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Short communication

Effect of Fe(III) on hydrogenation of citral over Pt supported multiwalled carbon nanotube

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ABSTRACT

Nano-platinum granules were affixed to MWCNTs via a liquid-reduction method. Different methods were utilized to introduce Fe(III) into the Pt/MWCNT catalyst. The influence of Fe(III) on the performance of a selective citral hydrogenation over the Pt/MWCNTs in isopropanol was investigated. Characterization techniques such as XRD, TEM, TPR, XPS and N_2 physisorptions were used. Changes in the absorbance and wavenumber for the C=O bond in the citral were monitored with a high-pressure in situ infrared spectrometer. When 0.25 wt.% Fe(III) was added, the citral conversion remained unchanged, but the selectivity toward the unsaturated alcohols increased from 33.7 to 90.7%.

1. Introduction

Citral (3,7-dimethyl-2,6-octadienal) is an important monoterpenoid aldehyde with pairs of conjugated C=O and C=C bonds in addition to an isolated C=C bond. Compared with other α,β-unsaturated aldehydes, citral has a unique structure that renders hydrogenation reaction complex (Fig. S1). The products generated by hydrogenating the C=O bond, nerol and geraniol (N + G), are two important intermediates with widespread applications in the fine chemical, perfume and pharmaceutical industries [1,2]. However, obtaining unsaturated alcohols is thermodynamically disfavored because the C=C bond has a lower bond energy than the C=O bond [3]. Platinum is able to facilitate the selective hydrogenation of C=O bonds and its use has been closely examined in the hydrogenation reactions of α,β-unsaturated aldehydes [4–6]. Because Pt is expensive, support materials [7–9] and promoters [10–14] are often used to reduce the cost of the catalysts and make them more efficient. Carbon materials are common support materials for catalysts [15–18]. Promoters enhance the catalytic performance of oxide of metals such as Ge [10], Co [11], Sn [12], Fe [13], Ce and Mg [14]. The high promoter-driven selectivity can be attributed to two factors: First, the promoters interact with the catalytic active sites [19,20]. Second, electrons may be transferred from the promoters to noble metals [21]. As reported by Zgolicz [22], the metallic impurities and oxidative groups contained in the MWCNTs influence the particle size of the supported Pt and exert a positive effect on the selectivity for the unsaturated alcohols. Solvent choice also affects the selectivities of the hydrogenation reactions [23,24]. Chatterjee [25] reported that the selectivity for geraniol formation reached 98.8% with a 99.8% conversion during a selective citral hydrogenation using Pt-MCM-41 as a catalyst with supercritical CO_2 as a solvent.

The influence of Fe(III) on the hydrogenation of citral was investigated using Pt/MWCNTs prepared via an impregnation method. A mechanism was proposed for the catalytic hydrogenation of citral.

2. Experimental

2.1. Catalyst preparation

The MWCNTs were pretreated with a mixture of concentrated HNO_3 and H_2SO_4 prior to introducing the functional oxygen-containing groups onto the MWCNT-supported catalyst surfaces.

The Pt/MWCNTs were prepared using a liquid-reduction method [5], and the mass fraction of the loaded platinum was 5 wt.%.

A two-step procedure was utilized to incorporate the Fe(III) into the Pt/MWCNTs. First, the Pt/MWCNTs were impregnated with various quantities of $FeCl_3$ or $Fe(NO_3)_3$ in a solution (pH = 3). Then, the samples were dried at 120 °C for 12 h. The catalysts containing $FeCl_3$ or $Fe(NO_3)_3$ were labeled 5%Pt–y%Fe/MWCNTs-1 and 5%Pt–y%Fe/MWCNTs-2.

To determine if the Fe(III) affected the average size of the platinum granules supported on the MWCNTs, the preparation method for the Pt/MWCNTs was modified. A solution of H_2PtCl_6 and $FeCl_3$ or

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$Fe(NO_3)_3$—not H_2PtCl_6 alone—(pH = 3) diluted with ethylene glycol was dropped into a mixture containing MWCNTs and ethylene glycol. The catalysts obtained were labeled 5%Pt–Fe/MWCNTs-3 and 5%Pt–Fe/MWCNTs-4.

2.2. Characterization of supports and catalysts

The changes in the oxygen-containing groups on the MWCNTs before and after pretreatment were evaluated using a Bruker-Tensor 27 FT-IR spectrometer.

The X-ray diffraction (XRD) was conducted with a Bruker D8 Advance apparatus using Cu Kα radiation (λ = 0.1542 nm) from 20 to 70° operating at 40 kV and 40 mA.

The high-resolution transmission electron microscopy (HRTEM) was performed with a JEM-2100 transmission electron microscope using a 200-kV accelerating voltage. The average particle size and distribution on the support surfaces were calculated by selecting 100 particles from the TEM images.

The BET specific surface areas and the porosities based on the BJH calculation of the desorption branches were measured on a BEL SORP-max (BEL JAPAN, INC.) using N_2 as an adsorbent at the liquid-nitrogen temperature. Prior to measurement, the catalyst sample was completely degassed at 300 °C for 12 h.

