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Article

Confinement effect of carbon nanotubes on the product distribution of selective hydrogenation of cinnamaldehyde

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ABSTRACT

The catalytic activity of metal catalysts can be modulated by confinement within the channels of carbon nanotubes (CNTs). Here, we show that the product distribution of cinnamaldehyde hydrogenation can be modified by confinement of Ru nanoparticles in CNTs. A catalyst composed of Ru nanoparticles dispersed on the exterior walls of CNTs gave hydrocinnamaldehyde as product. In contrast, confinement of the Ru nanoparticles within CNT channels facilitated hydrogenation of C=O bonds and complete hydrogenation, and both cinnamyl alcohol and hydrocinnamyl alcohol formed in addition to hydrocinnamaldehyde. High-resolution transmission electron microscopy, Raman spectroscopy, hydrogen temperature-programmed reduction, and hydrogen temperature-programmed desorption were used to investigate the characteristics of the catalysts. The results indicate that the different interactions between the confined Ru nanoparticles and the exterior and interior walls of the CNTs, as well as spatial restriction and enrichment within the narrow channels likely play important roles in modulation of the product distribution.

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1. Introduction

Carbon nanotubes (CNTs) are composed of graphene layers with a tubular morphology [1], which distinguishes them from other carbon materials such as activated carbon and carbon nanofibers. The tubular morphology leads to the π electron density shifting from the interior to the exterior surface [2]. Therefore, the nanochannels of CNTs are frequently used as a container and they provide an intriguing confinement environment for catalysis [3,4]. A number of substances and materials have been introduced into the channels of CNTs, and they exhibit different properties and behavior from those in the bulk and on the exterior walls of CNTs [5,6].

It was reported that the interaction of transition metal atoms with CNT walls significantly differs from their interaction with planar graphite layers with regard to the bonding sites, magnetic moments, and charge-transfer directions [7], which could modify their physiochemical properties. For example, reduction of metal nanoparticles such as Fe [6] and Ru [8] is facilitated when they are confined within CNT channels compared with when they are dispersed on the exterior walls of CNTs. Reduction is facilitated more within smaller nanotubes owing to more distorted sp^2 hybridization and hence stronger confinement effects [5]. This could affect the catalytic activity,

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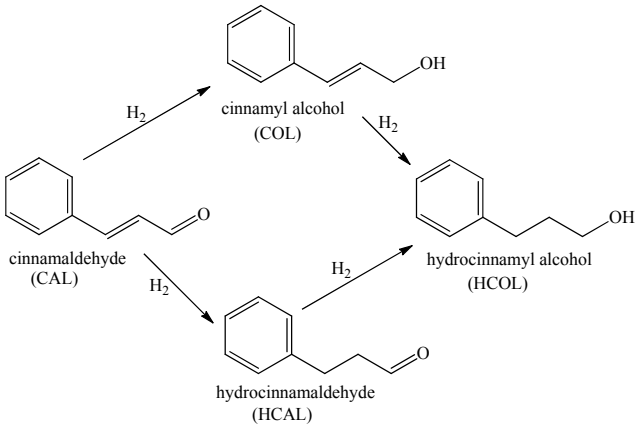
particularly for reactions involving reduction and oxidation. For example, the CNT-confined Fe catalyst exhibits higher activity in Fischer-Tropsch synthesis [9,10]. The CNT-confined RhMn catalyst also exhibits higher activity than nanoparticles dispersed on the exterior walls of CNTs in C_2 oxygenate synthesis [11]. Confinement within the CNT channels also provides protection for metallic nanoparticles [12] and their oxidation is retarded. This allows generation of highly active and durable oxidation catalysts. For instance, CNT-confined Pt nanoclusters exhibit high activity and stability for oxidation of methylbenzene compared with conventional Al_2O_3, zeolite, and high surface area activated carbon supported Pt catalysts [13]. Although many studies have reported different activities by introducing metal nanoparticles into CNT channels, few studies have discussed the effect on the product selectivity. Serp and co-workers [14] reported enhanced activity for confined PtRu nanoparticles in selective hydrogenation of cinnamaldehyde (CAL) within CNTs with an average inner diameter as large as 40 nm. They found that the product selectivity was related to the location of the PtRu nanoparticles (inside or outside the CNTs) [14]. We wonder if similar effects are present in smaller nanotubes.

