Available online at www.sciencedirect.com
ScienceDirect
Journal of Power Sources 169 (2007) 103–109
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Hydrogen production by thermo-catalytic decomposition of methane: Regeneration of active carbons using CO_2 ☆

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Available online 30 January 2007

Abstract

Thermo-catalytic decomposition of methane using carbons as catalyst is a very attractive process for free CO_2–hydrogen production. One of the main drawbacks for the sustainability of the process is catalyst deactivation. In this work, regeneration of a deactivated active-carbon catalyst has been studied using CO_2 as activating agent under different regeneration conditions. It has been stated that during the regeneration stage, a compromise between the regeneration of the initial properties of the catalyst and the burn-off is needed in order to keep the sustainability of the process. Three deactivation–regeneration cycles have been performed for two sets of regeneration conditions. A progressive decreasing in the burn-off, surface area and surface oxygenated groups after each decomposition/regeneration cycle is observed. It can be explained considering that the carbon removed during the regeneration steps is not the carbon deposited from methane but the remaining initial catalyst, which is less resistant to gasification. The implication is that after three cycles of decomposition/regeneration, most of the carbon sample consists of carbon formed during the process since the initial catalyst has been gasified.

Keywords: Hydrogen production; Methane decarbonization; Carbon catalysts; Catalyst regeneration

1. Introduction

Emissions of carbon dioxide (CO_2), the main greenhouse gas (GHG) from human activities, are the subject of a worldwide debate about energy sustainability and the stability of global climate [1]. Conventional hydrogen production processes from natural gas (e.g., steam methane reforming) produce large amount of CO_2 emissions. One alternative to conventional processes is single-step thermo-catalytic decomposition (TCD) of natural gas (NG) into hydrogen and carbon [2–5]. Due to the absence of oxidants (e.g., H_2O and/or O_2), no carbon oxides are formed during the process, thus obviating the need for water gas shift and CO_2 removal stages, which significantly simplifies the process. In addition, pure carbon, instead of carbon dioxide, is produced [6].

Two different nature catalysts have been used for this process: metallic and carbonaceous catalysts [7–10]. Carbon catalysts have been proposed as an alternative to metallic ones [11–15] because they offer several advantages: (i) higher fuel flexibility and no sulphur poisoning; (ii) lower price; (iii) the carbon formed can be used as catalyst precursor, so that, the process is self-consistent. However, one of the main drawbacks for the use of these materials is catalyst deactivation mainly as a consequence of: (i) the reduction in catalyst surface area due to carbon deposition and (ii) the lack of catalytic activity of the carbon crystallites formed from methane decomposition.

Muradov et al. [14] have reported that the catalytic activity of deactivated carbon samples can be re-established by treatment with activating agents at elevated temperature. It was demonstrated that the treatment of carbon particles with steam resulted in the increase in surface area and simultaneously in the increase in methane decomposition rate. Authors suggest that at industrial scale, the activation of carbon particles with activating agents could be accomplished in an external reactor where the carbon particles are heated and then recycled into the TCD reactor as energy carrier for the endothermic decomposition reaction.

It is well known that generation of surface area by activation of a carbonaceous material proceeds removing carbon atoms

☆ This paper presented at the 2nd National Congress on Fuel Cells, CONAPPICE 2006.

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doi:10.1016/j.jpowsour.2007.01.045