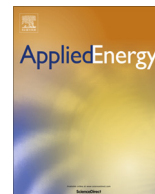




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Simultaneous production of hythane and carbon nanotubes via catalytic decomposition of methane with catalysts dispersed on porous supports

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HIGHLIGHTS

- Simultaneous production of hythane and carbon products via CDM was realized.
- Product hythane with hydrogen concentration around 10–30 vol% was obtained.
- Effect of different catalyst supports on CDM was investigated.
- Carbon products with different morphologies were detected.
- Two different growth modes for the carbon products were evidenced.

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ABSTRACT

A process coupling simultaneous production of hythane and carbon products via catalytic decomposition of methane (CDM) was carried out using iron catalysts dispersed on porous supports. The effect of different supports such as HZSM-5 zeolite, HBETA zeolite, and porous precipitated Al_2O_3 on catalytic decomposition of methane was investigated. The results showed that the ratio of hydrogen is around 10–30 vol% in the gaseous product which could be directly utilized as the clean fuel in the internal combustion engine. The solid carbon products with different morphologies such as open end or closed end carbon nanotubes (CNTs) were detected. The pore structure of the supports may have significant influence on the CNTs growth mechanism and production of hythane.

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1. Introduction

The research of alternative fuel has been highly attractive with the concern of environmental protection and growing energy demand. Natural gas, mainly containing methane, is considered as one of the most promising alternative fuels because of its high H/C ratio and excellent combustion properties such as high octane number, antiknock quality and reduced NO_x emissions [1]; so it has been widely used in engines [2]. However, there are some disadvantages for natural gas such as large cyclical variation and poor lean burning capability due to its low flame propagation rate [3]. Besides natural gas, hydrogen is also a widely investigated gas fuel for engines, which exhibits wide flammability range and allows a complete combustion due to the fast flame propagation speed. Thus the hydrogen combustion could reach high thermal efficiency and avoid the problems of liquid fuels such as inadequate vaporization and vapor lock. However, hydrogen used as the

engine fuel also generates serious problems such as backfire and explosion [4]. Consequently, there are researches [2,3,5,6] reporting that mixture of methane and hydrogen (hythane) could be directly utilized as high combustibility and environmentally benign mixture fuel.

Usually, hythane is produced directly by physical mixing between natural gas and hydrogen, but the cost is relatively high. Then several chemical and biological ways have been suggested to produce hythane, such as steam reforming of methane (SRM) [7], partial oxidation of methane (POM) [8,9], dark fermentation and anaerobic digestion from organic substrates (wheat straws, beer lees and sewage sludge) [10]. However, the CO_2 byproduct is unavoidable. Therefore, it is worth considering whether there is an efficient route. Recently, one of the most prospective technologies for obtaining hythane by catalytic decomposition of methane (CDM) is reported [11–13], however, the production of carbon was not fully discussed in these works.

Clean carbon could also be obtained as solid products while hythane is produced during the CDM process. The carbon products, including carbon blacks (CBs), carbon fibers (CFs) [14,15], carbon

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flakes [16] and carbon nanotubes (CNTs) [17–19], could be quite different depending on catalysts and reaction conditions. Among these, CNTs have been acknowledged as a high value added and widely applied product. Besides, there is a substantial relationship between the CNTs morphologies and their performance. For example, the open end CNTs have potential applications in heterogeneous catalysis because the inner surface of the tubes is ready for supporting foreign catalytic components and accessible for reactant molecules, while the close end CNTs need pretreatment to remove the cap. Furthermore, when CNTs are applied in field emission devices, comparing with the close end CNTs, the open end CNTs could produce irregular and changing patterns due to their sharp edges and dangling bonds [20]. Therefore, it is important to investigate different morphologies of carbon products in the CDM process. The carbon morphologies should be concerned with the catalyst structure, for example, the pore structure. To the best of our knowledge, few CDM works have discussed the effect of catalyst support pore structure on morphologies of carbon products.

In this paper, we selected several porous supports with different pore sizes and properties for the iron-based catalysts. Furthermore, the influence of pore structure on morphologies of carbon products and production of hythane in the CDM process was discussed.

2. Experiments

2.1. Preparation of catalysts

Three types of porous supports were selected to disperse iron catalysts. They are HBETA zeolite, HZSM-5 zeolite (Si/Al ratio of 25 for both, purchased from Nankai Catalyst Factory) and the porous Al_2O_3 . The porous Al_2O_3 support was prepared by the precipitation method as follows: firstly, a solution containing AlCl_3 , ethanol, PEG2000 and de-ionized water (DI-water) was prepared; then ammonia was added to obtain the solid precipitate; lastly, the precipitate was calcined in a muffle furnace under 800°C and the resulting powder was washed by DI-water.

