



# Extremely productive iron-carbide nanoparticles on graphene flakes for CO hydrogenation reactions under harsh conditions

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## ABSTRACT

For the highly productive nanocatalyst synthesis, ensuring the formation and stabilization of active nanoparticles with enlarged surface areas by increasing their metal loading and dispersion have been major issues. Herein, we report a facile method based on a simple melt-infiltration process for creating extremely productive Fe<sub>5</sub>C<sub>2</sub> nanoparticles (~14 nm) incorporated into graphene flakes (Fe<sub>5</sub>C<sub>2</sub>/G) with a stable and high Fe load (~35 wt%). They showed extremely high C<sub>5+</sub> hydrocarbon productivity (4.41 g<sub>C5+HC</sub> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>), CO conversion (91.8%), and Fe time yield (6.5 × 10<sup>-4</sup> mol<sub>CO</sub> g<sub>Fe</sub><sup>-1</sup> s<sup>-1</sup>) as well as good thermal stability in CO hydrogenation reactions under harsh conditions.

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## 1. Introduction

The catalytic carbon-monoxide (CO) hydrogenation reaction has been used as an effective route for producing valuable hydrocarbons [1,2]. In particular, the high-temperature Fischer-Tropsch synthesis (HT-FTS) reaction (a representative CO hydrogenation route), which is generally performed in the range of 300–350 °C using iron (Fe)-based catalysts, has been suitable for the selective production of gasoline-range (C<sub>5</sub>–C<sub>12</sub>) hydrocarbons and lower olefins [3,4]. In a practical HT-FTS reaction, the product yield per unit weight of the catalyst has a significant meaning [5]. In this respect, well-designed catalysts with high metal loading are good candidates to increase the number of active sites, if the active particle dispersion is ensured [6].

To enhance the catalyst performance, a new catalyst with an increased number of active sites/surfaces was developed [7], for which it was necessary to optimize the particle embedding skills needed for formation and stabilization of the active surfaces. In general, the particle agglomeration readily occurs when the active nanoparticles are not strongly anchored to the surface of the support [8]. Therefore, only 10–20 wt% of the active metals in conventional catalysts have been incorporated into the supporting

materials such as porous alumina, silica, and various forms of carbons, in order to ensure the proper size of active particles by preventing severe particle agglomeration [9–13]. Unfortunately, it can only be achieved using novel approaches such as thermal decomposition of metal organic framework (MOF) precursors to synthesize the fine nanoparticles with the high Fe loads (>30 wt%) [14,15].

Recently, a melt-infiltration process has provided well dispersed nanoparticles during the synthesis of supported catalyst synthesis [16,17]. Compared with conventional wetness impregnation routes, the new method for preparing supported metal catalysts is convenient and eco-friendly; however, this method is also dependent on the qualities of porous supports, such as pore volume and structure.

Graphene, is an sp<sup>2</sup> hybridized carbon material with a hexagonal monolayer network, is often used as a catalyst support based on its intrinsic properties. These include high surface area and large pore volumes as well as excellent chemical and thermal stability [18,19]. In particular, the structural defects of the graphene can be used to enhance interactions with anchored molecules or nanoparticles by tailoring the localized properties to achieve new surface functionalities [20,21].

Recently, a research group have reported graphene oxide-supported iron oxide nanoparticles with more active sites exposed for FTS, based on the promoted reduction and carbonization behaviors [22,23]. In addition, iron oxide/reduced graphene

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