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Direct liquefaction of coal with oil-soluble iron-based catalysts

Майда дисперленген темірқұрамды катализаторлардың қатысында көмірді тікелей сұйылту

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Майда дисперленген Fe_2O_3 бөлшектері, темір олеаты және коммерциялық Fe_2O_3 ұнтағы көмірді тікелей сұйылтуда катализаторлар ретінде қолданылған. Fe_2O_3 нанобөлшектері темір олеаты прекурсорының термиялық ыдырауынан алынған. Майдың конверсиясы мен шығу деңгейіне, газдың шығымына байланысты көрсетілген катализаторлар келесі ретпен орналасады: Fe_2O_3 нанобөлшектері > темір олеаты > Fe_2O_3 коммерциялық ұнтағы. Қорытынды бойынша синтезделген майда дисперленген темірлі катализаторлар көмірді тікелей сұйылту процесінің тиімді катализаторлары болып есептеледі.

Диспергированные в масле наночастицы Fe_2O_3, олеат железа и коммерческий порошок Fe_2O_3 использованы в качестве катализаторов при прямом ожижении угля. Наночастицы Fe_2O_3 получены термическим разложением прекурсора олеата железа. По уровню выхода и конверсии масла, выхода газа указанные катализаторы располагаются в следующем порядке: наночастицы Fe_2O_3 > олеат железа > коммерческий порошок Fe_2O_3. Результаты показали, что синтезированные диспергированные в масле железные катализаторы являются перспективными катализаторами процесса прямого ожижения угля (ПОУ — DCL).

1. Introduction

In order to utilize fully of coal, much effort have been devoted to the DCL processes [1]. During the conversion of coal to liquid, the catalysts are widely investigated, which are used for cracking and hydrocracking of C–C bonds of coal [2, 3]. Up to now, various catalysts have been studied for DCL process [4–6], such as Co, Mo, Ni, Fe etc. Among them, iron-based catalysts have received intensive interest because of their low cost, high activity, low toxic and eco-friendly performance [7].

On the other hand, there are major drawbacks in the application of iron-based catalysts originating from the lower coal conversion and lower oil yield. Two major methods have been adopted to improve the iron-based catalytic property, including increasing the dispersion of the catalysts and reducing the size of the particles [8–10]. Suzuki [11] has studied iron pentacarbonyl ($Fe(CO)_5$) as the catalyst for the hydroliquefaction of a variety of coal samples. As a well dispersed iron-based catalyst, $Fe(CO)_5$ has been proved an active catalyst for DCL. However, $Fe(CO)_5$ is a noxious and expensive organometallic compound. Zhao et al. [12] have also reported that highly dispersed ferrihydrite and binary ferrihydrite compounds can be used as the catalysts for the DCL. Dadyburjor and co-workers [13] have prepared ferric sulfide-based catalysts using an aerosol reactor. And the catalyst activity of the synthesized particles with 3–20 nm in diameter was tested in liquefaction experiments of coal. Therefore, the research on increasing the dispersion of the catalysts and reducing the size of the particles for the DCL is required.

In this study, iron oleate was synthesized by reacting ferric chloride and sodium oleate. Subsequently, monodispersed Fe_2O_3 nanoparticles were prepared by the thermal decomposition of the iron oleate precursor [14]. The synthesized Fe_2O_3 nanoparticles were around 15 nm in diameter. The iron oleate and the monodispersed Fe_2O_3 nanoparticles were all oil-soluble and highly dispersive in the DCL system. In addition, the catalytic properties of the two oil-soluble iron-based catalysts for the DCL were compared with that of the commercial Fe_2O_3 powders. The DCL test results show that oil-soluble iron-based catalysts present higher catalytic performance than that of the commercial catalyst.

2. Experimental section

2.1. Materials

Ferric chloride ($FeCl_3 \cdot 6H_2O$, analytically pure) and oleic acid ($C_{18}H_{34}O_2$, analytically pure) were purchased from Tianjin Fuchen Chemical Reagent of China. Sodium oleate ($C_{18}H_{33}NaO_2$, chemically pure) and 1-octadecene ($C_{18}H_{36}$, 90 % pure) were obtained from Aladdin. The commercial Fe_2O_3 was purchased from Tianjin Zhiyuan Chemical Reagent of China. All reagents were used as received without any further purification.

