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Catalytic decomposition of methane over activated carbon

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Abstract

Methane decomposition over activated carbons was carried out in a fixed bed, quartz-tube flow reactor. The kinetics of methane decomposition and surface properties changes before and after reaction was investigated. As a non-carbon based material, active alumina was also used to compare and understand the catalytic decomposition mechanism of methane over different materials. A reaction order of 0.5 is obtained for methane decomposition over ACs and activation energies in the range from 117 to 185 kJ mol^{-1}. The pore size change in the course of methane decomposition over activated carbons indicates that the catalytic reaction occurs mainly in the micropores. Activated alumina has different pore properties and carbon deposition in mesopores of the alumina is responsible for the catalytic activity.
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1. Introduction

Recently, people show great concern about the climate changes resulting from the emission of greenhouse gases in particular CO_2 and at the same time environmental friendly energy source is strongly required. Hydrogen is the best choice because its combustion product is H_2O. However, conventional hydrogen production methods, such as methane steam reforming and methane partial oxidation, have disadvantages of hydrogen purification because of byproducts of CO, CO_2 and the consequence of CO_2 storage. While the direct thermal decomposition of methane has advantages over other methods because of the simple product of C and H_2 based on which the carbon black production has been industrialized. As it is known, methane is the most stable hydrocarbon having a high decomposition temperature without catalyst. So the activation of methane i.e., hydrogen production by catalytic decomposition of methane has been widely researched [1–6]. The catalysts used in these researches are mostly based on transition metal such as Ni, Fe, Co etc., which show remarkable activity. But

the regeneration of the deactivated catalyst is always by burning off or gasifying the deposited carbon on the catalyst surface leading to CO_2 production again.

A new process of hydrogen production by methane decomposition over carbon-based catalyst was proposed by Muradov recently [7–9]. The carbon catalyst shows several advantages over metal catalyst: (i) low price; (ii) needless regeneration of the catalyst; and (iii) valuable carbon byproduct; and (iv) hydrogen production without CO_x emission during the process. Muradov [9] investigated several kinds of carbon including activated carbon (AC), carbon black (CB), graphite, diamond, carbon fibers and the carbon nanotubes in a fixed bed reactor among which the ones having disordered forms of carbon, such as AC, CB, are more catalytically active than the ordered ones (e.g. graphite and diamond). Lee et al. [10] used a fluidized bed reactor to produce CO_2 free hydrogen by decomposition of methane with activated carbon catalyst. The authors concluded that the reaction rate and deactivation of carbon catalyst were similar to those of fixed bed reactor system and the deactivation of catalyst was resulted from the carbon deposition.

However, there are few references in literature on the catalytic decomposition of methane over activated carbon

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and many are not well understood about the process of catalytic decomposition of methane, such as the characteristic of the active site of carbon, catalytic performance differences between the carbon based catalyst and the non-carbon based catalyst, surface properties changes of activated carbon before and after the reaction and so on.

In this work, methane decomposition in a fixed bed reactor was studied to understand the differences of catalytic performance between carbon-based catalyst and the non-carbon based catalyst—active alumina. At the same time the kinetics of methane decomposition over activated carbon and the surface properties changes of carbon and the active alumina were also investigated.

2. Experimental

Several different commercial activated carbons (DX40, CB10, MZ10, ZL30) and an active alumina were employed as catalysts in methane decomposition. AC MZ10 is derived from hardwood and other activated carbons (ACs) are from coal with steam activation for all carbons. The surface area for MZ10 is 783 m^2/g, for CB10 is 734 m^2/g, for ZL30 is 738 m^2/g and for active alumina is 152 m^2/g. All catalysts were grinded and sieved to 246–833 μm and dried at 383 K for 24 h before the experiment. Methane (99.99%) was used directly without further purification.

