Regular Article

Well-dispersed rhenium nanoparticles on three-dimensional carbon nanostructures: Efficient catalysts for the reduction of aromatic nitro compounds

Pitchaimani Veerakumar [a,b,*], Pounraj Thanasekaran [c], King-Chuen Lin [a,b,*], Shang-Bin Liu [a]

[a] Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan
[b] Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan
[c] Institute of Chemistry, Academia Sinica, Taipei 11529, Taiwan

GRAPHICAL ABSTRACT

Ordered mesoporous carbon supported ReNPs (Re/OMC) exhibited superior performances compared to their unsupported colloidal metal nanoparticles.
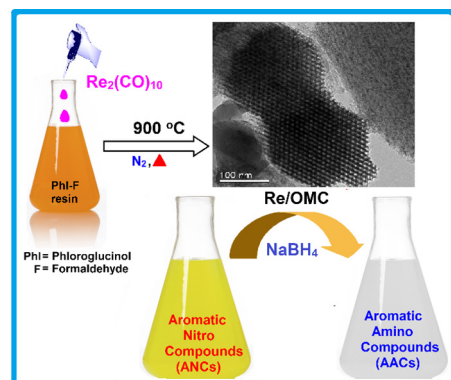
ARTICLE INFO

ABSTRACT

Rhenium nanoparticles (ReNPs) supported on ordered mesoporous carbon (OMC) as a catalyst (Re/OMC) through a solvent-evaporation induced self-assembly (ELSA) method were prepared. The synthesized heterogonous catalyst was fully characterized using X-ray diffraction, field emission transmission electron microscopy, N_2 sorption, metal dispersion, thermogravimetric analysis, Raman, Fourier-transform infrared, and X-ray photon spectroscopies. In addition, the catalyst was applied to reduce the aromatic nitro compounds (ANCs) for the first time in aqueous media and the reactions were monitored by following the intensity changes in the UV–vis absorption spectra with respect to time. This method provides the advantages of obtaining a high rate constant (k), green reaction conditions, simple methodology, easy separation and easy workup procedures. Moreover, the catalyst can be easily recovered by centrifugation, recycled several times and reused without any loss of activity. The higher activity of this catalyst was attributed to higher dispersion and smaller particle size of ReNPs as observed from FE-TEM and XRD results.

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* Corresponding authors at: Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.
  E-mail addresses: spveerakumar@gmail.com (P. Veerakumar), kclin@ntu.edu.tw (K.-C. Lin).

1. Introduction

Over the past decade, transition metal nanoparticles (MNPs) supported catalysts have received wide attention as heterogeneous catalysts due to their environmental benignity, low cost, structural integrity and high catalytic activities in various reactions [1–4]. By taking advantages of extraordinary properties of these nanomaterials including large specific surface area, high electrical conductivity and superior strength, the assembled 3D porous structures offer excellent opportunities for building high performance supercapacitors and electrochemical sensors [5]. Nevertheless, the catalytic activity of rhenium (Re) based nanomaterials used in the catalyst is limited compared to other metal catalysts [6–10]. Extensive effort has thus been devoted herein to synthesizing the carbon supported rhenium nanoparticles (ReNPs) and studied their catalytic activities. Several new techniques including pulsed-laser decomposition [11], electrodeposition [12], gamma irradiation [13], chemical vapour deposition (CVD) [14], wet chemical reduction [15,16], solvothermal [17], colloidal and microemulsion and other methods [18–20] were adopted to synthesize ReNPs materials. Apart from rhenium nanoparticles, other catalytic active MNPs, such as RuNPs [21], OsNPs [22,23], IrNPs [24], AuNPs [25] and, AgNPs [26] were also used as catalysts for the reduction of aromatic nitro compounds (ANCs).

Rhenium metals are the most promising catalytic materials that could be used as versatile catalysts. Apart from bare metals, ReNPs may serve as catalysts while they usually supported on polymer [27], DNA scaffold [28], carbon [29–31], and γ-Al$_2$O$_3$ [32], etc. Ordered mesoporous carbon materials (OMCs) as a support for transition metal catalysts [33,34] offer several advantages including easy modification, elimination of nanoparticle agglomeration, relatively low cost, high mechanical strength, chemical stability, and a pore structure along with an attractive surface chemistry. In addition, these nanocatalysts can make the products easily removable and the catalysts recyclable [35].

