Chinese Journal of Catalysis 34 (2013) 508–523

available at www.sciencedirect.com

ScienceDirect

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

Review (Special Column on Progress in Catalysis in China during 1982-2012)

Research progress in metal-free carbon-based catalysts

SUN Xiaoyan [a], WANG Rui [a,b], SU Dangsheng [a,*]

[a] *Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, Liaoning, China*
[b] *National Institute of Clean-and-Low-Carbon Energy, Beijing 102211, China*

ARTICLE INFO

Article history:
Received 10 November 2012
Accepted 6 January 2013
Published 20 March 2013

Keywords:
Nanocarbon
Metal-free
Heterogeneous catalysis

ABSTRACT

Metal-free carbon-based catalysts are one of the most active research directions in nanomaterials and catalysis. The advantages that nanocarbon catalysts have over metal catalysts include high efficiency, environmental compatibility, low energy consumption, and corrosion resistance. Nanocarbon can efficiently catalyze alkane conversion, chemical synthesis, energy catalysis and other heterogeneous catalytic processes. This review highlights recent progress in the development of metal-free carbon-based catalysts, including understanding their surface properties, catalytic performance and reaction mechanism and macroscopic architecture. The state-of-the-art and future challenges of metal-free heterogeneous catalysis are also discussed.

1. Introduction

Metal-free catalysts are newly emerging green catalytic materials that have attracted much attention in recent years for their advantanges of high efficiency, environment friendliness and economy in many industrial catalytic processes. There are a variety of organic metal-free catalysts, such as small organic molecules containing N, P electron-rich center, dendrimers, ionic liquids, etc., which have been widely used in various homogeneous organic reactions for rearrangement reactions, cycloaddition, condensation, alkylation and carbonylation [1–3].

An important type of inorganic metal-free catalysts developed in recent years are nanocarbon materials that have demonstrated superior catalytic performance to traditional metal catalysts in many fields, including hydrocarbon conversion, fine chemicals production, fuel cells, and solar energy [4,5]. Metal-free carbon-based catalysis has become one of the most promising research directions in nanomaterials and catalysis. The carbon material itself is used as the catalyst and no metal is loaded or added, so the active sites for the reaction are the defective structure or functional groups on the carbon surface. Compared with a metal-based catalyst, a nanocarbon catalyst has the advantages of low cost, no heavy metal pollution and environmental friendliness, while showing high selectivity and long term stability under mild conditions in many catalytic processes. This review focuses on the key issues of their catalytic properties in heterogeneous catalytic system, the reaction mechanism and macroscopic architecture of metal-free carbon-based catalysts.

2. Structure and surface chemistry of nanocarbon materials

Many carbon materials used in catalysis have the graphitic structure. These marterials include conventional activated carbon, carbon black and graphite, and also the new nanomaterials of fullerenes, nanotubes and nanofibers,

---

* Corresponding author. Tel: +86-24-83970029; Fax: +86-24-83970019; E-mail: dssu@imr.ac.cn

This work was supported by the National Natural Science Foundation of China (21133010, 21103203, and 50921004), the National Basic Research Program of China (973 Program, 2011CBA00504), and the Thousand Talents Program of the Central Organization Department.

DOI: 10.1016/S1872-2067(11)60515-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 34, No. 3, March 2013

graphene and mesoporous carbon.

Nanocarbon materials are prepared by severe chemical processes such as laser arc discharge, ablation and chemical vapor deposition, and thus a large amount of structural defects are introduced into the carbon surface. The terminating surface of a curved graphitic structure requires new foreign atoms to saturate the dangling bonds at the defects and edges. After chemical post-treatment, these sites can be modified with heteroatoms to provide strong chemical reactivity for acid-base and redox chemistry. Oxygen and nitrogen atoms are the most frequently incorporated atoms. Figure 1 summarizes the different oxygen and nitrogen functional groups found on carbon surfaces [4]. Oxygenated functional groups have been the most extensively studied because they are formed spontaneously by the exposure of the carbon material to the atmosphere. Acidic oxygen groups include carboxylic acids, anhydrides, lactones and phenols. Carbonyls and ether oxygen species, such as quinones, pyrones, and benzopyrans are generally alkaline or neutral oxygen functional groups.