In this study, we chose CNTs with an inner diameter of 1–3 nm and considered selective hydrogenation of CAL as a probe reaction to explore the effect of confinement on the product selectivity. Because CAL contains conjugated C=C and C=O double bonds, CAL hydrogenation could possibly lead to three different products: cinnamyl alcohol (COL), hydrocinnamaldehyde (HCAL), and hydrocinnamyl alcohol (HCOL) (Scheme 1). Therefore, we encapsulated Ru nanoparticles within the channels of CNTs and also deposited them on the outer walls of the same CNTs to investigate how the product distribution is influenced by confinement.

2. Experimental

All the chemicals used in this study were analytical grade and they were not subjected to further treatment.

2.1. Catalyst preparation



Scheme 1. Possible reaction pathways for hydrogenation of CAL.

Raw CNTs were purchased from Chengdu Organic Chemicals and purified in HNO_3 and H_2SO_4 (Tianjin Kermel Chemicals Co., Ltd., China) (volume ratio = 1:3) for 4.5 h at 40–50 °C, followed by thorough washing with deionized water. The CNT aqueous dispersion was then subjected to freeze drying for 84 h. Subsequently, the sample was heated to 1000 °C at a rate of 5 °C/min in Ar atmosphere and kept at this temperature for 4 h.

Volatile bis(2,4-dimethylpentadienyl)ruthenium (99%, Strem Chemicals) was used as the precursor of Ru. The CNTs were evacuated to 10^{-4} Pa for 16 h at 450 °C before exposure to the precursor vapor. The mixture was kept at 120 °C for 48 h to allow diffusion of the precursor into the CNT channels. The catalyst was then reduced in H_2 (60 mL/min) at 230 °C for 3 h. The obtained catalyst is denoted Ru@CNT.

For comparison, Ru was also dispersed on the exterior walls of CNTs by the impregnation method. Bis(2,4-dimethylpentadienyl)ruthenium dissolved in toluene was used. After drying at 60 °C for 12 h, the catalyst was subjected to reduction under the same conditions as those used to produce Ru@CNT. The resulting catalyst is called Ru/CNT.

2.2. Reaction test

Hydrogenation of CAL was performed in a 300-mL Parr high-pressure reactor equipped with a stirrer, a thermocouple, a gas inlet, and a vent. In each experiment, 1 g of CAL (Sinopharm Chemical Reagent Co., Ltd, China), 100 ml of isopropanol (Tianjin Kermel Chemicals Co., Ltd., China), and 10 mg of catalyst were added into the reactor. After the reactor was purged three times with high purity H_2 (99.999%), it was heated to 100 °C. The reactor was then pressurized to 2.0 MPa with H_2. The reaction was performed for 2 h. The products were analyzed by gas chromatography (GC)-mass spectroscopy (MS) and quantified by a gas chromatograph (Agilent 7890 A) equipped with a flame ionization detector and a DB-5 capillary column, and 7000 triple quadrupole MS.

2.3. Catalyst characterization

Transmission electron microscopy (TEM) was performed with an FEI Tecnai F30 microscope operated at an accelerating voltage of 300 kV. The catalyst was well dispersed in ethanol under ultrasonic treatment before the measurements. Energy dispersive X-ray (EDX) analysis of the catalysts was performed using the same instrument.

The Ru loading of the catalysts was measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) on a PerkinElmer ICP-OES 7300DV. The catalysts were first oxidized in air at 600 °C for 2 h and Ru was then dissolved in aqua regia (HNO_3:HCl = 1:3) in a microwave reactor (MARS, CEM Inc.).

Raman spectroscopy was performed with a LabRam I confocal microprobe Raman instrument (Dilor) at an excitation wavelength of 632.8 nm.

H_2-temperature programmed desorption (H_2-TPD) was performed with a Micromeritics Autochem II chemisorption analyzer. The catalyst charge was 8 mg for all tests. Prior to tests, the pre-reduced catalysts were further reduced in situ in

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