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# An experimental investigation into the CO<sub>2</sub> gasification of deactivated activated-carbon catalyst used for methane decomposition to produce hydrogen

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## ARTICLE INFO

### Article history:

Received 12 August 2009

Received in revised form

17 October 2009

Accepted 23 October 2009

Available online 11 November 2009

### Keywords:

CO<sub>2</sub> gasification

Catalytic methane decomposition

Hydrogen production

Activated carbon

Characterization

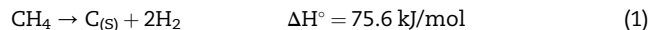
## ABSTRACT

A series of experiments was conducted to study the CO<sub>2</sub> gasification of a deactivated palm-shell-based activated-carbon (ACPS) catalyst used for the thermocatalytic decomposition of methane to produce hydrogen. This catalyst becomes deactivated due to the accumulation of carbon deposits during the methane-decomposition process. The CO<sub>2</sub> gasification was carried out at 850, 900, 950 or 1000 °C to study the deactivated ACPS, which was used at methane-decomposition temperatures of 850 or 950 °C. A series of six methane-decomposition cycles at 950 °C alternating with five gasification cycles using CO<sub>2</sub> at 900, 950 and 1000 °C was also carried out to evaluate the stability of the catalyst. The experiments were conducted using a thermobalance by monitoring the change in mass of the catalyst with time, i.e., the mass gain during methane decomposition or the mass loss during CO<sub>2</sub> gasification. Gasification of the virgin and deactivated ACPS showed strong temperature dependence, with the half and complete gasification times having an exponential dependence on temperature. The gasification reactivity at different conversions was higher for the virgin ACPS and increased with increases in the decomposition temperatures used for deactivation of the ACPS. The activation energies of virgin ACPS and ACPS deactivated at a decomposition temperature of 850 °C decreased with an increase in conversion, while they increased for the ACPS deactivated at a decomposition temperature of 950 °C; the activation energies varied between 81 and 163 kJ/mol. The gasification reactivity changed with methane conversion, showing maximum values for both the virgin and deactivated ACPS at a decomposition temperature of 950 °C. The initial gasification reactivity of the catalyst decreased after three gasification cycles at 1000 °C, while no significant change was observed with gasification cycles at 950 or 900 °C.

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## 1. Introduction

Hydrogen appears to be one of the most promising energy vectors since it is considered environmentally benign [1,2]. Methane can be thermally or thermocatalytically decomposed into carbon and hydrogen according to the following reaction:-



Methane decomposition is a moderately endothermic reaction, and, due to the strong C–H bonds, noncatalytic

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doi:10.1016/j.ijhydene.2009.10.072

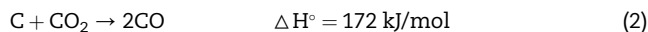
thermal cracking of methane requires a temperature higher than 1200 °C in order to obtain a reasonable yield. In thermocatalytic processes, catalysts such as metals and carbonaceous materials have been widely used, and among the metal catalysts, Ni [3], Fe [4] or a combination of metals, such as, Co/Mo/Al<sub>2</sub>O<sub>3</sub> or Ni/Cu/Al<sub>2</sub>O<sub>3</sub> [5] and Ni/Al or Ni/Cu/Al [6] have been studied most often. Significant attention in the last few years has been focused on carbons as catalysts for methane decomposition. Carbon catalysts offer several advantages over metal catalysts such as (1) low cost, (2) high-temperature stability, (3) tolerance to sulfur and other potentially harmful impurities in the feedstock, (4) production of a marketable by-product carbon (which could substantially reduce the net cost of hydrogen production), and (5) avoidance of metal-carbide formation, which complicates the regeneration of metal catalysts [7]. Among the various types of carbonaceous materials, most of the research activities have focused on activated carbon (AC) and carbon black (CB) [8–14].

During the thermocatalytic decomposition (TCD) of methane, the catalyst becomes deactivated due to intensive carbon deposition. The carbon resulting from the cracking process has been found in different structures ranging from amorphous to crystalline depending on the conditions in which the carbon is formed. This deposit normally has a lower surface area and activity compared to the virgin carbon catalyst and its activity is influenced by its structure. The carbon deposit produced from the TCD of methane has been found to have a more ordered structure compared to amorphous carbons; however, it is less structurally ordered than graphite (which is characteristic of turbostratic carbon). The order of the catalytic activities of carbons for methane decomposition according to their structures is amorphous > turbostratic > graphite [10].

