



# Ruthenium nanoparticles loaded on functionalized graphene for liquid-phase hydrogenation of fine chemicals: Comparison with carbon nanotube



Yong Wang, Zeming Rong\*, Yue Wang, Jingping Qu

State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, PR China

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## ABSTRACT

A facile way to prepare graphene-supported Ru catalysts was developed here. For the first time, functionalized graphene obtained from thermal exfoliation of graphite oxide at low temperature (200 °C) under air atmosphere was used to support Ru nanoparticles (2.3 nm) with the simple method of incipient wetness impregnation. Heat treating at 700 °C in N<sub>2</sub> flow did not change the mean size but made Ru nanoparticles electron rich. The electronic effect had a great influence on the activities of benzene and *p*-chloronitrobenzene hydrogenation but little influence on the activity of cinnamaldehyde hydrogenation and its selectivity of C=O bond. A geometric effect benefited from the distinctive preparation method was supposed to be another factor accounting for these catalytic phenomena. Comparing with CNTs-supported Ru catalysts obtained from a similar method, we can see clearly that graphene with the two-dimensional flexible graphitic surface could modulate the electronic and geometric structures of Ru catalysts in an unusual way. Additionally, this work provides the possibility of producing graphene-based precious metal catalysts on a large scale.

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## 1. Introduction

Catalytic hydrogenation is the most useful method for the reduction of fine chemicals and has found numerous applications in research laboratories and industrial processes [1]. Precious metals are widely employed as active components due to their remarkable high performance on the activation of unsaturated groups and H<sub>2</sub>. They are usually loaded on support to reduce cost, which can simultaneously modulate the electronic or geometric structures of metal catalysts. Carbon materials have many significant advantages to be served as supports for precious metal catalysts, such as resistance to acid or basic media, easy recovery of precious metals, and possibility to control the porosity and surface chemistry [2]. Graphene, a single atomic layer of sp<sup>2</sup> hybridized carbon, is a new member among them [3]. It is considered to be an ideal two-dimensional catalyst support due to its excellent electrical and thermal conductivity, mechanical strength, and high surface area [4].

Actually, Ru [5–12], Rh [11–13], Pd [14–18], Pt [19–24], Ag [25], and Au [26–29] nanoparticles (NPs) have been loaded on graphene as high-performance catalysts for various hydrogenation reactions,

and graphene exhibited many advantages over than other carbon materials, such as carbon black [21], active carbon [15], mesoporous carbon [10], and multi-walled carbon nanotubes (CNTs) [20]. First-principles-based calculations were performed by Liu et al. [10] to investigate the interaction between Ru and carbon substrate. It was found that the C-sp orbitals of defective graphene with sp<sup>2</sup> dangling bonds hybridize more strongly with the Ru-dsp orbitals than that of amorphous carbon with both sp<sup>3</sup> and sp<sup>2</sup> dangling bonds do. Thus, the catalytic activity can be affected by modulating the electronic structure of Ru NPs. This hybridization would result in electron transfer from Ru to graphene and would further impede the oxidation of Ru [30], which can also be seen from other metals. For example, Pd [15] and Pt [21] NPs loaded on graphene possess the higher fraction of zero-valent metal compared with the corresponding ones loaded on active carbon and carbon black, respectively; thus, they showed higher performance on hydrogenation reactions. However, for CNTs with the similar sp<sup>2</sup> dangling bonds at the defects as graphene, little research was involved in the comparative study of their modification on metal catalyst for hydrogenation. Previously, we found both the activity and the selectivity to cinnamyl alcohol (COL) of cinnamaldehyde (CAL) hydrogenation are higher for the graphene-supported Pt catalyst than the CNTs-supported one, and the easier adsorption of CAL on graphene was supposed to be responsible for this [20], while some intrinsic reasons should be further revealed. Recently,

\* Corresponding author.

E-mail address: [zeming@dlut.edu.cn](mailto:zeming@dlut.edu.cn) (Z. Rong).

we further studied the catalyst system of CNTs-supported Ru in the perspective of confinement effect [31], and various factors influencing the selectivity of CAL hydrogenation were discussed and clarified by the combination of multiple characterizations and another two model reactions testing. Based on those acquired information, we would like to investigate what and how graphene affects on Ru catalyst for hydrogenation.

First thing is the preparation of graphene-supported Ru catalyst. In order to make the catalyst comparable with the CNTs-supported Ru catalyst, an identical H<sub>2</sub> reduction at high temperature is preferred. As surveyed on above literatures, most of the methods were based on liquid-phase reduction which needs sophisticated control on multiple parameters, particularly the concentrations of metal precursors, reductants, stabilizers, and other additives. Only three samples of graphene-supported Pd [18] and Ru [7,8] catalysts were prepared by gas-phase synthesis due to its simpler control. But the graphene in the three samples was all synthesized by mechanical exfoliation of natural graphite which is time-consuming and low-yield, and it even needed to be further functionalized with oxygenated surface groups (OSGs) for immobilizing metal NPs. In this work, a more facile way was developed. Thermal exfoliation of graphite oxide (GO) under mild conditions was adopted to prepare functionalized graphene as support, and then a simple method of incipient wetness impregnation (IWI) was used to disperse metal precursors on this thermally exfoliated graphite oxide (TEGO). After a simple reduction in H<sub>2</sub> flow, Ru NPs with a mean size around 2.3 nm can be firmly loaded on TEGO.

