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Short Communication

Microwave-assisted green synthesis of uniform Ru nanoparticles supported on non-functional carbon nanotubes for cinnamaldehyde hydrogenation

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ABSTRACT

Uniformly dispersed ruthenium nanoparticles supported on non-functional carbon nanotubes (CNT) have been successfully synthesized by using a facile and solvent-free microwave-assisted thermolytic method with dodecacarbonyltriruthenium as the precursor. The results show that 2–4 nm sized spheres of Ru nanoparticles were uniformly dispersed and supported on non-functional CNT by several minutes' exposure to microwave irradiation without solvent. The Ru/CNT catalysts show the desired conversion of about 80% and selectivity to hydrocinnamaldehyde of about 72% in the selective hydrogenation of cinnamaldehyde, where the catalytic performance has been found to depend on both the Ru loading and the surface properties of CNT.

1. Introduction

Carbon nanotubes (CNT) supported metal catalysts have shown superior catalytic activity and selectivity in some chemical reactions, such as ammonia decomposition/synthesis [1,2], Fischer–Tropsch synthesis [3], CO oxidation [4], and fine chemical synthesis [5]. This has been attributed to the unique structure of CNT, together with the interaction between CNT and metal nanoparticles [6–10]. Various chemical and physical techniques have been developed to synthesize highly dispersed metal nanoparticles on the oxidized CNT which was generally obtained by nitric acid oxidation method. However, controlled synthesis of highly dispersed metal nanoparticles on non-functional CNT still remains a big challenge in catalysis and nanotechnology.

Supported Ru catalysts have been extensively studied and applied in various fields. However, various conventional preparation methods for Ru-based catalysts required modify supports, and use solvents in the process, which generated a lot of contaminants. Most importantly, there are difficulties in controlling preparation steps and in obtaining highly dispersed metal particles due to the effects of the solvent on the adsorption and drying process. Conventional chemical vapor deposition has been shown to be a powerful method for generating dispersed Ru catalysts in a controlled and reproducible manner [11–13]. However, it generally takes on the order of tens of hours due to a multistage temperature program under high-vacuum conditions.

Microwave techniques have been successfully used in syntheses and have been confirmed to be more environmental friendly than the conventional processes [14]. Recently, we have successfully prepared non-functional CNT-supported nanostructured carbides by a microwave-assisted thermolytic method [15], which is able to quickly and simply generate supported carbide catalysts. Meanwhile, we had investigated the effect of Pd on cinnamaldehyde hydrogenation over functional CNT-supported Ru catalysts, which were prepared by conventional incipient wetness impregnation technique [16]. Herein, we extend the solvent-free route to prepare uniformly dispersed Ru nanoparticles supported on non-functional CNT. To the best of our knowledge, this is a novel report on synthesis of uniform Ru nanoparticles supported on non-functional CNT by the facile and solvent-free microwave thermolytic route, which is of great potential in the controlled synthesis of non-functional carbon material supported catalysts.

2. Experimental

2.1. Preparation of Ru/CNT and Ru/FCNT

Ru nanoparticles on non-functional CNT (surface area: 103 m^2/g, pore volume: 0.73 cm^3/g, pore diameter: 2.7 nm) catalysts (Ru/CNT) were prepared via a one-step microwave-assisted thermolytic process

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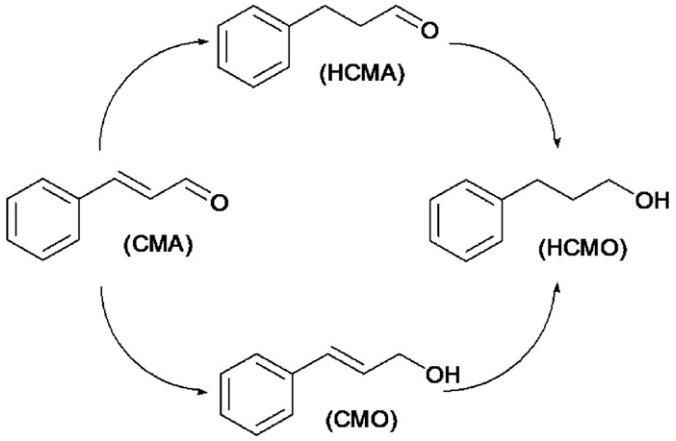

Scheme 1. Hydrogenation pathways of CMA.

with dodecacarbonyltriruthenium [$Ru_3(CO)_{12}$] as the precursor. Typically, CNT and $Ru_3(CO)_{12}$ were put in an agate mortar and mixed for 20 min. The homogeneous precursor mixture was put in a quartz-tube reactor and fluidized with argon for 2 h at room temperature in order to keep the reaction under an inert atmosphere. Then, the reactor was placed in a domestic microwave oven operating at 2.45 GHz with a power of 800 W. Finally, the resulting products were cooled to room temperature under argon. The level of Ru loading depends on the amount of the precursor, 5 wt.%, 10 wt.% and 15 wt.% (0.0059 mol/mol, 0.0119 mol/mol and 0.0178 mol/mol), respectively.

For comparison, functionalized CNT (FCNT) (surface area: 138 m^2/g, pore volume: 0.89 cm^3/g, pore diameter: 3.5 nm) was obtained by the following process. 3.0 g CNT was dispersed in 300 mL solution of distilled water, nitric acid and sulfuric acid (volume ratio 1:1:3), in order to introduce oxygen-containing groups to the outer surface of CNT. The obtained solution was ultrasonically agitated for 5 min and then heated to 120 °C for 4 h. Ru nanoparticles on FCNT (Ru/FCNT) catalysts have also been prepared via microwave-assisted thermolytic method.

