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Mo/Co/ZSM-5 Catalyst Prepared by Cold Plasma Under Atmospheric Pressure and Its Application

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Abstract: A catalyst preparation method using a dielectric barrier discharge (DBD) plasma was investigated. The Mo/Co/K/ZSM-5 catalysts were prepared using DBD plasma. The Mo/Co/K/ZSM-5 catalysts were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscope (SEM). The results show that the catalysts prepared using DBD plasma and traditional roasting process have similar performance. The former can obtain smaller size of particles and lower agglomeration degrees. The activity tests also show that the catalysts prepared by DBD plasma have higher activities towards synthesizing hydrocarbon (C_{5+}) directly from synthesis gas than those obtained by the traditional roasting method.

Key words: catalyst preparation; dielectric barrier discharge plasma; calcination; synthesis gas

The increasing consumption of fossil fuel forces people to look for new alternative energy resources nowadays. Fischer-Tropsch Synthesis (F-TS) is an important technique for the production of liquid fuel from synthesis gas. In general, cobalt (Co) and iron are commonly used in traditional catalysts [1,2]. Molybdenum (Mo) has shown a promise for the conversion of synthesis gas to liquid hydrocarbons as it has cobalt on the zeolite (ZSM-5) support. However, this catalytic converter can produce a wide range of hydrocarbons ($C_1 \sim C_{60}$) during the reaction [3,4]. The activity and selectivity of hydrocarbon fuels are not high enough and catalyst stability is still unsatisfactory. Catalyst preparation technique plays a very important role in bi-functional catalytic processes. In order to ensure an efficient reaction in bi-functional catalysis, the active phase (usually the metal) on the catalyst surface must be highly dispersed over a large specific surface area and the specific activity maximized. To achieve this goal, catalytically active species are usually deposited as very fine particles on the surface of a highly porous support material (such as zeolites) with high thermal stability and high surface area.

In recent years, the methods of using plasmas for catalyst

preparation have attracted considerable attention [5-16]. Plasma is a substance in which part of the atoms or molecules are effectively ionized. Plasma is usually classified into high temperature plasma and low temperature plasma. Low temperature plasmas are important for the synthesis and processing of catalytic materials. The cold plasmas have been exploited for the catalyst preparation in the previous papers [5]. Dielectric barrier discharge (DBD) plasma [7] is one of the cold plasma phenomena; it can be operated at atmospheric pressure conditions. It is different from other plasma phenomena, because both of the electrodes are covered by the dielectric-barrier materials (quartz or ceramic materials). However, cold plasmas are different from the high electron temperature [8,9] and the gas temperature can remain at room temperature. Some characterizations have been obtained when DBD plasma was involved in the pretreatment of catalyst surface, which has led to efforts to directly apply plasmas to prepare catalysts more effectively. For this work, we attempt to use the DBD plasma for the preparation of Mo/Co catalysts, and the catalysts were tested by F-TS for producing hydrocarbons (C_{5+}) from synthesis gas.

1   Experiment

1.1   Catalyst preparation

The Mo/Co/K/ZSM-5 catalyst was prepared using incipient wetness impregnation. The bi-functional metal impregnation on the ZSM-5 catalyst was carried out with drop-by-drop immobilized ionic solution and continuously stirred at room temperature. The support material of ZSM-5 ($SiO_2/Al_2O_3 = 50$) (50 g) obtained from the catalyst plant of Nankai University was impregnated with an aqueous solution of 4.6 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and mixtures of Mo/ ZSM-5 were dried at 110 °C overnight and ground to fine powders. Cobalt was impregnated on the Mo/ZSM-5 with an aqueous solution of 12.4 g $Co(NO_3)_2 \cdot 2H_2O$, and then mixtures of Mo/Co/ZSM-5 were also dried at 110 °C overnight and ground to fine powders. Potassium was impregnated on the Mo/Co/ZSM-5 with an aqueous solution of 1.3 g K_2CO_3. Finally the samples of Mo/Co/K/ZSM-5 were dried in a vacuum drying oven at 110 °C.

