Production of CO$_x$-free hydrogen by the thermal decomposition of methane over activated carbon: Catalyst deactivation

CrossMark

Amjed A. Al-Hassani [a,b], Hazzim F. Abbas [c], W.M.A. Wan Daud [a,*]

[a] Department of Chemical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
[b] Department of Petrochemical Engineering, Technical College/Basrah, 61001 Basrah, Iraq
[c] Department of Chemical Engineering, University of Nizwa, Al-Dakulaya, Oman

ARTICLE INFO

ABSTRACT

Hydrogen, an environment-friendly energy source, is deemed to become strongly in demand over the next decades. In this work, CO$_x$-free hydrogen was produced by the thermal catalytic decomposition (TCD) of methane by a carbon catalyst. Deactivated catalysts at four-stage of progressive were characterized by nitrogen sorption and scanning electron microscopy. TCD of methane at 820 and 940 °C was about 13- and 8-folds higher than non-catalytic decomposition, respectively. High temperatures positively affected the kinetics of hydrogen production but negatively influenced the total amount of hydrogen and carbon products. The total pore volume was a good indicator of the total amount of hydrogen product. Catalyst activity was decreased because of the changes in the catalyst's textural properties within three ranges of relative time, that is, 0 to 45, 0.45 to 0.65, and 0.65 to 1. Models for specific surface area and total pore volume as functions of catalyst deactivation kinetics were developed.

Introduction

Scientists have serious concerns about CO$_x$ emissions and their effects on climate change. Thus, environment-friendly energy sources have been strongly demanded recently. Hydrogen is considered as a promising clean energy source and releases large amounts of the heating value (141.86 MJ/kg) [1]. Hydrogen is not naturally free but is rather produced from a variety of sources, which include fossil-fuels (natural gas and coal gasification) and renewable sources (biomass and water) [2]. To date, hydrogen is produced about 48% from natural gas, 30% from naphtha/oil reforming, and 18% from coal gasification [3]. To release hydrogen, its compounds must be decomposed or reformed through processes such as electrolysis, thermochemical, steam electrolysis, and biomass transformation [4].

Methane, which is the main component of natural gas, has the highest hydrogen content. Hydrogen is conventionally produced through steam methane reforming but is not

environment-friendly due to a mole of CO_2 is emitted per the mole of CH_4 decomposed [5]. CO_2 separation and capture by additional units increase the cost of the hydrogen product. Direct thermal decomposition (TD) of methane is an alternative process to produce hydrogen without CO_x emissions [1]. This process is more economic than steam methane reforming because it needs substantially lower energy, removal units for CO_x are unnecessary, and the carbon by-products can be marketed [6]. The Gibbs energy of methane TD is zero at 545 °C [7]; therefore, methane decomposition can occur above this temperature.

Catalysts reduce the threshold temperature of the Gibbs energy and improve the reaction kinetics [8]. Metal catalysts, such as iron, cobalt, and nickel are commonly used for TCD of methane because of their high activities at high temperatures. However, these catalysts suffer from several drawbacks, such as limited thermal and chemical tolerance and reduced activity when their active sites are blocked [9]. The regeneration of metal catalysts through burning or gasifying also emits CO_x [10]. With these circumstances, scientists have focused on carbon-based catalysts that offer numerous advantages, such as low cost, high thermal stability, and enhancement of gas-to-solid heat transfer [11,12].

Several controversies result from the comparison of different carbon catalysts obtained by different precursors or its preparations [13]. For instance, activated carbon (AC) has high initial catalytic activity but is rapidly deactivated [14], whereas carbon black has low initial catalytic activity but a long catalytic lifetime [15]. Serrano et al. [16] concluded that having high initial catalytic activity results in a high defect concentration for AC and carbon black catalysts. Nevertheless, ordered mesoporous carbons consider as the most active catalysts with long lifetimes. Recently, Shilapuram et al. [17] used that the carbide-derived carbon has a lower threshold temperature and better catalytic activity compared with ordered mesoporous carbons because of their higher total pore volume.

