



Different active sites in a bifunctional Co@N-doped graphene shells based catalyst for the oxidative dehydrogenation and hydrogenation reactions



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ABSTRACT

Low-cost, active and stable catalysts, with a bifunctional capability if possible, are required to achieve the chemical transformations between saturated and unsaturated N-heterocycles. In this work, Co@N-doped graphene shells (Co@NGS) was used as a bifunctional catalyst with high activity and stability for the oxidative dehydrogenation (ODH) and hydrogenation (HYD) of quinolines. The excellent performance can be attributed to the synergetic effect of N-doped graphene, underlying Co nanoparticles, and the encapsulation structure in which carbon shells protect Co from leaching and aggregation. Poisoning tests with KSCN and spectroscopic analysis clearly unveil that the active sites for ODH and HYD are quite different: N-doped graphene shells modified by Co NPs via electron transfer serve as active sites for the O₂ activation in ODH, while the underlying Co NPs promoted by N dopants favor the H₂ activation in HYD. This finding challenges the previous concept of N-doped carbon sites as active sites for both ODH and HYD. The bifunctional property is due to the access of both N-doped graphene and Co sites to small molecules in our one-pot pyrolyzed Co@NGS catalysts.

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1. Introduction

Catalytic hydrogenation (HYD) and dehydrogenation of N-heterocycles are of fundamental importance in organic synthesis, because both saturated and unsaturated N-heterocycles are very important structure units in pharmaceuticals and natural products [1–3]. Compared with the direct dehydrogenation pathway via removal of H₂, the oxidative dehydrogenation (ODH) route can effectively decrease thermodynamic energy barriers required for dehydrogenation with the assistance of active oxygen species, which makes ODH to occur under a milder reaction condition such as low temperature. Heterogeneous noble metal based catalysts such as Pt [4,5], Pd [6–8], Rh [9], Ir [10], and Ru [11,12] are widely used in both the HYD and ODH of N-heterocycles because of their capability of H₂ and/or O₂ activation. Some of them show a bifunctional property for both HYD and ODH reactions [4,6,8]. Despite their high catalytic performance achieved, high cost and scarcity greatly limit the development of noble metal catalysts in practical

applications. It is desirable to develop an inexpensive, earth-abundant non-noble metal catalyst, with a bifunctional capability if possible, to fulfill the chemical transformations between saturated and unsaturated N-heterocycles via HYD and ODH, respectively.

Recently, non-noble metals such as Fe, Co and Ni based N-doped carbon hybridized materials (MNCs) have attracted much attention and been viewed as a potential substitute for Pt-group metal catalysts in electrochemical oxygen reduction/evolution reactions [13–17], and heterogeneously catalytic ODH of alcohols [18–21] and amines [22], and selective HYD of nitroarenes [23–28], nitriles [29,30], and N-heterocycles [31,32]. Such wide applications of MNCs can be expressed by their intrinsic capability of the activation of both O₂ and H₂ molecules [33–37]. However, most of MNC catalysts are still suffering from an unavoidable deactivation caused by metal leaching and aggregation especially under harsh reaction conditions, even though many groups have claimed that metal nanoparticles (NPs) can be immobilized and stabilized by N dopants modified carbon matrix [27,32,38–41].

The encapsulation structure of metal NPs in protective carbon shells (M@C) has proved effective in enhancing the stability of MNC catalysts without distinct loss of their catalytic activity

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[25,27,37,42–46]. So far, the identification of active sites for both O_2 and H_2 activation in M@C catalysts is still controversial. Beller et al. have reported several efficient MNC catalysts for the ODH and HYD reactions, and they roughly attributed their high activities to the MO- N_x centers (metal oxide coordinated with N atoms) or the entire units of M-MO $_x$ @NG (metal-metal oxide embedded in N-doped graphene shell) [23,24,31,35,47]. To further clarify real active sites in M@C core-shell units, Bao and co-workers developed Pod-Fe and CoNi@NC catalysts for the oxygen reduction/evolution, and they claimed metal-modified nitrogen doped graphene (NG) shells via electron transfer as active sites for O_2 activation [42,46]. Meanwhile, NG surface sites modified by Co are also believed to serve as active sites for H_2 activation in Co^0 Co_3O_4 @N-doped carbon nanotubes-catalyzed HYD of nitrobenzene and quinolines reported by Wang's group [27,32]. Similarly, underlying metallic Ni was believed to enable inert carbon nitride (CN) shells to directly adsorb and activate H_2 in the CN/Ni/ Al_2O_3 catalyst [25]. It should be noted that these judgments were subjected to an assumption that small molecules cannot diffuse to metal surfaces which are totally blocked by carbon. Small cracks and defects normally coexist, along with the generation of curved graphene shells via base metal-catalyzed graphitization of amorphous carbons under pyrolysis at high temperatures, as reported in previous works [48,49]. In fact, the literature has shown that small molecules such as CO , H_2 and O_2 can intercalate the van der Waals gap between graphene and metal surface through a defect-aided intercalation mechanism [50,51]. Recently, Corma's group reported Co NPs coated by thin carbon layers with small cracks for H_2 diffusion as a catalyst for the selective HYD of nitroarene-derived compounds, and thin carbons were demonstrated as spectators in H_2 activation [44,52]. One can find that, compared to the generally accepted O_2 activation at carbon shell sites, it remains an intense debate on the identification of true active sites for direct H_2 activation between core metals and carbon shells.

