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Research Paper

Embedded iron nanoparticles by graphitized carbon as highly active yet stable catalyst for ammonia decomposition

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ABSTRACT

The Fe nanoparticles embedded by graphitized carbon were developed through a strategy of hydrothermal and thermal treatment. The resulting materials, with high surface area and porosity, well dispersed iron nanoparticles (NPs) associated with graphitized carbon structure, show high activity and durability in ammonia decomposition reaction. Among the serial Fe-based catalysts, Fe@GC-4 of a low iron content (1.29 wt%) exhibits significant ammonia decomposition activity (~71% conversion and 22.1 mol_{H2} $g_{Fe}{}^{-1}$ h^{-1}) at a gas hourly space velocity of 6000 $cm^3 g_{cat}{}^{-1} h^{-1}$ and 600 °C. After an extended period of reaction conducted over the representative Fe@GC-3 catalyst, most of the embedded Fe NPs transform to nitride species with relatively smaller particle size, while the embedded structure still retains. This study provides new insights into the development of cheap metal-based catalysts functionalized by graphitized carbon (graphene) for the current reaction and other potential applications.

1. Introduction

Hydrogen is considered one of the most important clean energy carriers for future energy systems [1]. The implementation of sustainable hydrogen production and subsequent hydrogen conversion to energy is called “hydrogen economy”. Unfortunately, its physical properties make the transport and handling of hydrogen gas difficult [2]. Liquid ammonia, as a hydrogen-rich molecule, can be easily stored, transported and converted to CO_x-free hydrogen for the demand of proton-exchange membrane fuel cells (PEMFCs). Therefore, on-site generation of hydrogen via NH_3 catalytic decomposition has attracted extensive attention for easy handling and relatively low cost [3–6].

In the past few decades, most efforts have been devoted to Ru-, Ni-, Fe- and Co-based catalysts [3–6]. Among them, carbon supported catalysts showed advance performance for NH_3 decomposition, which was thought to be the electronic promotion effect of carbon support on active metal species, facilitating the recombinative desorption of surface nitrogen atoms [7–10]. Carbon nanotubes (CNTs) supported Ru catalyst was found to be the most active catalyst known to date [7]. Zhang et al. [11,12] adopted CNTs containing residual Co, Fe or their alloy nanoparticles as catalysts for NH_3 decomposition, achieving superior activity and structural maintenance during the reaction. Other types of carbon materials, such as carbon nanofibers (CNFs), ordered nanostructured carbons (CMK-5) and graphitized carbon, were also employed as supports in ammonia decomposition [13–17].

In recent years, the unique properties have been observed by confining/embedding metal NPs into inorganic channels or cavities, which offer new opportunities to design advanced catalytic systems [18,19]. How to introduce catalytic active species (such as metal or metal oxide NPs) dispersed homogeneously in graphitized carbon matrix remains challenging. Several works have shown that functional nanoparticles encapsulated into ordered mesoporous carbons can be synthesized through either a hard-templating approach using ordered mesoporous silica as a template [10,20–22] or a soft-templating approach based on co-assembly of triblockcopolymers pluronic F127 and resol or resorcinol-formaldehyde in the presence of metal salts [23–25]. However, these methods require the preparation of ordered mesoporous silica or low-polymerized phenolic resol as the scaffold, which certainly increases technical complexity as well as cost of catalyst fabrication. Yu and co-workers designed a one-pot hydrothermal cohydrolysis-carbonization process using glucose and metal nitrate as starting materials, and succeeded in fabrication of uniformly embedded iron oxide NPs in carbonaceous spheres [26]. Despite it showed remarkable stability and selectivity in Fischer-Tropsch synthesis, high graphitization degree as well as porosity of carbon

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Table 1
Physical properties of prepared Fe@GC catalysts.

Samples	Metal content (wt%)[a]	S_{BET} ($m^2 g^{-1}$)	V_{micro} ($cm^3 g^{-1}$)	V_t ($cm^3 g^{-1}$)	D_p (nm)
Fe@GC-1	56.05	279.7	0.07	0.24	3.5
Fe@GC-2	20.47	274.8	0.06	0.22	3.3
Fe@GC-3	9.56	368.6	0.11	0.28	3.1
Fe@GC−3#[b]	–	370.6	0.13	0.34	3.7
Fe@GC-4	1.29	447.4	0.16	0.22	2.0

[a] The metal amounts of different samples measured by ICP-AES.
[b] The used catalyst Fe@GC-3 after stability test (600 °C and 20 h).

