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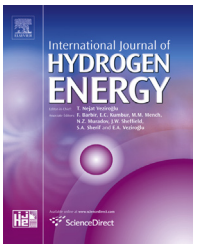

Evaluation of activated carbons based on olive stones as catalysts during hydrogen production by thermocatalytic decomposition of methane

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ABSTRACT

Catalytic decomposition of methane over carbon materials has been intensively studied as an environmental approach for CO_2-free hydrogen production without further by-products except hydrogen and valuable carbon. In this work, we will investigate the catalytic activity of activated carbons based on olive stones prepared by two different processes. Additionally, the effect of three major operational parameters: temperature, weight of catalyst and flow rate of methane, was determined. Therefore, a series of experiments were conducted in a horizontal-flow fixed bed reactor. The outflow gases were analysed using a mass spectrometer. The textural, structural and surface chemistry properties of both fresh and used activated carbons were determined respectively by N_2 gas adsorption, X-Ray Diffraction and Raman and Temperature Programmed Desorption. The results reveal that methane decomposition rate increases with temperature and methane flow however it decreases with catalyst weight. The two carbon samples exhibit a high initial activity followed by a rapid decay. Textural characterization of the deactivated carbon presents a dramatic drop of surface area, pore and micropore volumes against an increase of average pore diameter confirming that methane decomposition occurs mainly in micropores. XRD characterization shows a turbostratic structure of fresh samples with more graphitization in deposed carbon explaining the lowest activity at the end of reaction. Raman spectra reveal the domination of the two bands G and D which varying intensities affirm that the different carbons tend to organise in aromatic rings. Finally the surface chemistry qualitatively changes greatly after methane dissociation for CAGOC unlike CAGOP but quantitatively a small difference is observed which indicates that these functionalities may have a role in this heterogeneous reaction but cannot be totally responsible. Among the two catalysts tested, CAGOC has the highest initial methane decomposition rate but CAGOP is the most stable one.

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Introduction

Fossil fuels are the primary source of energy for human societies which increasing dependence is dramatically affecting the environment in terms of greenhouse emissions, health and safety considerations [1]. As a consequent, the search of an alternate environmental fuel becomes necessary and inevitable. Nowadays, hydrogen is attracting a significant attention as a promising and a sustainable alternate fuel [2] since it is the most abundant element in the universe and it has the highest specific energy content of all conventional fuels [3]. Moreover, hydrogen is an energy carrier and not an energy source. This implies its production from a rich hydrogen feedstock. A wide variety of technologies are available for hydrogen production from both non-renewable (natural gas, hydrocarbons, coal) and renewable (solar, wind, water) energy sources [4]. However, hydrocarbons reforming including steam reforming, partial oxidation and autothermal reforming remain the major techniques currently used [5] with the highest air emissions. Therefore, a numerous researches are pursuing in order to enhance the hydrogen generation systems with the minimal environment impact. Among them, catalytic decomposition of methane is considered as the best hydrogen production process both environmentally [6] and economically [7]. The main obstacle facing the industrial implementation of methane decomposition over activated carbons is the rapid deactivation of the catalyst due to the deposition of carbon produced [8]. This issue has been the subject of numerous papers which reflect the contribution of the texture, structure and surface chemistry of these catalysts during this heterogeneous reaction. Various opinions of authors were reported in literature between a group who confirm that the capacity of activated carbons is related to its surface area and pore distribution [9]. As demonstrated by some studies, increasing these two parameters leads to an increase in the resistance to the deactivation of carbons [10,11]. While others deny this and affirm no discernible trend is observed [12]. This contradiction extends towards surface chemistry as some authors reveal a good correlation between the concentration of oxygenated surface groups on carbon materials and its activities. Moliner et al. [9] propose that methane decomposition occurs according two mechanisms; either with direct reaction of methane with oxygenated groups as a partial oxidation reaction or by the decomposition of this groups as CO and CO_2 creating active sites promoting methane dissociation. Whereas, others found that surface groups may contribute during methane decomposition but could not be the solely responsible [13,14]. Huang et al. [15] agree with them and demonstrate that methane molecules dissociate via interactions with the chemically reactive vacancies in graphene and with graphene edges. When comes to structure, an agreement is found indicating that catalytic activity of activated carbons varies according to the following order: amorphous > turbostratic > graphitic [13,16]. Besides, a number of lignocellulosic precursors, such as coconut [17], palm shell [18] and hardwood [19] were used as raw materials for activated carbons applied in methane decomposition. The aim of this work is to extend the range of activated carbons tested in order to gain further understanding of their behaviour during this reaction. In particular, the activated carbons used are based on olive stones and tested under different operational conditions. Both fresh and deactivated carbons were characterized to identify the changes occurring after their reaction.

Experimental

Catalysts preparation

Olive stones derived from an olive factory residue in South Tunisia were used as a raw material for the preparation of activated carbons via chemical activation and physical activation.

For the chemical activation process optimized by Gharib et al. [20] an amount of the raw material was impregnated, in the first place, with a solution of phosphoric acid (50% in weight). The impregnation ratio (weight of acid/weight of olive stones) was 3. This mixture was boiled at 110 °C for 9 h, then filtered and dried at room temperature. At a second place, the dried acid-impregnated olive stones were carbonized in a fixed bed stainless steel reactor under nitrogen flow at 410 °C during 2 h and a half. After cooling to room temperature under the same flow of nitrogen, the by-product was extensively washed with boiling distillate water until neutral pH. The final samples were dried overnight in an oven at 110 °C and labelled CAGOC.

The synthesis of activated carbons by physical activation [21] consists on the carbonization of the olive stones followed by the activation with steam. During the carbonization, the material was burned off under a nitrogen atmosphere at a temperature of 600 °C for 2 h to remove the mineral contents, and then the activation occurred at a temperature of 850 °C for 8 h using steam to promote and develop the porosity of the char. These activated carbons were labelled CAGOP.

Methane decomposition experiments

Methane (99.99%) and argon (99.99%), supplied by Air Liquide (France), were used directly without further purification and individually controlled by mass flow rate regulators (Brooks Instrument).

As a preliminary step towards methane decomposition experiments, the two samples of activated carbons: CAGOC and CAGOP were pre-treated at a temperature of 850 °C for 1 h under argon to stabilize their surfaces. All experiments were carried out, under atmospheric pressure, in a horizontal quartz tubular reactor inside which the activated carbons particles were well dispersed in a quartz plate. Before introducing the reactant gas, the system was heated by an electric furnace under argon flow (58 ml/min, 10 °C/min). At the required temperature, methane was introduced and the gazes produced were analysed for a residence time of one hour using a mass spectrometer type INFICON. The work realized was devised to three parts. First, to study the effect of temperature, a series of experiments were conducted at three temperatures of 800, 825 and 850 °C with a constant methane flow rate of 58 ml//min and catalyst weight of 0.245 g. Then, to better understand the effluence of the catalyst during this reaction, the temperature and flow rate of methane were

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