The CDM catalysts were prepared by microwave assisted impregnation method. For example, the catalyst Fe/HZSM-5 containing 20 wt% Fe was prepared in the following steps: the solution of $\text{Fe}_3\text{NO}_3 \cdot 9\text{H}_2\text{O}$ and ethanol was first prepared in a flask and then the powder of HZSM-5 zeolite was added into the solution. Next the flask was put in a microwave oven with the frequency of 2451 MHz, power of 200 W and rotational speed of 845 r/min; after that, the solvent was evaporated at $40\text{--}60^\circ\text{C}$ under vacuum. Finally, the resulting solid was calcined at 400°C for 4 h in air and reduced at 400°C in the H_2 flow. The obtained catalyst was marked as Z1. The other catalysts such as 20 wt% Fe/HBETA, 10 wt% Fe/HBETA and 20 wt% Fe/ Al_2O_3 were prepared in the same procedure and marked as B1, B2 and G1, respectively. By the way, except for the first two porous supports, the other chemicals were purchased from Sinopharm Chemical Reagent Corporation of China and the DI-water was prepared from tap water in lab. The catalyst characterizations were done by the field emission scanning electron microscope (FESEM, JSM-6700F, JEOL Corporation), transmission electron microscope (TEM, JEM-200CX, NEC Corporation), X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD, Kratos Corporation).

2.2. Catalytic decomposition of methane

The catalytic decomposition of methane experiments were carried out in a quartz tube mounted in the tube furnace with a temperature controller. For each trial, 0.4 g catalyst was loaded into the quartz tube reactor. At the beginning, the reactor was

swept for 1 h by a nitrogen flow of 40 ml/min; then the reactor was heated from room temperature until the set reaction temperature at the rate of $10^\circ\text{C}/\text{min}$. Next the nitrogen flow was shift to the methane flow of 40 ml/min to perform the CDM reaction. The outlet gas was sampled and analyzed by gas chromatography (GC, FL9500, ZHEJIANG FULI ANALYTICAL INSTRUMENT CO., LTD). After the catalytic decomposition reaction, the reactor was cooled to the ambient temperature with a nitrogen flow. The resulting solid product was collected for SEM, TEM, X-ray diffract meter (XRD, B/MAX-3C, Rigaku Corporation), and Raman spectrometer (HR 800, HORIBA JOBIN YVON).

3. Results and discussion

3.1. Catalytic activity analysis

The catalytic activity of three different supported Fe catalysts was tested for CDM reaction at 800°C and atmospheric pressure, and the results are shown in Fig. 1.

As shown in Fig. 1, all the iron based catalysts on three types of porous supports initially showed high methane conversion. The CDM process could be divided into four zones according to the reaction performance. In zone A, the iron catalysts were soon activated; in zone B, the methane conversion reached the maximum; in zone C, the catalysts became deactivated with the methane conversion and H_2 ratio in the gas product gradually decreased; in zone D, the reaction entered a quasi steady state. The four zones here could be defined as the induction, quasi-high, deactivation and quasi-low period, respectively. The catalysts were deactivated in the CDM process due to the carbon deposition. When the active metal sites were depleted, the reaction reached a quasi steady state with a low methane conversion.

Furthermore, the three catalysts with different pore structures exhibited their diversity. The alumina catalyst has the fastest deactivation rate. The methane conversion quickly dropped to a low level within 70 min, while the zeolite catalysts need 100 min or more. However, the alumina catalyst obtained the highest residual methane conversion of 19.6% in quasi-low period, while zeolite HBETA and HZSM-5 only obtained 15.9% and 6.0%, respectively. But anyway, the gaseous product composition in Table 1 shows that very pure hythane can be obtained. Only the methane peak (1.27 min) appeared in GC spectrogram of the cracking reaction can support this conclusion. The reason can be explained through the Gibbs free energy analysis. The Gibbs free energy for cracking of CH_4 , C_2H_6 , C_2H_4 , C_2H_2 and C_3H_6 are -19.18 , -109.4 , -118.28 , -170.03 and -181.38 kJ/mol (800°C , Standard atmospheric pressure), respectively. Therefore, even those intermediates (such as C_2H_6 , C_2H_4 , C_2H_2 and C_3H_6) could be produced from CH_4 , they will crack to C and H_2 much more easily than CH_4 under high temperature.

It is worth noting that the H_2 ratio in the gas product was around 10–30 vol%. Wang et al. [1] proposed that the hythane with 20 vol% of hydrogen can obtain the optimum combustion result. The optimum hydrogen fraction exists because hydrogen plays both positive and negative effects in the combustion. The hydrogen in the mixture could assist the combustion of methane and reduce carbon emissions. Simultaneously, the flame propagation rate of fuel could be improved and the cyclical variability could be reduced. The H_2 ratio in the quasi-low period of the CDM process is around this optimum value and the hythane gas may potentially be utilized in the internal combustion engine. If the H_2 with higher concentration is needed, more catalyst/methane ratio could be used or the effluent gas could be recycled to the reactor inlet for several runs to satisfy the demand.

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