INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 41 (2016) 10755–10765

Available online at www.sciencedirect.com

ScienceDirect

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

# Kinetic behavior of Pt catalyst supported on structured carbon nanofiber bed during hydrogen releasing from decalin

Yongxiao Tuo [a], Hao Jiang [a], Xing Li [a], Liujie Shi [a], Xinhai Yu [b], Ping Li [a,*]

[a] State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

[b] School of Mechanical and Power Engineering, East China University of Science and Technology, Shanghai 200237, China

ARTICLE INFO

*Article history:*
Received 3 February 2016
Received in revised form
11 April 2016
Accepted 12 April 2016
Available online 1 May 2016

*Keywords:*
Structured catalyst
Carbon nanofibers (CNFs)
Hydrogen releasing
Decalin
Kinetic behavior
Mass diffusion

ABSTRACT

It is of great significance to develop practical catalysts with macroscopic sizes for hydrogen releasing. In the present study, two kinds of structured carbon nanofiber (CNF) monoliths synthesized by growing CNFs on the graphite fiber felt in Ni–$C_2H_6$ and Fe–CO systems respectively have been used as the supports of Pt catalysts. The catalytic performances have been evaluated in the dehydrogenation of decalin for hydrogen releasing in a tubular flowing reactor. The structure characterization and the reaction kinetic analysis have been conducted upon different supports and catalysts to clarify the main factors influencing the apparent reaction rate. A comparison study has been made with the Pt catalysts supported on activated carbon (AC) pellets. The results show that two structured Pt catalyst beds perform much better at the aspects of both intrinsic catalysis and mass transfer than the catalysts based on AC pellets. The superior catalytic activity of the structured Pt catalysts can be assigned to the smaller Pt particle size and more proper interaction between the metal and the support. The excellent mass diffusion efficiency on both the external and internal sides of fibrous CNF interface can be correlated to the high large-pore porosity and the thin CNF layer in the structured supports, which have been manifested by the calculation of the mass diffusion limitation criteria.



## Introduction

Structured catalyst supports such as ceramic monoliths and metal foams have been successfully applied in the processes of automotive and stationary pollution abatement. Nowadays, their applications have been extended to wider industrial fields from the production of chemicals such as $H_2O_2$ to the energy-related processes, e.g. hydrogen generation for fuel cells, steam reforming of hydrocarbons, and Fischer–Tropsch synthesis [1–5]. The outstanding advantages of structured supports lie in that they can provide larger geometric surface areas, shorter diffusion distances, lower pressure drops and easier loading and handling in reactors, etc. as compared with

* *Corresponding author*. Tel.: +86 21 64251938; fax: +86 21 64253528.
E-mail address: lipingunilab@ecust.edu.cn (P. Li).

http://dx.doi.org/10.1016/j.ijhydene.2016.04.072

conventional pellet supports. Among the materials used for structured support fabrication, carbon materials have also been frequently adopted because they generally possess good corrosion resistance, high chemical and thermal stability, low mass density, and large specific surface area as well [6–8]. The tunable texture and surface chemistry of carbon materials are another important consideration in their application to being catalyst supports for objective reactions [9,10].

Being accompanied by a flourishing progress in the research and development of various nano-carbon materials, carbon nanofibers (CNFs) have attracted an intense interest worldwide due to their low synthesis cost in addition to the peculiar physic-chemical and mechanical properties. As a practicable form of CNFs devised for potential employment in commercial reactors, in fact, the structured catalyst supports based on CNFs have been synthesized and investigated extensively in the literature [11–13]. Making use of catalytic chemical vapor deposition (CVD) technique, CNFs can be configurated into structured CNFs/substrate supports by way of growing CNFs on the surface of macroscopic substrates such as metal foam, ceramic monolith and graphite felt (GF) [14–17]. The substrates just like scaffolds confer desired shape and size on CNFs-based supports. The structured CNFs/substrate supports combine the properties of the macroscopic host structure of the substrates and the advantages of the CNFs, especially the open interface with rare micropores, which can significantly reduce mass transfer limitation and allow fluid in high space velocity to be operated [18–20]. As reported, enhanced liquid–solid mass transfer by the introduction of CNFs on solid foam was observed at a considerably lower pressure drop than random packings [21]. In the study completed by Lefferts's research group on selective hydrogenation of 4-carboxybenzaldehyde over palladium catalysts supported on CNFs coated monolith, the superior internal mass transfer properties were assigned to high porosity, low tortuosity and short diffusion length of the CNF layer [22].

