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Macroscopically shaped monolith of nanodiamonds @ nitrogen-enriched mesoporous carbon decorated SiC as a superior metal-free catalyst for the styrene production

Housseinou Ba^{a,1}, Jingjie Luo^{a,c,1}, Yuefeng Liu^{a,b,*}, Cuong Duong-Viet^a, Giulia Tuci^d, Giuliano Giambastiani^{d,e}, Jean-Mario Nhut^a, Lam Nguyen-Dinh^f, Ovidiu Ersen^c, Dang Sheng Su^b, Cuong Pham-Huu^{a,*}

^a Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), ECPM, UMR 7515 du CNRS- University of Strasbourg (UdS), 25 rue Becquerel, 67087 Strasbourg, Cedex 02, France

^b Dalian National Laboratory for Clean Energy (DNL), Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, 116023 Dalian, China

^c Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504, CNRS-University of Strasbourg (UdS), 23, rue du Loess, 67034 Strasbourg, Cedex 02, France

^d Institute of Chemistry of OrganoMetallic Compounds, ICCOM-CNR and Consorzio INSTM, Via Madonna del Piano, 10-50019, Sesto F.no, Florence, Italy

^e Kazan Federal University, 420008 Kazan, Russian Federation

^f The University of Da-Nang, University of Science and Technology, 54 Nguyen Luong Bang, Da-Nang, Viet Nam

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ABSTRACT

Nanodiamonds (NDs) are recognized as a class of robust metal-free catalysts for the steam-free, direct dehydrogenation (DDH) of ethylbenzene (EB) to styrene (ST). In spite of that, some main drawbacks, such as their powdery form along with their tendency to form aggregates, limit their full exploitation at the industrial level. In this work, we describe the preparation of macroscopically shaped monoliths consisting of silicon carbide-based foams coated with a nitrogen-rich mesoporous carbon matrix (NMC) as a non-innocent glue for highly dispersed ND fillers. The NMC phase is prepared from cheap and non-toxic food-grade components and it prevents the undesired NDs agglomeration thus maximizing the reagents exposure throughout the catalytic DDH tests. Moreover, the NMC phase represents a key source of surface basicity capable of inhibiting the occurrence of EB cracking side reactions during the catalytic runs. As a result, the ND@NMC/SiC composite shows excellent dehydrogenation performance already at low ND loading if compared with the powdery NDs and/or the SiC-supported NDs of the state-of-the-art. Noteworthy, the ND@NMC/SiC composite presents its best catalytic performance under DDH conditions close to those used in industrial plants (reaction temperature up to 600 °C and EB concentrations up to 10 vol.%) with high ST rates ($\lambda_{\text{catal.}}$ of 9.9 mmol_{ST} g_{cat}⁻¹ h⁻¹), ST selectivity over 96% and long term stability on stream.

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1. Introduction

Styrene (ST) is mainly produced by the gas-phase direct dehydrogenation (DDH) of ethylbenzene (EB) [1–3]. The most widely employed catalyst for such reaction is a low surface area iron-based oxide promoted with different elements such as alumina or potas-

sium [4,5]. Nowadays, about 85% of the ST worldwide production is realized by means of these catalysts, which typically operate under high temperatures (ranging from 580 to 630 °C). The iron-based catalysts are cheap and they can ensure relatively high ST selectivity in the process. However, these metal-based catalysts list a number of serious disadvantages that significantly limit their catalytic performance, e.g. the drastic deactivation/passivation of their metal active sites due to the rapid generation of “coke” deposits. To overcome this problem, a large amount of steam is generally co-fed in the reactor with heavy energy wastes, estimated to be around 1.5×10^9 cal per ton of ST produced, together with large amounts of waste water containing traces of hydrocarbons which need to be purified before being discharged. Moreover,

* Corresponding authors at: Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), ECPM, UMR 7515 du CNRS- University of Strasbourg (UdS), 25 rue Becquerel, Cedex 02, Strasbourg 67087, France.

E-mail addresses: yuefeng.liu@dicp.ac.cn, yuefeng.liu@unistra.fr (Y. Liu), cuong.pham-huu@unistra.fr (C. Pham-Huu).

¹ These authors contributed equally.