



Ruthenium nanoparticles loaded on multiwalled carbon nanotubes for liquid-phase hydrogenation of fine chemicals: An exploration of confinement effect



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ABSTRACT

For the purpose as stated in title, three Ru catalysts were prepared with the same treated carbon nanotubes. One has most of Ru nanoparticles confined inside the channels, and the other two have most of Ru nanoparticles outside through different preparation methods. Heat treating was performed to obtain another three catalysts. Characterization by X-ray photoelectron spectroscopy indicated that heat treating made Ru nanoparticles electron rich. Hydrogenation of benzene, *p*-chloronitrobenzene, and cinnamaldehyde was chosen as model reactions to evaluate all these catalysts. Electronic effect plays an important role in catalytic performance. The electron-rich Ru would be favorable for *p*-chloronitrobenzene hydrogenation, but unfavorable for benzene hydrogenation. For cinnamaldehyde hydrogenation, the electron-rich Ru would be favorable for adsorption of C=O bond rather than C=C bond and thus promoted the selectivity to cinnamyl alcohol. A confinement effect induced by the electronic effect has different influences on these substrates, and it can be enhanced by heat treating for all the reactions. Finally, we drew a correlation of electronic structures between catalysts and substrates accounting for these phenomena.

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1. Introduction

Since 1994, carbon nanotubes (CNTs) were first used as supports for metal catalysts [1], and more and more attentions have been attracted in the field of catalysis during the last two decades [2]. Recently, Bao's group reported the effects of confinement inside CNTs (with an inner diameter smaller than 10 nm) on catalysis [3], mainly including four aspects: electronic interaction of metals with CNTs, space restriction on metal nanoparticles (NPs), enrichment of reactants inside CNTs, and diffusion inside the channels. Mostly, the confinement effects of CNTs were investigated in gas–solid catalytic reactions, such as syngas conversion to ethanol [4], Fischer–Tropsch synthesis [5–8], ammonia synthesis [9] and decomposition [10], CO preferential oxidation [11,12], methane dry reforming [13], and various hydrogenation [14–16] (benzene, methyl acetate, and butadiene) or oxidation [17,18] (ethylbenzene and benzyl alcohol) reactions. Fewer researches were involved in gas–liquid–solid three-phase reactions except for propylene epoxidation and benzene hydroxylation over double-walled

CNTs-based catalysts [19,20] and asymmetric hydrogenation of α -ketoesters and α , β -unsaturated carboxylic acid [21–23]. Some researchers induced Au [16], Pt [24], or PtRu alloy [25] NPs into CNTs for cinnamaldehyde (CAL) hydrogenation and obtained higher selectivities to hydrocinnamaldehyde (HCAL) on gold catalysts or to cinnamyl alcohol (COL) on the other two than on the corresponding ones with metals loaded outside CNTs. However, these interpretations on differences are ambiguous because of their inconformity of metal NPs or different surface chemistry of CNTs between the inside and the outside one.

Until now, it is still uncertain whether there is a confinement effect on liquid-phase hydrogenation of fine chemicals over CNTs-based metal catalysts. If indeed so, exact influences on different substrates should be further intensively studied. As we know, this kind of catalytic reaction is widely applied to laboratorial research and industrial processes [26]. Our group has done several related works on it, such as hydrogenation of aromatics [27–31], nitro-aromatics [32–34] and α , β -unsaturated aldehyde [35–37]. On this basis, we try to explore the confinement effects of CNTs on these reactions for developing high-performance hydrogenation catalysts instructively.

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In order to make the results comparable and reliable, we used the same treated CNTs with an inner diameter of 4–10 nm to prepare catalysts which have different locations of Ru NPs. Ru was employed as the active metal due to its versatility for hydrogenation of multiple unsaturated compounds. Based on our works, benzene, *p*-chloronitrobenzene (*p*-CNB), and CAL were chosen as model substrates to evaluate the nature of catalysts. Preparation methods of catalysts and heat-treating processes on them are crucial for this exploration, so strict characterizations should be adopted to avoid some faulty judgments. Then, a convincing conclusion can be reached, that is, a confinement effect derived from electronic effect indeed exists in liquid-phase hydrogenation, but has different influences on these substrates. This made us believe that there is a possible relationship of electronic structures between Ru and unsaturated groups.

2. Experimental

2.1. Catalyst preparation

Pristine CNTs (P-CNTs, purity >95%, outer diameter 10–20 nm and inner diameter 4–10 nm) were purchased from Chengdu Organic Chemicals. First, P-CNTs were treated by refluxing in concentrated HNO₃ (68 wt.%) at 140 °C for 14 h. Then, the mixture was dialyzed to be neutral and freeze-dried to obtain the catalyst support for use. These processing methods made CNTs easily redisperse in polar solvent, which could be attributed not only to the introduction of oxygenated surface groups (OSGs) but also to its looser macroscopic structure. The oxidized CNTs (O-CNTs) were obtained with about 60% yield. According to the analysis results of inductively coupled plasma-optical emission spectrometry (ICP-OES) and X-ray photoelectron spectroscopy (XPS), there is no nickel (the catalyst for producing P-CNTs) residual in O-CNTs.