On the basis of our previous works [20,31–34], hydrogenation of benzene, *p*-chloronitrobenzene (*p*-CNB), and CAL was chosen as model reactions to evaluate the nature of graphene-supported Ru catalysts. Heat treating on catalysts was crucial for this investigation. Through comparing with the performance of Ru catalysts loaded on CNTs, we found the peculiarity of graphene to modulate the electronic and geometric structures of Ru catalysts, which should be derived from its unique two-dimensional flexible structure and the rarely used gas-phase synthesis method. Our work also suggested that graphene should be a nice alternative to CNTs as support for metal catalysts, and this facile way could be a general path for the preparation of graphene-based metal or metal oxide catalysts with some unexpected properties at low cost and large scale.

## 2. Experimental

### 2.1. Support preparation

Graphite powder (purity >98%, Tianjin Damao Chemical Reagent Factory) was oxidized to prepare GO by an improved synthesis method [35]. Then, GO was placed in a U-type tube. After purging with a specific gas (Air, N<sub>2</sub>, or H<sub>2</sub>) for 10 min at room temperature, a rapid heating (~200 °C/min) was performed to exfoliate the GO. The explosive expansion occurred within 1 min in the range of 150 °C to 180 °C, which is lower than the decomposition temperature of OSGs (~200 °C, Fig. S5) due to the existence of diethyl ether and ethyl alcohol in interlayers, and the color turned from yellowish-brown to black. Once the expansion stopped, TEGO was taken out and heated at 110 °C for 11 h in a drying oven to remove some adsorbates, and then stored in an airtight desiccator for use. The samples obtained under different treating ambience are labeled as TEGO(a), TEGO(n), and TEGO(h) corresponding to air, N<sub>2</sub>, and H<sub>2</sub>, respectively. The yield for each sample is around 40%.

### 2.2. Catalyst preparation

The TEGO-supported Ru catalysts were prepared by the method of IWI with an acetone solution of RuCl<sub>3</sub>·3H<sub>2</sub>O (Ru containing

37 ± 0.3 wt.%, Heraeus). The needed volume of solution is as large as 40 ml per 1 g of TEGO. The Ru loading is fixed at 4 wt.% and confirmed by the analysis results of inductively coupled plasma optical emission spectrometry (ICP-OES) and X-ray photoelectron spectroscopy (XPS). After impregnation the solid was dried at room temperature overnight and heated at 110 °C for 11 h and finally reduced at 400 °C for 4 h in H<sub>2</sub> flow. The catalysts are denoted as Ru/TEGO(a), Ru/TEGO(n), and Ru/TEGO(h), and the Ru/TEGO(a) sample was further treated at 700 °C for 2 h in N<sub>2</sub> flow to obtain Ru/TEGO(a)-ht for comparison.

### 2.3. Characterization techniques

Scanning electron microscope (SEM) images were acquired on a Nova Nano SEM 450 microscope with a field-emission gun.

Transmission electron microscope (TEM) images were acquired on a FEI Tecnai G2 microscope operated at 200 kV. Approximately 300–400 Ru NPs were randomly counted to determine the particle size distribution. The mean diameter in each catalyst was calculated from the following formula:  $d = (\sum n_i d_i) / n_i$ . Some samples were tilted from 0° to 30° under the observation of high-resolution TEM (HRTEM), and the projected area of ellipse-like Ru NPs was calculated from the lengths of long axial and short axial measured in the HRTEM image.

X-ray diffraction (XRD) patterns of all samples were obtained with a RIGAKU D/MAX 2400 diffractometer using Cu K $\alpha$  radiation (40 kV, 100 mA) in the range of 5–85°.

N<sub>2</sub> adsorption–desorption isotherms were measured with a 3H-2000PS1 surface area porosity analyzer (Beijing Beishide Instrument S&T Co., Ltd.). The specific surface area (SSA) was calculated using the multipoint Brunauer–Emmett–Teller (BET) method.

Temperature programmed reduction (TPR) and temperature programmed desorption (TPD) were performed on a TP-5076 Adsorption Instrument (Tianjin Xianquan Industry and Trading Co., Ltd.): A sample of 5 mg (due to the too small density of TEGO) was heated from room temperature to 900 °C at a rate of 10 °C min<sup>-1</sup> (1.5 °C min<sup>-1</sup> for GO to avoid the explosive expansion) in a flow of 5% H<sub>2</sub>/Ar (30 ml min<sup>-1</sup>, STP) for TPR or high-purity Ar (99.999%) for TRD. It should be noted that, the as-dried samples (before H<sub>2</sub> reduction during preparation processes) were used to do the TPR testing.

Infrared (IR) spectrum was collected on a Thermo Scientific NICOLET 6700 FT-IR spectrometer in the range of 400–4000 cm<sup>-1</sup>.

Raman spectrum was collected on a Thermo Scientific DXR Raman microscope using a 532 nm laser source and a power of 0.1 mW to avoid the damage on the sample.

Elemental analysis (EA) was taken on an Elementar Vario EL III element analyzer to determine the carbon contents of GO and TEGO samples.

ICP-OES (Perkin Elmer, Optima 2000DV) was used to determine the actual Ru loading of all samples with a pretreatment of microwave digestion in mixed acid.

XPS measurement of each sample (protected by N<sub>2</sub>) was carried out on a high-resolution angle-resolved ESCALAB 250 Xi spectrometer using monochromatic Al K $\alpha$  radiation (1486.6 eV). The binding energies were calibrated based on the graphite C 1s peak at 284.5 eV. The CASA XPS program with a Gaussian–Lorentzian mix function and Shirley background subtraction was employed to deconvolute the XPS spectra.

### 2.4. Catalyst testing

The liquid-phase hydrogenation of benzene, *p*-CNB, and CAL was carried out in 70-ml autoclave reactor. Each catalyst (10 mg) was re-reduced in solvent (20 ml, tetrahydrofuran for benzene, methanol for *p*-CNB, and isopropanol for CAL) under reaction con-

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