After that, the catalyst powder obtained was placed on the quartz plate in the gap of the DBD reactor. The ratio of molybdenum metal component to the ZSM-5 in the finished catalyst was fixed at 5/100 by weight and the Mo:Co:K ratio was 5:5:1.4 by weight. The sample was decomposed under the influence of DBD plasmas and then directly applied for F-TS reaction from synthesis gas. For the purpose of comparison, a catalyst was also prepared using the traditional thermal decomposition, which was calcined at 600 °C for 5 h.

1.2   Experimental setup of DBD plasma

The experimental setup applied for the DBD plasma has been previously introduced in detail[10]. Fig.1 is a representative schematic of the DBD reactor. The top electrode and ground electrode are steel plate high voltage electrodes, which are attached to the inner surface of a quartz plate with a thickness of 2 mm. The diameter of the quartz plate is 60 mm, whereas it is 50 mm for the steel plate. The width of the discharge gap, which needs to be adjusted with different voltages, is 10 mm. The DBD decomposition operation was performed in stationary air under atmospheric pressure for 40 min. A high voltage generator was applied to supply a voltage from 0 to 30 kV with a continuous sinusoidal waveform at a frequency of about 25 kHz. The voltage was 25 kV and the input power was 100 W in this experiment. The DBD decomposition is quicker than the thermal decomposition.
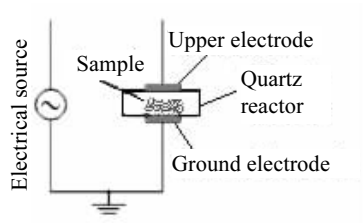

Fig.1   Representative schematic of DBD plasma reactor

1.3   Catalyst characterizations

X-ray fluorescence (XRF) analyses were applied to quantitatively determine the metals of Mo, Co and K of catalyst after pretreatment. The catalyst surface areas were measured by N_2 BET (Autosorb-iQ Quantachrome). The catalyst morphologies were investigated by a Carl Zeiss EVO50VP variable pressure scanning electron microscope (SEM) equipped with a Bruker Quantax 200 X flash energy-diffusive X-ray spectroscopy (EDS) spectrometer system, which simultaneously provided the surface elemental composition information. The accelerating voltage was 15 kV with a working distance of 10 mm. X-ray diffraction (XRD) analyses were conducted using a LabX-7000S/L diffract meter with Cu Kα radiation to identify the phases of the Mo/Co/K/ZSM-5 catalyst. The X-ray was operated at 30 mA and 30 kV. Diffuse reflectance infrared Fourier transform (DRIFT) spectra were collected on a thermo Electron Scientific Nicolet 6700 FTIR spectrometer with a diffuse reflectance attachment. The catalyst powder was held in a diffuse reflectance IR cell. The thermogravimetric analyses (TGA) for catalysts in different decomposition methods were evaluated by thermogravimetry (Shimadzu DTG-60).

1.4   Catalytic activity test

The catalytic activity tests were carried out in a 1000 mL stainless steel static reactor equipped with a catalyst fixing device which is 8.0 cm above the bottom of the reactor. Temperature and pressure were controlled by a reactor controller. The catalyst (Mo/Co/K/ZSM-5 for different preparation methods) was used with synthesis gas (molar ratio of $H_2/CO =1:1$). The catalyst was loaded and the reactor was purged with the reaction gas at room temperature. The reactant gas was used to pressurize the reactor so that 9.65 MPa would be achieved when reaching the selected reaction temperature.

The reactor was held at a reaction temperature of 280 °C for 15 h. Pressure was monitored with time. In a typical reaction, pressure decreased rapidly in the first few hours before the drop in pressure slowed and stopped within 10 h. After the pressure stabilized, the reactor was allowed to cool to room temperature where the final pressures ranged from 2.4 to 1.4×10^6 Pa. The major hydrocarbon (C_{5+}) was extracted from the reactor using ethyl acetate (LC-MS Grade) and then analyzed using GCMS (Shimadzu QP2010Plus) equipped with DB-1 column. The major hydrocarbon products were quantitatively analyzed by an internal standard method.