2.2. Preparation of the iron oleate and Fe_2O_3 nanoparticles

The preparation method of iron oleate and Fe_2O_3 nanoparticles was similar with the original paper by Hyeon and co-workers [14]. In a typical experiment, ferric chloride (5.4 g, 20 mmol) and sodium oleate (18.2 g, 60 mmol) were dissolved in a mixture of hexane (70 mL), ethanol (40 mL), and water (30 mL). The resulting solution was heated to 70 ^{o}C and kept at that temperature for 4 h under vigorous stirring. The upper organic layer was separated and washed 3 times with water in a separating funnel. Subsequently, the hexane was evaporated off, resulting in iron oleate in a reddish-brown viscous oil form. The iron oleate was used for the preparation of Fe_2O_3 nanoparticles and the DCL test.

In a typical experiment for Fe_2O_3 nanoparticles, the synthesized iron oleate (9.0 g, 10 mmol) and oleic acid (1.4 g, 5 mmol) were dissolved in 50 g of 1-octadecene. And the residual water of the mixture was removed under vacuum at 100 ^{o}C for 30 min. The reaction mixture was then heated slowly to 320 ^{o}C with stirring and aged at this temperature for 3 h under N_2 atmosphere. The resulting solution containing the nanoparticles was then cooled down to the room temperature, and excess ethanol was added into the solution to make the nanoparticles precipitation. Then the nanoparticles were washed and centrifuged with ethanol for three times. After that, the resultant nanoparticles were dried for the next catalytic reaction.

2.3. Characterization

The transmission electron microscopy (TEM) images of Fe_2O_3 nanoparticles were obtained on a Hitachi H-600 with an accelerating voltage of 100 kV. The scanning electron microscopy (SEM) images of commercial Fe_2O_3 was presented using LEO1450VP. The size distribution analysis of the obtained Fe_2O_3 nanoparticles and the commercial Fe_2O_3 were performed using MALVERN Nano-S90. The direct liquefaction of Jiangjunmiao coal from Xinjiang province of China was carried out in a batch 500 mL of autoclave reactor. And the activity of catalysts was evaluated by oil yield, conversion, and gas yield.

2.4. Reaction of the DCL

In a typical procedure of the DCL, 1.0 g of the as-prepared Fe_2O_3 nanoparticles, 0.3 g of sulfur, 30.0 g of pulverized Jiangjunmiao coal and 60.0 g of tetralin was mixed with ultrasonicating for 30 min to produce a viscous suspension. The reaction mixture was then transferred into an autoclave reactor. Before the liquefaction experiment, the reactor was sealed and flushed several times with hydrogen followed by pressuring the system to the initial hydrogen pressure of 6.5 MPa. Then the reactor was heated to 420 ^{o}C under stirring and kept for 75 min. The result product was extracted in sequence with *n*-hexane, toluene, and tetrahydrofuran (THF) in Soxhlet extractor. The *n*-hexane-soluble (HS), *n*-hexane-insoluble but toluene-soluble, toluene-insoluble but THF-soluble, and THF-insoluble substances were defined as oil and solvent, asphaltene, preasphaltene, and residue, respectively. The direct liquefaction of Jiangjunmiao coal with iron oleate and commercial Fe_2O_3 powders were also processed under similar procedures. In addition, the oil yield, conversion and gas yield of coal were determined using the following equations:

$$\text{Oil yield} = \left(W_{HS} - W_s\right) / W_{daf}\,; \quad (1)$$

$$\text{Conversion} = \left(W_{daf} - W_r\right) / W_{daf}\,; \quad (2)$$

$$\text{Gas yield} = \text{Conversion} - \text{Oil yield} - \left(W_A + W_{PA}\right) / W_{daf}\,, \quad (3)$$

where W_{daf} is the dry and ash-free weight of coal; W_r is the weight of residue; W_{HS} is the weight of HS; W_s is the weight of solvent, i.e. the 60.0 g of tetralin; W_A is the weight of asphaltene and W_{PA} is the weight of preasphaltene.

3. Results and discussion

The sizes and morphologies of synthesized Fe_2O_3 nanoparticles were investigated by TEM. A typical TEM image of the nano-Fe_2O_3 is shown in Figure 1. It can be seen that the Fe_2O_3 nanoparticles are well-disperse with a uniform size of 15 nm. The size distribution of the Fe_2O_3 nanoparticles is provided in Figure 2. The result shows that the majority size of the particles is 10–20 nm. The peak is sharp, indicating the particle size distribution is narrow.