It has been long known that during the cracking of hydrocarbons, carbonaceous material is deposited on the catalyst surface and as a result the catalyst must be regenerated. The catalyst used for the TCD of methane is rapidly deactivated due to intensive carbon deposition because carbon is one of the main reaction products. Different activating agents such as CO<sub>2</sub>, H<sub>2</sub>O and O<sub>2</sub> or their mixtures, which are used in the production of activated carbons from a variety of carbonaceous materials, can also be used to regenerate the deactivated catalyst. Carbon dioxide [15] and oxygen [16] have been used as the gasifying agents for deactivated metal catalysts used for methane TCD. Using different oxidizing agents, Muradov [17] reported that the treatment of deactivated carbon samples with steam and steam–CO<sub>2</sub> mixtures (1:1 by volume) resulted in a significant increase in the methane decomposition rate in TCD with the reactivated carbon, while using air as a gasifying agent was found to be less effective. There is a general agreement in the literature that the specific surface area as well as the surface chemistry of the catalyst, especially the concentration of oxygenated groups, play major roles in the behavior of carbon catalysts in methane TCD. It has been reported that the amount of oxygenated surface groups is related to the initial reaction rate and the specific surface area is related to the capacity for carbon accumulation [18]. Rodríguez-Reinoso et al. [19] reported that the maximum absolute micropore volume was obtained by the burn-off of approximately 40% of the carbon

catalyst and that CO<sub>2</sub> gasification creates not only a large number of oxygenated groups but more thermally stable groups than those produced by steam activation. This work also elucidated the mechanism of pore development and its relationship to the shape of the absolute micropore volume curve. Using CO<sub>2</sub> as a gasifying agent, it was reported that the maximum micropore volume occurs in the burn-off range of 40–50% for palm-shell-based activated carbon [20].

All carbonaceous materials gasified in CO<sub>2</sub> will produce CO via the following reverse-Boudouard reaction:



It is an endothermic reaction and the rate is relatively low. Generally, the reactivity of carbonaceous materials reacted with oxidizing gases is largely dictated by the type of carbon-based material and the conditions of carbonization employed. Additionally, reaction rate is influenced by particle size, temperature, the nature of the oxidizing gas and the content of mineral constituents in the carbon. For char particle sizes of less than 500 μm and temperatures less than 1000 °C the charCO<sub>2</sub> reaction is normally described by a first-order chemical reaction rate [21].

An analysis of the literature reports cited above indicates that the CO<sub>2</sub> gasification of deactivated ACs used as catalysts for methane TCD at a wide range of gasification temperatures has not yet been fully investigated. Furthermore, the relation between the gasification reactivity of AC after many reaction cycles with CO<sub>2</sub> gasification using different gasification temperatures has not been fully elucidated. In this context, the CO<sub>2</sub> gasification, at temperatures of 850, 900, 950 and 1000 °C, of several palm-shell-based activated carbons (ACPS), previously deactivated during methane TCD at decomposition temperatures of 850 or 950 °C, was investigated. The study also examined the change in gasification reactivity of deactivated ACPS at a decomposition temperature of 950 °C for a series of decomposition–gasification cycles using gasification temperatures of 900, 950 and 1000 °C.

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## 2. Experimental

### 2.1. Materials

Methane (99.99%) and carbon dioxide (99.99%), obtained from National Oxygen Pte. Ltd., and nitrogen (99.99%), supplied by Air Products, were used without further purification. Commercial ACPS was supplied by Bravo Green Sdn. Bhd. (Malaysia). The sample was crushed and sieved to a mean particle size of 117 μm and oven dried at 120 °C for a day prior to the study. The sample particle size was sufficiently small that the intraparticle mass-transfer effect was considered to be negligible [22].

### 2.2. Experimental set-up

The experiments were conducted using a Mettler-Toledo 850 Thermo-Gravimetric Analyzer (TGA). The experimental set-up allowed for continuous recording of sample weight change

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