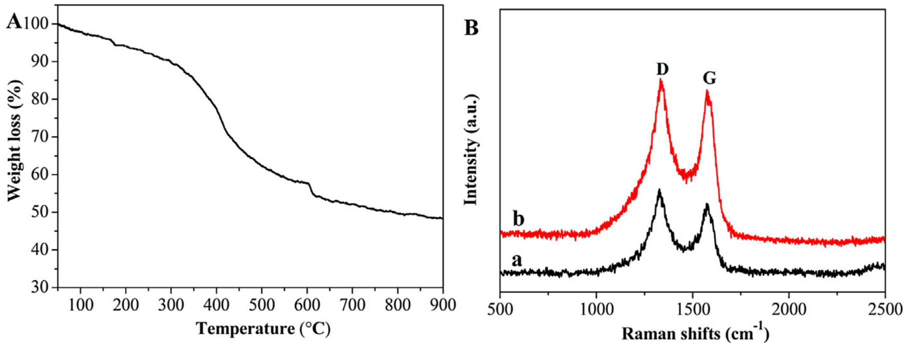

Fig. 1. (A) TGA profile of the pristine Fe@GC-3 before thermal treatment. (B) Raman spectrums of carbon (a) and representative Fe@GC-3 calcined at 700 °C respectively.

matrix is a prerequisite for many catalytic reactions. Bao's group recently reported that graphitized carbon could open up a route to enhance catalytic performance by coating of metal catalysts with controlled graphitized covers [27,28]. Deposition of graphitized carbon over metal oxides was also employed to improve high stability of electrocatalyst [29,30].

In this study, metal iron nanocatalysts encapsulated by graphitized carbon were synthesized via successive hydrothermal and calcination procedures, and applied for CO_x-free hydrogen production via ammonia decomposition. The aim of catalyst design is to construct a type of "embedded active phase" that is cheap metal-based and nanostructured. Due to the interaction between metal and graphitized carbon, the mesoporous Fe@GC composites with the unique nano-architecture could be efficient for ammonia decomposition, exhibiting notably low-temperature activity for the Fe-based catalyst, and high resistance against methanation by highly graphitized carbon networks.

2. Experimental section

2.1. Catalysts preparation

Embedded iron nanoparticles by graphitized carbon catalysts were prepared by a facile modified hydrothermal method [26] and subsequent thermal treatment. Typical synthesis procedure of Fe@GC composites as follows: glucose (0.1 mol) and $Fe(NO_3)_3{\bullet}9H_2O$ (0.01 mol) were dissolved into deionized water solution (30 mL) under stirring in sequence. After stirring for 0.5 h, the solution mixture was transferred into a 50 mL Teflon-lined autoclave and heated at 120 °C for 24 h. The resulting products were collected from the autoclave, centrifuged and washed with deionized water and ethanol for three times, and finally dried at 70 °C for 24 h. Then the resultant powder was calcined by heating it up to 700 °C at a temperature ramp of 4 °C min^{-1} under N_2 atmosphere and maintained for 4 h to get Fe@GC composites. A series of Fe@GC composites with different iron contents were realized by changing the amount of iron precursor salts. The corresponding samples were denoted as Fe@GC-1, Fe@GC-2, Fe@GC-3 and Fe@GC-4 composites, respectively.

2.2. Catalyst characterization

N_2 adsorption analysis was performed at 77 K using a Micromeritics ASAP 2020 to access the surface areas and pore size distributions. All the samples were outgassed at 200 °C for 6 h. Powder X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert MPD Pro X-ray diffractometer with graphite-monochromatized Cu Kα radiation at a scanning rate of 2°/min in the 2θ range from 20° to 80°.

TEM images were taken over a JEOL JEM-2000EX instrument operated at 200 kV. The SEM images were taken on a Hitachi S-4800 scanning electron microscope to determine the catalyst morphology and microstructure.

XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al-K radiations. The base pressure was approximately 3×10^{-9} mbar. The binding energies were referenced to the C1 s line at 284.8 eV from adventitious carbon.

The Raman spectra were collected on a Raman spectrometer (JY, HR 800) using a 514 nm laser. The metal loadings on porous carbon were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, PE OPTIMA 2100DV).

Thermogravimetric analysis (TGA) was simultaneously performed on a DTG-60 instrument (Shimadzu, Japan) at a heating rate of 10 °C/min under N_2 atmospheres.

2.3. Catalyst activity

For the ammonia decomposition reaction, the dried power catalysts (Fe@GC, 25 mg) were placed on a frit in the quartz tube, fixed-bed reactor with an internal diameter of 6 mm. The temperature-dependent conversion measurements of NH_3 were carried out as follows. Firstly, the temperature was raised to 600 °C in a pure ammonia stream and kept for 2 h, corresponding to a space velocity of 6000 cm^3 $g_{cat}{}^{-1}$ h^{-1}. After cooling down in the ammonia stream to 400 °C, the evaluated activity was started. Then the next