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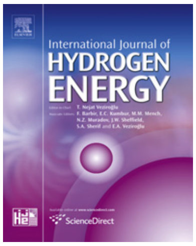

Kinetic and autocatalytic effects during the hydrogen production by methane decomposition over carbonaceous catalysts

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ABSTRACT

The reaction kinetics of methane decomposition to yield hydrogen and carbon has been investigated comparing different types of carbonaceous catalysts: two ordered mesoporous carbons (CMK-3 and CMK-5) and two commercial carbon blacks (CB-bp and CB-v). The evolution of the reaction rate along the time has been analyzed concluding that it is governed by different and opposite events: reduction of active sites by carbon deposition, autocatalytic effects of the carbon deposits and pore blockage and diffusional constraints. A relatively simple kinetic model has been developed that fits quite well the experimental reaction rate curves in spite of the complexity of the involved phenomena.

Both CMK carbons, and particularly CMK-5, present the highest initial reaction rates and the longest stability at long reaction times. In these materials, a part of the active sites remains accessible, since the carbon deposits formed from methane are capable of growing through the catalyst mesopores toward the outer part of the particles. The activation energies calculated from the initial reaction rates follow the sequence CMK-3 < CMK-5 < CB-bp < CB-v, whereas in all cases the reaction order was estimated to be 0.5 with respect to the methane partial pressure.

1. Introduction

Hydrogen is considered a promising clean fuel and energy carrier due to its CO_2-free combustion. Hydrogen can be produced from a wide variety of feedstocks and energy sources. As a consequence, a significant number of technologies and processes can be found nowadays for hydrogen production with different degree of maturity [1]. Among them, the most interesting ones are those based on the use of renewable or sustainable energy sources and feedstocks, such as biohydrogen, thermochemical or photocatalytic solar water splitting and photoelectrolysis. Nevertheless, these systems are still very far from being competitive, so much more research effort must be performed to achieve their large-scale applicability. Currently, most of the hydrogen production comes from fossil fuels, mainly by steam reforming of natural gas (SMR), which is characterized by significant emissions of greenhouse gases. In this way, by means of Life Cycle Assessment (LCA), it has been determined that the use of systems of capture and sequestration of the CO_2 emitted by hydrocarbon reforming may

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involve a high energy consumption, with significant damages to the environment in terms of acidification, production of heavy metals and winter smog [2].

Despite having lower H_2 production per mol of methane molecule consumed than SMR, methane decomposition ($DeCH_4$) is an interesting alternative since this reaction yields only hydrogen and solid carbon, according to the following reaction scheme [3]:

$$CH_4(g) \rightarrow C(s) + 2H_2(g) \quad \Delta H^\circ = 75.6 kJ/mol$$

Consequently, no direct CO_x emissions to the environment occur. Moreover, this endothermic reaction requires only 37.8 kJ to produce one mol of hydrogen, while 69 kJ/mol H_2 are consumed by SMR. However, thermal decomposition of methane requires very elevated temperatures, in the range 1100–1400 °C. In order to reduce the reaction temperature, as well as to enhance the kinetics of the process, a great effort is being put on the development of suitable catalysts for methane decomposition. First, most attention was paid to metal catalysts, such as Ni, Ni/Cu and Fe-based catalysts due to their high activity, operation at moderate temperatures and the possibility of obtaining carbon nanotubes or filaments as co-product [4–13]. Nevertheless, metal catalysts exhibit some drawbacks such as a limited thermal and chemical tolerance, as well as a prompt deactivation caused by the blocking of their active sites by carbon deposition. Thus, metal catalysts are usually very vulnerable to the presence of sulfur compounds, which would be the case of using methane from biogas. More recently, carbonaceous catalysts have been extensively explored [14]. Although these catalytic systems require higher temperatures than the metallic ones, the use of carbonaceous materials as catalysts offer important advantages: (a) higher thermal stability; (b) stronger resistance to sulfur and other chemical impurities, allowing the treatment of a large variety of methane feedstocks; (c) the catalyst regeneration may be not needed if the carbon produced in the process is or can be turned into catalytically active, and (d) the carbon product may have additional commercial applications due to its high purity and absence of metals. Using LCA tools, considering different energy scenarios, it has been concluded that autocatalytic decomposition of methane would represent a very promising and sustainable route for hydrogen production when compared with SMR [2]. Moreover, if biogas is employed as feed, the possibility of simultaneously achieving the production of energy (contained in the hydrogen) with a net carbon fixation has been reported [15].

