

available at [www.sciencedirect.com](http://www.sciencedirect.com)journal homepage: [www.elsevier.com/locate/chnjc](http://www.elsevier.com/locate/chnjc)

## Review

# Modulating the microstructure and surface chemistry of carbocatalysts for oxidative and direct dehydrogenation: A review



Zhongkui Zhao\*, Guifang Ge, Weizuo Li, Xinwen Guo, Guiru Wang

State Key Laboratory of Fine Chemicals, Department of Catalysis Chemistry and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China

## ARTICLE INFO

## Article history:

Received 13 January 2016

Accepted 22 February 2016

Published 5 May 2016

## Keywords:

Carbocatalysis

Microstructure

Surface chemistry

Modulation

Dehydrogenation

Olefin

## ABSTRACT

The catalytic performance of solid catalysts depends on the properties of the catalytically active sites and their accessibility to reactants, which are significantly affected by the microstructure (morphology, shape, size, texture, and surface structure) and surface chemistry (elemental components and chemical states). The development of facile and efficient methods for tailoring the microstructure and surface chemistry is a hot topic in catalysis. This contribution reviews the state of the art in modulating the microstructure and surface chemistry of carbocatalysts by both bottom-up and top-down strategies and their use in the oxidative dehydrogenation (ODH) and direct dehydrogenation (DDH) of hydrocarbons including light alkanes and ethylbenzene to their corresponding olefins, important building blocks and chemicals like oxygenates. A concept of microstructure and surface chemistry tuning of the carbocatalyst for optimized catalytic performance and also for the fundamental understanding of the structure-performance relationship is discussed. We also highlight the importance and challenges in modulating the microstructure and surface chemistry of carbocatalysts in ODH and DDH reactions of hydrocarbons for the highly-efficient, energy-saving, and clean production of their corresponding olefins.

© 2016, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

## 1. Introduction

Owing to their extensive use as chemical building blocks, olefins, including light olefins and styrene, are among the most important compounds in the chemical industry. Both light olefins and styrene are important monomers for polymer and copolymer synthesis. Light olefins are also the feedstock in the production of a vast array of chemicals including oxygenates like ethylene glycol, acetic acid, acetaldehyde, acetone, propylene oxide, ethylene oxide, 2-butanone, 1,2-epoxybutane, 2-butyl alcohol, etc. as well as important chemical intermedi-

ates like propyl aldehyde, vinyl chloride, acrylonitrile [1,2]. The production of light olefins and styrene has attracted continuously growing interest in the past century and would have this position for a long time to come. Therefore, the catalytic dehydrogenation of hydrocarbons including light alkanes and ethylbenzene to olefins has attracted considerable attention in both academia and industry.

The traditional DDH process for the production of olefins is normally performed a K promoted Fe-based catalyst [3,4]. However, the commercially available K-Fe catalyst has many disadvantages like quick deactivation due to potassium loss,

\* Corresponding author. Tel/Fax: +86-411-84986354; E-mail: [zkzhao@dlut.edu.cn](mailto:zkzhao@dlut.edu.cn)

This work was supported by the National Natural Science Foundation of China (21276041), the Program for New Century Excellent Talents in University of Ministry of Education of China (NCET-12-0079), the Natural Science Foundation of Liaoning Province (2015020200) and the Fundamental Research Funds for the Central Universities (DUT15LK41).

DOI: 10.1016/S1872-2067(15)61065-8 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 37, No. 5, May 2016

unstable  $\text{Fe}^{3+}$  state, coke deposition, and health injuries to human beings caused by the Cr used in this catalytic system. Moreover, the introduction of superheated steam into the feed is needed to give a thermodynamic driving force as heat due to its endothermic character (for DDH of ethylbenzene at 600 °C,  $\Delta H_{600} = 126.6$  kJ/mol), to shift the chemical equilibrium to higher styrene conversion. This also inhibits quick deactivation caused by coke deposition. However, the used excess steam (about 2–3:1 for current technology) leads to high energy consumption [3,4]. Oxidative dehydrogenation (ODH) is an alternative process with improved energy efficiency owing to its exothermic characteristic (for ODH of ethylbenzene at 600 °C,  $\Delta H_{600} = -111.1$  kJ/mol) [4–6]. However, a low selectivity due to the deep oxidation of alkane and the formed olefins is a bottle-neck for its application in olefin production since the formed olefins are more active than the starting hydrocarbons. The search for new catalyst systems is highly desirable, but remains a challenge.

