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Effect of hydrogen additive on methane decomposition to hydrogen and carbon over activated carbon catalyst

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ABSTRACT

The effect of H₂ addition on CH₄ decomposition over activated carbon (AC) catalyst was investigated. The results show that the addition of H₂ to CH₄ changes both methane conversion over AC and the properties of carbon deposits produced from methane decomposition. The initial methane conversion declines from 6.6% to 3.3% with the increasing H₂ flowrate from 0 to 25 mL/min, while the methane conversion in steady stage increases first and then decreases with the flowrate of H₂, and when the H₂ flowrate is 10 mL/min, i.e. quarter flowrate of methane, the methane conversion over AC in steady stage is four times more than that without hydrogen addition. It seems that the activity and stability of catalyst are improved by the introduction of H₂ to CH₄ and the catalyst deactivation is restrained. Filamentous carbon is obtained when H₂ is introduced into CH₄ reaction gas compared with the agglomerate carbon without H₂ addition. The formation of filamentous carbon on the surface of AC and slower decrease rate of surface area and pores volume may cause the stable activity of AC during methane decomposition.

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Introduction

Hydrogen is a clean fuel and considered as an attractive alternative for fossil fuels and renewable energy sources. Generally, the main sources of hydrogen are fossil fuels, water, and methane, in which fossil fuels are also the main source of air pollution that causes considerable damage to the environment. Conventionally, most of the industrial hydrogen production is based on the steam methane reforming (SMR) process, however, large amount of carbon oxides as by-product leads to the increasing cost of hydrogen production because of the necessary purification process [1,2].

Electrochemical splitting of water is a process to produce hydrogen without CO_x emission, and some efficient catalysts have been developed to improve the efficiency of process and reduce the production cost [3–7].

Catalytic methane decomposition (CMD), another simple and promising process for production of hydrogen and carbon material without by-products CO and CO₂, has received more and more attention. Many metal catalysts, such as Fe [8–10], Co [11–13] and Ni [14–16], were introduced into the process and proved as effective catalysts to promote methane decomposition. However, metal catalysts easily suffer the deactivation because the carbon deposition produced from methane encapsulates the surface active site of metals

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[17–19]. In comparison, carbon materials are considered as the alternative catalysts for methane decomposition to hydrogen owing to several advantages compared with metal catalysts such as low cost, high-temperature resistance, tolerance to sulfur and other potentially harmful impurities in the feedstock, and so on [20,21]. Activated carbon (AC) and carbon black are considered as more catalytically active materials than the more ordered ones such as graphite, diamond, carbon fibers and the carbon nanotubes [20,22], in which AC exhibits higher initial activity but lower sustainability. The rapid deactivation of AC catalysts is due to the blocking of the mouth of AC pores by growing carbon crystallites, which are generally in irregular agglomerate form [21,23]. Regeneration of carbon catalysts by carbonaceous deposit combustion with multiple cycles of reaction/regeneration or continuous supply of $\text{CO}_2/\text{H}_2\text{O}$ to methane decomposition can effectively remove the carbon deposits and recover the carbon catalysts [24–26]. However, the regeneration of carbon catalysts will lead to the generation of undesirable CO_x and even destroy the catalyst itself [27]. The type of carbon deposition is confirmed to be an important factor to influence the activity of catalyst during methane decomposition [19]. If the deposited carbon with higher activity is obtained and the production of the deposits with low activity is suppressed, the sustainability of AC for catalytic methane decomposition could be improved without regeneration. Muradov et al. [20] found that the activity of carbon deposition produced by decomposition of various hydrocarbons toward methane decomposition reaction are different. Many researchers added various hydrocarbons, such as ethylene [28,29], ethane [30], propane [20,31], ethanol [32], etc. to methane for improving the methane decomposition over carbon. They believed that the addition of hydrocarbons to methane will affect both the activity of carbon deposits and the methane decomposition. Malaika et al. [33] reported on hydrogen production by propylene-assisted decomposition of methane over activated carbon catalysts. They found that the addition of propylene to the CMD system effectively reduces deactivation of AC and permits fast stabilization of their catalytic activity at a high level, owing to the generation of carbonaceous deposit that can be catalytically active in CMD. However, it is inevitable to produce many other kinds of gases during the decomposition with addition of other hydrocarbons, which will complicate the separation process of products to obtain pure hydrogen and increase the cost. The addition of hydrogen in reaction system has been reported to remove the carbon deposits. Otsuka et al. [34] studied the catalytic decomposition of light alkanes, alkenes and acetylene over Ni/SiO_2 , and found that the hydrogenation of the carbon deposits produced by different hydrocarbons could be performed at 773 K by introducing and circulating hydrogen and only CH_4 was formed from these carbons. Bao et al. [35] and other workers [36,37] also considered that not all the coke but a part inert one causes the catalyst deactivation and the hydrogenation of inert coke facilitates the effective removal of coke and helps to revert the catalyst activity.