Here we employed N-doped graphene shells encapsulated Co NPs (Co@NGS) with a uniform structure as a bifunctional catalyst for both the ODH and HYD of quinoline compounds. The outer graphene shells can effectively prevent the leaching and aggregation of Co NPs, which accounts for the good stability of Co@NGS-800 in both reactions. In addition, we carried out KSCN-poisoning tests to unveil two different active sites for the ODH and HYD reactions: N-doped graphene shells with an electronic modification by underlying Co provide active carbon sites for O_2 activation while the HYD activity is attributed to the encapsulated metallic Co sites rather than carbon shells.

2. Experimental

2.1. Catalyst preparation

All chemicals were of analytical grade. The Co@NGS catalysts were prepared using a simple pyrolysis process. The aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.923 g, 3.17 mmol) and glucose (1 g) was added dropwise into the methanol solution with melamine (40 g, 317 mmol) under vigorous stirring and then the solvent was evaporated at $80^\circ C$. The obtained powder was pyrolyzed under high-purity Ar atmosphere. The mixture was first heated to $600^\circ C$ at a ramp rate of $2^\circ C \text{ min}^{-1}$ and held for two hours. Then the temperature was raised to the desired temperature at a ramp rate of $3^\circ C \text{ min}^{-1}$ and held for one hour. The final powder was treated in 0.5 M H_2SO_4 at $80^\circ C$ for 12 h. The leached samples were denoted as Co@NGS-T. For comparison, the non-leached samples were denoted as Co@NGS-T-NL, where T represents the pyrolysis temperature, and NL means "non-leached". In addition, to correlate the Co content with the catalytic activity, Co@NGS-800-NL was

further treated with 10 M H_2SO_4 at $80^\circ C$ for 36 h and the obtained sample was denoted as Co@NGS-800- H^+ . For comparison, we also prepared carbon supported Co sample (denoted as Co@C) and N-doped graphene catalyst (denoted as NGS) by using mixed precursors without melamine and metal source, respectively. Co/AC and Co/NAC were also prepared via a post-deposition method by using $Co(NO_3)_2 \cdot 6H_2O$ as the metal source and N-doped carbon as the support. The Co/AC and Co/NAC were reduced under high-purity H_2 atmosphere at $400^\circ C$ for 2 h to ensure Co in metallic state.

2.2. Catalyst characterizations

X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250Xi Spectrometer with a monochromatic X-ray source. All of the binding energies were calibrated by using the adventitious carbon ($C1s = 284.6 \text{ eV}$) as a reference. Powder X-ray diffraction (XRD) analyses of the patterns were recorded on a PANalytical X-ray diffractometer with a $Cu K\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation source. N_2 adsorption-desorption experiments were carried out on an ASAP 2020 Micromeritics Instrument at 77 K, each sample was degassed at $180^\circ C$ for 240 min before the measurement. The specific surface area was calculated from the adsorption data using the Brunauer-Emmett-Teller (BET) method and the pore size distributions were obtained from the desorption branch isotherms using the BJH (Barrett-Joyner-Halenda) method [53,54]. The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) was performed on a FEI JEM-1200-EX electron microscope operated at an acceleration voltage of 200 kV. TEM samples were prepared by placing a drop of catalyst dispersion onto a holey carbon film on a Cu grid. Raman spectra were performed at room temperature using a LabRam HR800 spectrometer (HORIBA Jobin Yvon) equipped with 532 nm excitation lasers at room temperature. Elemental analyses were performed by Perkin-Elmer OPTIMA 3300 DV Inductively coupled plasma atomic emission spectroscopy (ICP-AES). Temperature-programmed-desorption (TPD) measurements were carried out using a XIANQUAN tp-5080 instrument (Tianjin, China). The samples were pretreated at $600^\circ C$ under a flow of 10% v/v H_2/N_2 (40 mL min^{-1}) for 2 h and then cooled to room temperature under the same flow. After a saturated adsorption for 0.5 h, the samples were purged with pure He until the baseline was steady. Then the samples were heated from room temperature to $1000^\circ C$ at a rate of $10^\circ C \text{ min}^{-1}$, and the desorption curves was recorded during the process. Fourier transformed infrared spectra (FTIR) were measured on a Thermo Scientific Nicolet 870 Microscope. The scanning scope is $500\text{--}4000 \text{ cm}^{-1}$ and the spectra were acquired in transmission mode. Electron paramagnetic resonance (EPR) tests were performed using Bruker A300-9.5/12, with the following parameters: center field: 3362.000 G, microwave frequency: 9.450 GHz, and power: 24.689 mW.

2.3. Catalytic tests

Catalytic tests were carried out in a 50-mL Schlenk glass tube with a magnetic stirring bar. In a typical reaction, a mixture of 1,2,3,4-tetrahydroquinoline (1 mmol, 133 mg), catalyst (2.5 mol% Co, on a basis of the final Co content detected by ICP-AES), internal standard *n*-dodecane (80 mg), K_2CO_3 (1 mmol, 138 mg) and 2 mL methanol were added into a test tube. The tube was sealed and purged with O_2 three times before it was finally pressurized to 0.1 MPa. Subsequently, the reaction mixture was vigorously stirred at $80^\circ C$ for the specific time. After cooled to room temperature, excess O_2 was carefully released and then the catalyst was collected via magnetic separation. Finally, the resultant product mixtures were determined by gas chromatography-mass spectrometry (GC-MS, Agilent 7890A/5975C) and analyzed on a GC (Agilent

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