A wide variety of carbonaceous materials, obtained from different sources and methods, have been investigated as catalysts for hydrogen production via methane decomposition [16–36]. From these studies a general relationship between the catalytic activity of carbons and their structural and surface properties can be deduced. Thus, amorphous carbons, such as carbon blacks or activated carbons, are more active than crystalline phases such as graphite, due to a higher concentration of defects on the formers, which have been proposed as the main active sites of the reaction [36]. Concerning the textural properties, those carbons having higher external surface area or mesoporosity deactivate much more slowly because they offer a higher accessibility to methane molecules, even after the formation of large quantities of carbon deposits. In this way, we demonstrated the exceptional catalytic behavior in the $DeCH_4$ reaction of mesostructured carbons as catalysts, in particular of CMK-3 and CMK-5 ordered mesoporous carbons [33–36], characterized by having high surface areas and pore structures with hexagonal pore symmetry (*p6mm*) [37]. When compared with some representative commercial carbons, CMK materials exhibited very high activities, the best results being obtained over CMK-5. This material, characterized by possessing surface areas close to 2000 m^2/g and a bimodal mesopore system, led to the highest hydrogen production and strongest resistance to deactivation under the reaction conditions employed.

In the present work, the $DeCH_4$ kinetics at short and long reaction times is investigated to estimate different kinetics parameters, such as the reaction order and activation energy over the aforementioned CMK carbons. For this purpose, different temperatures and CH_4 partial pressures have been employed. The results have been compared with those obtained over two commercial carbon blacks. In all cases, particular attention has been paid to the possible presence of autocatalytic effects, as this would enhance strongly the large-scale feasibility of the process.

2. Experimental

2.1. Carbonaceous catalysts

The mesostructured carbons, CMK-3 and CMK-5, were synthesized according to a procedure published elsewhere [37], based on a nanocasting pathway using pure silica SBA-15 as hard template. SBA-15 was prepared by a soft-templating route, employing tetraethylorthosilicate (TEOS) and a non-ionic triblock copolymer (Pluronic 123) as silica source and mesopore liquid template, respectively. After calcination, the SBA-15 material was infiltrated with the carbon precursor solution, which was subsequently polymerized and carbonized by calcination under inert atmosphere. Furfuryl alcohol (FA) was used as carbon precursor, oxalic acid as polymerization catalyst and trimethylbenzene (TMB) as solvent. Once the silica template was removed by treatment with a basic solution (NaOH), the mesostructured carbons were attained. Two types of CMK materials were prepared by infiltrating pure FA (CMK-3) or a solution containing 60% FA in TMB (CMK-5), respectively. Details of the preparation procedure followed can be found in previous works [36,37]. Additionally, two commercial carbon blacks (black pearls 2000 and vulcan XC72, both from Cabot Corp.) were employed as reference catalysts.

2.2. CH_4 decomposition experiments

Methane decomposition reactions were performed on a simultaneous DSC-TGA thermobalance (TGA-DSC1, Mettler Toledo). As the methane decomposition takes place, carbon deposits are formed onto the catalyst allowing the reaction to be monitored through the measurement of the weight increase. Experiments were carried out at atmospheric pressure, using a flow rate of 160 ml/min of 10–40% CH_4 in Ar as reactive gas. The sample holder was a ceramic crucible with a