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Short Communication

Co-production of hydrogen and fibrous carbons by methane decomposition using K_2CO_3 /carbon hybrid as the catalyst

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ABSTRACT

Methane decomposition was conducted by using K_2CO_3 /carbon hybrids as the catalysts, and hydrogen-rich gas (with hydrogen content of about 87%) and fibrous carbons can be simultaneously obtained together with high and stable methane conversion (up to about 90% at 850 °C). Effects of K_2CO_3 on methane conversion, hydrogen content and fibrous carbons were investigated by changing the reaction temperature and space velocity. The results indicate that K_2CO_3 can greatly promote methane activation and conversion, taking responsibility for the continuous formation of CO and a trace of CO_2 . The oxygen transfer from K_2CO_3 probably provides convenience for the formation and growth of fibrous carbons.

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Introduction

The physical and chemical surface properties of carbon materials can be easily tailored to develop a large surface area and appropriate pore size distribution, and thus facilitating the diffusion of reactants and products to and from the active

sites on the surface [1]. Therefore, carbon materials have been widely used as catalyst supports or catalysts. In the last dozen years, specially, various carbon materials (such as activated carbon (AC), carbon black, coal-char (CC), mesoporous carbon, hierarchical porous carbon and so on) have been explored in hydrogen production by catalytic methane decomposition (CMD, $CH_4(g) \rightarrow 2H_2(g) + C(s)$) [2–7], which is considered as

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one promising eco-friendly hydrogen production process. Unfortunately, it is still difficult for carbon catalysts themselves to simultaneously prepare hydrogen and fibrous carbons by CMD except they are used as supports of metal catalysts [8–11]. In contrast, the fibrous carbons obtained by CMD with metal catalysts usually have to be further purified by acid treatment before utilization owing to the residual catalyst particles. More important, high cost and low stability against deactivation are also the inevitable challenges faced by using metal catalysts for CMD [3,12–15]. As a result, considerable effort has been made to develop diverse carbon-based catalysts for co-production of hydrogen and fibrous carbons by CMD. Up to now, however, little work has been done on the strategy with the catalyst of K_2CO_3 /carbon hybrid. Here a simple and effective method was reported for CMD by using the K_2CO_3 /carbon hybrid as the catalyst, achieving simultaneous preparation of hydrogen-rich gas and fibrous carbons.

Experimental

Materials

One CC sample (known as blue coke), with the particle size of 13–25 mm, was obtained from Shenmu Company of Five-continent Coal Chemical Industry, Shaanxi province, China. It is the residual product after pyrolysis of high volatile and weak or non-caking coal at about 600 °C. In the present work, the CC sample (its thermogravimetric analysis shown in Fig. S1, see Supplementary materials) was crushed and sieved to be particle size of 0.15–0.25 mm before use. K_2CO_3 was purchased from Tianjin Hedong Hongyan Chemical Reagent Factory, China. A commercial coconut shell-based activated carbon (AC-1, particle size of about 0.20 mm, Gongyi Yuanjie Water Purification Material Co., China) and another commercial coal-based activated carbon (AC-2, particle size of about 0.15 mm, Gongyi Yuanjie Water Purification Material Co., China) were utilized as the comparison samples of the CC sample. Their proximate and ultimate analyses are shown in Table 1.

Reaction system

CMD reactions were carried out in a traditional vertical stainless steel fixed-bed reactor (length of 450 mm and internal diameter of 16 mm) at atmosphere pressure. Isothermal CMD experiments were evaluated at 600–850 °C and the total

volumetric hourly space velocity (VHSV) of 600–9000 mL/(h•g_{CC}). In each experiment, the catalyst was placed at the center of the reactor, with the loading height ensured by pre-filling a certain amount of silica sand particles with the size of 0.85–1.70 mm. Then the reactor was heated at a rate of 10 °C/min from room temperature to the reaction temperature under a stream of nitrogen (99.999%, 25 mL/min). As soon as the desired temperature was achieved, the nitrogen stream was switched to a methane stream (99.999%) to start the CMD reaction. When each experiment was finished, nitrogen with a flow rate of 400 mL/min was used to purge the operating system for more than 15 min. Then the nitrogen flow rate was switched to 25 mL/min until the operating system become cool. The amount of the accumulated carbon from CMD was determined by the weight changes of the catalyst after reaction. The reproducibility of the operating system was evaluated and each experiment was repeated to ensure the reliability of the research results.

In the case of K_2CO_3 alone as the catalyst, specially, the initial VHSV was 900 mL/(h•g_{K₂CO₃}). When the K_2CO_3 /CC hybrid was used as the catalyst, the CC sample was mixed with K_2CO_3 by using porcelain mortar and pestle prior to the CMD reaction. Six types of the mixtures were prepared for the pre-tests with different K_2CO_3 /CC mass ratios: 0.25:1.00, 0.50:1.00, 0.75:1.00, 1.00:1.00, 1.50:1.00 and 2.00:1.00, where the CC amount was kept constant (5.00 g). The optimized ratio of K_2CO_3 /CC was 1.00:1.00 according to the resultant methane conversion and hydrogen content. Similarly, when K_2CO_3 /AC-1 or K_2CO_3 /AC-2 hybrid was used as the catalyst, the same preparation method was carried out at the ratio of 1.00:1.00.

Product analysis and characterization

The gas products were analyzed by an online gas chromatography (GC9560, Shanghai Huaai Chromatography Analysis Co., LTD). The GC analyzer has a thermal conductivity detector with two packed columns and argon as the carrier gas. A 5 m long and 2 mm diameter column packed with 13× molecular sieve was used to analyze H₂, N₂, CH₄ and CO while CO₂ was analyzed on a 2 m long and 2 mm diameter column with HayeSep Q packing. Methane conversion in the experiment was calculated by the following equation: $X = (F_{in} - F_{out})/F_{in} \times 100\%$, where X and F represent methane conversion and methane flow rate, respectively.

Nitrogen adsorption/desorption isotherms of the samples were conducted on a physical adsorption apparatus (AUTO-SORB-1C, Quantachrome) at –196 °C, and the porous structure parameters were obtained by using Brunauer–Emmett–Teller

Table 1 – Proximate and ultimate analyses of the CC sample and two commercial ACs.

Sample	Proximate analysis (wt.%, ad) ^a				Ultimate analysis (wt.%, daf) ^b				
	M	A	V	FC ^c	C	H	N	S	O ^c
CC	6.76	9.83	14.36	69.05	88.29	1.55	1.22	0.56	8.39
AC-1	18.38	2.68	22.70	56.24	78.36	1.92	0.35	0.14	19.23
AC-2	11.58	1.09	15.26	72.07	85.31	1.03	0.69	0.18	12.79

^a “ad” means air dry basis.

^b “daf” names dry ash-free basis.

^c By difference.

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