Over the last several years, numerous review articles have specifically addressed the toxicity and mutagenicity of ANCs. For example, the remediation of ANCs is of interest because it is a mutagen, anaemia and skin irritation [36]. Moreover, the reduced intermediates and products (such as amino-, and hydroxylamino-ANCs) often have greater toxicity and/or aqueous solubility than their parent compounds. Its ingestion can cause various health problems including eye, liver or kidney damages, aplastic anaemia, cyanosis, respiratory organs, as well as damage to neurological system [37]. Some ANCs are high-energy explosives. For example, 2,4,6-trinitrotoluene (TNT), 2,4,6-trinitrophenol (TNP) or picric acid are the primary constituents that were adopted in many unexploded landmines worldwide [38]. Therefore, it is necessary to remove such highly toxic pollutants. As the reduced products of ANCs, aromatic amino compounds (AACs) have attracted enormous attention in the chemical industry. They can also be used to synthesize drugs, pesticides, and explosives. In addition, these are key intermediates in many important fine chemicals, agrochemicals, pharmaceuticals, and polymer building blocks [39].

In the course of our studies on the development of heterogeneous catalysts, we report the potentiality of the Re/OMC catalyst that has been tested for the first time as a catalyst for the reduction of ANCs at room temperature, as illustrated in Scheme 1. In addition to the good catalytic properties, the synthesized catalyst could be easily separated from the reaction mixture and reused six times without loss of activity, indicative of its potential application in chemical industries.

2. Results and discussion

2.1. Structural properties

A highly mesoporous 3D structure of OMC was prepared via pyrolysis of phloroglucinol-formaldehyde resol by evaporation induced self-assembly (EISA) strategy (see Supporting Information, hereafter denoted as SI). Decomposition of dirhenium decarbonyl (Re$_2$(CO)$_{10}$, 217 mg, 0.33 mmol) used as a metal precursor may produce small ReNPs, which are embedded on the interior pore walls of the 3D carbon matrix (Scheme 1). Unlike previous methods adopted to synthesize on mesoporous carbon [8] and MWCNTs [29], the rhenium precursor Re$_2$(CO)$_{10}$ decomposes to the ReNPs upon microwave irradiation as shown in Eq. (1).

$$Re_2(CO)_{10} \rightarrow 2Re + 10CO \uparrow \tag{1}$$

Structural characterization based on X-ray diffraction pattern reveals that OMC showed two strong peaks appeared at 2θ = 24.6° and 44.6°, which can be attributed to the amorphous graphitic carbon (0 0 2) and (1 0 0), respectively (Fig. 1a) [40]. The related XRD pattern of the Re/OMC catalyst showed the peaks at 2θ = 37.7°, 40.6°, 43.0°, 56.6°, 68.4°, 75.3°, and 82.5°, confirming the formation of hexagonal rhenium. These results indicate that Re/OMC catalyst possessed a very small size ~2–5 nm of Re particle with a hexagonal closely-packed (hcp) structure of the bulk Re, which is in good agreement with previously published reports [11,40].

This fact verifies that ReNPs have been successfully loaded on to the three dimensional OMC material with rather good dispersion of the metallic phase. No other peaks have been observed; it is indicated that the rhenium dispersions have a highly textured, nanocrystalline structure with preferential growth orientation [20]. The crystallite size of Re in Re/OMC sample was determined according to the Scherrer formula (2):

$$d = \frac{0.9\lambda}{\beta \cos\theta} \tag{2}$$

where λ is the wavelength, β is the full width at half maximum (FWHM) of the Bragg's peak corrected using the corresponding peak in sample, and θ is the Bragg's angle.

Besides, pristine OMC and Re/OMC samples were also characterized by Raman spectroscopy (Fig. 1b). Both samples show the D and G bands at 1351 and 1598 cm^{-1}, respectively, which are in agreement with those reported [41]. Moreover, we observed an
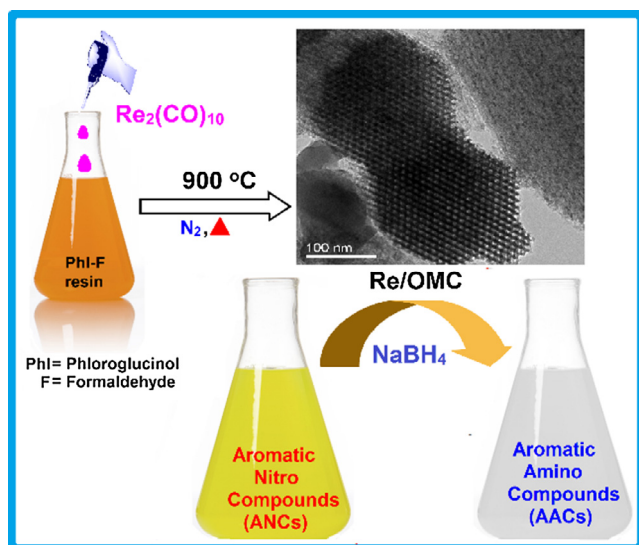
Scheme 1. Illustrated synthesis of Re/OMC nanocomposite from phloroglucinol-formaldehyde resin and its morphology and catalytic application.