2   Results and Discussion

The characterization of the catalyst using BET, XRD, SEM, EDX and DRIFT shows that the decomposition of Mo/Co/ K/ZSM-5 particles by DBD plasma has significant differences in the surface area, phase structure and surface composition compared to the particles prepared thermally. These differences promote a further difference in the catalytic activity as discussed below.

2.1 Catalyst element analysis and surface area

The different analysis confirms metals composition of Mo/Co catalyst at expected 1:1 ratio and the catalyst surface areas are listed in Table 1. Impregnating ZSM-5 with metals significantly reduced the surface area from about 420 m^2/g to 270 m^2/g, indicating that the added metal blocks some zeolite channels, resulting in a lower specific surface area. The photograph and EDS analysis are illustrated in Fig.2. The EDS analysis shows the presence of elements Mo, Co and K on the surface of the catalyst. In order to have representativeness of analytic results, the spectra were collected at different spots and the observed result did not differ at different spots, indicating well metal dispersion.

2.2 Thermogravimetric analyses for catalysts

Fig.3 shows the TG results of catalyst. It can be seen that thermal decomposition curves are basically the same between calcining and DBD plasma, indicating that two pretreatment methods have the same thermal decomposition ability.

Table 1   Catalyst elemental analysis and specific surface area

Catalyst	$S/m^2 \cdot g^{-1}$	Elemental content/at%		
		Mo	Co	K
ZSM-5	420.55	-	-	-
Calcining	299.83	4.87#	4.92#	1.35#
		4.90*	4.92*	1.35*
Plasma	272.24	4.94#	4.98#	1.39#
		4.92*	4.90*	1.41*

Note: ZSM-5: ZSM-5(SiO_2/Al_2O_3=50), Calcining: Mo/Co/K/ ZSM-5(calcining), Plasma: Mo/Co/K/ZSM-5(plasma); *S*-specific surface area, # XRF data, * EDS data
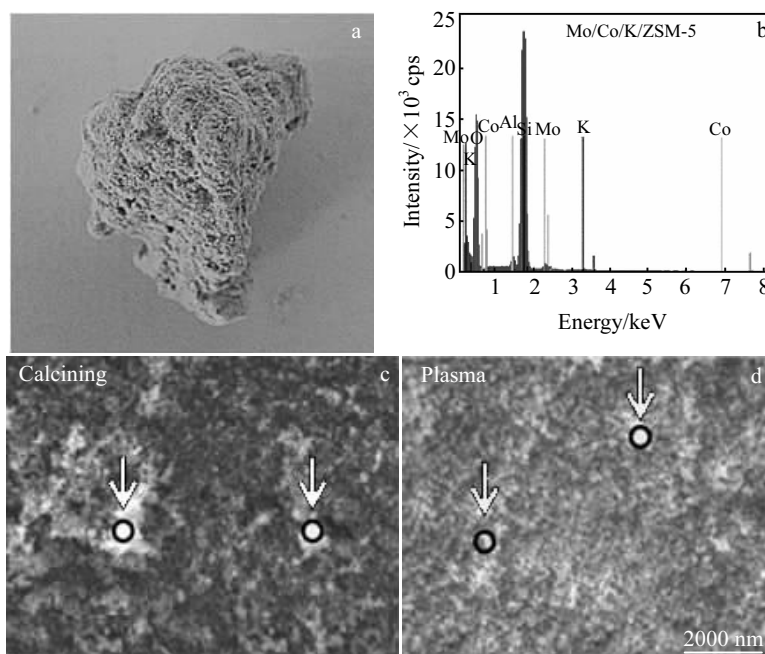

Fig.2   Photograph (a) and EDS analysis (b) of Mo/Co/K/ZSM-5 catalyst after pretreatment: (c) calcining and (d) plasma (the arrows indicate EDS analysis positions and the circles indicate the EDS spot size)
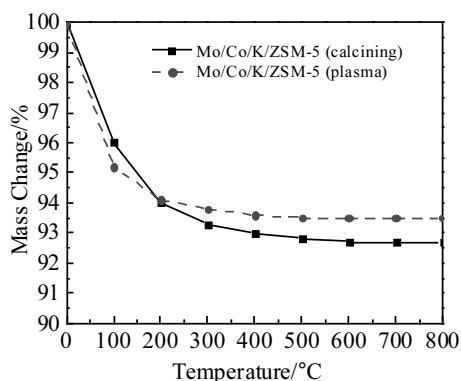