The development of low cost sustainable catalysts with high catalytic activity, selectivity, and stability under mild conditions remains at the heart of modern material chemistry, green chemistry, and catalysis from academic and practical aspects [7–9]. Although metal catalysts have currently played major roles in many industrial transformation processes, they suffer from many inherent disadvantages such as low availability, high cost, susceptibility to gas poisoning, detrimental effects on our environment, and residual metal in the products [10–13]. Owing to broad availability, environmental acceptability, corrosion resistance, and unique surface properties, nanocarbon materials are a promising and sustainable low cost metal-free alternative to metal-based catalysts for organic synthesis [14–20], hydrogen production [21,22], photo-degradation of organic pollutants [23,24], the crucial oxygen reduction reaction in fuel cells [25–27], and as the counter electrode catalyst for solar cells [28,29]. Nowadays, carbocatalysis has already attracted great attention throughout the world, and has become the forefront and a hot topic in heterogeneous catalysis and sustainable chemistry [10,11,30–42].

In fact, carbon materials, especially nanocarbons, have been reported in both ODH and DDH of hydrocarbons including that of light alkanes and ethylbenzene to their corresponding olefins. Numerous studies have been focused on the ODH process over different carbocatalysts, which exhibited many merits in comparison to DDH, such as higher activity and lower energy consumption, and not limited by thermodynamics due to its exothermic process [4,5]. However, it is worthwhile to point out that in fact the ODH process has some significant disadvantages. The use of a mixture containing oxygen and hydrocarbons leads to a low thermal stability of the carbocatalysts due to serious damage by oxygen under the relatively harsh reaction conditions, and there is a safety issue due to the use of a mixture containing oxygen and hydrocarbons, besides the above mentioned low selectivity owing to side reactions such as the combustion of hydrocarbons [43–46]. Recently, the carbon material catalyzed DDH of ethylbenzene to styrene under oxygen- and steam-free conditions was first reported by employing nanodiamond as an efficient metal-free catalyst, which

has a fascinating prospect for clean and energy-saving styrene production [47]. The exciting results have inspired researchers to develop novel and efficient carbon-based catalysts for the DDH reactions of different hydrocarbons including light alkanes and ethylbenzene. In the DDH process, the carbocatalysts exhibit outstanding coke tolerance behaviour in the absence of steam and oxidant in comparison to the industrially used K-Fe catalysts. In addition, DDH also eliminates the low thermal stability issues of ODH carbocatalysts, and the insufficient selectivity and the risks in handling flammable mixture including hydrocarbon and oxygen [47]. However, improvement in the catalytic activity of the carbocatalysts for DDH process is urgently required.

From the above, ODH and DDH as two ways for olefin production have demonstrated great potential for future industrial application. However, there still exist many issues to be resolved before the industrial use of carbocatalyst-mediated dehydrogenation processes of hydrocarbons, either ODH or DDH, can be realized. Especially, improvement in selectivity and stability for ODH and the enhancement in catalytic activity for DDH process are urgently required.

The catalytic performance of solid catalysts depends on the properties of the active sites and their accessibility to reactants, which are significantly affected by the microstructure (morphology, shape, size, texture, and surface structure) and surface chemical properties (elemental components and chemical states) [48–58]. This work reviews the state of the art in modulation of the microstructure and surface chemistry of carbocatalysts through both bottom-up and top-down approaches for both the ODH and DDH of hydrocarbons, including light alkanes and ethylbenzene to their corresponding olefins. We highlight the importance and challenges in modulating the microstructure and surface chemistry of carbocatalysts in both ODH and DDH reactions of hydrocarbons for applications in olefin production.

## 2. Active sites and mechanism

The surface chemical components, state, and structure of carbocatalysts are quite complex, which make it very difficult to identify and quantify the catalytically active sites for the dehydrogenation process. Since the catalytically active sites are very important for catalytic reactions, many studies have focused on their identification and quantification by employing powerful techniques like temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), Fourier Transform infrared spectroscopy (FT-IR), microcalorimetric analysis (MCA), chemical titration analysis, model catalysts experiment, and density functional theory (DFT) calculations [4,5,59–80]. Some fruitful results have been achieved which provided helpful guidance for designing and manipulating the microstructure and surface chemistry of carbocatalysts for olefin production from hydrocarbons through either the ODH or DDH process.

### 2.1. ODH reaction

General consensus in previously reported results of

Download English Version:

<https://daneshyari.com/en/article/59371>

Download Persian Version:

<https://daneshyari.com/article/59371>

[Daneshyari.com](https://daneshyari.com)