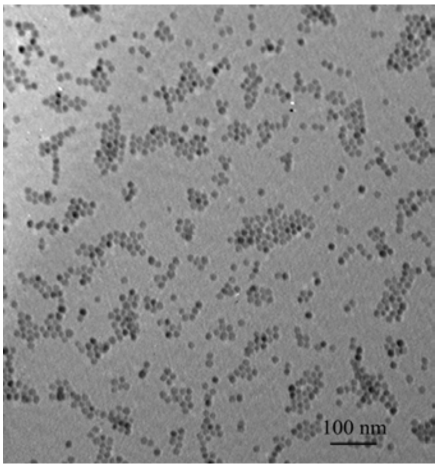

Fig. 1. TEM image of the synthesized Fe_2O_3 nanoparticles

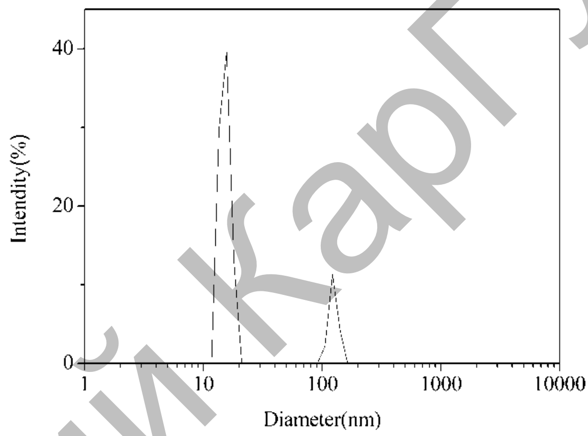

Fig. 2. Particle size distribution of the synthesized Fe_2O_3 nanoparticles

Figure 3 is the SEM image of the commercial Fe_2O_3 powders. It can be seen that the powders are the irregular spheres and agglomerate to form bulk materials. This indicates that the commercial Fe_2O_3 particles are poor dispersion. The average particles size is about 200 nm. The size distribution of the commercial Fe_2O_3 powders is provided in Figure 4, showing that the majority size of the particles is 300–700 nm. Broad peak demonstrates the polydispersion of the particles.

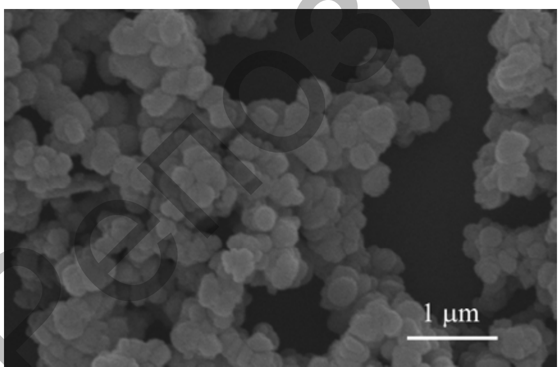

Fig. 3. SEM image of the commercial Fe_2O_3 powders

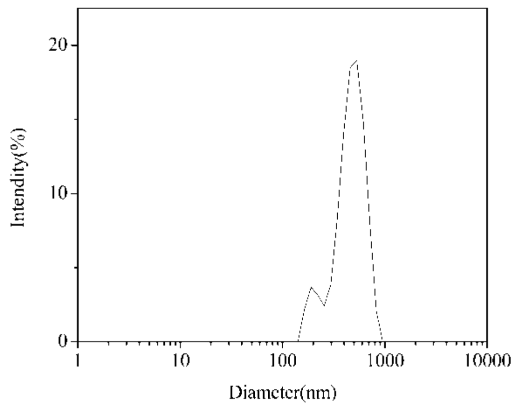

Fig. 4. Particle size distribution of the commercial Fe_2O_3 powders

The synthesized iron oleate, Fe_2O_3 nanoparticles and the commercial Fe_2O_3 powders were used as the catalysts for direct liquefaction of Jiangjunmiao coal. The result of reaction is shown in Figure 5. With the addition of commercial Fe_2O_3, the oil yield, conversion and gas yield are 76.62, 93.4 and 9.55 wt%, respectively. At the same reaction condition but with the addition of synthesized iron oleate, obtain oil yield of

80.33 wt%. Iron oleate exhibits 3.71 percentage points higher than commercial Fe_2O_3 catalyst. In particular, the oil yield increase about 10 percentage points used Fe_2O_3 nanoparticles comparing with the commercial Fe_2O_3, reach 86.45 wt% in the reaction. The conversion of 95.12 wt% and 97.18 wt% are obtained by using iron oleate and nano-Fe_2O_3 catalysts, respectively. It is noted that gas yield decreases to 6.13 wt% and 5.21 wt% respectively with the addition of iron oleate and Fe_2O_3 nanoparticles catalysts. This shows that the synthesized catalysts prevented effectively the conversion of obtained oil to gas.