The surface chemistry, crystallographic structures, and textural properties of carbon catalysts have significant effects on their activities. Moliner et al. [18] reported that microporous ACs exhibit high initial conversion rates but are rapidly deactivated. However, mesoporous ACs provide more stable catalytic lifetime. Serrano et al. [19] reported that mesoporous carbon catalysts with large surface areas present high initial catalytic activities and deactivation resistance. Other studies [14,15] reported that a large micropore volume can tolerate large accumulations of carbon deposits before complete deactivation occurs.

Literature survey reveals that the methane TCD through carbon catalysts depend on the catalytic activity and deactivation resistance; Thus, changes in the textural properties of the catalyst still require further investigation. In this study, AC was used as a catalyst for CO_x-free hydrogen production via methane decomposition. The kinetics of the non-catalytic and catalytic mechanisms in a fixed-bed reactor at the different temperatures were compared. The total amount of produced carbon and hydrogen at different temperatures were measured. Samples of fresh and deactivated catalysts at four-stage were characterized using nitrogen sorption isotherms and scanning electron microscopy (SEM). Empirical models for

the specific surface area (S_{BET}) and total pore volume (V_p), as functions of the kinetics of the catalyst deactivation, were developed.

Materials and methods

Materials and procedures

Methane, nitrogen, and helium gases, as well as liquefied nitrogen, were supplied by Mox-Linde Gases Sdn. Bhd., Malaysia. AC (Norit-RB3) was provided by Norit Nederland B.V., Netherlands. It has already been physically activated by steam and was used without further processing. Norit AC was ground, sieved, and dried to a particle size of 500–590 μm. The main properties of the AC and experimental setup were reported our previous study [20].

In this study, the flow rates for pure methane (F_{CH_4}) and nitrogen were adjusted at 717 and 700 cm^3/min, respectively. The nitrogen was flowed for 15 min before the methane effluent to purge moisture and gases in the internal spaces of the reactor. After purging, the nitrogen flow was arrested, and methane was supplied. The volumetric percentages of hydrogen (V_{H_2}) and methane (V_{CH_4}) with respect to time (t) were instantaneously measured by an online gas analyzer. The experiment was stopped upon complete catalyst deactivation, in which the slope of the plot of V_{H_2} versus time was nearly zero. Then, methane flow was arrested, and nitrogen was supplied again to purge the methane.

Isothermal non-catalytic methane TD at 740, 780, 820, 860, 900, 940, and 960 °C was conducted for 45 min. TCD experiments using 20 g of Norit AC at 820, 860, 900, and 940 °C were also conducted in a fixed-bed reactor. The threshold percentage of hydrogen ($V_{H_2}^i$) and ultimate percentage of hydrogen ($V_{H_2}^f$) at the final time (t^f) were identified. The numerical difference between $V_{H_2}^i$ and $V_{H_2}^f$ was divided into four equal stages, considering 25%, 50%, 75%, and 100% produced hydrogen. Times that correspond to each stage through their plot of V_{H_2} were specified. Other experiments for these times at previous temperatures were conducted to collect the samples of the deactivated catalysts.

Catalysts characterization

Samples of fresh Norit AC and deactivated catalysts were characterized by nitrogen sorption isotherms, but the details were reported elsewhere [20]. The specific surface area per weight of sample (S_{BET}) was measured according to Brunner-Emmett-Teller (BET) theory at 0.05 to 0.35 relative pressure (P/P_o) [21]. The total pore volume per weight of sample (V_p) was calculated using the ideal gas law at P/P_o of 0.99 [22]. The average pore size (d_p) was calculated based on the cylindrical pore geometry [23]. The micropore surface area (S_{mic}), and volume (V_{mic}) were measured according to t-plot method [24]. Typical t-plot method is related between a volume of nitrogen adsorbed (V_{ads}) versus the statistical thickness of the adsorbed film at 0.2–0.5 P/P_o. The total micropore (V_{mic}) is obtained by the intercept of the fitting straight line, and their slope was mesopore and macropore surface area. The micropore surface area (S_{mic}) was measured by, $S_{mic} = S_{BET} -$ slope. SEM images