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On the role of water in selective hydrogenation of cinnamaldehyde to cinnamyl alcohol on PtFe catalysts

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A series of carbon nanotube (CNT)-supported bimetallic PtFe nanoparticles were synthesized and employed as catalysts for hydrogenation of cinnamaldehyde in pure water. A synergy between water and bimetallic PtFe catalysts has allowed the efficiently selective production of cinnamyl alcohol. With the aid of water, an initial reaction rate of >1200 h^{-1} and a high selectivity of >97%, as well as a good cycling stability, were achieved with a Pt_3Fe/CNT catalyst under mild reaction conditions. Isotopic labeling studies and theoretic calculation results demonstrated that the water-involved hydrogen-exchange pathway occurred with a lower energy barrier, which coexisted with the pathway of direct H_2 dissociation–hydrogenation. This work also suggested that water participated in the catalytic hydrogenation reaction by serving as a hydrogen-exchange bridge.

1. Introduction

The chemoselective hydrogenation of carbonyls in multiunsaturated hydrocarbons, particularly α,β-unsaturated aldehydes and ketones, is a longstanding challenge, since both thermodynamics and kinetics favor the hydrogenation of C=C bonds over C=O bonds [1]. A variety of heterogeneous metallic catalysts have been developed to control the selectively of the reaction by means of alloying, ligand modification, and support optimization [2–10]. The elucidation of geometric and electronic effects on Pt-catalyzed hydrogenation reactions has been attempted. The selectivity of C=O hydrogenation exhibits a strong dependence on the particle size distribution, and the reaction rate is also sensitive to the structure of the Pt nanoparticles [11–13]. The electronic modification of Pt in bimetallic catalysis is an effective strategy for improving catalytic performance. However, the lack of structural control limits further enhancement because the second metal promoter unselectively blocks the Pt active sites. Surface science studies have suggested that direct adsorption of substances on the self-assembled layers of ligands is critical to adjusting the selectivity of the hydrogenation. The arrangement and the orientation of ligands with different chain lengths on the metal surfaces can be used to tune the adsorption geometry of the aldehyde molecule and boost the hydrogenation selectivity [14]. The confinement of metallic Pt or Pd sites in porous metal–organic frameworks also promotes the selectivity of the C=O activation due to steric hindrance of the C=C group as it approaches the active sites [15–17]. In addition, the catalytic performance depends on the manipulation of kinetic parameters (e.g., temperature, pressure, and humidity).

The use of water as a promoter or inhibitor to enhance the activity and selectivity of a catalyst has been demonstrated in many types of reactions, including CO oxidation, methanation, Fischer–Tropsch synthesis, oxygen evolution reactions, and various processes used in organic synthesis [18–23]. The extensive interest in the utilization of water is due to its substantial economic and ecological advantages, as well as its various functions, including solvation effects, carbon removal, and surface reconstruction [24–27]. A reaction pathway followed by a water-mediated Mars–Van Krevelen reaction has been reported in single-atom Pt_1/CeO_2-catalyzed CO oxidation. The intermediate is formed via the interaction of CO and the hydroxyl group from the dissociation of water rather than the direct reaction of CO with the lattice oxygen [28] The Au-catalyzed oxidation of CO has also been enhanced by water-promoted decomposition and conversion of the reaction intermediates [29]. Recently, water-assisted hydrogen diffusion

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across the surface of a metal oxide was directly confirmed by scanning tunneling microscopy (STM) movies, suggesting that catalytic hydrogenation, hydrogen evolution, or the reformation of hydrogen may be accelerated by the presence of water [30]. For instance, it was found that water could take part in the synthesis of C_{2+} alcohols via CO_2 hydrogenation by serving as the hydrogen source [31]. Despite the great progress and valuable insights from the above investigations, the details of the role of water in heterogeneous catalytic hydrogenation processes remain elusive.

For conjugated C=O hydrogenation, the replacement of organic solvent with water has been proven available to improve both the activity and selectivity of Au and Pt catalysts [32,33]. Trace amounts of water have also been shown to enhance the activity on Pt-based catalysts [34]. The orientable chemisorption of the hydrophilic C=O moiety in dipolar water solvent leads to satisfactory selectivity to unsaturated alcohol, according to the kinetic characterizations and adsorption spectra data [35–37]. Furthermore, isotopic-exchange studies have clarified the evolution of catalytically active sites in the pathway of direct hydrogenation by the dissociated H_2 [38,39]. The essential effect of water merits further investigation for selective hydrogenation on heterogeneous catalysts.

In this work, we employ carbon nanotube (CNT)-supported bimetallic PtFe nanoparticles (NPs) to efficiently achieve the chemoselective hydrogenation of cinnamaldehyde (CALD) to cinnamyl alcohol (CALA) with water as the only solvent. We illustrate the role of water as both a hydrogen carrier and a polar solvent by isotopic labeling experiments and theoretical calculations. The coexistence of two reaction pathways for water-mediated hydrogen exchange and dissociative hydrogenation with H_2 is also confirmed.