However, from the viewpoint of chemical engineering, there are still far more efforts required prior to putting the structured CNF supports into service in industrial reactors. Comprehensive kinetic analysis concerning the structured CNFs-based catalysts at catalytic bed level is much in demand for the succeeding design of reactor architectures. Nevertheless, there is rare literature on the relevant subject. Furthermore, the exploitation of structured CNF supports for more catalytic processes is also of great value [23,24]. In the present study, therefore, we attempt to utilize the structured CNFs/GF material fabricated elaborately as the support of Pt catalyst and subsequently employ the latter in the process of decalin dehydrogenation for hydrogen releasing.

It is increasingly recognized that hydrogen is a kind of promising clean energy to replace the traditional fossil fuel in the future. Nevertheless, the transportation and storage of hydrogen in mild conditions is as yet the most intractable issue of hydrogen technology. Among the broad options, the transportation and storage of hydrogen via organic hydrides is very competitive due to their simplicity and other merits [25–27]. Hydrogen can be released simply through dehydrogenation process over catalysts. As a kind of low-cost organic hydride, decalin owns very high hydrogen content (7.3 wt%, 64.8 $kgH_2/m^3$), which can meet the short-term target for hydrogen storage (5.5 wt%, 40 $kgH_2/m^3$) proposed by the US Department of Energy [28].

Although the research on the catalytic dehydrogenation of organic hydrides to release hydrogen with high efficiency has made progress in the past decades, its practical implementation in a pilot-plant scale is still undeveloped [29,30]. Our previous work revealed that the catalysts of Pt supported on powdery CNFs showed remarkable performance during the dehydrogenation of decalin [31,32]. In the present study, we will focus on the kinetic behaviors of the Pt catalytic beds based on structured CNFs/GF supports during decalin dehydrogenation in vapor phase in a tubular flowing reactor. Since the structured catalytic bed stowed in a reactor can occupy the whole space in the radical of the reactor, the configuration of the integrative bed may guide the hydrodynamic behavior of fluid that streams through the reactor and the mass transfer from external and internal sides of the cellular structure interface as well. Therefore, the textural properties of the structured support may have the impact not only on the Pt particle dispersion but also on the transference of reactive media during reaction [7,33]. For the structured CNF supports it is fortunate that their texture can be manipulated by altering CNF growth catalysts and carbon sources according to CNF growth mechanism, making possible the rational design of catalytic beds based on CNF supports on the significant aspects from micro-catalysis to macro-kinetics. On consideration, we will synthesize two kinds of structured CNFs/GF supports using Ni and Fe as CNF growth catalysts and $C_2H_6$ and CO as carbon sources, respectively, and further investigate the influence of their texture on the overall catalytic performance. A comparison between the structured CNFs/GF support and conventional activated carbon (AC) pellet beds will be emphasized in order to clarify the superiority of the structured CNFs/GF support on the basis of kinetic study. In view of the scarce report on the application of structured CNFs in the field of hydrogen energy, the purpose of the study is hereby with quantitative evidence to demonstrate the structured CNFs/GF supports where the excellent kinetic performance of the supported Pt catalysts could be achieved during hydrogen releasing from decalin in vapor phase under mild reaction conditions. The results obtained will be also useful for the further optimization of the reactor specification devised for the process concerned.

## Experimental

### *Synthesis of structured CNFs/GF supports and their supported Pt catalysts*

The GF substrate made of skeins of graphite microfibers each with a mean diameter of 19 μm was commercially available from the Shanghai Q-Carbon Material Co. Ltd. The specific surface area of GF is below 1 $m^2/g$ while it could be tailored to be cylindrical monoliths with an approximate size of 35 mm in diameter and 10 mm in height.

Two kinds of structured CNFs/GF supports synthesized using different growth catalysts and carbon sources, denoted by Ni–$C_2H_6$ and Fe–CO, were prepared through the growth of CNFs on the surface of GF monoliths by the method of