Journal of Power Sources 192 (2009) 100–106

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Influence on hydrogen production of the minor components of natural gas during its decomposition using carbonaceous catalysts

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ARTICLE INFO

Article history:
Received 15 October 2008
Received in revised form 16 December 2008
Accepted 16 December 2008
Available online 27 December 2008

Keywords:
Catalytic decomposition
Natural gas
Hydrogen production
Carbon catalysts

ABSTRACT

In this work, the catalytic decomposition of the minor hydrocarbons present in natural gas, such as ethane and propane, over a commercial carbon black (BP2000) is studied. The influence of the reaction temperature on the product gas distribution was investigated. Increasing reaction temperatures were found to increase both hydrocarbon conversion and hydrogen selectivity. Carbon produced by ethane and propane was predominantly deposited as long filaments formed by spherical aggregates with diameters on the order of nanometres. Furthermore, the influence of ethane and propane on methane decomposition over BP2000 was also investigated, showing enrichment in hydrogen concentration with the addition of small amounts of these hydrocarbons in the feed. Additionally, the positive catalytic effect of H_2S on methane decomposition over BP2000 is addressed.

1. Introduction

Catalytic decomposition of natural gas (CDNG), with carbon captured as a product of added value, is an interesting alternative to steam reforming for hydrogen production [1–5]. In previous works, it has been established that carbonaceous catalysts are suitable for the catalytic decomposition of methane (CDM) [6–25]. Particularly, active carbons show high initial reaction rate, but are rapidly deactivated. However, carbon blacks, displayed lower reaction rates, providing a sustainable behaviour in CDM during several hours on stream, predominantly due to the high textural development [16,17,24]. The activation energy of the BP2000 carbon black in methane decomposition was found to be 236 kJ mol^{-1}, significantly lower than the methane C–H bond energy of 440 kJ mol^{-1}, pointing out the catalytic effect of such carbonaceous material [16].

Methane, as the major component of natural gas, has been the hydrocarbon feedstock most commonly studied for catalytic decomposition over carbonaceous materials. However, for future process scale-up, natural gas should be the preferred feed, given its availability. Natural gas is defined as a mixture of hydrocarbons, with methane as the major component. Depending on the origin of the natural gas, it can also be composed of other minor hydrocarbons, such as ethane, propane and ethylene, as well as nitrogen, CO_2 and H_2S. Accordingly, in order to gain knowledge about the CDNG, the role of the minor components of the natural gas must be elucidated.

Increasing attention has been devoted to the study of the production of hydrogen and added value carbon by means of the decomposition of light alkanes and alkenes using metal catalysts [26–33]. For example, ethane decomposition for carbon nanofiber and rich H_2 stream co-production has been accomplished over metal catalysts, obtaining 100% conversion with temperatures lower than 600 °C [31]. The use of carbonaceous catalysts for the decomposition of non-methane hydrocarbons, to the best of our knowledge, has only been carried out by Muradov et al. In these studies, the decomposition of propane and methane–propane mixtures was examined [5,34], showing that the addition of hydrocarbons higher than methane increased the hydrogen concentration without catalyst deactivation. Additionally, for carbonaceous catalysts, higher temperatures are needed to reach complete conversion (around 800 °C). According to the same author, one of the major advantages of the use a feed composed of higher hydrocarbons, such as propane, ethylene, acetylene and benzene, is that carbon deposits seem to be more active toward methane decomposition than the carbon produced by the methane decomposition itself [5].

The general equation for alkane decomposition is

$$C_nH_{2n+2} \rightarrow nC + (n+1)H_2 \tag{1}$$

In the case of ethane and propane, thermal decomposition leads to carbon and hydrogen production, but some methane is also formed by hydrogenation of the produced carbon [30], according to the following reactions:

$$C_2H_6 \rightarrow 2C + 3H_2 \rightarrow C + CH_4 + H_2 \tag{2}$$

$$C_3H_8 \rightarrow 3C + 4H_2 \rightarrow 2C + CH_4 + 2H_2 \tag{3}$$

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doi:10.1016/j.jpowsour.2008.12.074