Catalysts were prepared according to the procedures described in the literature [38] with some modifications. For the preparation of Ru confined inside the channels of O-CNTs (denoted as Ru@CNTs), RuCl₃·3H₂O (Ru containing 37 ± 0.3 wt.%, Heraeus) was dissolved in acetone, then adding O-CNTs. After O-CNTs were dispersed to form a homogeneous solution promoted by ultrasound, acetone was evaporated at room temperature under continuous stirring. The resulting solid was heated at 1 °C/min to 110 °C in air, held at 110 °C for 11 h, and then reduced at 400 °C for 4 h in H₂ flow. For the preparation of Ru loaded outside CNTs, a key step is the protection of inner channels by inducing a medium as temporary blocker during impregnation with a solution containing metal salts. Here, we used two kinds of blockers, acetone and xylene. The first step is the formation of well-dispersed O-CNTs in acetone or xylene separately accompanying with ultrasound. In the acetone one, once an acetone solution of RuCl₃·3H₂O was added into the O-CNTs suspension, the mixture was heated at 60 °C under continuous stirring for evaporating acetone within 1 h. Subsequently, the solid was subjected to the same drying and reduction treatment as above, and this sample is labeled as Ru/CNTs(a). For the slurry of O-CNTs and xylene, after adding an aqueous solution of RuCl₃·3H₂O, a solution of NH₄HCO₃ dissolved in NH₃·H₂O (26–28 wt.%) was also added in order to transfer O-CNTs into the aqueous phase. Then, the same evaporation, drying, and reduction procedures as Ru/CNTs(a) were adopted to obtain Ru/CNTs(x). The nominal loading of each sample is 4 wt.% in this study and confirmed by ICP-OES.

In order to investigate the thermal stability of Ru NPs and to remove most of the OSGs, the three above-mentioned freshly reduced catalysts were treated at 700 °C for 2 h in N₂ flow. Their mass losses are negligible after heat treating. The resulting catalysts are named as Ru@CNTs-ht, Ru/CNTs(a)-ht, and

Ru/CNTs(x)-ht. Their actual loadings are also around 4 wt.% as detected by ICP-OES.

2.2. Catalyst characterization

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

Transmission electron microscope (TEM) images were acquired on a FEI Tecnai G2 microscope with a single tilt holder operated at 200 kV. Approximately 400–500 Ru NPs were randomly counted to determine the particle size distribution. The mean diameter in each catalyst was calculated from the following formula: $d = (\sum n_i d_i) / n_i$.

X-ray diffraction (XRD) patterns of all samples were obtained with a RIGAKU D/MAX 2400 diffractometer using Cu K α radiation (40 kV, 100 mA) in the range of 20° to 80°.

N₂ 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. The pore size distribution (PSD) was calculated by the Barrett–Joyner–Halenda (BJH) method from the adsorption branch of isotherms.

H₂ temperature programmed reduction (TPR) was performed on a TP-5076 Adsorption Instrument (Tianjin Xianquan Industry and Trading Co., Ltd.): A sample of 50 mg was heated from room temperature to 800 °C at a rate of 10 °C min⁻¹ in a flow of 5% H₂/Ar (40 ml min⁻¹, STP).

XPS measurements of pre-reduced catalysts were carried out on a high-resolution angle-resolved ESCALAB 250 Xi spectrometer using monochromatic Al K α 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.

2.3. Catalyst testing

The liquid-phase hydrogenation of benzene, *p*-CNB, and CAL was carried out in 70-ml autoclave reactors. Typically, 2 mmol of each substrate, 10 mg of each pre-reduced catalyst (>180 mesh), and 20 mL solvent (tetrahydrofuran for benzene, methanol for *p*-CNB, and isopropanol for CAL) were added into a reactor. The autoclave was sealed and replaced by N₂ for several times before being placed in a water bath. When the inner temperature reached 70 °C, H₂ was filled into the system with 1 MPa, and then the time was recorded once agitated (ca. 700 rpm). Samples were extracted through a micro-syringe at intervals and analyzed using Agilent 6890 N gas chromatograph with FID detector (HP-INNOWAX capillary column for benzene and HP-5 capillary column for *p*-CNB and CAL). Experimental data were obtained and verified by repeating each reaction two or three times, which showed reproducible results.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. TEM

TEM technique is a direct method to observe the morphology of CNTs and to verify the location and size of Ru NPs. Fig. 1 presents the TEM images of P-CNTs and O-CNTs. It can be seen that the tips of P-CNTs are closed and the residual nickel catalysts are confined inside the channels. After oxidation with acid, CNTs were

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