3. Catalytic performance of nanocarbon materials

The excellent catalytic performance of nanocarbon materials is due to their unique properties. First, most nanocarbons with a nanographite structure possess good electrical conductivity and ability to store/release electrons, which facilitates the rate of electron transfer in the critical step of the catalytic reaction and increases the overall reaction rate. Second, nanocarbon materials have very high specific surface areas and mesopore volumes, and have more surface active sites than conventional materials, thus improving the catalytic performance by the faster diffusion of reactant molecules in the mesopores. Finally, the higher concentration of surface defects on the nanocarbon materials can be functionalized with more oxygen and nitrogen heteroatoms. Table 1 lists some common reactions that are catalyzed by nanocarbon materials and the required surface functional groups or active sites [5].

Table 1
Overview of reactions catalyzed by carbon, and the surface chemistry and active sites [5].

Reactions	Surface chemistry/active sites
Gas phase	—
Oxidative dehydrogenation	quinones
Dehydration of alcohols	carboxylic acids
Dehydrogenation of alcohols	lewis acids and basic sites
NO_x reduction (SCR with NH_3)	acidic surface oxides (carboxylic and lactone) + basic sites (carbonyls or N5, N6)
NO oxidation	basic sites
SO_2 oxidation	basic sites, pyridinic—N6
H_2S oxidation	basic sites
Dehydrohalogenation	pyridinic nitrogen sites
Liquid phase	
Hydrogen peroxide reactions	basic sites
Catalytic ozonation	basic sites
Catalytic wet air oxidation	basic sites

3.1. Gas phase reactions

In the past few years, most studies of gas phase reactions catalyzed by nanocarbons were focused on the oxidative dehydrogenation system. In 2001, Robert Schlögl's research group carried out the oxidative dehydrogenation (ODH) of ethylbenzene using carbon nanofibers as the catalyst [6,7] and found that the carbon nanofibers showed a higher catalytic activity than highly dispersed graphite at the reaction temperature of 547 °C, and also had a far superior stability to traditional amorphous carbon black. A series of studies subsequently demonstrated that many nanostructured carbons can efficiently catalyze the ODH reaction of ethylbenzene to styrene (Fig. 2), and that these catalysts exhibited comparable or even better activities than the traditional iron oxide catalysts [8–13]. This is because the defects of the carbon surface can anchor functional groups as the active sites, while the graphitic structure can tightly hold the active sites to give excellent thermal stability even under an oxidative atmosphere [14]. In 2008, Su et al. [15] first reported that the oxidative dehydrogenation of butane to butene and butadiene can be catalyzed by carbon nanotubes. When the carbon nanotubes were additionally modified by passivation of the defects with phosphorus oxide, the resulting CNTs gave improved catalytic activity, while the reaction temperature was further decreased by 100–200 °C below the industrial catalytic process. The surface oxygen species on the surface of nanocarbon materials can be classified into electrophilic and nucleophilic types. Nucleophilic oxygen species preferentially react with electron-poor saturated bonds in al-

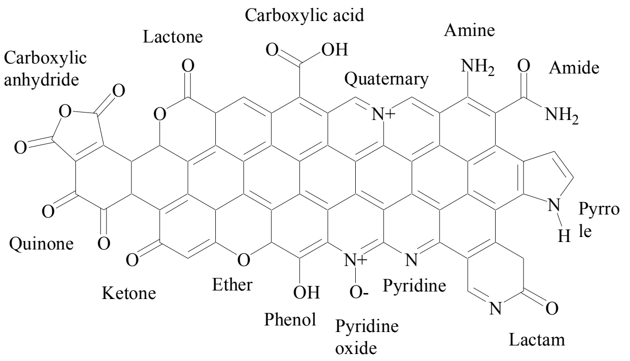

Fig. 1. Nitrogen and oxygen surface groups on nanocarbon [4].

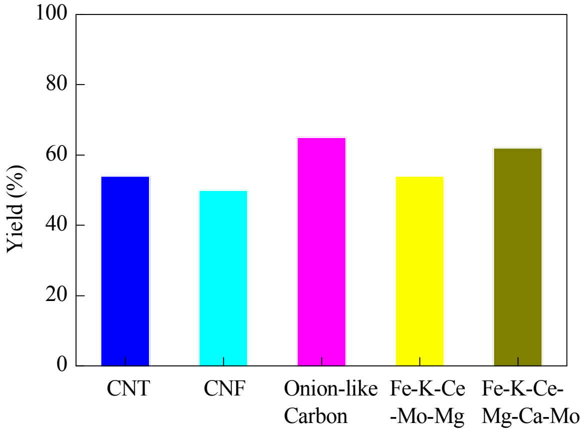

Fig. 2. Styrene yield over nanocarbon materials and metal catalysts in oxidative dehydrogenation [13].