The temperature-programmed reduction (TPR) experiments were performed with a Micromeritics Autochem 2920 instrument. First, a 0.05-g sample was loaded into a U-shaped tube and flushed with Ar at 30 mL min^{-1} and 100 °C for 30 min. Next, the flowing gas was switched to 10 vol.% H_2 in Ar while maintaining the 30-mL min^{-1} flow rate; the samples were heated at 10 °C min^{-1} from 100 to 900 °C. The H_2 consumption rate was monitored with a thermal conductivity detector (TCD) that was calibrated using the reduction of CuO as a reference. Finally, the samples were cooled to room temperature.

The X-ray photoelectron spectroscopy (XPS) determinations were carried out on a Thermo Scientific Specs Photoemission Electron Spectrometer equipped with an X-ray source using Al Kα radiation. The pressure of the analysis chamber was maintained below 10^{-9} Pa. The samples were prepared via treatment at 150 °C under 10^{-6} Pa for 12 h. The binding energies (BE) of the signals were referenced to the C_{1s} peak at 284.8 eV. The peak areas and BE values were estimated by fitting the curves with a combination of variably proportioned Lorentzian–Gaussian curves using Thermo AvantageV4.51 and CasaXPS peak-fit software.

2.3. Catalytic performance test

The citral was hydrogenated in a 100-mL SCF-1A-40200 high-pressure stainless steel batch reactor. For each experiment, 1 mL citral,

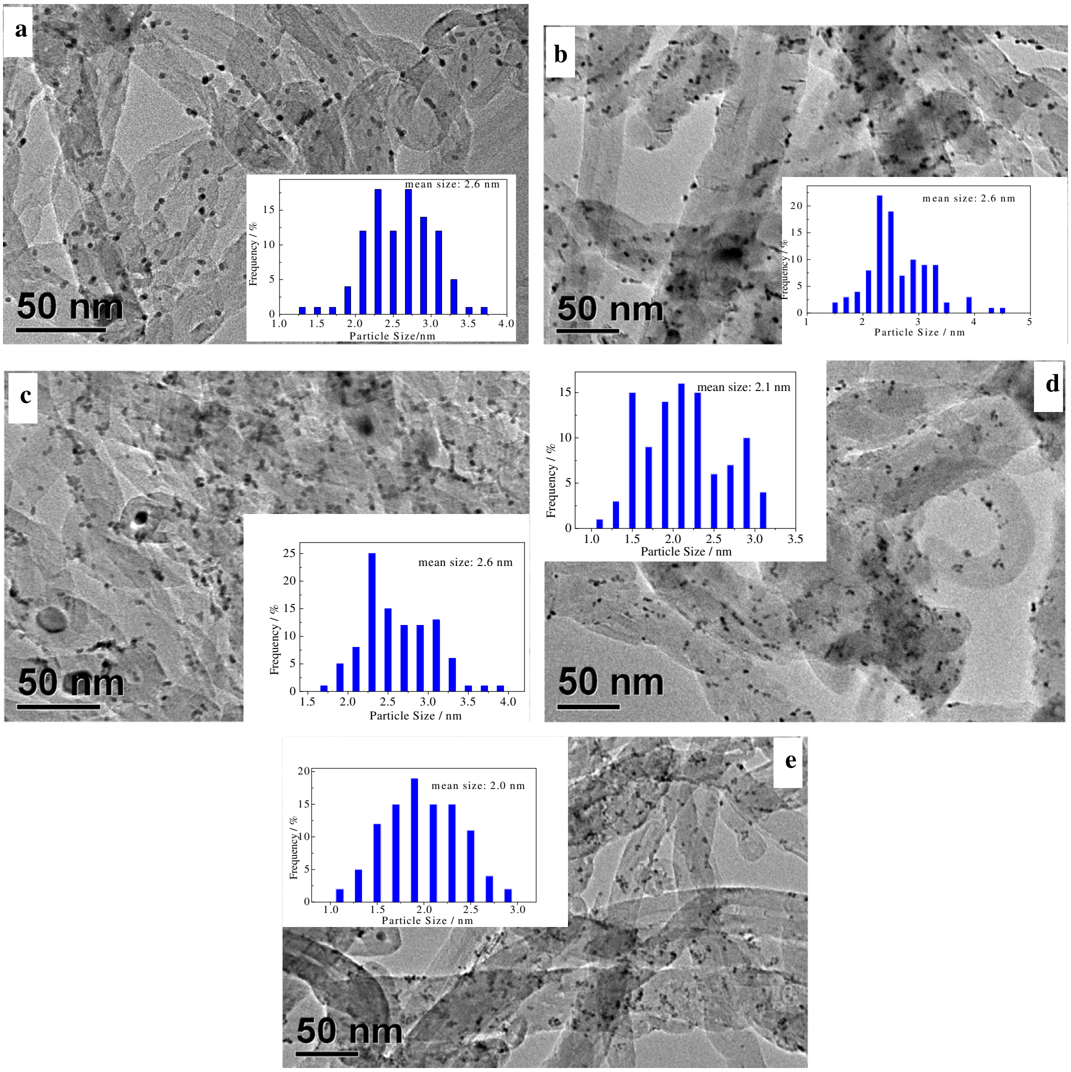

Fig. 1. TEM images and particle size distribution of (a) Pt/MWCNTs; (b) 5%Pt–0.25%Fe/MWCNTs-1; (c) 5%Pt–0.25%Fe/MWCNTs-2; (d) 5%Pt–0.25%Fe/MWCNTs-3 and (e) 5%Pt–0.25%Fe/MWCNTs-4.