Fig.3   Thermogravimetric curves of catalysts

2.3 Catalyst characterization by XRD

Fig.4 shows the XRD patterns of Mo/Co/K/ZSM-5 calcined and Mo/Co/K/ZSM-5 prepared using DBD plasma. From the XRD patterns, the full widths at half maximum of Mo/Co of Mo/Co/K/ZSM-5 (plasma) (2θ=24.02°, 26.51°, 45.06°) are basically matched with those of Mo/Co/K/ZSM- 5(calcining), but the peak intensity of Mo/Co of Mo/Co/K/ ZSM-5(plasma) (2θ=24.02°, 26.51°, 45.06°) are slightly weak, compared to that of the catalyst prepared thermally. The catalyst prepared using DBD plasma exhibits lower agglomeration degree of Mo/Co and smaller particle size.

2.4 Catalyst characterization by SEM

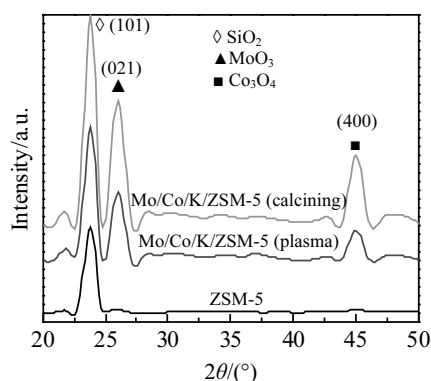The SEM images of Mo/Co/K/ZSM-5 confirm that the DBD plasma decomposition generates smaller particles and loose

Fig.4　XRD patterns of catalysts

Fig.6　DRIFT spectra of the Mo/Co/K/ZSM-5 (calcining) and Mo/Co/K/ZSM-5 (plasma) with the bulk Mo/Co ratio of 1:1

surface structure, as shown in Fig.5. The particle sizes and surface structure of aggregation are different because of the different decomposition methods, and the DBD plasma can prevent the phenomenon of agglomeration caused by excessive temperature and higher dispersion metals on the catalyst support surface.

2.5　DRIFT spectra characterization

Fig.6 shows the DRIFT spectra of the Mo/Co/K/ZSM-5 (calcining) and the Mo/Co/K/ZSM-5(plasma) samples with the bulk Mo/Co ratio of 1:1. The catalyst supports by ZSM-5 band show the most intensive peaks at 1069 and 794 cm^{-1}. However, the Mo/Co (calcining) band shows the more intensive peaks at 1635, 1456 and 1319 cm^{-1} than the corresponding Mo/Co (plasma) bands. These results give evidence that the DBD plasma decomposition induces template
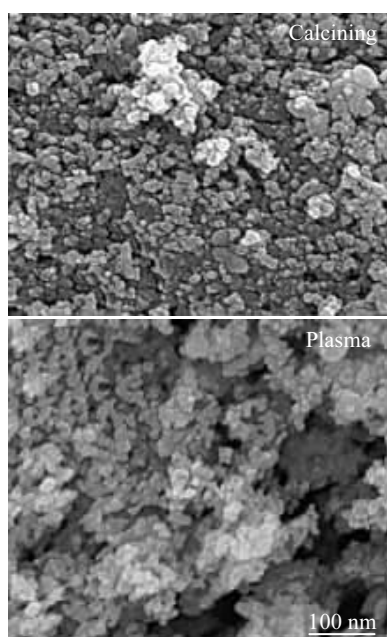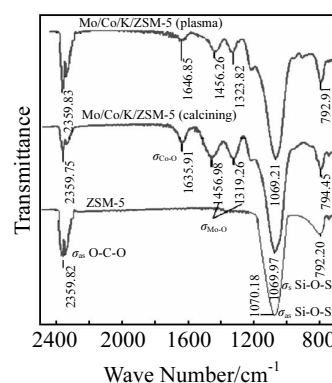
in $(NH_4)_6Mo_7O_{24}$ and $Co(NO_3)_2$ compared to the thermal decomposition. The fine structure is more stable in high-temperature-calcined than in DBD plasma and its ZSM-5 band peak intensity basically unchanged when using two different pretreatment methods. These results also indicate that the DBD plasma treatment removes the template without rearranging the remaining surface to an appreciable extent.