2.2. Catalyst characterization and measurement

Pristine CNT and Ru/CNT samples with different microwave irradiation time were dissolved in n-octane for 24 h. The supernatant liquor was examined using Fourier transform infrared spectroscopy (FT-IR) in order to investigate the thermal decomposition time of $Ru_3(CO)_{12}$.

X-ray diffraction (XRD) analyses of the samples were carried out using a Rigaku D/Max-RB diffractometer with Cu *K*α monochromatized radiation source (λ = 1.54178 Å), operated at 40 kV and 100 mA.

High-resolution transmission electron microscopy (HRTEM) was performed using a Philips CM200 FEG TEM. The composition distribution analysis with a resolution of a few nanometers was performed in the STEM mode in combination with energy dispersive X-ray spectroscopy (EDX) using a DX4 analyzer system (EDAX) in the same microscope.

The catalytic properties of this material for cinnamaldehyde (CMA) hydrogenation have been tested. As one of α, β-unsaturated aldehydes, CMA is of particular importance because its partial hydrogenation into either cinnamyl alcohol (CMO) or hydrocinnamaldehyde (HCMA) is a critical step for the industrial production of many fine chemicals, especially perfumes and pharmaceutical intermediates. It is well established that the hydrogenation of CMA which is a structure sensitive reaction occurs through the classical pathway shown in Scheme 1. The

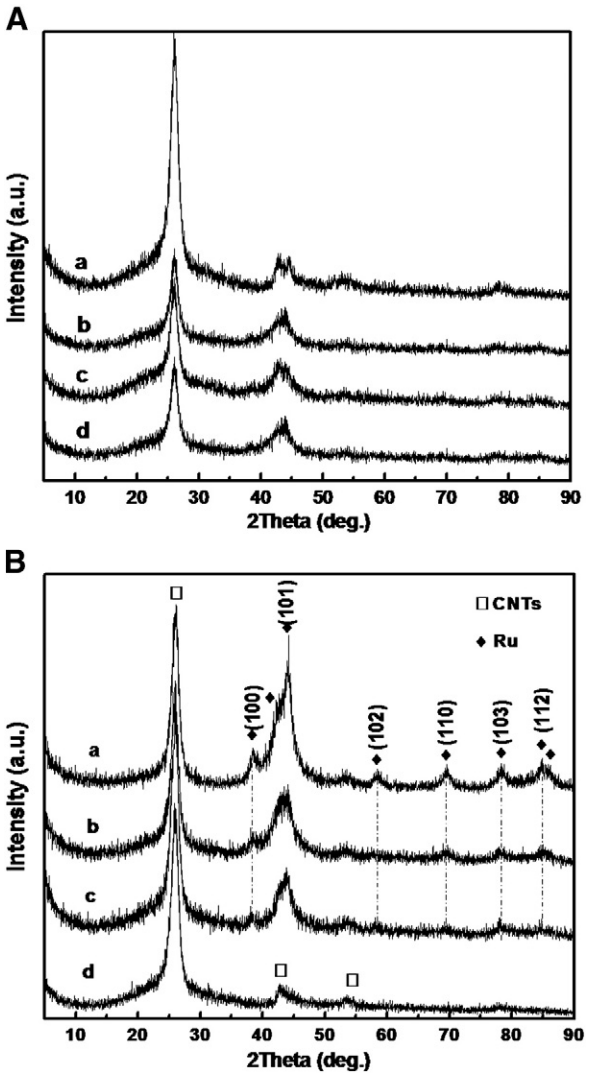

Fig. 1. (A) XRD patterns of CNT (a), 15.0 wt.% Ru/CNT (b), 10.0 wt.% Ru/CNT (c), 5.0 wt.% Ru/CNT (d). (B) XRD patterns of 15.0 wt.% Ru/FCNT (a), 10.0 wt.% Ru/FCNT (b), 5.0 wt.% Ru/FCNT (c), FCNT (d).

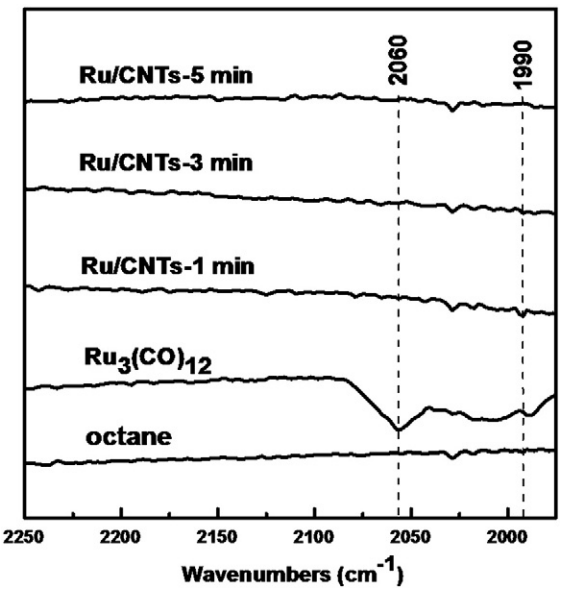

Fig. 2. FT-IR spectra of the extract liquor by octane from the Ru/CNT samples with microwave irradiation from 1 to 5 min.