2. Experimental

2.1. Materials

$Pt(acac)_2$ (97.0%), $Fe(acac)_3$ (97.0%), benzyl alcohol (99.0%), cinnamaldehyde (CALD, 99.0%), phenylpropyl aldehyde (HCALD, 95.0%), cinnamyl alcohol (CALA, 98.0%), 3-phenylpropanol (HCALA, 99.0%), isopropanol (99.9%), n-heptane (98.0%), ethyl acetate (99.8%), cyclohexane (99.5%), and n-hexane (97.0%) were obtained from Sigma-Aldrich (Shanghai, China). HNO_3 (69%) and H_2SO_4 (98%) were provided by Aladdin Reagent Corp. (Shanghai, China). The deuterated solvent D_2O (deuteration degree > 99.8%) was provided by J&K Scientific (Shanghai, China). CO (99.99%), H_2 (99.999%), and Ar (99.999%) were supplied by Nanjing Special Gas Factory (Nanjing, China). Multiwalled carbon nanotubes (purity 97.1%, SBET 241 m^2/g, bulk density 0.05 g/cm^3) were purchased from CNano Technology (Zhenjiang, China).

2.2. Catalyst preparation

CNTs were chosen as the support due to their anchoring effect; the CNT surface with abundant oxygen-containing groups can stabilize the metallic sites via strong interactions. Supported Pt-based nanoparticle (NP) catalysts were prepared according to a modified procedure using benzyl alcohol and carbon monoxide as the co-reductant. The method affords a moderate size distribution of bimetallic NPs that have clean surfaces and do not contain residual organic ligands [40]. Consequently, the effects of the ligand can be ruled out, and the intrinsic activity of the Pt-based catalysts in water is truly reflected in the selective hydrogenation reaction.

2.2.1. Pretreatment of CNT support

The pristine CNTs were pretreated with concentrated HNO_3 at 120 °C for 4 h to remove impurities and to introduce surface oxygen-containing groups to enhance the metal dispersion. The treated CNTs were washed with deionized water several times and dried in a 100 °C oven overnight. The CNT supports were kept dry before use.

2.2.2. Preparation of supported Pt-based catalysts

In a typical synthesis of the supported Pt catalyst, $Pt(acac)_2$ (100 mg, 0.25 mmol), 40 mL of benzyl alcohol and 800 mg of dry support were mixed together at room temperature and then stirred for 10 min. The resulting homogeneous yellow suspension was transferred to a glass pressure vessel. The sealed vessel was charged with 1 bar of CO gas and then heated for 3 h with vigorous stirring in an oil bath that had been preheated to 180 °C. After the vessel was cooled to room temperature, the catalyst was collected by centrifugation and washed several times with ethanol. For supported PtFe catalysts, the same preparation procedure was used and certain amounts of $Pt(acac)_2$ and $Fe(acac)_3$ were employed as metal precursors to obtain the desired Pt/Fe mole ratio. The Pt loadings were fixed at approximately 6.2 wt% for all Pt-based catalysts and confirmed by ICP-OES measurements. The identified real Pt/Fe ratios were 3.3, 8.5, and 58.7 for the Pt_3Fe/CNT, Pt_9Fe/CNT, and $Pt_{60}Fe$/CNT catalyst, respectively.

2.2.3. Acid washing of the Pt_3Fe/CNT catalyst

The reference catalyst was prepared via acid washing. The acid-washed sample without surface Fe species (Pt_3Fe/CNT-H_2SO_4) was obtained as follows: Pt_3Fe/CNT (100 mg) was soaked in 20 mL of H_2SO_4 (0.5 M) for 30 min, and the slurry was filtered and repeatedly washed with deionized water. Based on ICP-OES analysis, approximately 10% of the Fe has been removed, and the estimated Pt/Fe ratio of the Pt_3Fe/CNT-H_2SO_4 sample was 3.7.

2.3. Characterizations

The metal loadings for all catalysts were quantified using inductively coupled plasma optical emission spectrometry (ICP-OES, Avio 200, Perkin Elmer) by measuring the metal concentrations in solutions of the complexes dissolved in 40% hydrofluoric acid. X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Focus diffractometer using Ni-filtered CuKα radiation (λ = 0.154 nm) at 40 kV and 40 mA. Diffraction data were collected between 10° and 70° with a resolution of 0.02° (2θ). Transmission electron microscopy (TEM) images were obtained on a JEOL JEM 3010 instrument operated at 300 kV. Scanning transmission electron microscopy (STEM) and elemental line scanning were carried out on an FEI Tecnai G^2 F20 S-TWIN system operated at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were acquired using a VG Scientific ESCALAB Mark II spectrometer equipped with two ultra-high-vacuum (UHV) chambers. All binding energies were referenced to the C1*s* peak at 284.6 eV.

2.4. Catalytic tests

Selective hydrogenations of CALD were carried out in a stainless steel reactor with a Teflon liner (Parr 4950, controller 4843). A 10-mg portion of catalyst, a certain amount of CALD (200, 400, or 1000 μL), and 10 mL of the solvent were added into the reactor. The molar ratio of CALD to total Pt atoms in the catalysts was approximately 500, 1000, or 2500, based on the CALD sampling amount. The residual air inside the reactor was expelled by pressurizing and releasing hydrogen several times. The reaction was performed at 60 °C under 20 bar of hydrogen. The stirring speed was set at 700 rpm for all the experiments in this study to eliminate the external mass transfer limitation. The equivalents of CALD, hydrogen pressure, and reaction temperature, as well as reaction time, were controlled in the tests of catalytic performance.