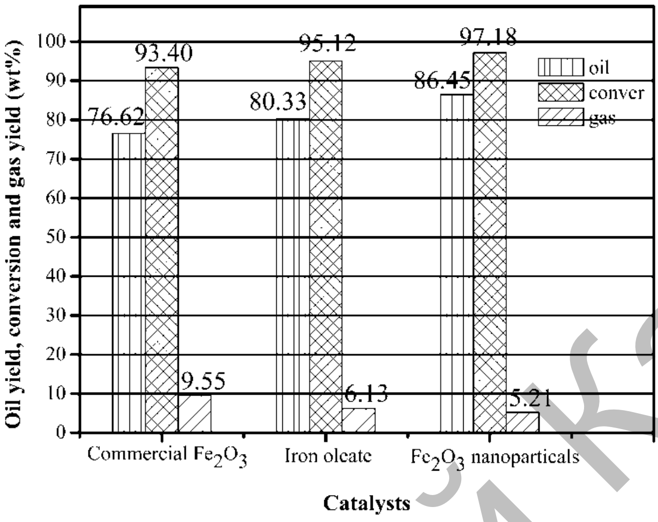

Fig. 5. Results of the direct liquefaction of Jiangjunmiao coal with different catalysts

In our study, it was found that Jiangjunmiao coal had a higher oil yield and conversion with the synthesized iron-based catalysts than that with the commercial Fe_2O_3 catalyst. The possible reason is that the long-chain organic molecules are existed in synthesized catalysts. The highly catalytic activity of the oil-soluble catalysts is result form their high dispersity in the reaction solvent. Furthermore, the exciting result of DCL using nanoscale Fe_2O_3 catalyst also attribute to the smaller size of particles. High specific surface and vast active sites of synthesized nano-Fe_2O_3 are beneficial to break down the structure of the coal and transfer hydrogen to coal fragment radicals. And the related further research is still in progress.

4. Conclusions

In summary, iron oleate and 15 nm sized Fe_2O_3 nanoparticles are synthesized by a simple and environmentally-friendly method. The synthesized catalysts are oil-soluble and highly dispersion in reaction system. Compared with commercial Fe_2O_3 powders, the synthesized iron-based catalysts are more effective for the DCL. The order of activity in reactions with the different catalysts is Fe_2O_3 nanoparticles > iron oleate > commercial Fe_2O_3 powders.

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The heat recovery equipment design of the primary furnace/exhaust gas: coil heat exchanger

Біріншілік жанған/қолданған газдан шыққан жылуды утилдеу құралын жобалау

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Мақалада сызықты регрессия көмегімен есептелген ASPEN бағдарламасынан алынған параметрлердің қасиеттері берілген. Үрімші қаласындағы петрохимиялық компаниясында жылуды утильдеу құралдың есептеулері EXCEL бағдарламасы көмегімен орындалған. Есептеулер бойынша қолданған газдың температурасы 175 ºС-тен 150 ºС және 90 ºС-қа дейін төмендеген.

В статье дан параметр свойства, взятый из большой выборки данных программы ASPEN, рассчитанный с помощью линейной регрессии. Расчет оборудования по утилизации тепла для петрохимической компании г. Урумчи выполнен с помощью программы EXCEL. Расчет показал, что температура отработанного газа снизилась с 175 ºС до 150 ºС и 90 ºС.

The primary reformer in Urumqi Petrochemical Company fertilizer plant ammonia plant in the second section was designed by TECNOMONT and manufactured by KIRCHNER, which had radiation section and convection section. Combustion reaction was occurred in radiation section and the fuel for the combustion was natural gas, waste gas, refining gas and synthesis purge gas, combustion improver was fuel turbine exhaust gas and the methane-steam transforming reaction was occurred in reformer tube with the heat released by the combustion reaction. The products of combustion was mixed with another fuel turbine exhaust gas well in the bottom of convection section, and then enter in convection section to recovery heat. There are six groups of convection section coil, from top to bottom boiler feedwater coil and feed gas preheating coil and preheating coil and mixing feed coil and air preheating coil and overheating coil respectively, and after recovering heat stack gas was discharged by means of induced draft fan. The temperature of the conversion furnace gas was higher, the actual exhaust gas temperature is about 247 ºC. Because of their large capacity of discharge and high temperature the