The addition of hydrogen in methane also affects the type and amount of carbon deposits, and the catalytic performance of catalysts in CMD. Kuvshinov et al. [38–40] investigated the effect of $\text{CH}_4\text{--H}_2$ mixture composition and reaction temperature on catalytic filamentous carbon formation in methane

decomposition over Ni-containing catalyst. They found that the texture of the produced catalytic filamentous carbon could be changed by varying the H_2 concentration. The amount of carbon deposition was also greatly enhanced by the H_2 addition. Therefore, H_2 plays an important role on the formation of carbon deposits and improving the activity of Ni-based catalysts during methane decomposition. However, few studies were reported about the effect of H_2 on the catalytic performance of AC for methane decomposition and the properties of resultant carbon deposits. In this paper, the effect of H_2 addition amount in methane on hydrogen production and carbon formation from $\text{CH}_4\text{--H}_2$ mixture over ACs were investigated.

Experimental

Catalysts

AC was used as the catalyst for catalytic $\text{CH}_4\text{--H}_2$ mixture decomposition (CMHD). Shenmu coal, a bituminous coal from China, was used as the carbon precursor and KOH (Shantou Xilong Chemical Technology Co., China) as the activation agent for preparation of AC. The coal was physically mixed with KOH in a mass ratio of 1:2. Thereafter, the mixture was carbonized in a horizontal furnace under nitrogen atmosphere with a flow rate of 110 mL/min. Carbonization procedures and washing methods were described elsewhere [41] with the only difference on carbonization temperature of 850 °C in this work. The resultant AC was labelled as SM-AC.

Characterization

X-ray diffraction (XRD) patterns of the samples were obtained by a D/MAX-2400 with a $\text{Cu K}\alpha$ radiation at 30 kV and 30 mA. Scanning electron microscopy (SEM, QUANTA 450) was conducted to record the morphology images of AC samples before and after CMD reaction. Temperature-programmed reduction (TPR) was performed in a conventional apparatus equipped with a thermal conductivity detector. About 0.03 g sample was preheated at 400 °C for 30 min before cooling to 120 °C under Ar atmosphere, then heated to 950 °C at a heating rate of 5 °C/min under pure H_2 atmosphere. The gas product was collected and analyzed by an online gas chromatograph. Raman spectra of fresh and spent ACs were measured at room temperature by using a laser Raman spectrometer (DXR Microscope). The textural properties of the samples were measured by N_2 adsorption at 77 K with a physical adsorption apparatus (ASAP 2420). The specific surface area was obtained by Brunauer-Emmett-Teller (BET) and the micropore volume (V_{mic}) calculated by using t-plot method. Thermogravimetric (TG) analysis of the samples was conducted under the air flow of 60 mL/min in a TG analyzer (Mettler Toledo TGA/SDTA851^e) to identify types of carbon deposits generated from CMHD.

$\text{CH}_4\text{--H}_2$ decomposition reaction

CMHD was carried out in a vertical fixed-bed reactor at atmospheric pressure. The reactor charged with 0.2 g catalyst was first heated to 850 °C under nitrogen atmosphere, and

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