The decomposition reaction was carried out in a quartz-tube fixed bed reactor heated by an electric furnace. The experiments were conducted at temperature ranges from 1023 to 1173 K and the volumetric hourly space velocity (VHSV) was from 3.0 to 18.0 $l\,g^{-1}\,h^{-1}$. Before introducing the reactant gas, the system was heated up to the set temperature under Ar. In the kinetic study, the reaction conditions for all catalysts are the same as follows: catalyst charge of 1g, methane flow rate of 100 ml/min, i.e., VHSV of 6.0 $l\,g^{-1}\,h^{-1}$, which has been proved eliminating the influence of diffusion. The activated carbon and the active alumina were weighed before and after each experiment. All experiments were conducted at atmospheric pressure.

The outflow gas was analyzed by gas chromatography equipped with a 5A molecular sieve column and TCD detector using Ar as a carrier. Another gas chromatography with a n-octadecane column and FID detector was used to analyze C_1–C_4 hydrocarbon. The first analysis was done 5 minutes after methane was flowed to flush out the argon gas.

Very small amount of hydrocarbon other than methane (<0.1 vol.%) is detected in the effluent gas during the experiment and there are no liquid products. So carbon and hydrogen can be regarded as the only products of methane decomposition, that is, only the following reaction occurs during the process:

$$CH_4 \rightarrow C + 2H_2, \quad \Delta H^0 = 75.6\,kJ/mol \tag{1}$$
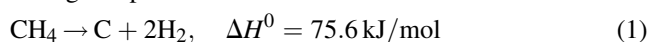
The conversion of methane can be calculated using the concentration of hydrogen in the effluent gas as the following formula:

$$X_{CH_4}\% = \frac{H_2\%}{(200 - H_2\%)} \times 100\% \tag{2}$$

where $X_{CH_4}\%$ is methane conversion at given time and $H_2\%$ the hydrogen concentration in the effluent gas (% by volume) determined by gas chromatography.

The surface properties of the fresh and the used samples were measured by N_2 adsorption at 77 K in a Tristar 3000 physical adsorption apparatus. The specific surface area and pore volume were calculated applying the BET method and Barrett–Joyner–Halenda (BJH) numerical integration method, respectively. BJH desorption model was used to calculate the pore size distribution of the samples. The SEM images of the samples were analyzed by H600 electron microscope.

3. Results and discussion

3.1. Methane decomposition over activated carbons

Fig. 1 shows the general performance of five activated carbons on methane decomposition at 1123 K. For all catalysts methane conversion shows the highest value of 25–35% at the beginning of the reaction and then it gradually decreases. The highest activity of ACs in the initial stage follows a rapid drop and then a smooth decrease until to a steady state which is similar as another work [9]. AC CB10 shows the highest initial activity on methane decomposition while AC ZL30 shows the lowest. Methane decomposition over ZL30 shows lower conversion than other four ACs during the whole process, which is not proportional to its surface area of 738 m^2/g. One reason is that only a part of the surface of AC ZL30 is active for methane decomposition [11] even though its whole surface area is only a little smaller than others' The deactivation behavior of catalyst is
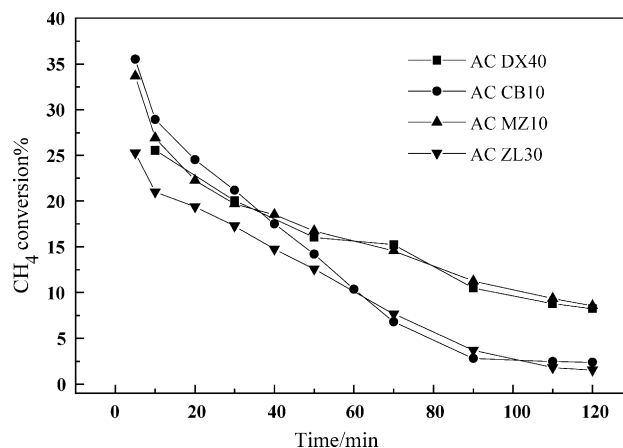

Fig. 1. Methane conversion as a function of time over five ACs at 1123 K (VHSV = 3.0 $l\,g^{-1}\,h^{-1}$).