt sources.

The results of XPS spectra, SEM and TEM observation reveal that different cobalt phases can be obviously found among the catalysts. Besides the cobalt oxides, which were confirmed by HRTEM and XPS spectra, a fibrous or filamentous structure is found as a different phase from spherical clusters. One part of the cobalt phase in aerogels can connect with -O- during the hydrolytic and polycondensation and form -O-Co-O- bridge with a chain structure.



Fig. 4. The Co 2p XPS spectra of CoCl₂/SiO₂-solgel-400 sample.



Figure S6. The SEM micrographs of: (1) 10CoCl/SiO₂sol, (2) 20CoCl/SiO₂-sol, (3) 20CoCl/SiO₂-im, (4) 20CoNO/SiO₂-im



Fig. 6. The HRTEM bright field images and selected area diffraction of CoCl₂/SiO₂-solgel-20%-400 sample.

After the characterization of the catalyst samples, the plasma-catalysis promoted FTS experiments were conducted to evaluate the catalytical performance. The total flow rate of 30 mL_n/min and the frequency of 3000 Hz were chosen for the experiments with catalysts. The H₂ to CO ratio was fixed at 2. The liquid products were condensed for 90 mins for the offline analysis via GC-MS. These series of experiments were repeated twice. As shown in Fig. 7, the introduction of Co/SiO₂ increased the SIE compared with the blank sample due to the change of conductivity. At the same time, the SIE of the samples with higher loading amount prepared by the impregnation method became lower. This can be explained that as the dispersion of cobalt was not uniform via the impregnation method, the excessive cobalt could result to more collapses and blocking of the pore structure, which was also reflected in the decrease of surface area

The gas and liquid products analysis formed after plasma treatments with different catalysts are presented in Table and Table 4, respectively. Only a negligible portion of methanol was found in the liquid product with the introduction of aerogels. Compared with the blank sample, all the samples with cobalt remarkably promoted the formation of hydrocarbons, a part of methanol, ethanol, and acetaldehyde, which is also interesting as these organic oxides are essential chemicals, was also found among the liquid products. Thus, the cobalt catalysts were confirmed to promote the hydrocarbon synthesis and decrease the energy barrier of the formation of oxides such as alcohols and aldehydes. As we found the cobalt in the samples prepared by the sol-gel method was partially connected with SiO₂ bone structure and well dispersed on the surface. The selectivity of CO_2 in the gas products was a little lower than those prepared via the impregnation method. Meanwhile, the well-dispersed part of Co is risky to oxidize again after H₂ reduction, the reduction reaction of oxidized Co and CoO-SiO₂ bone structure by H₂ and CO in DBD plasma reactor can explain the remarkably high concentration of water in the liquid products. Moreover, more metallic cobalt particles were detected in the samples prepared by the impregnation method. Consequently, the concentration of hydrocarbons and organic oxides in the gas and liquid products was higher, as well as the concentration of CO₂. As the cobalt crystallite size of the samples prepared by nitrate precursor was lower than those prepared via chloride precursor, the catalytic performance was better with a higher concentration of C2-C5 hydrocarbons and organic oxides.



Fig. 7. Conversion rate of H_2 and CO and SIE as a function of different catalysts.

Table 3. Gas product analysis of the experiments with different catalysts after plasma treatment.

Catalysts	CO ₂ (%)	CH ₄ (%)	C ₂ H ₆ (ppm)	C ₂ (ppm)	C ₃ (ppm)	C ₄ (ppm)	C ₅ (ppm)
blank	5.21	2.30	1916	45	801	194	46
10C1-S	4.70	2.91	2703	51	941	273	61
20C1-S	5.09	3.31	3431	59	1261	386	92
20Cl-I	5.60	3.50	3016	49	1014	264	67
20NO-I	6.61	4.39	4608	66	1523	498	164

Table 4. Liquid product analysis of the experiments with different catalysts after plasma treatment.

_	Catalysts	CH4O (%)	C ₂ H ₄ O (%)	C ₂ H ₆ O (%)
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blank	1.0	trace	trace
10C1-S	6.1	0.58	0.28
20C1-S	6.2	0.74	0.26
20C1-I	6.1	0.62	trace
20NO-I	13.4	1.3	0.32

5. Conclusion

This work aimed to explore the possibility of the nonthermal plasma promoted FTS at ambient condition. It was very remarkable that C1 to C5 hydrocarbons can be synthesized via our reactor at ambient condition with a very low energy consumption compared to existing work in which the external pressure, heating and high SIE were essential. The introduction of the cobalt catalysts significantly enhanced the hydrocarbon synthesis from syngas by a plasma catalysis pathway. Moreover, methanol, ethanol, and acetaldehyde were synthesized and detected. This non-thermal plasma approach provides a new perspective of FTS at ambient condition with lower energy consumption and broadens the field of further improvement on FTS.

6.References

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