2.6　Catalytic activity

The decreased reducibility induced by the potassium doping may be a direct consequence of the increased electron density around the cobalt sites, thus inhibiting the reduction process. In addition, the Mo/Co/K/ZSM-5 catalysts could also exhibit high activity and selectivity to hydrocarbon (C_{5+}), which is possibly due to the insensitivity of cobalt to water gas shift reaction and less tendency to carbon deposition of catalyst and molybdenum for enhancing the ability to hydrogen and adjusting the acidity of catalyst surface.

Catalyst activity tests were performed using the catalyst of Mo/Co/K/ZSM-5(calcining)　and　Mo/Co/K/ZSM-5(plasma). 5.0 g of Mo/Co/K/ZSM-5 catalysts was weighed and placed in the reaction basket, and the reactor was then charged with $3.4×10^6$ Pa of CO/H_2 (50/50) at room temperature. Heating to 280 °C, the reaction pressure approximately reached $9.7×10^6$ Pa. Following completion of the reaction (15 h) and cooling to 25 °C, collected hydrocarbon (C_{5+}) were extracted with ethyl acetate and placed in a 25 mL volumetric flask and diluted to 25 mL with additional ethyl acetate. The products were analyzed by GC-MS, calculated as the percentage of major hydrocarbon (C_{5+}), and percentage of converted CO transformed to hydrocarbon (C_{5+}) was compared in Table 2.

Table 2 shows that the distribution and percentage of the hydrocarbon (C_{5+}) are basically consistent in the reactions with Mo/Co/K/ZSM-5(calcining) and Mo/Co/K/ZSM-5(plasma). For the catalyst, the smaller the particle size and the larger the surface area, the higher the catalytic activity. However, the surface area of the catalysts treated by calcinations is slightly larger than that by the plasma method. Overall, the percentage

Fig.5　SEM images of Mo/Co/K/ZSM-5(calcining) and Mo/Co/K/ZSM-5(plasma) with the bulk Mo/Co ratio of 1:1

Table 2   Major hydrocarbon (C$_{5+}$) product yields (%)

Catalyst	C$_5$	C$_6$	C$_7$	C$_8$	C$_9$	C$_{10}$	C$_{11}$	C$_{12}$	C$_{5+}$
Mo/Co/K-ZSM-5(calcining)	18.9	12.5	15.5	31.3	18.4	1.8	0.9	0.7	39.1
Mo/Co/K-ZSM-5(plasma)	16.3	10.7	15.4	34.2	19.3	1.6	1.4	1.0	43.2

of converted CO transformed to hydrocarbon (C$_{5+}$) slightly increases (4%) when using Mo/Co/K/ZSM-5 (plasma) catalyst.

3   Conclusions

1) DBD plasma is effective and efficient in preparing Mo/Co/K/ZSM-5 catalyst.

2) Compared to the catalyst prepared thermally, the DBD plasma generated catalyst shows a smaller particle size and higher dispersion metals on the catalyst surface.

3) The DBD plasma decomposition rate is quicker than the thermal decomposition rate. And the activity of the hydrocarbon (C$_{5+}$) directly from synthesis gas is well.

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介质阻挡低温等离子体法辅助制备钼钴基催化剂及其应用研究

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摘　要：对介质阻挡(DBD)低温等离子体法辅助制备催化剂的方法进行了研究。用 DBD 等离子体法制备了 Mo/Co/K/ZSM-5 催化剂。利用 X 射线衍射、热重分析、扫描电子显微镜等对催化剂进行表征。结果表明，等离子体法和传统焙烧处理制备的催化剂性能相近，并且利用 DBD 低温等离子体处理的催化剂在预处理速度，催化剂微观颗粒尺寸，分散度等方面均优于传统焙烧的处理方式。预处理后的催化剂表面活性更有利于直接通过合成气制备液体烃类燃料。

关键词：催化剂制备；介质阻挡等离子体；焙烧；合成气

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